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Synthesis of a new tetradentate phosphine and its coordination chemistry with group 10 metals

Colleen Margaret Duff
Iowa State University

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Duff, Colleen Margaret, Ph.D.

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Synthesis of a new tetradentate phosphine and its coordination chemistry with group 10 metals

by

Colleen Margaret Duff

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1987

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DEDICATION

To Michelle Louise and Richard McCloud

INTRODUCTION: QUALITATIVE AND QUANTITATIVE LIGAND EFFECTS AND THEIR APPLICATION IN GROUP 10 METAL COMPLEXES

LIGAND DESIGN

Metal phosphine complexes display a tremendous range of reactivity and selectivity. The versatility of phosphines makes them particularly well suited as ligands for transition metals and through new synthetic routes, organometallic chemists are rapidly becoming able to custom design ligands to display the electronic and geometric and steric properties they desire. The physical and chemical properties of such metallic compounds vary with the electronic and steric properties of the coordinated ligands.

Changing substituents on the phosphorus markedly alters the character of a phosphine. Electron withdrawing groups such as halides or alcoxides decrease the Bronsted basicity of the phosphorus lone pair by induction. This is accompanied by an increase in the availability of phosphorus orbitals for back donation from filled metal d orbitals. Conversely, alkyl or other electron donating substituents on phosphorus increases the basicity of the phosphorus lone pair and decreases the availability of phosphorus orbitals for back donation from the metal. In 1967 Strohmeier and Muller found that the carbonyl stretching frequencies in a variety of monosubstituted metal carbonyl complexes could be used to order phosphorus ligands in an electronic series.[1]

Historically, the character of phosphine ligands was rationalized almost entirely on the basis of electronic effects until Tolman introduced the steric parameter θ.[2] The steric bulk of the phosphine is measured as the angle (θ) of the cone of space it requires when bound to a metal. Since the cone angle is determined from models, it provides a useful tool in predicting the coordination chemistry of phosphines. Tolman investigated the electronic component of phosphine coordination in a manner similar to Strohmeier. Tolman, however, narrowed his study to mono-substituted $LNi(CO)_3$ complexes, thus eliminating possible artifacts due to changes in metal centers. Compilation of values of ν_{CO} for numerous phosphines generated the electronic parameter χ, which is related to ν_{CO} by the equation:[2]

$$\text{for } PX_1X_2X_3 \quad \nu = 2056.1 + \Sigma\chi_i$$

Here χ is an electronic factor related to each substituent on the phosphorus atom, and the compilation of χ values allows the prediction of ν_{CO}. The stretching frequency, in turn, can be used as a measure of the overall basicity of the phosphine.

Today, it is readily recognized that the observed character of a phosphine is a combination of both electronic and steric effects which can be manipulated to yield the desired properties. Yet, while the electronic and steric parameters are useful tools in predicting the nature of a phosphine, they fall short in two important respects. The coordinating ability of a phosphine is strongly dependent upon the nature of the remaining ligands and their geometry relative to the phosphine. Strong π acids such as CO trans to the phosphorus atom compete for filled metal d orbitals involved in backbonding and cause an increase in the M-P bond distance. Electronegative groups trans to phosphorus decrease the M-P bond distance by increasing the Lewis acidity of the metal through induction, and by weakly competing for filled metal d orbitals. The limit of strain that can be tolerated within the molecule must also be considered and is not an easily determined variable. The cone angle, θ, may predict the steric bulk of a phosphine, but in real complexes, the toleration of strain is a complex balance of bonding, steric and geometric parameters that must be considered for each individual molecule.

Ligand design has been done in a qualitative sense by synthetic chemists as efforts to develop a quantitative measure that includes all variables continue. Comprehensive quantitative treatments are difficult because of the flexibility of phosphines and the interdependence of the steric, σ and π factors.

Giering et al.[3] have developed a method (QALE:

qualitative analysis of ligand effects) for separating the steric, σ and π factors in phosphine bonded complexes. Tolman's cone angle, θ, was used as a measure of steric bulk and the pK_a values for the protonated phosphines were used as a measure of the basicity of the phosphorus lone pair. In previous work, they had observed deviations in the reduction potentials from those predicted by the pK_a values. Complexes of electron withdrawing substituted phosphines, which were less basic, but involved π back bonding were more easily reduced than predicted. This deviation of the reduction potentials from those predicted was defined as $E\pi_a$, and was used as a measure for the extent of π back bonding of the phosphine. Correlation of heat of reaction data for the displacement of a weakly coordinated ligand with the phosphine of interest (e.g., equation 1) with θ, pK_a, and $E\pi_a$ afforded an

$$MePt(PhMe_2P)_2(THF)^+ + L \longrightarrow MePt(PhMe_2P)_2(L)^+ + THF \qquad (1)$$

analysis of the three paramters. The observed heat of reaction (ΔH) is composed of a σ electronic ($\Delta H\sigma$), π electronic ($\Delta H\pi$), and steric ($\Delta H\theta$) components, which are proportional to pK_a, $E\pi_a$, and θ, respectively. The results of this treatment included two distinct classes of phosphines: σ donors (class I), and δ donors/π acceptors (class II). Within these two classes thresholds were observed for the steric and the π contributions which are specific to the class of metal complexes being studied. As the cone angle increases in class I phosphines, there is no change in the coordinating ability of the phosphine until the steric threshold for σ donation (θ_σ) is reached. After this point there is a sharp drop in ligating ability due to destabilization of the complex by the large cone angle (Figure 1). As the π acceptor character of the phosphine is increased, evidence of π electronic effects are not observed until the π threshold is reached (π_t), after which the phosphines behave as class II ligands. As the cone angle is increased in class II phosphines, the increasing steric bulk of the complex causes a lengthening of the M-P bond distance until the steric threshold for π donation is reached (θ_π), after which the phosphine becomes a σ donor.

Back donation of filled metal d orbitals to phosphorus donor ligands has been a subject of controversy.[4] Although it is generally accepted that π interactions between the phosphorus and metal occur in some complexes, the prevalence of back bonding in organometallic systems and the identity of the orbitals on phosphorus that are used has remained a subject for discussion. As we have seen, QALE can be used to identify π interactions in

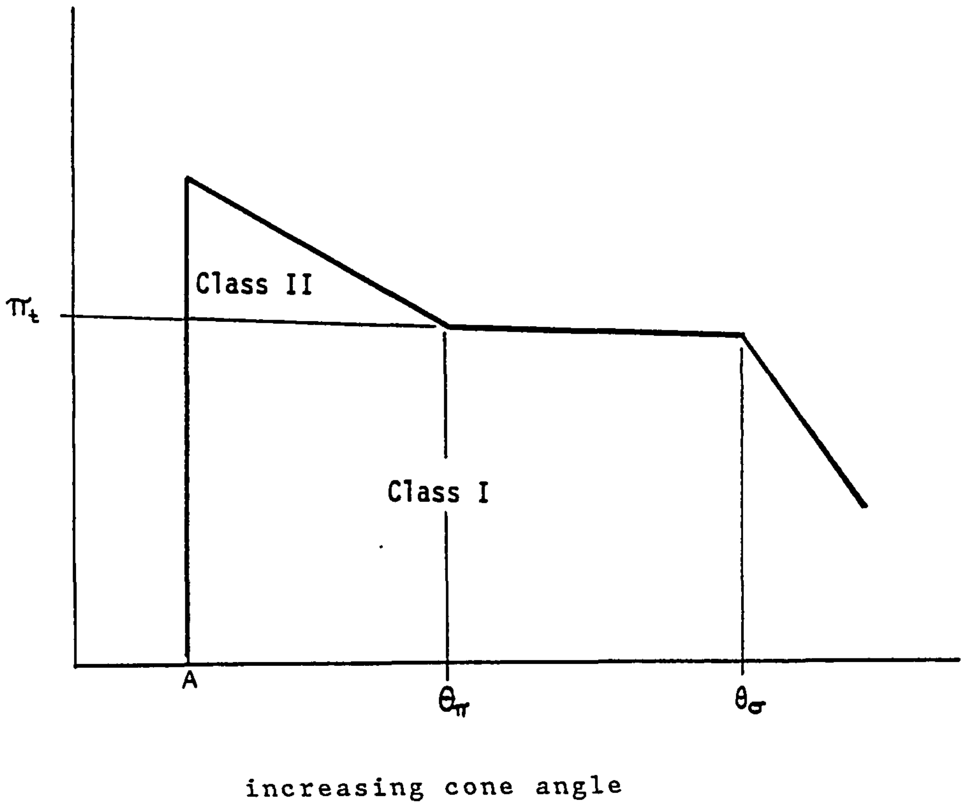


Figure 1. Graphic representation of the steric, σ, and π thresholds determined from QALE. Beginning at A, with a Class I ligand, the π accepting ability increases until π_t is reached, when it becomes a Class II ligand. The cone angle increases until θ_π , after which the M-P distance is too long for π interaction and again becomes Class I. At θ_σ, the cone angle begins to destabilize the complex.

organometallic systems, and Ellis et al. have applied X_α calculations to identify the low lying orbitals that could be used in π back bonding.[5] Previously, empty phosphorus d orbitals have been invoked in metal to phosphorus back π donation.[6] In identifying the frontier orbitals of PF_3, PH_3 and PMe_3, Ellis et al. have determined that the π overlap may involve p orbitals on phosphorus. The highest unoccupied orbital (HOMO) on phosphorus consists primarily of a lone pair s-p hybrid (Figure 2). The orbital energies follow the order PMe_3 (11% s) < PH_3 (14% s) < PF_3 (29% s), which parallels the percent s character and is the expected trend based on electron withdrawing groups on phosphorus. The lowest unoccupied orbitals (LUMO) are shown in Figure 3 (same plot parameters as Figure 2) and have the correct symmetry for back donation along the principal axis. All three have similar symmetry, however there are several important differences. The energy of the PF_3 (-1.05 ev) LUMO is lower than that in PH_3 (0.88 ev) or PMe_3 (0.85 ev) and should enhance the back-bonding to PF_3 relative to PH_3 or PMe_3. Second, the nature of LUMO changes from 36% 3p and 23% 3d on phosphorus in PH_3, 14% 3p and 10% 3d in PMe_3, to 44% 3p and 23% 3d in PF_3. More electronegative substituents on phosphorus in PX_3 cause a more ionic P-X

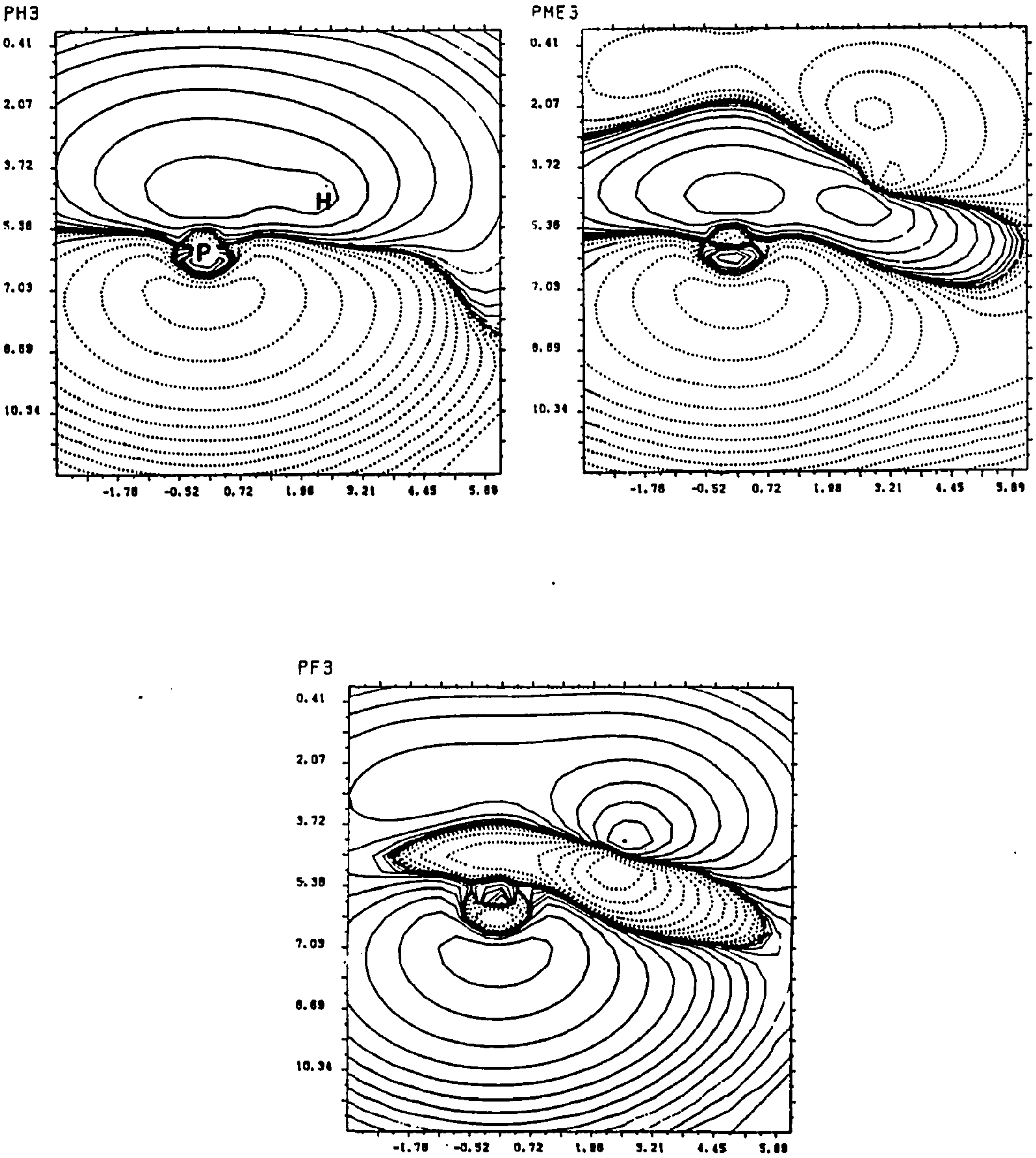


Figure 2. Contour plots of the HOMO (lone pair) orbitals in a) PH_3, b) PMe_3, and c) PF_3

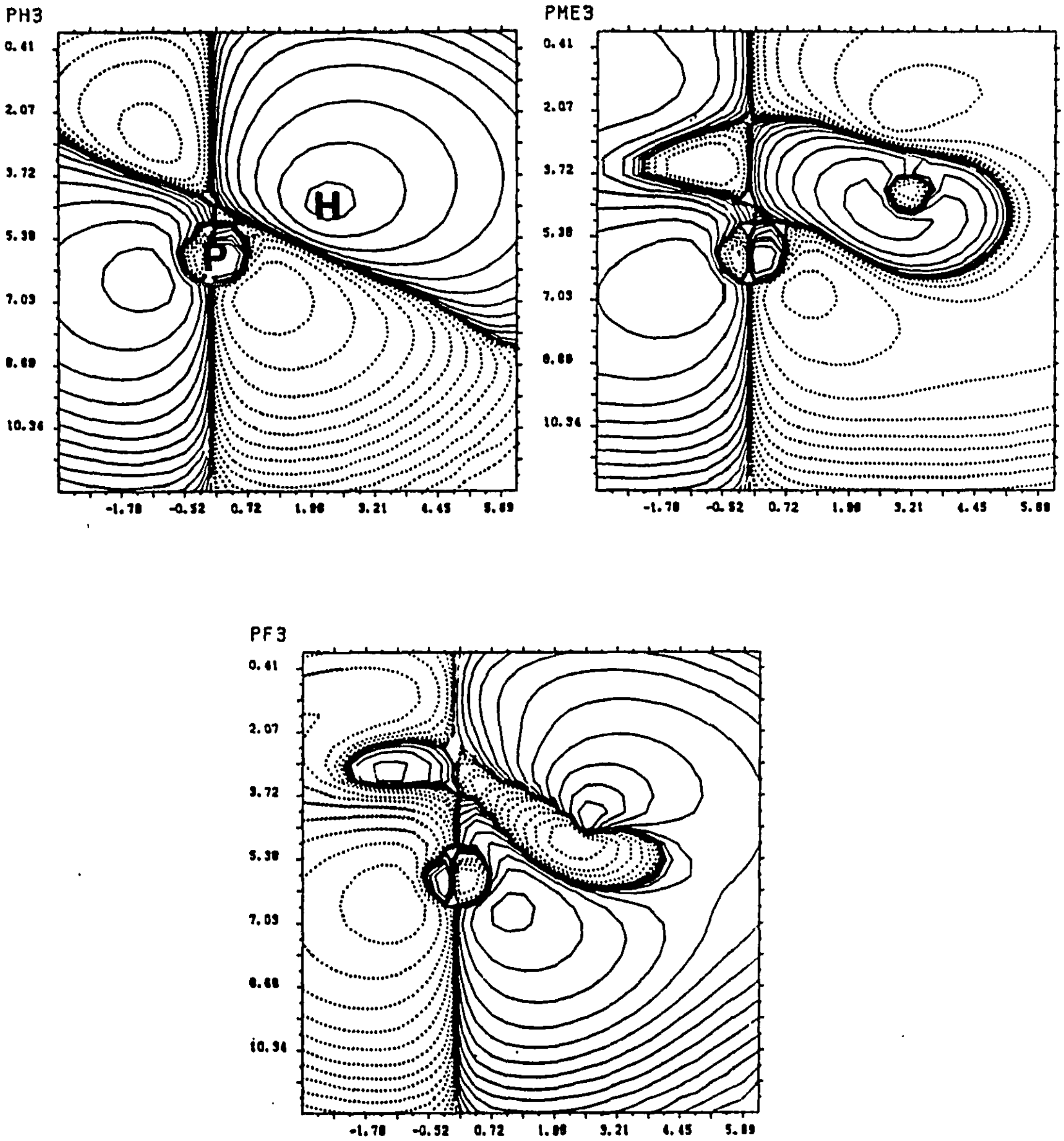


Figure 3. Contour plots of the LUMO (π acceptor) orbitals in a) PH_3, b) PMe_3, and c) PF_3

bond. Thus, the valence orbitals on X will dominate the occupied bonding orbitals and the antibonding levels will have more phosphorus 3p character.

Ab initio molecular orbital theory was used by Marynick to further investigate the π accepting orbitals on phosphorus.[6] Wave function plots identified the 3p orbitals (LUMO) on PH_3 as having σ* local symmetry. To test the importance of the σ* orbitals in π back-bonding, ab initio calculations were done on the tetrahedral complex $Ni(NH_3)_3(PH_3)$ with, and without the inclusion of 3d orbitals in the phosphorus basis set. There is very little difference in the Ni d orbital occupancy between the two (0.03 e in d_{xz}, d_{yz}; 0.02 e in d_{xy}, $d(x^2-y^2)$) with significant delocalization from the metal to phosphorus. While this is not a completely quantitative treatment, it indicates that d orbitals on phosphorus are not necessary for a qualitative explanation of back-bonding.

Numerous spectroscopic techniques have been used to study the nature of the phosphorus-metal bond.[7-9] The use of ^{31}P NMR is particularly attractive because it is readily accessible. Bartik and Himmler have reported a linear correlation between δ from the ^{31}P NMR of trans-$(PR_3)_2PdCl_2$ complexes and the steric parameter theta of the free ligand.[10] Plotting the chemical shift of 49 different phosphine complexes against theta gave a straight line with a correlation coefficient of 0.936. This line excludes four very bulky phosphines: Cy_3P, *ortho*-, *meta*-, and (*para*-tolyl)$_3$P which did not follow the correlation. An equation of the line allows an approximation of the cone angle from the ^{31}P NMR data (equation 2).

$$\theta = 0.474\ (\ \delta(^{31}P\ \underline{t}\text{-}(PR_3)_2PdCl_2) + 122.1 \qquad (2)$$

The above considerations of phosphines can be extended to chelating polyphosphines, although no parameters currently exist that include the chelate effect. Upon coordination of an initial phosphorus atom, the carbon backbone holds subsequent phosphorus atoms in close proximity to the metal. The most widely used chelating phosphines are the series, $R_2P(CH_2)_nPR_2$. Investigations of metal phosphine complexes have shown a dramatic increase in reactivity, selectivity, and stability when diphosphines are employed.[11] This has generated studies into the effects of chelate ring size, the number of such rings and the spatial arrangement of the phosphorus atoms within the polydentate phosphine ligands.

The study of $^{31}P\{^1H\}$ chemical shifts as a function of chelate ring size was undertaken by Garrou.[12] He compared several metal complexes containing $Ph_2P(CH_2)_nPPh_2$ where n = 1, 2, or 3 with their *bis*-alkyldiphenylphosphine analogues.

By tabulating the difference in chemical shifts between analogous monodentate phosphine complexes and bidentate phosphine complexes, he found a significant deshielding effect for those containing five-membered chelate rings. The deshielding contribution ranged from -21 to -33 ppm in fifteen complexes of Cr, Mo and W. Although fewer suitable examples were available for $n = 1$, δ ranged from +12 to +25 ppm in three examples. Similarly, the case for $n = 3$ fell between +2 and +17 ppm in four examples.

Since three different metals were employed in the study, the effects due to a change in metal size were also studied.[12] Within the Group 6 metals, no correlation could be found between ^{31}P NMR data and metal ion radius. However any generalization of this observation should be done cautiously since there is only a small change in metal radius within the group.[4] The idea of a negligible effect due to metal radius is further supported by Hancock et al.[13,14] In their study of the formation constants of metal tetra-azamacrocylic complexes (Figure 4a), there was no correlation between the formation constant and agreement between the metal diameter and ligand cavity size. Ligands predicted to have too large a cavity to coordinate favorably to a small metal ion such as Ni(II), and ligands predicted to have too small a cavity to coordinate the larger ion Pb(II) formed stable complexes with unexpectedly

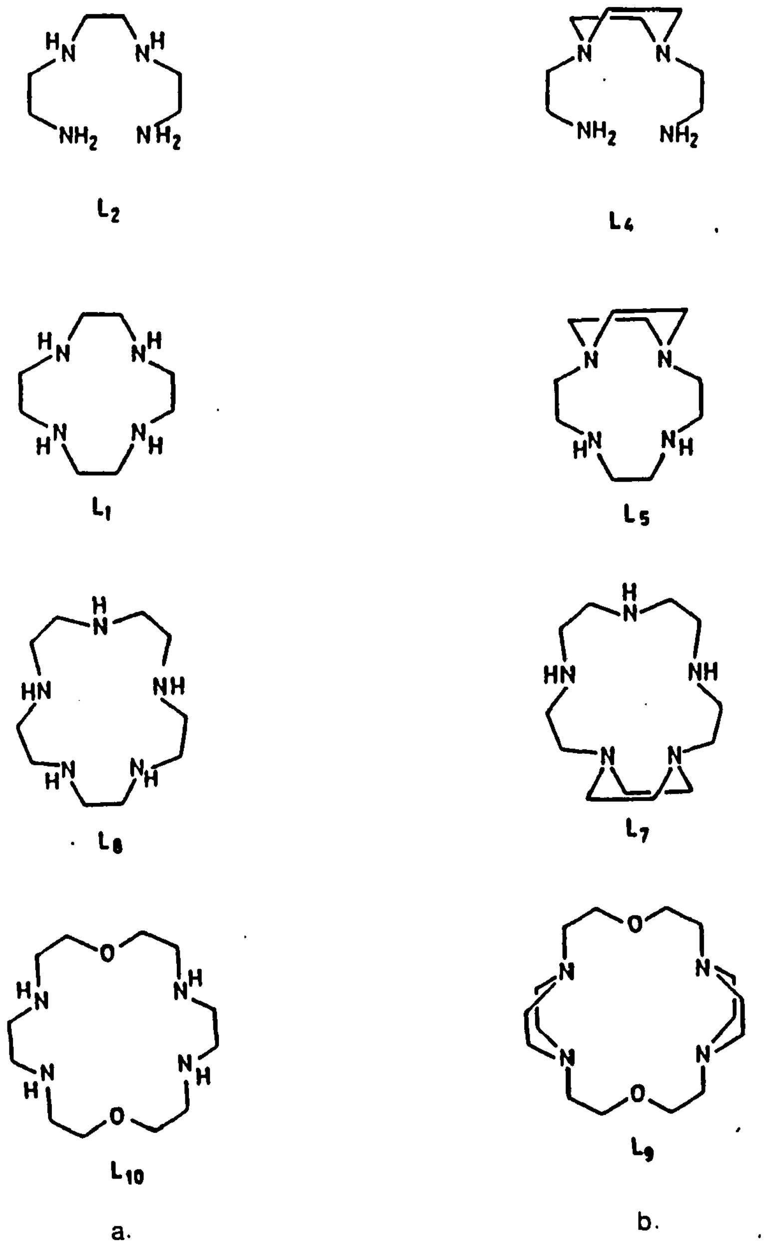
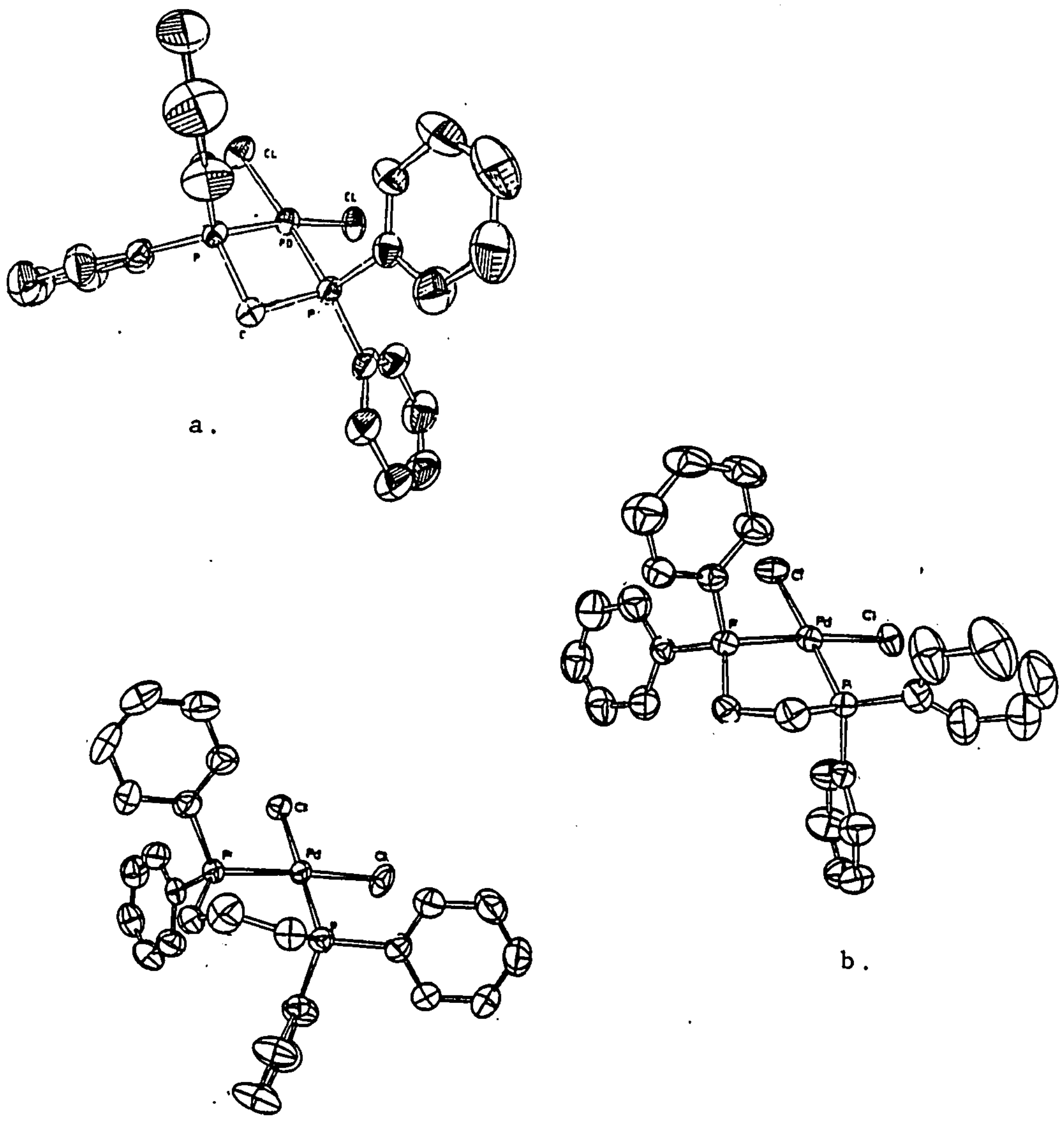


Figure 4. Tetraaza macrocyclic ligands, a) non-rigid, ethylene bridged, b) rigid doubly ethylene bridged macrocycles

large formation constants. The tetra-azamacrocycles are not rigid structures and the experimental results were rationalized by the fact that distortion in the planarity of the ligand could allow a more favorable interaction between the metal and nitrogen atoms. This hypothesis was investigated via the synthesis of more rigid analogues of the ligands (Figure 4b) and the formation constants of their complexes as a function of metal radius. The results indicate a slight dependence of the formation constants on the metal radius. These results, however, are complicated by new variables such as the ring conformation and folding that are generated by the double bridging ethylene.

The chelate studies of Garrou are nicely complemented by structural studies by Palenik et al.[15,16] Crystallographic analyses were done for the series of Pd(II) complexes $(Ph_2P(CH_2)_nPPh_2)PdX_2$ where n = 1 (dppm), 2 (dppe), or 3 (dppp), and X = Cl^- or NCS^-. This allowed the direct comparison of the metal-phosphorus bond lengths in a homologous series as a function of chelate ring size (Figure 5). The results indicate an increased metal-phosphorus interaction for the dppe (n = 2) five-membered chelate ring.

The P-Pd-P bond angle increases from dppm to dppp as the bite of the chelate increases with the added methylene



a.

b.

c.

Figure 5. Ortep diagrams for the series $Cl_2Pd(Ph_2P(CH_2)_nPh_2P)$: a) n = 1, dppm, b) n = 2, dppe, c) n = 3, dppp

groups between the phosphines (Table I). The P-Pd bond lengths are an absolute measure of the metal-phosphorus interaction. The Pd-P bond lengths for dppm, which provides a four-membered chelate ring, are complicated by inequivalency. The values are significantly different for dppm due to distortion in the molecule induced by the small bite of the chelate. The small Pd-P bond length for dppe (five-membered chelate ring) indicates a marginally stronger interaction between the Pd and P relative to the

Table I. Average bond lengths and angles in $(Ph_2P(CH_2)_nPPh_2)PdX_2$

	n = 1	n = 2	n = 3
X = NCS^-			
P-Pd-P (°)	73.33(5)	85.2	89.32
X-Pd-X (°)	90.9	90.2	89.8
Pd-P (Å)	2.282(2) 2.264(2)	2.242(3) 2.258(3)	2.241(1) 2.248(1)
X = Cl^-			
P-Pd-P (°)	72.68(3)	85.82(7)	90.58(5)
X-Pd-X (°)	93.63(3)	94.19(7)	90.78(5)
Pd-P (Å)	2.234(1) 2.250(1)	2.233(2) 2.226(2)	2.244(1) 2.249(2)

six-membered chelate ring compounds. This is rationalized as the result of a reduction in strain imposed on the complex by the ethylene backbone.

The successful utilization of chelating diphosphines has led to the natural extension of including higher polydentate phosphines, and a number of reviews have been published.[17]

As the number of phosphine complexes which have been analyzed by X-ray crystallography grows, the bond length and bond angle data provide clear information concerning ligand effects. Clark and Hampden-Smith studied deviations in Cy_3P (Cy = cyclohexyl) complexes as a function of steric bulk of the complex.[18] The extensive use of Cy_3P in organometallic chemistry has provided numerous crystallographic analyses from which to work, particularly for cis and trans-$[L_2PtZ_2]^{n+}$. Based on Tolman's cone angle[2], $Pt(PPh_3)_4$ and $Pt(PCy_3)_3$ should not exist because of the large cone angles of PPh_3 (145°) and PCy_3 (170°). However, these complexes are known and θ describes the ligand size but does not describe how such ligands can be accomodated about the metal center. This study reveals that steric overcrowding is accommodated progressively by the following types of distortion: a) lengthening of the Pt-P bond, b) deviations from square geometry at the Pt atom (but retaining planarity), c) deviation of the Pt-P-C angles in the phosphine ligand, d) deviation from planar geometry. This is nicely illustrated in the comparison of three the <u>trans</u> complexes: $H_2Pt(PCy_3)_2$ (A),[19] $[HPt(PhCy_2P)_2(PCy_3)_2]^+$ (B),[20] and $(PhCl_2Si)Pt(PCy_3)_2$ (C).[20] In the hydride complex A, there is little evidence of crowding when compared to mono-substituted PCy_3 complexes, such as $Cl_2Pt(PCy_3)(PMe_3)$ in which there is assumed to be no steric crowding. In A the average Pt-P bond distance is 2.26(1) Å (Table II). In complex **B**, more steric crowding created by the replacement of an hydride with the larger phosphine is reflected in highly distorted P-Pt-P bond angles, and an increase in the Pt-P bond length (2.346(3) and 2.337(3) Å). This is accompanied by a decrease in the P-Pt-P bond angle to 167.8 °.

Table II. Bond distance and angles in PCy_3 complexes of Pt(II)

compound	Pt-P distance (Å)	P-Pt-P angles (°)
$H_2Pt(PCy_3)_2$ **A**	2.26(1)	180
$[HPt(PhCy_2P)-(PCy_3)_2]^+$ **B**	2.346(3) 2.337(3)	167.8
$(PhCl_2Si)_2Pt(PCy_3)_2$ **C**	2.350(1) 2.388(1)	142.7

Displacement of the second hydride by a larger ligand further increases the Pt-P bond distance and decreases the P-Pt-P bond angle to 142.7°. The ligand substituents adopt a staggered conformation with respect to each other and the crowding distorts the Cy_3P ligand. In complex A, the Pt-P-C bond angles are between 109° and 111°. In complex C, these angles are between 123° and 125°.

COMPLEXES OF GROUP 10 METALS

The Group 10 metals are conveniently divided into Ni complexes, and Pd and Pt complexes. The covalent radii of divalent Pd and Pt are very similar (Pd:1.31 Å ; Pt: 1.32 Å).[21] A direct result of this similarity in radii is a close parallel in several of the types of organometallic compounds formed by Pd and Pt.[21] Since the divalent ions of the Group 10 metals are d^8, there is a strong tendency to form four-coordinate square planar complexes. Five-coordinate complexes are also known, although most commonly for Ni. Both square pyramidal and trigonal bipyramidal geometries have been observed, although the majority of five-coordinate Group 10 metal complexes have a distorted geometry that is closer to square pyramidal.[22]

The reaction of Ni(II) salts with monodentate phosphines yields four-coordinate complexes of the formula $Ni(PR_3)_2X_2$, where $X = Cl^-$, Br^-, I^-, or CN^-. The phosphine ligands in these compounds are sensitive to oxidation, in contrast to the analogous Pd and Pt complexes which are quite stable. Red-brown diamagnetic as well as blue to green paramagnetic complexes of this formula have been reported.[22] The diamagnetic complexes are square planar, the paramagnetic are tetrahedral. The preference for these two forms has been studied as a function of solvent,[23] substituents on phosphorus,[24] and anion.[25]

Isomerization between the two forms was found to occur more readily in polar solvents at elevated temperatures favoring the diamagnetic square planar isomer. The use of less polar solvents in the initial preparations favored formation of the tetrahedral product.[23] As the coordinating anion and substituents on phosphorus increased in steric bulk, the tetrahedral product was favored. For the series of phosphines n-Bu_3P, n-Bu_2PhP, and n-$BuPh_2P$, the complexes L_2NiX_2 yielded square planar products in the reaction of n-Bu_3P or n-Bu_2PhP with NiX_2 salts. As the steric bulk of the ligand increases in n-$BuPh_2P$, the interligand repulsions increase and the tetrahedral form is favored.[24] This reduces some of the strain by removing the planarity of the four phosphines. The same trend is observed for the series of anions Cl^-, Br^- and I^-. Coordination of I^- increases the steric interactions, and the paramagnetic tetrahedral form is favored.[25] When a Ni(II) salt of a non-coordinating anion, such as ClO_4^-, is reacted with Me_3P, $[Ni(PMe_3)_4](X)_2$ is formed.[25] The red product is diamagnetic and has a square planar geometry.

The coordination number and geometry of the Ni(II) product is strongly dependent on the anion and can not be completely rationalized by steric considerations. Deep blue-black tris-phosphine complexes ($[Ni(PMe_3)_3X]X$) have been isolated from the reaction of NiX_2 salts with Me_3P, as well as five-coordinate complexes ($Ni(PMe_3)_3X_2$). The ligand PMe_3 is the only phosphine known to form five-coordinate complexes containing halides.[26]

Ni complexes containing CN^- readily form five-coordinate species of the formula $[(CN)_{5-n}Ni(PMe_3)_n]^{-3+n}$ with a variety of phosphines. The ability of PMe_3 to form stable five-coordinate complexes more readily than other phosphines lies in a combination of its small cone angle and increased Lewis basicity. A crystallographic analysis of $Ni(CN)_2(PhPMe_2)_3$ showed it to have a distorted trigonal bipyramidal geometry very similar to that of $Ni(CN)_5^{3-}$ (Figure 6).[27] The three phosphine ligands occupy the equatorial positions with bond angles between them of 117°, 127, and 116. The more electronegative CN^- groups occupy the axial sites with P-Ni-CN angles between 89 and 91 , and a N-P angle of 177°.

Multidentate ligands can be used to favor or rigidly enforce desired geometries in metal complexes. The tripod ligands np_3, nas_3 and pp_3 have been used to produce five-coordinate trigonal bipyramidal complexes (Figure 7).[22] Sacconi et al. reported the structural characterization of a Ni(II) complex of np_3 in which the geometry about the Ni atom is distorted trigonal bipyramidal (Figure 8).[28] The phosphines are required to occupy the equatorial positions by the design of the ligand, and have P-Ni-P bond angles of

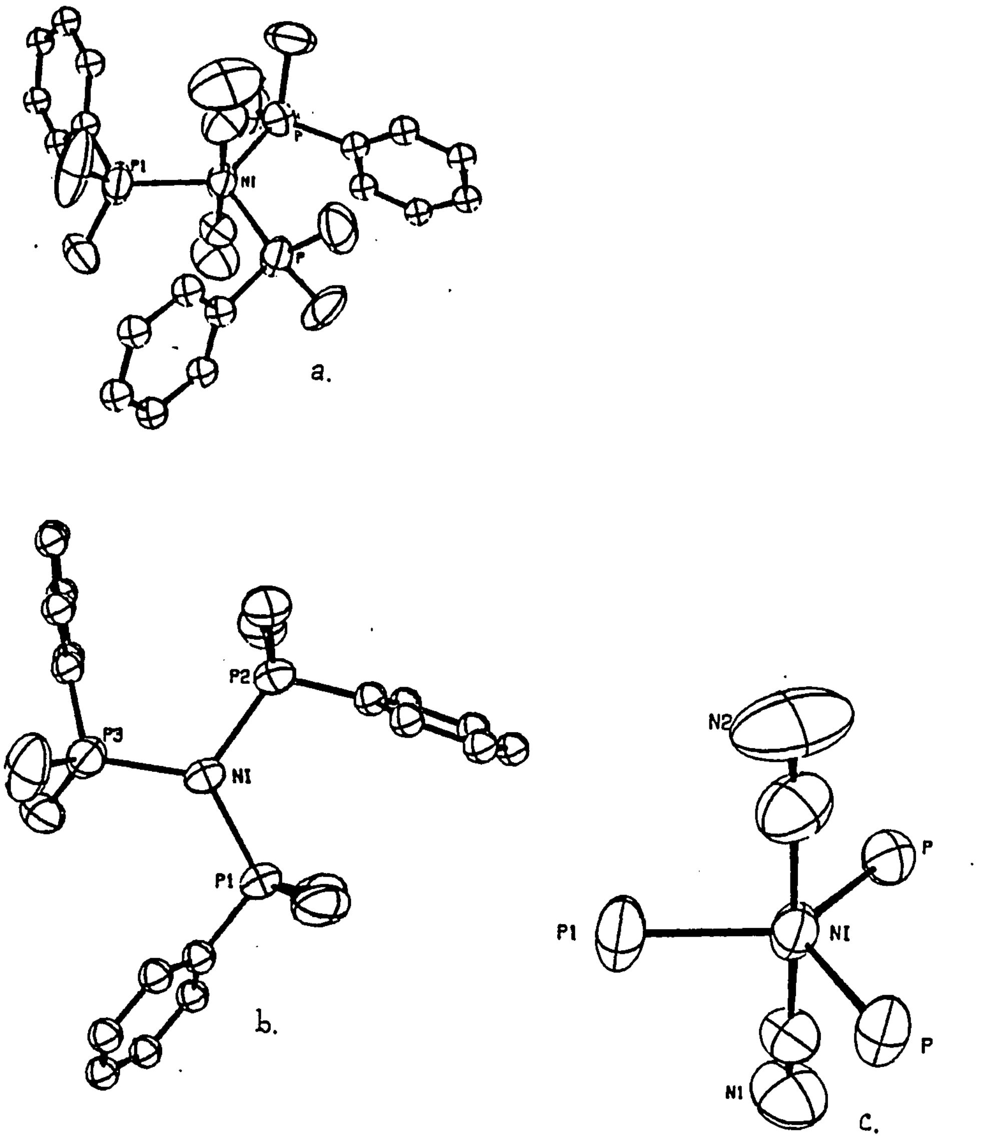


Figure 6. Ortep diagrams of $(CN)_2Ni(PhMe_2P)_3$: a) complete molecule, b) View down the three-fold axis, c) Ortep diagram with the phenyl rings removed to show the trigonal pyramidal geometry

126°, 113°, and 117°. The nitrogen donor of the ligand and the acyl group occupy the axial positions with a N-Ni-C angle of 174°.

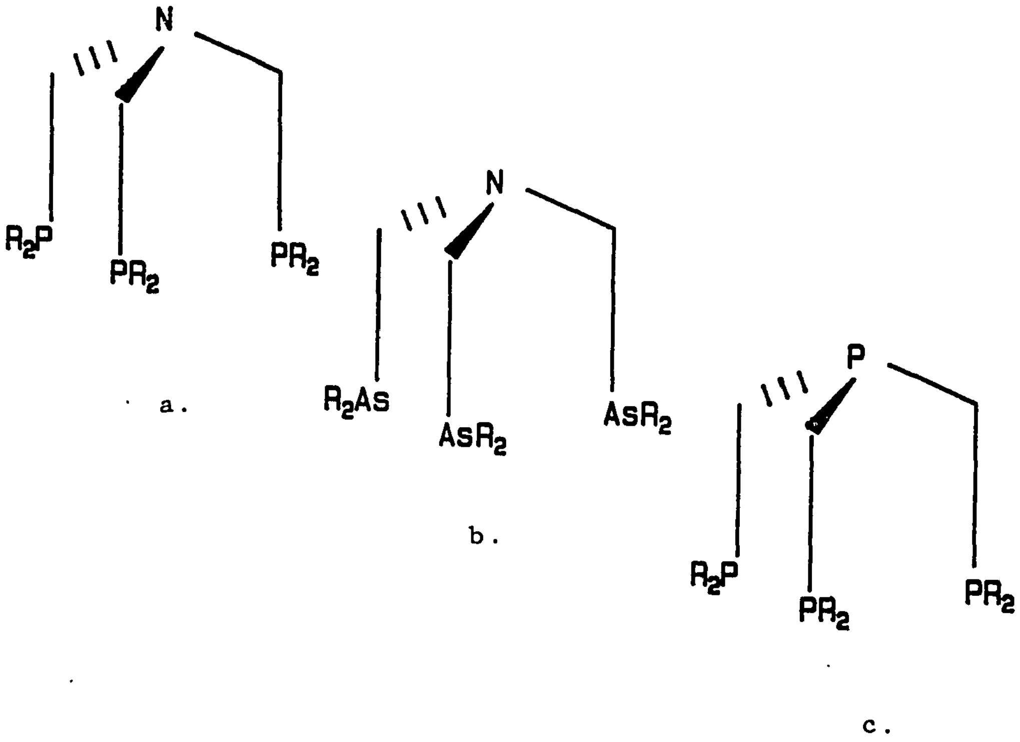


Figure 7. Tripod ligands a) np$_3$, b) nas$_3$, and c) pp$_3$.

Four-coordinate square planar and five-coordinate square pyramidal Ni(II) complexes of o-phenylenebis-(dimethylarsine) (diars), and the phosphorus analogue (diphos) have been reported.[29] Halide exchange was noted in the five-coordinate complexes during characterization

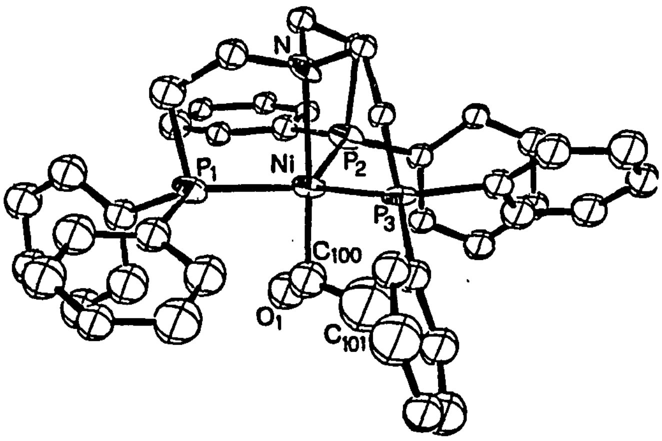


Figure 8. Ortep diagram of $[Ni(np_3)(COCH_3)]^+$

and in order to study halide exchange, the monophenyl substituted diars and diphos ligands were prepared. The phenyl substitution gives rise to ligand diasteriomers which were separated prior to coordination to Ni(II) (Figure 9a). Upon coordination of two of these bidentate ligands, further stereochemistry is generated.

Of interest in this study is the yellow syn-[(Ni(RS-bidentate$)_2$](PF$_6$)$_2$ in which all four methyl groups lie above the plane of the metal. In the presence of halide, the yellow compound turns a deeper yellow orange as the five-coordinate complex is formed. In the case of the syn isomer, a pair of chemically distinct adducts is possible in which the halide lies syn or anti to the methyl groups on the donor atom (Figure 9b). At room temperature (310 K), a single peak is observed in the ^{1}H NMR for the methyl resonances due to rapid exchange of the halide. The spectrum is temperature dependent and at 213 K, two signals of equal intensity are observed for the two halide adducts. ^{1}H NMR spectra of mixtures of the [Ni(bidentate)$_2$]$^{2+}$ isomers gave distinct signals for each of the isomers, thereby excluding the possibility of redistribution of the ligands to account for the experimentally observed phenomenon.

The best known examples of phosphine complexes of palladium and platinum in the +2 oxidation state are of the formula $X_2M(PR_3)_2$. They are readily prepared by the reaction of metal salts or LMX_2 (X = PhCN, COD, SMe$_2$) with the appropriate phosphine and are air- stable, diamagnetic, pale yellow to cream colored solids.[21]

The effect on the metal-phosphine bond of changing the chelate ring size in the series of compounds $Cl_2Pd(Ph_2P(CH_2)_nPPh_2)$ has been discussed for n = 1 to

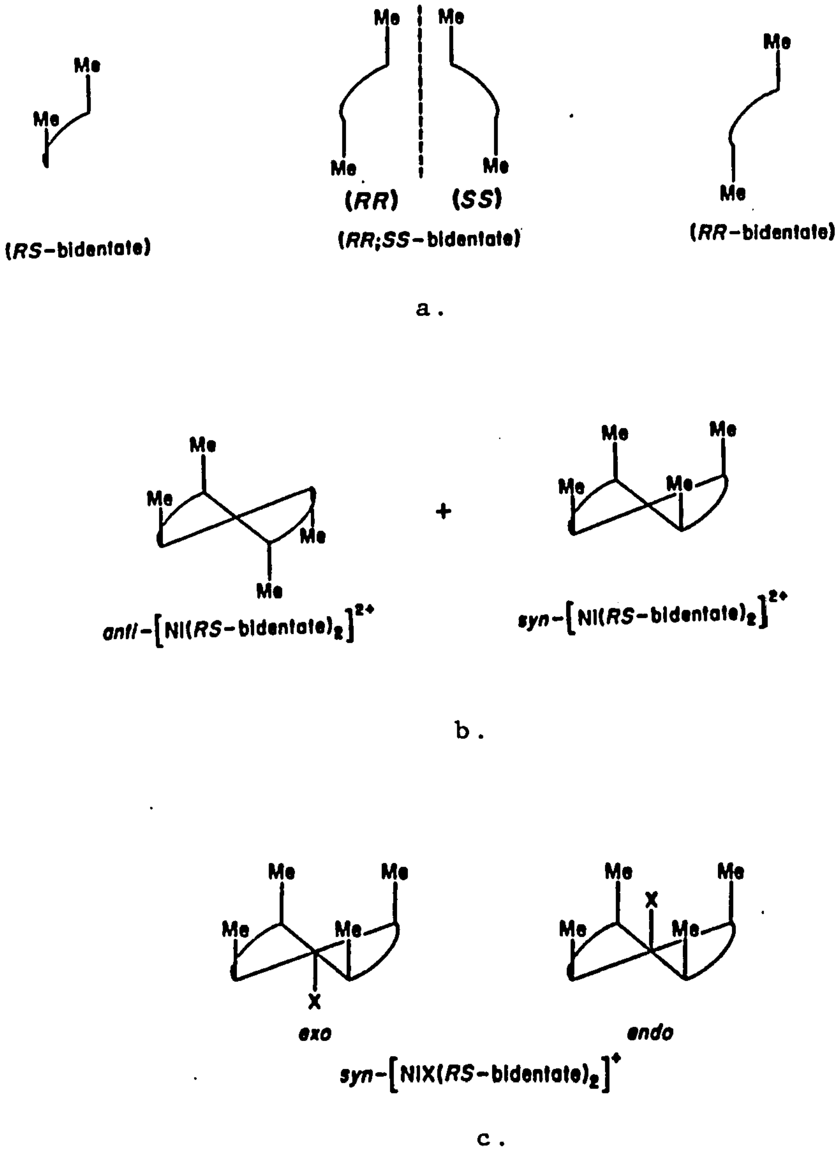
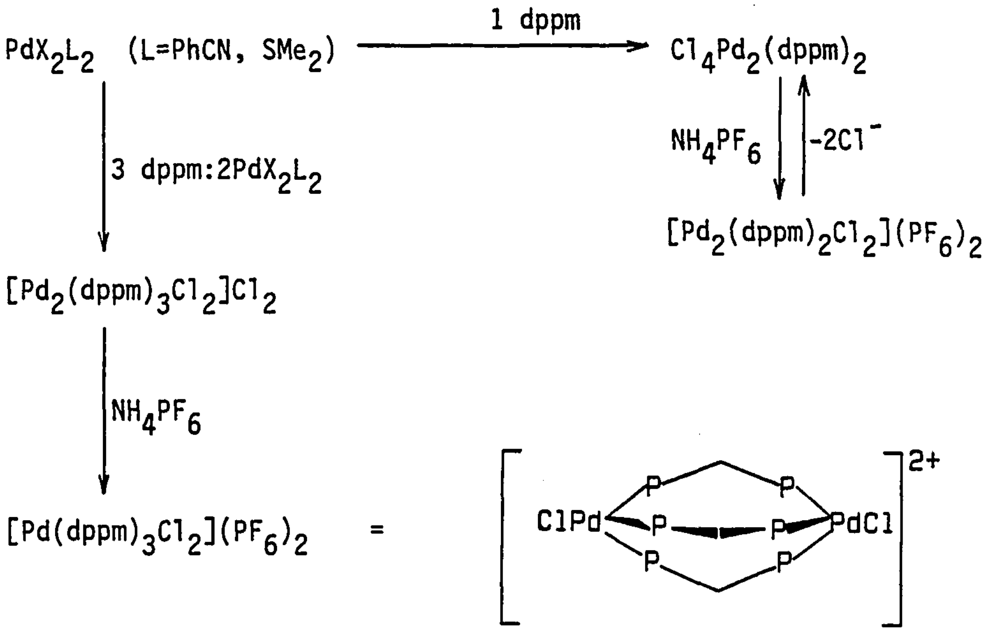


Figure 9. Possible stereochemistry of a) the ligand: RR, SS, and RS, b) of four-coordinate $[Ni(bidentate)_2]^{2+}$, and c) Possible orientations of the halide in syn-$[NiX(bidentate)_2]^+$

3.[15,16] An extension of this work was to determine the limiting value for n which would still allow cis coordination of the diphosphine. As already noted, the methylene bridged diphosphine, n = 1 (dppm), was determined not to be well suited to the series because of its small bite. The formation of a four-membered chelate ring induces a large amount of ring strain and has been found to be better suited to spanning two metals and the ligand dppm has proven very useful in this regard.[30]

In addition to $X_2Pd(dppm)$, another mode of coordination has been recently reported by Puddephatt and coworkers for the coordination of dppm to Pd(II) and Pt(II).[31] Reaction of $(PhCN)_2PdCl_2$ or $(Me_2S)_2PtCl_2$ with dppm produced dinuclear compounds in which the dppm serves as a bridging ligand. In Scheme 1, the reaction sequence is given for Pd(II). An analogous series has been obtained for Pt(II). A molar ratio of one to one yielded the bridging phosphine dimer, while reactions with a molar ratio of three dppm to two M(II) produced a dinuclear product of the same ratio in which three dppm ligands are bridging. The proposed structure is based on supporting evidence in the $^{31}P\{^1H\}$ spectrum, which shows an equivalence of all phosphines, conductance measurements



Scheme 1. Reactions of M(II) with dppm, the phenyl groups on phosphorus are not shown

consistent with a two to one electrolyte, and the removal of two chlorides by exchange.

As n is increased to 4, the chelate ring becomes too large for the ligand to coordinate cis to a single metal, yet it is not sufficiently expanded to allow trans coordination. The result is that stable phosphine bridged complexes are formed. In reactions with Pd(II) and Pt(II) this ligand has been shown to form trinuclear cis complexes, $\{Cl_2M(Ph_2P(CH_2)_4Ph_2P)_3$, based on solution molecular weight determinations and infrared spectral data.[32]

The chelating diphosphine with the largest chelate ring that has been reported to coordinate cis to Pd(II) or Pt(II) is bis(diphenylphosphino)-3,6-dioxaoctane (dpo) which has 8 atoms between the two phosphorus atoms.[33] Both cis-$PdCl_2$(dpo) and trans-MI_2(dpo) (M = Ni, Pd) have been structurally characterized (Figure 10). The $^{31}P\{^1H\}$ NMR spectra show a single peak, with the exception of the Pt complexes, in which there is coupling between P and Pt. The change in chemical shift from cis to trans is approximately +3 ppm, which agrees with that observed for the analogous n-Bu_3P complexes which showed a change in shift of +2.6 ppm.

Both complexes are square planar, with a small deviation from planarity in the trans complex. The angles and distances around the Pd atoms are given in Table III.

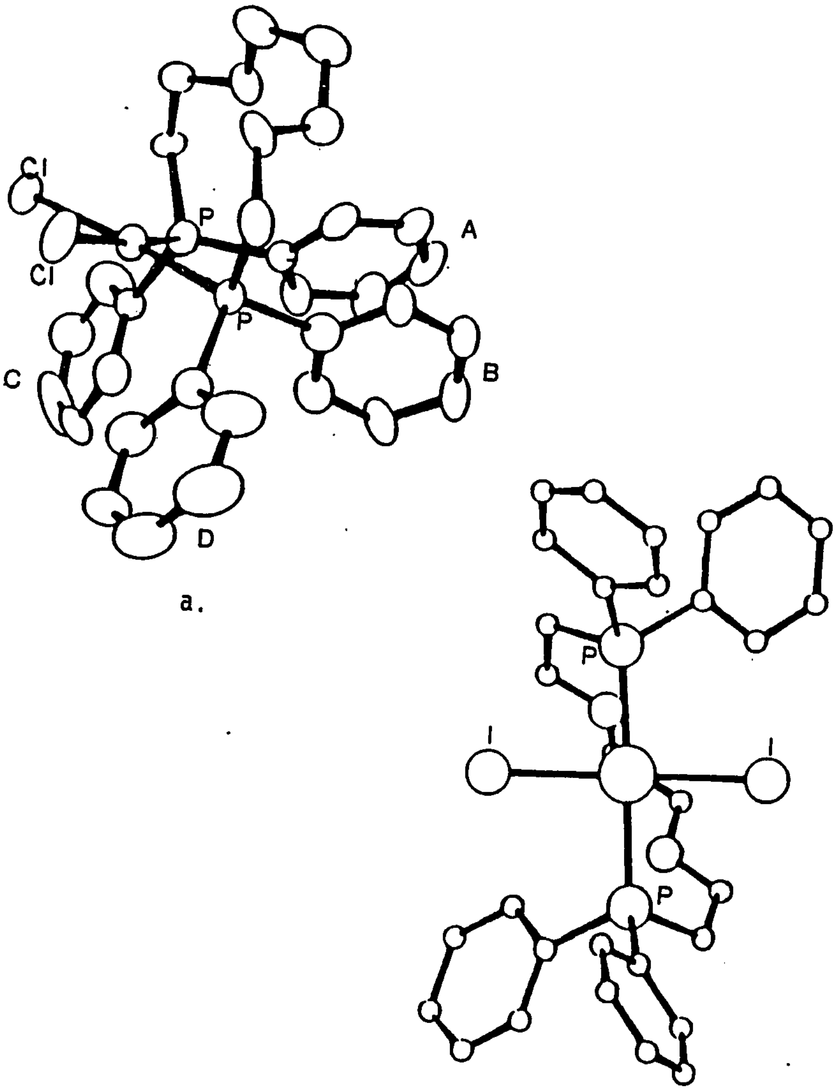
The bond distances compare favorably with similar compounds, demonstrating the ability of metal complexes to overcome steric strain through balancing their geometric and electronic variables. The P-Pd-P angle is significantly larger than the ideal 90 ° and this is ascribed to the large chelate ring of ligand.

Table III. Bond angles and distances for X_2M(dpo).

	cis-$PdCl_2$(dpo)	*trans*-PdI_2(dpo)
P-Pd-P (°)	105.4(1)	164.9(1)
X-Pd-X	88.1(1)	146.8(1)
P-Pd-X	82.5(1)	87.9(1)
P-Pd-X	84.0(1)	89.1(1)
P-Pd (Å)	2.268(1) 2.263(1)	2.330(2) 2.321(2)

Two pairs of the phenyl rings (A,B; C,D) lie almost parallel in the solid state structure of *cis*-$PdCl_2$(dpo). The angle between phenyls A and B is 17° and is 19° between C and D. The distances between the phenyl rings in each pair lie between 3.26 and 3.90 Å. The authors suggest a corresponding lengthening of the C-C bond lengths within these phenyl rings, with average distances of 1.368(3) Å compared to 1.377(3) Å in phenyl rings that lie approximately perpendicular to one another. These observations may indicate an interaction between the pi systems, although, the phenyl C-C bond distances lie within three standard deviations of one another and may be due to experimental error.

Halides are readily displaced from X_2Pt(dppe) by an additional chelating diphosphine but require the addition

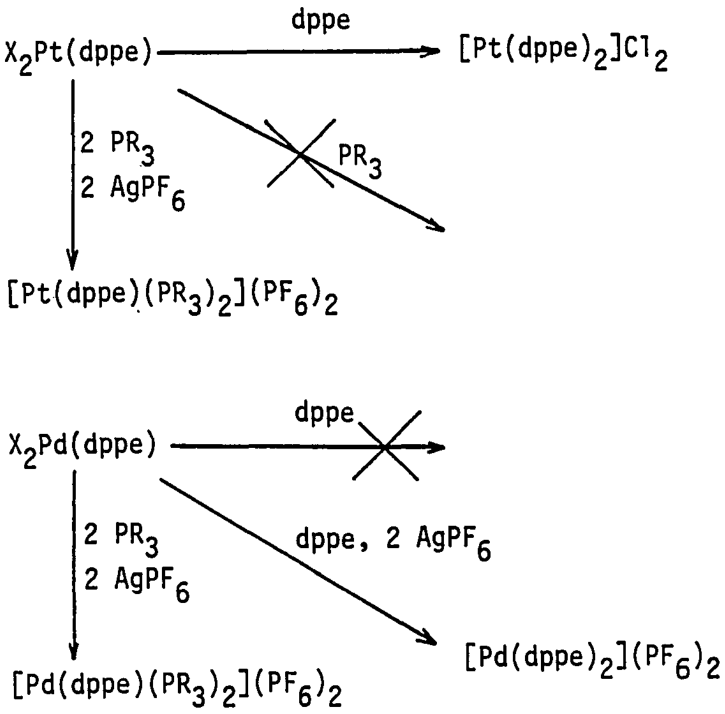


a.

b.

Figure 10. Ortep diagrams of: a) <u>cis</u>-(dpo)$PdCl_2$, b) <u>trans</u> -(dpo)PdI_2

of $AgBF_4$ to remove the halides in PdX_2(dppe).[34-38] When the halides are replaced by monophosphines, a silver salt is required to remove the second halide from Pt also. These methods have been used to prepare an additional series of Pt(II) and Pd(II) compounds in which three and four phosphine ligands are coordinated to the metal (Scheme 2).



Scheme 2. Ligand substitution chemistry of X_2M(dppe), where M = Pt, Pd, X = Cl^-, Br^-

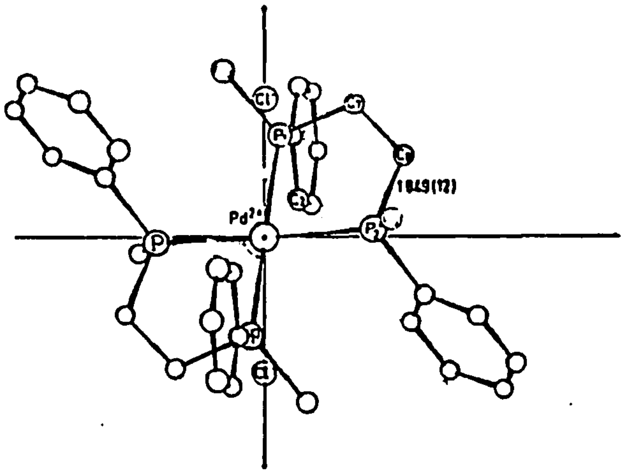


Figure 11. Ortep diagram of $[Pd(pMepe)_2]Cl_2$

The bis-bidentate complexes, $[M(dppe)_2]X_2$, have been structurally characterized for M = Pd and Pt, as well as for the methyl substituted ligand bis-(phenylmethylphosphino)ethane (pMepe) (Figures 11 and 12).[36,38] The trans effect of replacing chlorine by phosphorus trans to the phosphine, is quite pronounced, causing a lengthening of the M-P bond. The Pd-P bond lengths in $Cl_2Pd(dppe)$ are 2.233(2) and 2.226(2) Å, while in $[Pd(dppe)_2]Cl_2$ the bond lengths are 2.342(2), 2.332(2), 2.347(2), and 2.335(2) Å. The bond angles around Pd in $[Pd(dppe)_2]Cl_2$ are 81.65(8) °,

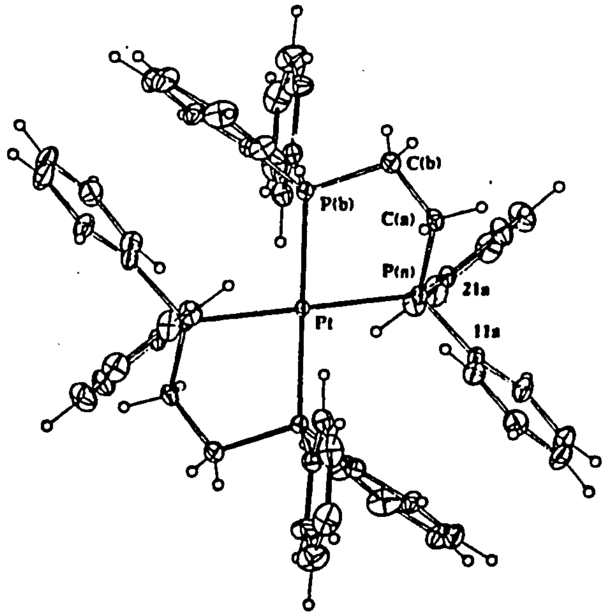


Figure 12. Ortep diagram of $[Pt(dppe)_2]Cl_2$

82.04(7)°, 98.35(8)°, and 97.96(7)°. In $Cl_2Pd(dppe)$ the P-Pd-P angle is 85.82(7)°, the Cl-Pd-Cl angle 94.19(7)°, and the P-Pd-Cl angles are 99.78(3)° and 94.39(3)°. The difference in angles around the Pd atoms can be attributed to the difference in steric requirements. There is also a conformational change between the bis-diphos and mono-diphos compounds in the ethylene bridge of the ligand. In $[Pd(dppe)_2]Cl_2$, both carbon atoms of each ethylene bridge lie on the same side of the MP_4 plane, whereas in

$Cl_2Pd(dppe)$ one of the carbon atoms lie above and the other below the MP_4 plane.

Stable five-coordinate complexes of Pt(II) and Pd(II) were virtually unknown before the late 1960s. Prior to that time, only three such compounds were identified. In 1964, Collier and coworkers reported the initial work on the structural characterization of compounds of the formula $(R_3P)_3PdBr_2$ in which the Pd atom is five-coordinate.[37] The geometry around the Pd is a distorted square pyramid with one Br^- lying well below the plane of the Pd and three P atoms (Figure 13). Cramer et al. reported a five-coordinate Pt(II) complex in 1965 in which five trichlorotin groups are bound to Pt.[39] It was proposed to have trigonal bipyramidal geometry (tbp) by comparison of

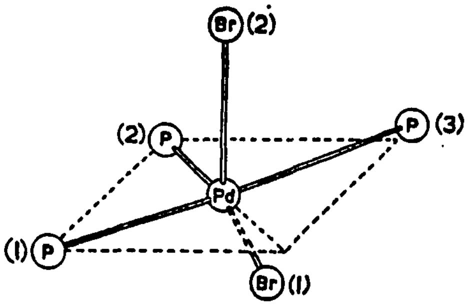


Figure 13. Ortep diagram of $[(PMe_3)_3PdBr_2]$

spectral data with $(Pt(CN)_5)^{3-}$ which is known to have tbp geometry.

Although not structurally characterized, $[Pt(dppm)_2](PF_6)_2$ was investigated by Grossel et al.[35a] They observed an equilibrium between the four-coordinate starting complex and a five-coordinate form in the presence of halide in which a halide is bound to the Pt. The five-coordinate complexes, $[XPt(dppm)_2]X$, were identified as being the major species in solutions of the previously reported $[Pt(dppm)_2]X_2$ four-coordinate complexes. $^{31}P\{^1H\}$, ^1H, and ^{195} Pt NMR and conductance measurements were used to verify five coordination. A small (2 ppm) upfield shift in the ^{31}P NMR chemical shift of the dication in CH_3CN, versus that in CH_2Cl_2 was observed, suggesting the coordination of CH_3CN in solution. The coupling $^1J_{Pt-P}$ ranged from 2000 to 2190 Hz, indicative of *trans*-phosphines. Upon coordination of the halide to the fifth coordination site, a downfield shift of 7 ppm was observed for $X = Cl^-$, and upfield shifts of 10 and 20 ppm for $X = Br^-$ and I^-, respectively. The Pt-P coupling constants exhibit a small change (30 to 100 Hz), remaining in the range expected for P trans to P. The significant changes in chemical shift show that the species in solution cannot be the four-coordinate Pt complex and the variation in the shift illustrates the dependence on the coordinated halide.

Reaction of $Cl_2Pd(PhMe_2P)_2$ with I^- has been reported to produce two polymorphic crystalline products of the formula $I_2Pd(dppe)$.[40] One polymorph crystallizes as deep red needles, the second as yellow plates. The red form converts to the yellow upon heating to 120°, then melts to an orange liquid at 160°. Both have been structurally characterized (Figure 14). The red form is five-coordinate in the solid state with bridging I^-. In addition, one ortho-H of the phenyl ring on each P is bent over the Pd atom. The yellow form is formally four-coordinate, but there is interaction between Pd and the ortho-H of one phenyl ring from each of the two P atoms to give an elongated octahedron.

In the red isomer, the equatorial non-bridging I^- lies 2.638(3) Å from the Pd. The bridging I-Pd bond distances are 2.619(3) Å for the equatorial Pd-I bond and 3.290(3) Å for the axial bond. One ortho H of each of the Me_2PPh units are 2.84 and 2.85 Å from the Pd. The average Pd-I bond length in the yellow form is 2.592(3) Å. The average Pd-H distance is 2.333(7) Å, which is significantly shorter than that found in the red isomer.

The hydrogen atoms were not located in the structure determination, but were derived assuming normal phenyl geometry. The Pd-H distances are sufficiently long that direct interactions are questionable, and their proximity

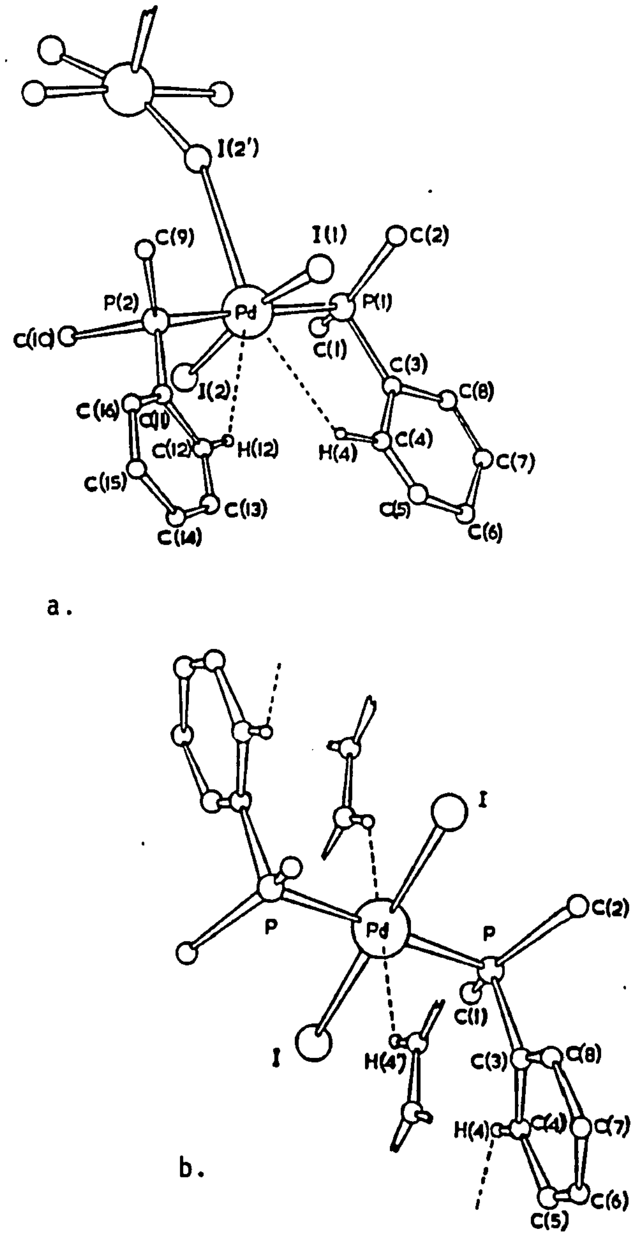


Figure 14. Ortep diagrams of $I_2Pd(PhMe_2P)_2$, a) red isomer, b) yellow isomer

may be a function of steric requirements.[40]

Macrocyclic phosphine ligands have been used to form five-coordinate Pd complexes of the general form PdP_4X. Stelzer and coworkers used Pd(II) and Ni(II) in the template synthesis of a cyclam-like tetraphosphine.[41] Four-coordinate and five-coordinate complexes were isolated depending on the isomeric structure of the ligand (Figure 15). In the process of a template synthesis of the ligand, two isomers are formed in which the substituents on the macrocycle are either trans, trans (A) or cis, cis (B). When cis, cis is formed, the chloride anion coordinates to the Pd to form the five-coordinate complex. The Pd-P bond distances are comparable between the two structures, 2.274(1) and 2.278(1) Å in the trans, trans, and 2.290(3) and 2.282(3) Å in the cis, cis. The Pd-Cl bond distance in cis, cis is 2.831(3) Å.

The difference in coordination geometry between the trans, trans and cis, cis complexes is rationalized by distortion within the cis, cis complex caused by the steric requirements of the ligand. The Pd atom in this isomer lies 0.26 Å out of the basal plane formed by the four P atoms, and it may be this deviation from planarity that activates the fifth coordination site forming the five-coordinate complex of ligand B.

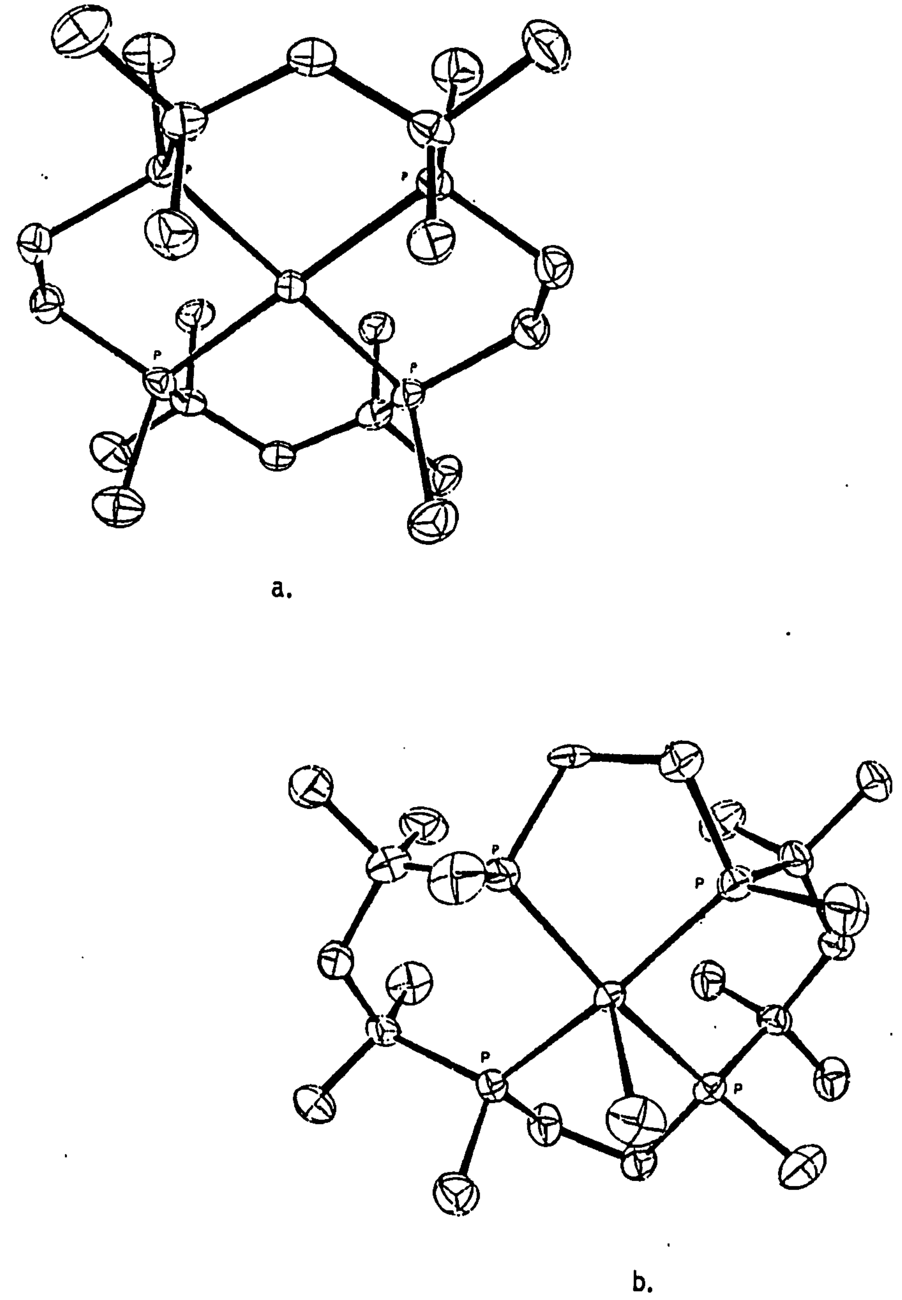


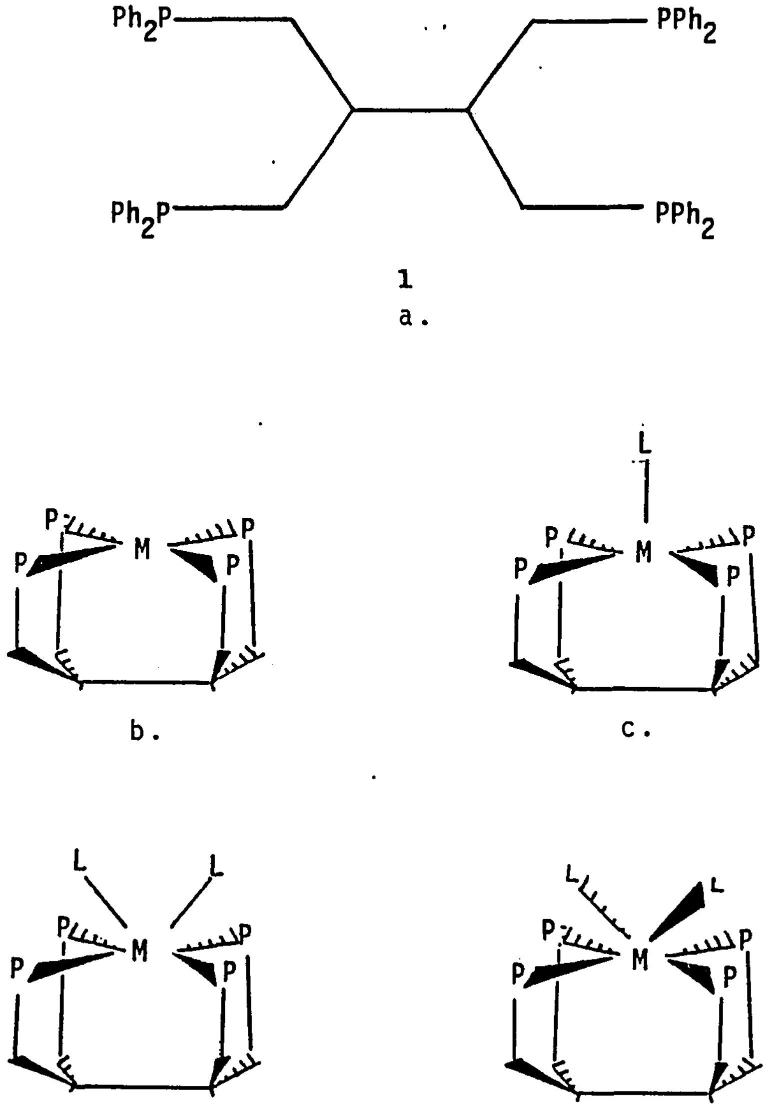
Figure 15. Ortep diagrams of the two isomers of Pd(macrocycle)Cl_2 a) [Pd(A)]Cl_2 and b) [Pd(B)]Cl_2

STATEMENT OF RESEARCH PROJECT

Ligand design is acquiring an entirely new outlook in the field of organometallic chemistry. It encompasses a variety of applications from asymmetric organic reactions mediated by organometallic complexes to solid supported phosphines as ligands which can be used an alternative to homogeneous catalysis.

The goal of this research was to synthesize a new tetradentate phosphine based on the skeletal structure of 1,1,2,2-(tetrahydroxymethyl)ethane (Figure 16a) and to investigate its coordination chemistry. The carbon skeleton of the ligand, 1,1,2,2-(tetra(diphenylphosphinomethyl)ethane (**1**), places strict geometric and steric restraints on metal complexes.

When coordinated to a single metal as shown in Figure 16b-e, two important features of the ligand emerge. First, although there is some degree of freedom in the carbon skeleton of **1**, it is not possible for a metal to achieve true tetrahedral geometry in a monomeric complex of the type M(**1**). When an additional monodentate ligand is added, a true trigonal bipyramidal geometry is also forbidden. Second, the carbon backbone of the ligand sterically inhibits formation of an octahedral complex. Coordination of **1** to transition metal ions must therefore lead to the formation of four and five-coordinate complexes that are



1
a.

b.
c.

d.
e.

Figure 16. Ligand 1 (a), and possible coordination geometries for M(1) complexes: b) square planar, c) square pyramidal, d) trigonal prismatic, and) distorted octahedral

square planar or square pyramidal, respectively (Figure 16, b & c).

Metal ions that typically form six-coordinate octahedra may be forced to be coordinatively unsaturated or achieve six-coordination through trigonal prismatic geometry as shown in Figure 16d. Molecular models show that the phenyl rings are oriented towards the edges of the square plane formed by the four P atoms and away from the corners. This also allows six-coordination by forming a highly distorted octahedron in which two monodentate ligands lie above the P atoms and eclipse diagonal M-P bonds as shown in Figure 16e.

Coordinative unsaturation has been proven to be an important factor in transition metal catalyzed reactions, the initial step of mechanisms often being the dissociation of a ligand to form the active site. It may be argued that a coordinatively unsaturated metal complex of ligand 1 may also inhibit catalyzed reactions by its steric restraints. However the activity of metal complexes is a function of a complicated mixture of both electronic and steric factors, and the reactivity of M(1) type compounds may be significant. If the activity is indeed inhibited by the steric bulk of 1, model complexes using ligand 1 may be used to parallel more reactive complexes whose catalysis is not always readily observed because of fast reaction rates and short-lived intermediates.

Coordination of ligand 1 to metal ions which assume tetradedral, trigonal bipyramidal, or octahedral geometries in complexes of mono-dentate ligands could lead to a highly distorted geometry about the metal, or geometries that are unusual for that metal ion. Investigation of the spectral, physical, and chemical properties of these compounds would provide information concerning bonding and relative stabilities of the geometric conformations.

Group 10 metal ions were initially chosen to investigate the coordination chemistry of 1 because they are well known to form four-coordinate square planar and five-coordinate square pyramidal complexes.[5] Four-coordinate Ni(II), Pd(II), and Pt(II) complexes of 1 and five-coordinate complexes of Pd(II) have been prepared. Within this group of compounds, three modes of coordination of ligand 1 have been observed in which: all four phosphorus atoms are coordinated to a single metal; the ligand bridges two metal centers; and two phosphorus atoms are coordinated and two are uncoordinated.

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SECTION I. PALLADIUM(II) AND NICKEL(II) COMPLEXES OF A PHOSPHINE POCKET LIGAND

INTRODUCTION

In attempts to control the character of coordinated transition metal ions, organometallic chemists have increasingly turned to ligand design. Subtle changes in the basicity, geometry and steric requirements of a ligand can have profound effects on the behavior of the metal.[1] The use of phosphines has proven especially useful in this regard and a tremendous number and variety of phosphine ligands have been reported.[2]

Multidentate phosphines have the additional factor of the chelation effect and variations of the "bite" and the physical arrangement of the donor atoms have been used to impose desired geometries around the coordinated metal center.

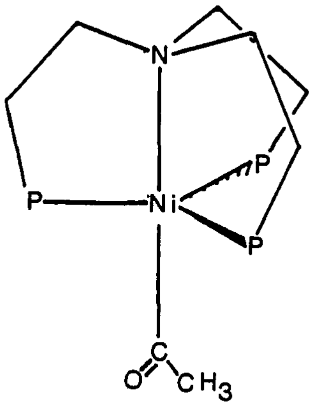


Figure 1. Utilization of a tripod ligand to favor trigonal bipyramidal geometry in $[Ni(np_3)(OCOCH_3)]^+$

Well known examples of this property include the tripod ligands which have been used to favor five-coordinate trigonal bipyramidal complexes, such as $[Ni(Np3)(OCOCH_3)][BF_4]$ (Figure 1)[3] and tetraphosphine analogues of cyclam which have been used to form square planar, square pyramidal and octahedral complexes (Figure 2).[4]

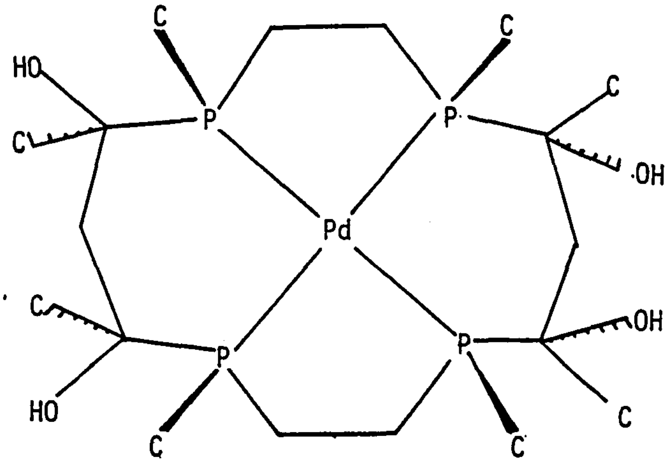


Figure 2. Tetraphosphine macrocylic complex of Pd(II)

We report here a new chelating tetraphosphine (1) (Figure 3) that is unique in its steric and geometric constraints. Four-coordinate complexes are required by the geometry of the ligand to be square planar. Five-coordinate complexes must be square pyramidal, and six coordination can only be achieved through trigonal prismatic or distorted octahedral geometry.

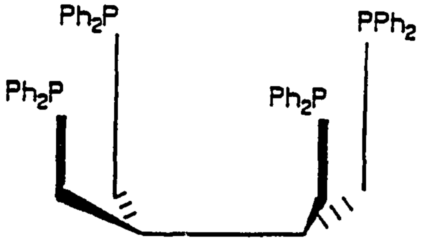


Figure 3. Ligand 1

Group 10 metal ions were chosen to investigate the coordination chemistry of 1 because they are well known to form four-coordinate square planar and five-coordinate square pyramidal complexes.[5] Four and five-coordinate Pd(II) complexes involving two modes of coordination of ligand 1 and a four-coordinate complex of Ni(II) will be presented.

EXPERIMENTAL

General Procedures

All reactions were carried out under an inert atmosphere using solvents that were distilled from an appropriate drying agent under N_2 or Ar prior to use. Reagents were used without further purification unless otherwise noted.

Solution ^{31}P NMR spectra were taken on a Bruker WM-300, or a Bruker WM-200 spectrometer operating in the Fourier mode. Chemical shifts were referenced to an external 85% H_3PO_4 standard. Positive values are downfield of the standard. Solution ^1H and ^{13}C NMR spectra were taken on a Nicolet NT-300 spectrometer operating in the Fourier mode. Both were referenced to internal TMS.

Mid-infrared (4000 to 400 cm^{-1}) and far-infrared (600 to 150 cm^{-1}) spectra were taken on an IBM Fourier IR/98 spectrometer. Mid-IR range samples were prepared as KBr pellets or Nujol mulls on KBr plates; far-IR range samples were prepared as Nujol mulls on polyethylene plates.

Conductance measurements were made with a Markson ElectroMark Analyzer on solutions that were approximately 10^{-3} molar. Elemental analyses were carried out by Schwarzkopf Analytical Laboratory.

Preparation of 2,3-di(hydroxymethyl)-1,4-butanediol (2)

The title tetraalcohol was prepared by a modified version of a synthesis previously reported.[6] A 2 L three neck r.b. flask fitted with a reflux condenser, addition funnel and N_2 inlet was charged with 800 mL THF and 45.0 g (0.919 mol) $LiAlH_4$. The flask was cooled in an ice bath and 88.6 g (0.280 mol) 1,1,2,2-tetracarboxylato-ethane-tetraethyl ester[6] dissolved in 200 mL THF was added over 1.5 h. The reaction mixture was allowed to warm to room temperature followed by heating at reflux overnight. After cooling to room temperature and then to 0 ° in an ice bath, the mixture was quenched by very slow addition of 90 mL H_2O mixed with 200 mL THF. The mixture was stirred for 2 h and refluxed for 1 h. The solid residue was separated by filtration and then extracted with the filtrate in a Soxhlet extractor for three days. The low solubility of the tetraalcohol necessitates extraction to maximize the yield. Evaporation of the solvent and recrystallization from dioxane yielded 18.7 g (45% yield) of 2. (m.p. 111-112 °; lit. 110 °) (^1H NMR (d_6-DMSO): δ 4.48 (5H, t, OH plus presumed trace H_2O), 3.44 (8H, overlying ABX quartets, CH_2), 1.65 (2H, apparent pentet, CH)

Preparation of 2,3-dichloromethyl)-1,4-dichlorobutane (3)

The title tetrachloride was prepared as previously reported.[6] (m.p. 53-54 °; lit. 52-53 °) (^{1}H NMR ($CDCl_3$): δ 3.90 (4H, A part of ABX system, $^2J_{AB}$ = 11.5 Hz, $^2J_{AX}$ = 2.8, CH_2), 3.73 (4H, B part of ABX system, J_{BX} = 6.0, CH_2), 2.29 (2H, m, X part of ABX, CH))

Preparation of 2,3-bis(diphenylphosphinomethyl) 1,4-bis(diphenylphosphino)butane (1)

Ph_2PH was prepared according to the procedure of Bianco and Doronzo.[7] Ph_2PK was generated <u>in situ</u> from 9.0 mL (52 mmol) $HPPh_2$ and 2.02 g (52 mmol) K in 100 mL THF. The reaction was complete after 3 h yielding a red orange solution. This was filtered into a r.b. flask (equipped with reflux condenser and addition funnel) to remove excess K. The phosphide solution was cooled to 0° and 2.65 g (11.9 mmol) of 3 in 50 mL THF was added over 1.5 h. The reaction was allowed to warm to room temperature upon completion of the addition, and then refluxed for 3 h. The excess phosphide was converted to Ph_2PH by addition of H_2O at 0° until the red color of $KPPh_2$ faded. Once isolated, 1 is stable to oxidation in air, but it is highly susceptible to oxidation in the presence of $HPPh_2$ and $H(O)PPh_2$. For this reason, the entire procedure is done with careful exclusion of air in a glove bag or under an Ar blanket.

The reaction mixture was filtered through Celite to remove KCl and then the volume was reduced by half under reduced pressure. Methanol was added to initiate precipitation and the mixture refridgerated overnight. The white product was filtered and recrystallized from 3:1 (v/v) MeOH/C_6H_6. White needles (6.16 g, 63% yield) were filtered, washed with methanol and dried in vacuo.

Further purification was achieved by flash chromatographic separation using Kieselgel 60 silica and benzene.[8] (m.p. 91-93°) (HRMS: m/e 821.817 (calculated m/e 821.769)) (elemental analysis ($C_{54}H_{50}P_4 \cdot 1/2\ C_6H_6$): 79.56% C, 6.31% H, 13.58% P (calc.: 79.62% C, 6.68% H, 13.69% P)) (^{1}H NMR ($CDCl_3$): δ 7 - 7.5 (40H, m, Ph), 2.28 (4H, A part of an ABX system, $^2J_{H-H}$ = 12.37 Hz, $^3J_{H-H}$ = 5.80 Hz, CH_2), 2.05 (6H, m, CH_2, CH) (^{13}C NMR ($CDCl_3$): δ 138.8 (d, $^1J_{CP}$ = 12.7 Hz, Ph-ipso), 133.0 (d of d J_{CP} = 8.8, 8.6 Hz, Ph-ortho, meta), 128.2 (d, $^3J_{CP}$ = 6.7 Hz, Ph-para), 35.92 (triplet of triplets, $^2J_{P-C}$ = 11.91 Hz, $^3J_{P-C}$ = 7.95 Hz, CH), 32.72 (multiplet, CH_2))

Preparation of $[CH(CH_2P(O)Ph_2)_2]_2$ (4)

The ligand 1 was easily oxidized by DMSO. Strong heating (100-130°) of 1 (0.321 g, 0.391 mmol) in DMSO in the presence of a catalytic amount of water for 24 h or sonication of the solution for 16 h quantitatively yields

4. Sonication was carried out by immersion of the reaction flask into a Branson 50-60 Hz ultrasonic cleaning bath. The solvent and side product Me_2S were removed *in vacuo*, and the product recrystallized from CH_3CN to give 0.331 g (96% yield). (m.p. 148 - 150 °) (^1H NMR ($CDCl_3$): δ 7.76 (8H, A part of an ABX system, $^3J_{P-H}$ = 29.85 Hz, $^3J_{H-H}$ = 7.49 Hz, Ph-*ortho*), 7.62 (8H, A' part of an A'BX system, $^3J_{P-H}$ = 29.72 Hz, $^3J_{H-H}$ = 7.62 Hz, Ph-*ortho"*), 7.30-7.45 (24H, multiplet, Ph-m, p), 2.95 (4H, multiplet, CH_2), 2.63 (6H, multiplet, CH_2, CH)), (^{13}C NMR ($CDCl_3$): δ 131.40 (s, Ph-ipso), 130.71 (d, $^2J_{P-C}$ = 6.31 Hz, Ph-ortho), 130.71 (d, $^3J_{P-C}$ = 8.28 Hz, Ph-meta), 128.56 (d, $^4J_{P-C}$ = 11.74 Hz, Ph-para), 35.63 (multiplet, CH_2), 29.67 (multiplet, CH))

Preparation of $PdCl_2)_2(1)$ (5)

Separate solutions of 0.219 g (0.570 mmol) $(PhCN)_2$-$PdCl_2$ and 0.235 g (0.290 mmol) of **1** in 20 mL benzene each were added to 50 mL stirred benzene over 0.5 h at room temperature with the aid of syringes and a syringe drive. The reaction was complete within 5 h, with precipitation of the pale yellow product. Filtration yielded 0.575 g of 5 (86% based on Pd) which was highly insoluble, dissolving only in DMSO. The complex was not purified before use in the next preparation. Recrystallization can be achieved by slow evaporation of a DMSO solution of 5 in air. (^1H NMR

(DMSO-d_6): δ 7.7 (16H, A part of ABX system, $^3J_{P-H}$ = 2.00 Hz, $^3J_{H-H}$ = 2.75 Hz, Ph-ortho), 7.50 (8H, m, Ph-meta), 7.34 (4H, m, Ph-para), 2.18 (4H, m, CH_2), 2.09 (2H, m, CH), 1.14 (4H, m, CH_2)

Preparation of [(DMSO)Pd(1)]Cl_2 (6)

Further reaction of 5 (0.575 g, 0.490 mmol) with an equivalent of 1 (0.403 g, 0.490 mmol), in 100 mL DMSO produces the mononuclear complex 6. The conversion is slow, requiring two to three weeks at room temperature. Completion of the reaction was determined by ^{31}P NMR. The volume of solvent was reduced <u>in vacuo</u> by approximately two thirds. An equal amount of $CHCl_3$ or CH_2Cl_2 was added to increase miscibility with the ether which was added to initiate precipitation. The product was isolated as a pale yellow solid (0.372 g; 76% yield). The solid was separated by filtration, washed with ether and dried <u>in vacuo</u>. (^{13}C NMR (DMSO): δ 131.87 (m, Ph-ipso), 131.00 (s, br, Ph-ortho), 129.89 (s, br, Ph-meta), 128.56 (s, br, Ph-para), CH_2 and CH not observed)

Preparation of [(DMSO)Pd(1)]$^{2+}$(7)

It is simplest to proceed directly from the preparation of 5 to 7 via 6 without purification of 5 or 6. The chlorides were easily removed from 6 with Ag(BF_4)

or Ag(AsF_6) to give 7. In 75 mL of 50:50 (v/v) $CHCl_3$/DMSO, 0.372 g (0.372 mmol) of 6 was stirred with 0.145 g (0.730 mmol) $AgBF_4$ for 2 h. AgCl (0.096 g) was collected (92% theoretical based on 2 Cl per Pd). The volume of the filtrate was reduced by half and ether added to initiate precipitation. Cooling of the mixture yielded 0.358 g (87% yield) of 7 as a pale yellow powder. The product is soluble in DMSO and CH_3CN. Complex 7 is stable in air in the solid state, but slowly decomposes in solution. In a similar experiement, 0.110 g (0.110 mmol) of 6 was reacted with 0.062 g (0.022 mmol) $AgAsF_6$ yielded 78% of complex 7. (^1H NMR (DMSO): δ 7.6 (40 H, br, m, Ph), 2.73 (4H, m, CH_2), 2.50 (8H, s, DMSO), 2.21 (6H, m, CH_2, CH)) (^{13}C NMR (DMSO): δ 131.61 (m, Ph-ipso), 130.38 (s, Ph-ortho), 129.79 (s, Ph-meta), 128.90 (s, Ph-para), 39.70 (s, DMSO))

Preparation of $[(CH_3CN)Pd(1)]^{2+}$(8)

Reprecipitation of 7 from CH_3CN with ether affords the title complex in which one molecule of CH_3CN remains associated with the metal complex in the solid state (8). (^1H NMR (CD_3CN): δ 7.5 (40H, br, m, Ph), 2.75 (4H, m, CH_2), 2.25 (6H, m, CH_2, CH), 1.96 (3H, s, CH_3CN-Pd)) (^{13}C NMR (CD_3CN): δ 133.2 (A part of an AXX' system, $^1J_{P\text{-}C}$ = 20.53 Hz, $^3J_{P\text{-}M\text{-}C}$ = 37.25 Hz, Ph-ipso), 131.6 (s, Ph-ortho), 129.9 (s, Ph-meta), 128.1 (s, Ph-para), CH_2 and CH not observed, 117.28 (s, CN), 0.40 (pentet, CH_3 of CH_3CN & CD_3CN))

Preparation of $[Ni(1)][ClO_4]_2$ (9)

Anhydrous $[Ni(CH_3CN)_6][ClO_4]_2$ was prepared from the hydrated salt by stirring overnight in 2,2-dimethoxypropane followed by addition of CH_3CN. The volume was reduced and ether added to precipitate the lavender blue product which was recrystallized from CH_3CN prior to further use.

Ligand 1 (0.0354 g, 0.0431 mmol) was dissolved in 5 mL benzene and added via syringe to a stirred solution of 0.0217 g (0.0431 mmol) $[Ni(CH_3CN)_6][ClO_4]_2$ in 50 mL CH_3CN at room temperature. During the addition, the solution turned orange brown but remained homogeneous. The reaction was stirred 16 h to produce the light yellow color characteristic of the product. The volume of the solution was reduced to approximately half under reduced pressure and the solution refridgerated to crystallize the product as light yellow prisms. (^1H NMR (CD_3CN): δ 7.63 (24H, m, Ph), 7.3-7.5 (16H, m, Ph), 2.75 (4H, m, CH_2), 2.50 (6H, m, CH_2, CH)) (^{13}C NMR (CD_3CN): δ 131.0 (m, Ph-ipso), 130.0 (m, Ph-ortho, meta), 128.1 (m, Ph-para), CH_2 and CH not observed)

X-ray Crystallographic Procedure for 4

Data Collection and Reduction

Crystals were grown from an CH_3CN solution of 4 by slow evaporation in air. A suitable crystal for data collection, approximately 0.10-0.12 mm on a side was selected, placed in a glass capillary and mounted on a standard goniometer. All intensity data were collected at room temperature. The unit cell parameters were initially calculated using an automatic indexing procedure[10] and subsequently verified by oscillation photographs. Final lattice constants were determined by a least squares fit to the $+2\theta$ values of 14 higher angle reflections. The intensity data were corrected for Lorentz and polarization effects. The standard deviation of a reflection was computed using the relationship:

$$I^2 = C_T + k_T C_B + (0.03C_T)^2 + (0.03C_B)^2$$

where C_T and C_B represent total and background counts and k_T is a counting time factor. Table I contains a tabulation of the pertinent information relevant to data collection and reduction.

Structure Solution and Refinement

The majority of the non-hydrogen atom positions was identified using direct-methods routines.[11] The remaining non-hydrogen atoms were located via alternate cycles of least squares calculations[12] and electron density difference density calculations.[13] The atomic scattering factors used were those found in the International Tables.[14a] Positions of the hydrogen atoms were calculated using an assumed C-H bond distance of 1.0 Å and a C-H bond angle of 109 .

Analysis of residual electron density on an electron density difference map (maximum = 0.4 e/Å^3) indicated all atoms were accounted for by the model.

X-ray Crystallographic Procedures for 5[9]

Data Collection and Reduction

A crystal suitable for data collection, approximately 0.08-0.15 mm on a side was selected, attached to a glass fiber and mounted on a standard goniometer. All intensity data were collected at room temperature. The unit cell dimensions and Bravais lattice type were initially calculated using an automatic indexing procedure[10] and subsequently verified by oscillation photographs. The observed systematic absences of 0k0, k = 2n+1 and h0l, h+l = 2n+1 indicated the space group $P2_{1/n}$. Final lattice constants were determined by a least squares fit to the +2θ values of 12 higher angle reflections. The intensity data were corrected for Lorentz and polarization effects. Table

II contains a tabulation of the pertinent information relevant to data collection and reduction.

Structure Solution and Refinement

Analysis of palladium-palladium vectors from the three-dimensional Patterson map revealed the appropriate positions for the palladium atoms in the unit cell. The remaining non-hydrogen atoms were located via alternate cycles of least squares calculations[12] and electron density difference density calculation.[13] The atomic scattering factors used were those found in the International Tables.[14a] Positions of the hydrogen atoms were calculated using an assumed C-H bond distance of 1.0 Å. Thermal parameters for the phenyl rings and the DMSO atoms were refined isotropically. The data were reweighted prior to the final least squares cycle so that $\omega(|F_0| - |F_c|)^2$ was approximately constant as a function of sinθ.

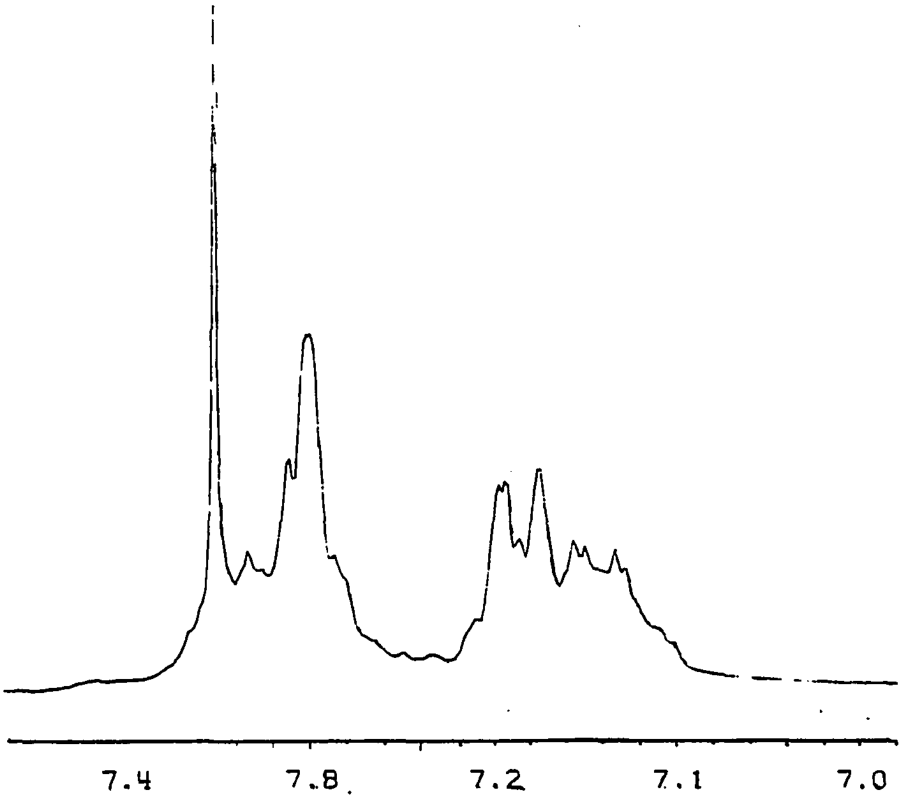
Restraints[14b] were imposed upon the C-C bond distances in the phenyl rings due to the relatively small contribution to the total scattering made by the individual carbon atoms when compared to the scattering power of the molecule and possible disorder in the ring positions. Analytical scattering factors were used[15], and the targets for the restrained phenyl distances were set to 1.40 . Residual electron density found on an electron density difference map indicated the possible presence of one or more highly disordered DMSO groups and some disorder in the phenyl ring orientations. These artifacts were not modelled due to the small occupancies of these disordered sites (<0.16). Since estimated standard deviations are not obtainable from RESLSQ, the parameters were used without restraints in a full-matrix least squares procedure. The esd's were obtained from the inverse of the normal equations matrix and therefore represent maxima for these values.

RESULTS AND DISCUSSION

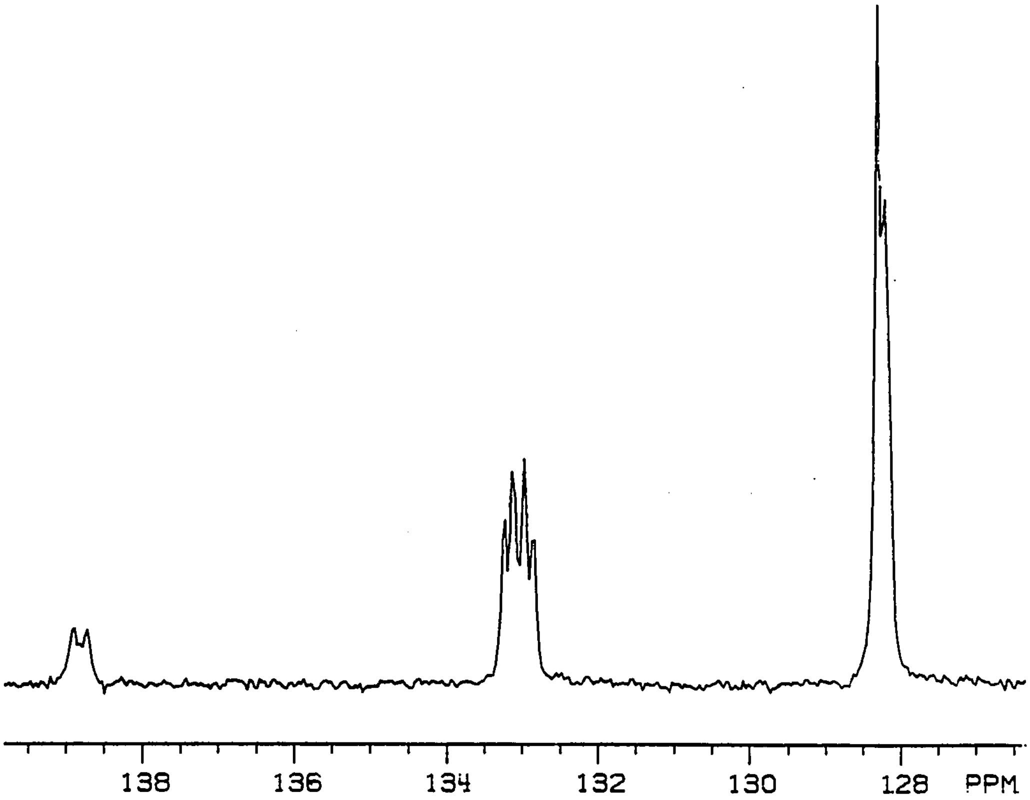
Tetraphosphine 1 and its oxide derivative 4

Ligand 1 was prepared in moderate yields (50 - 60%) and recrystallized from benzene to give a crystalline product at room temperature. It is stable in air, but susceptible to oxidation as a DMSO solution. The tetraphosphine 1 is very soluble in most organic solvents such as benzene and CH_2Cl_2, and oxidation was not observed when these solutions were exposed to air.

The ^{31}P NMR spectrum (Table III) shows a single sharp resonance at -22.0 ppm. The phenyl region of the ^{1}H NMR spectrum has two broad multiplets between 7.36 and 7.22 ppm, and 7.20 and 7.08 ppm (Figure 4a). In all of the tetra-functional derivatives of 2, the methylene hydrogens are diastereotopic and appear as ABX quartets. The resonances due to the methylene hydrogens in 1 are seen as multiplets at 2.25 and 2.05 ppm. The high-field multiplet is complex, and represents one set of diastereotopic methylene hydrogens and the methine hydrogens. The ABX pattern of the low-field CH_2 resonance is well resolved, with a two-bond coupling between the geminal hydrogens of 12.37 Hz, and a vicinal three-bond H-H coupling of 5.8 Hz. The peaks are broadened with shoulders due to a two-bond and probably a four-bond coupling to phosphorus which is small, on the order of 1 Hz.



a.



b.

Figure 4. Phenyl region of a) ^{1}H NMR spectrum and b) ^{13}C NMR spectrum of 1

In the ^{13}C NMR spectrum (Figure 4b), the resonances for the phenyl group carbon atoms appear as doublets with P-C coupling constants of 12.7 Hz (*ipso*), 8.6 Hz and 8.8 Hz (*ortho*, *meta*), and 6.7 Hz (*para*). The methine carbon is coupled to all four phosphorus atoms, giving a triplet of triplets which appear as an uneven pentet with $^{2}J_{P-C}$ = 11.91 Hz and $^{3}J_{P-C}$ = 7.95 Hz. The methylene carbon appears as an unsymmetrical singlet.

In the presence or absence of air, DMSO solutions of 1 containing 1 mole percent water are easily oxidized by heating or sonication, and are more slowly oxidized at room temperature. The oxidation of tertiary phosphines by DMSO in the presence of catalytic amounts of iodine, acid, or transition metal ions has been reported (equation 1).[16-19] In each case the function of the catalyst is to increase

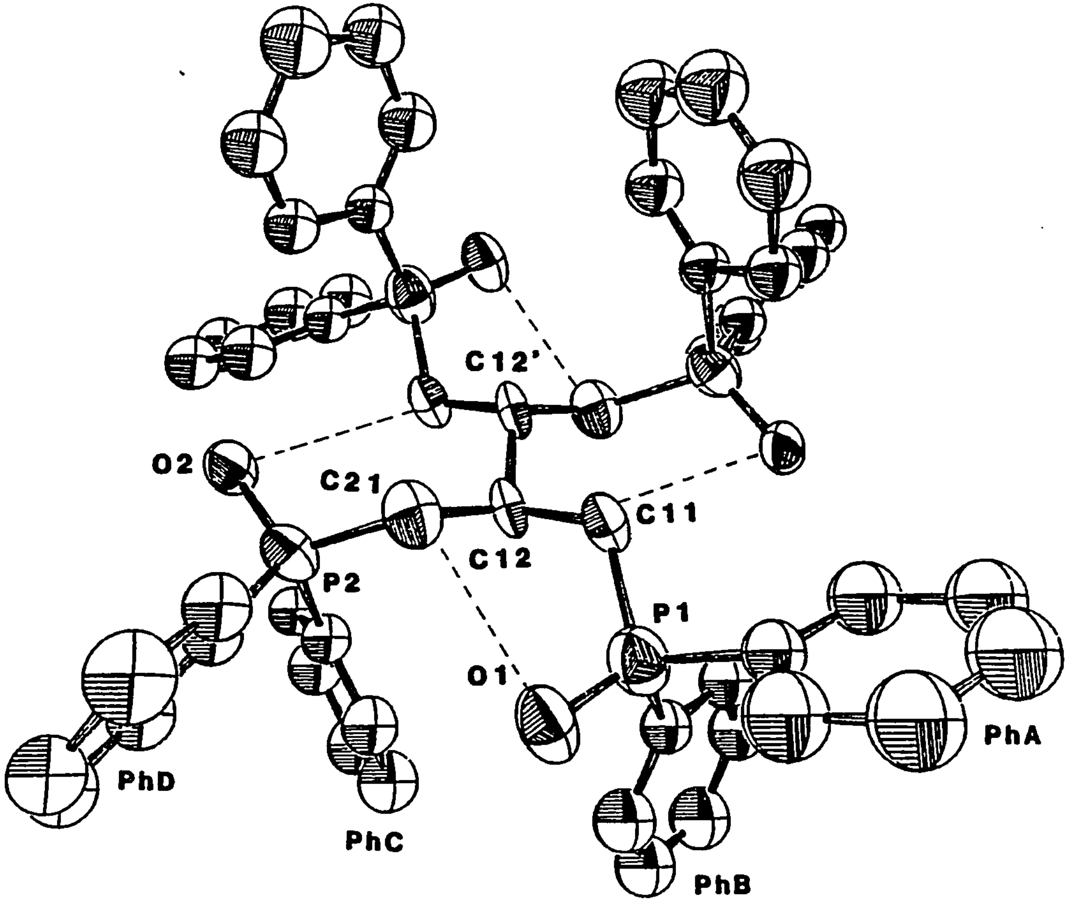
$$R_3P + (CH_3)_2SO \longrightarrow R_3P(O) + (CH_3)_2S \qquad (1)$$

the electrophilic nature of either the phosphorus or sulfur, causing nucleophilic attack by oxygen or phosphorus, respectively. In the strict absence of water or other impurities, oxidation is only achieved in low yield at temperatures over 180°.[19] The oxidation of aryl tertiary phosphines by DMSO has not been widely used in synthesis because of inefficiency and the subsequent difficulty in separating the products. We have found the oxidation of 1 by DMSO to be greatly enhanced by sonication, leaving only volatile dimethyl sulfide, excess DMSO and the product phosphine oxide.

A single crystal of the oxide derivative 4, isolated from an acetonitrile solution, was suitable for X-ray crystallographic analysis. The ORTEP diagram of 4,[20] together with a labeling scheme is presented in Figure 5, the unit cell is given in Figure 6. Selected bond distances, bond angles and interplanar angles can be found in Tables IV,V, and VI; positional parameters appear in Table VII. Tables of anisotropic thermal parameters, hydrogen atom coordinates and structure factors appear in Appendix I.

There are two crystallographically unique molecules in the unit cell. One half of each molecule is related to its second half by an inversion center at the center of the skeletal CH-CH bond. In both molecules the phosphoryl oxygen atoms are oriented in the same direction in a paddle wheel fashion due to hydrogen bonding which is indicated in Figure 5 by dashed lines. The difference between the two molecules is found in the angles of the phenyl ring planes (A, B; C, D; E, F;and G, H) relative to the remainder of the molecule. The greatest deviation lies between the pairs of rings C, D and E, F which are rotated by almost 60° relative to one another.

The oxide of bis(diphenylphosphino)methane (dppm) similarly crystallizes with two unique molecules in the unit cell, and has P-O bond lengths varying from 1.484(5) to 1.500(5) Å.[21] Other non-hydrogen bonded systems have P-O bond distances that fall between 1.48 and 1.50 Å.[22-23] Three of the P-O distances in 4 fall at least at the upper limit, if not outside of this range: 1.468(1) Å at P1, 1.511(1) Å at P2, 1.547(2) Å at P3, and 1.515(1) Å at P4. The lengthening of the P-O bonds may be due to weak intramolecular hydrogen bonding. Each phosphoryl oxygen atom is hydrogen bonded to a methylene of an adjacent "arm". This also accounts for the paddle wheel orientation of the four arms, each one being pulled over the following methylene. Bond distances between oxygen and hydrogen bonded atoms are typically between 2.5 and 2.8 Å.[22] The distances between the hydrogen bonded oxygen and carbon atoms in 4 are 3.18(1) Å at O1, 3.20(1) Å at O2, 3.16(1) Å at O3 and 3.17(1) Å at O4. The long P3-O3 bond distance (1.547(2) Å) approaches the distance of a P-O single bond, which typically falls between 1.55 and 1.59 Å. The bond distances between the phosphoryl oxygen and the methylene carbons are long for hydrogen bonding. However, the long P-O bond distances suggest some interaction.


C12'
O2
C21
C11
C12
P2
P1
O1
PhA
PhD
PhC
PhB

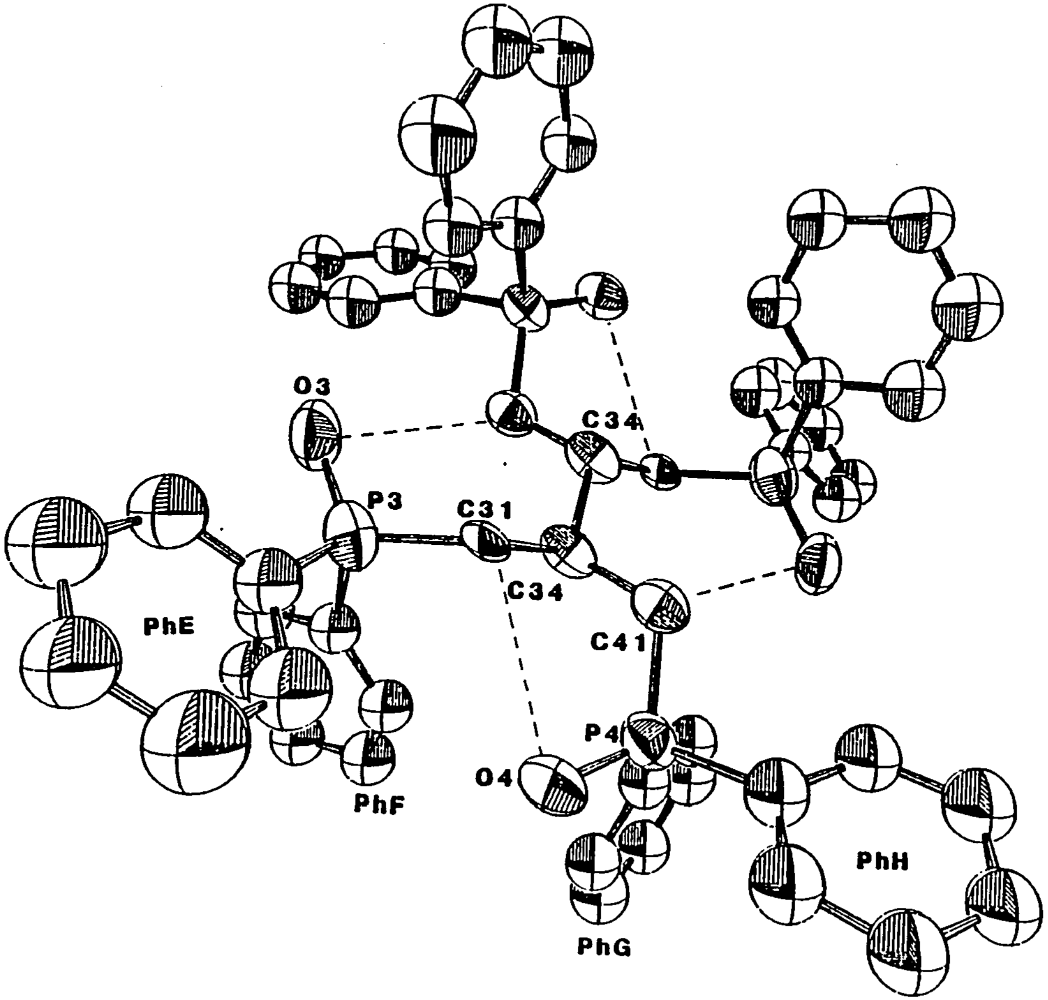


Figure 5. Ortep diagram of the two crystallographically unique molecules of 4

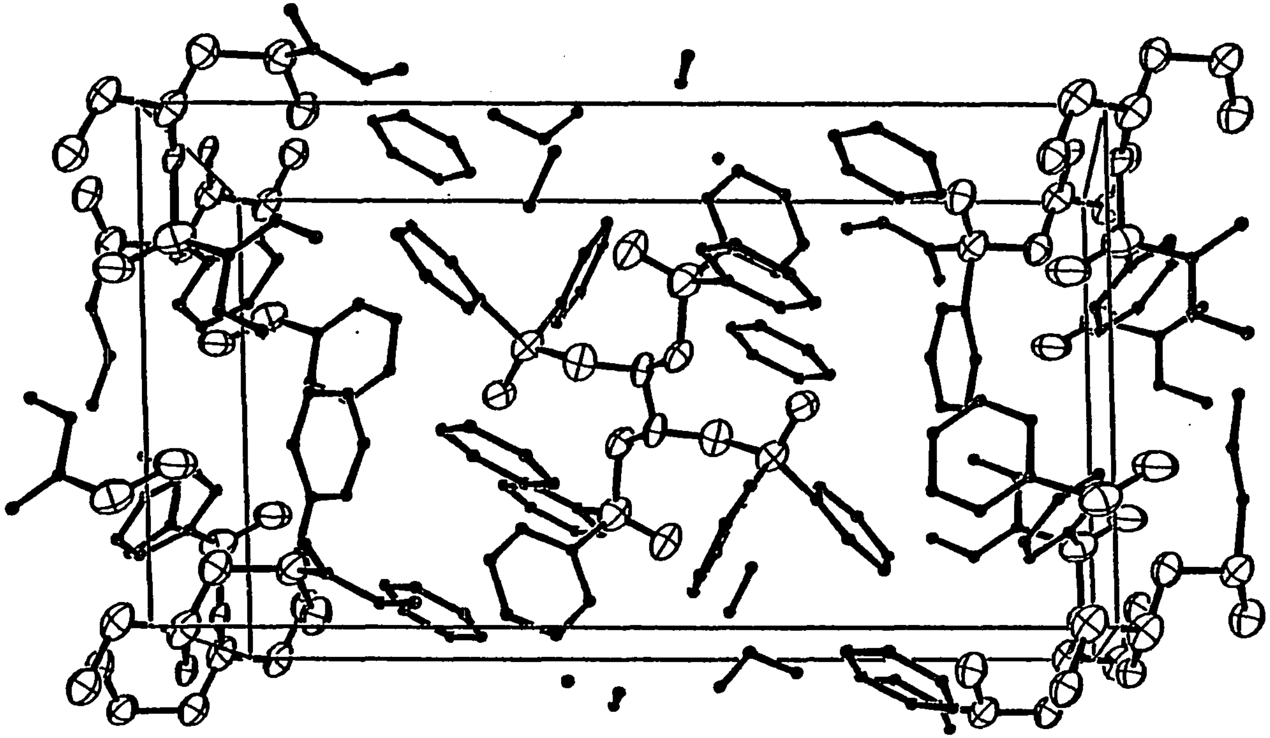
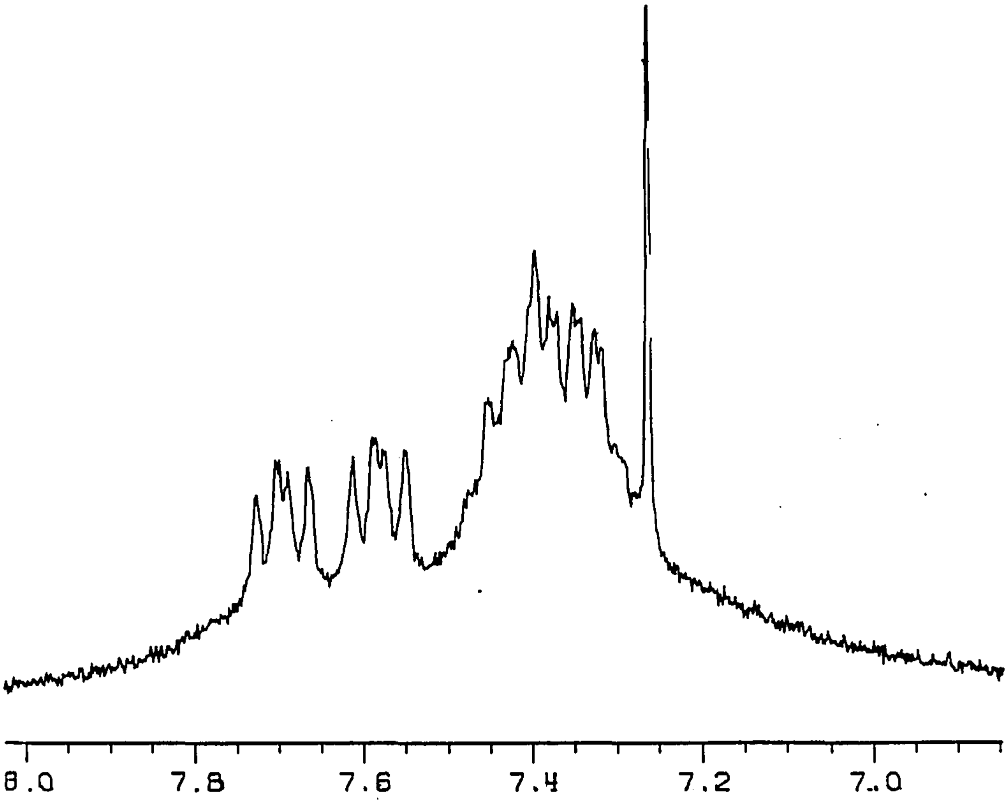


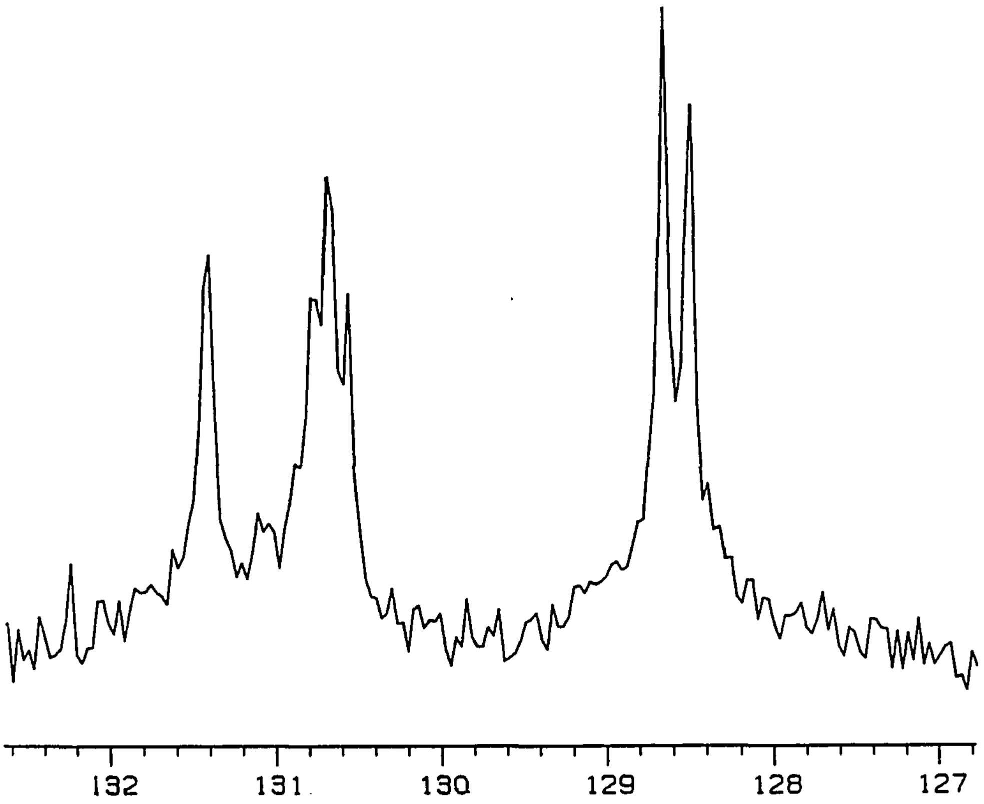
Figure 6. Diagram of the unit cell of 4

The O-H distances are 2.37(1) Å at O1, 2.20(1) Å at O2, 2.17(1) Å at O3, and 2.34 Å at O4, with O-H-C angles of 138.6(3)°, 172.0(3)°, 169.7(2)°, and 140.4(3)°, respectively. However, the hydrogen atom positions were calculated based on idealized tetrahedral geometry at carbon and C-H bond lengths of 1.00 Å, and may not accurately reflect the bonding situation.

The ^{31}P NMR shift of 4 occurs at 37.6 ppm. In the ^{1}H NMR spectrum, two ABX patterns are observed for the *ortho* hydrogens of the phenyl groups with coupling constants of 7.65 and 7.62 Hz, and 29.85 and 29.72 Hz (Figure 7). The *meat* and *para* hydrogens appear as a complicated eleven line multiplet that was not resolved. In the solid state, inequivalency arises from the orientation of one ortho hydrogen toward the phosphoryl oxygen and the other toward the bulk of the molecule. In solution, however, these should become equivalent through rotation. Since strong hydrogen bonding is prevalent in the solid state, it is likely to be responsible for the inequivalency in solution through restricted rotation about the P-Ph bond. The ^{13}C NMR spectrum does not exhibit the same inequivalency, giving single resonances for the *ipso*, *ortho*, *meta*, and *para* carbons with J_{P-C} values of 6.13 and 8.28 Hz for the *ortho* and *meta*, and 11.74 Hz for *para* carbons. No coupling to phosphorus was observed for the *ipso* carbon. The ^{1}H and



a.



b.

Figure 7. Phenyl region of the a) ^{1}H NMR spectrum of 4, and b) ^{13}C NMR spectrum of 4

^{13}C NMR spectra were taken for the same sample, and it is not clear why the inequivalency of the _ortho_ hydrogens is absent in the ^{13}C spectrum.

Metal Complexes of 1

Attempts to produce Pd(II) and Pt(II) complexes of 1 met with complicated results prior to the discovery of the synthetic route discussed below. Reaction of 1 with $PdCl_2$ in ethanol, DMSO, or CH_3CN, or with $[PdCOCl]_n$ in CH_2Cl_2 yielded inconsistent product distributions with ^{31}P NMR resonances of various intensities in the regions 31 - 30, 20, -5 ppm, and for the uncoordinated ligand 1 at -22 ppm.

Dipalladium Complex 5

Reaction of $(PhCN)_2PdCl_2$ with 1 in benzene yielded the dinuclear complex 5 regardless of the stoichiometry of the reactants. When the reaction was done with mole ratios ranging from one ligand to one $(PhCN)_2PdCl_2$, to one ligand to two $(PhCN)_2PdCl_2$, 5 precipitates, leaving the excess ligand in solution. The product is a pale yellow solid soluble only in DMSO and stable in both the solid state and in solution. Plate-like crystals for X-ray analysis were grown from a DMSO solution by slow evaporation in air.

The ORTEP diagram and labeling scheme is given in Figure 8.[20] A view containing only the heavy atoms and the skeletal carbons is given in Figure 9. Selected bond distances and bond angles appear in Tables VIII and IX. The atomic positional parameters are listed in Table X. Tables of anisotropic thermal parameters, hydrogen atom coordinates, and structure factors are given in Appendix II.

The stereochemistry at Pd is essentially square planar with the Pd atom residing 0.071 Å out of the plane. The six-membered rings formed by the Pd, two P, and three C atoms of the ligand skeleton are in the chair conformation and are approximately orthogonal. The phenyl rings are anti-diaxial rather than syn-diaxial to avoid 1,3-syn-diaxial steric interactions.

Considering each half of the complex as a P_2-Pd-Cl_2 unit, gives rise to an analogue to the structurally characterized $Cl_2Pd((PPh_2)_2(CH_2)_n)$ series of compounds, where n = 1 (dppm), 2 (dppe), or 3 (dppp).[23,24] Within this series there is no reason to expect the electronic properties of the phosphorus donor to vary except as a function of steric constraints in the complexes. The steric and resulting electronic properties of 1 relative to dppe and dppp can be qualitatively understood by including $(PdCl_2)_2$(1) in the series Cl_2Pd(diphosphine) (Figure 10).

For this consideration, the L = dppm (n = 1) case will be omitted. In this case the electronic and steric factors were determined to be much more complex for dppm than for

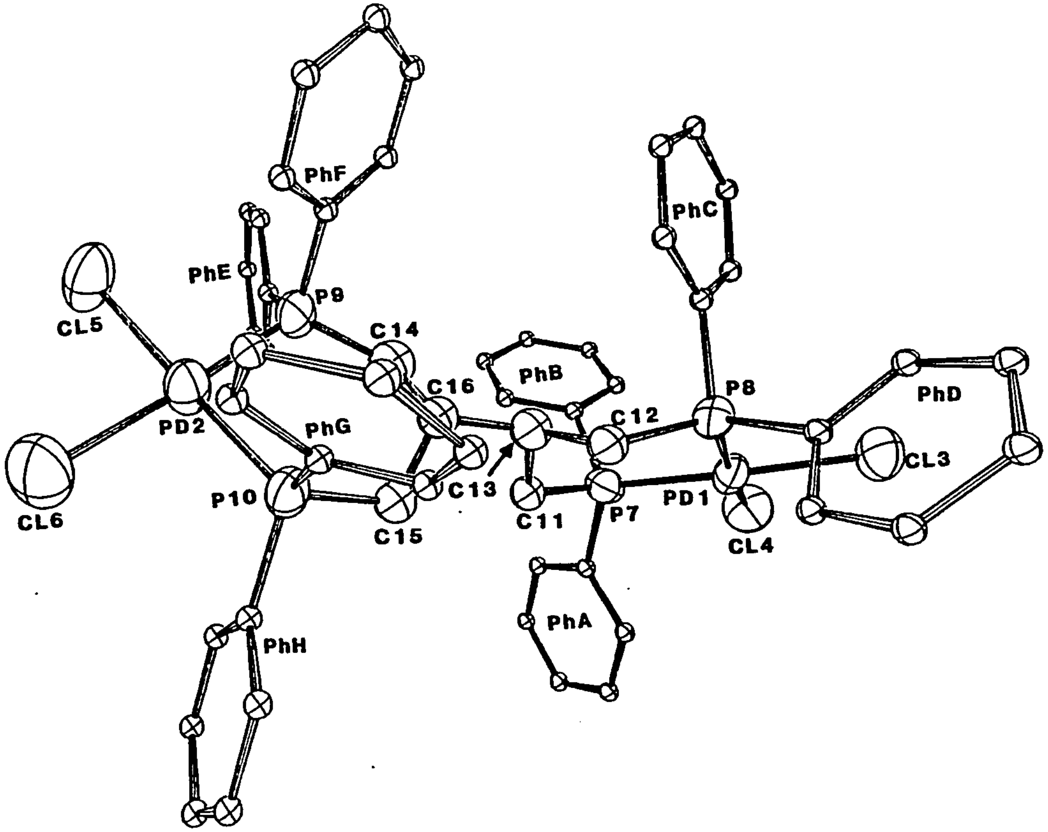


Figure 8. Complete ortep diagram of 5

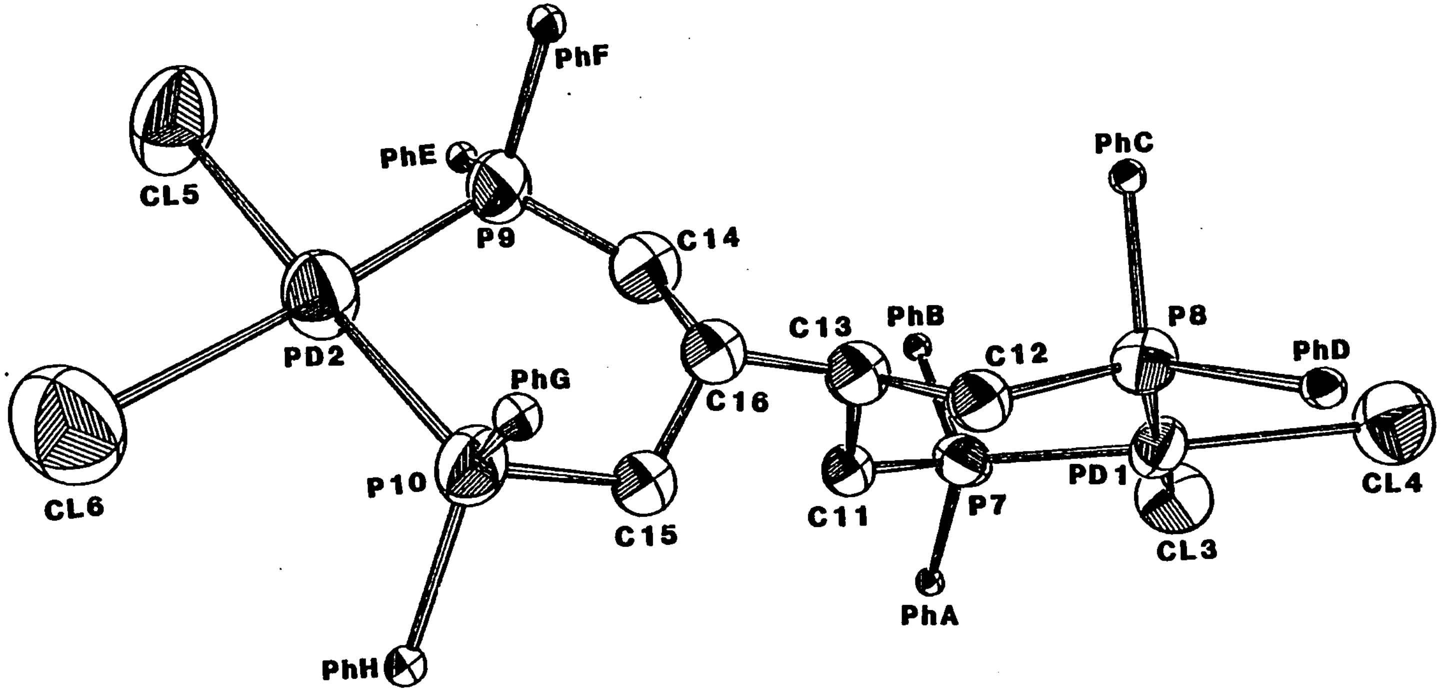
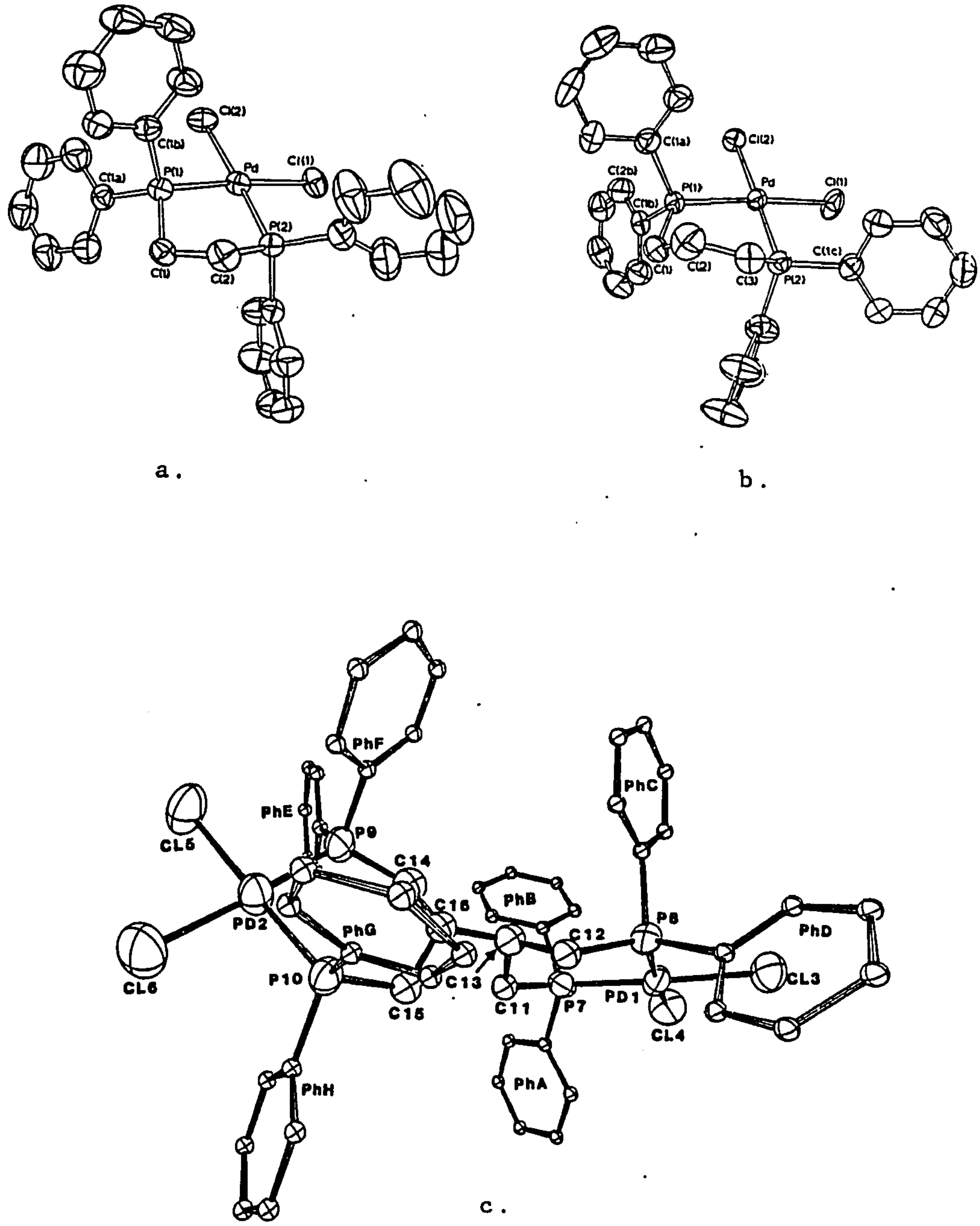


Figure 9. Ortep diagram of 5, showing only the heavy atoms and skeletal carbons

dppe and dppp owing to the small bite angle of dppm which places the P atoms unusually close to the Pd.[25]

The steric bulk in $Pd(L)Cl_2$ increases as L is changed from dppe (n = 2), to dppp (n = 3) and this increase would be expected to be very similar between dppp and ligand 1. The bond angles around the Pd and P atoms are an indication of steric strain, and the Pd-P and Pd-Cl bond distances provide a simple measure of this effect on the electronic nature of the phosphines. Coordination of dppe forms a five-membered chelate ring which creates the least strain and forms a nearly ideal square planar geometry around Pd. The addition of another methylene in the chelate ring to form dppp or 1 causes a widening of the P-Pd-P angle. For dppe the P-Pd-P angle is 85.82(7) °; for dppp, it is 90.58(5) ° and in the L = 1 analogue, the angle is further increased to 93.7(4) and 94.5(5) °. There is a corresponding decrease in the Cl-Pd-Cl angle from 94.19(7) for dppe, to 90.78(5)° for dppp, and 89.6(4)° and 90.65(6)° for 1. The Cl-Pd-Cl angle in $(PdCl_2)_2(1)$ does not decrease as much as might be predicted based on the increase in the P-Pd-P angle. The angle between the Cl atoms appears to have reached a minimum relative to the distortion in the complex. The conformational strain induced by the propylene ring and the interactions among



a.

b.

c.

Figure 10. Ortep diagrams of a) $Cl_2Pd(dppe)_2$, b) $Cl_2Pd(dppp)_2$, and c) $(Cl_2Pd)_2(\mathbf{1})$

phenyl groups must now be alleviated by deviation from planarity in the P_2-Pd-Cl_2 unit.

There is a similar trend between the dppe and dppp complexes in the lengthening of the P-Pd bonds and concomitant shortening of the Cl-Pd bonds. The P-Pd bond length increases from 2.233(2) and 2.226(2) Å for the dppe complex to 2.244(1) and 2.249(2) Å for the dppp complex. The bond distances in 5 are similar to those values for the dppe and dppp analogues, although large standard deviations in the bond distances of 5 due to disorder in the molecule, prevent the identification of a trend. The Pd-P bond lengths in 5 are between 2.23(1) and 2.26(1) Å. The Cl-Pd bond lengths are between 2.357(2) and 2.362(1) Å in $PdCl_2$dppe, 2.351(1) and 2.358(2) Å in $PdCl_2$dppm, and between 2.32(1) and 2.36(1) Å in 5.

The length of the Pd-Cl bonds can be used as a measure of the trans effect of the phosphine, which is dependent upon the basicity of the phosphine. A large trans effect causes the lengthening of the Pd-Cl bond by strong sigma electron donation of the phosphorus. Within the series being discussed, the dppe complex has the longest Pd-Cl bond distances, and thus is the more basic phosphine. The substituents on the phosphorus atoms within the series are equivalent so that electronic arguments can not be used to rationalize this difference in bond lengths. The five membered chelate ring of dppe induces the least steric strain and this results in an effectively more basic phosphine. In comparing dppp and 1, there is little difference in the bond lengths around the Pd atom but there is a substantial increase in the P-Pd-P bond angle. It is unclear why this angle in $(PdCl_2)_2(1)$ is larger than in the dppp analogue. There are no interactions within the $PdCl_2(1)$ unit or between the two units in the molecule which could be used to rationalize this observation.

Monopalladium Complexes

Further reaction of 5 with an equivalent of the ligand 1 yields the monopalladium complex 6 in which all four phosphines are apparently coordinated to one metal atom.

The reaction of 5 with ligand 1 occurs in DMSO and requires relativley long reaction times of 2 to 3 weeks. Mild heating reduces the reaction time, but an inert atmosphere and dry DMSO are required to prevent oxidation of the ligand. In the presence of air, or in the absence of air at temperatures over 80 °C, extensive oxidation of the ligand resulted with minor yield of the Pd product.

Monitoring the reaction by ^{31}P NMR initially showed two sharp resonances at +21.4 and -22.0 ppm for 5 and the ligand, respectively. As the reaction progressed, these peaks divided into multiplets and began to disappear as a group of 3 to 5 peaks centered at $+31 \pm 6$ ppm grew. The end of the reaction was signalled by the presence of a single sharp resonance at +30.8 ppm. No absorptions were observed in the IR that could be assigned to Pd-Cl and the conductance of 6, 42.6 cm^{2} $^{-1}$molΩ^{-1}, in DMSO is consistent with a two to one electrolyte (Table III). The ^{1}H NMR of 6 is equivalent to that of 7 in DMSO and the cation was further characterized as 7.

The monopalladium dication was characterized as the tetrafluoroborate salt (7). Crystals of 7 could not be obtained, thus eliminating the possibility of an X-ray structure analysis. A single resonance in the ^{31}P NMR spectrum indicated equivalence of the four phosphine arms. The ^{1}H NMR spectrum is consistent with equivalency, giving a pattern very similar to the free phosphine. The phenyl resonances remain a complicated multiplet but shifted downfield by 2 ppm. The methylene protons appear as two complex ABX multiplets, one overlying the methine protons, and shifted downfield by 0.4 and 0.2 ppm from the uncoordinated ligand 1. The ^{13}C NMR spectrum was not very informative, giving broadened signals from which coupling constants could not be determined. The resonance for the ipso carbon, at 131.6 ppm has shifted upfield by 7 ppm from the free ligand, and the ortho and meta carbons are similarly shifted upfield by 3 ppm. The para carbon remains close to that of the free ligand at 128.9 ppm. The methylene and methine carbons were not observed, and the solvent, DMSO appears at 39.7 ppm.

It is interesting to note that in all of the metal complexes of 1 studied, the methylene and methine carbons were not observed in the ^{13}C spectra. The intensity of the resonances representing these carbons is already diminished in the spectrum of the free ligand because of altered relaxation times due to proximity to the phosphorus atom and the presence of only one hydrogen on the methine carbon. Coordination of 1 to metal ions further increases the relaxation times, thus decreasing the intensity of those signals.[26]

When 7 as the BF_4^- salt was isolated from a DMSO solution, DMSO remains in the complex. In CH_3CN the ^1H NMR spectrum did not show a shift in the resonance for coordinated DMSO relative to free DMSO, which may be due to exchange with residual DMSO that was difficult to remove. Coordinated CH_3CN was not observed in the spectrum. When run in DMSO, the ^1H NMR spectrum showed only one broad peak for DMSO. A shift in the resonances for DMSO upon coordination to Pd may not be observed because of fast exchange with free DMSO on the NMR time scale. On the other hand, the change in the chemical shift may be very small. DMSO coordinated to Pd (as verified by IR spectral data) shows changes in shifts in the ^{1}H NMR spectra from 0.02 to 0.80 ppm.[27]

Generally, DMSO coordinates to soft metals such as Pd and Pt via the sulfur atom. When DMSO is bonded through S, ν_{S-O} is shifted from 1055 cm^{-1} in free DMSO to higher energy, i.e., between 1116 and 1157 cm^{-1} in the complex.[28,29] Recently it has also been determined that DMSO will coordinate through the oxygen atom when the other ligands are bulky.[29] In this case ν_{S-O} shifts to lower energy, between 900 and 1100 cm^{-1}. The infrared data are diagnostic regarding sulfur vs. oxygen coordination, but such spectra are complicated by the presence of several other medium to strong absorptions in the same region. The IR spectrum of 7 shows a strong absorption at 1008 cm^{-1}, indicating coordination of DMSO to Pd through the O atom, which is most reasonable considering the steric bulk of the ligand.

When 7 is precipitated from CH_3CN with ether, one molecule of solvent is retained in the solid to give 8. The ^{1}H NMR spectrum of 8 taken after 16 h of drying at 0.10 mm Hg continued to show one CH_3CN molecule per molecule 8. In the ^{1}H NMR there is a downfield shift of CH_3CN of 0.03 ppm. Other coordination complexes in which CH_3CN is bonded to a metal show a downfield shift of 0.50 ppm,[28] which is significantly larger than that observed for 8.[27] The ^{13}C

NMR spectrum taken at 45 ° does show upfield shifts of 1 ppm for the nitrile carbon and 0.9 ppm for the methyl carbon. The phenyl region of this spectrum is similar to that of 7, giving broad, poorly resolved signals.

The possibility of fast exchange of the phosphines on the NMR time scale was explored with variable temperature NMR. The ^{31}P NMR remains a single resonance at -43°, suggesting all four phosphine arms are coordinated to the Pd. However, as we have seen in the ^{13}C NMR spectrum, at this temperature, the phenyl region of the spectrum remains broad and poorly resolved. The temperature was limited by the solvent, CH_3CN, and a mechanism in which coordinated and uncoordinated phosphine arms are exchanging remains a possibility. Removal of both chlorides from the system was verified by precipitation of a stoichiometric amount of AgCl, and the absence of ν_{Pd-Cl} in the IR spectrum. Additionally, the conductance of 8 as the BF_4^- salt in CH_3CN, 195 $cm^2\,\Omega^{1}mol^{-1}$, lies within the expected range for a two-to-one electrolyte. The amibiguity of the low temperature ^{31}P and ^{13}C NMR spectra gives rise to possible displacement of a phosphine by DMSO or CH_3CN and fast rearrangement of the phosphines on the NMR time scale.

Ni Complex 9

Reaction of 1 with Ni salts did not yield a dinuclear complex analogous to 5. In ethanol, reaction of $Ni(PF_6)_2$

hydrate yielded a variety of products including an insoluble compound which gave multiple resonances in the ^{31}P NMR spectrum and was assumed to be polymeric in nature. The solution phase of the reaction gave resonances in the +31, +26, and +15 regions of the spectrum. Free ligand 1 was not observed in the spectra.

When an anhydrous Ni(II) salt was treated with ligand 1 in CH_3CN, a single product was obtained. Reaction of $[(CH_3CN)_6Ni](ClO_4)_2$ with 1 yielded the yellow complex 9 as the only product. Crystals of 9 were isolated, but were thin plates and unsuitable for X-ray diffraction. The ^{31}P NMR chemical shift for 9 is very close to that for the palladium analogue 8 (31.5 ppm and 30.9 ppm, respectively). The ^1H NMR in CH_3CN is also very similar to that of complex 8. The phenyl hydrogens appear as broad multiplets at 7.63 and 7.4 ppm, the methylene and methine hydrogens at 2.75 and 2.50 ppm, respectively. No residual CH_3CN was detected in the spectrum suggesting that complex 9 is four-coordinate.

Numerous Group 10 metal compounds have been reported that incorporate the ligand dppe. In addition to the metal diphosphine dichloride compounds which have already been discussed, homoleptic analogues such as $[Pd(dppe)_2](PF_6)_2$ can be obtained by the addition of another diphosphine in the presence of $AgPF_6$ (Figure 11).[30] This complex is analogous to $[(DMSO)Pd(1)]^{2+}$ (7). The dppe complexes of Pd and Pt have been structurally characterized, as well as $[Pd(pMepe)_2]Cl_2$, pMepe = $PhMeP(CH_2)_2PPhMe$ (Figure 12).[31] When either two dppe or pMepe ligands are coordinated to a single metal ion, space-filling molecular models show that the substituents on P have greater freedom than the phenyl rings in 7. To reduce repulsions, they can be oriented

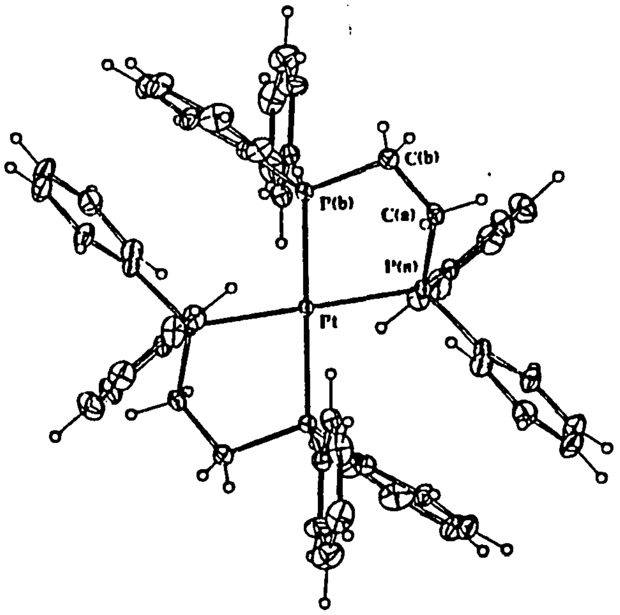


Figure 11. Ortep diagram for $[Pt(dppe)_2]Cl_2$

above and below the P_2-Pd-P_2 plane as seen in Figures 11 and 12. In 7, however, the carbon backbone forces the two phenyl rings on P to be on the same side of the metal plane.

In molecular models of 7, the phenyl rings are forced to be locked in a very nearly vertical position by steric repulsions among the rings. Furthermore, the phenyl rings and one of their <u>ortho</u> hydrogen atoms form a very protected cavity for the coordinated metal. Figure 13 shows a side-on view and a view down the two-fold axis of this cavity.

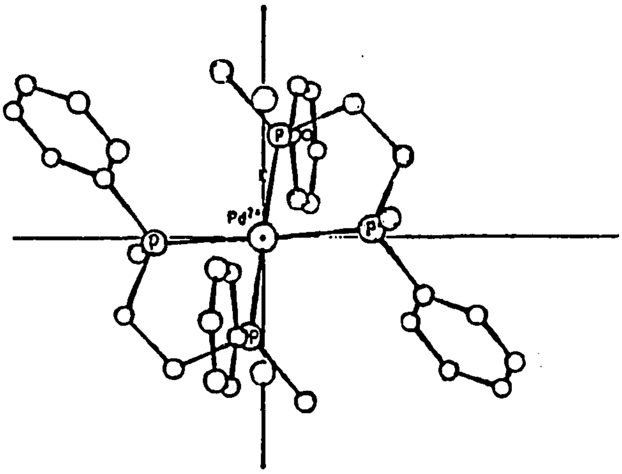


Figure 12. Ortep diagram for $[Pd(pMepe)_2]Cl_2$

For simplification, two phenyl groups have been omitted from the front phosphorus atoms.

The protected environment afforded by ligand 1 should increase the stability of these complexes, but the steric and ring strain induced by the ligand may also play a counter role here. When all four P atoms of 1 are bonded to a single metal, the strain due to formation of 6 and 7 membered chelate rings and the repulsions among the phenyl rings might be expected to destabilize the complex, causing dissociation of one or more phosphine arms. The coordination of DMSO or CH_3CN to Pd in 7 indicates that there is some flexibility within the molecule, although it was noted that the changes in chemical shifts between the coordinated and free solvents were very small. It may be that the interaction between Pd and O of DMSO, or N of CH_3CN is weak due to the steric bulk of the ligand 1.

The opposing effects caused by the protected metal environment, the steric bulk of the phenyl rings, and what may be substantial ring strain are combined in complex 7. This combination has led to interesting chemistry involving small molecules and is being investigated further.

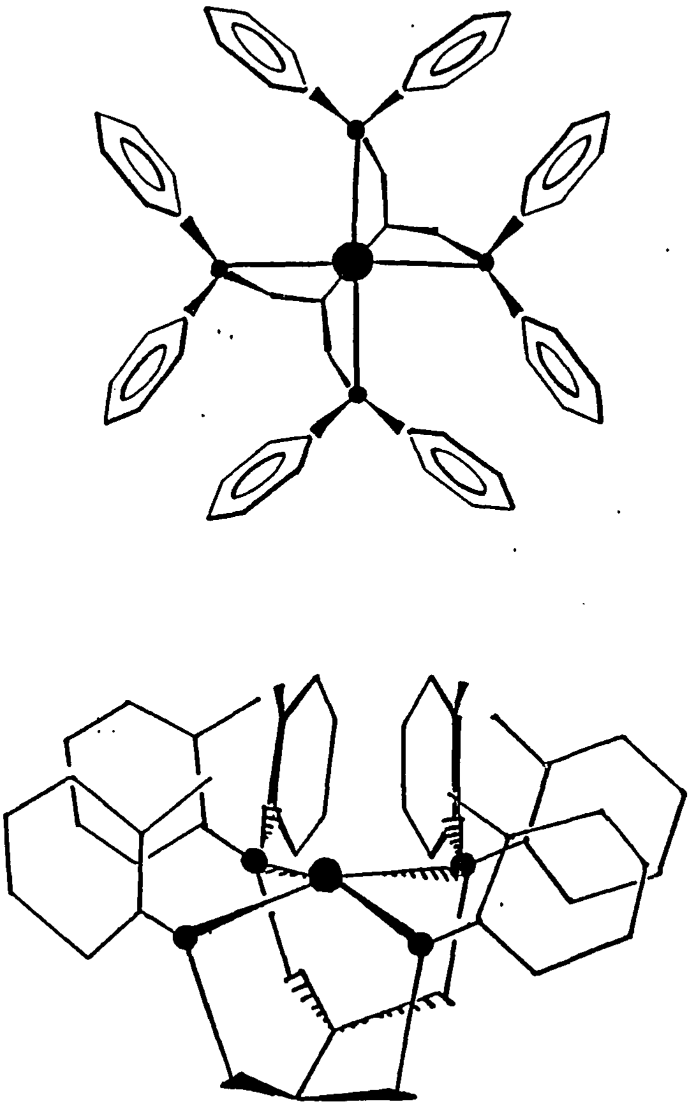


Figure 13. Two views of the metal cavity in M(1) complexes. Two phenyl rings have been omitted from the side view for clarity

TABLES

Table I. Crystal data for 4

Empirical Formula	$C_{54}H_{50}P_4O_4$
Formula weight	886.83
Space Group	P_1
a (Å)	11.70(3)
b (Å)	21.80(3)
c (Å)	9.28(6)
α (°)	94.0(3)
β (°)	102.7(3)
γ (°)	88.4(2)
V ($Å^3$)	2302
$\mu(MoK_\alpha)$ (cm^{-1})	2.04
ρcalc (g cm^{-3})	1.28
T (K)	290
Diffractometer	DATEX
Monochromator	oriented graphite
Reflections measured	hkl,hkl, hkl, hkl
Standard reflections[a]	1(measured every 100)
Reflections collected	3116
$2\theta_{max}$ (°)[b]	40.0
$2\theta_{min}$ (°)	3.5
Number of unique reflections	1207 ($I>2\theta(I)$)

---

[a] No decay in the standard intensity was noted.

[b] The 2 maximum was limited due to a rapid decrease in intensity above this point.

Table I. continued

Maximum number of parameters refined	319
R	0.0653
R^{c}	0.0533

$^{c}R_{\omega} = [\sigma(|F_{o}|-|F_{c}|)^{2}/\Sigma\omega F_{o}^{2}]^{\frac{1}{2}}$, $\omega=\sigma^{-2}(F_{o})$.

Table II. Crystal data for 5

Empirical formula	$C_{54}H_{50}Cl_{4}P_{4}Pd_{2}$
Formula weight	1177.44
Crystal system	monoclinic
Space group	$P2_{1/n}$
a (Å)	21.798(8)
b (Å)	13.927(5)
c (Å)	22.802(9)
α (°)	115.81(4)
V (Å^{3})	6231.(4)
$\mu(MoK_{\alpha})$ (cm^{-1})	8.56
ρcalc (g cm^{-3})	1.34
T (K)	290

Table II. continued

Diffractometer	DATEX
Reflections measured	hkl, hkl, hkl
Standard reflections[a]	1 (measured every 100)
Reflections collected	6287 collected, 1946 observed $(I>2\theta(I))$
$2\theta_{max}$ ( )	50.0
$2\theta_{min}$ ( )	3.5
Number of unique reflections	1996 $(I>2\ (I))$
Maximum number of parameters refined	353
R	0.13
R_{ω}[b]	0.11

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[a] No decay correction applied.

[b] $R_{\omega}=[\sigma(|F_o|-|F_c|)^2/\Sigma\omega F_o{}^2]^{\frac{1}{2}}, \omega=\sigma^{-2}(F_o)$.

Table III. $^{31}P\{^1H\}$ NMR, infrared, and conductance data.

Compound		$\delta\ ^{31}P$ (ppm)	ν M-X (cm^{-1})
1	$[HC(CH_2PPh_2)_2]_2$	-22.0	-
4	$[HC(CH_2P(O)Ph_2)_2]_2$	+38.2	-
5	$(PdCl_2)_2(1)$	+21.4	316 w 296 m
6	$[(DMSO)Pd(1)]Cl_2$	+30.8	*[b]
7	$[(CH_3CN)Pd(1)]^{2+}$	+30.9	*
8	$[(DMSO)Pd(1)]^{2+}$	+30.9	*
9	$[Ni(1)][ClO_4]_2$	+31.4	-

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[a] Acceptable ranges for 1:1 and 2:1 electrolyte in DMSO are 20-40 and 45-90, respectively. In CH_3CN, acceptable ranges are 120-140 for 1:1, and 190-240 for 2:1.[32]

[b] No absorption was observed in the expected region (150 tp 400 cm^{-1}).

$\nu_{P=O}$ (cm^{-1})	Λ_M (cm^{2}mol$^{-1}\Omega^{-1}$) (solvent)[a]
-	-
1186	-
-	5.16 (DMSO)
-	42.1 (DMSO)
-	195 (CH_3CN)
-	44.6 (DMSO)
-	198 (CH_3CN)

Table IV. Selected bond lengths (Å) in 4

atoms	distances	atoms	distances
P1 - O1	1.468(1)	P2 - O2	1.511(1)
P1 - C1A	1.814(2)	P2 - C1D	1.819(2)
P1 - C1B	1.816(2)	P2 - C1C	1.825(2)
P1 - C11	1.817(2)	P2 - C21	1.833(2)
P3 - O3	1.547(2)	P4 - O4	1.515(1)
P3 - C1E	1.801(2)	P4 - C1G	1.822(2)
P3 - C1F	1.832(2)	P4 - C1H	1.803(2)
P3 - C31	1.815(2)	P4 - C41	1.771(2)
C11 - C12	1.526(3)	C31 - C34	1.573(3)
C12 - C21	1.558(3)	C34 - C41	1.581(3)
C12 - C12	1.572(3)	C34 - C34	1.573(3)

Table V. Selected bond angles (°) in 4

atoms	angle	atoms	angle
O1 P1 C11	114.2(8)	O2 P2 C21	114.8(8)
O1 P1 C1A	113.5(9)	O2 P2 C1C	113.2(9)
O1 P1 C1B	109.0(8)	O2 P2 C1C	113.2(9)
C11 P1 C1A	103.5(9)	C21 P2 C1D	105.3(9)
C11 P1 C1B	107.7(9)	C21 P2 C1D	104.0(9)
C1A P1 C1B	108.6(9)	C1C P2 C1D	105.5(9)
O3 P3 C31	116.3(8)	O4 P4 C41	115.4(8)
O3 P3 C1E	111.6(9)	O4 P4 C1G	110.8(8)
O3 P3 C1F	111.5(9)	O4 P4 C1H	112.8(9)
C31 P3 C1E	103.(1)	C41 P4 C1G	107.2(9)
C31 P3 C1F	106.6(9)	C41 P4 C1H	104.2(9)
C1E P3 C1F	107.(1)	C1G P4 C1H	105.8(9)
P1 C11 C12	117.(1)	P2 C21 C12	123.(1)
P3 C31 C34	128.(1)	P4 C41 C34	116.(1)
C11 C12 C12	110.(2)	C31 C34 C34	110.(1)
C11 C12 C21	107.(1)	C31 C34 C41	108.(1)
C12 C12 C21	112.(2)	C34 C34 C41	112.(2)

Table VI. Selected interplanar angles (°) in 4

ring 1	ring 2	angle	ring 1	ring 2	angle
A	B	66.09[a]	A	C	92.08
A	D	65.15	B	C	73.63
B	D	60.06	C	D	27.27
E	F	103.07	E	G	115.67
E	H	43.05	F	G	100.60
F	H	89.54	G	H	78.78

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[a] Equation of plane given by $coeff_1*x + coeff_2*y + coeff_3*z = result$.

Table VII. Atom coordinates (fractional x 10^4) and isotropic thermal parameters[a] ($Å^2$ x 10^3) for isotropic atoms in 4[a,b]

atom	x	y	z	U
P1	2867.(5)[c]	5505.(3)	6967.(7)	71.
P2	3799.(5)	3634.(3)	4430.(6)	61.
P3	2323.(6)	185.(3)	8534.(7)	76.
P4	-1237.(5)	1333.(3)	8363.(6)	59.
O1	2288.(10)	4931.(5)	7109.(12)	71.
O2	4746.(10)	3276.(5)	3853.(12)	59.
O3	3008.(10)	-401.(6)	9090.(15)	86.
O4	-370.(10)	1473.(5)	7439.(13)	69.
C11	4308.(15)	5399.(8)	6549.(20)	53.
C12	4410.(13)	4949.(8)	5245.(20)	47.
C21	4321.(15)	4287.(8)	5740.(19)	61.
C31	749.(15)	177.(7)	8367.(21)	58.
C34	43.(19)	299.(8)	9622.(19)	59.
C41	-1204.(16)	567.(8)	8892.(19)	56.
C1A	3139.(15)	6006.(8)	8684.(20)	56.(6)

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[a] P, O, and skeletal C atoms were refined anisotropically. The remaining atoms were refined isotropically.

[b] U = 1/3 U_{ij}a-i a-$_j$a$_i$a$_j$ x 10^3 where the temperature factors are defined as exp(-2pi sum $h_ih_ja_ia_jU_{ij}$).

[c] Estimated standard deviations are given in parentheses for the least significant digits.

Table VII. continued

atom	x	y	z	U
C2A	2731.(17)	5795.(9)	9805.(926)	87.(7)
C3A	2874.(18)	6165.(10)	11121.(24)	91.(8)
C4A	3422.(18)	6713.(10)	11227.(24)	90.(7)
C5A	3795.(16)	6949.(9)	10105.(25)	78.(7)
C6A	3681.(16)	6570.(9)	8762.(22)	75.(7)
C1B	1957.(16)	5919.(19)	5491.(19)	47.(5)
C2B	2362.(15)	6446.(8)	4993.(20)	56.(6)
C3B	1613.(18)	6734.(9)	3887.(21)	71.(6)
C4B	473.(17)	6530.(21)	3307.(21)	82.(7)
C5B	88.(17)	6023.(9)	3842.(21)	71.(6)
C6B	861.(17)	5710.(8)	4949.(21)	69.(6)
C1C	2685.(16)	3954.(8)	2969.(21)	49.(5)
C2C	2878.(15)	3802.(7)	1503.(20)	52.(6)
C3C	2015.(19)	4039.(9)	297.(23)	75.(7)
C4C	1050.(19)	4328.(9)	606.(24)	79.(7)
C5C	835.(17)	4454.(9)	2012.(25)	78.(7)
C6C	1695.(18)	4239.(8)	3179.(21)	63.(6)
C1D	3003.(15)	3173.(8)	5436.(21)	54.(6)
C2D	3424.(15)	3159.(8)	6956.(21)	59.(6)
C3D	2882.(18)	2756.(9)	7663.(23)	93.(7)
C4D	1962.(17)	2402.(8)	6920.(23)	66.(6)
C5D	1560.(15)	2440.(8)	5472.(23)	69.(6)

Table VII. continued

atom	x	y	z	U
C6D	2119.(17)	2819.(9)	4672.(20)	71.(6)
C1E	2466.(17)	328.(9)	6693.(21)	61.(6)
C2E	3238.(17)	-53.(9)	6143.(23)	73.(7)
C3E	3475.(18)	31.(10)	4738.(25)	86.(7)
C4E	2898.(18)	489.(10)	4041.(22)	75.(7)
C5E	2049.(20)	869.(10)	4453.(27)	102.(8)
C6E	1855.(18)	795.(10)	5873.(24)	84.(7)
C1F	2861.(16)	869.(8)	9726.(19)	54.(6)
C2F	2237.(15)	1393.(9)	9934.(19)	60.(6)
C3F	2723.(18)	1886.(9)	10871.(21)	68.(6)
C4F	3919.(18)	1862.(9)	11535.(21)	73.(7)
C5F	4530.(17)	1356.(10)	11316.(23)	84.(7)
C6F	4031.(18)	837.(9)	10439.(22)	74.(6)
C1G	-1013.(16)	1835.(8)	10052.(21)	60.(6)
C2G	-1468.(16)	1722.(8)	11227.(22)	64.(6)
C3G	-1331.(18)	2157.(10)	12474.(24)	94.(8)
C4G	-776.(17)	2705.(10)	12438.(22)	77.(7)
C5G	-372.(17)	2822.(10)	11206.(24)	84.(7)
C6G	-442.(15)	2381.(9)	10038.(21)	66.(6)
C1H	-2737.(17)	1458.(8)	7421.(23)	67.(6)
C2H	-2917.(18)	1713.(9)	6134.(23)	75.(7)
C3H	-4051.(19)	1862.(8)	5343.(20)	71.(6)

Table VII. continued

atom	x	y	z	U
C4H	-4988.(16)	1754.(8)	5982.(21)	65.(6)
C5H	-4856.(17)	1453.(9)	7237.(24)	76.(7)
C6H	-3708.(18)	1334.(8)	8047.(20)	72.(7)

Table VIII. Selected bond lengths (Å) in 5

atoms	distances	atoms	distances
Pd1 - P7	2.26(1)	Pd2 - P9	2.23(1)
Pd1 - P8	2.24(1)	Pd2 - P10	2.25(1)
Pd1 - C13	2.32(1)	Pd2 - C15	2.34(1)
Pd1 - C14	2.34(1)	Pd2 - C16	2.36(1)
P7 - C11	1.90(4)	P8 - C12	1.82(4)
P7 - C1A	1.84(5)	P8 - C1C	1.87(4)
P7 - C1B	1.83(5)	P8 - C1D	1.81(5)
P9 - C14	1.78(5)	P10 - C15	1.80(4)
P9 - C1E	1.84(5)	P10 - C1G	1.78(4)
P9 - C1F	1.81(5)	P10 - C1H	1.82(5)
C11 - C13	1.50(6)	C12 - C13	1.54(6)
C13 - C16	1.62(6)	C14 - C16	1.61(6)
C15 - C16	1.47(5)		

Table IX. Selected bond angles (°) in 5

atoms	angle	atoms	angle
C13 Pd1 C14	89.6(4)	C15 Pd2 C16	90.6(6)
C13 Pd1 P7	88.0(5)	C15 Pd2 P9	86.8(5)
C13 Pd1 P8	174.0(4)	C15 Pd2 P10	173.5(5)
C14 Pd1 P7	176.0(4)	C16 Pd2 P9	176.5(6)
C14 Pd1 P8	88.4(4)	C16 Pd2 P10	87.8(6)
P7 Pd1 P8	93.7(4)	P9 Pd2 P10	94.5(5)
Pd1 P7 C11	118.(1)	Pd1 P8 C12	118.(1)
Pd1 P7 C1A	114.(1)	Pd1 P8 C1C	107.(1)
Pd1 P7 C1B	111.(2)	Pd1 P8 C1D	118.(1)
C11 P7 C1A	98.(2)	C12 P8 C1C	103.(2)
C11 P7 C1B	102.(2)	C12 P8 C1D	103.(2)
C1A P7 C1B	113.(2)	C1C P8 C1D	106.(2)
Pd2 P9 C14	119.(2)	Pd2 P10 C15	119.(1)
Pd2 P9 C1E	114.(1)	Pd2 P10 C1G	108.(2)
Pd2 P9 C1F	110.(1)	Pd2 P10 C1H	115.(2)
C14 P9 C1E	100.(2)	C15 P10 C1G	105.(2)
C14 P9 C1F	103.(2)	C15 P10 C1H	96.(2)
C1E P9 C1F	109.(2)	C1G P10 C1H	113.(2)

Table IX. continued

atoms	angle	atoms	angle
P7 C11 C13	114.(2)	P9 C14 C16	114.(3)
P8 C12 C13	114.(2)	P10 C15 C16	112.(3)
C11 C13 C12	112.(4)	C13 C16 C14	106.(3)
C11 C13 C16	111.(4)	C13 C16 C15	113.(3)
C12 C13 C16	111.(3)	C14 C16 C15	116.(3)

Table X. Atom coordinates (fractional x 10^4) and equivalent isotropic thermal parameters[a,b] (x 10^3) for 5

atom	x	y	z	U
Pd1	2759.(2)[c]	551.(2)	2192.(2)	53.
Pd2	5486.(2)	5439.(3)	1970.(2)	70.
C13	1843.(7)	-268.(9)	1402.(7)	78.
C14	2707.(6)	-457.(8)	2992.(6)	72.
C15	6407.(7)	5552.(10)	1707.(7)	100.

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[a] $U = 1/3\ U_{ij}a_i\ a_ja_ia_j \times 10^3$ where the temperature factors are defined as exp $(-2\ h_ih_ja_ia_jU_{ij})$.

[b] Pd, Cl, and P atoms were refined anisotropically. The remaining atoms were refined isotropically.

[c] Estimated standard deviations are given in parentheses for the least significant digits.

Table X. continued

atom	x	y	z	U
C16	5556.(9)	7102.(8)	2198.(10)	134.
P7	2810.(7)	1431.(8)	1383.(6)	53.
P8	3708.(6)	1204.(7)	2965.(5)	38.
P9	5489.(7)	3865.(8)	1786.(6)	64.
P10	4688.(6)	5341.(8)	2341.(6)	61.
C11	3303.(21)	2601.(23)	1611.(18)	36.(9)
C12	3943.(21)	2408.(23)	2828.(18)	36.(9)
C13	3991.(23)	2519.(26)	2177.(21)	47.(10)
C14	4770.(24)	3166.(28)	1687.(22)	61.(12)
C15	4107.(19)	4344.(26)	2091.(17)	40.(9)
C16	4466.(22)	3421.(26)	2197.(20)	43.(11)
C1A	1982.(25)	1909.(28)	800.(23)	62.(12)
C2A	1839.(36)	2052.(40)	149.(34)	110.(19)
C3A	1219.(42)	2454.(45)	-281.(36)	129.(22)
C4A	739.(35)	2709.(37)	-58.(32)	106.(18)
C5A	822.(39)	2566.(40)	593.(36)	114.(19)
C6A	1502.(35)	2166.(39)	1024.(32)	104.(19)
C1B	3253.(26)	774.(31)	984.(25)	6.(11)
C2B	3559.(34)	1309.(42)	667.(32)	31.(15)
C3B	3749.(46)	869.(55)	222.(440)	68.(24)
C4B	3634.(48)	-109.(54)	91.(45)	65.(25)
C5B	3329.(56)	-644.(76)	408.(52)	106.(32)

Table X. continued

atom	x	y	z	U
C6B	3139.(39)	-202.(44)	854.(38)	45.(21)
C1C	4444.(20)	458.(31)	3017.(18)	43.(8)
C2C	4360.(24)	-483.(38)	2788.(21)	68.(12)
C3C	4926.(38)	-1042.(40)	2882.(32)	102.(18)
C4C	5579.(28)	-658.(37)	3205.(25)	80.(15)
C5C	5663.(30)	283.(39)	3436.(27)	87.(17)
C6C	5097.(25)	843.(26)	3341.(22)	53.(12)
C1D	3775.(19)	1271.(24)	3798.(18)	31.(9)
C2D	3627.(25)	2150.(29)	4000.(23)	57.(12)
C3D	3761.(32)	2290.(37)	4650.(30)	94.(17)
C4D	4043.(28)	1547.(34)	5097.(26)	76.(15)
C5D	4192.(21)	670.(28)	4895.(20)	50.(11)
C6D	4060.(20)	527.(32)	4245.(19)	50.(9)
C1E	5552.(27)	3575.(29)	1029.(24)	59.(12)
C2E	4994.(32)	3764.(36)	437.(31)	86.(15)
C3E	5006.(41)	3475.(50)	-144.(39)	132.(24)
C4E	5576.(33)	3002.(35)	-128.(30)	84.(16)
C5E	6135.(33)	2817.(35)	464.(32)	93.(17)
C6E	6124.(36)	3105.(40)	1046.(34)	112.(20)
C1F	6181.(24)	3287.(29)	2462.(22)	53.(12)
C2F	6580.(34)	3867.(38)	2989.(32)	88.(16)
C3F	7118.(34)	3470.(41)	3531.(31)	96.(17)

Table X. continued

atom	x	y	z	U
C4F	7256.(36)	2492.(45)	3544.(32)	101.(18)
C5F	6855.(45)	1910.(52)	3019.(43)	134.(25)
C6F	6317.(35)	2308.(41)	2478.(33)	99.(18)
C1G	5112.(23)	5273.(28)	3209.(21)	50.(11)
C2G	4829.(35)	4802.(38)	3572.(34)	104.(20)
C3G	5180.(36)	4776.(40)	4250.(34)	103.(20)
C4G	5815.(48)	5218.(52)	4563.(43)	149.(27)
C5G	6097.(33)	5690.(39)	4199.(32)	106.(18)
C6G	5746.(23)	5719.(26)	3523.(21)	49.(11)
C1H	4043.(27)	6278.(32)	2050.(26)	73.(14)
C2H	3841.(39)	6729.(41)	2483.(34)	109.(19)
C3H	3336.(40)	7433.(45)	2261.(37)	115.(20)
C4H	3034.(36)	7686.(43)	1604.(36)	113.(20)
C5H	3235.(58)	7236.(67)	1170.(51)	182.(34)
C6H	3740.(40)	6531.(48)	1392.(37)	121.(22)
S	2925.(18)	4458.(26)	10026.(16)	211.(11)
C1	2340.(49)	4910.(49)	10345.(47)	163.(32)
C2	2895.(52)	5126.(52)	9431.(49)	170.(33)
O	3329.(27)	3701.(37)	330.(25)	143.(16)

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SECTION II. REACTION OF HALIDES WITH A STERICALLY HINDERED TETRAPHOSPHINE Pd(II) COMPLEX

INTRODUCTION

Five-coordinate complexes of the divalent Group 10 metals have long been proposed intermediates in substitution reactions and catalytic mechanisms.[1,2] While several examples of five-coordinate Ni(II) are known, relatively few examples of well-defined five-coordinate complexes of Pd(II) and Pt(II) can be found in the literature.[2,3] Pd(II) complexes of the tetradentate ligand 1 (Figure 1) have been reported in which a molecule of solvent (DMSO or CH_3CN) is coordinated to the metal to produce five-coordinate species, $[(solvent)Pd(1)](AsF_6)_2$ (2).[1] In these complexes solvent coordination was determined from ^{13}C NMR and IR data. However, there was some ambiguity as to the nature of the interaction because of the small coordination chemical shifts.

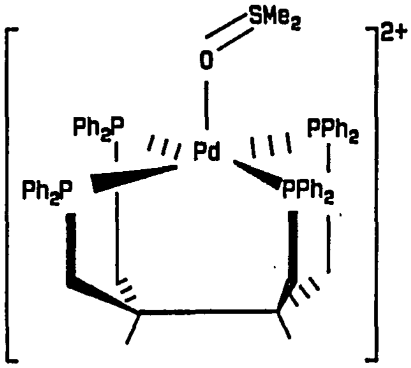


Figure 1. Proposed structure of $[(DMSO)Pd(1)]^{2+}$

Complex 2 is soluble in DMSO and CH_3CN, thus limiting the use of variable temperature NMR as a tool to investigate the system.

We have expanded this work to include five coordinate complexes of the formula [XPd(1)]X by displacing coordinated DMSO with halides. Based on the affinity of Pd(II) for halides, they should readily displace coordinated DMSO or CH_3CN.[4] However, in complex 2 there are eight phenyl rings surrounding the metal creating a protective cavity which may inhibit halide coordination. By studying the extent of coordination of the halide series we intended to probe the space that is available for coordination of a fifth ligand.

EXPERIMENTAL

General Procedures

All reactions were carried out under an inert atmosphere using solvents that were distilled from an appropriate drying agent under N_2 or Ar prior to use. Reagents were used without further purification unless otherwise noted. $[(DMSO)Pd(1)](AsF_6)_2$ (2), $[(CH_3CN)Pd(1)](AsF_6)_2$ (3), and $[(DMSO)Pd(1)]Cl_2$ (4) were prepared as previously reported.[3]

Solution ^{31}P NMR spectra were taken on a Bruker WM-300, or a Bruker WM-200 spectrometer operating in the Fourier mode. Chemical shifts were referenced to an external 85% H_3PO_4 standard, and downfield shifts are given as positive values. Solution ^1H NMR spectra were taken on a Nicolet NT-300 spectrometer operating in the Fourier mode and were referenced to internal TMS.

Mid-infrared (4000 to 400 cm^{-1}) and far-infrared (600 to 150 cm^{-1}) spectra were taken on an IBM Fourier IR/98 spectrometer. Mid-IR range samples were prepared as KBr pellets or Nujol mulls on KBr plates; far-IR range samples were prepared as Nujol mulls on polyethylene plates.

Conductances were measured with a Markson ElectroMark Analyzer on solutions that were approximately 10^{-3} molar.

Reactions of $[(DMSO)Pd(1)][BF_4]_2$ with X^-

For X = F, Cl, Br, I, approximately 30 mg of 2 in 2 mL 50/50 (v/v) $CHCl_3$/DMSO was placed in a 10 mm NMR tube. The addition of DMSO was required to completely dissolve 2. Various amounts of Bu_4NF, Bu_4NCl, Bu_4NBr or Et_4NI were added and the reactions monitored by ^{31}P NMR.

X = F, Cl

For X = F, Cl an equilibrium was established. The spectra were taken at 10 to 20 minute intervals until equilibrium was reached as signified by no further changes in consecutive spectra. The relative amounts of the species in solution were determined by peak integration of the ^{31}P NMR spectrum.

X = Br

When Bu_4NBr was added to a solution of 2, a greyish precipitate formed immediately that was insoluble in organic solvents. The ^{31}P spectrum of the solution showed the presence of uncoordinated 1 (δ -22.0).

X = I in DMSO

$[Pd(1)][AsF_6]_2$ (0.0610 g, 0.467 mmol) was reacted with 0.240 g (0.934 mmol) Et_4NI in 20 mL of DMSO. The color immediately changed from pale yellow to a deep orange upon addition of iodide and remained homogeneous. Separation from Et_4NAsF_6 was achieved by chromatography using Fluorosil as the adsorbent and acetone as the eluent. Addition of ether followed by cooling precipitated 0.031 g of $I_2Pd(Ph_2PCH_2)_2(CH)_2$-$(CH_2P(O)Ph_2)_2$ (7). (^1H NMR ($CDCl_3$): δ7.94 (8H, m, PhPO-ortho), 7.77 (8H, m, PhPO-meta), 7.59 (4H, m, PhPO-para), 7.1-7.5 (22H, m, PhPPd), 2.74 (5H, m, CH_2PO), 2.12 (7H, m, CH_2P-Pd, CH))

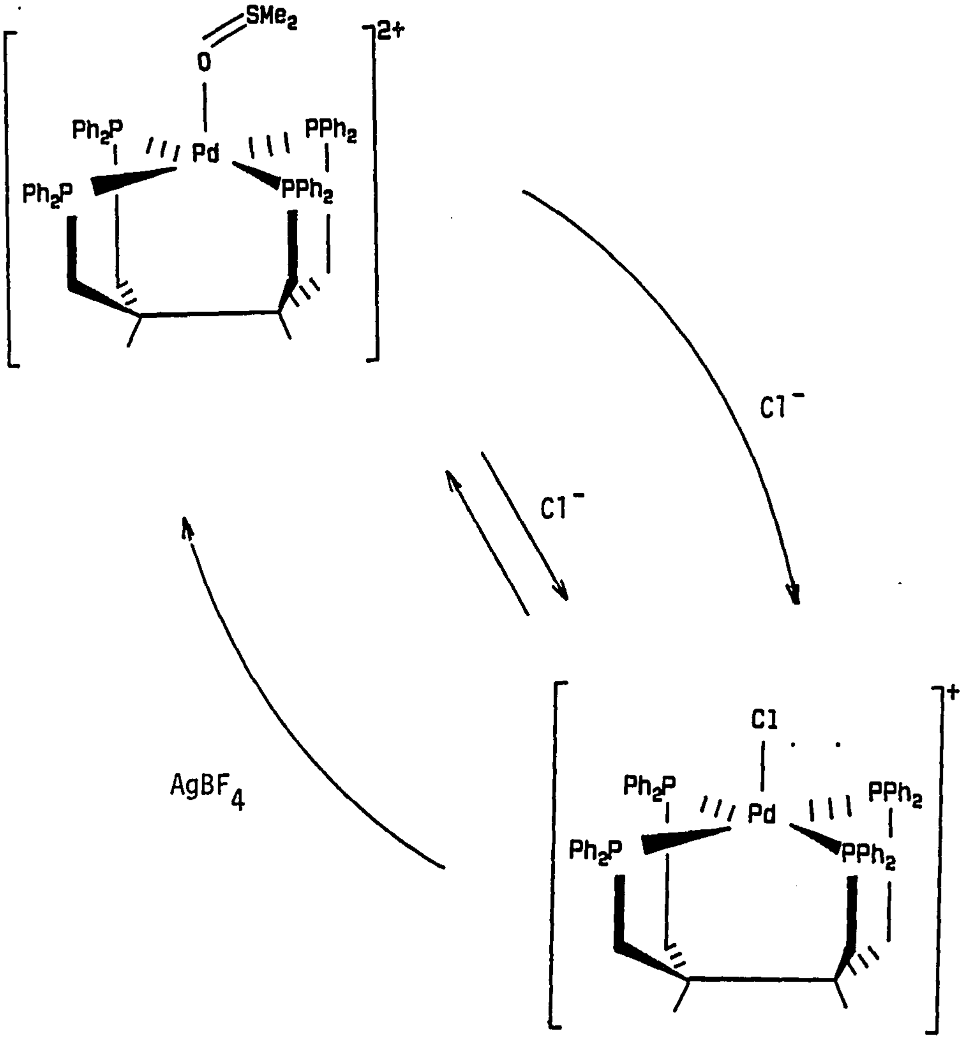
X = I in CH_3CN

Reaction of 3 (0.1096 g, 0.0811 mmol) with 0.0417 g (0.572 mmol) Et_4NI in CH_3CN yielded two products. Separation from Et_4NAsF_6 was achieved by chromatography as in the previous reaction. Deep red needle crystals (8), and orange hexagonal prismatic crystals (9) were separated by repeated fractional crystallization from CH_3CN. (mp (8) 191 dec.) (mp (9) 226-232 dec.) (^1H NMR (8) (DMSO): δ 7.64-7.29 (42H, m, Ph & $CDCl_3$), 2.66 (4H, m, CH_2), 2.34 (6H, m, CH_2, CH)) (^1H NMR (9) (DMSO): δ 7.71- 7.34 (40H, m, Ph), 2.69 (4H, m, CH_2), 2.48 (6H, m, CH_2, CH))

RESULTS

Reaction with Cl^-

Complex 4 is prepared in DMSO and gives a single ^{31}P resonance at 30.8 ppm (Table I). In DMSO, the conductivity is consistent with a two-to-one electrolyte, and no absorptions were observed in the IR spectrum that could be assigned to ν_{Pd-Cl}.[2] When 4 was dissolved in solvents less polar than DMSO, a second chemical shift was observed in the ^{31}P NMR spectrum at 20.4 ppm. Addition of $AgAsF_6$ to this mixture removed chloride from solution and again a single peak corresponding to 2 at +30.9 ppm is seen in the ^{31}P spectrum. Conversely, beginning with the dication 2, addition of two mole equivalents of Bu_4NCl to a 50/50 DMSO/$CHCl_3$ solution caused the appearance of the +20.4 resonance. When the equilibrium mixture was isolated from solution and redissolved in DMSO, it reverted completely to 4 over a period of days (Scheme 1). The +20.4 ppm resonance was assigned to the five-coordinate complex in which one of the chloride atoms is bound to the palladium, [ClPd(1)]Cl (5). Although evidence for the Cl^- coordinated complex 5 was found in solution, it could not be isolated due to an equilibrium with the DMSO coordinated complex 4. The coordination of Cl^- to Pd was verified by the presence of a medium-intensity ν_{Pd-Cl} mode in the infrared spectrum at 299 cm^{-1} (Table I).



Scheme 1. Reaction of $[Pd(1)]Cl_2$ (4) with $AgBF_4$, and equilibrium reactions involving 4

No absorption was observed between 150 to 400 cm^{-1} that could be assigned to $_{Pd-Cl}$ for complexes 2, 3, or 4.

Conductance measurements are consistent with the formation of a five coordinate complex. In DMSO, $[Pd(1)]Cl_2$ gives a conductance measurement that corresponds to a two-to-one electrolyte, Λ_m = 42.1 $cm^2mol^{-1}\ \Omega^{-1}$. The same compound in ethanol, has a conductance of 57.7 $cm^2mol^{-1}\Omega^{-1}$, which is midway between the expected values for a one to one (35 - 45) and a two to one electrolyte (70 - 90).[4] DMSO and CH_3CN solutions in which the chloride anions had been removed to give complexes 2 or 3 gave conductance measurements indicative of two to one ionic systems (Table I).

Mole ratios of 5 to 4, based on the integration of the corresponding resonances in the ^{31}P NMR spectrum, were determined as a function of solvent polarity and temperature (Tables II and III). There appears to be a correlation between solvent polarity and the amount of the Cl^- coordinated complex present in solution. The ratio of complexes 4 to 5 in solution increases to a limit with the polarity of the solvent. Of the solvents employed, chloroform has the lowest dielectric constant (least polar). In chloroform the ratio of 4 to 5 remained high, with a one to one ratio, thus eliminating the possibility of isolating complex 5 from 4. More polar solvents may be better able to support the dication 4. As the polarity decreases, the monocation 5 becomes favored. However this explanation is too simplistic and what is observed experimentally is undoubtedly the combination of solvent polarity, the relative coordinating ability of DMSO and Cl^-, and the steric properties of the ligated metal. Since the starting complex 4 has a molecule of DMSO coordinated, the observed equilibrium is perhaps a combination of equilibria between two five-coordinate complexes in which DMSO or Cl^- are bonded to Pd and an intermediate in which the metal is four-coordinate (Scheme 2).

$$[(DMSO)Pd(1)]Cl_2 \rightleftharpoons [Pd(1)]Cl_2 \rightleftharpoons [ClPd(1)]Cl$$

Scheme 2.

At higher temperatures, the coordination of chloride is slightly favored over DMSO (Table II). In chloroform at 40C, formation of 5 is favored giving a ratio of almost two to one relative to 4. It is not clear why the coordination of Cl^- is favored at higher temperatures. It may be that increased freedom within the phenyl rings of the ligand allows the larger Cl^- to gain closer proximity to the Pd atom. It has been shown that the DMSO coordinates to Pd via the O atom which has a smaller radius than the Cl^-.[2] The Cl is a softer base, however, and is known to displace O donor ligands.[4]

Reaction with F^-

Based on the ^{31}P NMR data, addition of n-Bu_4NF to 2 produced the fluoride analogue to 5, $[FPd(1)](AsF_6)$ (6). A four-fold excess of F^- was required to produce the second resonance at 19.8 ppm, and no coupling between phosphorus and fluorine was observed. The absence of coupling could be due to fast exchange on the NMR time scale. Low temperature ^{31}P NMR was limited to the melting point of the solvent (-47 ° C), however at - 45 no coupling to F was observed. Solid state ^{31}P NMR was not useful because line widths are typically 100 Hz and the expected coupling of 30 to 40 Hz for F _cis_ to P would not be detected.[5]

Reaction with I^- in DMSO

Addition of iodide to a solution of 2 in a 50/50 (v/v) DMSO/$CDCl_3$ solvent mixture resulted in the displacement of two arms of the ligand which were then oxidized by the DMSO to form complex 7. Two resonances were seen in the ^{31}P NMR spectrum at 31.6 ppm corresponding to the oxidized phosphine and 10.7 ppm corresponding to the phosphine bonded to the palladium. The ν_{P-O} appeared at 1184 cm^{-1}, but the ν_{Pd-I} was not observed in the expected region (150 - 400 cm^{-1}). The identification of this product was based on the ^{1}H, ^{31}P NMR and the IR spectra in comparison to the chloride analogue $Cl_2Pd(PPh_2CH_2)_2C_2H_2(CH_2P(O)Ph_2)_2$ (10) which has been structurally characterized.[6] ^{1}H NMR has been particularly useful in distinguishing between complexes in which all four phosphines are bound to the metal, and those which have two phosphines bound, and the remaining two oxidized and uncoordinated. The ortho hydrogens of the oxidized ligand, $[Ph_2P(O)CH_2)_2CH]_2$ appear characteristically downfield as two ABX quartets at 7.9 and 7.7 ppm.[6] The inequivalency arises from hydrogen bonding of the phosphoryl oxygens.

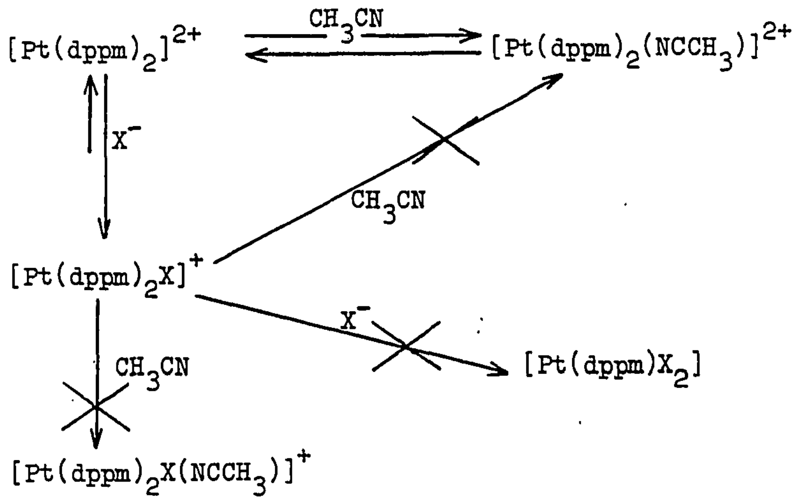
The phenyl region in the ^{1}H NMR of complex 10 clearly shows two ABX quartets at 7.86 and 7.65 ppm, and the remainder of the phenyl hydrogens appear upfield as a complicated multiplet centered at 7.39 ppm. The phenyl region of complex 7 is very similar, with two broadened multiplets at 7.90 and 7.60 ppm and the remainder of the phenyl hydrogens as a multiplet centered at 7.3 ppm.

Reaction with I^- in CH_3CN

When the reaction of 2 with I^- is done in CH_3CN, two products (8 and 9) were isolated. Both give a single resonance in the ^{31}P NMR indicating the equivalence of the four P atoms. During the course of the reaction between 4 and I^-, the resonances for complexes 8 and 9 in the ^{31}P NMR grew in, as well as a peak at -22 ppm correspondng to free ligand which was oxidized over ca. 16 h in air to give the phosphine tetraoxide. The resonances for 8 and 9 are well outside the range for oxidized ligand (37.6 ppm), In the far-IR spectra, neither 8 nor 9 have absorptions that could be assigned to ν_{Pd-I}. This is not a definitive indication of the absence of a Pd-I bond because the weak absorptions of M-I are not always observed. Compounds 8 and 9 are very soluble in organic solvents and were separated by fractional crystallization from a mixture of CH_3CN and $CHCl_3$. Compound 8 crystallized as dark red needles which were too thin to diffract sufficiently for X-ray analysis. Compound 9 crystallized as bright orange hexagonal prisms. The crystallographic analysis of this compound is currently in progress.

DISCUSSION

Platinum and palladium complexes of the formula $[M(bidentate)_2]X_2$ are analogous to complex 4. $[Pd(dppe)_2]Cl_2$, $Pt(dppe)_2Cl_2$, and $[Pd(pMepe)_2]Cl_2$ have been structurally characterized.[7] In all complexes, the solid state structures are four-coordinate square planar. Grossel et al.[8] has recently studied the solution chemistry of $[Pt(dppm)_2]X_2$ and determined each member of the series for $X = Cl^-$, Br^-, I^- to be five-coodinate. He proposes an equilibrium reaction between the four-coordinate and five-coordinate complexes as shown in Scheme 3.



Scheme 3. Proposed solution chemistry of $[Pt(dppm)_2]Cl_2$[8]

Unlike the equilibria observed between four and five-coordination in complex 4, the same equilibria in $[Pt(dppm)_2]X_2$ lie far to the side of the five-coordinate complexes. The ^{31}P NMR chemical shifts of the four-coordinate and five-coordinate complexes showed an upfield shift upon coordination of X to the fifth position. When X = Cl^-, the phosphorus resonance shifts 6.2 ppm upfield. On coordination of Cl^- to 2, an upfield change of 10.7 ppm is observed. They also note a slight (0.1 ppm) downfield shift of the ^{31}P NMR resonance of $[Pt(dppm)_2]^{2+}$ in CH_3CN relative to CH_2Cl_2, and suggest a separate equilibrium between $[(CH_3CN)Pd(dppm)_2]^+$ and $[ClPd(dppm)]^+$ in which CH_3CN does not displace the phosphine but plays a part in the equilibria.

In the reactions between halides and 4, only Cl^- and F^- were found to form five-coordinate complexes, but neither could be isolated from their equilibrium partners. Since halides readily displace coordinated solvents in similar systems,[2,8] the reason for the limited halide coordination in 4 must lie with the steric constraint of the ligand. The relative steric constraints placed on the two compounds by the phosphine ligands has been discussed.[3] It has been shown that DMSO coordinates through the small O atom, and displacement by the larger Cl^- may be inhibited by the steric restrictions of the ligand. Although the F^-

is much smaller in radius, now the controlling factor is probably electronic. Fluoride is a hard base, which only coordinates very weakly to soft metals such as Pd and Pt.[1]

When I^- was added to 2, displacement of two arms of the phosphine resulted, allowing coordination of I^- to the Pd. This suggests that the much larger radius of I^- relative to Cl^- prevents it from forming a five-coordinate complex.

Both complexes 8 and 9 are non-conducting in DMSO (Table I). The presence of a single resonance in the ^{31}P NMR spectrum for these compounds at 16.0 ppm for 8 and 17.1 ppm for 9, indicates an equivalency of all four phosphine arms. The deep colors, which are in contrast to the pale yellow of the starting complex 2, suggests coordination of iodide. To account for this data,formation of an oligomeric or six coordinate complex, or extensive rearrangement must be considered. It does not seem likely that 8 and 9 are oligomeric because of their crystalline nature. Ligand 1 creates a very protected, sterically crowded cavity for the Pd, and six coordination appears difficult, suggesting rearrangement of the tetraphosphine, which is substantiated by the loss of phosphine during the reaction.

On the basis of these results, it would seem that the fifth coordination site on 2 is sterically restrained by the ligand 1. Coordination of chloride in an equilibrium reaction indicates that its radius is nearing the limit allowed by the phosphine ligand. Coordination of DMSO and CH_3CN suggests possible coordination of other small molecules that have small donor atoms to occupy the relatively small volume available.

TABLES

Table I. $^{31}P\{^{1}H\}$ NMR, Infrared and Conductance measurements

	compound	$\delta^{31}P$	$\nu Pd\text{-}Cl$
1	$((Ph_2PCH_2)_2CH)_2$	-22.0	-
2	$[(DMSO)Pd(1)](AsF_6)_2$	30.9	*[b]
3	$[(CH_3CN)Pd(1)](AsF_6)_2$	31.0	*
4	$[(DMSO)Pd(1)]Cl_2$	30.8	*
5	$[ClPd(1)]Cl$	20.1	299 m, br [c]
6	$[FPd(1)]AsF_6$	19.8	*
7	$I_2Pd((Ph_2PCH_2)_2C_2H_2\text{-}(CH_2P(O)Ph_2)_2)$	8.1[d] 31.6	*
8	$I_2Pd(1)$	16.0	*
9	$I_2Pd(1)$	17.1	*

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[a] Acceptable ranges for 1:1 and 2:1 electrolyte in DMSO are 20-40, and 45-90, respectively. In CH_3CN, acceptable ranges are 120-140 for 1:1 and 190-240 for 2:1.[9]

[b] The IR spectrum was taken in the expected region; no absorption was observed.

[c] This value is for an equilibrium mixture of 4 and 5.

[d] The downfield resonance at +31.6 ppm corresponds to the oxidized phosphine.

ν_{P-O} (cm^{-1})	Λ_M cm^{2}mol^{-1}ohm^{-1} (solvent)[a]
-	-
-	
-	195 (CH_3CN)
-	42.1 (DMSO)
-	57.7 (EtOH)
-	-
1188	0.56
-	0.19
-	0.21

Table II. Mole ratio of 4 to 5 as a function of solvent

4 : 5	solvent
1 : 1	$CDCl_3$
1.4 : 1	CD_2Cl_2
1.5 : 1	MeOH, EtOH
2.1 : 1	CH_3CN
only 4	DMSO

Table III. Mole ratio of 4 to 5 as a function of temperature in $CDCl_3$

4 : 5	temperature(C)
1 : 1	-2
1 : 1.4	32
1 : 1.7	40

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SECTION III. OXIDATION OF DIMETHYLSULFOXIDE TO DIMETHYLSULFONE BY A Pd(II) TETRAPHOSPHINE COMPLEX

INTRODUCTION

Recently we reported the preparation and characterization of a Pd(II) complex of the new tetradentate phosphine 1 (Figure 1).[1] In the process of investigating the chemistry of $[(DMSO)Pd(1)](BF_4)_2$ (2), it was discovered that DMSO solutions of 2 left open to air catalytically oxidize DMSO to dimethylsulfone ($DMSO_2$).

Pd(II) salts and complexes are well known to catalyze numerous organic syntheses. These include alkyl and aryl coupling reactions, carbonylation of organic substrates, the oxidation of olefins in the Wacker process and the oxidation of organic substrates through palladium dioxygen species.[2,3] However, in each of these catalytic systems, the Pd cycles between oxidation states (0) and (II) which seemed improbable for DMSO solutions of 2. To clarify the oxidative ability of 2 towards DMSO, the catalysis has been repeated under controlled conditions and compared with the reactivity of analogous Pd(II) complexes of mono- and diphosphine ligands.

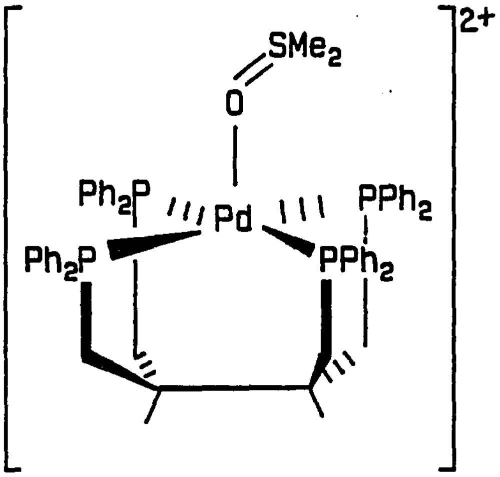


Figure 1. Proposed structure of $[(DMSO)Pd(1)](Z)_2$; 2 Z = BF_4^-; 3 Z = Cl^-

EXPERIMENTAL

General Procedures

Preparative reactions were carried out under an inert atmosphere using solvents that were distilled from appropriate drying agent under N_2 or Ar prior to use. Reagents were used without further purification unless otherwise noted. $[(DMSO)Pd(1)](BF_4)_2$ (2), $[(DMSO)Pd(1)]Cl_2$ (3), $(PdCl_2)_2(1)$ (5),[1] $[Pd(dppe)_2](BF_4)_2$ (6),[4] and $Pd(Ph_2MeP)_4](BF_4)_2$ (7)[5] were prepared as previously reported.[1]

Solution ^{31}P NMR spectra were taken on a Bruker WM-300, or a Bruker WM-200 spectrometer operating in the Fourier mode. Chemical shifts were referenced to an external 85% H_3PO_4 standard. Positive values are downfield of the standard. Solution ^1H and ^{13}C NMR spectra were taken on a Nicolet NT-300 spectrometer operating in the Fourier mode. Both were referenced to internal TMS.

Mid-infrared (4000 to 400 cm^{-1}) and far-infrared (600 to 150 cm^{-1}) spectra were taken on an IBM Fourier IR/98 spectrometer. Mid-IR range samples were prepared as KBr pellets or Nujol mulls on KBr plates; far-IR range samples were prepared as Nujol mulls on polyethylene plates.

Conductance measurements were made with a Markson ElectroMark Analyzer on solutions that were approximately 10^{-3} molar.

Oxidation of DMSO to $DMSO_2$

Reactions of Pd complexes with DMSO

Approximately 30 mg of each of the Pd complexes 2, 3, 5, 6 and 7 was dissolved in 2.5 ml DMSO and the solution stirred for three weeks while open to air. The DMSO was dried over CaH_2 and distilled under partial vacuum. Ligand 1 in DMSO and a flask containing only DMSO were stirred in air for three weeks as controls.

Isolation of dimethylsulfone

At the end of the allotted reaction time, the ^{31}P NMR spectrum of the reaction solution was taken to determine the fate of the Pd complex. Water (10 mL) was then added and the dimethylsulfone extracted from the solution with three 5 mL portions of $CHCl_3$. The organic phases were combined, dried over anhydrous Na_2SO_4 and evaporated to dryness using a rotary evaporator. The crude product was weighed, then sublimed at 145 °C under an inert atmosphere before characterization. (m.p. 106 - 109°; lit. m.p. 108-110°)[6a] (^1H NMR (CD_3CN): δ 2.90 (s); lit. 2.91 (s))[6b] (^{13}C NMR (CD_3CN): δ 42.82)

Ligand 1

Stirring ligand 1 (0.0091 g, 1.1×10^{-2} mmol) in 2.5 mL DMSO and 75 μL water caused partial oxidation of 1 over the three week reaction period. The odor of Me_2S was detected over the reaction mixture and the presence of the phosphine oxide, $[Ph_2P(O)CH_2)_2]_2$ (8), was identified by ^{31}P NMR (+37.6 ppm).[1] Oxidation of 1 to 8 by DMSO has been reported to occur under sonication or long reaction times.[1]

$[(DMSO)Pd(1)](BF_4)_2$ (2)

Complex 2 (0.269 g (0.227 mmol)) stirred in 3 mL DMSO with 75 μL water, in air for three weeks yielded 0.127 g (1.35 mmol) $DMSO_2$. In a repeat experiment, 0.056 g of 2 ($4.7x10^{-2}$ mmol) yielded 0.024 g $DMSO_2$ (0.26 mmol).

In the absence of water, 0.0562 g of 2 in DMSO for three weeks provided trace amounts of $DMSO_2$ detected by ^1H NMR that were not isolated.

The oxidationof DMSO was performed in the presence of ^{18}O labelled water (>1.5%). Complex 2 (0.0034 g, $2.9x10^{-3}$ mmol) was stirred in 2.5 mL DMSO with 100 L $^{18}OH_2$ for three weeks. $DMSO_2$ (0.0017 g, $1.7x10^{-2}$ mmol) was isolated from the reaction, purified by sublimation and submitted for exact mass spectral analysis to determine the extent of incorporation of ^{18}O. A control reaction was included in which 0.0015 g $DMSO_2$ was stirred in 2.5 mL DMSO with 100 μL $^{18}OH_2$ for the same time period, the DMSO isolated, and submitted for mass spectral analysis. The resultant percentage incorporation of ^{18}O was: 4.90% ± 0.03 when no ^{18}O was present, 4.92% 0.03 when $DMSO_2$ was stirred with $^{18}OH_2$, and 4.94% 0.03 when the $DMSO_2$ resulted from the oxidation of DMSO in the presence of $^{18}OH_2$.

Addition of 0.0035 g ($6.0\text{x}10^{-2}$ mmol) NaCl to 0.0328 g ($2.71\text{x}10^{-2}$ mmol) of 2 in 2.5 mL DMSO and 75 µL water produced a trace amount of $DMSO_2$ detected by ^1H NMR, which was not isolated.

[(DMSO)Pd(1)]Cl_2 (3)

A DMSO solution of complex 3 loosely capped and set aside in air for ca. 1.5 year reacted to produce a detectable amount of $DMSO_2$. Unreacted 3 remained in solution while 0.0160 g ($1.55\text{x}10^{-2}$ mmol) of $Cl_2Pd((Ph_2PCH_2)_2C_2H_2(P(O)Ph_2)_2)$ (4) crystallized and was structurally characterized. (^1H NMR (4) ($CDCl_3$): δ 7.86 (6H, m, Ph); 7.65 (12H, m, Ph); 7.2 - 7.5 (35H, m, Ph + $CHCl_3$); 2.32 (4H, complicated m, CH_2); 2.09 (6H, m, CH_2 + CH)) (^{13}C NMR ($CDCl_3$): δ 148.4 (m, Ph-P(O) ipso); 133.1 (m, Ph-PPd ipso); 131.7 (m, Ph); 130.9 (m, Ph); 130.5 (m, Ph); 128.5 (m, Ph); 126.6 (m, Ph); CH_2 and CH not observed).

Repetition of the reaction over three weeks in the presence of H_2O yielded no detectable $DMSO_2$.

$(PdCl_2)_2$(1) (5)

Stirring 0.0299 g ($2.54\text{x}10^{-2}$ mmol) 5 in 2.5 mL DMSO and 75 µL water for three weeks yielded no detectable $DMSO_2$.

$[Pd(Ph_2MeP)_4](BF_4)_2$ (6)

DMSO was not detectably oxidized to $DMSO_2$ by 0.0199 g ($2.57\text{x}10^{-2}$ mmol) of 6 in 2.5 mL DMSO and 75 µL water after three weeks.

$[Pd(dppe)_2](BF_4)_2$ (7)

Complex 7 crystallized from a solution of 0.0987 g ($9.17x10^{-2}$ mmol) 7 in 2.5 mL DMSO and 75 μL water over three weeks and $DMSO_2$ was not detected.

X-ray Crystallographic Procedures for 4[7]

Data Collection and Reduction

A pale yellow pinacoidal crystal of approximate dimensions 0.20 x 0.20 x 0.60 mm was mounted on a glass fiber in a random orientation. Cell constants and an orientation matrix for data collection were obtained from least-squares refinement, using the setting angles of 25 reflections in the range $22 < 2\theta < 34$. The data were collected using the θ- 2θ technique.

A total of 7783 reflections were collected, of which 3896 were unique and not systematically absent. As a check on crystal and electron stability, three representative reflections were measured every 60 min. No significant loss of intensity was observed throughout the data collection, so no decay correction was applied. Lorentz and polarization corrections were applied to the data. The linear absorption coefficient is 6.2 cm^{-1} for MoK_α radiation. An empirical absorption correction, based on a series of psi-scans, was applied to the data. Relative transmission coefficients ranged from 0.965 to 0.999 with an average value of 0.987. Intensities of equivalent reflections were averaged. The agreement factors for the averaging of the 3896 observed and accepted reflections was 2.0% based on intensity and 1.7% based on F_o. Table I contains a tabulation of the pertinent information relevant to data collection and reduction.

Structure Solution and Refinement

The position of the Pd atom was given by a Patterson interpretation method.[8] The remainder of the non-hydrogen atoms were located from subsequent difference-Fourier and least-squares refinement cycles. Following least-squares refinement of all of the non-hydrogen atoms in the Pd complex, the oxygen atom of a water molecule and a partially disordered molecule of DMSO were located in the lattice. The DMSO molecule was disordered such that the oxygen atom and the two methyl groups defined a plane, on either side of which were located half-occupancy atoms. The total occupancy of the solvent molecule refined to a value of 0.88.

The parameters thus defined were refined in full-matrix least-squares calculations. Scattering factors were taken from Cromer and Waber.[9] Anomalous dispersion effects were included in F_c;[9] the values for f' and f" were those of Cromer.9 Only those reflections having intensities greater than 3.0 times their standard deviation were used in the refinements.

Analysis of residual electron density on an electron density difference map (maximum = 2.2e/Å^3, located 0.23 from Pd) indicated all atoms were accounted for by the model.

RESULTS

The production of $DMSO_2$ by the oxidation of DMSO in the presence of Pd(II) complexes is summarized in Table II. The control reactions in which the uncoordinated ligand 1 was stirred in DMSO and a blank in which no other substance was added to the DMSO/H_2O solution gave no oxidized product. In fact the solution of 1 resulted in a reduction of DMSO to DMS and the oxidation of the phosphine to $[(Ph_2P(O)CH_2)_2CH]_2$ (8). The oxidation of 1 by DMSO has been reported by us, and occurs either in the presence or absence of air.[1] The oxidized phosphine 8 was easily identified by the downfield shift in the ^{31}P NMR spectrum (37.5 ppm) relative to -22.0 ppm for 1 (Table III). The oxidation was not complete, and in the region of 36 to 38 ppm, several signals were observed, in addition to signals in the -15 to -22 ppm region.

In the presence of complex 2, air, and water, more than 5 equivalents of DMSO is oxidized relative to the initial amount of 2, and in the strict absence of H_2O, no oxidation was detected. If this observation were due to a stoichiometric reaction in which DMSO and the phosphine ligand were simultaneously oxidized, the maximum mole ratio of $DMSO_2$ to starting Pd complex would be 4. In order to verify that this system is catalytic and gain insight into the reaction, the fate of the Pd complex must be considered. ^{31}P NMR spectrometry was used to identify the Pd complexes once the oxidation reactions were ended. The ^{31}P NMR spectral data and infrared data for the starting materials are given in Table III.

In each of the reactions involving complex 2, the composition of the Pd complexes in solution was altered. The starting complex 2 gives a single resonance at 30.8 ppm. The spectra at the end of each oxidation reaction showed a much more complex mixture. In one example, resonances (with relative peak areas in parentheses) were observed at 40.2 ppm (1P), 38.0 ppm (1.5P), 31.7 ppm (2.4P), and 20.0 ppm (2.5P), but the major peak remained at 30.9 ppm (8.2P). In subsequent runs involving 2, the same general pattern was observed in the final ^{31}P NMR spectra.

When the BF_4^- anion in 2 is replaced with a coordinating anion, as in complex 3, only a trace amount of $DMSO_2$ was detected after three weeks. When the reaction was allowed to proceed for 1.5 years, two moles of $DMSO_2$ was isolated for each mole of complex 4 that was recovered from the solution. In this reaction, two of the phosphines were oxidized and displaced by the chlorides to give the final complex 4. Complex 4 crystallized from the reaction mixture, and after 1.5 year, unreacted 3 was still detected in solution over the crystals by ^{31}P NMR. Numerous other peaks representing partially oxidized phosphine, and complex 4 were also present. Repetition of the reaction with a three week reaction time yielded no detectable $DMSO_2$ and no detectable destruction of 3. Crystals of complex 4 were submitted for X-ray crystallographic analysis. The ORTEP diagram of 4 is shown in Figure 2, the heavy atoms and carbon skeleton are shown in Figure 3, and the unit cell is shown in Figure 4. Selected bond distances, bond angles and isotropic positional parameters are given in Tables IV, V, and VI, respectively. Anisotropic thermal parameters, hydrogen atom positions and structure factor tables can be found in Appendix III.

The dinuclear complex 5 and the tetraphosphine oxide of 1 have also been structurally characterized.[1] Since both 4 and 5 have the same $Cl_2Pd(Ph_2PCH_2)_2CH$ subunits, the bond angles and distances should compare favorably. The Pd atom in 4 is square planar with minor deviations from planarity. The Pd is 0.034(1) Å out of the P_2Cl_2 plane, and the sum of the bond angles about Pd is 360°. In complex 5, the Pd is nearly square planar with a deviation of 0.071 Å out of the P_2Cl_2 plane. The P-Pd-P bond angle at 94.6(1)°, is very close to the P-Pd-P angles in complex 5 (93.7(4) and 94.5(5)°. The Cl-Pd-Cl bond angles are

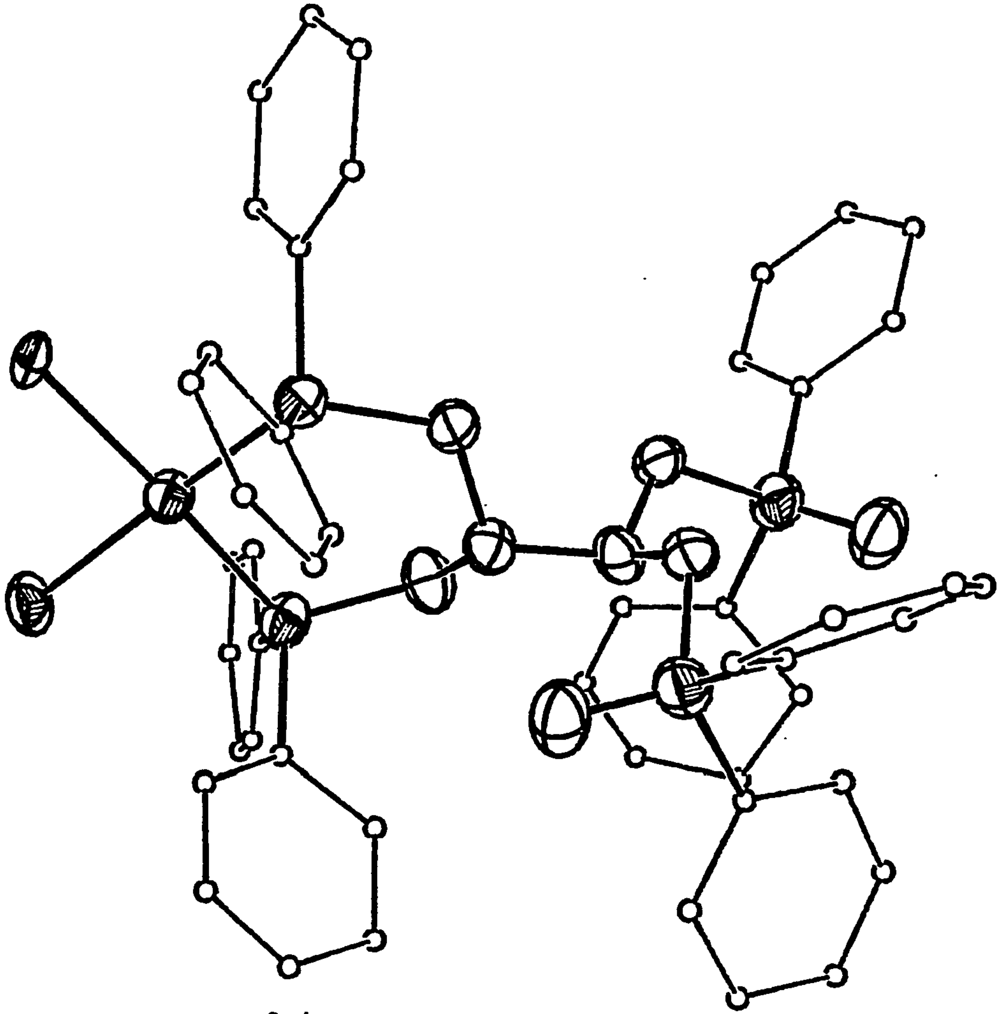


Figure 2. Complete ortep diagram of 4

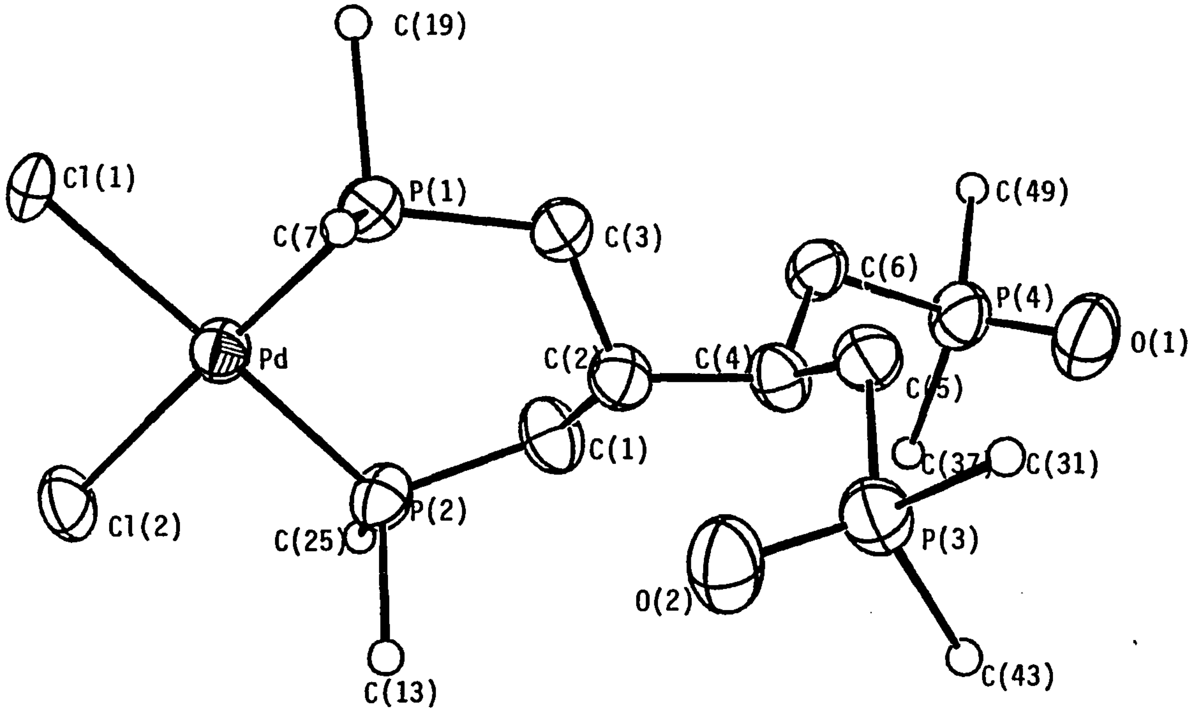


Figure 3. Ortep diagram of 4, showing only the heavy atoms and skeletal carbons

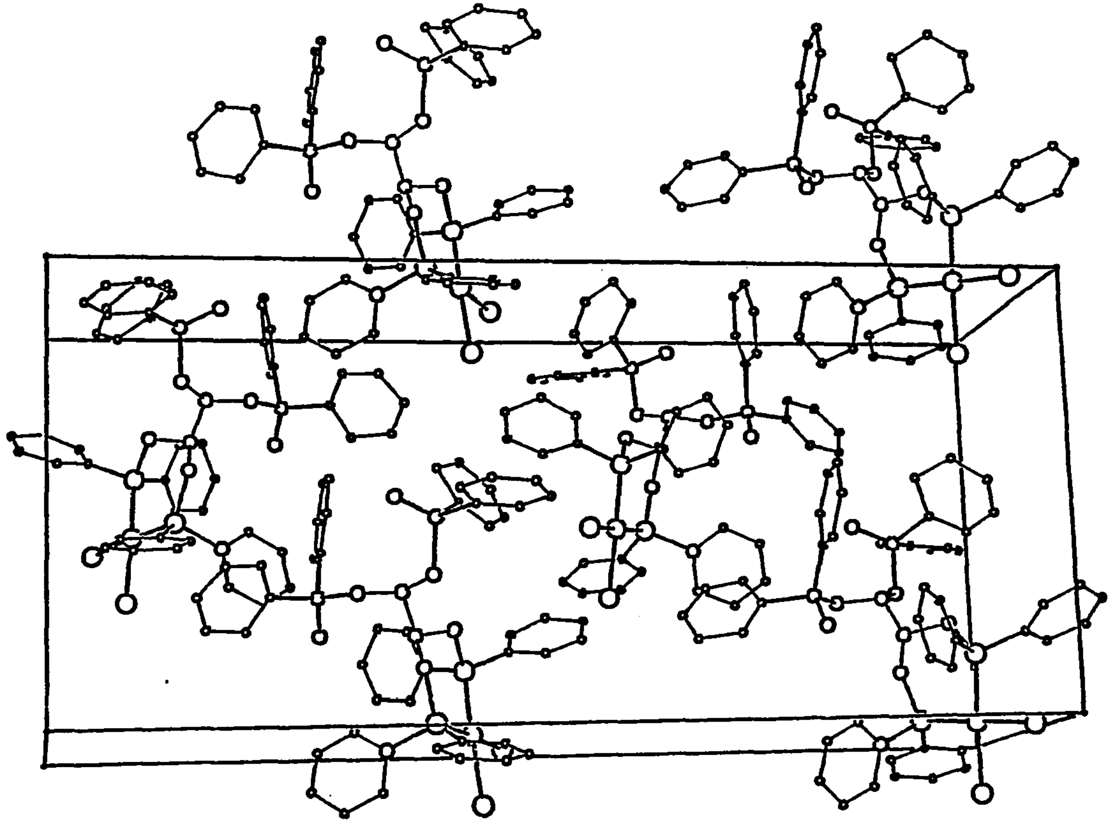


Figure 4. Unit cell diagram of 4

92.21(9)Å in 4, and 89.6(4) and 90.65(6)Å in 5. The Pd-Cl bond lengths are from 2.32(1) and 2.36(1) Å in 5, and 2.415(2) and 2.386(3) Å in 4.

The P-Pd bond lengths in 5 are between 2.23(1) and 2.26(1) , and in 4 they are 2.243(3) and 2.229(3) . The strain created by the formation of a six-membered chelate ring has already been discussed in relation to complex 5.[1] Comparing complexes 4 and 5, the increased freedom of the uncoordinated phosphine oxide arms appears to have decreased the strain caused by the adjacent chelate ring in 5 and thus decreased the distortion in the square plane around Pd in 4. There is no evidence for hydrogen bonding through the phosphoryl oxygen as was observed in the tetraphosphine oxide.

When two equivalents of Cl^- was added to 2 in DMSO/H_2O, the presence of the coordinating anion inhibited the oxidation of DMSO, and only a trace amount of $DMSO_2$ was detected in the ^1H NMR spectrum after three weeks.

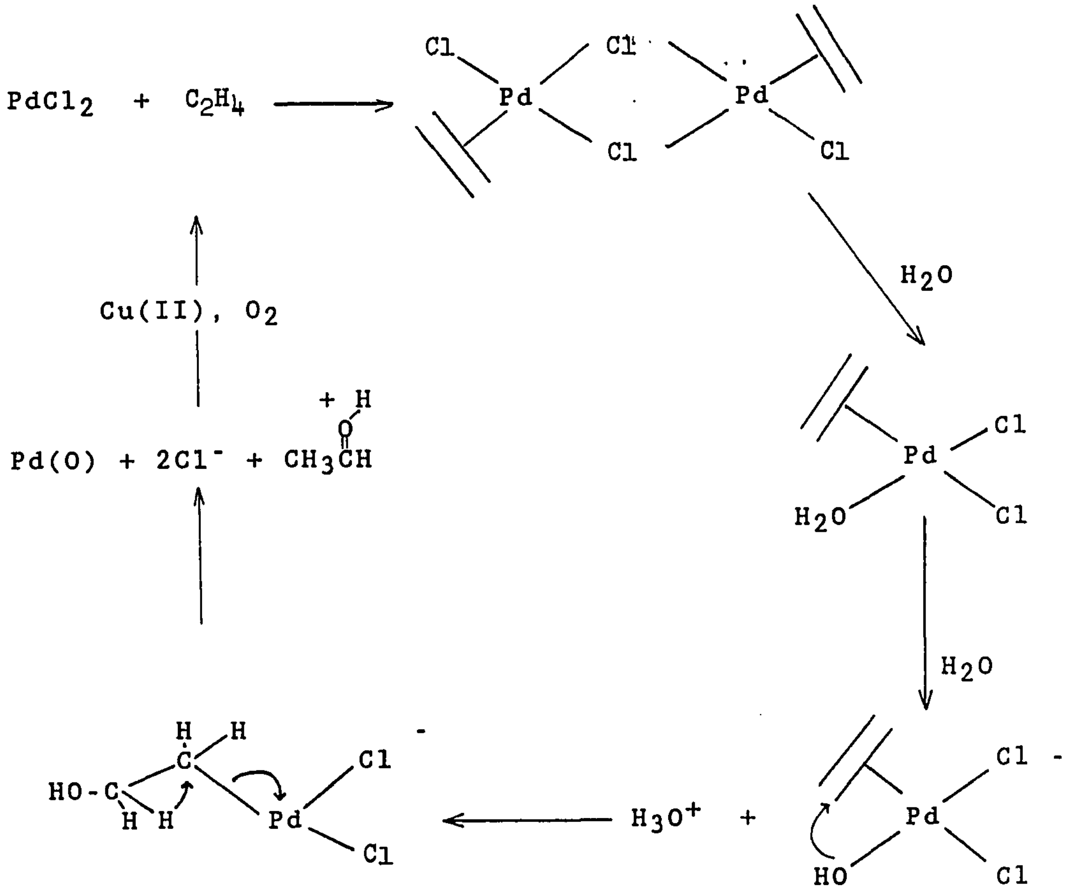
The dipalladium complex 5 in which two chlorides are bound to the Pd atom, also did not produce any $DMSO_2$ over a three week period in DMSO and H_2O.

DISCUSSION

The catalysis of organic reactions by transition metals can be reduced to three basic steps: 1)oxidative addition to a reduced species, 2) insertion into a metal substrate bond, and 3) reductive elimination of the product. During this sequence Pd phosphine catalysts must be able to cycle between a reduced species and Pd(II). It is this ability to alternate between oxidation states that qualifies the Pd complex for catalytic activity. Additionally, the catalyst must be in a state of coordinative unsaturation allowing coordination of the substrate, or oxidative addition.

Catalytic oxidation of organic substrates by Pd is known to proceed through palladium hydroxide (Wacker process), palladium dioxygen compounds, and palladium nitro compounds.[2] Since nitrate is not present in DMSO solutions of 2, the latter oxidation process can be dismissed.

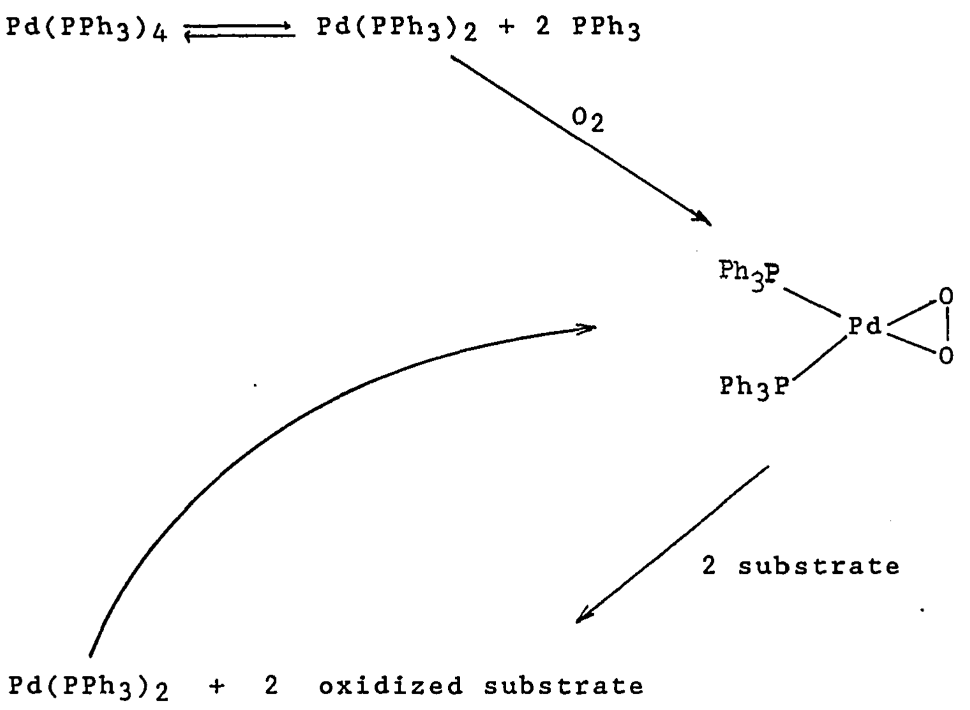
The Wacker process is the industrially important oxidation of olefins by $PdCl_2$. The catalysis requires the presence of H_2O to produce a Pd-OH or Pd-OH_2 species which is the active catalyst. Because of the importance of this process, it has been studied in detail. The mechanism for this oxidation is given in Scheme 1. The key step in this process is nuceophilic attack of OH^- or H_2O on the



Scheme 1. Wacker process for oxidation of olefins catalyzed by Pd

coordinated olefin. The role played by Pd involves increasing the electrophilic nature of the olefin by removing electron density from the pi orbitals upon coordination and thus increasing susceptibility towards nucleophilic attack.

In catalytic oxidation by dioxygen complexes, a



Scheme 2. Catalytic oxidation by palladium dioxygen phosphine complexes

reduced Pd phosphine complex such as $Pd(PPh_3)_4$ oxidatively adds molecular O_2 in situ to give the active catalyst. The mechanism for this process is shown in Figure 2.

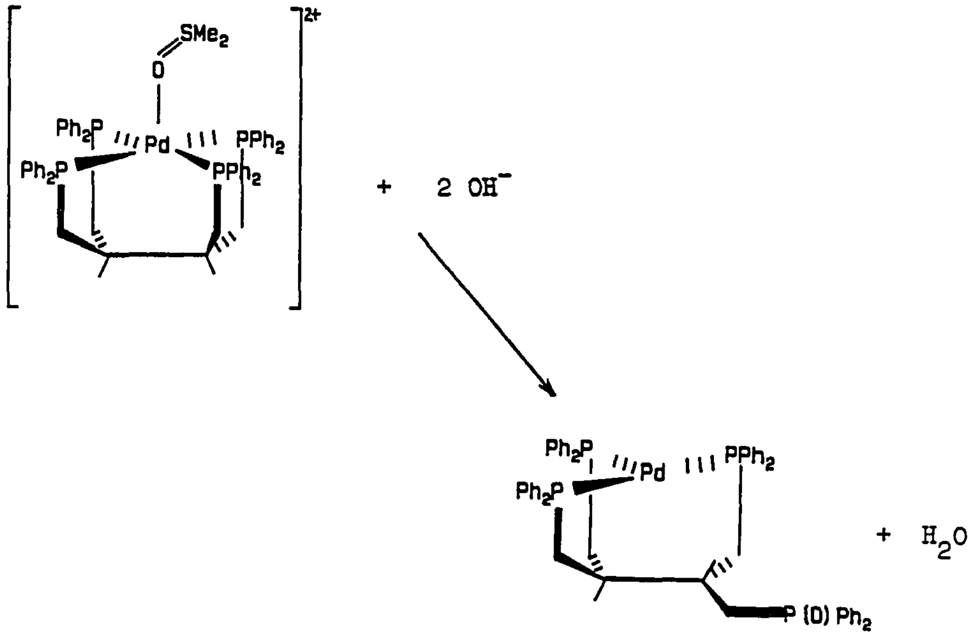
The oxidation of DMSO to $DMSO_2$ is catalyzed by 2, in which Pd is in the +2 oxidation state. The active catalyst therefore must be a Pd(II) species, or is the result of reduction in the reaction mixture to give Pd(0).

Consideration of Pd(II) as the active species in solution further leads to two possible mechanisms.

Coordination of DMSO to 2 in the solid state has been shown to occur through the O atom.[1] By induction of electron density, coordination should increase the electrophilic nature of the S of DMSO. However, direct nucleophilic attack of molecular oxygen on a substrate has not been reported. Nucleophilic attack by H_2O or OH^- as in the Wacker process is more reasonable.

The presence of water was found to be necessary for catalytic oxidation of DMSO by 2 and would appear to be consistent with the Wacker process for oxidation. However, the amount of water added to the DMSO solutions was less than the stoichiometric amount needed to produce the observed amounts of $DMSO_2$. In one such reaction, 4.2×10^{-6} mol H_2O was added to the reaction and 2.6×10^{-4} mol of $DMSO_2$ was obtained from the oxidation. Application of the Wacker process to catalytic oxidation by 2 presents the additional problem of how the resulting Pd(0) complex could be oxidized back to the active Pd(II) catalyst.

If a palladium dioxygen complex is the active catalyst, the question arises as to how the starting Pd(II) complex was reduced to Pd(0). Perhaps this question has already been answered in the discussion of Wacker-type chemistry in which Pd(II) is reduced to Pd(0) in the first cycle. An additional consideration is the reduction of Pd(II) by the phosphine ligand which would yield a three-



Scheme 3. Possible pathway for reduction of 2 by a phosphine arm

coordinate Pd(0) phosphine complex (Scheme 3). This could then oxidatively add O_2 to yield the active catalyst.

The addition of Cl^- inhibits the oxidation of DMSO by 2. The reduction in catalytic activity upon replacement of a non-coordinating with a coordinating anion indicates blockage of an active site on the Pd which leads to a catalytically dead Pd complex. As indicated by NMR studies, coordinated DMSO in complex 2 is displaced to a substantial extent (50%) by chloride in $CHCl_3$ but is not displaced in DMSO solutions.[1] In DMSO, the dipalladium complex 5 reacts with an equivalent of the ligand 1 to form

2. Since free ligand 1 displaces Cl^- in DMSO solution, displacement of one or more of the phosphine arms of 1 by Cl^- to produce an inactive complex can be ruled out.

The fate of the Pd in the reaction of 3 with DMSO has been determined. When Cl^- is the anion, the Pd in the final product is coordinated to two of the four phosphines of ligand 1 and two Cl^-, the two remaining phosphine arms having been oxidized. However this reaction proceeds much more slowly than the oxidation of DMSO by 2 and may not follow the same reation pathway.

The role played by water in the oxidation of $DMSO_2$ by complex 2 remains unclear. However, in the absence of water, no oxidation was observed in the presence of 2. The results of the $^{18}OH_2$ labelling experiment are inconclusive. When unlabelled water was added to the reaction of 2 and DMSO, 4.90% ±0.03 ^{18}O was found in the resultant $DMSO_2$ by mass spectral analysis. Stirring unlabelled $DMSO_2$ with $^{18}OH_2$ followed by reisolation of the $DMSO_2$ showed 4.92%± 0.03 incorporation of ^{18}O, and the addition of $^{18}OH_2$ to the reaction of 2 with DMSO gave 4.94% ±0.03 ^{18}O in the $DMSO_2$ produced. The percentages of ^{18}O incorporation are not sufficient to draw any conclusions concerning the role H_2O plays in the oxidation process, and should be repeated with an initially higher percentage labelled H_2O.

There have been no reports in the literature of a similar oxidation of DMSO by a Pd(II) phosphine complex. For this reason, Pd(II) complexes containing Ph_2MeP and $Ph_2PCH_2CH_2PPh_2$ (dppe) analogous to 2 were prepared in order to investigate their activity towards the oxidation of DMSO. Complexes 6 and 7 did not show any activity towards the oxidation of DMSO, producing no detectable $DMSO_2$ after three weeks reaction time. In the course of this time, complex 6 crystallized from the solution as pale yellow plates. Complex 7 began to decompose producing a black silt in the reaction flask and Ph_2MePO in solution.

The catalytic oxidation of DMSO to $DMSO_2$ by complex 2 is complicated. The ^{31}P NMR spectrum of the final product yields several peaks in the regions expected for both the starting material, and oxidized phosphine. Further study of this system should include the separation and characterization of the resulting Pd species which may provide more information about the active catalyst. The production of $DMSO_2$ as a function of temperature and pressure of O_2 should also be studied.

TABLES

Table I. Crystal Data for 4

Formula	$PdP_4O_2Cl_2C_{54}H_{50}$, C_2H_6SO
Formula weight	1126.3
Space Group	$P_{na}2_1$, No.33
α,	33.375(5)
β,	11.125(2)
γ,	14.886(3)
V, ^{3}	5527(3)
Z	4
calc, g/cm^3	1.354
Crystal size, mm^3	0.2 x 0.2 x 0.6
$\gamma(MoK_\alpha)$, cm^{-1}	6.2
Data collection instrument	Enraf-Nonius CAD4
Radiation (monochromated in incident beam)	MoK_α (= 0.71073Å)
Orientation reflections, number, range (2)	25, 22-34
Temperature, C	21
Scan method	θ-2θ
Data col. range, 2 ( )	0 - 50
No. unique data, total with $F_o{}^2 > 3\sigma(F_o{}^2)$	3896, 3031
Number of parameters refined	592
R^a_ω	0.0662

$^aR = \sigma\ |F_o| - |F_c|)^2/\Sigma\omega F_o{}^2]^{\frac{1}{2}}$, $\omega = \sigma(F_o)$.

Table I. continued

Quality-of-fit indicator	2.07
Largest shift/esd, final cycle	0.03
Largest peak, e/Å^3	2.2

Table II. Oxidation of DMSO by Pd(II) phosphine complexes to form $DMSO_2$, reaction time 3 weeks

compound	conditions	mole $DMSO_2$ produced/initial mole compound
$[(Ph_2PCH_2)CH]_2$	$DMSO/air/H_2O$	0
$[(DMSO)Pd(1)]^{2+}$	$DMSO/air/H_2O$	5.95
	$DMSO/air/H_2O$	5.40
	$DMSO/air/H_2{}^{18}O$	5.92
	DMSO/air	trace
	$DMSO/air/H_2O/2Cl^-$	trace
$[(DMSO)Pd(1)]Cl_2$	$DMSO/air/H_2O$[a]	2
$(PdCl_2)_2(1)$	$DMSO/air/H_2O$	0
$[Pd(dppe)_2](BF_4)_2$	$DMSO/air/H_2O$	0
$[Pd(Ph_2MeP)_4](BF_4)_2$	$DMSO/air/H_2O$	0
-	$DMSO/air/H_2O$	0

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[a] Reaction time was ca. 1.5 years, open to air on a bench top.

Table III. $^{31}P\{^{1}H\}$ NMR and infrared data.

compound	$\delta\ ^{31}P\{^{1}H\}$ (ppm)	ν M_{-X}(cm^{-2})
$(Ph_2PCH_2)_4C_2H_4$ (1)	-22.0	-
$[(DMSO)Pd(1)](BF_4)_2$ (2)	+30.9	-
$[(DMSO)Pd(1)]Cl_2$ (3)	+30.8	*[a]
$Cl_2Pd(Ph_2PCH_2)_2C_2H_2$-$(CH_2P(O)Ph_2)_2$ (4)	+31.6[b] +20.4	303 m 291 m
$(PdCl_2)_2(1)$ (5)	+21.4	316 w 296 m
$[Pd(dppe)_2](BF_4)_2$ (6)	+68.3	-
$[Pd(Ph_2MeP)_4](BF_4)_2$ (7)	+13.5	-
$[(Ph_2P(O)CH_2)_2CH]_2$ (8)	+37.6	-

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[a] No absorptions were observed that could be assigned to ν_{PdCl} between 400-150 cm^{-1}.

[b] +31.6 ppm corresponds to P=O; +20.4 ppm corresponds to P bonded to Pd.

Table IV. Selected bond distances for 4

atoms	distances	atoms	distances
Pd-Cl1	2.415(2)	Pd-Cl2	2.386(3)
Pd-P1	2.243(3)	Pd-P2	2.229(3)
P1-C3	1.84(1)	P1-C7	1.82(1)
P1-C19	1.80(1)	P2-C1	1.81(1)
P2-C13	1.79(1)	P2-C25	1.78(1)
P3-O2	1.480(9)	P3-C5	1.80(1)
P3-C31	1.80(1)	P3-C43	1.78(1)
P4-O1	1.485(9)	P4-C6	1.81(1)
P4-C37	1.81(1)	P4-C49	1.80(1)
C1-P2	1.81(1)	C1-C2	1.54(1)
C2-C3	1.54(1)	C2-C4	1.55(1)
C3-P1	1.84(1)	C3-C2	1.54(1)

Table V. Selected bond angles for 4

atoms	angle	atoms	angle
Cl1-Pd-Cl2	92.21(9)	Pd-P1-C3	120.4(3)
Cl1-Pd-P1	87.91(9)	Pd-P1-C7	107.4(4)
Cl1-Pd-P2	177.3(1)	Pd-P1-C19	115.7(4)
Cl2-Pd-P1	174.9(1)	C3-P1-C7	106.3(6)
Cl-Pd-P2	85.3(1)	C3-P1-C19	98.9(5)
P1-Pd-P2	94.6(1)	C7-P1-C19	107.2(6)
Pd-P2-C1	116.8(3)	O2-P3-C5	114.5(5)
Pd-P2-C13	112.6(4)	O2-P3-C31	110.2(6)
Pd-P2-C25	112.3(4)	O2-P3-C5	112.7(5)
C1-P2-C25	106.6(5)	C5-P3-C31	103.8(5)
C1-P2-C25	99.3(6)	C5-P3-C43	106.8(5)
C13-P2-C25	108.0(5)	C31-P3-C43	108.3(6)
O1-P4-C6	113.7(5)	P2-C1-C2	116.2(8)
O1-P4-C37	113.9(6)	C1-C2-C3	110.8(8)
O1-P4-C49	112.3(5)	C1-C2-C4	108.9(8)
C6-P4-C37	105.1(5)	C3-C2-C4	112.7(8)
C6-P4-C49	104.6(5)	P1-C3-C2	118.8(7)
C37-P4-C49	106.4(6)	C2-C4-C5	111.1(8)
C2-C4-C6	111.2(8)	C5-C4-C6	111.6(8)
P3-C5-C4	116.4(7)	P4-C6-C4	113.1(7)

Table VI. Anisotropic positional parameters; starred atoms were refined isotropically.

atom	x	y	z	B(A^2)
Pd	0.08823(2)	0.18637(6)	0.000	2.88(2)
Cl1	0.08154(8)	0.2404(2)	0.1564(2)	2.93(5)
Cl2	0.04891(8)	0.0091(2)	0.0194(2)	3.70(6)
P1	0.13000(8)	0.3429(2)	-0.0155(2)	3.00(6)
P2	0.09183(8)	0.1314(3)	-0.1438(2)	3.07(6)
P3	0.24083(9)	0.2768(3)	0.7076(2)	3.56(7)
P4	0.13353(9)	0.5084(3)	-0.4386(2)	3.64(7)
O1	0.1735(2)	0.5271(7)	-0.4801(6)	5.0(2)
O2	0.2365(2)	0.1897(7)	-0.2179(6)	4.6(2)
C1	0.1063(3)	0.246(1)	-0.2235(8)	3.6(3)
C2	0.1468(3)	0.3089(9)	-0.2059(7)	2.9(2)
C3	0.1432(3)	0.3992(9)	-0.1280(7)	3.2(2)
C4	0.1615(3)	0.3681(9)	-0.2941(7)	3.0(2)
C5	0.2062(3)	0.4005(9)	-0.2886(7)	3.3(2)
C6	0.1355(3)	0.4794(9)	-0.3188(6)	3.0(2)
C7	0.1771(4)	0.3023(9)	0.0386(8)	3.8(3)
C8	0.2059(3)	0.237(1)	-0.0074(9)	3.8(2)
C9	0.2413(4)	0.203(1)	0.0347(9)	5.1(4)

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[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as:(4/3) * [a^2 * B(1,1) + b^2 * B(2,2) + c^2 * B(3,3) + ab(cos gamma) * B(1,2) + ac(cos beta) * B(1,3) + bc(cos alpha) * B(2,3)].

Table VI. continued

atom	x	y	z	B(A^2)
C10	0.2484(4)	0.228(1)	0.121(1)	5.1(4)
C11	0.2194(5)	0.296(1)	0.1705(8)	5.5(4)
C12	0.1828(4)	0.332(1)	0.1303(80	5.1(3)
C13	0.1248(3)	0.007(1)	-0.1612(8)	3.8(3)
C14	0.1378(7)	-0.054(2)	-0.097(1)	10.3(7)
C15	0.1676(9)	-0.146(2)	-0.109(1)	14(1)
C16	0.1813(5)	-0.171(2)	-0.190(1)	8.6(6)
C17	0.1668(7)	-0.110(2)	-0.190(1)	9.1(6)
C18	0.1416(8)	-0.010(2)	-0.248(1)	10.0(7)
C19	0.1134(4)	0.482(1)	0.0343(7)	4.0(3)
C20	0.0725(5)	0.501(1)	0.042(1)	6.9(4)
C21	0.0572(6)	0.613(2)	0.073(1)	7.7(5)
C22	0.0831(8)	0.704(2)	0.092(1)	8.4(6)
C23	0.1257(9)	0.686(1)	0.085(1)	8.4(6)
C24	0.1404(5)	0.572(1)	0.055(1)	6.0(4)
C25	0.0440(3)	0.093(1)	-0.1889(7)	3.6(3)
C26	0.0360(5)	-0.009(1)	-0.237(1)	6.2(4)
C27	-0.0004(6)	-0.032(2)	-0.276(1)	9.2(6)
C28	-0.0330(5)	0.057(2)	-0.258(1)	6.9(5)
C29	-0.0258(4)	0.153(2)	-0.209(1)	7.0(5)
C30	0.0124(5)	0.178(2)	-0.176(1)	7.7(5)

Table VI. continued

atom	x	y	z	B(A^2)
C31	0.02893(5)	0.178(2)	-0.287(1)	4.6(3)
C32	0.3001(4)	0.439(1)	-0.345(1)	7.3(5)
C33	0.3347(6)	0.499(2)	-0.336(2)	10.2(8)
C34	0.3612(7)	0.480(2)	-0.272(2)	10.1(9)
C35	0.3514(6)	0.398(3)	-0.213(2)	12.2(9)
C36	0.3126(4)	0.318(2)	-0.217(1)	8.0(5)
C37	0.1059(4)	0.383(1)	-0.4854(9)	4.9(3)
C38	0.0729(4)	0.329(1)	-0.443(1)	5.2(4)
C39	0.0533(9)	0.233(2)	-0.474(2)	9.0(7)
C40	0.064(1)	0.188(3)	-0.542(3)	12(1)
C41	0.097(1)	0.225(2)	-0.597(2)	14(1)
C42	0.1236(6)	0.339(2)	-0.568(1)	8.1(5)
C43	0.2355(4)	0.209(1)	-0.3997(9)	4.2(3)
C44	0.2369(5)	0.083(1)	-0.403(1)	6.7(4)
C45	0.2311(6)	0.026(1)	-0.492(2)	8.8(5)
C46	0.2272(6)	0.095(2)	-0.569(1)	7.5(5)
C47	0.2259(6)	0.215(2)	-0.562(1)	7.0(5)
C48	0.2308(5)	0.274(1)	-0.4783(8)	6.0(4)
C49	0.1017(4)	0.639(1)	-0.4496(8)	4.4(3)
C50	0.0599(6)	0.640(1)	-0.443(1)	7.3(5)
C51	0.0370(6)	0.746(2)	-0.450(1)	8.2(5)
C52	0.0564(6)	0.849(1)	-0.467(1)	7.2(5)

Table VI. continued

atom	x	y	z	B(A$_2$)
C53	0.0979(6)	0.857(1)	-0.474(1)	7.9(6)
C54	0.1216(6)	0.748(1)	-0.468(1)	6.9(4)
S1	-0.0097(4)	0.445(1)	0.2503(8)	8.3(3)*
S2	-0.0187(4)	0.468(1)	0.3408(8)	8.6(3)*
O3	-0.0424(5)	0.537(2)	0.273(1)	10.9(5)*
C55	0.0348(8)	0.470(3)	0.307(2)	11.8(8)*
C56	-0.029(1)	0.325(3)	0.317(2)	13.0(9)*
O4	9.7141(4)	0.008(1)	0.3495(8)	8.3(3)*

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SECTION IV. REACTIONS OF (COD)PtI$_2$ AND THE FORMATION OF AN OLIGOMERIC FIVE-COORDINATE Pt(II) PHOSPHINE COMPLEX

INTRODUCTION

The formation of Pd(II) complexes of the tetraphosphine ligand 1, (Figure 1), has yielded dinuclear complexes in which the ligand bridges two Pd atoms, mononuclear complexes in which only two of the four phosphine arms are coordinated, and mononuclear, five-coordinate "pocket" complexes.[1]

The coordination chemistry of Pd(II) and Pt(II) are very similar[2], and it was a natural progression of this work to attempt to extend to Pt(II) the chemistry that has been observed for Pd(II). However, in the reaction of ligand 1 with many Pt(II) precursors, intractable solids were formed. However, the reaction of (COD)PtI_2 with 1 has yielded an oligomeric five-coordinate complex as the major product.

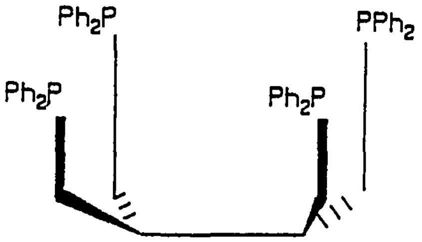


Figure 1. Ligand 1

EXPERIMENTAL

General Procedures

Preparative reactions were carried out under an inert atmosphere using solvents that were distilled from appropriate drying agent under N_2 or Ar prior to use. Reagents were used without further purification unless otherwise noted.

Solution ^{31}P NMR spectra were taken on a Bruker WM-300, or a Bruker WM-200 spectrometer operating in the Fourier mode. Chemical shifts were referenced to an external 85% H_3PO_4 standard. Positive values are downfield of the standard. Solid state ^{31}P NMR spectra were taken on a Bruker MSL-300 spectrometer and were referenced to $(NH_4)_2PO_4$. Solution ^1H and ^{13}C NMR spectra were taken on a Nicolet NT-300 spectrometer operating in the Fourier mode. Both were referenced to internal TMS.

Mid-infrared (4000 to 400 cm^{-1}) and far-infrared (600 to 150 cm^{-1}) spectra were taken on an IBM Fourier IR/98 spectrometer. Mid-IR range samples were prepared as KBr pellets or Nujol mulls on KBr plates; far-IR range samples were prepared as Nujol mulls on polyethylene plates.

Conductance measurements were made with a Markson ElectroMark Analyzer on solutions that were approximately 10^{-3} molar.

Cyclic voltammogram experiments were done with a

Bioanalytical Systems CV-1B Cyclic Voltammograph. A three-electrode configuration was employed, consisting of a stationary, Pt disc working electrode, a Pt wire counter electrode and a Ag/AgCl reference electrode. Solvents were distilled immediately prior to use and contained ca. 0.1 M *t*-Bu_4NPF_6 (TBAP) as the supporting electrolyte. Analyte concentration was ca. $1x10^{-3}$ M in a solution volume of 15 mL. Solutions were deoxygenated with Ar and measurements were made under Ar at room temperature.

Unsuccesful reactions of 1 with Pt(II) precursors

Reactions of ligand 1 with $(COD)PtCl_2$, $(MeS_2)_2PtCl_2$, $(PhCN)_2PtCl_2$, and $(PhCN)_2PtI_2$ in benzene yielded beige to white solids that were insoluble and not characterized, but were presumed to be polymeric or Magnus type salts $([Pt(1)][PtCl_4])$, which are characteristically insoluble.

Reaction of $(COD)PtI_2$ with 1

Stirring 0.297 g (0.361 mmol) $(COD)PtI_2$ with 0.198 g (0.361 mmol) ligand 1 in 150 mL benzene overnight at room temperature precipitated $[IPt(1)]_nI_n$ (2) as the major product. The product was isolated by filtration, washed with benzene followed by ether, and dried *in vacuo* to give 0.410 g of 2 (91.0% yield based on Pt). Complex 2 is slightly soluble in DMSO, and insoluble in other organic solvents. When initially isolated from the reaction mixture, 2 is orange in color, changing to a pale yellow color after repeated washes of benzene. It is stable in air as a solid, but as a DMSO solution decomposes over time (1 week). (mp >310 °C) (^{31}P NMR (DMSO): δ -0.50 (J_{Pt-P} = 2263 Hz))

From the filtrate, a second product was isolated by reduction of the volume of solvent and the addition of ether to initiate precipitation. The pale yellow solid, identified as $I_2Pt(Ph_2PCH_2)_2C_2H_2(CH_2P(O)Ph_2)_2$ (3), was formed as a minor product, yielding 0.017 g of 3 (3.63% based on Pt). Unlike complex 2, it is very soluble in organic solvents. (^1H NMR ($CDCl_3$): δ 7.84 (4H, m, Ph-ortho (P=O)), 7.60 (4H, m, Ph-ortho (P=O)), 7.3-7.4 (32H, m, Ph), 2.63 (4H, m, CH_2), 2.50 (2H, m, CH), 1.88 (4H, m, CH_2)) (^{13}C NMR ($CDCl_3$): 135.3 (m, Ph-ipso (P=O)), 133.4 (m, Ph-ipso (P-Pt)), 132.1 (m, Ph-ortho), 131.1 (d, $^3J_{P-C}$ = 5.43 Hz, Ph-meta(P-Pt)), 130.8 (d, $^3J_{P-C}$ = 8.32 Hz, Ph-meta(P=O)), 128.9 (d, $^4J_{P-C}$ = 11.29 Hz, Ph-para(P=O)), 128.3 (A part of an AB_2X system, J_{AB} = 4.26 Hz, J_{AX} =26.4 Hz, Ph, coupling unassigned))

Reaction of 2 with $AgAsF_6$

Complex 2 (0.010 g, $7.9x10^{-6}$ mol) was stirred with 0.002 g ($7.x10^{-6}$ mol) $AgAsF_6$ in 5 mL of 50/50 DMSO/$CHCl_3$.

AgI (0.001 g) precipitated from the solution, amounting to 65% of the theoretical. In a separate reaction, 0.014 g (1.1×10^{-5} mol) of 2 was reacted with 0.006 g $AgAsF_6$ to give 0.005 g of AgI (92% yield).

In subsequent reactions of $(COD)PtI_2$ and 1 in benzene, complex 2 was consistently obtained as the major product, and was isolated in yields ranging from 61% to 91%. The more soluble species in the reaction solution, however, gave various product distributions, with four to ten ^{31}P NMR peaks between -5 ppm and 36 ppm.

Preparation of $[(I_2Pt)_2(1)]_n$ (4)

Ligand 1 (0.096 g, 0.17 mmol) was stirred with 0.065 g (0.17 mmol) $(COD)PtI_2$ in 5 mL DMSO for 30 h. The reaction was followed by ^{31}P NMR, which indicated that the reaction was completed after 20 h. The solvent was removed and the resultant solid washed with acetone to remove the excess ligand, followed by a wash with ether, and dried in vacuo. The filtered product, $(I_2Pt)_2(1)$ (4), is a yellow powder (0.081 g, 81.5% yield). Complex 4 is insoluble in organic solvents, except for limited solubility in DMSO, and is air stable as a solid and in solution. (^{31}P NMR (DMSO): δ 0.40 (t, $^1J_{Pt-P}$ = 2286 Hz))

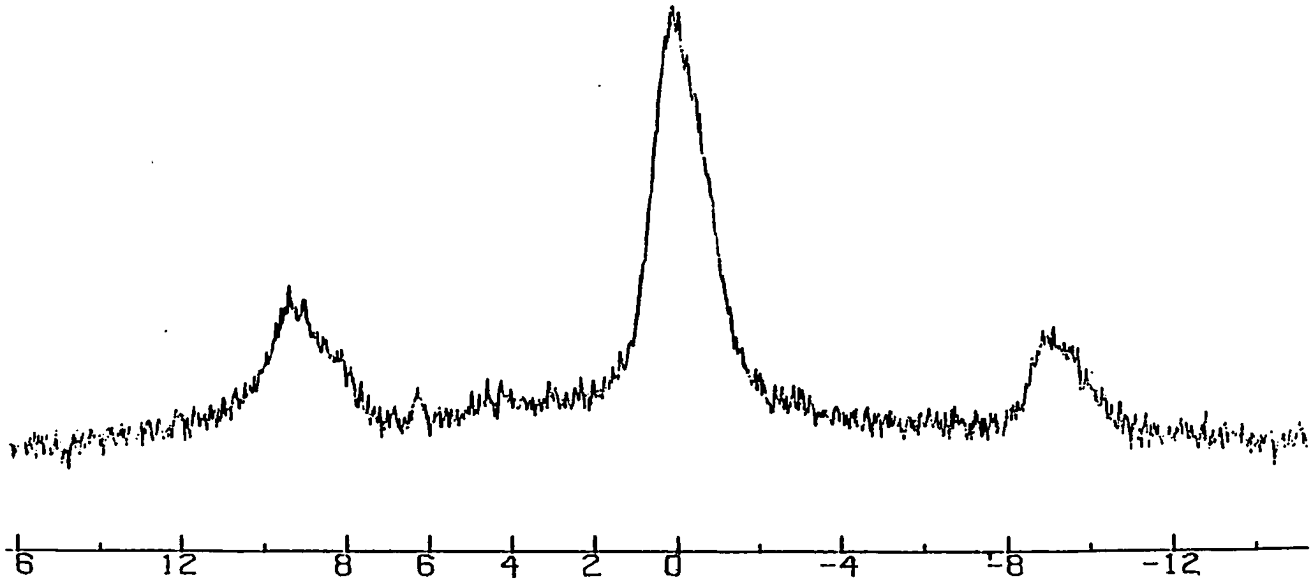
RESULTS

$[IPt(1)]_nI_n$

$[IPt(1)]_nI_n$ is the major product of the reaction of $(COD)PtI_2$ and 1 in benzene, but the yield varied between preparations from 61 to 91%. It is extremely insoluble, being only slightly soluble in DMSO. This limited the use of NMR techniques in characterization. The solution ^{31}P NMR spectrum shows a triplet at -0.50 ppm with a coupling between Pt and P of 2263 Hz, (Figure 2a and Table I). In the solid state ^{31}P NMR spectrum, two signals were observed at -5.50 and 3.07 ppm (Figure 2b).

Solution ^{1}H and ^{13}C NMR were not useful because of the low solubility of 2. The solid state ^{13}C NMR spectrum was taken to determine if COD was present in the product. The spectrum consisted of two signals, one at 130 ±10 ppm representing the phenyl carbons, and 32 ±12 ppm representing the alkyl carbons of the ligand (Figure 3). The resonance at 32 ppm appears to be two overlying signals for the ligand methylene and methine carbons. No resonances appear for coordinated or free COD in the region of 90-110 ppm, verifying the absence of COD in the product.

A sample of 2 was submitted for Fast Atom Bombardment mass spectral analysis. The highest molecular weight peak of significant intensity from a glycerol matrix was m/e 1145.5, corresponding to $[IPt(1)]^+$, mass 1145. This is



a.

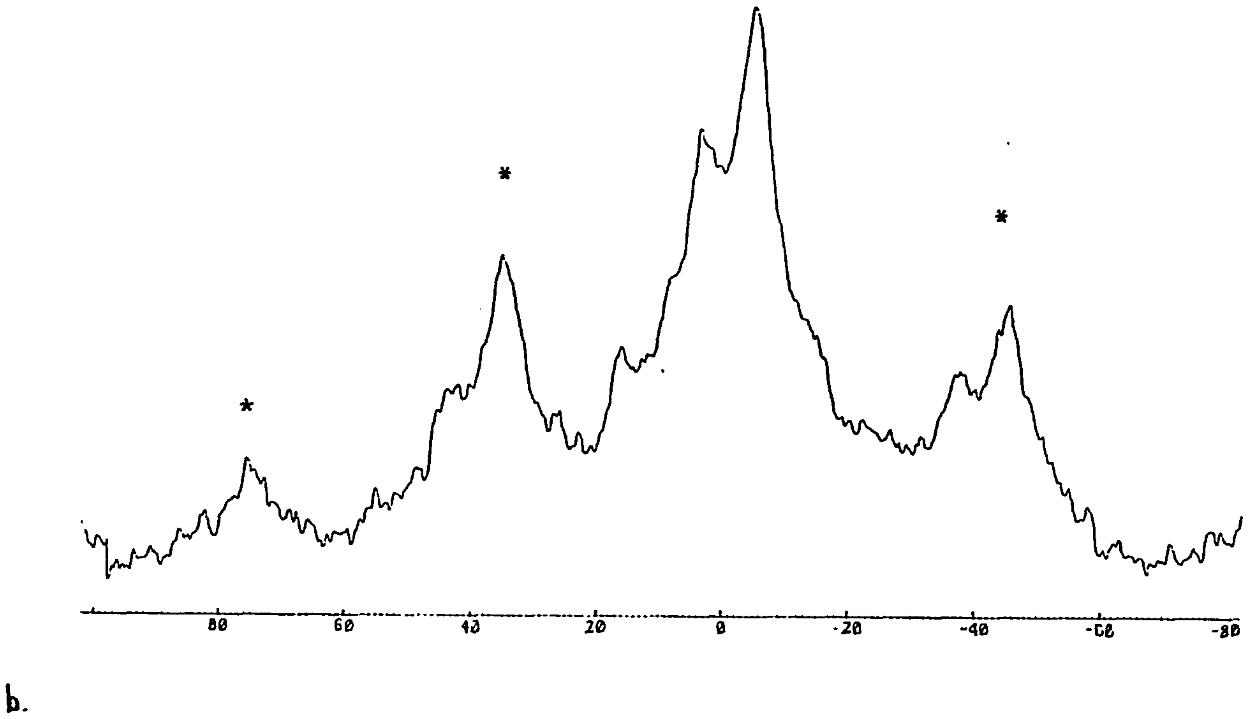


Figure 2. ^{31}P NMR spectra of 2, a) solution (DMSO), b) solid state, * denote spinning side bands

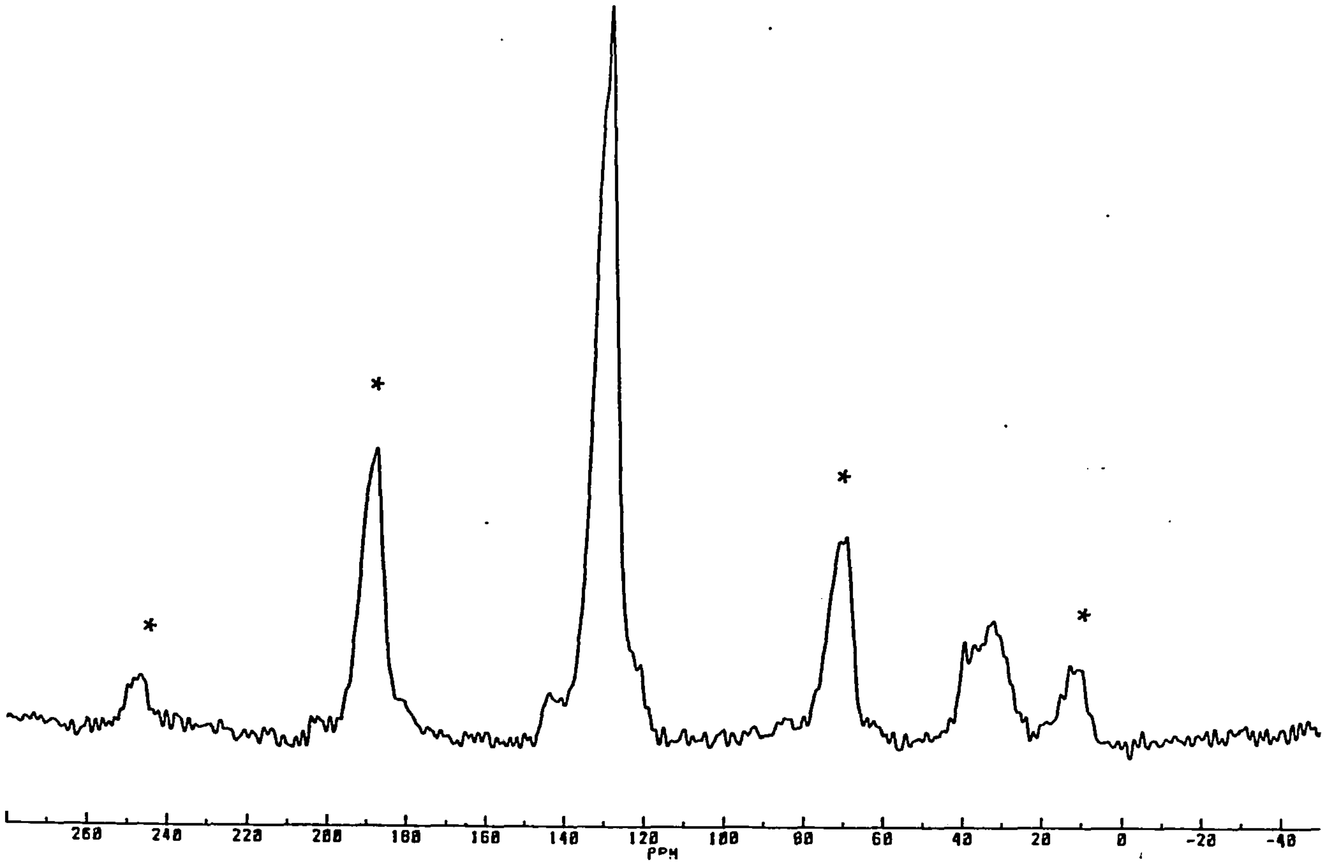


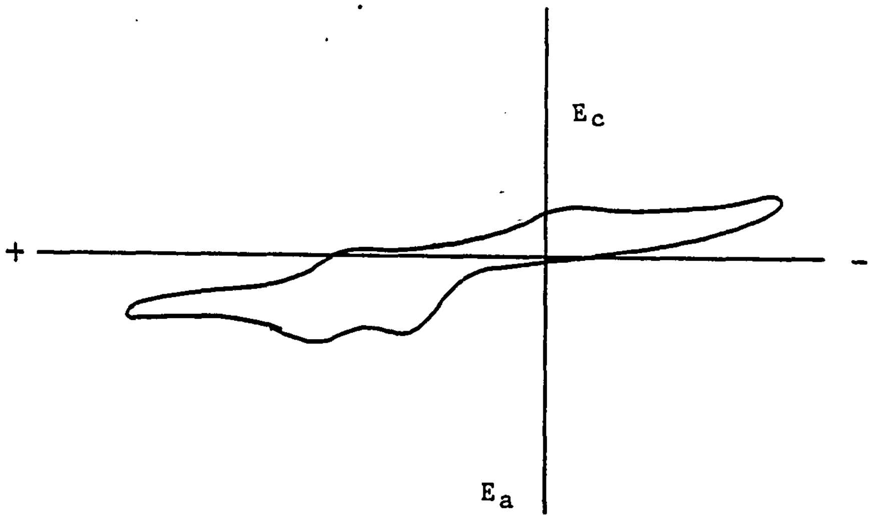
Figure 3. Solid state ^{13}C NMR spectrum of 2, * denote spinning side b

followed by loss of iodide to give m/e 1017.5 and loss of Pt to give m/e 885.5, which is the tetra-oxidized ligand 1 (mass 1 = 885.4). The remainder of the spectrum consists of a decomposition pattern typical of the ligand.

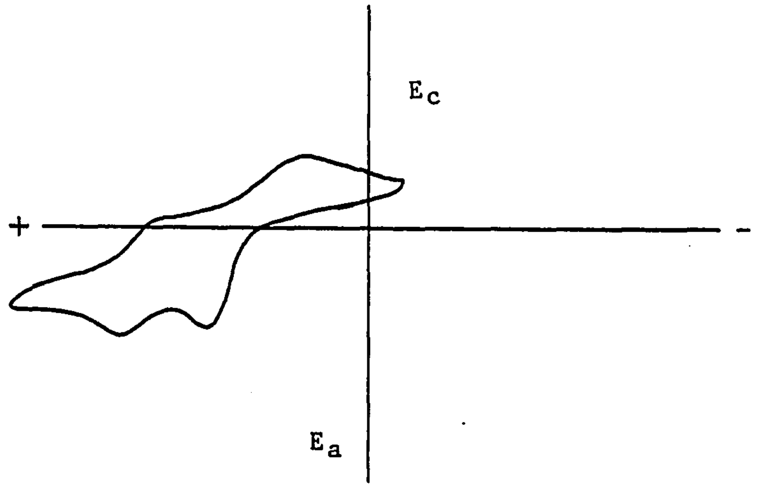
The presence of iodide was verified by the precipitation of AgI with a silver salt. Separate experiments in which 2 was reacted with one, and two equivalents of $AgAsF_6$, verified the presence of two I in the formula of 2.

The conductance of 2 in DMSO is 26.0 $cm^2\Omega^{-1}mol^{-1}$ and is consistent with a one-to-one electrolyte, indicating the coordination of one iodide in solution. However no absorptions were observed in the far-range IR that could be assigned to Pt-I (Table I).

Cyclic voltammogram experiments were done with complex 2 in CH_2Cl_2 and DMSO. In CH_2Cl_2, a two step non-reversible cycle is observed (Figure 4a), with reduction waves at 0.56 ±0.01 V and -0.06 ±0.03 V, and oxidation waves at 0.65 ±0.01 V and 0.38 ±0.01 V. In DMSO two nearly reversible couples are observed with reduction waves at 0.58 ±0.01 V and 0.20 ±0.01 V, and oxidation waves at 0.71± 0.01 V and 0.47 ±0.01 V (Figure 4b). The values given are averages with standard deviations from a series of runs at different scan rates. Plots of the anodic and cathodic potentials vs. scan rate are shown in Graphs 1

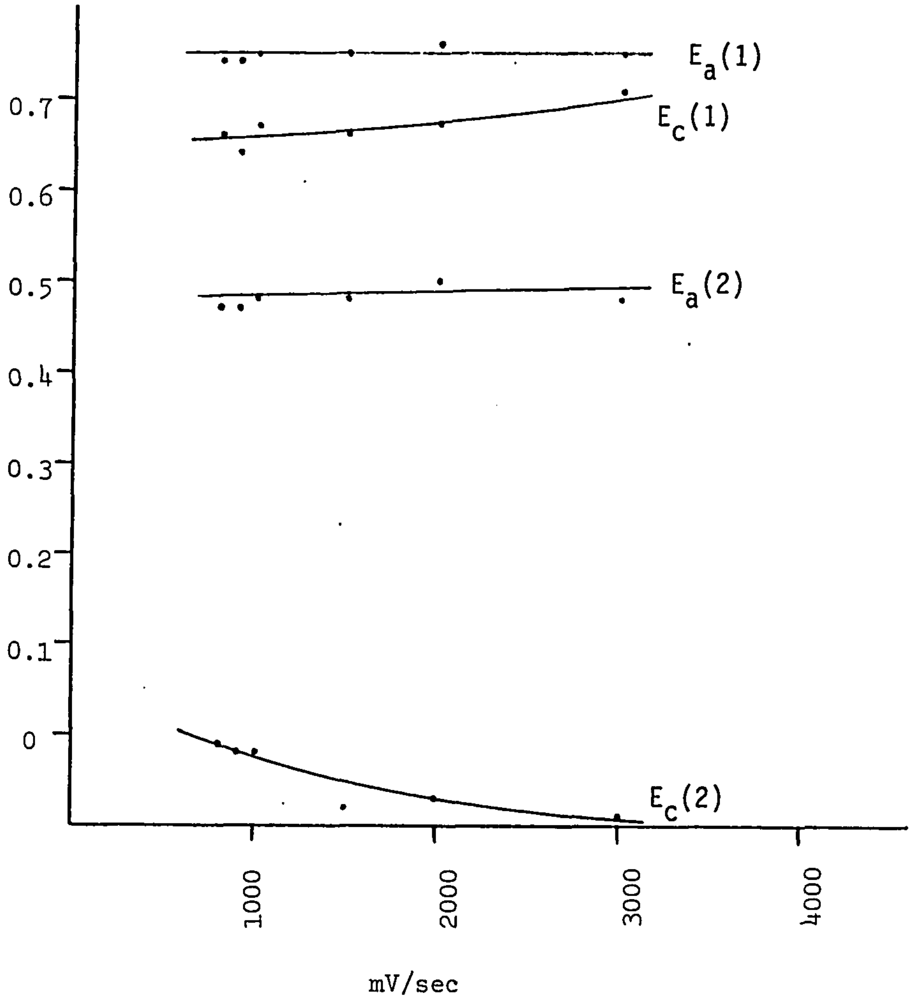


a. 2 in CH_2Cl_2 with 0.1 M TBAP, scan rate = 2000 mV/sec
E_a = 0.66, 0.40, E_c= 0.57, -0.07 eV vs. SCE

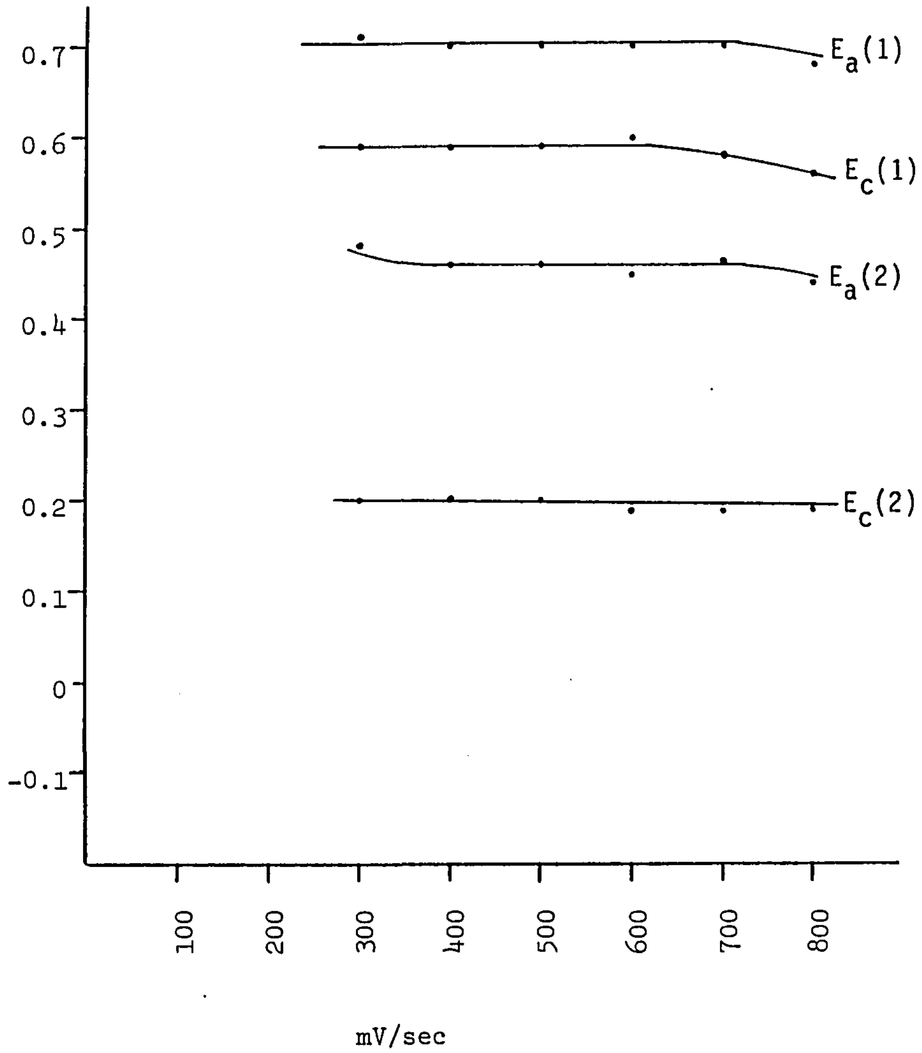


b. 2 in DMSO with 0.1 M TBAP, scan rate = 600 mV/sec
E_a= 0.68, 0.19, E_c= 0.57, 0.19 eV vs. SCE

Figure 4. Cyclic voltammograms for 2



Graph 1. E_a and E_c vs. scan rate (mV/sec) for 2 in CH_2Cl_2



Graph 2. E_a and E_c vs. scan rate (mV/sec) for 2 in DMSO

(CH_2Cl_2) and 2 (DMSO). The data for these graphs are given in Tables II and III. In Graph 1, the potential of the second reduction step changes substantially with scan rate. In Graph 2, the potentials are relatively constant, indicating a nearly reversible system.

$I_2Pt((Ph_2PCH_2)_2C_2H_2(P(O)Ph_2)_2)$ (3)

Complex 3 was produced as a minor product from the reaction of (COD)PtI_2 and 1 in benzene. In several repetitions of this reaction, several minor phosphorus containing products were present, however, 3 was always observed to be present as evidenced by the ^{31}P NMR. The ^{31}P NMR spectrum consists of a singlet at 29.9 ppm for the uncoordinated, oxidized phosphines, and a triplet at -4.2 ppm with Pt-P coupling of 3220 Hz (Figure 5 and Table I).

The ^{1}H and ^{13}C NMR spectra are consistent, indicating inequivalent phosphorus atoms. Three multiplets appear in the phenyl region of the ^{1}H NMR spectrum of 3, and in the ^{13}C NMR spectrum, seven signals are observed in the phenyl region (Figure 6a). This compares to a maximum of three multiplets in the phenyl region of the ^{1}H NMR spectrum, and four in the ^{13}C NMR spectrum when all four phosphine complexes are equivalent. Thin layer chromotography using silica gel plates and a variety of organic solvents verified the presence of a single compound. The final identification of 3 was made by the comparison of spectral data with a structurally characterized Pd analogue, $Cl_2Pd((Ph_2PCH_2)_2C_2H_2(CH_2P(O)Ph_2)_2)$ (5).[1] The ^{13}C NMR spectra of 3 and 5 are shown in Figure 6a and b. The Pt-I stretching mode was not observed in the far-range IR spectrum.

Complex 3 is a non-conductor, with a molar conductance of 19.0 $cm^{2-2}mol^{-1}$ in CH_3CN (Table I). No absorptions were observed in the expected region of the far-range IR spectrum (200-120 cm^{-2}) for the coordinated iodides. In the mid-range IR spectrum, however, $_{P-O}$ was observed at 1188 cm^{-2} (Table I).

$[(I_2Pt)_2(1)]_n$ (4)

The reaction of $(COD)PtI_2$ with ligand 1 in DMSO afforded a five-coordinate oligomeric product. Similar to complex 2, it is insoluble in organic solvents, except DMSO, in which it is slightly soluble. The reaction was followed by ^{31}P NMR (Figure 7). The reactants were added in a one to one stoichiometry, and after completion of the formation of 4, the only observed reaction was the oxidation of excess ligand 1. Prior to the addition of $(COD)PtI_2$, the ^{31}P NMR spectrum showed only the resonance

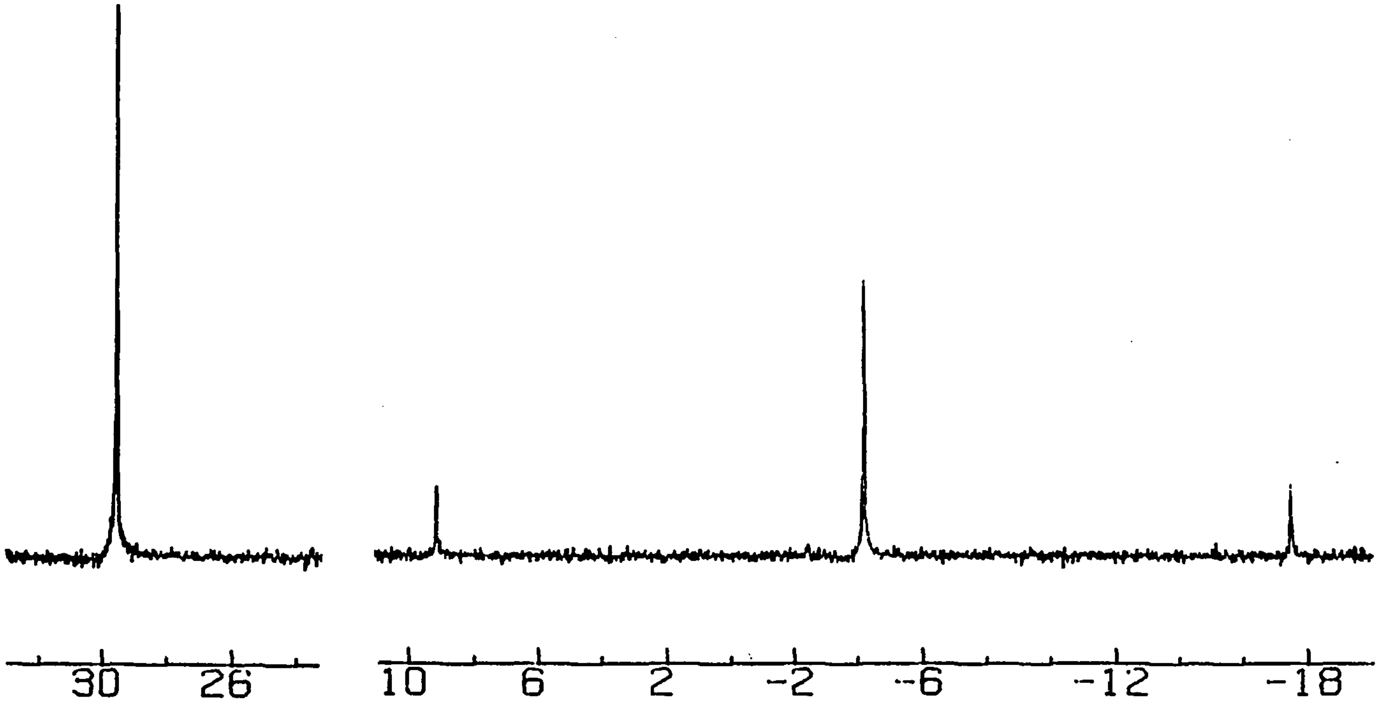
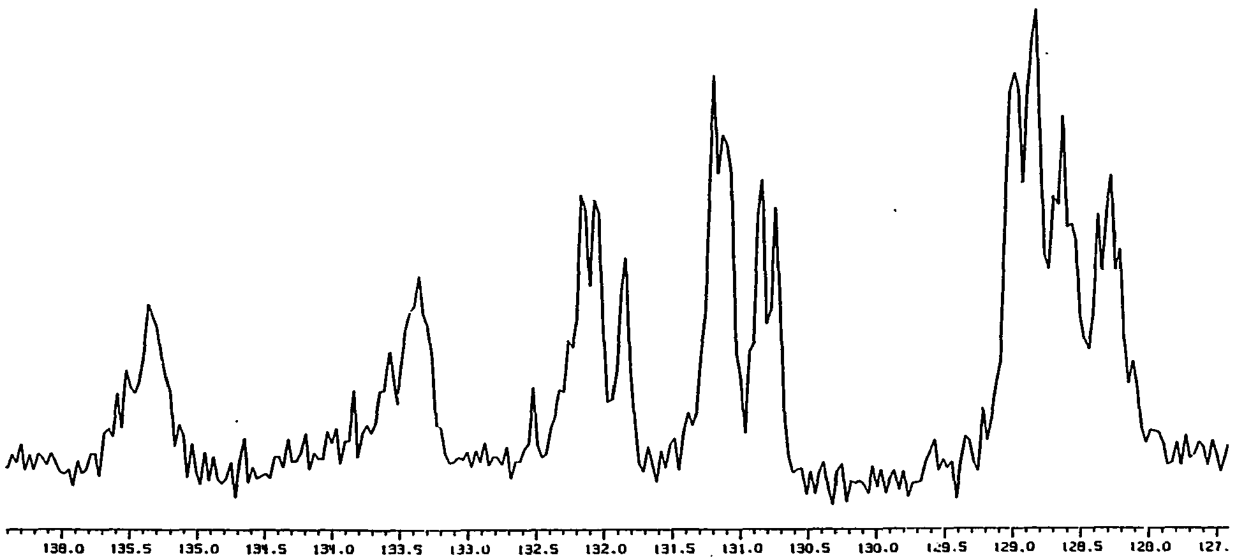


Figure 5. ^{31}P NMR spectrum of 5 in $CHCl_3$


136.0
135.5
135.0
134.5
134.0
133.5
133.0
132.5
132.0
131.5
131.0
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128.5
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a.

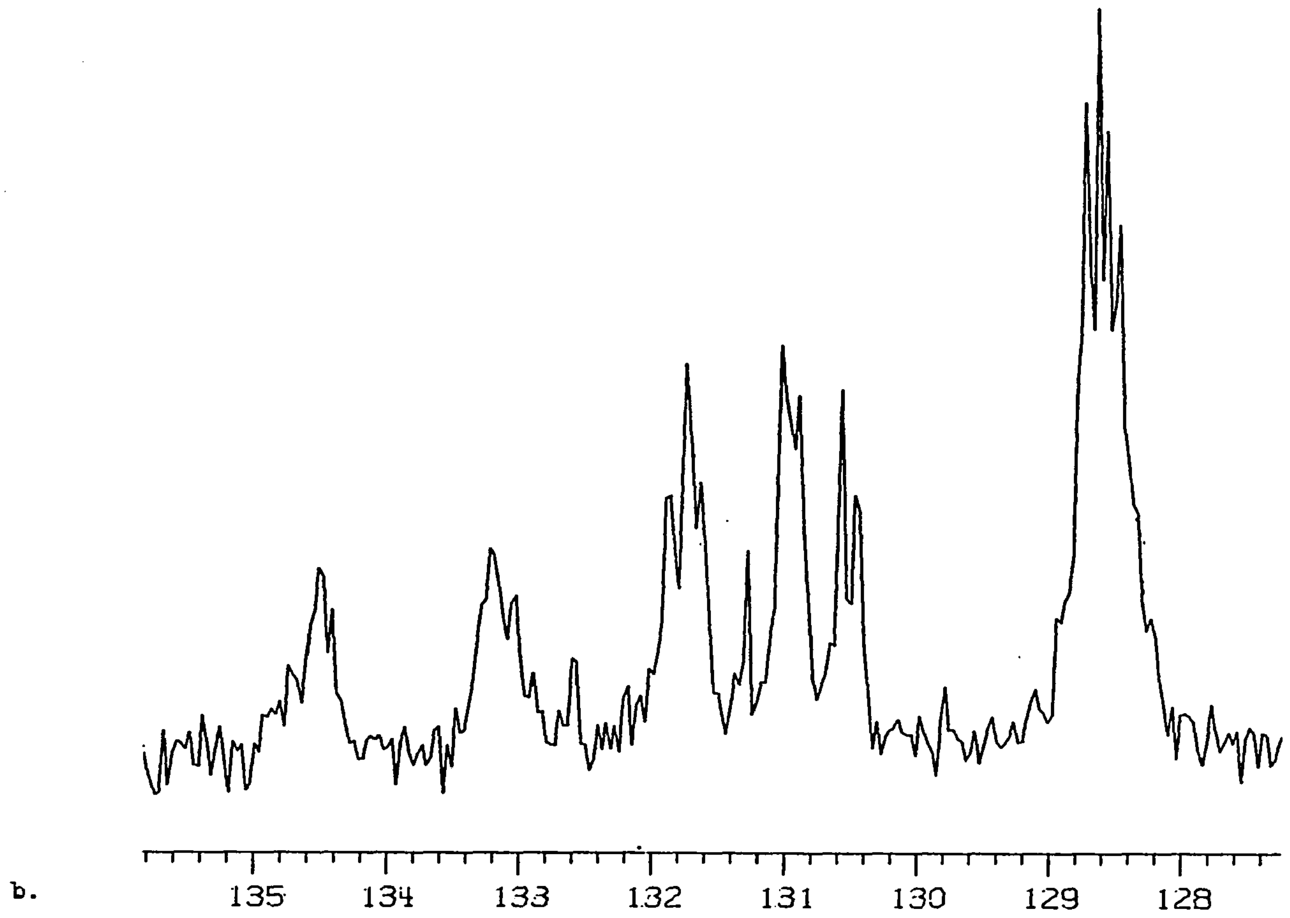
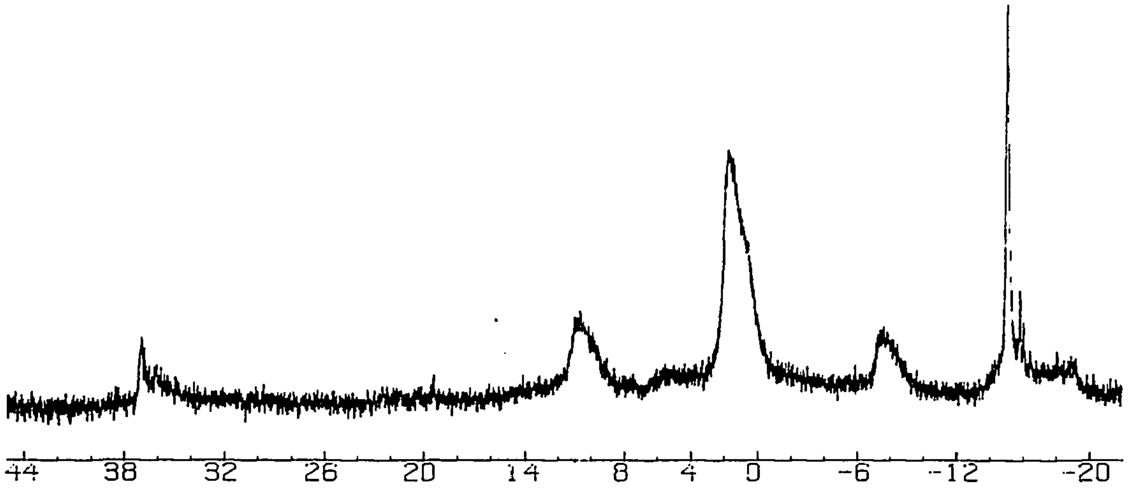


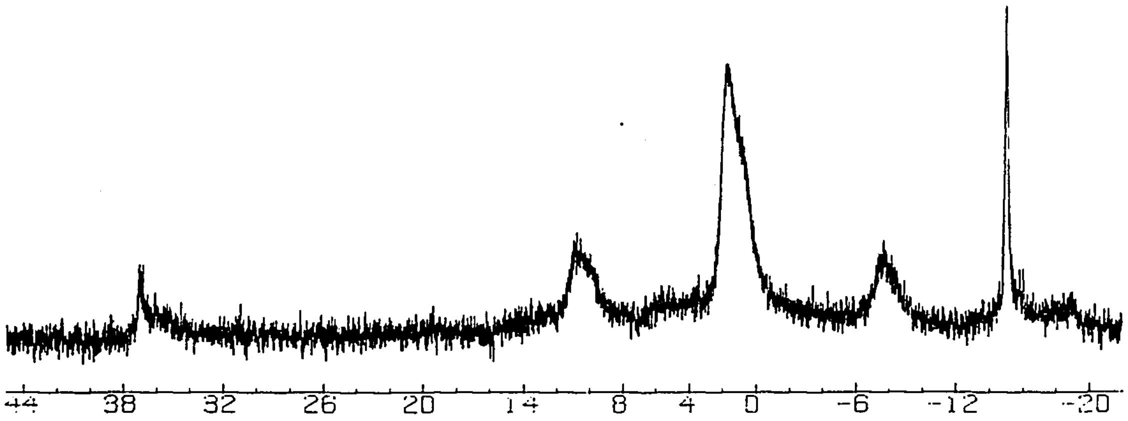
Figure 6. Phenyl region of a) ^{1}H NMR spectrum and b) ^{13}C NMR spectru of 3

for 1 at -22.0 ppm. Upon addition of the Pt reagent, a second peak appeared at -5 ppm. After 10 minutes, the coupling to Pt became visible with a coupling constant of 2230 Hz, and a third peak appeared at 29.9 ppm. As the reaction ensued, the peak at 29.9 ppm increased slowly, and the peak representing the title complex increased rapidly while shifting downfield by almost 1 ppm. After 20 h the reacton was complete, with peaks at 29.9 ppm, representing partial oxidation of ligand 1 (integration:2), 0.40 ppm, representing 3 ($^1J_{Pt-P}$ = 2286 Hz, integration:4), and -22.0 ppm, representing free ligand (integration:2).

The molar conductance of 4 is 17.6 $cm^2 \Omega^{-1} mol^{-1}$ in DMSO, which is in the range for a non-conductor, but close to the lower limit for a one-to-one electrolyte (Table I). The accepted range in DMSO for a one-to-one system is 23 to 42 $cm^2 \Omega^{-1} mol^{-1}$.[3]



a.



b.

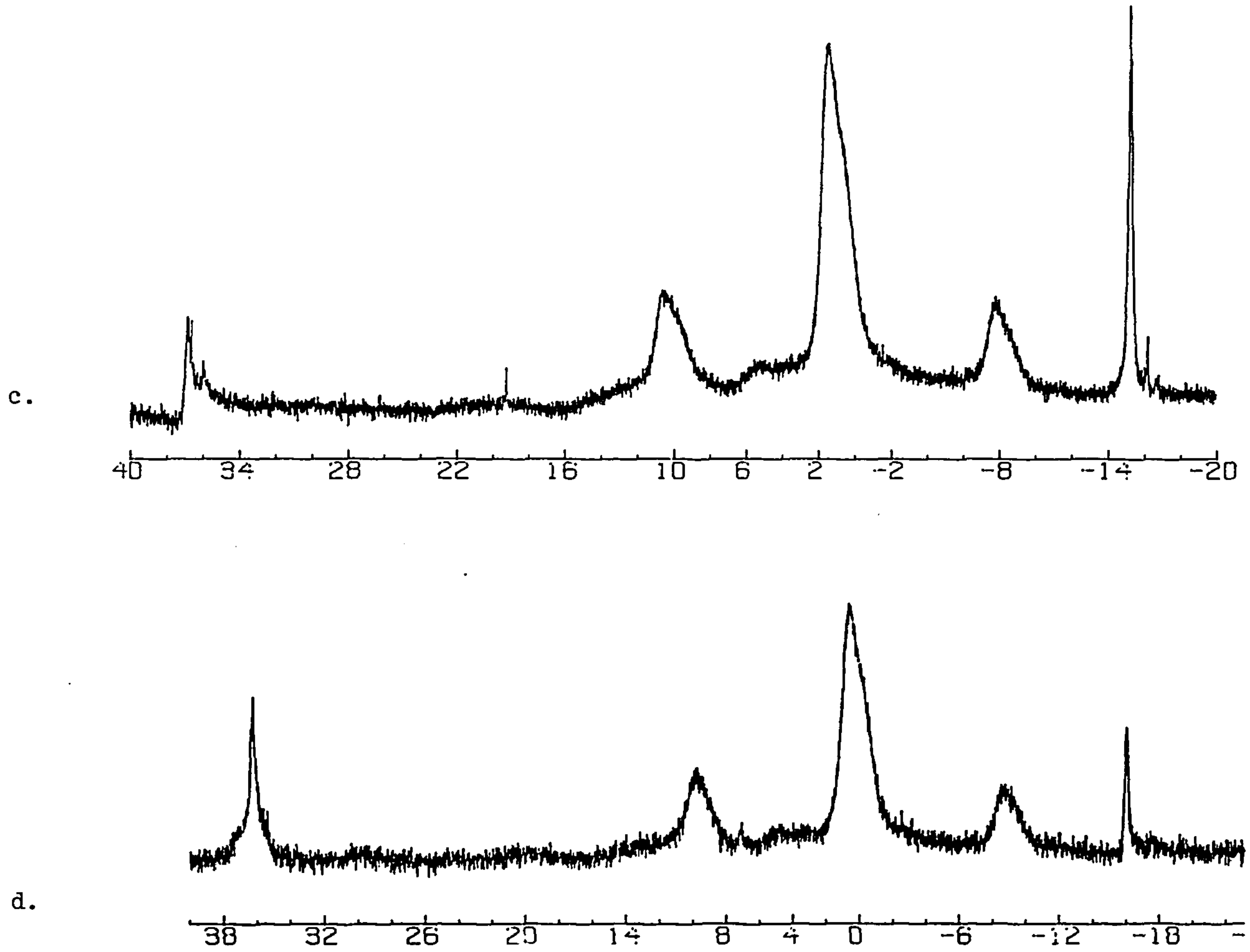


Figure 7. Reaction of (COD)PtI$_2$ and ligand 1 in DMSO at a) 10 min, b) 45 min, c) 6 h, d) 45 h

DISCUSSION

$[IPt(1)]_nI_n$ (2)

The ^{31}P NMR spectrum of 2 (Figure 2a) shows a single resonance at -0.50 with a coupling constant of 2263 Hz, indicating the equivalency of all four phosphine arms of ligand 1 in the complex. The solid state ^{13}C NMR spectrum (Figure 3) verified the absence of COD in the product. It has been previously noted that resonances for the methylene and methine carbons are usually absent in the solution ^{13}C NMR spectra of metal complexes of ligand 1.[1] This was ascribed to altered relaxation times of these carbons due to the proximity of the metal and dipolar interactions with phosphorus.[1] In the solid state ^{13}C spectrum of 2, these peaks are relatively intense, which suggests that the relaxation mechanism that predominates in solution is intermolecular and is thus absent in the solid state.

Coupling constants for trans-$(PR_3)_2PtX_2$ complexes are typically between 2300 and 2400 Hz, and for cis phosphine ligands, the coupling ranges from 3200 to 3400 Hz.[4] In dicationic $[Pt(PR_3)_4]X_2$ complexes the Pt-P coupling is intermediate, around 2600 Hz.[4] The P-Pt coupling constant in the ^{31}P NMR spectrum of complex 2, 2263 Hz, appears to indicate a trans arrangement of the phosphines. It is not possible, however, for the four carbon skeleton of 1 to span the Pt to give a trans complex. The diphosphine with the shortest linking chain known to coordinate trans consists of six carbon atoms and two oxygen atoms between the phosphines for a total of eight atoms, as opposed to four in ligand 1.[5] Grossel et al.[6] has recently shown that the complexes, $[Pt(dppm)_2]X_2$, are five-coordinate in solution. The ^{31}P NMR spectrum of $[IPt(dppm)_2]I$ in CH_3CN has a resonance at -61.0 ppm with a Pt-P coupling constant of 2194 Hz. This value is within reasonable range of Pt-P coupling found for 2, which we propose to be an oligomeric five-coordinate complex (Figure 8). The FAB mass spectrum has a major peak at m/e 1145.5, representing the unit $[IPt(1)]^+$, and the conductance is consistent with this formulation, indicating a one-to-one electrolyte. The Pt-I

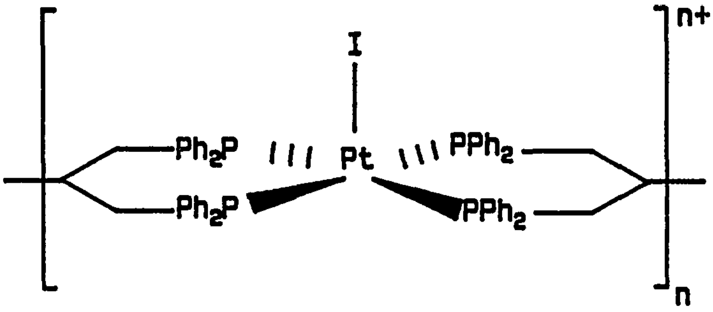
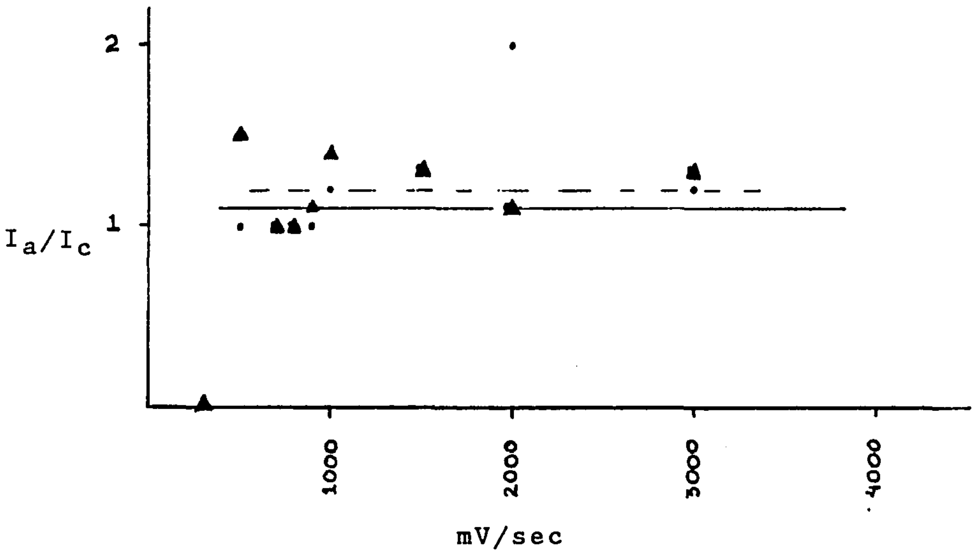


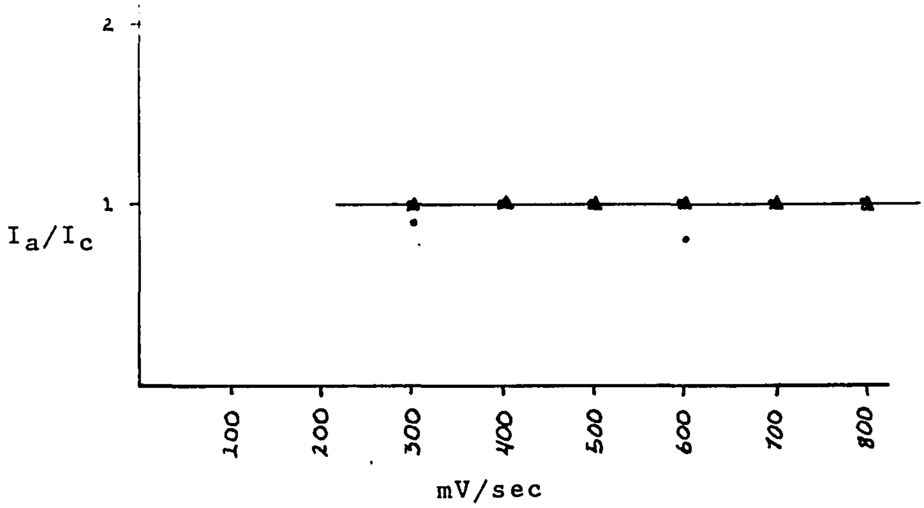
Figure 8. Proposed structure of $[IPt(1)]_nI_n$ (2)

stretching mode was not visible in the far-range IR. However, this is not conclusive since metal iodide stretching frequencies are of medium to weak intensity and are frequently absent.[7]

The solid state ^{31}P NMR spectrum of 2 shows two signals whose Pt-P coupling constants could not be measured because of the large line widths (Figure 2b). The difference between the single resonance in the solution spectrum and two in the solid state can be rationalized by site inequivalency imposed by the crystal, and has been observed for other Pt phosphine complexes that are known to have equivalent phosphorus atoms from crystal structure analysis.[3] It is also possible that the one signal observed in solution is an average of the two in the solid state due to fast exchange on the NMR time scale. This could not be explored, however, because of the high melting point of DMSO (5°).

There are inconsistencies in the cyclic voltammograms of 2. In CH_2Cl_2 or DMSO, the ratio of intensities of the anodic to cathodic waves (I_a/I_c) is one, or very close to one. Graphs 3a (CH_2Cl_2) and 3b (DMSO) show the dependence of I_a/I_c on the scan rate and the data for these graphs is given in Tables IV and V. Assuming we begin with a Pt(II) complex in solution, as reduction occurs, some of the reduced species is removed from the electrode surface by diffusion or solution chemistry. The result is that less of the reduced species remains at the electrode for oxidation in the return anodic wave. The Pt(II) complex is continually replaced at the electrode surface from the bulk solution and $I_a>I_c$. Conversely, if Pt(0) is the starting complex, $I_c>I_a$. From Tables IV and V, we see that in CH_2Cl_2 there is a greater deviation from a ratio of one, but in general $I_{a\_}I_c$, which is consistent with a Pt(II) species. However, in DMSO, the deviation from a ratio of one is such that $I_{a\_}I_c$, which is consistent with a Pt(0) species. This anomaly may be due to a difference in the rates of electron transfer between the oxidation and reduction steps that is dependent on solvent. If the rate of electron transfer in the reduction step is slow, the observed intensity of that wave will be diminished. Since the reduction process continues until the wave returns in the oxidation step, the amount of reduced species present builds up. If the rate of electron transfer for the oxidation process is fast relative to that for reduction, the intensity of the oxidation wave is greater, and $I_c<I_a$. The dependence on solvent indicates different pathways for the electron transfer in DMSO and CH_2Cl_2. It may be the stronger donating ability of DMSO relative to CH_2Cl_2 stabilizes an intermediate, thus altering the pathway of electron transfer.





Graph 3. I_c/I_a vs. scan rate for a) voltammogram of 2 in CH_2Cl_2, and b) voltammogram of 2 in DMSO

The reversability of the reduction of complex 2 differs from the electrochemistry of the "pocket" Pd(II) complex $[(CH_3CN)Pd(1)](BF_4)_2$ (6) (Figure 9).[1] The cyclic voltammogram of **6** in CH_3CN is completely non-reversible (Figure 9). The Pd is reduced in a two step process, but the reduced species is unstable and an unidentified rearrangement occurs to give a new, electrochemically active complex. In the returning anodic wave, the oxidation corresponding to the reduction of the initial complex is not observed. Instead, the generated species is

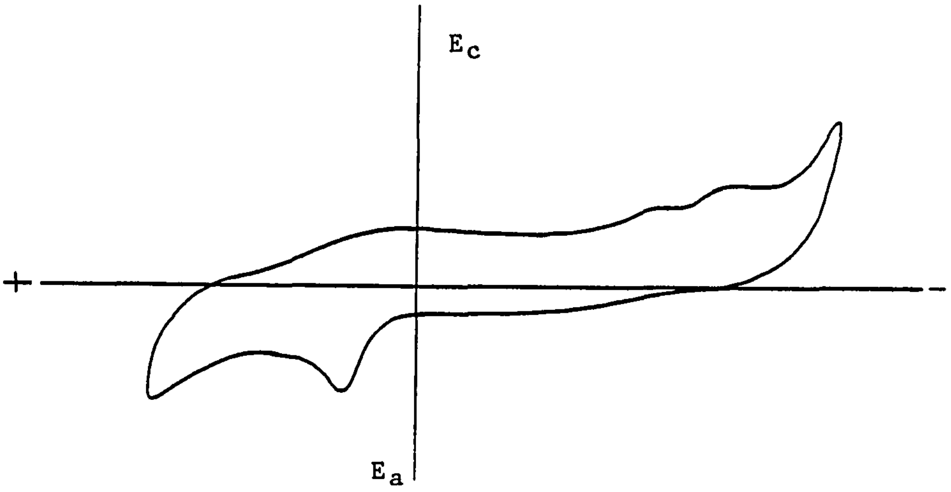


Figure 9. Cyclic voltammogram of 6 in CH_3CN, 0.1 M TBAP, $E_c = -0.95$ V, -1.20 V; $E_c' = 0.27$ V, $E_a' = -0.29$ V; scan rate = 500 mv/sec

oxidized to Pd(II) and a second one step reduction/oxidation couple is observed.

This difference in reversability between complexes 2 and 6 can be attributed to the difference in their structures. Complex 2 is oligomeric and five-coordinate, with four phosphines and one iodide coordinated (Figure 8). Complex 6 is similar in structure, being monomeric, five-coordinate with four phosphines and an CH_3CN coordinated. When 6 is reduced to Pd(0), it is constrained by ligand 1 to be square planar. Reduced group 10 metal complexes are d^{10} and have a tetrahedral geometry.[2] Imposing a square planar geometry destabilizes the reduced complex, and rearrangement or solution chemistry ensues. When complex 2 is reduced, it is not constrained to be square planar by ligand 1 because of its oligomeric nature, and rotation of the two ligands to which the Pt is bound allows the reduced species to attain a near tetrahedral geometry. This serves to stabilize the reduced species and increases the reversability of the reduction/oxidation cycle.

$I_2Pt((Ph_2PCH_2)_2C_2H_2(CH_2P(O)Ph_2)_2)$ (3)

The ^{31}P NMR spectrum of 3 shows two inequivalent phosphorus atoms, one of which is coupled to Pt with a coupling constant of 3220 Hz. This coupling is indicative of <u>cis</u> coordination of the phosphines, and the uncoupled resonance (29.5 ppm) is in the region of the oxidized ligand 1.

The ^{1}H and ^{13}C NMR spectra clearly show the inequivalency of the phosphine arms. ^{13}C NMR was particularly useful in the identification of 3 by comparison with the Pd(II) analogue 5. The phenyl region of the ^{13}C NMR spectra of 3 and 5 are shown in Figure 6a and b. The methylene and methine carbons were not observed in either spectrum. The pattern of this region is characteristic of the general structure of 3 and 5 in which two phosphine arms of ligand 1 are coordinated to the metal forming a six-membered chelate ring, and the remaining two have been oxidized and are uncoordinated (Figure 10). The ^{13}C NMR spectrum of 3 should be more complicated than 5 due to coupling to Pt. This coupling is small however,[4] and

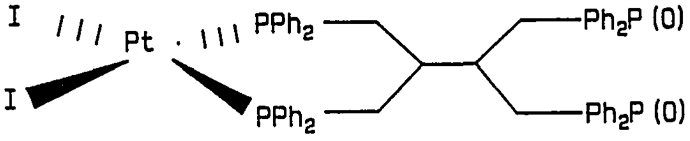


Figure 10. Proposed structure of 3

was not detected. At the high-field end of the ^{13}C NMR spectrum of 3, an AB_2X pattern is observed for which there is no apparent explanation. Based on the chemical shift, it is assigned as a para-carbon. If it is a phenyl bonded to a P coordinated to Pt, the splitting may be due to coupling to Pt. However, this would be a five-bond coupling and would be expected to be very small. If the carbon is in the para position of a phenyl bonded to an oxidized phosphine, the observed splitting may be due to coupling to other phosphorus atoms through hydrogen bonding of the phosphoryl oxygen. The tetraphosphine oxide of ligand 1 has been reported by us, and hydrogen bonding in solution gives rise to inequivalency of the phenyl hydrogens in the ^1H NMR.[1]

$[PtI_2)_2(1)]_n$ (4)

The formulation for this compound is based in part on the stoichiometry of the preparative reaction. Reaction of one 1 with one $(COD)PtI_2$ in DMSO yielded 4, with the excess phosphine being partially oxidized. Upon completion of reaction, the ^{31}P NMR spectrum consists of signals at 29.9 ppm (integration:1) representing oxidized phosphine, 0.40 ppm (integration : 4) with coupling to Pt of 2285 Hz, and -22 ppm (integration: 3) for unreacted ligand 1. The coupling to Pt suggests the presence of _trans_ phosphines.

This leads us to conclude it is oligomeric in nature.

The conductance (17.6 $cm^2 \Omega^{-1} mol^{-1}$) is below the range expected for a one to one electrolyte in DMSO (23-42 $cm^2 \Omega^{-1} mol^{-1}$), but high for a non-conductor. Perhaps 4 disocciates only to a very limited extent in solution. Based on the stoichiometry of two Pt to one ligand, and the fact that it is at least very weakly conducting, the proposed oligomeric structure of 4 is shown in Figure 11. It is interesting that in DMSO a nonconducting four coordinate Pt complex is formed, while in the much less polar solvent, benzene, a five coordinate one to one electrolyte is produced. This may be the result of the ability of DMSO to act as a ligand for Pt, and altering the path by which it reacts.

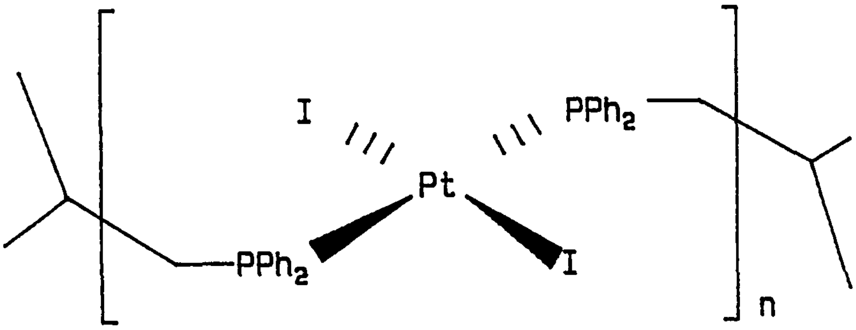


Figure 11. Proposed structure for $[(PtI_2)_2(1)]_n$

CONCLUSIONS

The coordination chemistry of ligand 1 with Pd(II) and Pt(II) is markedly different. Pd(II) formed dinuclear and mononuclear monomeric complexes from Pd(II)chloro precursors. In contrast, Pt(II)chloro precursors yielded only intractable solids. Reaction of 1 with $(COD)PtI_2$ has given two oligomeric products of the formulas $[IPt(1)]_nI_n$ and $[(I_2Pt)_2(1)]_n$, respectively, and a monomeric product in which two phosphines are coordinated and two have been oxidized and are free, $I_2Pt((Ph_2PCH_2)_2C_2H_2(CH_2P(O)Ph_2)_2)$. The reason for this observed difference is not clear. There is a small difference in the covalent radius of Pd(II) (1.31) and Pt(II) (1.32).[8] This difference in size between the two metals is very small. Nevertheless, the striking contrasts observed in the chemistry of Pd and Pt with ligand 1 appear to be due to different tendencies to oligomerize and it is difficult to dismiss the 0.01 difference in their radii.

TABLES

Table I. $^{31}P\{^{1}H\}$ NMR, infrared, and conductance data

Compound	$\delta^{31}P$ ($^{1}J_{Pt-P}$,Hz)	ν_{M-X} (cm^{-1})
$[(Ph_2PCH_2)_2CH]_2$	-22.0	-
$[IPt(1)]_nI_n$	-0.05 (2263)	*[a]
$I_2Pt((Ph_2PCH_2)_2C_2H_2$- $(CH_2P(O)Ph_2)_2)$	29.9[c] 4.2 (3220)	*
$[I_2Pt)_2(1)]_n$	0.40 (2286)	*
$Cl_2Pd((Ph_2PCH_2)_2C_2H_2$- $(CH_2(O)PPh_2)_2)$	31.6[e] 20.4	303, 291
$[(CH_3CN)Pd(1)](BF_4)_2$	30.9	-
$[(Ph_2P(O)CH_2)_2CH]_2$	37.6	-

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[a] Absorptions were not observed in the expected region (400-150 cm^{-1}).

[b] Accepted range for 1:1 electrolyte in DMSO: 23 - 42 $cm^{2}\,\Omega^{-1}mol^{-1}$.[9]

[c] The chemical shift at 29.9 represents the oxidized phosphines, the 20.4 shift represents the phosphines bonded to Pd.

[d] Accepted range for 1:1 electrolyte in CH_3CN is 120-190 $cm^{2}\,\Omega^{1}mol^{-1}$.[10]

[e] The chemical shift at 31.6 represents the oxidized phosphines, the 20.4 shift represents the phosphines bonded to Pt.

ν_{P-O} (cm^{-1})	Λ_M $(cm^{2-1}mol^{-1})$(solvent)
-	-
-	26.0 (DMSO)[b]
1188	19.0 (CH_3CN)[d]
-	17.6 (DMSO)
1180	23.0 (CH_3CN)
-	195 (CH_3CN)
1186	-

Table II. Data for Graph 1, E_a and E_c vs. scan rate for the cyclic voltammogram of 2 in CH_2Cl_2

$E_a(1)$[a]	$E_a(2)$	$E_c(1)$	$E_c(2)$	scan rate (mV/sec)
0.64	0.37	0.56	-0.01	800
0.64	0.37	0.54	-0.02	900
0.65	0.38	0.57	-0.02	1000
0.65	0.38	0.56	-0.08	1500
0.66	0.40	0.57	-0.07	2000
0.65	0.38	0.61	-0.09	3000

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[a] In this and subsequent tables of cyclic voltammetric data, (1) denotes the first reduction or oxidation, (2) denotes the second.

Table II. Data for Graph 2, E_a and E_c vs. scan rate for the cyclic voltammogram of 2 in DMSO

$E_a(1)$	$E_a(2)$	$E_c(1)$	$E_c(2)$	scan rate (mV/sec)
0.71	0.48	0.59	0.20	300
0.70	0.46	0.59	0.20	400
0.70	0.46	0.59	0.20	500
0.70	0.45	0.60	0.19	600
0.70	0.46	0.58	0.19	700
0.68	0.45	0.57	0.19	800

Table IV. Data for Graph 3a, I_a/I_c vs. scan rate for cyclic voltammogram of 2 in CH_2Cl_2

I_c/I_a (1)	I_c/I_a (2)	scan rate (mV/sec)
0	0	300
1	1.5	500
1	1	700
1	1	800
1	1.1	900
1.2	1.4	1000
1.3	1.3	1500
1.8	1.1	2000
1.2	1.3	3000

Table V. Data for Graph 3b, I_a/I_c vs. scan rate for cyclic voltammogram of 2 in DMSO

I_c/I_a (1)	I_c/I_a (2)	scan rate (mV/sec)
0.9	1	300
1	1	400
1	1	500
0.8	1	600
1	1	700
1	1	800

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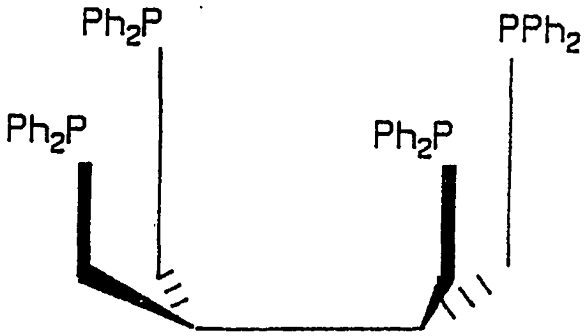
SUMMARY

The synthesis of a new tetradentate phosphine (1) was accomplished by treatment of the corresponding tetrabromide with Ph_2M (M = K, Na, Li) in THF. Ligand 1 is of interest because of the unique steric and geometric constraints placed on a coordinated metal in M(1) complexes. A square planar geometry is required for M(1) complexes, and square pyramidal geometry is required for complexes of the formula [LM(1)] in which L is an additional ligand. Coordination of two additional ligands, $[L_2M(1)]$, would form a trigonal prism in which the M-L bonds ie staggered between M-P bonds of ligand 1, or a distorted octahedron in which the M-L bonds eclipse two opposite M-P bonds.



Ligand 1

Complexes of the group 10 metals have been prepared with ligand 1. Five coordination modes have been observed in this work. Reaction of anhydrous Ni(II) salts with 1 yielded the mononuclear product $[Ni(1)](X)_2$ (2) (X = BF_4, ClO_4^-) or insoluble polymers. There was no evidence for coordination of solvent or anion, and the geometry is proposed to be square planar.

Reaction of $(PhCN)_2PdCl_2$ with 1 yielded a dinuclear product, $(PdCl_2(1)$ (3), in which two adjacent phosphine ares are coordinated <u>cis</u> to a $PdCl_2$ unit forming two six-membered chelate rings. Further reaction of the dinuclear product with 1 in DMSO forms a mononuclear product similar to Ni, $[(solvent)Pd(1)](BF_4)_2$ (4). Unlike the Ni complex, the Pd if five-coordinate with retention of one solvent molecule (DMSO, CH_3CN). The solvent can be displaced by Cl^- in an equilibrium that lies in favor of solvent coordination. Chloride should coordinate preferentially over DMSO or CH_3CN, although the steric bulk of ligand 1 may inhibit coordination of larger donor atoms. Complex 4 was found to catalytically oxidize DMSO in the presence of water and air, producing five equivalents of dimethylsulfone per complex 4 over a three week time period. In the presence of Cl^-, complex 4 forms only a trace amount of dimethylsulfone and rearranges to a mononuclear product in which two adjacent phosphines are coordinated to Pd and two have been oxidized, $[Cl_2Pd((Ph_2PCH_2)_2C_2H_2(CH_2P(O)PPh_2)_2]$ (5).

Reaction of 1 with Pt reagents largely produced polymeric products which were not characterized. However, two oligomeric and one mononuclear product were obtained in reaction of $(COD)PtI_2$ with 1. When this reaction is done in benzene, an oligomer is formed in which two pairs of adjacent phosphines from different molecules of 1 are coordinated to a PtI unit to give a five-coordinate compels. A minor product of this reaction is the PtI_2 analogue of complex 5. When this reaction is done in DMSO, an oligomeric product is formed of the formula $[(PtI_2)_2(1)]_n$ in which one phosphine of two different molecules of 1 are coordinated to a PtI_2 unit to give a coordination number of four.

APPENDIX I. SUPPLEMENTARY DATA FOR THE CRYSTALLOGRAPHIC ANALYSIS OF $[(Ph_2P(O)CH_2)_2CH]_2$

Table I. Anisotropic thermal parameters[a] (Å x 10^3) for 4

atom	U_{11}	U_{22}	U_{33}
P1	78.(5)	65.(5)	70.(5)
P2	59.(5)	61.(5)	63.(5)
P3	64.(5)	91.(5)	71.(5)
P4	58.(5)	60.(5)	61.(5)
P1	86.(11)	60.(9)	67.(10)
P2	56.(9)	59.(9)	62.(10)
P3	48.(10)	102.(13)	107.(12)
P4	83.(10)	62.(9)	63.(9)
C11	63.(15)	45.(13)	51.(14)
C12	66.(17)	30.(12)	45.(14)
C21	78.(16)	63.(15)	42.(13)
C31	48.(14)	40.(14)	86.(17)
C34	76.(16)	65.(17)	36.(14)
C41	67.(16)	51.(14)	50.(15)

[a] The form of the temperature factor is exp(-2 $U_{ij}h_ih_ja_ia^j$).

$U_1{}^2$	U_{13}	U_{23}
-17.(4)	31.(4)	-7.(4)
-18.(4)	16.(4)	6.(4)
-10.(4)	28.(4)	6.(5)
-14.(4)	6.(4)	7.(4)
-26.(8)	26.(8)	-4.(8)
-11.(7)	24.(8)	-21.(8)
8.(9)	23.(9)	32.(10)
-10.(8)	25.(9)	21.(8)
-20.(12)	15.(11)	-8.(12)
-16.(13)	5.(12)	-9.(12)
-8.(13)	1.(12)	4.(13)
-2.(11)	20.(13)	42.(13)
-17.(14)	20.(13)	19.(12)
-11.(12)	14.(13)	-5.(12)

Table II. Hydrogen atom coordinates[a] (fractional x 10^4) for 4

atom	x	y	z
H111	4845	5253	7438
H112	4557	5810	6325
H12	3697	5018	4387
H211	3810	4305	6474
H212	5138	4172	6249
H311	500	-245	7958
H312	420	478	7607
H34	471	643	10372
H411	-1717	553	9618
H412	-1525	298	7995
H2A	2355	5382	9717
H3A	2585	6006	11956
H4A	3510	6971	12173
H5A	4178	7356	10190
H6A	3964	6723	7914
H2B	3178	6597	5403
H3B	1892	7105	3500
H4B	-70	6750	2515

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[a] The hydrogen atom parameters were calculated and not refined. The isotropic U values were set to a value of 76.

Table II. continued

H5B	-731	5878	3436
H6B	575	5338	5328
H2C	3596	3538	1315
H3C	2147	3952	-726
H4C	452	4470	-252
H5C	122	4676	2195
H6C	1571	4325	4204
H2D	4095	3420	7506
H3D	3179	2729	8750
H4D	1577	2117	7456
H5D	884	2179	4930
H6D	1827	2841	3585
H2E	3676	-391	6730
H3E	4050	-244	4351
H4E	3055	551	3041
H5E	1615	1209	3882
H6E	1259	1070	6254
H2F	1383	1415	9445
H3F	2259	2268	11033
H4F	4300	2221	12184
H5F	5380	1328	11802
H6F	4499	455	10266
H2G	-1879	1321	11230
H3G	-1645	2068	13352

Table II. continued

H4G	-693	3015	13309
H5G	20	3218	11802
H6G	-124	2465	9147
H2H	-2230	1802	5701
H3H	-4179	2059	4385
H4H	-5803	1853	5444
H5H	-5543	1363	7667
H6H	-3583	1140	9015

Calculated and Observed Structure Factors

L = 0

H	K	Fo	Fc
-10	5	164	142
-8	6	303	362
-8	7	206	-225
-7	2	195	206
-7	3	363	-394
-7	6	396	-406
-7	8	204	-242
-7	12	203	-212
-7	14	169	-191
-6	1	122	141
-6	3	528	541
-6	4	319	-347
-6	9	228	232
-5	2	243	236
-5	3	361	351
-5	4	338	310
-5	8	424	425
-5	10	436	411
-5	11	253	270
-4	1	633	-627
-4	2	351	385
-4	3	161	-179
-4	4	346	369
-4	7	259	313
-4	9	467	-470
-4	16	144	-205
-4	19	124	-84
-3	1	832	-837
-3	2	474	-487
-3	3	1367	1373
-3	4	392	-408
-3	6	292	316
-3	8	307	-322
-2	1	579	-608
-2	2	850	-853
-2	3	407	-397
-2	4	278	-274
-2	5	339	337
-2	14	178	241
-1	1	310	295
-1	4	1141	1157
-1	5	891	871
-1	6	340	-325
-1	10	278	-276
-1	13	149	193
-1	14	268	268
-1	15	187	200
-1	17	183	224
0	3	328	347
0	4	643	-620
0	5	656	680
0	6	585	592
0	7	775	750
0	10	262	-264
0	11	137	-192
0	17	174	-152
0	19	239	-249
1	1	334	311
1	4	287	-293
1	5	419	-401
1	6	1180	-1161
1	7	784	782
1	8	181	170
1	11	442	-442
1	12	141	-175
1	13	281	-291
1	14	122	-128
1	17	209	-213
2	0	1217	-1262
2	1	454	442
2	2	353	-372
2	3	747	-742
2	4	155	192
2	5	1054	-1068
2	6	493	493
2	10	432	-442
2	13	291	-297
2	17	210	197
3	0	363	354
3	1	478	457
3	2	842	857
3	3	529	519
3	4	436	436
3	5	249	263
3	6	180	191
3	8	328	344
3	11	598	580
3	12	424	-422
3	13	246	268
3	14	264	-284
4	0	216	216
4	1	584	582
4	2	505	502
4	3	329	345
4	5	319	319
4	6	121	-126
4	8	227	225
4	10	172	190
4	11	254	-292
4	16	258	-246
4	17	144	-149
5	0	169	-190
5	2	459	-463
5	4	192	-202
5	7	609	-602
5	8	111	114
5	11	177	-211
5	12	135	213
5	13	244	-248
5	14	264	263
5	15	161	-164
5	16	299	-276
5	18	166	-206
6	0	175	-186
6	2	515	-506
6	5	222	-232
6	9	231	-235
6	11	253	-296
6	13	294	301
6	14	257	-250
7	3	172	-209
7	10	189	-196
7	15	182	147
8	1	239	252
8	4	274	-285
8	8	215	216
8	12	132	-152
8	14	179	181
9	1	225	210
9	2	297	296
9	5	147	-150
9	10	196	133
9	11	237	-257
10	8	187	-169

L = 1

H	K	Fo	Fc
-11	-1	251	178
-10	-6	219	-184
-10	8	150	-8
-9	-11	202	-158
-9	-10	287	-287
-9	-4	252	-282
-9	0	260	266
-8	-12	167	198
-8	-11	313	-277
-8	-10	191	217
-8	-6	373	352
-8	0	198	237
-8	2	292	308
-7	-14	297	269
-7	-5	430	408
-7	5	333	-345
-7	7	287	-323
-6	-14	203	221
-6	-11	263	286
-6	-10	330	-328
-6	-8	358	-338
-6	-7	186	-208
-6	-3	275	-253
-6	-1	591	-548
-6	0	267	-290
-6	1	319	-297
-6	12	314	-358
-6	15	195	-261
-5	-16	186	-213
-5	-14	409	-368
-5	-13	286	284
-5	-11	208	-211
-5	-5	220	-207
-5	-3	461	-459
-5	-2	344	-352
-5	0	483	-490
-5	1	444	444
-5	2	655	-603
-5	3	323	334
-5	6	397	399
-5	7	190	197
-5	9	308	316
-5	12	263	248
-5	13	160	194
-5	18	170	158
-4	-15	517	-485
-4	-14	184	-164
-4	-12	384	-382
-4	-11	166	188
-4	-10	255	262
-4	-8	619	614
-4	-7	343	-359
-4	-5	369	379
-4	-4	285	279
-4	-2	186	173
-4	2	345	361
-4	4	178	-194
-4	5	666	659
-4	8	394	403
-4	10	245	-281
-4	12	317	348
-4	14	259	312
-3	-19	255	-235
-3	-13	297	-313
-3	-12	234	258
-3	-10	247	-264
-3	-9	740	729
-3	-8	150	-210
-3	-5	678	-686
-3	-4	246	233
-3	-1	256	309
-3	0	1013	1049
-3	1	311	-333
-3	5	220	-247
-3	6	385	-393
-3	9	278	-261
-3	11	201	-224
-3	17	204	-227
-2	-13	281	262
-2	-10	760	-729
-2	-9	349	387
-2	-8	463	-452
-2	-7	351	371
-2	-6	536	-539
-2	-5	241	-306
-2	-4	594	544
-2	-3	725	-746
-2	-2	1830	1862
-2	2	1260	-1276
-2	3	1367	1311
-2	5	1072	-1047
-2	7	325	338
-2	9	261	287
-1	-18	232	-241
-1	-13	164	-190
-1	-11	150	-130
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-1	-9	580	-565
-1	-8	153	210
-1	-6	287	292
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-1	-4	512	-527
-1	-3	1104	-1087
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-1	0	444	482
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-1	14	184	150
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0	-7	332	345
0	-5	825	806
0	-4	775	-802
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0	-1	787	823
0	0	87	-122
0	1	1279	1283
0	2	1064	1052
0	3	412	-428
0	4	491	488
0	5	608	-620
0	6	373	-376
0	7	368	370
0	8	513	521
0	9	269	293
0	10	393	385
0	11	200	-207
0	12	524	-515
0	13	122	200
0	15	370	350
1	-12	330	352
1	-11	234	265
1	-10	202	-200
1	-9	207	-228
1	-6	211	197
1	-5	419	420
1	-4	712	734
1	-3	269	-264
1	-2	725	731
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1	2	521	556
1	3	555	539
1	4	2491	2461
1	5	168	181
1	6	784	767
1	9	659	642
1	11	200	237
1	12	214	-242
1	15	294	-304
2	-18	195	-174
2	-17	171	181
2	-13	161	157

2	-11	348	329
2	-10	477	442
2	-7	124	-117
2	-6	145	-116
2	-5	244	-222
2	-4	1453	1413
2	-2	1889	-1887
2	-1	844	803
2	1	699	675
2	2	536	534
2	3	324	330
2	4	221	-232
2	7	621	-616
2	8	274	262
2	9	391	-373
2	10	309	-303
2	15	369	-353
2	18	128	152
2	20	168	-136
3	-19	149	22
3	-12	299	249
3	-10	219	231
3	-9	246	-233
3	-8	197	-195
3	-7	267	-263
3	-6	439	-444
3	-5	635	596
3	-4	183	150
3	-3	589	607
3	-2	441	-464
3	-1	748	-760
3	0	137	-136
3	2	798	-803
3	5	851	-840
3	6	599	-592
3	7	335	-353
3	8	279	-302
3	9	222	-221
3	12	204	211
3	14	202	-229
3	16	252	-265
4	-15	177	-147
4	-13	229	-217
4	-6	695	-692
4	-5	298	288
4	-4	453	448
4	-3	644	605
4	2	151	156
4	3	421	430
4	4	294	295
4	6	316	336
4	7	331	318
4	8	446	436
4	9	248	298
4	11	367	382
5	-9	376	359
5	-7	346	335
5	-5	771	-769
5	-4	557	555
5	-3	238	252
5	-2	693	630
5	-1	491	481
5	0	103	-137
5	1	147	-147
5	4	436	436
5	5	324	338
5	6	223	222
5	7	358	366
5	15	155	-105
5	18	149	-60
6	-10	273	232
6	-8	509	488
6	-6	293	327
6	1	145	164
6	7	212	-218
6	8	124	-152
6	9	195	-216
6	10	362	-353
6	11	362	-370
6	13	335	-331
6	14	215	231
7	-6	141	-81
7	-4	346	-340
7	3	177	-193
7	6	204	-244
7	7	136	-188
7	9	265	-272
8	-10	280	-234
8	-8	500	-481
8	-7	198	213
8	-4	180	173
8	-3	363	-404
8	6	123	-171
8	9	427	414
8	10	138	135
9	1	188	203
9	3	159	201
9	5	152	120
10	1	140	-68
10	2	239	242
10	7	166	-141

L = 2

H	K	Fo	Fc
-10	-4	164	-174
-10	4	210	-189
-9	-2	214	-222
-9	1	237	263
-9	2	329	343
-9	3	217	-224
-9	7	242	246
-8	-14	157	-135
-8	-11	397	377
-8	-10	219	-215
-8	-5	190	207
-8	-1	275	-243
-8	3	396	363
-8	11	196	219
-7	-12	336	277
-7	-10	188	209
-7	-7	334	-321
-7	-6	368	353
-7	-4	443	466
-7	-1	172	228
-7	0	176	-214
-7	2	155	138
-6	-18	233	253
-6	-13	200	182
-6	-10	291	320
-6	-8	216	-174
-6	-1	321	305
-6	0	310	-332
-6	3	137	131
-6	5	211	-221
-6	7	161	-193
-6	9	174	-220
-6	12	250	270
-6	13	190	-98
-6	14	319	-365
-5	-12	311	-301
-5	-11	285	292
-5	-8	194	-195
-5	-7	277	-288
-5	-3	238	-248
-5	-1	461	-475
-5	0	269	274
-5	1	644	-643
-5	4	371	-348
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-4	-14	257	-245
-4	-13	226	-226
-4	-12	220	-233
-4	-9	556	545
-4	-7	222	-235
-4	-5	288	-301
-4	-4	187	-184
-4	-3	393	373
-4	-1	150	173
-4	0	335	-341
-4	2	497	-484
-4	7	422	431
-4	8	330	-332
-4	9	175	199
-4	13	189	197
-4	16	244	184
-3	-20	183	-141
-3	-10	146	175
-3	-9	421	-381
-3	-8	144	198
-3	-7	427	432
-3	-6	262	-255
-3	-4	216	191
-3	-3	145	-175
-3	-2	545	507
-3	-1	831	831
-3	0	220	241
-3	1	743	763
-3	2	341	357
-3	9	558	567
-3	11	224	-243
-2	-13	254	-266
-2	-12	179	157
-2	-11	283	-277
-2	-10	319	-269
-2	-8	210	236
-2	-7	536	-473
-2	-6	383	-360
-2	-5	380	403
-2	-3	739	713
-2	-1	257	-264
-2	0	101	-150
-2	1	124	-124
-2	2	635	662
-2	3	1042	-1010
-2	4	725	734
-2	7	249	-286
-2	8	264	223
-2	9	224	-230
-2	12	429	-402
-2	14	172	-155
-1	-14	192	-217
-1	-13	505	466
-1	-10	171	-176
-1	-8	230	-268
-1	-7	222	233
-1	-6	235	-217
-1	-3	1083	-1120
-1	-2	1345	-1378
-1	-1	558	-572
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-1	1	244	-231
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-1	3	301	-292
-1	5	256	-284
-1	6	833	-852
-1	9	358	352
-1	16	297	305
0	-20	168	-171
0	-15	328	-324
0	-12	226	253
0	-9	621	-599
0	-8	277	-275
0	-7	442	-445
0	-4	708	-663
0	-3	123	148
0	-1	510	510
0	0	493	480
0	1	478	-450
0	3	1006	985
0	4	308	323
0	5	507	513
0	6	448	-442
0	7	519	-514
0	8	294	-344
0	9	354	358
0	10	587	567
0	11	378	373
0	12	303	326
0	13	378	-381
0	16	254	260
0	17	219	226
1	-13	352	-337
1	-11	128	-149
1	-10	167	-228
1	-8	618	-637
1	-6	570	-552
1	-5	150	186
1	-4	271	304
1	-3	503	489
1	-2	298	-268
1	-1	626	622
1	0	457	-446
1	2	298	287
1	3	280	291
1	5	428	423
1	6	374	384
1	7	242	280
1	8	362	393
1	11	191	223
1	12	130	137
1	14	336	-336
1	16	407	-416
1	17	152	236
2	-16	181	234
2	-11	240	271
2	-10	322	311
2	-4	738	709
2	-3	231	-258
2	-2	313	330
2	1	640	-637
2	4	721	735
2	6	473	476
2	7	366	355
2	8	549	-582
2	15	260	-255
3	-14	180	-238
3	-11	245	267
3	-9	294	318
3	-8	406	407
3	-7	703	-678
3	-6	442	453
3	-4	424	407
3	-3	726	699
3	-2	595	-578
3	0	227	-224
3	1	346	-351
3	2	152	148
3	3	122	133
3	5	365	373
3	7	233	-266
4	-17	141	134
4	-13	327	-355
4	-6	413	-436
4	-5	439	-400
4	-2	208	212
4	-1	435	415
4	1	150	182

4	2	262	-294
4	3	231	-240
4	5	336	323
4	6	262	-258
4	9	385	-373
4	11	233	-256
4	16	141	-121
5	-16	145	82
5	-12	277	-253
5	-7	274	308
5	-6	373	-364
5	-3	273	258
5	-1	231	256
5	0	463	462
5	1	204	223
5	2	219	-227
5	3	277	269
5	6	365	355
5	8	278	295
5	11	125	119
5	13	188	131
5	15	227	222
5	16	213	-210
6	-8	453	470
6	-6	302	267
6	-3	239	264
6	0	251	254
6	2	228	244
6	3	130	119
6	5	206	208
6	7	286	281
6	12	250	-245
7	8	250	-257
7	11	256	-289
7	13	386	-352
8	-4	185	-159
8	7	259	-237
9	7	186	180

L = 3

H	K	Fo	Fc
-11	0	163	181
-10	-3	197	-169
-10	1	172	188
-10	5	212	-185
-9	-9	289	-247
-9	-7	405	-372
-9	-1	194	-192
-8	-13	249	-196
-8	-8	473	-453
-8	-2	258	-243
-8	1	246	-262
-8	2	431	429
-8	5	264	298
-7	-14	271	-264
-7	-11	209	172
-7	-9	446	461
-7	-4	210	188
-7	-3	176	191
-7	-2	726	683
-7	-1	183	-155
-7	3	256	257
-7	8	152	-174
-6	-11	189	172
-6	-10	276	262
-6	-9	152	127
-6	-8	363	381
-6	-6	303	281
-6	-4	313	339
-6	-3	328	319
-6	-2	185	190
-6	3	236	251
-6	5	178	188
-6	15	174	-184
-5	-18	199	156
-5	-11	301	-341
-5	-6	535	-529
-5	-5	193	-243
-5	-4	181	-203
-5	-3	191	167
-5	-1	328	338
-5	1	330	-352
-5	4	301	302
-4	-12	227	-250
-4	-11	213	-219
-4	-6	304	-298
-4	-5	279	321
-4	-4	347	-345
-4	-3	753	-737
-4	-2	375	361
-4	0	557	538
-4	1	396	-425
-4	10	421	-422
-3	-19	167	-136
-3	-18	187	-149
-3	-16	239	-233
-3	-10	254	-309
-3	-9	370	368
-3	-6	444	430
-3	-3	181	192
-3	-2	232	234
-3	-1	801	778
-3	0	154	177
-3	1	277	283
-3	2	142	174
-3	3	406	405
-3	4	219	-225
-3	6	658	-617
-2	-15	157	142
-2	-11	300	-313
-2	-8	357	-327
-2	-5	237	-225
-2	-4	723	746
-2	-3	324	312
-2	1	310	349
-2	3	901	893
-2	4	349	-364
-2	5	425	430
-2	7	144	-190
-2	8	456	473
-2	16	334	-310
-1	-15	169	-189
-1	-14	338	359
-1	-12	293	284
-1	-11	230	248
-1	-9	368	-346
-1	-7	250	-251
-1	-5	444	458
-1	-4	485	-504
-1	-3	530	-527
-1	-2	552	-534
-1	-1	765	-796
-1	0	436	411
-1	2	414	-387
-1	3	464	463
-1	4	464	429
-1	7	1058	-1031
-1	10	178	226
-1	12	306	-350
-1	13	221	-234
-1	14	279	-284
0	-20	151	82
0	-14	326	-323
0	-10	126	-133
0	-9	330	326
0	-8	366	-377
0	-6	441	-423
0	-5	626	-631
0	-4	380	374
0	-2	221	223
0	0	140	-155
0	1	720	-700
0	3	339	-336
0	5	267	294
0	6	328	-324
0	8	486	-607
0	13	254	264
0	15	211	-221
1	-14	270	-285
1	-11	365	-365
1	-9	347	-329
1	-8	468	453
1	-7	284	-322
1	-4	527	-527
1	-3	264	239
1	-2	347	362
1	0	255	-268
1	1	183	222
1	2	199	-230
1	3	181	-161
1	5	648	633
1	9	155	175
1	12	505	465
1	14	249	222
2	-11	185	185
2	-7	212	-237
2	-4	507	-516
2	-3	859	804
2	-2	359	-363
2	-1	239	278
2	2	295	-299
2	3	195	225
2	5	472	471
2	6	778	735
2	7	180	-197
2	8	220	212
2	9	213	-228
2	11	366	372
2	13	389	373
3	-7	306	296
3	-4	420	415
3	-3	459	-435
3	-2	389	373
3	3	563	-543
3	5	219	-219
3	10	151	-175
3	17	138	-115
4	-12	206	-240
4	-8	280	236
4	-3	393	-404
4	-2	281	261
4	0	506	500
4	2	266	-262
4	4	576	-564
4	6	376	383
4	11	245	-254
5	-11	307	-304
5	-10	330	-329
5	2	268	247
5	3	152	179
5	4	208	-205
5	6	165	-181
5	7	170	236
5	8	338	363
5	10	300	264
5	11	238	-254
5	13	166	130
6	-9	136	63
6	1	127	142
6	2	151	177
6	4	242	247
6	6	175	195
7	-11	283	238
7	0	223	221
7	2	136	207
7	3	223	236
7	8	159	-174
7	9	152	147
7	11	167	202

L = 4

H	K	Fo	Fc
-9	-7	170	-190
-9	6	140	-42
-9	9	165	-172
-8	-7	282	-287
-8	-6	178	-186
-8	2	322	-313
-7	-13	317	-347
-7	-9	179	230
-7	-6	230	-222
-7	-3	182	189
-7	6	380	384
-7	8	204	217
-6	-13	166	123
-6	-12	230	-278
-6	-9	298	306
-6	-7	199	242
-6	-4	266	235
-6	-2	586	594
-6	-1	348	349
-6	1	326	335
-6	7	242	243
-5	-16	207	218
-5	-11	302	-318
-5	-10	216	218
-5	-8	445	422
-5	-6	499	503
-5	-3	259	276
-5	-1	296	314
-5	0	336	332
-5	2	230	-241
-5	4	478	-464
-4	-14	202	269
-4	-10	373	-416
-4	-6	348	345
-4	-5	320	-314
-4	-4	603	-572
-4	-3	310	-312
-4	-2	599	-607
-4	5	409	-390
-4	8	323	304
-3	-17	318	-283
-3	-10	305	-297
-3	-8	142	-163
-3	-6	322	-360
-3	-5	326	-335
-3	-3	488	-480
-3	-2	416	423
-3	-1	269	267
-3	3	213	211
-3	4	469	470
-3	5	507	-506
-3	7	172	160
-3	8	301	-347
-3	9	411	430
-3	12	186	226
-2	-11	238	247
-2	-7	412	-403
-2	-6	407	407
-2	-5	727	740
-2	-4	357	357
-2	-3	254	289
-2	-2	332	312
-2	-1	183	185
-2	0	412	393
-2	1	420	414
-2	2	392	358
-2	3	324	359
-2	5	415	436

-1	-17	269	251
-1	-12	437	469
-1	-10	311	296
-1	-9	140	163
-1	-5	308	314
-1	-2	212	-232
-1	2	163	-209
-1	3	162	183
-1	5	536	527
0	-15	151	-197
0	-8	219	254
0	-7	148	173
0	-6	591	-585
0	-4	290	-280
0	-3	263	-259
0	-1	167	-215
0	1	316	-330
0	2	384	-391
0	3	676	-664
0	4	619	610
0	5	512	-485
0	10	181	-190
0	16	156	-157
1	-12	404	-407
1	-10	432	-426
1	-7	316	-317
1	-5	406	-427
1	-4	215	234
1	-3	317	-285
1	0	531	542
1	1	235	-283
1	3	258	-245
1	4	219	-244
1	5	383	369
1	7	127	191
1	10	312	-321
2	-11	169	-158
2	-4	249	244
2	-3	231	-277
2	-2	312	289
2	-1	409	405
2	0	241	-213
2	1	490	491
2	2	191	-185
2	4	139	130
2	6	162	182
2	12	164	184
3	-7	271	280
3	-6	185	242
3	-4	176	-195
3	-2	174	-232
3	1	448	446
3	2	202	-215
3	4	326	-325
3	6	267	275
4	-7	277	243
4	-5	185	-183
4	-3	180	-193
4	0	133	169
4	2	584	578
4	3	242	-229
4	4	277	-296
4	6	390	-408
4	11	168	-164
5	-1	360	-347
5	1	290	328
5	5	174	-165
6	0	157	-151
6	3	203	175
6	8	228	204
7	-1	249	281
7	0	191	-217
7	2	211	206
7	4	313	323

L = 5

H	K	Fo	Fc
-9	-5	319	300
-8	-5	340	-326
-8	1	248	-195
-8	3	335	-314
-7	-11	314	-341
-7	-5	243	-256
-7	-3	234	-258
-7	0	191	-245
-7	1	212	284
-6	-15	179	-225
-6	0	509	503
-6	2	194	147
-6	6	304	290
-6	8	295	297
-5	-15	197	163
-5	-13	289	319
-5	-12	185	-256
-5	-10	410	-376
-5	0	192	207
-5	1	180	225
-5	2	320	342
-5	6	383	-410
-5	7	459	443
-4	-13	358	332
-4	-12	261	301
-4	-9	266	-327
-4	-3	334	-344
-4	0	161	-185
-4	1	241	229
-4	6	303	-294
-4	9	237	236
-4	13	279	-314
-3	-15	271	-315
-3	-7	179	-248
-3	-6	202	-230
-3	-1	244	-251
-3	8	248	284
-2	-15	170	-245
-2	-14	266	-297
-2	-8	575	-569
-2	-1	186	-238
-2	1	235	-237
-2	2	305	313
-2	4	241	297
-2	7	213	238
-1	-14	234	-230
-1	-13	240	278
-1	-12	160	-187
-1	-11	324	342
-1	-10	243	233
-1	-8	238	307
-1	-5	159	154
-1	-3	133	-122
-1	-2	405	393
-1	-1	401	387
-1	2	195	250
-1	3	346	355
-1	4	305	304
-1	5	339	328
-1	6	339	292
-1	14	172	127
0	-15	203	166
0	-12	193	216
0	-10	149	179
0	-6	166	203
0	-2	260	-253
0	-1	307	308
0	0	109	-124
0	1	300	302
0	4	327	-345
0	6	263	-237
1	-11	289	-298
1	-6	172	-208
1	-2	144	-174
1	1	215	-259
1	3	620	-614
1	5	306	-283
2	-12	239	-213
2	-10	306	-281
2	-7	291	-271
2	-1	373	-351
2	0	513	511
2	5	182	221
2	8	170	166
2	9	218	234
3	-11	174	-234
3	-4	208	161
3	1	339	348
3	2	166	231
3	4	212	246
3	6	179	-187
4	-13	184	128
4	-11	158	121
4	-5	341	315
4	3	197	200
4	5	350	-352
4	7	230	-218
4	8	179	-170
5	-3	179	214
5	-1	165	-158
5	1	348	-344
5	2	287	287
5	4	236	-248
6	0	189	-219
6	5	268	259
7	-2	150	141
7	3	256	209
7	6	152	85

L = 6

H	K	Fo	Fc
-9	-6	172	238
-9	-1	274	287
-8	-7	290	225
-8	1	256	239
-8	5	228	-258
-7	-1	372	-396
-7	4	372	-328
-7	5	147	-97
-7	6	174	-154
-6	-14	177	102
-6	-11	219	-232
-6	-5	183	-217
-6	-3	235	-210
-6	0	185	-242
-6	4	234	-231
-6	6	281	-285
-6	8	351	306
-6	10	213	199
-5	-15	239	-202
-5	-9	241	-267
-5	-8	185	-287
-5	-6	163	174
-5	-5	306	319
-5	1	229	209
-5	2	203	221
-5	3	225	204
-5	4	577	544
-5	5	180	-200
-5	9	160	134
-4	-16	174	-188
-4	-11	169	191
-4	-9	187	220
-4	1	154	-178
-4	2	244	228
-4	3	182	241
-4	10	273	-272
-3	-10	293	333
-3	-6	317	-336
-3	-5	345	-311
-3	0	182	-190
-3	2	207	-243
-3	8	208	-247
-2	-9	178	-163
-2	-7	222	-255
-2	2	214	-223
-2	5	190	222
-2	6	188	205
-1	-15	164	-147
-1	-13	350	-357
-1	-11	289	-284
-1	-9	290	245
-1	-8	222	-275
-1	0	229	289
-1	2	170	145
-1	4	270	253
-1	6	163	186
0	-10	204	229
0	-9	167	179
0	-7	298	279
0	-2	201	255
0	0	162	195
1	-14	208	220
1	-8	279	264
1	-4	233	-253
1	4	243	-243
2	-11	200	-177
2	-8	168	-215
2	-2	224	-233
2	4	182	150
2	5	341	-330
3	-9	174	-155
3	-1	220	-229
3	3	212	236
4	-4	268	218
4	-3	272	258
4	3	238	235
4	5	267	272
4	7	202	-202
4	8	180	195
5	2	362	-341
5	4	142	99
5	8	171	-131
6	-1	157	-80

L = 7

H	K	Fo	Fc
-7	2	326	294
-6	-7	218	-215
-6	-1	330	-297
-6	4	157	-112
-5	-9	164	-117
-5	-7	219	-258
-5	0	173	-180
-5	3	162	225
-4	-11	155	-148
-4	-8	203	206
-4	-6	186	-318
-4	1	191	-184
-4	4	545	538
-3	-9	347	301
-3	0	198	229
-3	1	283	-290
-3	2	206	-188
-3	5	173	144
-2	-12	173	-115
-2	-5	291	-299
-2	2	441	-421
-2	3	168	-188
-1	-12	177	-171
-1	-9	323	-298
-1	-6	172	-199
0	-10	165	-176

0	-4	314	-312
0	-3	153	170
0	0	406	409
0	2	219	187
0	3	141	-179
1	-4	328	298
1	3	155	-153
2	0	208	-190
2	1	265	253
2	2	234	-250
2	3	159	176
3	3	161	142
3	4	191	212
3	7	153	-68
4	-2	219	164

L = 8

H	K	Fo	Fc
-5	-5	196	-164
-5	-2	262	283
-4	-8	266	220
-4	-5	174	-159
-3	-1	183	183
-3	3	186	-219
-2	2	213	-241
-1	-2	340	-270
-1	4	151	-128
-1	6	172	-164
0	-9	222	-185
0	-2	250	-230
1	1	155	168
2	-5	230	-181
2	-4	260	228

APPENDIX II. SUPPLEMENTARY DATA FOR THE CRYSTALLOGRAPHIC ANALYSIS OF $(Cl_2Pd)_2(1)$

Table I. Hydrogen atom coordinates[a] (fractional x 10^4) for 5

atom	x	y	z
H111	3045.2	3113.3	1709.3
H112	3398.5	2839.1	1232.3
H13	4210.5	1917.6	2127.4
H121	3580.4	2898.5	2823.1
H122	4385.0	2617.6	3190.8
H141	4908.8	2455.6	1745.5
H142	4396.6	3244.3	1239.7
H16	4861.5	3417.2	2653.1
H151	3836.5	4381.4	2333.3
H152	3820.5	4426.8	1613.3
H2A	2183.6	1868.0	-11.4
H3A	1116.8	2556.5	-748.1
H4A	294.1	2995.4	-365.3
H5A	538.0	2749.9	753.5
H6A	1604.3	2063.4	1491.1
H2B	3641.1	2011.4	760.3
H3B	3967.7	1253.9	-5.1
H4B	3770.3	-424.9	-228.1
H5B	3246.1	-1345.7	314.5

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[a] The hydrogen atom parameters were calculated and not refined. The isotropic U values were set to a value of 76.

Table I. continued

H6B	2920.1	-587.1	1080.9
H2C	3891.3	-758.9	2555.0
H3C	4865.0	-1717.5	2717.0
H4C	5984.8	-1058.0	3273.1
H5C	6131.9	558.5	3669.1
H6C	5158.5	1518.0	3506.3
H2D	3423.6	2682.7	3678.7
H3D	3654.6	2920.6	4794.9
H4D	4139.5	1647.1	5563.7
H5D	4395.7	137.3	5216 4
H6D	4166.3	-103.6	4100.6
H2E	4585.1	4102.8	426.5
H3E	4605.1	3608.4	-569.4
H4E	5584.3	2795.3	-544.5
H5E	6544.5	2478.2	475.1
H6E	6524.8	2971.6	1471.0
H2F	6482.0	4570.2	2978.3
H3F	7405.3	3886.2	3908.0
H4F	7641.4	2206.4	3931.8
H5F	6953.7	1207.5	3029.8
H6F	6030.1	1891.8	2100.4
H2G	4374.5	4483.5	3347.4
H3G	4977.6	4437.8	4511.3
H4G	6066.8	5198.4	5049.2

Table I. continued

H5G	6552.0	6008.5	4424.2
H6G	5948.5	6057.1	3262.2
H2H	4058.4	6546.9	2954.6
H3H	3191.8	7755.8	2572.0
H4H	2671.8	8191.0	1444.7
H5H	3018.3	7417.3	699.2
H6H	3885.0	6207.9	1081.0
H661	2309.8	5633.7	10395.4
H662	2493.2	4674.1	10851.9
H663	1861.4	4656.0	10122.9
H664	2139.1	4342.3	10524.9
H665	2579.7	5328.9	10786.2
H666	1945.6	5292.4	10059.0
H671	2801.9	5821.9	9413.5
H672	3458.4	5190.2	9475.1
H673	2688.3	4838.6	8988.6
H674	3164.7	4745.6	9171.8
H675	3276.7	5729.2	9596.2
H676	2507.2	5375.9	9109.2

Table II. Anisotrpic thermal parameters[a] (A^2 x 10^3) for 5

ATOM	U_{11}	U_{22}	U_{33}
Pd1	56.(3)	42.(2)	62.(3)
Pd2	79.(3)	49.(2)	82.(3)
C13	68.(9)	84.(10)	80.(10)
C14	75.(8)	56.(6)	86.(9)
C15	90.(10)	84.(8)	127.(10)
C16	136.(14)	64.(9)	202.(19)
P7	58.(9)	53.(8)	49.(9)
P8	27.(7)	54.(7)	33.(8)
P9	66.(10)	57.(7)	69.(10)
P10	63.(8)	45.(8)	75.(9)

[a] The form of the temperature factor is exp(-2 $U_{ij}h_ih_ja_ia_j$).

U_{12}	U_{13}	U_{23}
-6.(3)	39.(2)	-2.(2)
-5.(3)	59.(3)	-4.(2)
-14.(8)	22.(9)	-9.(7)
-28.(10)	78.(10)	-20.(9)
-12.(9)	127.(16)	-24.(9)
15.(7)	27.(8)	9.(6)
-9.(6)	6.(7)	0.(5)
4.(7)	51.(9)	12.(7)
-5.(7)	48.(8)	-3.(7)

Calculated and Observed Structure Factors

K = 0

H	L	Fo	Fc
0	2	4710	-4731
0	4	2270	2919
0	6	2470	1831
0	8	1079	-1072
0	10	1571	1586
0	12	1142	-1203
0	14	1261	1206
0	16	430	-439
1	-17	685	-565
1	-15	1604	1451
1	-13	1113	-866
1	-11	1363	1134
1	-5	392	-1085
1	-3	1780	1095
1	3	2462	1797
1	5	3888	-3119
1	7	1958	2005
1	9	770	-837
1	11	1085	-1036
1	13	1546	1471
1	15	827	-822
2	-16	904	906
2	-14	1957	-1936
2	-12	1739	1589
2	-10	366	-165
2	-8	2238	-2360
2	-6	640	1009
2	-4	720	208
2	-2	448	-360
2	2	2291	-1972
2	4	1864	1460
2	8	880	-745
2	10	970	995
3	-15	780	-799
3	-13	1496	1306
3	-11	1217	-1140
3	-7	379	-528
3	-5	394	-247
3	-3	1377	1484
3	-1	2811	-3038
3	1	3172	3187
3	3	307	-278
3	5	785	-1045
3	7	1619	1501
3	9	974	-833
4	-10	505	628
4	-8	2494	-2377
4	-6	2485	2851
4	-4	1623	-2073
4	-2	803	-182
4	2	3775	-3215
4	4	2160	2050
4	6	1103	-1047
4	8	625	788
4	12	597	-488
4	14	647	572
5	-19	470	517
5	-17	835	-756
5	-15	890	942
5	-13	1111	-1021
5	-3	4095	-2870
5	-1	2275	-2450
5	1	463	-722
5	5	1900	-1739
5	7	1404	1246
5	9	1277	-1260
5	11	640	608
5	21	509	258
6	-24	487	-324
6	-22	467	418
6	-16	844	961
6	-14	2423	-2385
6	-12	2777	2679
6	-10	2678	-2569
6	-8	365	335
6	-6	1419	1409
6	-4	1456	-1883
6	0	1358	-1113
6	2	1885	1488
6	4	1522	-1215
7	-17	413	-687
7	-15	418	456
7	-13	907	831
7	-11	2569	-2547
7	-9	5097	5099
7	-7	3659	-3890
7	-5	929	1320
7	-3	733	321
7	-1	2081	-1733
7	1	1331	1660
7	3	2920	-2976
7	5	1118	1054
7	7	531	-432
8	-26	459	-378
8	-24	773	613
8	-14	542	-600
8	-8	475	-280
8	-4	2474	-2388
8	-2	2164	1745
8	0	459	-574
8	2	1483	-1019
8	4	2078	2016
8	6	908	-971
8	8	493	512
8	10	455	-573
9	-17	503	-429
9	-15	465	556
9	-13	1697	-1721
9	-11	2050	1984
9	-7	2189	-1672
9	-5	1670	1490
9	-3	1185	-1118
9	1	827	769
9	9	518	-480
9	11	633	542
10	-26	415	271
10	-12	2358	2297
10	-10	2466	-2684
10	-8	2304	2233
10	-6	757	-523
10	-2	1703	1593
10	0	807	-735
10	2	1427	1302
10	12	549	-478
11	-23	399	307
11	-15	712	582
11	-9	624	621
11	-7	745	-908
11	-5	1515	1580
11	-3	2597	-2438
11	-1	2386	2104
11	3	633	-510
11	5	838	957
12	-26	514	-513
12	-24	689	600
12	-22	417	-426
12	-12	1080	-982
12	-8	605	722
12	-6	819	-870
12	-2	1561	1227
12	0	1609	-1590
12	2	1307	1254
12	8	400	76
12	10	560	-720
12	12	634	786
13	-23	555	-650
13	-21	808	803
13	-19	627	-554
13	-11	1027	893
13	-9	598	-873
13	-7	555	622
13	-1	747	661
13	11	382	569
14	-18	930	830
14	-16	496	-720
14	-14	1157	1021
14	-8	1300	1275
14	-6	1330	-1169
14	-4	1954	1701
14	-2	1456	-1343
14	2	694	894
14	4	893	-875
14	6	534	718
14	8	373	-384
15	-13	525	-484
15	-7	457	-506
15	-5	1136	1014
15	-3	1601	-1525
15	-1	1496	1099
15	1	423	-563
15	9	536	398
16	-22	941	-835
16	-20	815	841
16	-18	744	-578
17	-21	460	525
17	-19	842	-956
17	-17	1174	1189
17	-15	643	-779
17	-13	425	467
17	-9	1138	-952
17	-7	1001	864
18	-12	1504	-1487
18	-10	1286	1292
18	-8	512	-375
18	-4	478	428
18	-2	974	-768
18	0	671	709
18	2	460	-476
19	-21	483	-396
19	-15	536	-464
19	-11	626	563
19	-5	633	-590
19	1	624	-736
20	-14	568	-461
20	-10	614	646
20	-8	1117	-988
21	-15	816	-760
21	-13	1032	1004
21	-11	852	-980
21	-5	506	-490
21	-1	709	-643
21	1	497	498
22	-14	609	540
22	-12	773	-759
22	-10	869	861
22	-8	744	-618
22	-6	473	260
22	0	558	562
22	2	467	-391
23	-7	388	-61
24	-4	513	-178
25	-13	428	286

K = 1

H	L	Fo	Fc
0	2	567	-30
0	3	513	1464
0	4	1311	-1164
0	5	3822	-3706
0	7	1298	1136
0	11	1838	-1622
0	13	1330	1260
0	23	492	319
1	-12	878	-829
1	-10	574	650
1	-9	359	-418
1	-8	1497	-1267
1	-6	456	628
1	-5	1097	-837
1	-3	331	-31
1	-2	456	-129
1	2	2294	-3014
1	3	729	1165
1	4	895	1094
1	5	1020	-1081
1	7	424	340
1	10	524	-403
1	12	462	581
1	14	419	-649
2	-7	886	792
2	-5	3818	-3095
2	-3	3591	3717
2	-2	1461	-589
2	-1	3065	-3807
2	0	842	195
2	1	616	1426
2	3	3031	2918
2	5	1293	-1539
2	6	903	1223
2	7	2379	2275
2	8	869	-896
2	9	2624	-2484
2	10	838	973
2	11	1385	1328
2	12	607	-624
2	13	493	-454
3	-13	383	-530
3	-12	1056	992
3	-11	566	580
3	-10	616	-542
3	-9	608	572
3	-7	489	606
3	-6	768	-961
3	-5	727	745
3	-4	627	488
3	-3	1030	-1418
3	-2	2583	-1891
3	-1	2039	2756
3	0	2707	1939
3	2	811	-1131
3	3	395	83
3	4	1669	1690
3	5	530	-492
3	6	314	-443
3	8	1674	-1663
3	10	2061	2049
3	11	575	-603
3	12	1673	-1649
3	14	628	539
4	-23	458	333
4	-21	494	-564
4	-19	922	710
4	-17	1007	-925
4	-13	418	433
4	-12	402	-285
4	-11	1334	-1302
4	-10	857	995
4	-9	1316	1459
4	-8	792	-973
4	-7	1284	-1087
4	-6	387	455
4	-4	927	-769
4	-3	1590	-2098
4	-1	585	-298
4	0	347	842
4	1	398	-72
4	2	2156	-1610
4	4	1422	1210

4	5	713	-850
4	6	303	-580
4	13	369	390
5	-18	557	-599
5	-17	461	450
5	-16	1286	1116
5	-15	610	-576
5	-14	1092	-1140
5	-12	1066	1241
5	-11	1961	1643
5	-9	1781	-1642
5	-8	507	-654
5	-7	716	789
5	-6	2656	2256
5	-5	479	369
5	-4	2799	-2368
5	-3	1018	1168
5	-2	3023	3014
5	0	320	97
5	2	964	1017
5	3	887	1007
5	4	1078	1277
5	5	1309	-1346
5	6	310	-339
5	7	689	859
5	8	819	984
6	-15	535	449
6	-13	655	570
6	-11	571	-721
6	-10	602	-585
6	-9	1711	1635
6	-8	1007	979
6	-7	992	-856
6	-6	971	-756
6	-4	1293	1218
6	-3	1227	1136
6	-2	1758	-1489
6	-1	1400	-1173
6	0	475	161
6	1	2712	2580
6	2	476	-524
6	3	1622	-1539
6	7	714	450
6	9	860	-886
6	11	1088	1070
6	13	386	-580
7	-23	411	376
7	-22	524	583
7	-20	780	-751
7	-14	863	-715
7	-12	1082	1084
7	-10	1469	-1445
7	-5	1513	-1511
7	-4	808	-652
7	-2	1104	735
7	-1	897	-756
7	0	1136	1038
7	1	348	-481
7	2	2475	-2333
7	4	1361	1023
7	14	547	587
8	-17	626	-611
8	-15	1434	1371
8	-14	716	-576
8	-13	1158	-1189
8	-11	479	449
8	-9	1890	2039
8	-8	1362	-1343
8	-7	2330	-2542
8	-6	801	836
8	-5	2915	2739
8	-4	806	-794
8	-3	787	-498
8	-1	1349	979
8	0	414	-169
8	1	764	-637
8	2	583	488
9	-14	891	-1003
9	-13	785	833
9	-12	2376	2190
9	-11	784	-731
9	-10	1766	-1992
9	-8	1148	1335
9	-5	646	-651
9	-4	1080	-1236
9	-3	783	680
9	-2	2519	2443
9	-1	1050	-1096
9	0	2943	-2551
9	1	1074	1126
9	2	1914	1925
9	4	329	-376
10	-19	634	-492
10	-11	680	-560
10	-10	930	1089
10	-8	786	-721
10	-7	1622	-1445
10	-6	889	887
10	-5	1319	1396
10	-3	1322	-1382
10	-1	1116	-1145
10	0	610	535
10	1	2152	2043
10	3	1827	-1925
10	5	742	632
10	11	425	512
10	13	392	-620
11	-16	665	-692
11	-14	1238	1288
11	-12	1401	-1469
11	-9	560	681
11	-8	992	1093
11	-7	728	-753
11	-6	507	-727
11	-4	725	622
11	-1	416	475
11	0	592	512
12	-23	489	-305
12	-15	994	1026
12	-14	605	-593
12	-13	1858	-1994
12	-12	420	597
12	-11	1784	1745
12	-9	382	-592
12	-6	634	789
12	-5	833	828
12	-4	556	-501
12	-3	2513	-2345
12	-2	670	753
12	-1	2626	2422
12	0	501	-533
12	1	1703	-1611
13	-14	669	-747
13	-13	790	725
13	-12	551	579
13	-11	378	-544
13	-9	469	455
13	-8	593	769
13	-6	1208	-1072
13	-2	575	556
13	0	1494	-1462
13	2	1397	1344
13	4	769	-785
13	6	383	461
13	13	409	105
14	-20	477	-439
14	-19	788	-749
14	-15	693	-681
14	5	391	405
15	-24	498	443
15	-17	424	-479
15	-16	773	-873
15	-14	1120	1088
15	-12	1106	-1196
15	-10	717	744
15	-3	473	345
16	-21	457	481
16	-19	806	-794
16	-13	489	-408
16	-11	1340	1315
16	-9	1374	-1417
16	-7	829	853
16	-1	572	548
16	1	662	-622
16	3	455	620
17	-11	478	-389
17	-10	445	-486
17	-8	749	768
17	-6	884	-729
17	-4	601	507
17	2	489	603
17	4	409	-563
18	-25	467	-500
18	-23	605	554
18	-17	633	649
18	-15	923	-946
18	-13	962	971
18	-11	983	-918
19	-24	452	466
19	-18	415	-486
19	-14	453	524
19	-12	1215	-1206
19	-10	1634	1664
19	-8	1140	-1060
20	-9	558	-530
20	-7	690	714
20	-5	668	-545
20	-3	483	477
22	-21	456	-296
22	-14	399	131
22	-11	582	-547
22	-9	454	581
23	-4	456	-336
24	-10	397	-25
K =		2	
H	L	Fo	Fc
0	0	4079	3080
0	1	2446	-2529
0	2	2363	-2329
0	3	725	943
0	4	682	728
0	6	1275	1006
0	8	1676	-1552
0	9	383	487
0	10	797	1096
0	11	601	-664
0	12	593	-697
0	13	646	754
0	14	472	594
0	15	579	-588
1	-22	414	-186
1	-12	670	659
1	-10	702	-686
1	-4	733	1111
1	-3	1195	-1883
1	-2	1563	1298
1	-1	596	1188
1	0	2140	-1826
1	1	1283	-646
1	3	799	919
1	4	788	-790
1	5	2210	-1949
1	6	1824	1368
1	7	1365	1313
1	8	978	-962
1	9	649	-760
1	11	887	-852
1	13	980	1027
1	14	436	-529
1	16	396	373
2	-21	572	435
2	-19	488	-511
2	-18	493	-433
2	-17	534	649
2	-16	1020	989
2	-15	632	-634
2	-14	1102	-1017
2	-13	752	778
2	-12	774	812
2	-10	878	-684
2	-7	853	1082
2	-5	1357	-1612
2	-4	4844	-3405
2	-3	401	-13
2	-2	328	-198
2	-1	1084	-1073
2	0	525	134
2	1	506	136
2	2	1947	-1223
2	4	425	217
2	5	1038	-982
2	6	803	647
2	8	1283	-1201
2	11	502	-460
3	-16	741	-807
3	-15	810	-814
3	-14	1016	1102
3	-13	1391	1190
3	-12	1279	-1125
3	-11	483	-617
3	-10	588	-614
3	-9	1358	1346
3	-8	527	552
3	-7	1409	-1361
3	-6	1619	-1223
3	-5	1316	862
3	-4	465	-953
3	-3	1480	1854
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3	-1	1356	-1418
3	1	4865	3663
3	2	2032	-1874
3	4	347	577
3	7	888	764
3	8	392	-537
3	9	693	-615
3	11	826	893
4	-11	762	722
4	-10	727	779
4	-8	1492	-1619
4	-7	1180	892
4	-5	691	-394
4	-4	2164	1599
4	-3	384	329
4	-2	2416	-2275
4	0	2881	3379
4	2	656	-919
4	3	1588	1751
4	4	1952	1726
4	5	980	-1018
4	6	2186	-1975
4	7	1037	1098
4	8	887	939
4	9	928	-969
4	12	927	-1026
5	-22	427	-419
5	-20	614	506
5	-17	988	-928
5	-15	833	884

5	-13	603	-698
5	-9	789	-663
5	-8	714	757
5	-5	504	514
5	-4	1136	1099
5	-3	1655	-1536
5	-2	1974	-1696
5	-1	1177	936
5	0	689	403
5	1	1231	-991
5	2	716	468
5	5	794	-908
5	7	1585	1635
5	8	1128	-1149
5	9	824	-890
5	10	1066	1162
5	12	445	-679
6	-22	652	618
6	-16	917	1047
6	-15	559	-686
6	-14	1514	-1532
6	-13	986	1017
6	-12	1727	1665
6	-11	839	-943
6	-10	1367	-1374
6	-8	1302	1404
6	-4	722	-932
6	-3	976	-1134
6	-2	2093	1918
6	0	720	-778
6	1	970	813
6	2	465	-291
6	3	1433	-1329
6	5	383	672
6	9	479	672
7	-18	619	-540
7	-15	441	481
7	-12	1417	-1322
7	-11	1062	-1005
7	-10	1538	1497
7	-9	1946	1898
7	-8	913	-863
7	-7	2476	-2341
7	-6	1250	1143
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7	1	896	919
7	2	1410	-1262
7	3	471	-596
7	4	1127	1277
7	5	544	628
7	6	367	-438
7	8	388	461
8	-25	446	164
8	-13	599	460
8	-11	663	580
8	-8	389	-453
8	-7	1293	1273
8	-6	997	940
8	-5	1848	-1666
8	-4	1225	-1142
8	-3	1809	1618
8	-2	821	727
8	1	986	-941
8	3	1147	972
8	4	943	1100
8	6	762	-701
9	-21	417	502
9	-15	770	866
9	-14	652	-678
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19	-7	467	614
20	-17	391	239
20	-6	923	-921
20	-4	793	795
20	-2	445	-472
21	-19	443	249
22	-12	499	-446
22	-10	514	494
23	-12	430	-262

K = 6

H	L	Fo	Fc
0	0	1261	-1197
0	1	2284	-2473
0	2	893	907
0	3	1787	1766
0	4	706	-695
0	5	1271	-1191
0	8	659	750
0	9	956	886
0	10	531	-552
1	-16	462	498
1	-8	403	390
1	-5	717	-698
1	-4	890	935
1	-3	459	485
1	-2	1467	-1551
1	-1	498	-736
1	0	1028	1086
1	2	493	561
1	3	1105	-951
1	4	2508	-2676
1	5	770	839
1	6	2439	2596
1	8	1038	-1039
1	9	703	-532
1	16	477	491
2	-17	614	620
2	-7	1114	1043
2	-6	789	-667
2	-5	954	-995
2	-4	686	678
2	-2	379	-394
2	-1	994	1015
2	0	407	338
2	1	1617	-1601
2	2	439	-500
2	4	447	564
2	5	414	331
2	7	547	-713
2	9	565	707
2	11	481	-852
3	-12	976	-880
3	-10	1309	1300
3	-8	772	-828
3	-5	515	-527
3	-4	513	612
3	-2	2355	-2466
3	0	2042	1894
3	1	640	-753
3	2	1465	-1384
3	3	1052	940
3	4	954	1052
3	8	538	-770
4	-11	548	592
4	-9	1081	-1045
4	-7	1802	1721
4	-5	1155	-1168
4	-3	511	742
4	-1	919	911
4	1	1567	-1465
4	3	2885	2871
4	4	518	-498
4	5	2056	-2094
4	7	1122	1205

4	13	552	811
5	-14	590	-655
5	-1	405	545
5	0	410	666
5	4	543	-598
5	6	1052	1145
5	8	902	-915
5	10	579	719
6	-15	1368	-1345
6	-14	557	646
6	-13	1562	1531
6	-11	1291	-1186
6	-5	609	-531
6	-3	827	759
6	-1	424	-740
7	-10	962	1038
7	-9	630	-640
7	-8	2259	-2333
7	-6	2190	2003
7	-3	408	-623
7	0	799	850
7	2	1121	-949
7	4	602	605
7	5	444	-565
8	-16	482	522
8	-14	501	-453
8	-13	733	664
8	-11	1188	-1308
8	-9	800	711
8	-6	404	-476
8	-3	1735	1679
8	-1	1361	-1368
8	5	749	-779
8	7	767	1061
9	-14	487	-595
9	-9	580	562
9	1	514	-431
9	2	439	-680
10	-11	1205	-1178
10	-9	1827	1849
10	-7	2286	-2221
10	-6	818	774
10	-1	1158	-1234
10	3	488	-693
11	-16	599	492
11	-8	1301	-1301
11	-6	2915	2825
11	-4	2564	-2523
11	-2	1519	1498
11	6	562	-978
12	-21	530	556
12	-20	380	-234
13	-22	607	606
13	-20	544	-632
13	-18	555	691
13	-6	565	-640
14	-17	719	-735
14	-7	1021	-1105
15	-2	771	715
15	0	574	-653
16	-18	398	227
17	-20	511	-610
17	-18	983	931
17	-16	1143	-1095
17	-14	672	786
17	-10	464	-491
17	-8	648	774
17	-4	556	537
18	-15	763	857
18	-13	1029	-989
18	-11	677	852
18	-1	709	678
20	-18	413	287
20	-17	620	716
20	-16	547	-446
20	-15	488	-512
20	-9	546	-617
21	-18	442	479

K = 7

H	L	Fo	Fc
0	1	530	436
0	2	724	591
0	3	498	-531
0	8	506	680
0	9	494	-575
0	10	594	-687
1	-10	539	-560
1	-9	1311	-1241
1	-8	904	881
1	-7	2088	2036
1	-6	1345	-1235
1	-5	1175	-1240
1	-4	676	756
1	-1	1358	1315
1	1	1680	-1635
1	2	460	546
2	-8	499	610
2	-7	1011	-1007
2	-6	1152	-1179
2	-5	1406	1366
2	-4	1353	1347
2	-3	440	-563
2	-2	1461	-1442
2	-1	617	804
2	0	534	712
3	-9	605	589
3	-6	524	695
3	-1	775	892
3	1	627	-628
3	2	415	693
4	-15	469	446
4	-10	795	815
4	-8	1296	-1320
4	-7	603	664
4	-6	665	640
4	0	695	598
5	-15	697	-784
5	-13	918	921
5	-7	982	973
5	-6	1031	-1002
5	-3	1661	1600
5	3	597	584
5	5	734	-837
6	-5	549	646
6	-2	1594	-1714
7	-21	477	-190
7	-18	591	-537
7	-11	1044	-961
7	-8	462	470
8	-17	554	552
8	-16	829	922
8	-15	848	-816
8	-14	1085	-1050
8	-12	418	437
8	-4	1611	-1791
8	-3	536	661
8	-2	616	582
9	-22	451	-54
9	-16	493	-585
9	-13	459	556
9	-9	903	953
9	-5	544	-590
9	-3	1282	1168
9	0	484	619
10	-20	409	-422
10	-18	566	589
10	4	423	557
11	-19	456	370
11	-17	662	-675
11	-6	530	589
12	-23	402	204
12	-9	526	598
12	0	577	-594
14	-18	433	460
14	-2	468	520
15	-16	665	679
15	-15	496	576
15	-12	410	399
15	-11	697	613
16	-15	669	-582
16	-13	740	748
16	-12	462	417
16	-11	654	-620
16	-9	473	626
18	-15	525	541
19	-9	580	-687
19	-7	702	641
20	-4	455	613
22	-16	448	119
23	-7	461	446

K = 8

H	L	Fo	Fc
0	0	1125	-1261
0	1	755	-766
0	2	1294	1289
0	3	736	855
0	4	1008	-959
0	10	568	-622
1	2	778	988
2	-10	563	549
2	-7	605	639
2	-4	537	616
2	-3	495	-429
2	-1	513	514
3	-13	740	-671
3	-12	729	-689
3	-11	723	857
3	-9	776	-885
3	-3	737	-820
3	-1	1452	1432
3	0	462	563
3	1	1369	-1508
3	2	450	-728
3	3	1030	1165
4	-15	432	-483
4	-12	870	813
4	-10	1269	-1328
4	-8	1235	1232
4	-6	651	-652
4	-2	1108	1088
4	0	896	-1011
4	1	930	-1084
4	2	651	865
4	3	1126	1117
5	-17	531	465
5	-8	834	-888
5	-6	601	597
5	-1	1009	-954
5	1	507	704
6	-16	902	-812
6	-15	409	-410
6	-14	1096	1229
6	-13	735	875
6	-12	873	-797
7	-13	606	-641
7	-11	851	835
7	-9	1039	-901
7	-6	858	837
8	-9	579	588
9	-15	424	-543
10	-18	389	-236
10	-12	745	-804
10	-5	704	634
11	-17	423	311
11	-11	500	608
11	-6	787	787
13	-21	450	-544
13	-13	469	413
14	-18	533	-676
14	-15	567	604
15	0	599	-581
16	-14	433	-238
16	6	413	-76
17	-21	503	-218
17	-16	624	-646
17	-14	697	690
18	-16	452	472
18	-14	594	-624
18	-12	508	527
20	-18	469	571
20	-9	425	-354
22	-12	427	300

K = 9

H	L	Fo	Fc
0	4	467	-476
0	11	664	713
1	-10	831	-763
1	-8	675	745
1	-6	654	-760
1	2	636	903
1	4	599	-747
2	-9	492	581
2	-7	728	-759
2	-5	472	633
2	-3	783	-849
2	-1	447	622
3	-16	424	-52
3	-2	465	441
3	-1	555	683
5	-18	424	233
5	-15	788	-692
5	-13	502	590
5	0	711	862
5	3	628	829
6	-13	509	-540
6	-11	711	767
6	-3	755	-831
6	1	1086	-877
6	3	478	371
7	-20	435	389
7	-2	865	888
7	0	1142	-1065
7	2	612	741
7	10	504	-432
7	14	468	-270
8	-17	605	680
8	-15	957	-895
8	-13	698	753
8	-7	1006	1017
8	-5	797	-944
8	-3	926	797
8	1	470	464
9	-14	785	732
9	-12	886	-822
9	-2	895	-892
9	0	484	519
10	1	675	-567
10	3	940	823
11	-20	559	336
11	-14	469	-442
12	-15	545	-494
12	-11	646	-661
12	1	810	690
12	3	565	-461
12	8	399	96
13	-10	424	610
13	-8	423	-427

13	0	840	736
13	2	920	-765
13	4	527	539
14	-13	505	-389
14	0	496	-272
14	1	515	-408
14	4	401	-122
15	-14	652	-759
15	4	425	-131
16	-19	472	374
16	-9	516	639
18	-15	478	516
18	-13	433	-394
19	-10	456	-499
21	-11	426	164

K = 10

H	L	Fo	Fc
0	0	2200	-2077
0	2	1457	1438
0	3	566	534
0	4	457	-574
0	12	438	569
0	14	586	-559
1	-1	554	-792
1	1	1164	1044
1	3	1419	-1302
1	5	904	805
1	7	562	-574
1	13	695	-637
1	17	513	-331
2	-14	565	586
2	-1	664	683
2	0	414	471
2	1	841	-751
2	3	604	733
2	5	474	-383
2	10	515	-514
2	13	453	297
3	-20	443	-42
3	-13	494	-625
3	-11	723	778
3	-1	775	736
3	1	1102	-953
3	2	497	526
3	3	646	593
4	-10	635	-621
4	0	548	-725
4	2	1180	1141
4	4	780	-630
4	12	432	297
5	1	763	883
5	5	577	560
5	12	416	-329
6	-14	1003	1116
6	-12	1343	-1285
6	-10	939	993
6	0	760	748
6	2	577	-481
7	-13	423	-456
7	-11	1018	976
7	1	484	-483
7	14	473	226
8	2	492	330
8	3	490	-294
8	4	674	-545
8	10	584	339
9	-13	565	610
9	9	454	283
10	-18	499	-300
10	-15	401	-298
10	-12	683	-713
10	-10	1002	1002
10	-8	929	-1026
10	2	547	-473
11	-9	524	-531
11	-3	521	526
11	3	492	328
11	11	428	154
12	-9	407	379
14	-16	497	394
14	-6	451	237
16	-7	380	-157
16	0	453	453
17	-5	390	190
18	-2	479	354
18	0	516	-341

K = 11

H	L	Fo	Fc
0	2	372	462
0	4	551	-555
0	8	722	-748
0	10	650	654
0	11	574	515
0	12	419	-370
0	15	393	219
1	-10	565	-522
1	-5	550	759
1	-3	801	-983
1	2	551	644
1	4	503	-489
1	11	411	-360
2	-5	576	661
2	-3	841	-884
2	-1	782	1011
2	5	652	591
2	7	829	-751
2	9	905	824
2	11	731	-630
3	-15	462	-121
3	-2	552	646
3	0	705	-817
3	10	773	-657
3	12	688	649
5	-16	457	-392
5	-8	402	297
5	-6	513	-462
5	-2	654	-792
5	6	420	289
6	-6	465	523
6	-1	767	863
6	0	567	-494
6	1	1011	-868
6	3	599	511
6	11	547	-386
7	2	612	479
8	-19	476	-256
9	-12	568	-675
9	-10	721	823
9	0	1238	1056
9	2	574	-619
10	-20	399	293
10	-7	487	477
10	1	767	-740
10	3	729	636
11	-5	367	-50
12	-11	714	-760
12	-6	552	491
12	-1	739	-749
13	0	473	483
13	2	687	-562
14	2	501	245
15	-14	545	-541
16	-15	428	28
16	-9	622	546
16	1	484	276
19	-12	605	522
19	-11	396	-46
19	-10	582	-560

K = 12

H	L	Fo	Fc
0	0	1442	-1414
0	1	704	701
0	2	1004	1012
0	8	496	513
0	10	570	-582
1	5	755	665
2	-14	421	390
2	2	665	656
2	4	668	-438
2	7	547	435
2	15	531	-241
3	-3	657	-916
3	-1	741	975
3	0	637	-663
3	1	502	-460
3	2	686	701
3	7	479	-371
3	11	385	-109
4	1	519	471
4	2	813	692
4	3	584	-522
4	4	966	-836
4	6	547	540
5	5	393	218
5	9	523	438
6	-15	405	199
6	-10	445	622
7	-5	420	-575
7	1	680	-697
7	2	445	379
7	3	650	429
8	3	524	-481
8	5	502	393
8	6	430	313
9	-13	500	495
9	-4	376	-271
9	10	496	-214
10	-12	627	-595
10	0	586	583
11	-14	388	124
11	4	526	-452
12	0	488	542
14	-6	500	520
14	-1	391	-171
16	-12	524	354
16	0	464	44

K = 13

H	L	Fo	Fc
0	3	615	-607
0	5	394	459
1	0	495	-535
1	1	520	404
1	3	625	-586
2	-4	554	-682
2	8	552	450
2	10	448	-394
3	2	606	632
3	9	621	-415
4	-12	422	170
4	1	445	-251
5	-15	412	282
5	-5	681	722
6	0	409	-407
10	-5	527	-574
10	0	607	-496
12	0	481	450
14	-8	393	10
14	-5	407	-112
15	-12	412	105
15	-10	419	-98

K = 14

H	L	Fo	Fc
0	1	653	683
0	2	469	483
0	3	531	-339
4	-7	409	-235
4	5	572	487
5	5	439	233
7	-10	633	-661
7	2	464	322
7	4	614	-384
13	-5	444	-124

K = 15

H	L	Fo	Fc
1	-5	406	379
4	-4	411	396
5	-4	396	-77

APPENDIX III. SUPPLEMENTARY DATA FOR THE CRYSTALLOGRAPHIC ANALYSIS OF $Cl_2Pd(Ph_2PCH_2)_2C_2H_2CH_2P(O)Ph_2)_2$

Table I. General displacement parameter expressions

atom	U(1,1)	U(2,2)	U(3,3)
Pd	0.0373(4)	0.0378(4)	0.0344(4)
Cl1	0.048(2)	0.043(1)	0.021(1)
Cl2	0.048(2)	0.044(1)	0.049(2)
P1	0.043(1)	0.037(1)	0.034(2)
P2	0.036(2)	0.047(2)	0.034(2)
P3	0.039(2)	0.041(2)	0.055(2)
P4	0.057(2)	0.047(2)	0.034(2)
O1	0.061(5)	0.070(5)	0.059(5)
O2	0.047(5)	0.066(5)	0.063(5)
C1	0.038(6)	0.048(7)	0.051(7)
C2	0.035(6)	0.039(6)	0.037(6)
C3	0.055(7)	0.037(6)	0.030(5)
C4	0.039(6)	0.035(5)	0.041(5)
C5	0.040(6)	0.036(5)	0.051(6)
C6	0.047(6)	0.037(6)	0.030(6)
C7	0.057(7)	0.043(6)	0.043(6)
C8	0.043(6)	0.060(6)	0.042(6)
C9	0.068(9)	0.064(8)	0.064(9)
C10	0.051(8)	0.054(7)	0.09(1)
C11	0.09(1)	0.076(9)	0.043(7)
C12	0.07(7)	0.086(9)	0.034(7)

U(1,2)	U(1,3)	U(2,3)
0.0010(3)	0.0038(4)	0.0018(4)
-0.004(1)	0.011(1)	0.002(1)
-0.013(1)	0.009(1)	0.010(1)
-0.001(1)	-0.000(1)	0.010(1)
-0.006(1)	0.001(1)	-0.001(1)
0.004(1)	0.005(1)	0.007(1)
0.009(1)	0.003(1)	0.008(1)
0.016(4)	0.021(4)	0.014(4)
0.006(4)	0.011(4)	0.016(4)
-0.013(6)	-0.004(5)	0.008(6)
-0.007(5)	-0.001(5)	0.001(6)
-0.008(5)	0.002(4)	-0.003(5)
0.002(5)	-0.001(5)	0.009(5)
0.004(5)	0.010(5)	0.001(5)
0.010(5)	0.002(4)	0.003(4)
-0.011(6)	-0.007(5)	0.002(5)
0.003(5)	0.002(6)	-0.001(7)
0.011(7)	-0.015(7)	0.000(6)
0.003(6)	-0.022(7)	0.005(7)
-0.024(8)	-0.025(7)	0.015(7)
-0.034(8)	-0.013(6)	0.014(6)

Calculated and Observed Structure Factors

Values of 10*Fobs and 10*Fcalc for PdCl2(f-0-Pphenyl2-02)

Page 1

H	K	L	Fobs	Fcalc	SigF
0	0	2	2400	2641	14
0	0	4	4562	4610	20
0	0	6	3010	2703	7
0	0	8	1353	1252	9
0	0	10	516	525	12
0	0	12	579	554	14
0	0	14	957	884	13
0	0	16	259	231	11
0	1	1	2419	2532	12
0	1	3	2382	2260	5
0	1	5	2842	2515	7
0	1	7	2537	2415	8
0	1	9	813	774	10
0	1	11	893	828	12
0	1	13	889	831	13
0	1	15	433	400	12
0	2	0	1472	1372	5
0	2	2	1663	1760	5
0	2	4	946	880	7
0	2	6	1663	1548	8
0	2	8	568	516	11
0	2	10	990	959	11
0	2	12	314	302	9
0	2	14	628	563	15
0	3	1	1368	1137	6
0	3	3	671	631	7
0	3	5	1367	1171	8
0	3	7	664	640	10
0	3	9	381	385	9
0	3	11	471	481	12
0	3	13	478	461	12
0	4	0	2369	1910	7
0	4	2	1381	1348	7
0	4	4	591	645	9
0	4	6	662	574	9
0	4	8	1011	946	10
0	4	10	379	357	8
0	4	12	234	226	10
0	4	14	234	242	12
0	5	1	982	1047	8
0	5	3	571	540	10
0	5	5	664	695	10
0	5	7	593	620	12
0	5	9	832	771	12
0	5	11	258	253	10
0	5	13	159	167	16
0	6	0	1969	1891	9
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0	6	4	1746	1594	9
0	6	6	828	827	11
0	6	8	457	455	12
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0	6	12	377	353	8
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0	7	3	1525	1459	10
0	7	5	1142	1126	11
0	7	7	382	355	9
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0	8	2	489	484	11
0	8	4	699	620	13
0	8	6	728	720	13
0	8	8	438	471	12
0	8	10	708	726	15
0	9	1	180	229	12
0	9	3	439	401	10
0	9	5	628	641	14
0	9	7	275	239	10
0	9	9	598	587	13
0	10	0	495	460	13
0	10	2	365	378	9
0	10	4	496	489	14
0	10	6	180	236	15
0	11	1	130	143	20
0	11	3	162	188	18
0	11	5	320	329	10
0	12	0	286	271	12
0	13	1	294	281	13
1	1	1	1061	966	17
1	1	2	942	1070	5
1	1	3	960	869	9
1	1	4	1111	1013	6
1	1	5	1093	1034	10
1	1	6	759	729	8
1	1	7	551	585	9
1	1	8	941	940	9
1	1	9	120	111	11
1	1	10	590	587	12
1	1	11	249	228	8
1	1	12	465	444	12
1	1	13	250	232	15
1	1	14	344	333	10
1	1	15	204	192	13
1	2	0	738	622	5
1	2	1	1729	1612	5
1	2	2	1780	1682	9
1	2	3	750	666	11
1	2	4	1030	998	7
1	2	5	1393	1350	7
1	2	6	285	268	12
1	2	7	640	615	9
1	2	8	166	198	8
1	2	9	325	332	9
1	2	11	475	500	11
1	2	12	496	489	11
1	2	13	526	507	12
1	2	14	232	205	11
1	2	15	328	320	9
1	3	0	1127	1082	6
1	3	1	225	223	5
1	3	2	1100	1014	6
1	3	3	820	750	17
1	3	4	562	638	8
1	3	5	772	790	11
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1	3	7	383	322	9
1	3	8	373	426	9
1	3	9	604	602	17
1	3	10	257	253	18
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1	4	1	1128	1085	8
1	4	2	394	357	8
1	4	3	740	808	8
1	4	4	131	139	19
1	4	5	660	631	15
1	4	6	272	273	6
1	4	7	713	693	10
1	4	8	668	634	11
1	4	9	603	644	12
1	4	10	244	230	15
1	4	11	473	453	12
1	4	12	459	438	11
1	4	13	564	577	28
1	4	14	201	208	14
1	4	15	352	339	10
1	5	0	926	955	9
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1	5	9	273	292	10
1	5	10	674	653	13
1	5	11	187	169	12
1	5	12	544	539	13
1	5	13	312	307	25
1	5	14	356	341	9
1	6	0	712	671	27
1	6	1	478	470	10
1	6	2	980	950	9
1	6	3	625	559	10
1	6	4	545	541	11
1	6	5	508	529	12
1	6	6	303	310	17
1	6	7	510	497	15
1	6	8	382	390	10
1	6	9	301	286	8
1	6	10	341	332	10
1	6	11	430	428	10
1	6	12	290	293	10
1	6	13	253	239	24
1	7	0	243	231	7
1	7	1	334	278	12
1	7	2	579	577	14
1	7	3	352	387	15
1	7	4	264	255	12
1	7	5	665	622	22
1	7	6	251	207	8
1	7	7	287	309	11
1	7	8	148	141	14
1	7	9	476	462	12
1	7	10	225	216	15
1	7	12	410	415	10
1	8	0	189	149	18
1	8	1	194	216	10
1	8	2	234	212	9
1	8	3	164	148	12
1	8	5	228	211	17
1	8	6	483	480	17
1	8	7	151	134	17
1	8	11	257	254	12
1	9	1	340	345	9
1	9	2	212	206	11
1	9	3	204	171	11
1	9	4	183	140	13
1	9	5	296	280	13
1	9	9	180	168	15
1	9	10	179	148	23
1	10	1	239	216	10
1	10	3	526	534	13
1	10	4	370	363	11

```
Values of 10*Fobs and 10*Fcalc for PdCl2(f-0-Pphenyl2-02)                                                          Page  2

 H  K  L   Fobs  Fcalc  SigF      H  K  L   Fobs  Fcalc  SigF      H  K  L   Fobs  Fcalc  SigF      H  K  L   Fobs  Fcalc  SigF
 -  -  -   ----  -----  ----      -  -  -   ----  -----  ----      -  -  -   ----  -----  ----      -  -  -   ----  -----  ----

 1 10  5    195    159    13      2  2  9    421    423    21      2  6  3   1076    985    11      2 13  0    194    219    20
 1 10  6    194    167    15      2  2 10    442    382    11      2  6  4    634    547    11      3  1  0    723    656     4
 1 11  0    254    257    11      2  2 11    842    863    12      2  6  5   1012    989    10      3  1  1   1378   1345    24
 1 11  1    192    197    15      2  2 12    504    519    12      2  6  6    363    364     9      3  1  2   2035   1924    36
 1 11  2    375    356     9      2  2 13    679    659    17      2  6  7    875    860    11      3  1  3    789    723     6
 1 11  3    421    413    10      2  2 14    199    197    16      2  6  8    297    302     8      3  1  4    798    762     7
 1 11  4    591    549    13      2  2 15    405    374    21      2  6  9    977    963    12      3  1  5    467    474     9
 1 11  5    175    155    16      2  3  0   1619   1459     6      2  6 10    457    436    12      3  1  6   1018    903    10
 1 11  6    336    330    11      2  3  1    456    445    12      2  6 11    623    611    15      3  1  7    589    618     9
 1 12  0    281    270    15      2  3  2    784    777     7      2  6 12    212    224    13      3  1  8    289    260     7
 1 12  1    353    338    10      2  3  3    228    212     6      2  6 13    170    149    15      3  1  9    162    144     9
 2  0  2   1258   1264     7      2  3  4    732    655     8      2  7  0    440    429    14      3  1 11    335    352     9
 2  0  3    758    591     6      2  3  5    249    238     7      2  7  1    178    188     9      3  1 12    241    221     9
 2  0  4   2284   2171     6      2  3  6    349    274     9      2  7  2   1129   1099    26      3  1 13    417    408    10
 2  0  5   1538   1546     8      2  3  7    193    186     7      2  7  3    717    734    14      3  1 15    270    274    11
 2  0  6    711    716     8      2  3  8    843    729    17      2  7  4   1053   1057    19      3  2  0   1340   1306     5
 2  0  7   2553   2402    10      2  3  9    159    121    10      2  7  5    242    236     8      3  2  1   1442   1318     5
 2  0  8    751    754    10      2  3 12    476    482    19      2  7  6    587    607    13      3  2  2    355    352     7
 2  0  9   1089   1154    18      2  3 13    221    201    11      2  7  7    449    457    11      3  2  3    535    470    11
 2  0 10    334    302     8      2  3 14    168    164    15      2  7  8    410    384    11      3  2  4    191    201     5
 2  0 11    697    688    12      2  4  1    584    544     9      2  7  9    364    362     8      3  2  6   1279   1259     8
 2  0 12    738    682    13      2  4  2    434    336     9      2  7 10    540    558    13      3  2  7    375    356     9
 2  0 13    869    832    13      2  4  3    584    459    14      2  7 11    317    297    10      3  2  8    588    609    22
 2  0 14    240    257    10      2  4  4    462    337    11      2  7 12    262    244    11      3  2 10    267    251    12
 2  0 15    207    196    20      2  4  5    915    838     9      2  8  1    781    832    16      3  2 11    235    248     9
 2  1  0   3126   3028    12      2  4  6    196    185     7      2  8  2    218    185    10      3  2 12    381    371     9
 2  1  1   1454   1342    14      2  4  7    398    410    10      2  8  3   1049   1003    11      3  2 13    206    208    17
 2  1  2   1364   1499    14      2  4  8    413    427    19      2  8  4    380    397     9      3  2 14    523    489    16
 2  1  3    769    806     6      2  4  9    749    665    11      2  8  5    617    635    13      3  3  1    610    687     7
 2  1  4   1813   1621    16      2  4 11    210    236    10      2  8  8    377    375    16      3  3  2    582    628     9
 2  1  5    959    921     9      2  4 12    167    155    13      2  8  9    514    459    28      3  3  3    563    601     8
 2  1  6   2214   2145     7      2  4 13    220    201    11      2  8 10    316    323    10      3  3  4    668    603    11
 2  1  7    198    192     6      2  4 15    474    466    13      2  8 11    484    463    12      3  3  6    739    707     9
 2  1  8   1192   1208     9      2  5  0    547    543    13      2  9  0    274    283    11      3  3  7   1351   1312    10
 2  1  9    295    314     7      2  5  1    631    582     9      2  9  2    620    603    14      3  3  8    321    297    13
 2  1 10    581    587    12      2  5  2   1086    979     8      2  9  3    327    270    15      3  3  9    170    199    10
 2  1 11    383    356    18      2  5  3    328    290    11      2  9  4    659    689    14      3  3 11    383    357    10
 2  1 12    635    621    13      2  5  4    592    530    10      2  9  7    315    300     9      3  3 12    163    130    23
 2  1 13    307    314    15      2  5  5    389    396    14      2  9  8    227    219    32      3  3 13    597    575    12
 2  1 14    743    707    14      2  5  6    257    282     8      2  9  9    245    251    12      3  3 14    186    161    14
 2  1 15    362    342    10      2  5  7    315    316     8      2  9 10    389    393    13      3  3 15    373    377    11
 2  2  0   1186   1095     8      2  5  8    856    780    26      2 10  1    317    303     9      3  4  0   1754   1710     7
 2  2  1   1145   1065     8      2  5  9    208    179    16      2 10  2    325    314     9      3  4  1    174    190    14
 2  2  2   1340   1323    26      2  5 10    292    284     8      2 10  3    436    405    16      3  4  2    863    895     8
 2  2  3    590    554     9      2  5 11    131    142    20      2 10  4    254    240    17      3  4  3    316    307    16
 2  2  4   1070    822     7      2  5 12    183    158    12      2 10  5    396    361    20      3  4  4   1045   1054     8
 2  2  5   1184   1039     7      2  5 14    429    439    11      2 10  7    211    225    13      3  4  5    293    254     7
 2  2  6    578    584    12      2  6  0    763    686    10      2 10  8    193    192    15      3  4  6   1040    994     9
 2  2  7    766    808    25      2  6  1    813    812    10      2 11  4    149    156    19      3  4  7    299    282     9
 2  2  8    181    141     7      2  6  2    702    719    10      2 11  6    290    284    11      3  4  8    834    847    11
```

Values of 10*Fobs and 10*Fcalc for PdCl2(f-0-Pphenyl2-02)

H	K	L	Fobs	Fcalc	SigF
3	4	10	723	707	13
3	4	11	223	224	10
3	4	12	627	614	14
3	4	14	490	461	13
3	4	15	190	181	15
3	5	0	531	512	10
3	5	1	1026	951	8
3	5	2	930	782	9
3	5	3	1294	1207	9
3	5	4	371	367	10
3	5	5	809	821	10
3	5	6	264	248	12
3	5	7	965	941	13
3	5	8	277	273	8
3	5	9	389	372	10
3	5	11	625	596	15
3	5	13	491	504	13
3	6	0	703	724	10
3	6	1	217	217	7
3	6	2	935	917	9
3	6	3	141	126	10
3	6	4	895	887	10
3	6	5	231	199	9
3	6	6	714	738	11
3	6	7	173	145	11
3	6	8	413	383	8
3	6	9	153	188	14
3	6	10	610	580	13
3	6	11	182	203	26
3	6	12	457	454	12
3	7	0	488	409	20
3	7	1	150	130	10
3	7	2	547	493	12
3	7	3	367	344	10
3	7	4	293	280	7
3	7	5	582	559	13
3	7	7	462	475	14
3	7	8	137	116	15
3	7	11	419	426	12
3	8	0	364	364	16
3	8	1	447	434	12
3	8	2	278	266	8
3	8	3	375	342	10
3	8	4	504	508	14
3	8	5	348	380	12
3	8	6	234	212	10
3	9	0	160	171	13
3	9	1	190	192	12
3	9	3	260	249	9
3	9	4	141	139	16
3	9	5	207	197	16
3	9	6	322	305	12
3	9	8	168	157	15
3	9	9	319	309	10
3	10	1	122	77	18
3	10	2	421	449	13
3	10	3	242	249	19
3	10	4	406	407	10
3	10	6	331	317	9
3	10	8	339	315	10
3	11	0	186	166	15
3	11	1	532	522	13
3	11	3	615	579	13
3	11	4	144	159	19
3	11	5	540	534	14
3	12	0	222	205	14
3	13	1	272	253	13
4	0	0	1812	1783	4
4	0	1	1696	1517	13
4	0	2	2935	2940	37
4	0	3	215	241	6
4	0	4	426	511	8
4	0	5	1805	1665	7
4	0	6	1190	1153	8
4	0	7	1388	1210	16
4	0	8	690	695	10
4	0	9	637	721	23
4	0	10	802	754	11
4	0	11	603	612	15
4	0	12	669	655	13
4	0	13	944	935	13
4	0	14	503	482	12
4	0	15	430	405	10
4	1	0	1156	1102	10
4	1	1	1693	1728	12
4	1	2	857	927	11
4	1	3	822	873	6
4	1	4	624	622	7
4	1	5	1656	1577	15
4	1	6	1427	1339	8
4	1	7	845	879	19
4	1	8	930	918	9
4	1	9	752	705	10
4	1	10	252	268	10
4	1	11	200	206	10
4	1	12	743	713	13
4	1	13	493	458	13
4	1	14	519	525	23
4	1	15	307	297	10
4	2	0	340	63	8
4	2	1	1289	1123	16
4	2	2	1075	1046	9
4	2	3	1141	1057	10
4	2	4	509	563	9
4	2	5	1417	1250	14
4	2	6	1045	1039	11
4	2	7	735	701	9
4	2	8	1070	1046	9
4	2	9	420	355	24
4	2	10	291	306	8
4	2	11	565	570	14
4	2	12	602	562	13
4	2	13	569	536	22
4	2	14	334	321	9
4	2	15	209	227	13
4	3	0	327	221	10
4	3	1	681	692	7
4	3	2	458	428	14
4	3	3	420	387	9
4	3	4	628	532	8
4	3	5	1017	869	9
4	3	6	338	309	8
4	3	7	368	353	12
4	3	8	323	259	24
4	3	9	357	347	20
4	3	10	181	139	15
4	3	11	283	242	8
4	3	12	348	369	13
4	3	14	234	214	16
4	3	15	185	190	15
4	4	0	790	766	8
4	4	1	1206	993	7
4	4	2	743	658	16
4	4	3	1015	895	10
4	4	4	443	420	10
4	4	5	368	341	9
4	4	6	525	547	11
4	4	7	769	697	10
4	4	8	844	803	11
4	4	9	569	504	16
4	4	10	360	366	8
4	4	12	283	314	9
4	4	13	120	139	18
4	5	0	179	145	7
4	5	1	322	304	8
4	5	2	847	784	10
4	5	3	771	744	9
4	5	4	307	280	7
4	5	5	205	200	7
4	5	6	125	168	11
4	5	7	673	666	11
4	5	8	725	767	12
4	5	9	348	361	8
4	5	10	334	327	8
4	5	11	317	301	8
4	5	12	229	233	12
4	5	13	147	141	17
4	5	14	233	230	12
4	6	0	1169	1218	11
4	6	1	865	775	10
4	6	2	1113	1019	18
4	6	3	1286	1233	18
4	6	4	609	624	11
4	6	5	805	754	11
4	6	6	273	259	9
4	6	7	736	758	30
4	6	8	471	468	11
4	6	9	551	530	11
4	6	10	336	320	9
4	6	11	484	494	14
4	6	12	273	258	11
4	6	13	225	211	19
4	7	0	614	621	11
4	7	1	467	475	13
4	7	2	990	960	13
4	7	3	929	934	11
4	7	4	978	905	11
4	7	5	454	487	15
4	7	6	387	384	9
4	7	7	640	613	13
4	7	8	333	353	16
4	7	9	409	377	9
4	7	10	583	562	13
4	7	11	425	417	11
4	7	12	221	207	13
4	8	0	202	198	10
4	8	2	565	579	13
4	8	3	760	772	12
4	8	4	521	477	12
4	8	5	280	277	9
4	8	6	375	354	9
4	8	7	360	346	9
4	8	8	338	352	11
4	8	9	553	520	12
4	8	10	604	599	13
4	8	11	477	461	17
4	9	2	527	512	12
4	9	3	324	320	8
4	9	4	549	553	12
4	9	5	222	207	11

Values of 10*Fobs and 10*Fcalc for PdCl2(f-0-Pphenyl2-02)

H	K	L	Fobs	Fcalc	SigF
4	9	6	264	257	10
4	9	8	252	247	11
4	9	9	411	392	11
4	9	10	418	420	10
4	10	1	508	482	13
4	10	3	561	578	13
4	10	4	161	187	15
4	10	5	397	416	12
4	10	6	150	146	17
4	11	2	308	318	10
4	11	4	263	266	12
4	11	5	272	276	12
4	12	0	226	237	14
4	13	0	224	231	15
4	13	1	146	133	21
5	1	1	335	352	7
5	1	2	1388	1265	9
5	1	3	475	490	11
5	1	4	184	174	5
5	1	5	930	939	7
5	1	6	982	969	9
5	1	7	730	720	11
5	1	8	874	848	10
5	1	9	680	650	11
5	1	10	210	196	9
5	1	12	402	402	15
5	1	13	215	196	11
5	1	14	245	247	14
5	2	0	3119	2851	18
5	2	1	1964	1874	17
5	2	2	1143	1008	6
5	2	3	866	763	7
5	2	4	185	215	6
5	2	5	347	343	19
5	2	6	640	593	18
5	2	7	1115	1122	18
5	2	8	458	439	13
5	2	9	341	345	8
5	2	10	402	387	8
5	2	11	432	415	11
5	2	12	168	151	13
5	2	13	591	593	13
5	2	14	191	175	14
5	2	15	316	325	11
5	3	0	786	747	9
5	3	1	1261	1260	7
5	3	2	1597	1608	10
5	3	3	664	572	8
5	3	4	855	891	8
5	3	5	941	860	10
5	3	6	1305	1259	20
5	3	7	107	122	12
5	3	8	889	823	10
5	3	9	453	462	10
5	3	10	375	337	10
5	3	11	428	419	12
5	3	12	369	372	10
5	3	13	521	481	15
5	3	14	506	461	28
5	3	15	393	409	11
5	4	0	1245	1093	11
5	4	1	1439	1351	7
5	4	2	715	746	11
5	4	3	852	769	8
5	4	4	786	769	9
5	4	5	626	640	10
5	4	6	710	722	10
5	4	7	858	827	10
5	4	8	393	360	11
5	4	9	497	503	11
5	4	10	229	239	9
5	4	11	485	494	12
5	4	12	218	216	12
5	4	13	493	476	20
5	4	14	255	265	11
5	5	0	797	752	11
5	5	1	516	477	10
5	5	2	839	874	9
5	5	3	730	660	9
5	5	4	736	750	10
5	5	5	748	754	12
5	5	6	1084	1035	10
5	5	7	363	337	18
5	5	8	797	785	20
5	5	9	784	732	12
5	5	10	591	555	14
5	5	11	334	344	14
5	5	12	599	556	13
5	5	13	137	149	18
5	5	14	245	251	12
5	6	0	134	146	12
5	6	1	874	861	12
5	6	2	529	474	11
5	6	3	740	751	10
5	6	4	268	259	7
5	6	5	619	608	12
5	6	6	468	454	12
5	6	7	314	325	9
5	6	8	516	476	21
5	6	9	322	322	9
5	6	10	141	158	16
5	6	11	480	466	13
5	6	12	214	189	13
5	6	13	202	192	13
5	7	0	547	531	14
5	7	1	382	375	9
5	7	2	605	595	12
5	7	3	430	404	11
5	7	4	724	698	12
5	7	5	339	358	12
5	7	6	193	189	11
5	7	7	543	512	12
5	7	8	335	327	8
5	7	10	222	216	11
5	7	11	161	130	16
5	7	12	264	271	11
5	8	3	263	236	9
5	8	4	587	593	14
5	8	5	201	182	11
5	8	6	329	342	9
5	8	8	186	188	12
5	8	9	191	180	16
5	8	10	159	153	17
5	8	11	195	178	30
5	9	2	471	444	11
5	9	3	351	329	10
5	9	4	374	358	9
5	9	7	188	168	12
5	9	8	215	182	13
5	9	10	182	166	16
5	10	1	382	363	16
5	10	3	513	476	17
5	10	4	244	234	11
5	10	5	284	285	10
5	10	6	148	113	17
5	11	1	245	252	12
5	11	2	434	417	13
5	11	3	314	295	10
5	11	4	477	456	14
5	11	5	207	199	15
5	12	0	265	243	17
5	12	1	350	333	20
5	13	0	289	266	15
6	0	0	2979	2903	16
6	0	1	870	895	5
6	0	2	4172	3937	55
6	0	3	908	927	6
6	0	4	753	744	7
6	0	5	254	211	6
6	0	6	1644	1635	8
6	0	7	679	639	9
6	0	8	1028	933	9
6	0	9	781	754	11
6	0	10	494	496	11
6	0	12	751	747	13
6	0	14	810	747	14
6	0	15	136	153	18
6	0	17	226	221	14
6	1	1	1091	1123	7
6	1	2	1014	912	6
6	1	3	649	612	7
6	1	4	367	342	9
6	1	5	1343	1198	15
6	1	6	388	341	8
6	1	7	1944	1867	8
6	1	8	418	422	10
6	1	9	347	324	10
6	1	10	375	340	10
6	1	11	524	537	13
6	1	12	178	169	12
6	1	13	879	823	13
6	1	14	213	180	12
6	1	15	268	240	11
6	2	0	3968	3833	19
6	2	1	1023	994	6
6	2	2	1308	1210	6
6	2	3	1557	1400	6
6	2	4	1179	1164	7
6	2	5	643	567	14
6	2	6	797	781	16
6	2	7	472	477	11
6	2	8	655	636	21
6	2	9	214	198	8
6	2	10	308	324	7
6	2	11	150	109	17
6	2	12	598	576	14
6	2	13	136	133	17
6	2	14	541	511	14
6	2	15	213	165	13
6	3	0	501	532	8
6	3	1	611	496	7
6	3	2	644	578	8
6	3	3	442	506	10
6	3	4	303	312	8
6	3	5	930	762	9
6	3	6	525	504	10
6	3	7	841	758	10
6	3	8	270	256	6
6	3	9	467	480	11
6	3	11	560	542	16

Values of 10*Fobs and 10*Fcalc for PdCl2(f-0-Pphenyl2-02)

H	K	L	Fobs	Fcalc	SigF	H	K	L	Fobs	Fcalc	SigF	H	K	L	Fobs	Fcalc	SigF	H	K	L	Fobs	Fcalc	SigF
6	3	13	487	475	11	6	8	0	230	199	9	7	2	8	499	516	13	7	5	13	323	292	16
6	3	15	146	169	18	6	8	1	565	565	13	7	2	9	760	759	13	7	5	14	362	333	36
6	4	0	509	473	9	6	8	2	683	667	13	7	2	10	175	161	10	7	6	0	363	328	9
6	4	1	725	653	8	6	8	3	690	670	18	7	2	11	346	341	10	7	6	1	460	441	9
6	4	2	855	707	8	6	8	4	818	785	12	7	2	12	199	214	17	7	6	2	676	697	10
6	4	3	686	646	9	6	8	5	185	193	19	7	2	13	342	328	15	7	6	3	536	538	12
6	4	4	843	697	9	6	8	6	282	258	10	7	2	14	345	351	9	7	6	4	458	461	10
6	4	5	112	83	14	6	8	7	165	159	13	7	2	15	341	312	9	7	6	5	591	557	12
6	4	6	391	362	10	6	8	8	433	440	11	7	3	0	1691	1676	12	7	6	6	648	645	23
6	4	7	410	410	9	6	8	10	686	681	14	7	3	1	2043	1818	18	7	6	8	390	401	10
6	4	8	459	367	10	6	8	11	209	182	14	7	3	2	1231	1166	12	7	6	9	515	492	12
6	4	9	202	208	9	6	9	1	278	243	9	7	3	3	1299	1193	7	7	6	10	348	364	9
6	4	10	251	255	11	6	9	2	179	196	13	7	3	4	1157	1116	10	7	6	11	238	234	10
6	4	11	301	299	8	6	9	3	868	879	13	7	3	5	1585	1512	8	7	6	12	425	393	11
6	4	12	215	207	11	6	9	4	192	177	12	7	3	6	1043	1019	17	7	6	13	203	201	14
6	5	0	1202	1177	8	6	9	5	587	539	12	7	3	7	1156	1055	13	7	7	1	523	532	12
6	5	1	672	652	9	6	9	7	343	329	10	7	3	8	1079	1103	10	7	7	3	523	521	10
6	5	2	731	673	9	6	9	8	207	214	13	7	3	9	952	935	11	7	7	4	153	139	16
6	5	3	906	887	9	6	9	9	515	510	13	7	3	10	582	575	13	7	7	5	815	811	15
6	5	4	683	648	10	6	10	0	223	211	20	7	3	11	477	462	12	7	7	6	392	362	9
6	5	5	1005	972	10	6	10	1	206	198	12	7	3	12	418	397	13	7	7	7	413	393	13
6	5	6	346	339	10	6	10	2	426	423	11	7	3	13	518	479	12	7	7	8	234	205	10
6	5	7	144	133	14	6	10	3	385	364	10	7	3	14	480	461	17	7	7	9	506	504	19
6	5	8	233	205	9	6	10	4	433	437	12	7	3	15	250	242	12	7	7	11	233	237	12
6	5	9	659	632	13	6	10	6	139	131	18	7	4	0	1415	1310	11	7	8	1	286	284	12
6	5	10	230	237	10	6	10	8	314	288	17	7	4	1	1290	1202	8	7	8	2	433	421	12
6	5	11	424	442	10	6	11	3	178	166	24	7	4	2	1040	998	8	7	8	3	581	550	13
6	5	12	175	128	17	7	1	0	1692	1569	29	7	4	3	1203	1148	11	7	8	5	135	109	15
6	5	14	173	199	16	7	1	1	872	769	6	7	4	4	963	901	9	7	8	7	152	143	16
6	6	1	423	367	10	7	1	2	1866	1812	6	7	4	5	1221	1250	9	7	8	8	168	194	14
6	6	2	1296	1219	9	7	1	3	514	472	7	7	4	6	689	632	10	7	9	0	238	216	10
6	6	3	240	207	11	7	1	4	644	642	10	7	4	7	862	839	10	7	9	1	225	211	14
6	6	4	1011	992	10	7	1	5	258	200	6	7	4	8	744	733	11	7	9	3	373	342	14
6	6	5	344	336	9	7	1	6	726	719	9	7	4	9	706	691	19	7	9	4	448	438	12
6	6	6	458	433	11	7	1	7	112	130	11	7	4	10	379	387	17	7	9	6	246	213	15
6	6	7	751	737	12	7	1	8	284	274	6	7	4	11	434	426	15	7	9	8	323	319	25
6	6	8	601	586	13	7	1	9	463	434	23	7	4	12	346	332	17	7	9	9	219	240	13
6	6	9	250	227	9	7	1	10	239	245	9	7	4	13	430	435	10	7	9	10	277	275	12
6	6	10	361	344	8	7	1	11	216	194	9	7	4	14	224	202	12	7	10	0	342	332	11
6	6	11	333	325	9	7	1	12	188	193	11	7	5	0	1031	1029	9	7	10	2	419	371	20
6	6	12	298	300	10	7	1	13	272	288	13	7	5	1	444	505	24	7	10	3	389	364	10
6	7	1	554	532	12	7	1	14	295	278	10	7	5	2	1497	1397	15	7	10	4	499	496	16
6	7	3	938	873	14	7	1	15	320	314	12	7	5	4	1200	1190	9	7	10	5	401	363	10
6	7	4	461	477	12	7	2	0	1880	1860	9	7	5	5	686	692	22	7	10	6	267	279	11
6	7	5	689	679	12	7	2	1	1151	1199	6	7	5	6	554	547	12	7	10	7	188	200	15
6	7	6	473	476	12	7	2	2	368	265	10	7	5	8	504	454	21	7	10	8	196	181	15
6	7	7	385	367	9	7	2	3	1109	1046	7	7	5	9	302	283	8	7	11	0	304	280	10
6	7	9	715	690	14	7	2	4	345	368	8	7	5	10	519	493	12	7	11	2	453	444	12
6	7	10	279	257	9	7	2	5	984	950	9	7	5	11	206	198	11	7	11	3	414	393	10
6	7	11	587	565	17	7	2	7	1138	1122	18	7	5	12	421	403	10	7	11	4	451	440	11

Values of 10*Fobs and 10*Fcalc for PdCl2(f-0-Pphenyl2-02)

H	K	L	Fobs	Fcalc	SigF	H	K	L	Fobs	Fcalc	SigF	H	K	L	Fobs	Fcalc	SigF	H	K	L	Fobs	Fcalc	SigF
7	12	0	242	227	13	8	3	3	826	748	8	8	6	12	417	415	10	9	1	14	173	197	15
7	12	1	251	231	13	8	3	4	569	600	9	8	7	0	370	385	9	9	1	15	164	165	16
8	0	0	869	770	6	8	3	5	270	254	8	8	7	1	139	119	13	9	2	0	1149	1223	7
8	0	1	1268	1195	6	8	3	6	870	849	19	8	7	2	787	821	11	9	2	1	827	795	7
8	0	2	1146	995	6	8	3	8	527	514	11	8	7	3	311	313	10	9	2	2	1363	1283	7
8	0	3	752	727	7	8	3	9	271	272	7	8	7	4	738	735	12	9	2	3	119	109	9
8	0	4	164	150	6	8	3	10	326	334	12	8	7	6	327	334	8	9	2	4	1018	981	13
8	0	5	1456	1319	7	8	3	11	152	158	16	8	7	7	248	232	21	9	2	5	284	267	6
8	0	6	982	962	8	8	3	12	305	286	8	8	7	8	478	469	11	9	2	6	1013	983	15
8	0	7	1261	1326	15	8	3	13	260	230	10	8	7	9	219	217	15	9	2	7	516	506	17
8	0	8	965	892	10	8	3	14	185	193	14	8	7	10	500	485	13	9	2	8	1017	1033	11
8	0	9	496	474	13	8	3	15	163	160	22	8	7	11	281	277	16	9	2	9	229	223	15
8	0	10	400	354	17	8	4	0	529	564	17	8	7	12	322	311	28	9	2	10	580	592	12
8	0	11	628	604	13	8	4	1	784	643	12	8	8	1	483	483	11	9	2	11	220	203	10
8	0	12	261	253	9	8	4	2	959	899	8	8	8	2	192	177	15	9	2	12	453	424	16
8	0	13	931	866	13	8	4	3	909	815	9	8	8	3	969	962	12	9	2	13	232	230	11
8	0	14	415	412	11	8	4	4	371	330	15	8	8	5	668	641	28	9	2	14	528	517	13
8	0	15	409	364	9	8	4	5	455	368	23	8	8	7	560	542	21	9	3	0	1059	970	7
8	0	17	273	248	12	8	4	6	900	843	10	8	8	9	678	676	15	9	3	1	2104	2014	7
8	1	0	3865	3605	38	8	4	7	247	223	8	8	8	11	584	548	14	9	3	2	287	283	7
8	1	1	1064	983	7	8	4	8	716	708	20	8	9	0	297	293	9	9	3	3	1193	1200	8
8	1	2	932	998	6	8	4	9	542	538	13	8	9	1	197	166	22	9	3	4	551	549	15
8	1	3	256	235	6	8	4	11	563	599	12	8	9	2	630	655	14	9	3	5	1326	1378	9
8	1	4	1015	998	17	8	4	12	285	280	9	8	9	3	344	324	9	9	3	6	495	402	11
8	1	5	141	119	7	8	4	14	275	259	11	8	9	4	743	725	15	9	3	7	907	910	13
8	1	6	1196	1214	8	8	5	0	578	436	16	8	9	6	262	241	10	9	3	8	274	280	8
8	1	7	407	381	9	8	5	1	478	362	14	8	9	7	183	179	23	9	3	9	644	604	12
8	1	8	1016	961	16	8	5	2	743	698	10	8	9	8	245	262	21	9	3	11	707	681	13
8	1	10	385	379	15	8	5	3	296	270	7	8	9	9	173	188	16	9	3	12	266	250	9
8	1	11	280	273	8	8	5	4	469	398	10	8	10	1	181	152	13	9	3	13	672	642	19
8	1	12	751	757	18	8	5	5	503	495	11	8	10	2	304	298	10	9	4	0	1437	1349	8
8	1	13	202	219	19	8	5	6	319	315	8	8	10	3	567	540	13	9	4	1	737	691	9
8	1	14	701	641	15	8	5	8	430	395	15	8	10	4	393	378	10	9	4	2	1386	1412	8
8	1	15	282	270	15	8	5	9	244	232	9	8	10	6	205	188	19	9	4	3	487	380	10
8	2	0	318	302	7	8	5	10	241	224	10	8	10	8	251	240	13	9	4	4	1114	1113	9
8	2	1	1574	1471	6	8	5	11	178	184	13	8	11	2	179	192	16	9	4	5	355	371	10
8	2	3	490	477	8	8	5	12	298	286	14	8	11	3	244	228	13	9	4	6	1190	1151	10
8	2	4	409	320	15	8	5	13	169	153	15	8	11	5	260	238	12	9	4	8	714	744	12
8	2	5	1323	1220	20	8	6	0	94	116	14	9	1	0	415	373	8	9	4	9	343	340	9
8	2	7	1300	1220	9	8	6	1	447	466	10	9	1	1	921	923	14	9	4	10	720	689	13
8	2	8	112	120	12	8	6	2	322	263	9	9	1	3	198	198	5	9	4	11	161	114	15
8	2	9	524	556	12	8	6	3	655	653	11	9	1	4	442	385	15	9	4	12	628	638	14
8	2	10	603	585	13	8	6	4	253	233	8	9	1	5	449	470	9	9	4	14	665	589	15
8	2	11	429	387	10	8	6	5	511	518	10	9	1	6	263	253	6	9	5	0	254	218	11
8	2	12	547	554	29	8	6	6	286	284	8	9	1	7	1035	1010	16	9	5	1	165	192	8
8	2	13	752	738	14	8	6	7	122	127	15	9	1	8	283	241	7	9	5	2	225	204	7
8	2	15	162	167	17	8	6	8	371	365	10	9	1	9	542	583	22	9	5	3	1065	1066	9
8	3	0	1150	898	7	8	6	9	524	501	12	9	1	10	141	143	13	9	5	4	386	398	10
8	3	1	933	861	7	8	6	10	433	435	10	9	1	11	188	153	11	9	5	5	839	794	14
8	3	2	649	650	8	8	6	11	351	368	9	9	1	13	314	278	20	9	5	6	387	350	9

H	K	L	Fobs	Fcalc	SigF
9	5	7	1131	1109	11
9	5	8	181	163	11
9	5	9	636	603	13
9	5	10	228	218	10
9	5	11	799	768	14
9	5	12	171	161	15
9	5	13	428	418	20
9	6	0	440	382	10
9	6	1	250	244	12
9	6	2	305	329	7
9	6	3	106	139	14
9	6	4	1016	1036	10
9	6	5	515	535	12
9	6	6	359	367	9
9	6	7	199	185	10
9	6	8	318	351	17
9	6	9	238	228	11
9	6	10	624	613	15
9	6	12	331	316	9
9	7	0	340	297	15
9	7	1	342	322	8
9	7	2	707	633	31
9	7	3	661	618	12
9	7	4	300	294	15
9	7	7	277	293	9
9	7	8	325	322	8
9	7	9	230	202	10
9	7	11	211	190	13
9	8	1	289	279	8
9	8	2	270	256	9
9	8	3	325	303	12
9	8	4	188	193	12
9	8	5	364	396	10
9	8	6	252	244	10
9	8	7	189	186	12
9	8	8	157	123	15
9	8	9	135	138	19
9	9	0	308	284	9
9	9	1	599	580	12
9	9	2	245	252	11
9	9	3	541	491	11
9	9	4	283	260	9
9	9	5	523	527	13
9	9	6	283	275	10
9	9	9	268	261	11
9	10	2	689	662	15
9	10	3	197	197	13
9	10	4	511	473	12
9	10	6	293	266	10
9	11	1	274	251	11
9	11	3	400	379	10
10	0	0	654	582	7
10	0	1	2195	1973	16
10	0	2	880	876	7
10	0	3	283	321	8
10	0	4	767	643	8
10	0	6	1316	1349	8
10	0	7	743	705	10
10	0	8	967	1018	16
10	0	9	207	184	8
10	0	11	247	225	15
10	0	12	712	689	20
10	0	13	443	448	10
10	0	14	423	421	9
10	0	15	476	435	13
10	0	17	173	153	18
10	1	1	1477	1436	7
10	1	2	960	884	7
10	1	3	650	683	15
10	1	5	939	961	8
10	1	6	922	862	9
10	1	7	906	844	10
10	1	8	679	628	20
10	1	9	502	511	11
10	1	10	202	181	9
10	1	11	398	376	10
10	1	12	462	431	18
10	1	13	578	529	16
10	1	14	378	364	24
10	1	15	284	273	11
10	2	0	1733	1425	7
10	2	1	904	849	7
10	2	2	1094	970	7
10	2	3	260	286	6
10	2	4	932	914	8
10	2	5	635	567	16
10	2	6	659	637	10
10	2	7	879	849	10
10	2	8	853	807	15
10	2	9	533	534	12
10	2	10	280	297	23
10	2	11	423	378	10
10	2	12	657	643	16
10	2	13	347	362	8
10	2	14	262	254	11
10	2	15	355	336	10
10	3	0	583	526	9
10	3	1	590	526	11
10	3	2	974	1018	8
10	3	4	185	178	7
10	3	5	1186	1162	9
10	3	6	664	624	10
10	3	7	359	350	17
10	3	8	517	495	12
10	3	9	332	351	10
10	3	11	242	244	17
10	3	12	374	354	9
10	3	13	188	164	14
10	3	14	204	205	22
10	4	0	941	912	8
10	4	1	1405	1287	8
10	4	2	470	415	20
10	4	3	201	190	8
10	4	4	545	488	12
10	4	5	256	252	6
10	4	6	703	680	11
10	4	7	362	319	14
10	4	8	126	97	17
10	4	9	309	307	9
10	4	10	324	300	8
10	4	11	417	408	10
10	4	12	367	359	9
10	4	13	237	210	12
10	5	0	106	85	12
10	5	1	583	562	10
10	5	3	324	266	14
10	5	4	237	231	7
10	5	5	342	306	8
10	5	6	355	337	8
10	5	7	447	448	10
10	5	8	231	203	11
10	5	10	431	438	10
10	5	12	427	424	11
10	6	1	208	189	8
10	6	2	325	305	8
10	6	3	374	391	21
10	6	4	104	104	16
10	6	5	382	351	10
10	6	6	260	264	8
10	6	8	428	412	17
10	6	9	185	183	12
10	6	10	330	307	8
10	7	0	192	248	10
10	7	1	337	298	9
10	7	2	422	357	11
10	7	3	515	512	11
10	7	4	426	408	11
10	7	5	309	285	8
10	7	7	435	401	10
10	7	8	353	360	9
10	7	9	446	434	12
10	7	10	341	357	9
10	7	11	370	359	16
10	8	0	522	546	13
10	8	2	750	711	13
10	8	3	685	628	13
10	8	4	666	653	27
10	8	5	403	394	10
10	8	6	327	346	8
10	8	7	416	423	10
10	8	8	301	307	9
10	8	9	556	568	14
10	8	10	430	442	11
10	8	11	414	414	11
10	9	0	228	185	11
10	9	1	358	370	10
10	9	2	720	709	14
10	9	3	709	690	14
10	9	4	603	605	17
10	9	5	181	190	14
10	9	6	357	317	9
10	9	7	267	274	17
10	9	8	361	328	9
10	9	9	233	257	13
10	10	0	197	191	13
10	10	1	407	376	21
10	10	2	256	260	11
10	10	3	510	531	14
10	10	4	255	222	12
10	10	5	237	263	17
10	10	6	165	135	16
10	11	2	254	247	14
10	11	4	169	177	17
11	1	1	154	135	6
11	1	2	183	203	8
11	1	3	443	427	11
11	1	4	523	407	13
11	1	5	386	422	9
11	1	6	485	464	9
11	1	7	363	320	10
11	1	8	501	503	14
11	1	9	178	152	10
11	1	10	765	739	22
11	1	11	170	165	12
11	1	12	348	353	8
11	1	14	555	510	13
11	2	0	561	631	32
11	2	1	1431	1424	7
11	2	2	791	682	15
11	2	3	1002	1014	8

Values of 10*Fobs and 10*Fcalc for PdCl2(f-0-Pphenyl2-02)

H	K	L	Fobs	Fcalc	SigF	H	K	L	Fobs	Fcalc	SigF	H	K	L	Fobs	Fcalc	SigF	H	K	L	Fobs	Fcalc	SigF
11	2	4	494	422	9	11	6	2	246	243	8	12	0	13	285	267	9	12	4	9	198	225	11
11	2	5	766	729	9	11	6	3	577	569	12	12	0	14	618	601	13	12	4	10	245	255	9
11	2	6	366	365	8	11	6	5	490	480	11	12	0	15	276	246	11	12	4	12	331	336	8
11	2	7	1181	1197	13	11	6	6	166	156	14	12	1	0	680	800	101	12	5	0	412	448	10
11	2	8	217	212	8	11	6	7	173	198	12	12	1	1	1202	1109	16	12	5	1	617	530	17
11	2	9	901	897	23	11	6	8	262	263	12	12	1	2	621	619	8	12	5	2	279	269	7
11	2	10	186	186	10	11	6	9	335	323	9	12	1	3	180	213	6	12	5	3	497	412	17
11	2	11	437	384	10	11	6	11	524	499	13	12	1	4	172	184	7	12	5	4	176	159	9
11	2	12	176	165	13	11	7	2	338	297	8	12	1	5	632	592	12	12	5	5	641	597	33
11	2	13	650	618	13	11	7	3	279	245	9	12	1	6	419	378	27	12	5	6	543	518	12
11	2	15	385	373	10	11	7	4	568	545	13	12	1	7	1298	1193	23	12	5	8	251	258	9
11	3	0	2170	2035	7	11	7	6	427	412	10	12	1	8	490	519	10	12	5	9	355	327	19
11	3	1	245	219	7	11	7	8	453	436	12	12	1	9	482	466	10	12	5	10	258	261	11
11	3	2	1609	1492	8	11	7	10	478	427	13	12	1	11	204	215	10	12	5	11	471	465	12
11	3	3	231	203	6	11	8	0	183	133	22	12	1	12	319	282	8	12	5	12	231	208	12
11	3	4	1555	1537	18	11	8	1	172	165	13	12	1	13	769	767	23	12	6	1	273	280	8
11	3	5	269	266	10	11	8	4	358	362	28	12	1	15	289	262	11	12	6	2	599	577	12
11	3	6	1704	1634	9	11	8	5	358	321	12	12	2	0	2750	2548	7	12	6	4	508	458	11
11	3	7	97	75	14	11	8	7	141	163	16	12	2	1	681	664	8	12	6	5	406	400	10
11	3	8	1462	1448	10	11	8	9	301	306	10	12	2	2	648	500	8	12	6	6	253	247	9
11	3	9	324	284	22	11	9	0	160	185	15	12	2	3	784	729	8	12	6	7	283	265	13
11	3	10	814	812	23	11	9	1	339	312	8	12	2	4	522	484	9	12	6	8	405	374	10
11	3	11	250	248	9	11	9	2	588	550	13	12	2	5	574	517	10	12	6	9	191	191	12
11	3	12	818	784	24	11	9	3	286	258	12	12	2	6	897	861	12	12	6	10	469	468	11
11	3	13	277	244	10	11	9	4	553	561	13	12	2	7	233	236	7	12	6	12	167	140	17
11	3	14	515	499	14	11	9	6	460	418	16	12	2	8	478	433	18	12	7	1	423	435	16
11	4	1	1263	1268	9	11	9	7	180	135	23	12	2	9	478	455	20	12	7	2	390	388	9
11	4	2	464	352	11	11	9	8	337	325	9	12	2	10	214	183	15	12	7	3	684	658	13
11	4	3	1160	1151	9	11	10	1	324	317	9	12	2	11	524	503	12	12	7	4	196	192	11
11	4	4	145	155	9	11	10	3	564	510	19	12	2	12	364	360	11	12	7	5	610	608	14
11	4	5	1228	1232	10	11	10	4	251	241	25	12	2	14	406	394	10	12	7	6	169	177	13
11	4	6	448	434	10	11	10	5	519	497	23	12	3	0	204	216	6	12	7	7	226	212	10
11	4	7	1211	1157	10	11	10	7	253	225	15	12	3	1	453	434	63	12	7	8	163	150	16
11	4	8	305	296	8	11	11	0	146	129	19	12	3	2	434	357	9	12	7	9	558	572	13
11	4	9	587	538	13	11	11	2	430	413	10	12	3	3	767	757	9	12	7	10	167	186	16
11	4	10	155	137	13	11	11	3	270	265	12	12	3	4	122	116	17	12	7	11	459	454	11
11	4	11	767	749	13	11	12	1	225	200	14	12	3	5	626	634	10	12	8	0	684	670	13
11	4	12	231	218	11	12	0	0	700	733	7	12	3	6	145	157	10	12	8	1	331	322	8
11	4	13	509	471	13	12	0	1	1009	943	7	12	3	7	636	614	12	12	8	2	989	948	12
11	5	0	716	741	10	12	0	2	694	633	7	12	3	8	285	257	15	12	8	3	400	432	18
11	5	1	744	712	10	12	0	3	325	273	8	12	3	9	346	319	9	12	8	4	1102	1100	15
11	5	2	401	434	10	12	0	4	678	602	8	12	3	11	396	380	16	12	8	5	176	151	13
11	5	4	726	674	11	12	0	5	293	311	8	12	3	13	182	198	15	12	8	6	359	369	10
11	5	5	426	412	10	12	0	6	984	933	9	12	4	0	310	297	8	12	8	7	350	370	10
11	5	6	664	679	12	12	0	7	396	368	10	12	4	2	732	679	9	12	8	8	417	394	35
11	5	7	254	244	14	12	0	8	940	934	17	12	4	3	286	267	12	12	8	9	233	242	15
11	5	9	285	303	9	12	0	9	420	383	32	12	4	4	1004	961	10	12	8	10	503	483	12
11	5	10	703	669	14	12	0	10	479	438	11	12	4	5	276	288	7	12	9	1	605	579	13
11	5	12	651	621	15	12	0	11	387	416	11	12	4	6	631	591	17	12	9	2	341	340	10
11	6	1	347	321	9	12	0	12	388	382	10	12	4	7	297	274	7	12	9	3	918	925	19

Values of 10*Fobs and 10*Fcalc for PdCl2(f-0-Pphenyl2-02)

H	K	L	Fobs	Fcalc	SigF	H	K	L	Fobs	Fcalc	SigF	H	K	L	Fobs	Fcalc	SigF	H	K	L	Fobs	Fcalc	SigF
12	9	4	277	285	10	13	3	9	456	486	12	13	7	5	380	364	9	14	1	11	402	408	9
12	9	5	548	559	13	13	3	10	185	207	11	13	7	7	342	319	10	14	1	12	473	481	15
12	9	6	351	320	9	13	3	11	420	394	11	13	7	8	172	186	13	14	1	14	624	577	13
12	9	7	201	185	13	13	3	12	487	491	18	13	7	9	210	197	12	14	2	1	1365	1264	10
12	9	8	153	132	21	13	3	13	465	425	13	13	8	0	341	314	8	14	2	2	458	421	12
12	9	9	427	443	12	13	3	14	267	260	12	13	8	1	256	214	10	14	2	3	931	912	16
12	10	0	137	120	19	13	4	0	835	824	9	13	8	2	180	150	12	14	2	4	318	339	12
12	10	1	169	179	16	13	4	1	980	974	9	13	8	4	443	420	11	14	2	5	1075	998	10
12	10	2	386	397	18	13	4	2	1111	1111	21	13	8	6	281	244	9	14	2	6	869	805	10
12	10	3	228	202	13	13	4	3	647	647	10	13	8	7	169	181	14	14	2	7	1261	1162	10
12	10	4	461	440	11	13	4	4	809	787	25	13	8	8	236	235	14	14	2	8	462	441	11
12	10	6	229	185	19	13	4	5	846	800	10	13	9	0	305	270	9	14	2	9	762	739	12
12	11	3	289	281	11	13	4	6	802	792	16	13	9	1	396	392	10	14	2	11	372	365	8
12	12	0	337	295	11	13	4	7	604	630	12	13	9	2	239	208	11	14	2	12	358	361	9
13	1	1	395	314	8	13	4	8	548	486	11	13	9	3	618	581	13	14	2	13	618	596	14
13	1	2	432	453	9	13	4	9	459	420	11	13	9	4	282	288	10	14	2	14	322	285	10
13	1	3	676	646	18	13	4	10	505	490	14	13	9	5	291	289	14	14	3	0	1130	1058	8
13	1	4	243	256	6	13	4	11	334	330	12	13	9	6	227	213	12	14	3	2	349	325	9
13	1	5	413	430	9	13	4	12	524	508	13	13	9	7	197	181	16	14	3	3	478	445	11
13	1	6	237	229	6	13	4	13	287	266	10	13	9	8	215	225	28	14	3	4	662	732	10
13	1	7	637	597	11	13	5	0	491	486	11	13	10	0	293	290	10	14	3	5	399	373	10
13	1	8	182	182	9	13	5	1	365	392	11	13	10	1	207	242	18	14	3	6	580	560	13
13	1	9	520	513	19	13	5	2	436	446	10	13	10	2	392	362	9	14	3	7	214	189	10
13	1	10	136	155	14	13	5	3	478	489	13	13	10	3	467	424	13	14	3	8	383	359	9
13	1	11	127	142	17	13	5	4	202	201	9	13	10	4	541	504	14	14	3	9	160	129	12
13	1	13	227	222	11	13	5	5	1096	1080	11	13	10	6	170	191	17	14	3	10	309	292	8
13	1	14	178	192	15	13	5	6	418	375	15	13	11	0	216	193	14	14	3	12	223	217	11
13	2	0	1493	1412	9	13	5	7	400	401	9	13	11	2	185	165	20	14	4	1	404	458	11
13	2	1	675	675	8	13	5	8	317	322	13	14	0	1	912	917	15	14	4	3	443	412	9
13	2	2	714	744	15	13	5	9	753	720	31	14	0	2	301	256	8	14	4	4	464	433	11
13	2	3	371	380	9	13	5	10	224	184	10	14	0	3	423	357	10	14	4	5	483	458	12
13	2	4	434	434	10	13	5	11	502	478	14	14	0	4	1032	920	9	14	4	6	186	170	13
13	2	5	732	761	10	13	5	12	257	259	14	14	0	5	475	487	11	14	4	7	340	317	8
13	2	6	1018	981	10	13	5	13	260	245	17	14	0	7	1028	1070	10	14	4	8	184	180	11
13	2	7	543	506	12	13	6	0	393	423	10	14	0	8	407	393	23	14	4	9	355	321	10
13	2	8	886	848	11	13	6	1	355	376	8	14	0	10	627	618	13	14	4	10	371	369	9
13	2	9	384	374	9	13	6	2	374	365	15	14	0	11	415	412	10	14	4	11	662	653	13
13	2	10	377	378	13	13	6	3	257	257	8	14	0	12	619	586	16	14	4	12	294	299	10
13	2	12	411	387	10	13	6	4	382	385	10	14	0	13	798	762	14	14	4	13	262	240	14
13	2	13	324	318	12	13	6	5	450	419	15	14	1	0	2379	2277	169	14	5	1	598	507	11
13	2	14	393	365	11	13	6	6	421	412	12	14	1	1	262	229	7	14	5	2	460	426	10
13	3	0	1064	1081	11	13	6	7	307	285	11	14	1	2	696	737	10	14	5	3	510	472	12
13	3	1	2140	2058	13	13	6	8	526	509	13	14	1	3	823	695	9	14	5	4	642	631	12
13	3	2	1234	1139	8	13	6	9	239	245	10	14	1	4	442	480	10	14	5	6	429	416	11
13	3	3	715	675	9	13	6	10	371	370	8	14	1	5	475	491	10	14	5	8	336	332	10
13	3	4	504	503	10	13	6	12	409	383	10	14	1	6	1098	1018	10	14	5	9	159	157	13
13	3	5	1303	1283	9	13	7	1	508	513	11	14	1	7	386	414	16	14	5	10	202	194	12
13	3	6	696	714	10	13	7	2	353	328	9	14	1	8	509	521	20	14	5	11	187	203	14
13	3	7	974	933	11	13	7	3	302	271	8	14	1	9	223	207	17	14	5	12	344	328	9
13	3	8	756	766	17	13	7	4	147	128	14	14	1	10	340	346	11	14	6	0	266	251	7

Values of 10*Fobs and 10*Fcalc for PdCl2(f-0-Pphenyl2-02)

H	K	L	Fobs	Fcalc	SigF	H	K	L	Fobs	Fcalc	SigF	H	K	L	Fobs	Fcalc	SigF	H	K	L	Fobs	Fcalc	SigF
14	6	1	417	449	12	15	2	2	997	928	9	15	5	10	293	287	10	16	0	5	626	589	10
14	6	3	190	186	10	15	2	3	340	341	9	15	5	11	425	446	11	16	0	6	966	976	13
14	6	4	216	186	11	15	2	4	467	499	16	15	5	12	263	250	17	16	0	7	925	934	18
14	6	5	264	221	8	15	2	5	936	909	10	15	6	0	567	602	25	16	0	8	815	785	11
14	6	6	234	241	9	15	2	6	769	735	11	15	6	1	163	169	11	16	0	9	550	509	29
14	6	7	174	142	12	15	2	7	631	641	12	15	6	2	308	295	17	16	0	10	393	367	9
14	6	8	397	382	10	15	2	8	741	705	17	15	6	3	208	238	9	16	0	11	384	386	10
14	6	9	288	310	10	15	2	9	540	498	12	15	6	4	535	528	11	16	0	12	633	626	15
14	6	10	182	192	13	15	2	10	170	155	22	15	6	5	215	191	10	16	0	13	441	429	15
14	6	11	224	214	13	15	2	12	444	448	11	15	6	6	219	209	10	16	0	14	562	529	13
14	7	0	197	190	11	15	2	13	232	198	12	15	6	7	187	178	20	16	1	1	802	826	9
14	7	1	253	267	10	15	2	14	392	374	10	15	6	9	199	186	18	16	1	2	831	850	9
14	7	2	557	516	13	15	3	0	738	747	10	15	6	10	312	297	12	16	1	3	165	211	10
14	7	4	780	753	13	15	3	1	1381	1403	31	15	6	12	231	260	14	16	1	4	242	228	7
14	7	5	123	89	17	15	3	2	800	789	10	15	7	0	439	334	22	16	1	5	810	766	10
14	7	6	278	271	9	15	3	3	1225	1256	9	15	7	1	227	194	10	16	1	6	997	932	10
14	7	7	411	374	11	15	3	4	352	364	9	15	7	2	119	135	17	16	1	7	596	597	23
14	7	8	415	408	10	15	3	5	1043	1008	10	15	7	3	630	612	13	16	1	8	506	516	11
14	7	9	134	139	18	15	3	6	612	613	12	15	7	5	184	183	24	16	1	9	336	338	13
14	7	10	538	534	14	15	3	7	1281	1259	17	15	7	6	211	192	11	16	1	10	288	267	12
14	8	1	537	525	12	15	3	8	762	717	27	15	7	7	357	365	16	16	1	11	394	380	10
14	8	2	191	185	12	15	3	9	507	526	17	15	7	9	354	317	11	16	1	12	644	626	25
14	8	3	911	878	13	15	3	10	435	385	10	15	7	10	274	250	11	16	1	13	576	545	13
14	8	5	863	865	13	15	3	11	446	431	11	15	7	11	254	223	12	16	1	14	266	270	19
14	8	7	367	370	8	15	3	12	293	296	10	15	8	1	203	212	23	16	2	0	627	541	13
14	8	9	726	677	21	15	3	13	444	442	17	15	8	2	250	191	15	16	2	1	1489	1417	9
14	9	0	465	469	11	15	4	0	1187	1155	9	15	8	3	223	227	12	16	2	2	818	805	9
14	9	2	683	675	16	15	4	1	546	587	11	15	8	4	235	226	11	16	2	3	255	293	8
14	9	4	676	640	15	15	4	2	935	919	10	15	8	6	189	178	14	16	2	4	456	424	11
14	9	6	342	333	10	15	4	3	544	506	11	15	8	7	213	194	12	16	2	5	826	767	10
14	9	8	392	358	10	15	4	4	690	679	11	15	9	1	413	377	13	16	2	6	638	594	11
14	10	1	250	232	17	15	4	5	928	965	23	15	9	2	159	125	15	16	2	7	524	470	11
14	10	3	379	369	9	15	4	6	850	875	11	15	9	3	320	325	9	16	2	8	363	335	9
14	10	5	389	354	9	15	4	7	291	275	8	15	9	4	425	402	10	16	2	10	179	181	12
14	12	1	175	181	19	15	4	8	587	604	13	15	9	5	364	337	9	16	2	11	353	316	20
15	1	0	1085	1207	80	15	4	9	560	547	16	15	9	6	220	253	13	16	2	12	454	441	20
15	1	1	511	414	9	15	4	10	600	555	14	15	9	7	187	183	21	16	2	13	254	260	11
15	1	2	607	573	9	15	4	11	229	213	11	15	9	8	228	209	13	16	3	1	585	628	14
15	1	3	371	303	16	15	4	12	419	384	9	15	10	0	229	214	13	16	3	2	291	263	11
15	1	4	492	399	12	15	4	13	196	191	14	15	10	2	445	434	12	16	3	3	400	397	10
15	1	7	322	315	8	15	5	0	434	383	10	15	10	3	267	225	12	16	3	5	685	644	11
15	1	8	113	122	14	15	5	1	544	528	16	15	10	4	405	373	9	16	3	6	583	618	12
15	1	9	415	418	10	15	5	2	699	736	11	15	10	5	273	267	24	16	3	8	360	339	9
15	1	10	406	418	10	15	5	3	585	605	12	15	11	0	419	368	10	16	3	9	208	201	10
15	1	11	155	162	23	15	5	4	524	459	11	15	11	1	218	197	14	16	3	11	234	227	10
15	1	12	228	178	11	15	5	5	412	441	11	16	0	0	793	764	9	16	3	12	464	453	12
15	1	13	292	282	10	15	5	6	232	192	9	16	0	1	1544	1438	9	16	3	13	202	197	19
15	1	14	223	230	13	15	5	7	650	589	13	16	0	2	794	808	13	16	4	0	443	413	28
15	2	0	829	922	105	15	5	8	328	328	14	16	0	3	759	741	16	16	4	2	186	149	8
15	2	1	700	715	23	15	5	9	370	346	8	16	0	4	439	417	11	16	4	3	638	582	11

Values of 10*Fobs and 10*Fcalc for PdCl2(f-0-Pphenyl2-02)

H	K	L	Fobs	Fcalc	SigF
16	4	4	304	268	7
16	4	5	409	402	9
16	4	6	685	681	26
16	4	8	228	239	23
16	4	10	267	256	9
16	4	12	349	344	14
16	5	0	803	760	11
16	5	1	417	437	11
16	5	2	438	402	11
16	5	3	118	131	14
16	5	4	509	534	11
16	5	5	530	486	12
16	5	6	267	258	11
16	5	7	241	214	9
16	5	8	239	197	10
16	5	10	197	205	12
16	6	1	482	454	11
16	6	3	397	382	13
16	6	4	301	283	9
16	6	5	288	272	8
16	6	6	328	310	8
16	6	7	513	487	13
16	6	8	481	427	18
16	6	9	427	423	11
16	6	10	388	389	15
16	6	11	241	244	12
16	7	1	271	255	10
16	7	2	391	363	13
16	7	3	651	595	21
16	7	4	452	413	11
16	7	5	391	374	10
16	7	6	335	306	10
16	7	7	302	278	9
16	7	8	191	209	13
16	7	9	356	345	14
16	7	10	469	462	18
16	8	0	322	299	13
16	8	1	375	363	9
16	8	2	703	674	22
16	8	3	488	457	13
16	8	4	591	557	14
16	8	5	213	229	23
16	8	6	307	289	9
16	8	7	144	133	22
16	8	8	244	227	12
16	8	9	276	267	16
16	9	0	174	158	20
16	9	1	446	417	11
16	9	2	186	185	13
16	9	3	501	487	11
16	9	4	388	361	11
16	9	5	434	399	11
16	9	6	156	144	17
16	10	0	163	165	17
16	10	1	243	255	12
16	10	2	247	255	14
16	10	4	329	323	10
16	11	0	217	198	14
16	11	1	183	145	16
17	1	0	488	466	24
17	1	1	514	502	12
17	1	2	423	363	12
17	1	3	174	187	10
17	1	4	468	495	10
17	1	5	471	440	11
17	1	6	279	276	8
17	1	7	530	541	18
17	1	8	501	474	12
17	1	9	369	372	21
17	1	11	261	260	9
17	1	12	253	223	13
17	2	1	1143	1152	16
17	2	2	407	421	9
17	2	3	589	629	10
17	2	5	610	600	16
17	2	6	263	238	8
17	2	7	927	894	12
17	2	9	390	363	12
17	2	10	145	135	14
17	2	11	347	337	8
17	2	13	382	356	10
17	3	0	1279	1282	25
17	3	2	1096	1049	10
17	3	4	609	566	11
17	3	6	1210	1183	11
17	3	7	223	221	10
17	3	8	711	723	22
17	3	9	358	381	10
17	3	10	434	413	12
17	3	11	327	319	9
17	3	12	487	463	23
17	3	13	226	214	13
17	4	0	136	119	12
17	4	1	897	905	17
17	4	3	887	848	13
17	4	4	296	324	7
17	4	5	486	520	26
17	4	7	1053	1019	12
17	4	8	225	210	10
17	4	9	481	462	13
17	4	11	534	501	14
17	4	13	473	448	11
17	5	0	640	594	12
17	5	2	735	749	13
17	5	3	348	358	9
17	5	4	915	902	11
17	5	5	229	221	9
17	5	6	518	496	12
17	5	7	301	284	8
17	5	8	567	529	34
17	5	9	314	310	8
17	5	10	457	466	11
17	5	12	344	349	11
17	6	0	160	130	12
17	6	1	538	504	12
17	6	2	196	173	11
17	6	3	885	887	12
17	6	4	356	369	10
17	6	5	298	294	8
17	6	6	225	247	10
17	6	7	596	574	20
17	6	9	286	256	9
17	6	10	289	290	15
17	6	11	435	423	22
17	7	1	376	352	10
17	7	2	326	262	8
17	7	3	251	227	17
17	7	4	388	389	11
17	7	5	369	360	10
17	7	6	348	349	9
17	7	7	261	265	10
17	7	8	194	192	13
17	7	9	271	256	11
17	7	10	266	228	11
17	8	1	140	147	15
17	8	2	305	302	9
17	8	5	236	224	11
17	8	6	274	262	11
17	8	8	216	200	13
17	9	0	210	197	12
17	9	1	190	187	19
17	9	2	381	357	10
17	9	7	138	134	20
17	10	1	306	261	15
17	10	3	369	340	10
18	0	0	1365	1518	15
18	0	1	928	925	15
18	0	2	170	178	8
18	0	3	516	487	11
18	0	4	192	202	7
18	0	5	559	583	11
18	0	6	804	818	14
18	0	7	361	313	9
18	0	8	572	505	13
18	0	9	474	467	12
18	0	10	591	593	14
18	0	11	398	372	8
18	0	12	666	605	15
18	0	13	483	442	11
18	1	1	1289	1286	12
18	1	2	590	595	10
18	1	3	523	568	12
18	1	4	371	371	9
18	1	5	860	817	10
18	1	6	460	449	11
18	1	7	1131	1064	11
18	1	8	439	435	15
18	1	9	489	473	12
18	1	10	260	270	9
18	1	11	471	448	12
18	1	12	399	387	10
18	1	13	522	516	12
18	2	2	723	727	10
18	2	3	525	486	11
18	2	4	578	578	11
18	2	5	382	338	10
18	2	6	1057	1022	22
18	2	7	231	206	9
18	2	8	719	684	13
18	2	9	423	428	9
18	2	10	514	496	13
18	2	11	337	315	9
18	2	12	281	300	10
18	3	2	442	472	10
18	3	3	204	228	8
18	3	4	209	219	8
18	3	5	361	361	10
18	3	6	356	384	9
18	3	7	444	419	11
18	3	8	204	197	10
18	3	9	445	434	10
18	3	10	228	215	10
18	3	11	267	253	9
18	3	12	291	272	25
18	4	2	775	745	15
18	4	3	617	613	12
18	4	4	405	345	10
18	4	5	594	586	13
18	4	6	288	290	8
18	4	7	347	334	9

Values of 10*Fobs and 10*Fcalc for PdCl2(f-0-Ppheny12-02)

H	K	L	Fobs	Fcalc	SigF
18	4	8	425	411	11
18	4	9	382	350	10
18	4	10	191	201	12
18	4	11	173	174	15
18	4	12	349	341	19
18	5	3	358	358	10
18	5	4	312	290	7
18	5	5	620	581	19
18	5	6	214	197	10
18	5	7	150	140	14
18	5	9	541	533	31
18	5	11	159	200	17
18	5	12	163	155	17
18	6	0	283	276	8
18	6	1	193	186	22
18	6	2	557	479	25
18	6	3	337	328	8
18	6	4	635	624	16
18	6	6	209	189	18
18	6	7	378	347	11
18	6	8	323	326	9
18	6	9	132	139	19
18	6	10	401	386	9
18	7	1	335	313	8
18	7	2	298	286	17
18	7	3	651	650	14
18	7	4	291	259	9
18	7	5	417	426	11
18	7	7	267	278	27
18	7	8	166	171	16
18	7	9	496	502	10
18	7	10	211	210	20
18	8	0	500	457	16
18	8	1	169	203	13
18	8	2	620	609	14
18	8	3	209	202	18
18	8	4	734	715	15
18	8	5	194	180	13
18	8	6	393	357	17
18	8	7	196	187	14
18	8	8	484	440	16
18	9	1	257	287	26
18	9	3	526	487	12
18	9	4	321	286	10
18	9	5	394	363	10
18	9	6	241	232	16
18	10	1	250	272	18
18	10	3	274	269	12
18	11	0	230	234	18
19	1	1	700	691	18
19	1	2	608	613	11
19	1	3	251	258	6
19	1	4	136	129	11
19	1	5	449	406	11
19	1	6	361	322	9
19	1	7	332	340	9
19	1	8	207	243	10
19	1	10	134	118	15
19	1	11	191	168	12
19	1	12	180	146	14
19	1	13	216	204	13
19	2	0	643	643	39
19	2	2	866	838	17
19	2	3	192	179	8
19	2	4	353	353	9
19	2	5	192	177	10
19	2	6	800	769	12
19	2	7	220	217	10
19	2	8	538	497	11
19	2	10	207	190	11
19	2	12	311	299	10
19	3	0	603	658	47
19	3	1	641	768	62
19	3	2	528	486	15
19	3	3	678	608	24
19	3	4	513	541	11
19	3	5	546	540	11
19	3	6	286	245	8
19	3	7	879	865	12
19	3	8	468	467	12
19	3	9	455	430	14
19	3	10	118	122	17
19	3	11	285	295	20
19	3	12	179	194	25
19	4	0	1002	1006	11
19	4	2	734	696	11
19	4	4	623	603	13
19	4	5	478	501	12
19	4	6	646	647	13
19	4	7	260	251	23
19	4	8	746	684	13
19	4	9	297	294	9
19	4	10	320	309	8
19	4	12	486	469	19
19	5	0	246	264	13
19	5	1	852	828	36
19	5	2	458	473	21
19	5	3	844	852	12
19	5	5	622	580	16
19	5	6	637	615	14
19	5	7	541	536	12
19	5	8	366	315	12
19	5	9	436	445	11
19	5	10	146	147	17
19	5	11	349	344	11
19	6	1	335	347	9
19	6	2	841	831	32
19	6	4	379	397	9
19	6	5	544	519	29
19	6	6	325	297	9
19	6	8	312	322	9
19	6	9	243	225	12
19	6	10	290	276	27
19	7	0	424	434	11
19	7	1	311	293	10
19	7	2	554	498	13
19	7	3	159	117	14
19	7	4	155	165	21
19	7	5	267	268	10
19	7	8	216	203	17
19	7	9	185	138	19
19	8	1	258	231	10
19	8	3	140	107	17
19	8	5	245	222	12
19	9	3	226	201	13
19	9	4	261	244	12
19	9	6	257	239	12
19	10	2	200	196	15
19	11	1	222	200	15
20	0	1	1227	1212	9
20	0	2	233	247	7
20	0	3	878	790	10
20	0	4	382	350	10
20	0	5	883	946	11
20	0	6	455	435	18
20	0	7	1416	1372	11
20	0	8	245	253	9
20	0	9	681	675	14
20	0	10	472	419	13
20	0	11	383	380	10
20	0	12	392	415	11
20	0	13	663	634	36
20	1	0	1595	1654	93
20	1	1	596	573	39
20	1	2	767	735	10
20	1	3	190	166	11
20	1	4	623	616	25
20	1	5	426	382	17
20	1	6	964	957	11
20	1	7	183	199	11
20	1	8	708	702	13
20	1	10	441	415	18
20	1	11	185	187	23
20	1	12	346	334	15
20	1	13	241	230	12
20	2	1	993	908	64
20	2	2	265	232	7
20	2	3	774	796	11
20	2	4	248	217	10
20	2	5	373	369	9
20	2	6	237	220	18
20	2	7	744	695	12
20	2	8	297	292	11
20	2	9	188	166	15
20	2	11	413	410	12
20	2	13	353	331	16
20	3	2	572	513	14
20	3	3	419	391	11
20	3	4	532	514	12
20	3	6	294	278	13
20	3	7	176	185	22
20	3	8	182	171	12
20	3	9	180	207	23
20	3	10	265	233	9
20	3	11	196	165	13
20	4	1	423	529	11
20	4	4	562	512	13
20	4	5	633	560	18
20	4	6	248	263	9
20	4	7	179	168	18
20	4	8	209	229	17
20	4	9	311	308	9
20	4	10	436	415	11
20	4	11	160	160	16
20	5	0	444	396	29
20	5	2	693	677	26
20	5	3	301	279	8
20	5	4	483	457	11
20	5	5	211	214	11
20	5	7	273	270	9
20	5	8	442	435	10
20	5	9	284	296	16
20	5	10	168	154	16
20	6	0	235	252	10
20	6	1	493	520	12
20	6	3	662	628	13
20	6	5	521	537	13
20	6	6	168	159	16
20	6	7	457	452	14
20	6	8	273	281	11

Values of 10*Fobs and 10*Fcalc for PdCl2(f-0-Pphenyl2-O2)

H	K	L	Fobs	Fcalc	SigF	H	K	L	Fobs	Fcalc	SigF	H	K	L	Fobs	Fcalc	SigF	H	K	L	Fobs	Fcalc	SigF
20	6	9	671	635	17	21	4	0	363	369	19	22	0	4	846	820	11	22	5	4	518	480	12
20	6	10	209	194	14	21	4	1	358	466	11	22	0	5	609	605	13	22	5	5	214	228	11
20	7	0	453	401	12	21	4	3	300	323	8	22	0	6	866	851	12	22	5	6	152	160	15
20	7	1	255	256	9	21	4	4	417	412	10	22	0	7	397	398	10	22	5	7	405	361	10
20	7	2	621	608	15	21	4	5	579	543	14	22	0	8	714	668	13	22	5	9	396	374	12
20	7	4	788	771	19	21	4	6	224	226	10	22	0	9	352	317	8	22	5	10	244	237	27
20	7	6	480	475	13	21	4	7	322	325	9	22	0	10	294	269	17	22	6	0	790	749	16
20	7	8	571	559	15	21	4	8	456	413	11	22	0	11	376	346	12	22	6	2	562	607	13
20	8	0	154	128	15	21	4	9	397	388	10	22	0	12	576	549	14	22	6	3	421	358	9
20	8	1	575	552	13	21	4	10	314	294	9	22	1	1	1034	977	11	22	6	4	646	630	14
20	8	3	703	709	18	21	4	11	219	205	19	22	1	2	651	675	11	22	6	6	463	482	12
20	8	5	472	431	12	21	5	0	451	498	12	22	1	3	389	423	10	22	6	7	229	225	12
20	8	6	136	150	19	21	5	1	534	518	32	22	1	4	288	256	16	22	6	8	508	469	13
20	9	0	258	247	11	21	5	2	881	843	14	22	1	5	926	865	11	22	6	9	305	308	10
20	9	2	380	359	9	21	5	3	470	473	13	22	1	6	584	580	14	22	7	0	238	205	10
20	9	4	533	472	13	21	5	4	625	626	14	22	1	7	700	693	41	22	7	1	652	615	15
20	9	5	187	171	15	21	5	5	521	485	12	22	1	8	287	296	9	22	7	2	317	333	12
20	11	1	174	136	18	21	5	6	384	351	11	22	1	9	504	470	12	22	7	3	762	740	14
21	1	2	561	516	12	21	5	7	355	336	8	22	1	10	265	248	9	22	7	4	263	262	10
21	1	3	312	270	8	21	5	8	559	550	13	22	1	11	259	245	11	22	7	5	492	406	12
21	1	4	522	489	12	21	5	9	188	155	14	22	1	12	525	508	13	22	7	6	188	200	15
21	1	5	339	337	7	21	5	10	209	230	13	22	2	1	877	910	62	22	7	7	346	345	10
21	1	6	537	555	13	21	5	11	270	252	11	22	2	2	368	378	9	22	7	8	267	251	12
21	1	7	179	171	15	21	6	0	295	334	18	22	2	3	155	161	11	22	8	0	293	282	10
21	1	8	384	355	15	21	6	1	430	419	23	22	2	4	202	198	20	22	8	1	170	156	15
21	1	10	262	274	11	21	6	2	605	590	13	22	2	5	423	390	14	22	8	2	341	311	16
21	1	12	304	281	10	21	6	3	366	361	9	22	2	6	699	641	13	22	8	3	343	367	11
21	2	0	426	430	25	21	6	4	263	262	10	22	2	7	398	416	10	22	8	4	523	477	19
21	2	2	226	234	8	21	6	5	497	507	13	22	2	8	407	380	9	22	8	5	223	220	13
21	2	3	306	297	12	21	6	6	252	233	10	22	2	10	257	223	10	22	8	6	337	289	10
21	2	4	216	238	9	21	6	7	198	191	27	22	2	12	309	291	10	22	9	1	177	167	16
21	2	5	567	560	12	21	6	9	288	278	11	22	3	2	221	207	9	22	9	2	167	152	17
21	2	6	465	462	11	21	6	10	271	217	13	22	3	3	319	315	13	22	9	3	350	324	25
21	2	7	499	470	12	21	7	0	190	214	15	22	3	4	293	322	9	22	10	0	309	273	10
21	2	8	217	216	10	21	7	3	310	279	15	22	3	5	262	247	8	23	1	0	277	298	41
21	2	9	229	218	12	21	7	5	341	355	10	22	3	6	301	285	8	23	1	2	287	272	9
21	2	10	343	321	9	21	7	6	297	278	14	22	3	8	273	311	14	23	1	3	385	349	10
21	2	11	143	165	17	21	7	7	294	298	14	22	3	10	215	216	12	23	1	4	185	209	14
21	2	12	248	235	12	21	7	9	261	246	12	22	3	11	253	234	11	23	1	5	290	294	9
21	3	2	276	299	7	21	8	0	178	166	13	22	3	12	259	269	12	23	1	6	521	469	12
21	3	3	398	387	22	21	8	2	134	131	19	22	4	2	579	524	13	23	1	7	238	200	11
21	3	4	183	165	11	21	8	4	209	210	13	22	4	3	715	688	13	23	1	8	364	372	9
21	3	5	350	324	8	21	8	7	225	220	13	22	4	4	337	317	15	23	1	10	331	323	9
21	3	6	330	312	9	21	9	3	172	176	22	22	4	5	260	267	9	23	1	12	245	220	12
21	3	7	575	577	15	21	11	0	219	230	15	22	4	6	337	298	15	23	2	0	483	542	39
21	3	8	211	196	11	21	11	1	251	227	28	22	4	8	411	381	9	23	2	3	247	234	10
21	3	9	444	422	12	22	0	0	1614	1614	10	22	5	0	277	299	23	23	2	5	250	249	13
21	3	10	323	304	8	22	0	1	915	887	11	22	5	1	450	525	52	23	2	6	297	305	9
21	3	11	308	296	10	22	0	2	1215	1205	16	22	5	2	450	442	21	23	2	7	572	545	13
21	3	12	323	290	13	22	0	3	268	276	7	22	5	3	332	289	8	23	2	8	237	234	10

Values of 10*Fobs and 10*Fcalc for PdCl2(f-0-Pphenyl2-02)

H	K	L	Fobs	Fcalc	SigF
23	2	11	260	233	13
23	3	0	686	637	42
23	3	2	369	381	9
23	3	3	202	180	10
23	3	4	277	259	8
23	3	6	522	520	18
23	3	7	377	359	9
23	3	8	230	204	10
23	3	10	271	252	10
23	4	1	334	437	16
23	4	2	176	181	12
23	4	3	618	622	13
23	4	5	212	190	10
23	4	6	174	152	12
23	4	7	602	596	13
23	4	9	346	334	13
23	4	11	399	367	11
23	5	2	376	387	9
23	5	3	351	314	8
23	5	4	672	645	14
23	5	5	178	219	13
23	5	6	594	543	12
23	5	7	208	182	20
23	5	8	451	436	13
23	5	10	532	496	13
23	6	1	355	377	9
23	6	3	599	545	13
23	6	4	187	186	21
23	6	5	408	380	9
23	6	7	415	405	10
23	6	9	364	323	10
23	7	0	217	214	11
23	7	4	391	347	16
23	8	5	169	167	16
23	9	2	198	169	28
23	10	1	202	168	15
24	0	0	1047	1055	11
24	0	1	911	822	27
24	0	2	720	683	12
24	0	3	401	394	11
24	0	4	738	718	17
24	0	5	890	797	12
24	0	6	937	938	12
24	0	7	594	563	14
24	0	8	578	595	13
24	0	9	690	671	14
24	0	10	304	277	10
24	0	11	542	475	13
24	1	2	836	779	12
24	1	3	659	666	12
24	1	4	307	272	7
24	1	5	490	445	12
24	1	6	675	641	14
24	1	7	933	914	13
24	1	8	542	520	29
24	1	9	150	136	15
24	1	10	148	158	21
24	1	11	482	469	20
24	2	1	659	689	68
24	2	2	496	529	11
24	2	3	182	162	11
24	2	4	385	372	9
24	2	5	421	458	10
24	2	6	473	451	11
24	2	8	300	278	12
24	2	9	290	262	9
24	2	10	153	150	16
24	2	11	204	161	13
24	3	2	489	472	12
24	3	3	123	67	15
24	3	4	350	321	17
24	3	5	207	182	10
24	3	7	361	363	16
24	3	8	152	129	15
24	4	2	314	337	11
24	4	3	156	227	22
24	4	4	228	188	10
24	4	8	302	307	11
24	4	9	237	239	19
24	4	10	204	181	23
24	5	0	580	564	14
24	5	3	395	344	11
24	5	6	255	285	15
24	5	7	295	245	10
24	5	8	379	338	19
24	5	9	310	313	10
24	6	0	314	319	11
24	6	2	568	561	19
24	6	3	332	361	9
24	6	4	401	408	14
24	6	5	396	378	12
24	6	6	277	267	11
24	6	7	611	546	13
24	6	8	394	365	10
24	7	0	332	347	9
24	7	1	304	302	14
24	7	2	305	311	9
24	7	3	484	490	14
24	7	4	378	376	10
24	7	5	388	379	12
24	7	6	410	371	19
24	7	7	274	237	17
24	8	1	321	284	17
24	8	2	409	368	10
24	8	3	452	385	10
24	8	4	383	356	9
25	1	2	275	246	8
25	1	3	193	158	21
25	1	4	259	229	9
25	1	5	538	561	14
25	1	7	342	331	8
25	1	11	192	193	14
25	2	0	595	619	54
25	2	2	339	328	7
25	2	4	458	478	10
25	2	5	286	310	9
25	2	6	496	481	12
25	2	8	403	363	12
25	3	2	278	290	8
25	3	3	375	303	9
25	3	5	334	326	9
25	3	6	220	220	10
25	3	7	398	368	12
25	3	8	314	293	9
25	3	9	518	474	13
25	4	1	308	355	10
25	4	2	408	411	10
25	4	4	255	275	10
25	4	5	309	310	8
25	4	6	541	486	13
25	4	8	384	363	10
25	4	10	389	349	10
25	5	1	773	796	34
25	5	3	737	701	27
25	5	5	576	587	13
25	5	6	243	230	12
25	5	7	426	424	16
25	5	9	368	369	9
25	6	0	383	412	15
25	6	2	437	485	36
25	6	4	550	530	13
25	6	5	225	242	13
25	6	6	234	248	13
25	6	8	298	267	10
25	7	5	390	367	9
25	8	3	281	250	27
25	9	1	170	179	19
25	10	1	164	191	19
26	0	0	622	620	13
26	0	1	1246	1205	19
26	0	2	546	548	12
26	0	3	832	856	12
26	0	4	280	290	8
26	0	5	795	746	18
26	0	6	552	556	12
26	0	7	1178	1109	13
26	0	8	343	337	8
26	0	9	293	278	10
26	0	11	510	485	14
26	1	0	1262	1247	34
26	1	2	409	392	10
26	1	3	469	449	11
26	1	4	676	667	14
26	1	5	240	247	10
26	1	6	819	786	13
26	1	7	314	293	9
26	1	8	410	388	10
26	1	9	213	219	14
26	1	10	448	435	13
26	2	2	252	232	16
26	2	3	531	473	11
26	2	4	343	341	8
26	2	5	181	218	12
26	2	7	474	424	11
26	2	8	343	306	9
26	2	9	185	157	14
26	2	10	301	295	10
26	3	2	259	265	14
26	3	4	338	316	8
26	3	6	292	276	9
26	3	8	183	175	14
26	3	9	140	151	18
26	4	4	131	136	16
26	4	5	140	132	15
26	4	6	140	151	16
26	4	7	188	219	13
26	4	9	204	220	17
26	5	2	350	383	19
26	5	4	309	272	9
26	5	5	175	150	14
26	5	6	226	222	12
26	5	7	292	281	10
26	5	8	267	263	11
26	6	0	439	472	36
26	6	1	572	536	30
26	6	3	423	440	11
26	6	5	571	539	14
26	6	6	303	269	10
26	6	7	290	293	16
26	7	0	363	355	10

Values of 10*Fobs and 10*Fcalc for PdCl2(f-0-Pphenyl2-02)

H	K	L	Fobs	Fcalc	SigF
26	7	1	269	257	11
26	7	2	579	552	14
26	7	3	241	220	26
26	7	4	565	537	14
26	8	1	240	212	12
27	1	2	244	239	15
27	1	3	185	160	12
27	1	5	255	281	10
27	1	6	352	344	10
27	1	7	356	344	9
27	1	8	342	320	9
27	1	9	200	184	13
27	2	3	186	188	13
27	2	4	315	309	8
27	2	5	389	377	10
27	2	6	314	290	8
27	2	7	270	242	9
27	2	8	304	274	10
27	2	10	246	218	20
27	3	0	493	470	32
27	3	1	453	409	12
27	3	2	329	287	14
27	3	3	185	166	12
27	3	4	347	308	8
27	3	5	394	362	10
27	3	6	274	233	14
27	3	7	197	206	13
27	3	8	324	294	16
27	3	9	165	167	16
27	4	0	424	450	11
27	4	1	373	403	9
27	4	2	368	343	21
27	4	3	224	203	11
27	4	4	298	308	9
27	4	5	449	433	12
27	4	6	394	350	10
27	4	7	255	256	11
27	4	8	209	207	13
27	4	9	316	314	10
27	5	0	310	328	32
27	5	2	408	394	11
27	5	3	444	415	11
27	5	4	441	418	12
27	5	5	445	417	10
27	5	6	398	356	9
27	5	7	410	392	10
27	5	8	361	317	16
27	6	3	275	281	12
27	6	4	261	228	18
27	6	5	458	446	12
28	0	0	815	788	13
28	0	1	551	564	12
28	0	2	804	775	31
28	0	3	313	267	9
28	0	4	397	401	9
28	0	5	317	290	11
28	0	6	904	815	13
28	0	7	292	292	11
28	0	8	540	513	22
28	0	10	404	358	11
28	1	1	613	563	14
28	1	3	583	535	13
28	1	4	218	191	11
28	1	5	608	601	13
28	1	6	203	212	12
28	1	7	634	573	14
28	1	8	317	325	10
28	1	9	353	327	9
28	2	2	334	317	15
28	2	3	604	563	14
28	2	4	480	412	11
28	2	5	301	284	9
28	2	6	271	265	10
28	2	8	339	319	9
28	3	3	178	170	12
28	3	4	241	245	21
28	3	5	214	184	11
28	3	6	229	217	11
28	4	7	202	233	14
28	4	8	197	190	14
28	5	1	410	437	17
28	5	5	294	256	11
28	5	6	180	193	21
28	5	7	315	283	18
28	6	0	478	472	12
28	6	2	454	452	10
28	6	3	345	346	14
28	6	4	369	394	14
28	6	5	223	211	13
28	6	6	379	349	12
28	7	0	175	152	19
28	7	1	393	385	11
28	7	3	384	364	13
28	8	0	206	174	14
29	1	0	539	579	12
29	1	2	488	481	33
29	1	3	237	200	19
29	1	4	334	328	8
29	1	6	439	446	11
29	2	3	288	275	9
29	2	4	283	247	9
29	2	5	294	295	9
29	2	7	414	391	14
29	2	9	222	216	14
29	3	0	428	411	29
29	3	4	375	343	9
29	3	5	138	140	18
29	3	6	405	344	10
29	3	7	246	238	16
29	3	8	439	402	11
29	4	0	277	288	31
29	4	1	345	396	12
29	4	3	470	436	14
29	4	4	248	207	11
29	4	5	408	381	10
29	4	7	426	415	15
29	5	0	568	586	37
29	5	2	531	523	15
29	5	3	229	230	12
29	5	4	501	485	15
29	5	5	214	181	24
29	5	6	428	426	27
29	6	3	441	399	19
29	6	4	239	238	13
29	8	1	162	155	19
30	0	0	196	205	12
30	0	1	560	508	12
30	0	2	200	210	11
30	0	3	419	406	19
30	0	4	147	121	14
30	0	5	462	443	13
30	0	6	570	551	18
30	0	7	471	470	13
30	0	8	448	407	11
30	1	1	397	428	24
30	1	2	607	588	27
30	1	4	261	228	16
30	1	5	251	247	12
30	1	6	396	368	10
30	1	7	275	275	18
30	1	8	459	420	11
30	2	3	324	338	19
30	2	5	245	245	23
30	2	6	160	167	16
30	2	7	160	154	17
30	3	2	278	259	9
30	3	4	161	126	20
30	3	7	168	195	16
30	4	6	222	243	23
30	5	4	206	204	24
30	6	1	310	326	28
30	6	3	216	242	31
30	7	0	376	364	13
30	8	0	222	186	14
30	8	1	234	238	17
31	1	3	231	211	26
31	1	4	193	213	13
31	1	7	324	320	11
31	2	3	251	231	11
31	2	4	208	209	16
31	2	5	238	223	12
31	2	6	469	428	12
31	3	1	531	523	14
31	3	3	433	392	13
31	3	5	310	283	10
31	3	6	261	227	11
31	3	7	471	449	11
31	4	2	595	573	13
31	4	4	449	423	13
31	4	6	429	404	26
31	5	3	425	389	9
32	0	1	625	632	14
32	0	2	302	325	12
32	0	3	431	435	12
32	0	5	312	318	10
32	0	6	158	110	20
32	0	7	438	420	10
32	1	0	529	528	21
32	1	1	265	289	33
32	1	2	303	272	15
32	1	3	214	205	13
32	1	4	279	261	10
32	1	5	196	208	14
32	1	6	416	406	11
32	1	7	224	192	13
32	2	3	221	163	18
32	2	4	252	259	11
32	2	5	238	248	12
32	2	6	242	225	30
32	3	4	233	231	13
32	3	6	252	248	13
32	4	3	229	234	23
32	6	0	260	254	18
32	6	1	270	283	16
32	7	0	169	167	18
33	1	3	254	264	11
33	1	4	139	143	19
33	1	5	269	264	13
33	2	1	327	347	34
33	2	3	186	171	15

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