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Metal carbonyl complexes of a non-chelating phosphite-phosphine ligand

by

David Albert Allison

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Dean of Graduate College

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Ames, Iowa

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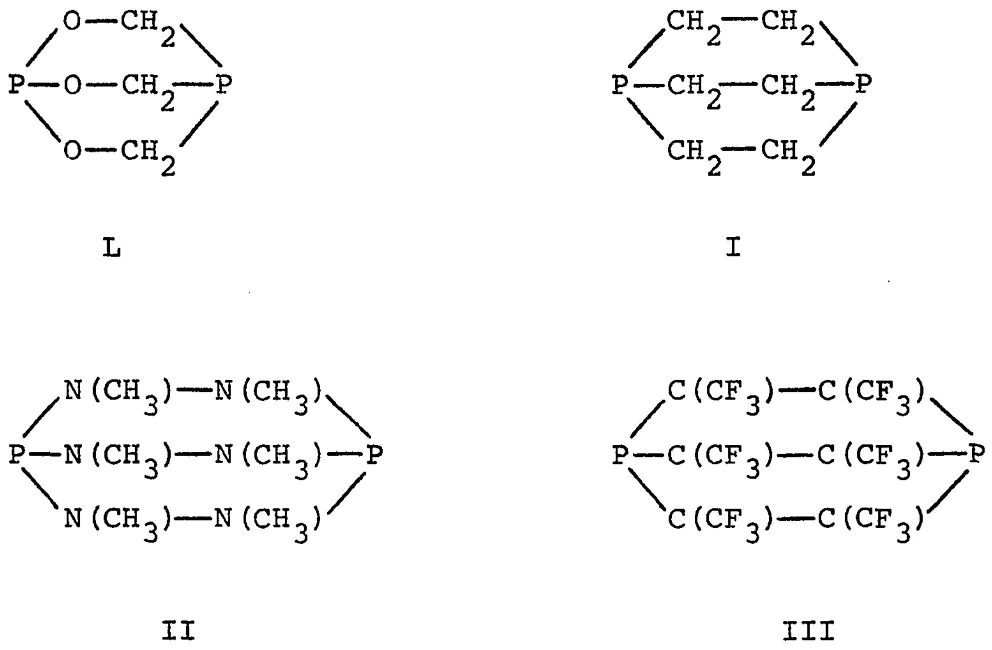
INTRODUCTION

The synthesis of the novel bifunctional phosphorus ligand L (Figure 1) was first reported in 1965 (1). It was thought that this molecule would provide an unique opportunity to study the relative coordinating properties of a phosphite and a phosphine ligand. Knowledge of the difference in chemical properties of phosphites and phosphines in coordination compounds would lead to a better understanding of the metal-phosphorus bond.



L

I

II

III

Figure 1. Schematic representation of the bicyclic diphosphorus ligands L and I-III

Most of the complicating factors normally present in a phosphite _versus_ phosphine study with two different ligands are eliminated with L. When monodentate open-chain phosphite and phosphine ligands are used in competition studies, a number of factors need to be considered in addition to chemical differences in explaining the results. Thus differences in ligand solubility and steric effects due to rotational effects of the alkoxy and alkyl groups on the ligands must be considered. The necessity of monitoring different ligands and products also complicates such a study.

The use of L simplifies these factors and permits direct comparison of the difference in chemical properties of a phosphite and a phosphine. The rigid nature of the bicyclic molecule insures that the substituents on phosphorus cannot rotate. Also the steric requirements have been reduced by the bicyclic system although some steric differences between the two phosphorus atoms must be present owing to the presence of four non-bonding electrons on each of the oxygens as well as two protons on each of the carbons.

It should be noted that the phosphine in L is slightly different than most phosphines since a P-C-O linkage exists rather than a P-C-C. Undoubtedly the more electronegative oxygen will influence the chemistry of the phosphine-phosphorus as was observed in $P(CH_2O)_3CCH_3$ where Boros _et al_. found the $B(CH_3)_3$ adduct surprisingly unstable (2), and phosphonium salts completely unstable (3). They also observed that $\nu(CO)$ values in $(OC)_5WL$ were closer to those for $P(OCH_2)_3CCH_3$ than $P(n\text{-}C_4H_9)_3$ (4). Thus, it is also of interest to learn more concerning the influence of the oxygen in determining the coordination properties of the phosphine end of the ligand.

Although the bicyclic diphosphorus ligands I (5), II (6), and III (7) (Figure 1) are also known, only a few coordination studies have been reported with these ligands. The complex $ClAuP(CH_2CH_2)_3P\ AuCl$ and the dimethyl diphosphonium salt of I have been prepared (5). Several derivatives of II including the dioxide, disulfide, the dimethyl diphosphonium salt, and the bis-borine adduct have been reported (6), and more recently the bis(triethylaluminum) adduct was described (8). Diborane was shown to react with III at low temperature, but the product is unstable at room temperature. A compound, P_2C_6, has been reported (9), but it is not certain that the structure is bicyclic (10). Because of the linear PCCP skeleton of $[(C_6H_5)_2PC]_2$, only complexes in which the ligand bridges to two metal atoms have been obtained (11-13). The geometry of 3,3'-bis(diphenylphosphino)biphenyl also appears to allow bridging of two AuCl groups in preference to chelation (14). It might be mentioned that chelating phosphorus ligands such as $[(C_2H_5)_2PCH_2]_2$ (15) or $[(CH_3)_2PCH_2]_2$ (16) are capable of forming a bridge between two metal atoms under certain conditions.

The presence of two chemically different phosphorus coordination sites permits the possibility of linkage isomerism in complexes, chalconides and phosphonium salts of L wherein one coordination site is used. Because the geometry of L does not permit chelation, two Lewis acid moieties can be bonded as illustrated with I-III above. When the two acid groups are different, two linkage isomers will be possible.

The nature of the metal-phosphorus bond has been debated for a number of years. The major point of disagreement concerns the existence of $d\pi$-$d\pi$ back bonding from the metal to the phosphorus. Contradictory conclusions on the bonding in metal-phosphorus links has been inferred from carbonyl stretching frequencies in substituted metal carbonyls. A number of reviews have covered metal carbonyl derivatives (17-20), and only a brief description of the cases for and against π-bonding will be given here. The basis for the various conclusions on metal-phosphorus bonding in carbonyl complexes is the generally accepted bonding model shown in Figures 2 and 3. Bonding involves both coordinate σ-bond formation in which the lone-pair

Figure 2. OC→M σ-bond formation

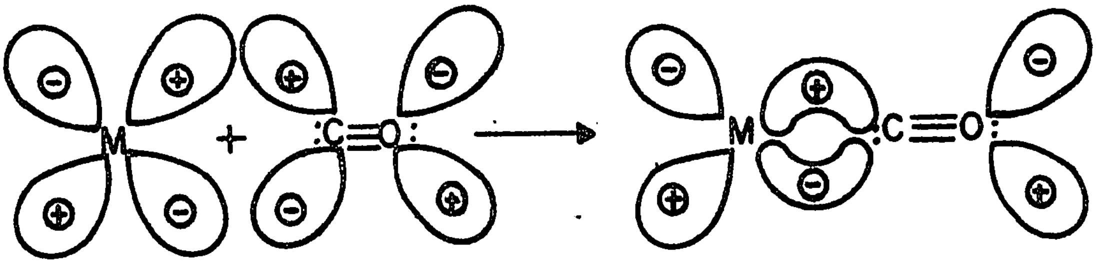


Figure 3. M→CO dπ→pπ "back bonding"

electrons on the carbon atom interact with a vacant metallic orbital (Figure 2) and metal-ligand π-bonding in which filled metallic d orbitals interact with low lying vacant antibonding π orbitals of the ligand (Figure 3).

Cotton and Kraihanzel have proposed a simple model through which sets of force constants for the series of metal carbonyl derivatives may be obtained (21, 22). Although the absolute values for these force constants have no significance, they are useful in assigning stretching frequencies and they are claimed to give internally consistent results for the series of derivatives $M(CO)_{6-n}L_n$. Differences in force constants should therefore bear a direct relation to the actual numbers of π electrons involved in the M-C and C-O bonds and to the bond orders. Cotton (22) has proposed that changes in the C-O force constants (and stretching frequencies) with different donor groups are a function only of the π-accepting ability of the ligand in question and that all $M(CO)_5L$ complexes in which there is no M-L π-bonding should have roughly similar C-O force constants. In a series of the type $M(CO)_5PY_3$, a rise in the electronegativity of Y is accompanied by an increase in the metal-phosphorus π-bonding. This in turn causes a depopulation of the C-O antibonding orbitals and an increase in the C-O force constants. Graham has used the Cotton force constants equations to separate the σ- and

π-bonding components of the metal-ligand bond (23). From such studies of $\nu(CO)$, a spectrochemical series of the π-bonding ability of a series of ligands has been proposed (23, 24).

Bigorgne and co-workers have extensively studied carbonyl stretching frequencies in metal carbonyl derivatives (25-31). They have observed that the phenomenon of the lowering of the C-O frequencies is closely related to that of the raising of the M-C frequencies. In addition the curve of C-O force constants is linear with the degree of substitution for a given ligand PY_3. For all the ligands the slopes of these straight lines are a function of the effective electronegativity of Y and they vary linearly with Taft's polar substituent constant σ^*. Since their plot of $\nu(CO)$ versus σ^* was linear, they concluded that the lowering of the C-O stretching frequencies when the ligand varies from PF_3 to PR_3 is fundamentally an inductive phenomenon (30). Because PR_3 has a donor capacity which is much larger than that of PF_3, the negative charge on the metal is distributed to the CO through the M-C-O π orbitals. From the observation that the plot of C-O force constants *versus* degree of substitution was a straight line, they concluded that ligands in complexes can not be characterized by definite donor-acceptor capacities but that this property varies in proportion to the degree of substitution (31).

If significant metal-phosphorus dπ-dπ bonding exists, the metal-phosphorus bond length should show a decrease. A great many metal-phosphorus bond lengths have now been determined (32-34) and the bond lengths are shorter than the sum of the covalent radii. Interpretations of this shortened bond length must take into consideration a number of factors. The single-bond covalent radii of transition metals are ambiguous numbers. The majority of structures have contained triphenylphosphine, and very few of the rest involve a more electronegative group than an alkyl. Also, the metal-phosphorus bond length will be affected by the bulk of the substituent on the phosphorus, the other ligands on the metal, the geometry of the complex and crystal packing distortions. Despite all of these factors, it is still possible to draw meaningful conclusions about the nature of the metal-phosphorus bond from the bond's length (34-38). Aslanov et al. (34) found that the metal-phosphorus bond length becomes shorter in MCl_4Y_2 and MCl_3Y_3 complexes as M goes from tungsten to platinum ($Y=P(CH_3)_2C_6H_5$). The metal-phosphorus bond length remains constant on going from MCl_3Y_3 to MCl_4Y_2 for these same metals. The metal-chlorine bond lengths behave in the opposite manner and are sensitive to a change in formal oxidation state, but not to the electronic configuration. The interpretation is that the more ionic metal-chlorine bond is much more sensitive to the formal oxidation state of the metal than the more covalent metal-phosphorus bond.

In platinum complexes it has been found that the metal-phosphorus bond length is more dependent on the other ligands than the charge or the geometry of platinum (35, 37). In complexes where the other ligands are capable of π-bonding, the metal-phosphorus bond length is 2.32-2.34A. The bond length shortens to 2.24-2.26A in complexes without ligands capable of π-bonding and in complexes containing only phosphorus ligands. This implies that phosphorus π-bonding to platinum is important when there is no competition for the metal electrons capable of π-bonding. How much, if any, back donation to the phosphorus occurs when the other ligands are better π acceptors can not be determined from these studies.

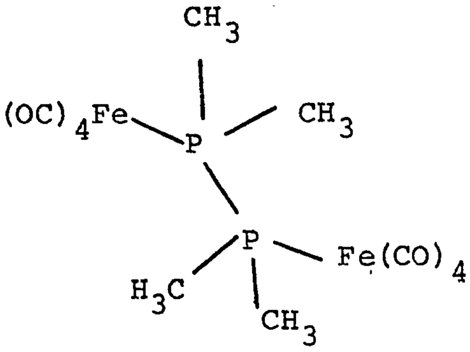
Recently a comparative study of the chromium-phosphorus bond lengths of the ligands triphenylphosphine and triphenylphosphite in $Cr(CO)_5L$ was reported (38). The π-bonding theory discussed earlier predicts for a $Cr(CO)_5L$ complex (where L is a weaker π acceptor than CO) that the carbon-oxygen bond length <u>trans</u> to L will be longer than the carbon-oxygen bond length of the <u>cis</u> carbonyls. Also, the chromium-carbon bond <u>trans</u> to L should be shorter than the <u>cis</u>-chromium-carbon bonds. These changes were indeed observed. Furthermore, triphenylphosphite is expected to be a better π acceptor than triphenylphosphine since oxygen is more electronegative than carbon. Not only should the chromium-phosphorus bond be shorter in the triphenylphosphite complex than in the triphenylphosphine complex, but the trans-chromium-carbon bond should be longer, the trans-carbon-oxygen bond shorter, the cis-chromium-carbon bond longer and the cis-carbon-oxygen bond shorter in the former complex. These predictions were all confirmed by the two structures.

The rhodium-phosphorus bond length in $[Rh(P(OCH_3)_3)_2][B(C_6H_5)_4]$ is 2.19A (39). This is considerably shorter than the 2.34A found for a number of triphenylphosphine complexes of rhodium (36). Although many factors must be considered, the large difference in the bond lengths is similar to that observed in the $Cr(CO)_5L$ study.

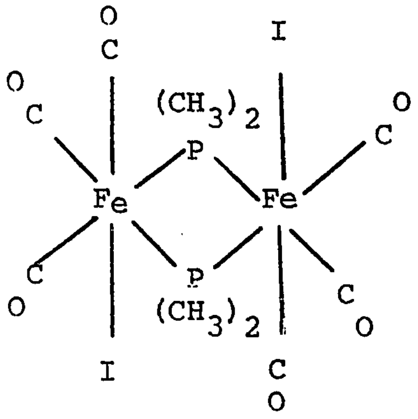
Only a few structures of iron complexes containing phosphorus ligands have been determined (Figure 4). Again, phosphine ligands appear to have longer metal-phosphorus bond lengths than phosphites. Compounds IV (40), V (41), VI (42), and VII (43) have iron-phosphorus bond lengths varying from 2.24-2.29A, while the iron-phosphorus distance in VIII (44) is 2.15A.

The purpose of this study was to learn more about the phosphorus-acceptor bond, particularly with metals. The

Figure 4. Schematic representation of the phosphorus containing iron complexes IV-VIII



IV



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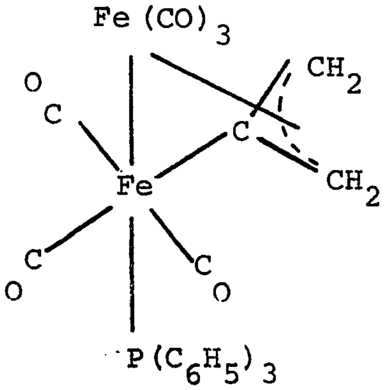
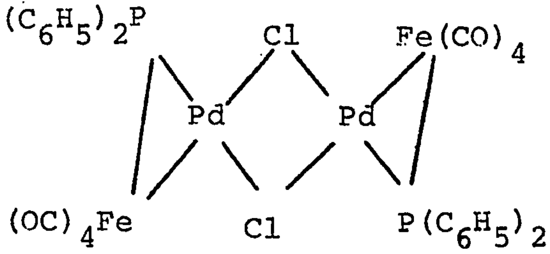
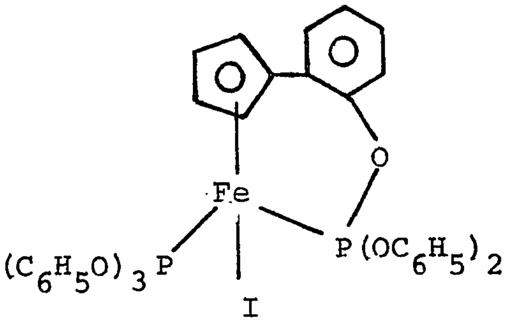


VI



VII



VIII

results of the study have been evaluated in terms of the bonding of phosphorus to the various moieties. In the dissertation are also discussed several aspects of the chemistry of L. Most of the varying types of derivatives mentioned earlier which can potentially form have been synthesized and characterized. In this study are included chalconides, phosphonium salts, borane adducts, and metal carbonyl complexes of L. Extensive use has been made of the proton and phosphorus nmr spectral parameters in characterizing the compounds as well as infrared spectra. Furthermore, the existence of linkage isomers in <u>trans</u>-$(OC)_3Fe[P(OCH_2)_3P][P(CH_2O)_3P]$ has been confirmed by means of a crystal structure determination carried out with the help of Dr. J. Clardy.

EXPERIMENTAL

The proton nmr spectra were obtained on a Varian A-60 nmr spectrometer while the nmr double-resonance experiments were performed on a Varian HR-60 nmr spectrometer. A detailed description of the instrumentation has been given elsewhere (45).

Infrared spectral data were obtained on a Beckman IR-12 spectrometer. An Atlas CH-4 single-focusing spectrometer operated at 70 and 18 ev gave the mass spectra except for the peak matching experiments which were performed on an AEI MS902 spectrometer.

Single crystals of trans-$(OC)_3Fe[P(OCH_2)_3P][P(CH_2O)_3P]$ were obtained by cooling a saturated acetonitrile solution to -20°C. Since the crystals decompose on prolonged exposure to the air, they were placed in thin walled Lindemann glass capillaries. Preliminary rotation photographs (CuK_α) indicated that the unit cell has orthorhombic symmetry. The space group was determined to be Pnma and the unit cell has the parameters: a=11.516A, b=9.780A, c=17.065A. Density calculations indicated that each unit cell contained four molecules. Since the space group Pnma must contain eight asymmetric units, the crystal must make use of a mirror plane through the molecule and this was verified. Similar situations were found for N-methyl-1,4-diazabicyclo[2.2.2]octonium trichloroaquonickelate(II)

(46) and for 1-oxo-4-methyl-2,6,7-trioxa-1-phosphabicyclo [2.2.2]octane (47). A list of the final calculated and observed structure factors is given in Table 1. Also listed are the final position parameters (Table 2) and the final thermal parameters (Table 3).

The borane exchange studies were performed in nmr tubes and the reaction progress followed by proton nmr spectroscopy. The equilibrium between L, $P(CH_2Cl)_3$ and their borane adducts was studied from both directions in acetonitrile while the other reactions were run in nitrobenzene. The peaks for both the complexed and uncomplexed forms of each ligand were easily distinguished and permitted measurement of the relative amounts of the four species in every case except the tri-n-butylphosphine reaction. In this case only the relative amounts of total phosphine to each of the two L species were measured due to the broad complex spectrum of the n-butyl groups.

The bicyclic compound $P(CH_2O)_3As$ was donated by J. W. Rathke and freshly sublimed prior to use. The tri-n-butylphosphine was obtained from Aldrich and used without further purification. The preparations of $P(CH_2Cl)_3$ (48) and $P(CH_2O)_3CCH_3$(2) have been reported. The adduct $H_3BP(CH_2Cl)_3$ was prepared by condensing B_2H_6 into an ether solution of $P(CH_2Cl)_3$. The solvent and excess diborane were removed under vacuum to give the white solid.

Table 1. FO and FC values for *trans*-(OC)$_3$Fe[P(OCH$_2$)$_3$P][P(CH$_2$O)$_3$P]

K = 0

H	L	FO	FC
0	2	194	243
0	4	185	134
0	6	612	614
0	8	1524	1527
0	10	223	280
0	14	583	588
0	18	168	133
0	20	106	93
1	1	1147	1458
1	2	252	241
1	3	120	147
1	4	873	988
1	5	72	39
1	6	798	825
1	7	1327	1452
1	8	484	440
1	9	265	322
1	10	267	320
1	11	154	152
1	13	223	246
1	14	89	108
1	15	317	360
1	17	320	318
1	18	147	149
1	19	97	105
1	20	99	88
2	0	585	513
2	1	296	242
2	2	101	158
2	3	730	785
2	4	227	232
2	5	55	31
2	6	616	588
2	7	600	647
2	8	428	500
2	9	319	405
2	10	257	285
2	11	644	655
2	13	359	333
2	15	155	183
2	16	350	356
2	17	224	249
2	19	140	160
3	1	885	945
3	2	1261	1304
3	3	1127	1158
3	4	588	529
3	5	803	810
3	6	440	386
3	7	218	228
3	8	73	62
3	9	203	200
3	10	455	480
3	12	626	725
3	14	143	187
3	16	129	124
3	20	164	155
4	0	405	417
1	11	471	486
1	12	226	208
1	13	384	401
1	14	204	180
1	15	243	225
1	17	101	46
1	18	348	333
1	19	191	183
2	0	1183	1060
2	1	1955	1989
2	2	776	690
2	4	78	42
2	5	124	95
2	6	1320	1279
2	7	763	698
2	8	834	858
2	9	526	510
2	10	437	412
2	11	308	315
2	12	157	133
2	13	269	284
2	16	473	479
2	18	190	169
2	19	103	108
3	1	455	543
3	2	264	279
3	3	177	145
3	5	587	567
3	6	823	813
3	7	126	138
3	8	186	177
3	9	663	640
3	10	281	308
3	11	289	283
3	13	291	276
3	14	323	336
3	15	347	295
3	16	238	250
3	17	210	214
3	18	96	81
3	20	89	43
4	0	812	764
4	1	499	482
4	2	457	456
4	3	88	89
4	4	51	57
4	5	309	321
4	6	220	273
4	7	323	345
4	8	358	384
4	9	98	115
4	10	137	115
4	11	91	126
4	12	216	196
4	15	330	329
4	16	295	299
4	18	82	60
4	20	140	132
5	1	304	320
5	2	240	226
2	9	300	264
2	10	314	254
2	11	392	333
2	12	446	412
2	14	149	119
2	15	203	189
2	16	231	219
2	17	236	230
2	18	96	88
2	19	228	186
3	1	328	249
3	2	867	862
3	3	641	600
3	4	395	333
3	5	337	278
3	6	246	285
3	7	63	61
3	8	278	277
3	9	111	91
3	10	302	299
3	11	597	540
3	12	486	454
3	13	99	100
3	16	115	117
3	18	91	59
3	19	168	152
3	20	151	143
4	0	609	541
4	1	339	333
4	2	720	671
4	3	770	792
4	4	249	213
4	5	960	967
4	6	418	364
4	7	162	158
4	9	533	490
4	10	474	456
4	11	252	246
4	13	69	44
4	14	82	57
4	15	349	304
4	16	119	106
4	17	100	112
4	18	100	72
4	19	256	249
4	20	124	119
5	1	335	352
5	2	898	867
5	3	300	314
5	4	721	681
5	5	459	442
5	6	270	276
5	7	694	685
5	8	278	253
5	9	170	129
5	10	518	516
5	11	263	241
5	12	287	257
5	13	102	94
5	14	177	170
3	6	304	294
3	7	164	158
3	8	161	169
3	9	828	854
3	10	572	553
3	11	123	134
3	13	248	245
3	14	211	206
3	15	332	316
3	16	177	172
3	17	177	151
3	18	120	112
4	0	775	791
4	1	302	284
4	3	489	427
4	4	255	266
4	5	101	88
4	6	547	502
4	7	339	340
4	8	626	570
4	9	347	329
4	10	397	361
4	11	87	77
4	13	126	110
4	14	166	159
4	15	136	136
4	16	242	250
4	19	87	28
5	1	440	467
5	3	404	386
5	4	719	679
5	5	273	241
5	6	91	81
5	7	189	191
5	8	77	56
5	9	73	73
5	12	403	397
5	13	229	186
5	15	186	203
5	17	110	98
6	0	72	50
6	3	937	887
6	4	303	296
6	5	451	444
6	6	157	130
6	7	92	106
6	8	186	161
6	10	123	136
6	11	675	677
6	12	154	147
6	13	204	225
6	14	77	12
6	15	86	57
6	16	82	81
6	17	91	42
7	1	110	130
7	2	209	205
7	3	208	201
7	4	1035	1018
7	6	480	443
5	12	234	243
5	13	90	80
5	14	136	128
5	15	216	200
5	18	89	79
6	0	193	174
6	1	219	216
6	2	106	84
6	3	293	262
6	4	100	95
6	5	402	372
6	6	306	289
6	7	122	132
6	9	443	465
6	10	293	278
6	11	118	111
6	13	138	104
6	14	317	304
6	15	114	113
7	1	136	147
7	2	170	144
7	3	382	377
7	4	509	483
7	5	436	437
7	6	79	82
7	7	128	110
7	8	195	173
7	9	89	117
7	10	125	118
7	13	145	138
8	0	135	105
8	1	68	63
8	2	427	425
8	3	305	283
8	4	279	254
8	5	440	396
8	6	177	188
8	9	76	47
8	10	133	151
8	12	142	132
8	13	197	199
8	14	117	113
9	1	180	161
9	2	326	333
9	3	310	296
9	4	372	362
9	5	149	147
9	6	131	133
9	7	123	100
9	8	80	90
9	10	85	70
9	12	301	288
10	2	67	45
10	3	241	233
10	4	78	44
10	5	214	201
10	10	158	134
10	11	127	121
10	12	134	115
10	13	162	139
11	1	169	169
11	2	122	104
11	4	130	141
11	5	83	90
11	7	120	131
11	9	87	102
12	2	159	145
12	6	116	146

K = 6

H	L	FO	FC
0	0	1567	1780
0	2	66	62
0	4	153	163
0	6	171	156
0	8	645	727
0	10	302	309
0	14	274	260
1	1	644	633
1	2	97	108
1	3	218	223
1	4	64	55
1	6	171	183
1	7	533	567
1	9	401	428
1	10	221	211
1	12	91	101
1	13	90	68
1	15	158	81
1	17	201	243
2	0	486	470
2	3	60	16
2	4	271	281
2	5	177	203
2	6	112	73
2	8	197	193
2	9	248	259
2	10	88	83
2	11	189	203
2	12	143	131
2	16	155	143
2	17	144	165
3	1	119	124
3	2	687	666
3	3	324	341
3	4	152	122
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3	6	153	185
3	8	193	209
3	10	212	230
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3	12	249	238
3	13	113	117
3	16	92	98
4	0	177	197
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4	2	469	456
4	3	496	485
4	5	456	466
4	6	388	395
7	6	276	272
7	7	131	119
7	9	88	91
7	11	90	89
7	12	168	184
7	13	96	69
8	0	106	113
8	1	125	128
8	2	97	93
8	3	200	204
8	5	177	186
8	6	129	122
9	4	112	110
9	5	107	114
9	8	99	83
10	6	156	138
10	7	95	67
11	1	121	108
11	2	108	77
11	4	111	109
11	5	107	115

K = 8

H	L	FO	FC
0	0	1113	1243
0	6	93	128
0	8	455	502
0	10	165	175
0	14	127	156
1	1	406	386
1	3	110	74
1	4	124	94
1	5	76	108
1	6	180	175
1	7	331	364
1	9	179	220
1	13	98	88
1	15	115	136
2	0	200	187
2	3	101	86
2	6	94	82
2	7	91	81
2	8	224	216
2	9	106	91
2	11	105	118
2	15	102	36
3	1	73	38
3	2	325	289
3	3	224	233
3	4	110	97
3	5	181	176
3	6	124	114
3	10	146	162
3	11	145	145
3	12	205	232
4	1	112	75
4	2	255	240
4	3	215	205
4	5	315	318
4	6	163	141

Table 1 (Continued)

4	1	937	926
4	2	387	447
4	3	235	239
4	4	261	289
4	5	910	986
4	6	661	711
4	7	234	284
4	9	217	206
4	10	324	363
4	11	393	430
4	14	107	79
4	15	397	453
4	16	108	103
4	17	192	185
4	19	316	311
4	20	114	127
5	1	147	152
5	2	161	171
5	3	429	433
5	4	667	758
5	5	80	41
5	6	191	192
5	7	311	324
5	8	665	747
5	9	241	246
5	10	290	338
5	11	303	371
5	12	257	288
5	13	119	136
5	14	248	306
5	15	292	318
5	16	97	135
5	18	125	115
6	0	637	752
6	1	207	240
6	2	284	301
6	3	127	143
6	6	270	273
6	7	256	290
5	8	298	342
6	9	265	322
6	10	208	202
6	13	115	137
6	14	421	420
6	15	138	125
6	17	83	72
6	19	155	158
7	1	85	79
7	2	216	220
7	3	422	488
7	4	230	239
7	5	287	299
7	7	235	283
7	8	140	121
7	9	121	139
7	10	92	158
7	12	167	155
7	15	142	162
8	0	255	266
8	2	390	448
8	3	239	265
5	3	428	400
5	4	1108	1169
5	7	199	183
5	8	320	317
5	9	116	128
5	10	107	103
5	12	217	191
5	13	277	274
5	14	142	113
5	15	150	146
5	18	121	105
6	0	493	490
6	1	174	152
6	2	257	246
6	3	607	644
6	4	130	131
6	5	364	357
6	6	62	62
6	7	192	195
6	8	81	61
6	9	139	152
6	10	124	128
6	11	495	492
6	12	87	91
6	13	353	354
6	14	122	104
6	15	98	111
6	16	119	142
7	1	110	94
7	2	295	290
7	3	176	179
7	4	677	744
7	5	167	187
7	6	649	675
7	7	347	367
7	8	156	165
7	9	283	290
7	10	87	87
7	11	164	158
7	12	355	344
7	13	129	114
7	14	326	337
8	0	195	196
8	1	245	248
8	2	204	173
8	3	262	295
8	5	370	371
8	6	258	242
8	7	176	204
8	8	155	164
8	9	84	70
8	11	83	79
8	12	102	125
8	13	325	334
8	14	95	68
8	15	140	141
9	2	75	87
9	3	129	166
9	4	228	240
9	5	273	261
9	6	131	147
5	15	219	202
5	17	80	16
5	18	116	84
5	19	120	96
6	0	776	788
6	1	141	120
6	2	107	116
6	3	71	63
6	4	182	185
6	5	337	314
6	6	480	472
6	7	388	374
6	8	97	100
6	9	439	404
6	10	151	136
6	13	159	168
6	14	358	340
6	15	132	98
6	16	92	96
7	2	57	53
7	3	442	427
7	4	608	585
7	5	354	360
7	6	196	198
7	7	209	203
7	8	107	95
7	13	95	89
7	15	113	140
8	0	78	75
8	1	87	104
8	2	452	466
8	3	317	318
8	4	187	175
8	5	467	449
8	8	89	57
8	10	314	296
8	11	149	168
8	12	89	65
8	13	255	257
8	14	189	176
9	1	187	171
9	2	230	235
9	3	261	264
9	4	428	425
9	5	76	78
9	6	228	211
9	7	178	169
9	8	97	63
9	10	87	61
9	12	387	371
9	14	103	88
9	15	96	83
10	0	144	138
10	1	144	131
10	2	131	123
10	3	234	228
10	5	244	224
10	9	102	87
10	11	171	159
10	12	152	142
10	13	164	181
7	8	338	303
7	9	131	135
7	10	150	151
7	11	148	136
7	12	266	252
7	14	218	198
8	0	84	75
8	1	182	195
8	2	183	193
8	3	408	414
8	4	69	15
8	5	350	325
8	6	192	180
8	7	78	58
8	11	155	134
8	12	142	161
8	13	292	253
8	14	128	112
8	15	120	126
9	1	73	56
9	2	150	146
9	3	122	131
9	4	239	210
9	5	347	335
9	13	192	178
9	15	112	109
10	1	188	206
10	2	216	221
10	5	117	112
10	6	298	296
10	7	113	83
10	8	147	143
10	11	85	47
10	14	153	141
11	1	158	145
11	2	202	212
11	4	168	186
11	5	121	113
11	6	99	111
11	7	136	124
11	9	107	104
11	10	89	82
11	11	190	178
12	1	81	64
12	2	199	172
12	3	121	119
12	6	109	94
12	7	110	81
12	10	133	118
13	2	81	41
13	6	102	53

K = 4

H	L	FO	FC
0	0	1687	1911
0	2	602	619
0	6	277	317
0	8	445	469
0	10	416	421
0	14	91	46
0	16	261	261
11	4	113	93
12	0	205	210
12	1	103	77
12	8	116	113
13	1	147	105
13	3	92	101

K = 5

H	L	FO	FC
0	1	260	282
0	3	548	620
0	5	166	149
0	7	416	391
0	9	99	131
0	11	597	666
0	13	203	199
0	15	120	85
0	17	233	231
0	19	88	71
1	1	339	319
1	2	99	115
1	3	90	105
1	4	420	435
1	5	150	162
1	6	334	377
1	7	535	587
1	8	100	132
1	9	139	174
1	10	320	336
1	11	279	274
1	12	116	134
1	13	79	41
1	15	173	187
1	18	256	279
1	19	100	120
2	0	936	953
2	1	601	565
2	2	89	107
2	3	194	169
2	4	124	116
2	5	212	220
2	6	506	540
2	7	258	294
2	8	562	611
2	9	186	223
2	10	193	203
2	11	147	184
2	13	171	151
2	14	118	145
2	16	277	280
2	18	137	111
3	1	733	728
3	2	428	403
3	3	149	119
3	4	100	94
3	5	203	231
3	6	224	230
3	7	234	259
3	8	86	141
3	9	556	598
3	10	267	287
4	7	130	105
4	9	208	219
4	10	225	231
4	11	172	194
4	15	205	218
5	1	198	174
5	2	248	246
5	3	277	267
5	4	293	278
5	5	269	260
5	6	158	153
5	7	229	241
5	8	231	240
5	10	212	197
5	11	124	124
5	12	151	148
5	14	157	174
5	15	112	102
6	0	357	319
6	4	106	78
6	5	176	136
6	6	209	191
6	7	270	261
6	10	89	104
6	11	80	41
6	13	151	135
6	14	227	218
6	15	122	127
7	1	78	64
7	3	282	280
7	4	283	260
7	5	157	150
7	7	110	92
8	2	189	198
8	3	114	100
8	5	198	208
8	10	141	143
8	11	89	72
8	13	204	191
9	1	132	147
9	2	126	117
9	3	122	130
9	4	218	189
9	6	153	168
9	7	142	141
9	12	253	258
10	0	136	136
10	1	74	77
10	2	126	89
10	3	180	154
10	5	179	198
11	4	97	123
11	6	86	65
11	8	77	40
12	0	138	144
12	2	90	70

K = 7

H	L	FO	FC
0	1	367	421
0	3	183	192
4	7	126	109
4	9	124	96
4	10	156	173
4	11	166	174
4	13	94	69
5	1	73	65
5	2	219	212
5	3	167	137
5	4	291	281
5	6	80	71
5	7	130	138
5	8	183	166
5	10	188	196
5	11	113	122
5	12	139	123
6	0	220	220
6	1	128	140
6	3	136	147
6	5	85	81
6	6	152	165
6	9	88	112
7	3	138	117
7	4	95	105
7	5	135	131
8	2	139	121
8	3	175	168
8	4	78	68
8	5	195	187
8	8	92	15
9	2	142	131
9	4	212	241
9	7	103	103
10	0	87	32
10	3	122	115
10	5	144	119

K = 9

H	L	FO	FC
0	1	102	97
0	5	102	94
0	7	183	176
0	9	88	34
0	11	125	111
1	1	110	115
1	2	134	144
1	6	225	225
1	7	93	109
1	9	158	152
1	10	124	135
1	11	141	164
2	0	153	138
2	1	323	302
2	2	164	175
2	4	100	97
2	5	139	161
2	7	130	138
2	8	227	229
2	9	104	126
2	10	168	172
2	11	90	83
3	1	208	192

Table 1 (Continued)

8	4	318	330
8	5	342	393
8	7	149	142
8	8	73	48
8	9	192	156
8	10	228	240
8	11	167	190
8	13	239	288
8	14	138	147
8	15	90	60
9	1	267	290
9	2	234	256
9	3	107	160
9	4	429	448
9	5	73	27
9	6	171	186
9	7	223	243
9	8	143	147
9	11	83	94
9	12	333	378
9	14	102	108
9	15	99	116
10	0	140	186
10	1	118	151
10	2	133	154
10	3	270	292
10	5	270	286
10	6	83	134
10	7	135	118
10	8	81	75
10	9	103	71
10	11	100	150
10	12	113	134
10	13	162	106
10	14	134	157
11	4	201	202
11	6	112	126
11	12	115	171
12	0	222	210
12	1	105	105
12	2	110	117
12	8	151	166
12	11	92	2
13	1	164	185
13	3	97	131
13	4	82	65
13	7	150	145
14	0	127	163
14	2	111	121

K = 1

H	L	FO	FG
0	1	925	882
0	3	183	39
0	5	159	147
0	7	580	566
0	9	132	115
0	11	502	451
0	13	304	315
0	15	144	138
0	17	390	348
0	19	88	81
1	1	1289	1217
1	2	667	577
1	3	995	880
1	4	1030	796
1	6	1109	1008
1	7	1052	935
1	8	327	292
1	9	346	339
1	10	552	545
9	7	109	115
9	8	103	111
9	9	134	116
9	13	172	167
10	1	171	152
10	2	189	212
10	5	142	147
10	6	256	284
10	7	118	135
10	8	148	158
10	14	147	168
11	1	161	184
11	2	141	129
11	3	109	127
11	4	171	179
11	5	214	214
11	7	146	158
11	8	113	75
11	9	121	146
11	10	98	60
11	11	159	159
11	12	90	60
11	13	136	145
12	1	81	73
12	2	229	256
12	3	150	153
12	6	179	201
12	7	113	142
12	10	119	125
13	5	101	89
13	6	107	73
14	0	92	92

K = 2

H	L	FO	FC
0	0	2738	3345
0	2	289	280
0	4	533	605
0	8	1119	1082
0	10	992	900
0	12	194	180
0	14	412	395
0	16	309	310
0	18	149	158
1	1	1194	1059
1	2	627	618
1	3	720	622
1	4	213	19
1	5	702	571
1	6	542	512
1	7	920	860
1	8	396	400
1	9	577	519
1	10	541	456
1	11	150	142
1	12	212	182
1	13	199	159
1	15	331	310
1	17	431	399
1	18	197	169
1	19	105	87
1	20	92	55
2	0	1303	1253
2	1	203	220
2	2	250	228
2	3	786	673
2	4	1259	1085
2	5	289	280
2	6	95	36
2	7	101	43
2	8	456	445
11	4	132	158
11	6	82	84
11	7	105	68
11	12	134	127
12	0	244	233
12	1	96	95
12	2	104	100
12	4	77	9
12	7	90	108
12	8	148	140
13	1	170	155
13	2	73	46
13	3	112	112
13	5	105	56
14	0	140	126
14	1	101	79

K = 3

H	L	FO	FC
0	1	218	262
0	3	1241	1135
0	5	385	397
0	7	611	622
0	9	359	389
0	11	988	903
0	13	518	518
0	15	207	189
0	17	286	274
0	19	92	85
1	1	63	118
1	3	73	116
1	4	585	570
1	5	309	288
1	6	436	491
1	7	604	653
1	8	219	251
1	9	93	81
1	10	419	385
1	11	480	477
1	12	163	140
1	14	107	86
1	15	282	266
1	16	114	116
1	17	130	133
1	18	336	341
1	19	186	187
2	0	1465	1363
2	1	486	475
2	2	456	381
2	3	102	120
2	4	321	311
2	5	386	405
2	6	717	685
2	7	479	483
2	8	795	746
2	9	123	129
2	10	293	262
2	11	235	228
2	12	188	170
2	13	238	210
2	14	173	156
2	15	153	150
2	16	378	363
2	17	79	23
2	18	236	215
2	19	93	121
3	1	1094	1023
3	2	437	431
3	3	213	220
3	4	175	165
3	5	263	257
0	18	101	151
1	1	952	929
1	2	641	601
1	3	412	388
1	4	157	185
1	6	619	646
1	7	577	627
1	8	87	76
1	9	483	514
1	10	462	476
1	11	130	118
1	14	119	156
1	15	143	153
1	17	363	381
2	0	612	570
2	1	333	345
2	2	268	283
2	3	346	283
2	4	620	612
2	5	403	439
2	6	390	360
2	7	239	234
2	8	359	328
2	9	451	501
2	10	499	505
2	12	474	476
2	15	134	132
2	16	211	206
2	17	139	132
2	19	116	128
3	1	476	423
3	2	361	330
3	3	133	106
3	4	115	99
3	5	69	35
3	6	397	414
3	8	157	165
3	9	131	152
3	10	157	148
3	11	379	357
3	12	338	297
3	13	92	111
3	14	156	144
3	16	174	146
3	19	187	183
4	0	332	278
4	1	429	418
4	2	586	570
4	3	210	185
4	5	703	673
4	6	318	314
4	7	600	570
4	8	84	93
4	9	335	311
4	10	445	464
4	11	300	295
4	12	117	104
4	13	280	296
4	14	77	66
4	15	198	212
4	16	100	90
4	17	110	127
4	19	194	199
5	2	784	741
5	3	591	563
5	4	346	350
5	5	83	45
5	6	414	423
5	7	509	483
5	8	134	107
5	10	463	443
5	11	336	318
3	11	82	115
3	13	152	174
3	14	154	160
3	15	230	251
3	16	134	155
3	17	136	126
4	0	441	416
4	3	130	122
4	4	165	163
4	5	165	133
4	6	306	295
4	7	269	258
4	8	313	331
4	9	142	155
4	10	252	271
4	14	78	59
4	15	188	204
4	16	211	200
5	1	291	257
5	3	400	386
5	4	647	634
5	5	182	183
5	6	90	65
5	7	129	94
5	8	124	134
5	10	93	80
5	12	253	258
5	13	125	111
5	15	119	133
6	0	104	90
6	1	66	26
6	3	692	637
6	4	110	88
6	5	377	393
6	6	160	157
6	7	73	52
6	8	76	70
6	9	85	110
6	10	96	83
6	11	398	398
6	12	109	96
6	13	171	201
7	3	102	75
7	4	678	625
7	6	321	286
7	7	94	29
7	8	112	94
7	9	172	145
7	12	228	225
7	13	113	64
7	14	199	203
8	1	111	121
8	2	111	108
8	3	268	252
8	5	253	240
8	6	167	154
8	7	150	144
8	11	163	145
8	12	84	86
8	13	231	244
8	14	111	75
9	1	84	10
9	2	108	117
9	3	121	120
9	4	183	172
9	5	158	135
9	9	78	47
9	13	123	103
10	1	97	115
10	2	133	113
10	6	192	190
10	8	129	108
0	7	159	169
0	9	119	146
0	11	125	128
0	17	141	155
1	1	521	517
1	2	327	314
1	3	161	161
1	4	135	140
1	5	79	81
1	6	265	295
1	7	365	385
1	8	136	170
1	9	138	174
1	10	278	291
1	11	114	130
1	12	91	92
1	13	159	156
1	14	96	75
2	0	426	405
2	1	639	611
2	2	419	428
2	3	66	47
2	4	95	79
2	6	432	497
2	7	334	352
2	8	355	371
2	9	144	180
2	10	148	164
2	12	83	78
2	13	132	143
2	16	190	220
3	1	317	309
3	2	99	100
3	3	136	121
3	4	80	62
3	5	200	177
3	6	308	322
3	7	95	110
3	9	335	343
3	10	126	123
3	11	97	115
3	13	115	106
3	14	169	178
3	15	158	143
3	16	117	109
4	0	77	59
4	1	127	107
4	2	134	120
4	5	72	84
4	6	85	87
4	7	192	199
4	8	211	180
4	15	183	188
4	16	168	153
5	1	111	112
5	3	176	151
5	4	460	438
5	5	78	48
5	9	85	90
5	12	121	113
5	13	91	123
5	14	83	47
6	0	121	141
6	3	281	248
6	4	74	36
6	5	239	233
6	7	111	108
6	11	205	207
6	12	87	61
6	13	216	227
7	2	112	135
7	4	378	334
3	2	216	205
3	4	113	115
3	5	131	124
3	6	150	167
3	9	229	235
3	10	121	131
4	0	238	248
4	2	100	115
4	3	91	96
4	6	142	170
4	8	178	152
5	1	100	101
5	3	137	104
5	4	228	222
5	8	105	84
5	11	116	87
6	3	307	282
6	5	190	169
7	2	144	155
7	4	281	287
7	6	154	180
7	8	97	74
8	1	71	46
8	3	121	110
8	4	84	26
8	5	113	132

K = 10

H	L	FO	FC
0	0	334	428
0	2	122	130
0	6	87	5
0	8	229	257
0	10	184	185
1	1	180	157
1	7	173	180
1	9	148	161
1	10	100	75
2	0	228	221
2	2	94	75
3	2	145	163
3	3	105	124
3	6	91	75
3	10	111	72
4	1	113	86
4	2	161	149
4	3	164	134
4	5	162	160
5	2	209	207
5	3	93	92
5	4	148	153
5	6	88	119
5	7	114	118
6	0	98	59
6	1	78	61
6	6	120	112
7	3	81	76
7	4	104	106

K = 11

H	L	FO	FC
0	3	141	136
1	1	134	125
1	2	117	100
1	7	92	109
2	0	229	242
2	1	118	85
2	2	91	98
2	6	113	139
2	7	110	93
3	1	165	141
4	0	122	77

Table 2. Final parameters for *trans*-$(OC)_3Fe[P(OCH_2)_3P][P(CH_2O)_3P]$

Atom	Positional Parameters		
	x	y	z
Fe	0.0755 (2)	0.2500	0.0645 (1)
P(1)	0.0168 (3)	0.2500	0.1820 (2)
P(2)	-0.0679 (4)	0.2500	0.3497 (2)
P(3)	0.1476 (3)	0.2500	-0.0543 (2)
P(4)	0.2603 (4)	0.2500	-0.2142 (2)
O(1)	0.121 (1)	0.2500	-0.2111 (6)
O(2)	0.2902 (7)	0.1202 (9)	-0.1567 (4)
O(3)	0.1906 (7)	0.5139 (8)	0.0990 (4)
O(4)	0.1166 (8)	0.2500	0.2445 (5)
O(5)	-0.0604 (6)	0.3788 (7)	0.2046 (3)
O(6)	-0.170 (1)	0.2500	0.0198 (6)
N	0.479 (2)	0.549 (3)	0.019 (2)
C(1)	0.049 (1)	0.2500	-0.1380 (9)
C(2)	0.242 (1)	0.111 (1)	-0.0803 (6)
C(3)	0.1454 (8)	0.413 (1)	0.0834 (5)
C(4)	0.090 (1)	0.2500	0.3279 (9)
C(5)	-0.108 (1)	0.391 (1)	0.2832 (6)
C(6)	-0.072 (1)	0.2500	0.0337 (8)
C(7)	0.448 (2)	0.644 (2)	0.051 (1)
C(8)	0.411 (1)	0.768 (3)	0.088 (1)

Table 3. Anisotropic thermal parameters

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Fe	0.0071 (2)	0.0097 (2)	0.00244 (7)	0.0	0.00013 (9)	0.0
P(1)	0.0072 (3)	0.0104 (4)	0.0026 (1)	0.0	0.0002 (2)	0.0
P(2)	0.0126 (5)	0.0171 (6)	0.0027 (1)	0.0	0.0011 (2)	0.0
P(3)	0.0076 (3)	0.0097 (4)	0.0024 (1)	0.0	0.0000 (1)	0.0
P(4)	0.0125 (5)	0.0174 (7)	0.0032 (2)	0.0	0.0015 (2)	0.0
O(1)	0.012 (1)	0.033 (3)	0.0032 (4)	0.0	-0.0010 (6)	0.0
O(2)	0.020 (1)	0.021 (1)	0.0043 (3)	0.009 (1)	0.0041 (5)	0.0026 (5)
O(3)	0.0150 (9)	0.012 (1)	0.0051 (4)	-0.0042 (8)	0.0006 (4)	-0.0005 (5)
O(4)	0.0094 (9)	0.026 (2)	0.0023 (3)	0.0	-0.0012 (4)	0.0
O(5)	0.0144 (8)	0.0131 (9)	0.0035 (3)	0.0039 (8)	0.0027 (4)	0.0006 (4)
O(6)	0.010 (1)	0.022 (2)	0.0047 (5)	0.0	-0.0021 (6)	0.0
N	0.0133	0.0138	0.0086	-0.0040	-0.0015	0.0011
C(1)	0.011 (2)	0.036 (4)	0.0021 (5)	0.0	-0.0010 (8)	0.0
C(2)	0.023 (2)	0.021 (2)	0.0042 (5)	0.013 (2)	0.0063 (8)	0.0033 (8)
C(3)	0.0077 (8)	0.011 (1)	0.0038 (4)	0.0007 (9)	-0.0014 (5)	0.0011 (6)

Table 3 (Continued)

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(4)	0.009 (2)	0.044 (5)	0.0031 (6)	0.0	-0.0005 (8)	0.0
C(5)	0.019 (2)	0.016 (2)	0.0038 (4)	0.005 (1)	0.0023 (7)	0.0002 (7)
C(6)	0.009 (1)	0.016 (2)	0.0035 (6)	0.0	0.0003 (8)	0.0
C(7)	0.0078	0.0090	0.0033	-0.0012	0.0011	0.0002
C(8)	0.0080	0.0059	0.0041	0.0034	0.0003	-0.0005

Preparation of $P(OCH_2)_3P$ (L), $OP(OCH_2)_3PO$, and $SP(OCH_2)_3PO$

The ligand L was prepared following the procedure published earlier (1) with the modifications given elsewhere (49). The chalconide derivatives were made from L as described before (1).

Preparation of $OP(OCH_2)_3P$ and $SP(OCH_2)_3PS$

A solution of 2.4 g (0.01 mole) of $Cu(NO_3)_2 \cdot 3H_2O$ in 35 ml of acetone was prepared. Over a period of twenty minutes, 6.4 g (0.04 mole) of L was added with vigorous stirring. The blue color of the solution disappeared and a white precipitate formed. The occasional bluish appearance of the precipitate may be due to co-precipitated $Cu(NO_3)_2$. The mixture was filtered and the filtrate collected over a small amount of magnesium sulfate. The solid was rinsed with 5 ml of acetone and the rinse collected with the filtrate. After two hours the magnesium sulfate was removed by filtration. The acetone was removed under reduced pressure until approximately 5 ml remained. Addition of hexane precipitated a white solid. The solid was recrystallized from an acetone-hexane solution to give 0.6 g of product. A mass spectrum contained a parent ion peak at 168, the molecular weight of $OP(OCH_2)_3P$.

The white solid from the original reaction was suspended in approximately 450 ml of acetonitrile in a three-neck round-bottom flask. The flask was fitted with a stopper, a gas dispersion tube and a gas outlet tube. The gas outlet tube was then connected to a mineral oil bubbler. A steady stream of hydrogen sulfide was introduced to the suspension through the gas dispersion tube for ninety minutes. The gas was introduced at a rate sufficient to cause a slow, steady flow of gas through the mineral oil. The hydrogen sulfide passing through the mineral oil was destroyed by passing it through a concentrated sulfuric acid solution containing manganese dioxide. The suspension was stirred vigorously during the addition of hydrogen sulfide with a magnetic stirrer. The system was flushed with nitrogen for several minutes, and the dark solid removed by filtration. The acetonitrile was removed under reduced pressure to give a white solid which was recrystallized from acetonitrile to give 4.9 g of product. A parent ion peak of 216 in the mass spectrum corresponds to $SP(OCH_2)_3PS$.

Mass spectral peak matching:	Calculated:	215.9234
	Found:	215.9263

Preparation of $SP(OCH_2)_3P$ and $P(OCH_2)_3PS$

To 700 ml of toluene was added 4.5 g (0.03 mole) L and 19.2 g (0.6 mole) sulfur. The mixture was refluxed for twenty-four hours. The toluene was removed under reduced pressure and the resulting solid was extracted with acetonitrile. The acetonitrile was removed under reduced pressure and the resulting solid extracted with carbon disulfide. The white solid remaining after the carbon disulfide extraction was recrystallized from acetonitrile to give 2.2 g of white crystals. The proton nmr corresponds to that of $SP(OCH_2)_3P$ reported earlier (1).

The carbon disulfide was removed under reduced pressure to give a white solid. The solid was recrystallized from acetonitrile to give 0.9 g $P(OCH_2)_3PS$. A parent ion peak appeared in the mass spectrum at 184.

Mass spectral peak matching: Calculated: 183.9513
Found: 183.9531

It was noted that when less than a twenty-fold excess of sulfur was used, some unreacted ligand remained and purification of the two compounds is extremely difficult under these conditions. Moreover this reaction should be worked up in a hood since the odor of $P(OCH_2)_3PS$ is even more obnoxious than that of carbon disulfide.

Preparation of $P(OCH_2)_3PO$

A solution of 2.0 g (12 mmoles) $H_3BP(OCH_2)_3P$ and 2.9 g (12 mmole) benzoyl peroxide in 50 ml dry acetonitrile was refluxed for two and a half hours. At this time an nmr spectrum of the reaction mixture showed nearly equal amounts of $H_3BP(OCH_2)_3P$ and $P(OCH_2)_3PO$.

Preparation of $H_3BP(OCH_2)_3P$

Into a solution of 0.45 g (3 mmoles) of L in 10 ml of anhydrous ether on a vacuum line was condensed 1.5 mmoles of diborane at -196°C. The reaction was warmed to room temperature and the ether removed under vacuum. The white solid remaining was identified as $H_3BP(OCH_2)_3P$ by its proton nmr.

Preparation of $H_3BP(OCH_2)_3PBH_3$

Into a solution of 0.45 g (3.0 mmole) of L in 10 ml of anhydrous ether on a vacuum line was condensed 4.5 mmoles of diborane at -196°C. The diborane was added in seven nearly equal portions over a four hour period. After the addition of each portion the reaction was allowed to warm up to room temperature. The ether and excess diborane were removed under vacuum after the final addition. The white solid remaining was identified as $H_3BP(OCH_2)_3PBH_3$ by its nmr spectrum. This compound is extremely water sensitive and any water in the solvent will react to give the monoadduct $H_3BP(OCH_2)_3P$.

Preparation of $[P(OCH_2)_3PCH_3]BF_4$ and $[CH_3P(OCH_2)_3P]BF_4$

A solution of 0.5 g (3.3 mmoles) of $[(CH_3)_3O]BF_4$ prepared by the method of Meerwein (50) was dissolved in 20 ml of dry acetonitrile. After 0.5 g (3.3 mmoles) of L was dissolved in the solution, it was cooled to -20°. The phosphine-coordinated isomer crystallized out in 27% yield (mp 140° dec). The mother liquor was found from analysis of the nmr spectrum to contain nearly equal amounts of the two isomers.

$(OC)_5CrP(OCH_2)_3P$ and $(OC)_5CrP(OCH_2)_3PCr(CO)_5$

A mixture of 170 ml of methylcyclohexane, 1.0 g (4.5 mmoles) of $Cr(CO)_6$ and 0.5 g (3.3 mmoles) of L was stirred under a nitrogen atmosphere while irradiating for two hours with a 673-A Hanovia lamp. The reaction mixture was filtered and the solvent removed under reduced pressure. The residue was subjected to chromatography on a silica gel column prepared and eluted with an equivolume hexane-benzene mixture. The bridged compound was eluted first followed by the complex of lower molecular weight. The parent ions in the mass spectra of the bridged compound (536) and of $(OC)_5CrP(OCH_2)_3P$ (334) were observed.

cis-$(OC)_4Cr[P(OCH_2)_3P]_2$

A mixture of 10 ml of methylcyclohexane, 10 ml of benzene, 0.32 g (2.1 mmoles) of L, and 0.26 g (1.0 mmole) of norbornadienetetracarbonylchromium prepared by the method of King (51), was stirred together for twenty-four hours at room temperature. The solution was cooled to

-20° and the liquid decanted. The residue was extracted once with acetonitrile and the extract evaporated to give the desired compound as a white solid in 4% yield. A parent ion peak of 468 was observed in the mass spectrum of the compound.

$(OC)_5MoP(OCH_2)_3P$ and $(OC)_5MoP(OCH_2)_3PMo(CO)_5$

A mixture composed of 60 ml of methylcyclohexane, 2.0 g (7.6 mmoles) of $Mo(CO)_6$, and 1.0 g (6.6 mmoles) of L was stirred under nitrogen atmosphere while refluxing for seven hours. The solvent was removed under reduced pressure and the white residue was subjected to chromatography on a silica gel columns prepared and eluted in the same manner as for the chromium analogs. A 20% yield (based on L) was obtained for $(OC)_5MoP(OCH_2)_3P$, and a 1% yield (based on $Mo(CO)_6$) was obtained for the bridged complex. A mass spectrum of the bridged complex revealed a parent peak at the calculated mass of 628 based on ^{98}Mo, and the $(OC)_5MoP(OCH_2)_3P$ complex showed a parent ion of 390 in its mass spectrum.

Anal.

Calculated: for $MoC_8H_6O_8P_2$: C, 24.76; H, 1.56; P, 15.96.

Found: C, 24.68, H, 1.72; P, 14.96.

$(OC)_5WP(OCH_2)_3P$ and $(OC)_5WP(OCH_2)_3PW(CO)_5$

A mixture of 50 ml of benzene, 0.26 g (1.7 mmoles) of L, and 0.72 g (1.7 mmoles) of $(OC)_5WNH_2C_6H_5$, prepared by the method of Angelici (52), was stirred together for twenty-four hours at room temperature. The white solid remaining after evaporation of the solvent was subjected to chromatography on a silica gel column with a 50% hexane-benzene solution. A trace of the bridged complex was eluted first, followed closely by the $(OC)_5WP(OCH_2)_3P$. The parent ion of mass 476 based on ^{184}W was observed in the mass spectrum of the latter compound. The $(OC)_5WP(OCH_2)_3P$ was obtained in 25% yield.

The bridged compound was prepared in better yield (23%) by using a lower ligand to metal ratio (1:2). Thus a mixture of 20 ml of benzene, 0.15 g (1 mmole) of L, and 0.84 g (2 mmoles) of $(OC)_5WNH_2C_6H_5$ was treated as described above. The crude white product obtained upon evaporation under reduced pressure was chromatographed as in the previous separation to give the pure product. A mass spectrum of this bridged complex revealed a parent ion peak at mass 800.

$[(OC)_5WP(OCH_2)_3PCH_3]BF_4$

A mixture of 50 ml of dichloromethane, 0.48 g (1 mmole) of $(OC)_5WP(OCH_2)_3P$, and 0.15 g (1 mmole) of $[(CH_3)_3O]BF_4$

was stirred under nitrogen for two hours at room temperature. The solvent was removed with a stream of dry nitrogen. The solid was recrystallized from acetonitrile to give a 10% yield of the complex.

$(OC)_4FeP(OCH_2)_3P$, $(OC)_4FeP(CH_2O)_3P$, and $(OC)_4FeP(OCH_2)_3PFe(CO)_4$

A solution of 2.0 ml (15 mmoles) $Fe(CO)_5$ and 2.3 g (15 mmoles) of $P(OCH_2)_3P$ in 60 ml ethylbenzene in a quartz tube was irradiated for two and one-half hours with a 673-A Hanovia lamp. The reaction was filtered and the solvent removed under reduced pressure. The residue was purified by chromatography on a silica gel column using an equivolume hexane-benzene solution as the elutant.

The first compound eluted had a parent ion peak in the mass spectrum which matched the calculated one for the bridged compound (488). The complex $(OC)_4FeP(CH_2O)P$ was eluted next, and was followed by the $(OC)_4FeP(OCH_2)_3P$ complex. Parent ion peaks of 320 were observed for both complexes.

<u>trans</u>-$(OC)_3Fe[P(OCH_2)_3P][P(CH_2O)_3P]$

A white precipitate formed when a hexane solution (600 ml) containing 4.6 g (30 mmoles) L and 40 ml (30 mmoles) $Fe(CO)_5$ was irradiated with a 673-A Hanovia lamp. After four and one-half hours of irradiation, the hexane solution was decanted and the solid was extracted with benzene. The benzene was then removed under reduced pressure and the residue chromatographed on a silica gel column. With a 9:1 benzene-hexane elutant, unreacted L was eluted first, followed closely by the complex. A parent ion peak of 444 was observed in the mass spectrum.

cis-$(OC)_4Mo[P(OCH_2)_3P][P(CH_2O)_3P]$

This complex was generously supplied by Patrick D. Plummer.

Uncharacterized Complexes of L

$Ni(CO)_4 + L$

To a benzene solution (15 ml) of 3.0 g (20 mmoles) of L was added 3.4 g (20 mmoles) of $Ni(CO)_4$ giving an immediate vigorous evolution of gas. After forty-five minutes, the reaction was cooled to -20°C until the solvent froze. The solution was warmed until the benzene just melted, and then was quickly filtered. A precipitate formed in the filtrate on standing. This was also filtered, and more precipitate was observed to form. The precipitate is insoluble in benzene and acetonitrile. Thin layer chromatography experiments showed a number of compounds, but no compounds were eluted when column chromatography was attempted. Apparently a polymer formed.

NiI_2 + 5L + $(CH_3CH_2)_2NH$

In 50 ml of acetonitrile was dissolved 0.48 g (2 mmoles) of NiI_2. The solution was filtered and 1.5 g (10 mmoles) of L dissolved in acetonitrile added to the filtrate followed by the dropwise addition of 0.5 ml diethylamine. The color rapidly disappeared, and a light brown precipitate formed. The precipitate should be NiL_4 (53) but was not characterizable due to its complete insolubility. Some $OP(OCH_2)_3P$ was found in the mother liquor indicating that the expected redox reaction took place but that polymer was produced instead of the NiL_4.

RESULTS AND DISCUSSION

The composition and molecular weights of all the compounds were confirmed by observation of the parent ion peaks in their mass spectra. Because most of the complexes showed evidence of decomposition on standing, commercial elemental analyses were not deemed reliable due to the time lapse involved. The analysis of the stable $(OC)_5MoP(OCH_2)_3P$ complex, however, is in agreement with its formulation as a monosubstituted complex.

The symmetries of the metal complexes of L can be determined from the characteristic infrared absorptions in the carbonyl region which were assigned by analogy to those for the analogous $P(OCH_2)_3CCH_3$ and $P(CH_2O)_3CCH_3$ complexes (see Table 4). Of the three and six possible bands in the $(OC)_5ML$ and $(OC)_5MLM(CO)_5$ systems, respectively, (where M = chromium, molybdenum and tungsten), only the A_1^2 and E modes were resolved. The cis-configuration of the disubstituted chromium and molybdenum complexes is supported by the observation of three of the characteristic four carbonyl modes (A_1^1, A_1^2, and B_1, B_2).

Three bands are possible for a monosubstituted iron pentacarbonyl complex with the ligand in the axial position. All three bands were observed in the $Fe(CO)_4$ L complexes. Again, when L bridges two iron carbonyl groups, only three

Table 4. Infrared frequency assignments in the carbonyl region

Compound	Frequencies (cm^{-1}) and assignments[a]			Solvent
	A_1^2	A_1^1	E	
$(OC)_5CrP(OCH_2)_3P$	2077 (w)		1951 (vs)	CH_2Cl_2
$(OC)_5CrP(OCH_2)_3CCH_3$[b]	2082 (w)	1995 (sh)	1960 (vs)	$CHCl_3$
$(OC)_5MoP(OCH_2)_3P$	2077 (w)		1948 (vs)	CH_2Cl_2
$(OC)_5MoP(OCH_2)_3CCH_3$[b]	2085 (w)	2001 (sh)	1962 (vs)	$CHCl_3$
$(OC)_5WP(OCH_2)_3P$	2085 (w)	1907 (sh)	1948 (vs)	CH_2Cl_2
$[(OC)_5WP(OCH_2)_3PCH_3]BF_4$	2085 (w)	1912 (sh)	1947 (vs)	CH_2Cl_2
$(OC)_5WP(OCH_2)_3CCH_3$[b]	2084 (w)	1993 (sh)	1958 (vs)	$CHCl_3$
$(OC)_5CrP(OCH_2)_3PCr(CO)_5$	2073 (m)		1956 (vs)	CH_2Cl_2
$(OC)_5MoP(OCH_2)_3PMo(CO)_5$	2078 (m)		1951 (vs)	CH_2Cl_2
$(OC)_5WP(OCH_2)_3PW(CO)_5$	2077 (m)		1948 (vs)	CH_2Cl_2
$(OC)_4FeP(OCH_2)_3P$	2068 (s)	1991 (s)	1954 (vs)	CH_2Cl_2
$(OC)_4FeP(OCH_2)_3CCH_3$[b]	2065 (s)	1996 (vs)	1965 (vs)	$CHCl_3$

[a] vs=very strong, sh=shoulder, s=strong, m=medium, w=weak. Values are precise to ± 2 cm^{-1}.

[b] See reference (54).

Table 4 (Continued)

Compound	Frequencies (cm^{-1}) and assignments[a]			Solvent
	$A_1{}^2$	$A_1{}^1$	E	
$(OC)_4FeP(CH_2O)_3P$	2065(s)	1993 (s)	1946 (vs)	CH_2Cl_2
$(OC)_4FeP(CH_2O)_3CCH_3$[c]	2059 (s)	1988 (s)	1949 (vs)	CH_2Cl_2
$(OC)_4FeP(OCH_2)_3PFe(CO)_4$	2068 (s)	1999 (s)	1963 (vs)	CH_2Cl_2
	$A_1{}^2$	$A_1{}^1$	B_1B_2	
cis-$(OC)_4Cr[P(OCH_2)_3P]_2$	2037 (m)	1946 (sh)	1924 (vs)	CH_2Cl_2
cis-$(OC)_4Cr[P(OCH_2)_3CCH_3]_2$[d]	2043 (m)	1950 (sh)	1925 (vs)	CH_2Cl_2
		E'		
trans-$(OC)_3Fe[P(OCH_2)_3P][P(H_2O)_3P]$		1927		CH_2Cl_2
trans-$(OC)_3Fe[P(OCH_2)_3CCH_3]_2$[b]		1933		$CHCl_3$

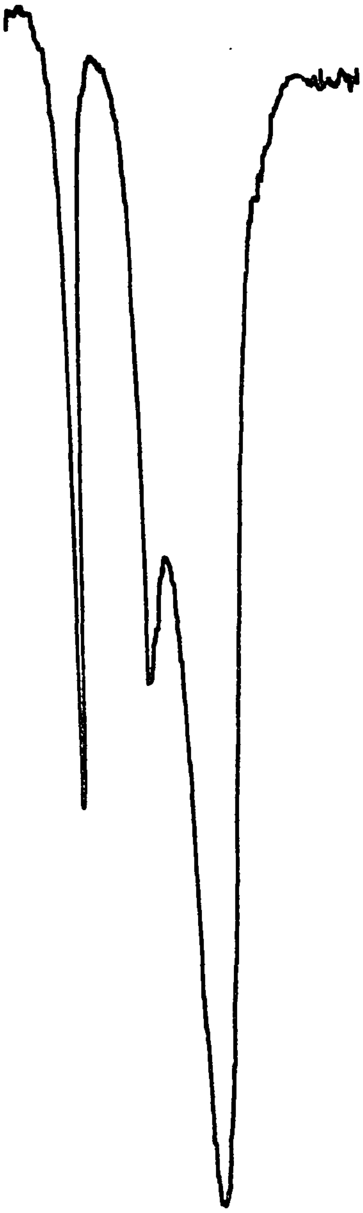
[c] See reference (2).

[d] See reference (55).

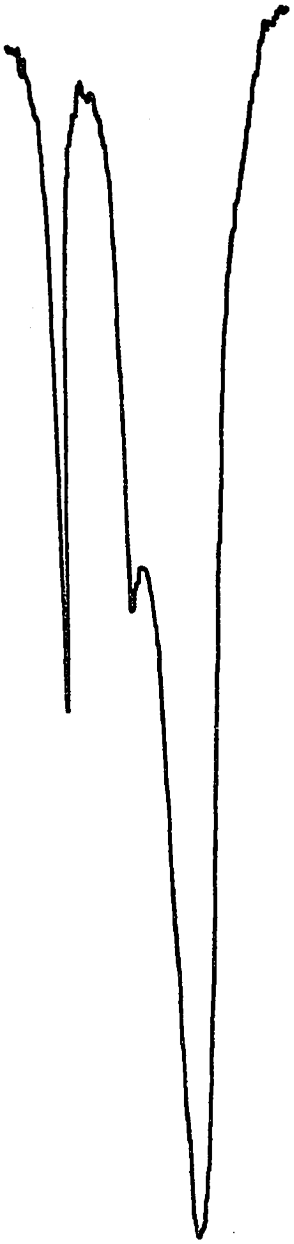
bands are observed instead of the six which are possible. The single band expected for a trans-disubstituted iron tricarbonyl complex is observed.

The mode of attachment of L to the metal can not be unambiguously assigned on the basis of the positions of the carbonyl infrared bands. The iron(O)tetracarbonyl series of complexes illustrates this fact. Three complexes were isolated which exhibited the characteristic carbonyl bands of $Fe(CO)_4L$. A comparison with the spectra of the analogous $P(OCH_3)_2CCH_3$ and $P(CH_2O)_3CCH_3$ complexes does not help in the assignment of the three possibilities: $(OC)_4FeP(OCH_2)_3P$, $(OC)_4FeP(CH_2O)_3P$, and $(OC)_4FeP(OCH_2)_3PFe(CO)_4$. It was expected that the infrared spectrum of the bridged compound would be the sum of the first two compounds. Thus six peaks were expected, or at least a broadening of the peaks if overlap of the bands took place. Figure 5 shows that no broadening is observed. Similarly no broadening of the bands for $(OC)_5MP(OCH_2)_3PM(CO)_5$ compared to those for $(OC)_5MP(OCH_2)_3P$ where M = Cr, Mo, and W was observed. The reason for this phenomenon is not obvious. Exchange of the metal carbonyl fragments on the ligand sites is unlikely since this would have been observed in the nmr spectra. For example, in a mixture of $(OC)_5WP(OCH_2)_3PW(CO)_5$ and free ligand, the proton resonances of both species are present and both occur at the same

Figure 5. Infrared spectrum in the carbonyl region for (a) $(OC)_4FeP(OCH_2)_3P$, (b) $(OC)_4FeP(OCH_2)_3PFe(CO)_4$



a



b

chemical shift as solutions of the pure compound. Hence, if exchange occurs, the free ligand is not involved as would be expected.

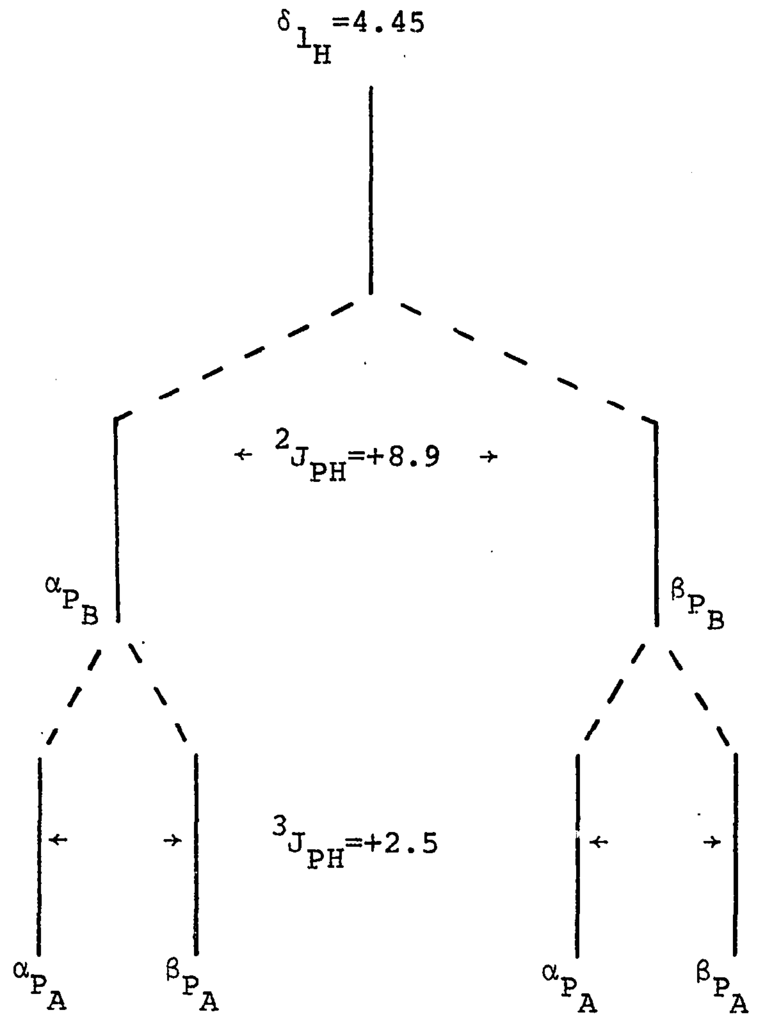
Distinguishing bidentate compounds of L from monodentate compounds and the mode of ligand attachment in the latter can be accomplished using nmr methods.

Because of the two chemically different phosphorus atoms of L, the proton nmr spectrum consists of a doublet of doublets (Figure 6). The phosphorus-proton coupling constants can be read directly from the proton spectrum (2.5 and 8.9 Hz), but distinguishing J_{POCH} ($^3J_{PH}$) from J_{PCH} ($^2J_{PH}$) is not possible without further information. The necessary information has been obtained in two different ways. The first method involves comparison of the proton nmr spectrum of L with that of $P(OCH_2)_3CCH_3$ and $P(CH_2O)_3CCH_3$. In the phosphite ligand $^3J_{PH}$=1.8 Hz (56) and $^2J_{PH}$=8.0 Hz (2) in the phosphine. From this comparison, the values of $^2J_{PH}$ and $^3J_{PH}$ in L are 8.9 and 2.5 Hz respectively. Confirmation of this assignment can be gained by examining the phosphorus nmr spectrum. Each phosphorus peak is split into a septet by the six equivalent protons and into a doublet by the other phosphorus. The spectrum consists of two doublets of septets (Figure 7). The splitting in each septet will be J_{PH}, and the distance between the center of the septets in each doublet will equal $^3J_{PP}$. The chemical shift of each

Figure 6. Schematic ^{1}H nmr spectrum of $P_A(OCH_2)_3P_B$

δ is in ppm with respect to tetramethylsilane

J values are in Hz

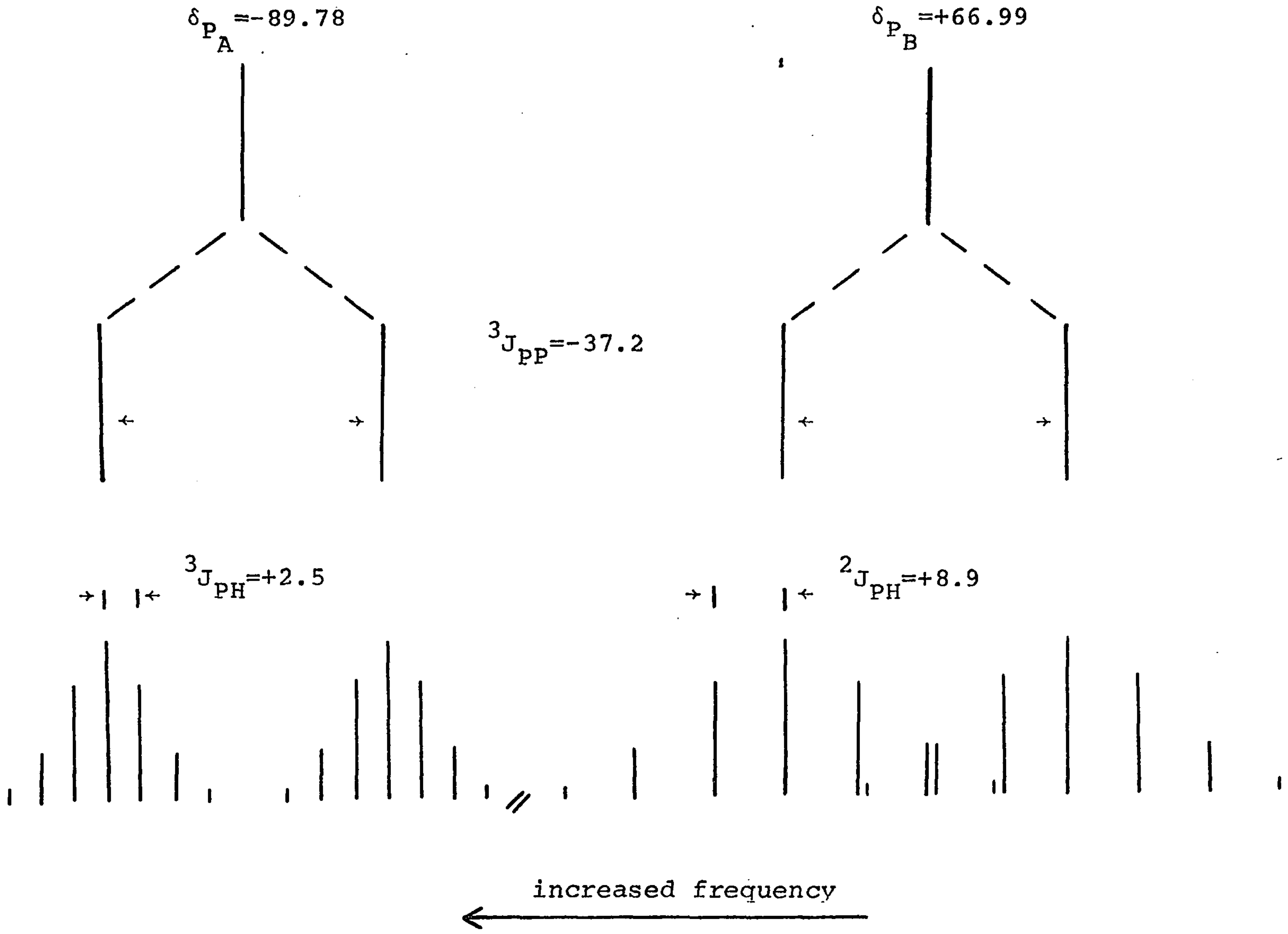


increasing frequency ←

Figure 7. Schematic ^{31}P nmr spectrum of $P_A(OCH_2)_3P_B$

δ values are in ppm with respect to 85% phosphoric acid

J values are in Hz


δ_{P_A}=-89.78
δ_{P_B}=+66.99
$^3J_{PP}$=-37.2
$^3J_{PH}$=+2.5
$^2J_{PH}$=+8.9
increased frequency

phosphorus atom corresponds to the middle of the appropriate doublet of septets. Comparison of the phosphorus nmr parameters of L with $P(OCH_2)_3CCH_3$ ($\delta\,{}^{31}P$=-91.5) and $P(CH_2O)_3CCH_3$ ($\delta\,{}^{31}P$=+80.5) permits assignment of the downfield peaks as the phosphite-phosphorus and the upfield peaks as the phosphine-phosphorus. The assignment of ${}^3J_{PH}$=2.5 and ${}^2J_{PH}$=8.9 follows from the septet splittings. These comparisons are summarized in Tables 5 and 6.

Coordination of the phosphorus lone pairs by chalconides, metal carbonyls, carbonium ions, boron groups and other groups will change the numerical values of ${}^2J_{PH}$, ${}^3J_{PH}$, and ${}^3J_{PP}$ but will not, in general, change the features of the spectra as described.

The procedures described afford chemical shifts and numerical values for the coupling constants but not their signs. To obtain sign information, INDOR (internuclear double resonance) techniques must be used. This technique has been described extensively elsewhere (57-60), and only a brief description of its application to this system will be given here.

As stated earlier, the proton spectrum of L at fixed field has absorptions at four different frequencies. Continuous irradiation at a fixed frequency corresponding to one of the four peaks gives constant absorption (assuming insufficient power is used to cause saturation).

Table 5. Nmr parameters for $P(OCH_2)_3P$, some analogous bicyclic compounds, and their transition metal derivatives[a]

Compound	$^2J_{PH}$[b]	$^3J_{PH}$[b]	δ^1H[b]	$^3J_{PP}$[c]	$\delta^{31}PO_3$[c]	$\delta^{31}P(CH_2)_3$[c]
$P(OCH_2)_3P$[d]	+8.9	+2.5	4.45	-37.2	-89.78	+66.99
$P(OCH_2)_3CCH_3$[e]		2	3.93		-91.5	
$P(CH_2O)_3CCH_3$[f]	8.0		4.30			+80.5[g]
$(OC)_5CrP(OCH_2)_3P$[h]	+8.4	+5.3	4.87	-3.0±0.3	-154.47	+68.57

[a] Spectra were obtained in acetonitrile unless otherwise indicated.

[b] The values and signs were obtained from ^1H and ^{31}P INDOR spectra, respectively. J values are precise to ± 0.2 Hz. δ^1H values are reported with respect to internal tetramethylsilane and are precise to ± 0.02 ppm.

[c] These values were obtained from ^{31}P INDOR spectra. $\delta^{31}P$ values are precise to 0.02 ppm and are reported with respect to external 85% phosphoric acid (see reference 45). J values are precise to ± 0.5 Hz.

[d] Determined in dimethylsulfoxide-d_6. See reference 45.

[e] Determined in deuterochloroform. See reference 61.

[f] Determined in carbon tetrachloride. See reference 2.

[g] Determined by direct observation in benzene. See reference 45.

[h] See reference 45.

Table 5 (Continued)

Compound	$^2J_{PH}$[b]	$^3J_{PH}$[b]	$\delta\,^1H$[b]	$^3J_{PP}$[c]	$\delta\,^{31}PO_3$[c]	$\delta\,^{31}P(CH_2)_3$[c]
cis-$(OC)_4Cr[P(OCH_2)_3P]_2$[h]	+8.4[i]	+5.3[i]	4.91	-2.4	-157.21	+68.52
$(OC)_5CrP(OCH_2)_3CCH_3$[e]		4.3	4.24		-162	
$(OC)_5MoP(OCH_2)_3P$[h]	+8.4	+5.2	4.85	-4.6	-130.82	+68.60
$(OC)_5MoP(OCH_2)_3CCH_3$[e]		4.2	4.20		-136	
$(OC)_5WP(OCH_2)_3P$[h]	+8.5	+5.5	5.02	-0.4	-109.09	68.75
$(OC)_5WP(OCH_2)_3CCH_3$[e]		4.4	4.25		-114	
$(OC)_4FeP(OCH_2)_3P$[h]	+8.4	+6.1	5.00	+8.6	-157.44	+71.38
$(OC)_4FeP(CH_2O)_3P$[h]	+0.4	+2.8	4.75	+47.1±2.5	-87.37	-22.42
$(OC)_5CrP(OCH_2)_3PCr(CO)_5$[h]	+2.0	+5.6	5.00	+66.1±0.8	-152.52	-8.21
$(OC)_5MoP(OCH_2)_3PMo(CO)_5$[h]	+2.3	+5.4	4.98	+63.7	-130.97	+18.94
$(OC)_5WP(OCH_2)_3PW(CO)_5$[h]	+1.5	+5.5	4.82	+73.8	-108.37	+36.34

[i] The ^1H nmr spectrum for this compound is not first order. See Discussion.

Table 5 (Continued)

Compound		$^2J_{PH}$ [b]	$^3J_{PH}$ [b]	$\delta\,^1H$ [b]	$^3J_{PP}$ [c]	$\delta\,^{31}PO_3$ [c]	$\delta\,^{31}P(CH_2)_3$ [c]
$(OC)_4FeP(OCH_2)_3PFe(CO)_4$[h]		+0.4	+6.3	5.15	+95.3	-160.40	-22.06
$[(OC)_5WP(OCH_2)_3PCH_3]BF_4$[h,j]		-5.8	+6.3	5.70	+143.2	-113.00	-2.98
cis-$(OC)_4Mo$[k]	$P(OCH_2)_3P$	+8.5	+5.2	4.84	-6.0	-133.3	+69.3
	$P(CH_2O)_3P$	+2.6	+2.6	4.46	+20.0	-88.0	+13.1
trans-$(OC)_3Fe$[l]	$P(OCH_2)_3P$	+8.7	+6.2	4.95	+9.0	-161.3	+68.0
	$P(CH_2O)_3P$	0.9	2.8	4.60			

[j] $^2J_{PCH_3}$ is 17.5 ± 0.2 Hz from the ^1H spectrum.

[k] $^2J_{PP}$ = 38.0 Hz.

[l] $^3J_{PP}$ = 38.0 Hz.

Table 6. Nmr parameters for non-metallic derivatives of $P(OCH_2)_3P$

Compound	$^2J_{PH}$ [a]	$^3J_{PH}$ [a]	δ^1H [a]	$^3J_{PP}$ [b]	$\delta^{31}PO_3$ [b]	$\delta^{31}P(CH_2)_3$ [b]	Solvent
$OP(OCH_2)_3P$	+7.5	+7.5	5.15	+65	+14.25	+69.98	CH_3CN
$OP(OCH_2)_3CCH_3$ [c]		6	4.48		+7.97		$(CH_3)_2SO$
$P(OCH_2)_3PO$	-8.1	+3.2	4.60	+140	-85.53	-7.45	CH_3CN
$OP(CH_2O)_3CCH_3$ [d]	7.5		4.40			-16.00	CD_3CN
$SP(OCH_2)_3P$ [d]	+7.6	+7.5	5.11	+48.1	-52.06	+70.89	$(CD_3)_2SO$
$SP(OCH_2)_3CCH_3$ [c]		7	4.48		-57.4		$(CH_3)_2SO$
$P(OCH_2)_3PS$	-5.8	+3.0	4.60	+118	-90.49	-6.30	CH_3CN
$SP(CH_2O)_3CCH_3$ [e]	5.6		4.49				$(CH_3)_2CO$

[a] The values and signs were obtained from ^1H and ^{31}P INDOR spectra respectively. J values are precise to ± 0.2 Hz. δ^1H values are reported with respect to internal tetramethylsilane and are precise to ± 0.02 ppm.

[b] These values were obtained from ^{31}P INDOR spectra. $\delta^{31}P$ values are precise to ± 0.02 ppm and are reported with respect to external 85% phosphoric acid (45).

[c] See reference 56. The values for $^3J_{PH}$ in this reference are reversed but are given correctly in this table.

[d] See reference 45.

[e] See reference 2.

Table 6 (Continued)

Compound	$^2J_{PH}$[a]	$^3J_{PH}$[a]	$\delta\,^1H$[a]	$^3J_{PP}$[b]	$\delta\,^{31}PO_3$[b]	$\delta\,^{31}P(CH_2)_3$[b]	Solvent
$OP(OCH_2)_3PO$[d]	-8.2	+8.3	5.09	+139.0	+18.17	-5.48	$(CD_3)_2SO$
$SP(OCH_2)_3PS$	-5.4	+8.6	5.07	+150	-49.28	-3.91	CH_3CN
$SP(OCH_2)_3PO$[d]	-9.0	+8.2	5.16	+151.3	-49.28	-5.50	$(CD_3)_2SO$
$[CH_3P(OCH_2)_3P]BF_4$[f]	+8.7	+6.1	5.45	+46.2	-51.03	+59.80	CH_3CN
$[CH_3P(OCH_2)_3CCH_3]BF_4$[g]		5.1	4.89		-60.15		CH_3CN
$[P(OCH_2)_3PCH_3]BF_4$[h]	-5.6	+3.1	5.15	+114.6	-89.58	-2.56	CH_3CN
$H_3BP(OCH_2)_3P$[i]	9.0	5.5	4.97	10		+66.25	CH_3CN
$H_3BP(OCH_2)_3CCH_3$[j]		4.2	4.30		-97		CD_3CN

[f] $^2J_{PCH_3}$ is 18.7 ± 0.2 Hz. See reference 45.

[g] $^2J_{PCH_3}$ is 19.0 ± 0.5 Hz. See reference 45.

[h] $^2J_{PCH_3}$ is 17.0 ± 0.2 Hz. See reference 45.

[i] δ_{BH} is 0.50 ppm with respect to tetramethylsilane. $^1J_{BH}$ is 100 ± 5 Hz and $^2J_{PBH}$ is 25 ± 3 Hz.

[j] See reference 62.

Table 6 (Continued)

Compound	$^2J_{PH}$[a]	$^3J_{PH}$[a]	$\delta\,^1H$[a]	$^3J_{PP}$[b]	$\delta\,^{31}PO_3$[b]	$\delta\,^{31}P(CH_2)_3$[b]	Solvent
$H_3BP(OCH_2)_3PBH_3$[k]	0	5.9	4.98				CH_3CN
$H_3BP(CH_2O)_3CCH_3$[e]	0.8		4.46				$CDCl_3$

[k] Only a broad peak is observed in the B-H region.

While remaining on the proton peak, the irradiation of a second frequency in the frequency range corresponding to one of the phosphorus nuclei will cause a perturbation of the monitored proton peak. As the frequency range of the phosphorus nuclei is swept, the perturbations give rise to an inverted spectrum corresponding to the phosphorus spin states responsible for the existence of the monitored proton peak. A complete phosphorus nmr spectrum of L can be obtained by performing INDOR experiments on proton peaks arising from the different spin states of the phosphorus nuclei. As can be seen from Figure 6, if the two outside or two inside proton peaks are chosen for the INDOR experiments, only two experiments are necessary. Otherwise three proton peaks will be needed.

Each of the two proton peaks used in the INDOR experiment is associated with one of the peaks of each phosphorus doublet. Sign information is obtained by observing which peaks of the three coupled nuclei are associated with respect to each other. (Since two frequencies of each nucleus are being discussed, they will be referred to as the higher and lower frequencies.) Four unique associations are possible. First, the higher frequencies of each of the three nuclei may be associated, in which case the signs of ${}^3J_{PH}$, ${}^2J_{PH}$ and ${}^3J_{PP}$ will all be the same. A second possibility involves the lower frequency of the phosphite-phosphorus nucleus associated with the higher frequency of the proton and phosphine-phosphorus nuclei. In this situation, $^{3}J_{PH}$ and $^{3}J_{PP}$ will be of the same sign but of the opposite sign to $^{2}J_{PH}$. Another possibility involves the lower frequency of the phosphine-phosphorus nucleus associated with the higher frequency of the proton and phosphite-phosphorus nuclei. The sign of $^{3}J_{PH}$ will then be the opposite of $^{2}J_{PH}$ and $^{3}J_{PP}$. The final possibility involves the higher proton nucleus frequency being associated with the lower frequency of each of the two phosphorus nuclei, in which case $^{3}J_{PP}$ will differ in sign from $^{2}J_{PH}$ and $^{3}J_{PH}$.

Absolute signs can only be determined when the sign of one of the three related coupling constants is known. Bertrand has found the absolute sign of $^{3}J_{PH}$ in $P(OCH_2)_3P$ and $OP(OCH_2)_3PO$ to be positive (60). The magnitude of the $^{3}J_{PH}$ values for all of the derivatives of L listed in Tables 5 and 6 lie between the magnitude of the $^{3}J_{PH}$ values for these two compounds and hence $^{3}J_{PH}$ is assumed to be positive in these derivatives. This assumption then permits the determination of the signs for $^{2}J_{PH}$ and $^{3}J_{PP}$.

The nmr spectrum of the disubstituted complexes is more complicated than for compounds containing only one ligand. Three of these complexes have been studied: cis-$(OC)_4Cr[P(OCH_2)_3P]_2$, cis-$(OC)_4Mo[P(OCH_2)_3P][P(CH_2O)_3P]$, and trans-$(OC)_3Fe[P(OCH_2)_3P][P(CH_2O)_3P]$. The spectra of the molybdenum and iron complexes are similar, and they will be discussed first. The proton spectrum of the iron complex consists of eight lines. Each ligand gives a four-line spectrum as discussed above and the proton nmr spectrum of trans-$(OC)_3Fe[P(OCH_2)_3P][P(CH_2O)_3P]$ is essentially the sum of the nmr spectra of $(OC)_4FeP(OCH_2)_3P$ and $(OC)_4FeP(CH_2O)_3P$ as shown in Figures 8, 9, and 10. The nmr parameters of the ligands in the disubstituted complex have changed only slightly from those of the corresponding monosubstituted complexes and the same is true in the molybdenum complex. The proton chemical shifts for the two ligands are clearly resolved in acetonitrile but overlap is observed in benzene.

The phosphorus nmr spectrum is not simply the sum of the two spectra of the monosubstituted complexes. The four phosphorus atoms are all chemically different, and in addition to the phosphorus-phosphorus coupling in each ligand, the two coordinated phosphorus atoms will be coupled ($^2J_{PP}$). Moreover, the possibility exists of coupling between the coordinated phosphorus of one ligand and the non-coordinated phosphorus of the other ligand ($^5J_{PP}$). The spectrum of cis-$(OC)_4Mo[P(OCH_2)_3P][P(CH_2O)_3P]$ obtained by the INDOR method contains twelve resonances. A schematic of the spectrum is given in Figure 11 while in Figure 12 is shown the INDOR spectrum of one of the twelve resonances.

Figure 8. ^1H nmr spectrum of $(OC)_4FeP(OCH_2)_3P$. $^2J_{PH}$ and $^3J_{PH}$ are +8.4 and +0.1 Hz, respectively

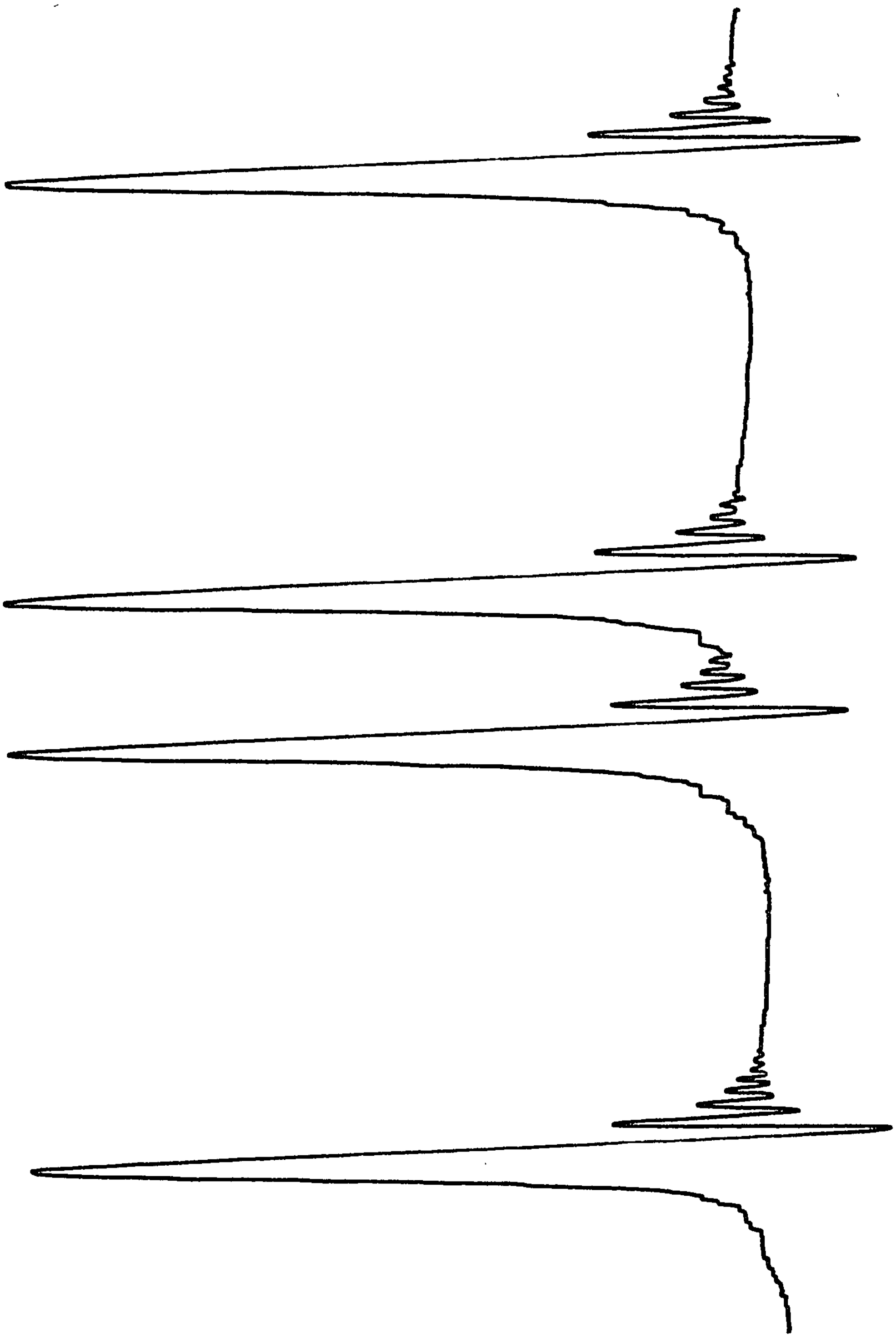


Figure 9. ^{1}H nmr spectrum of $(OC)_4FeP(CH_2O)_3P$. $^{2}J_{PH}$ and $^{3}J_{PH}$ are +0.4 and 2.8 Hz, respectively

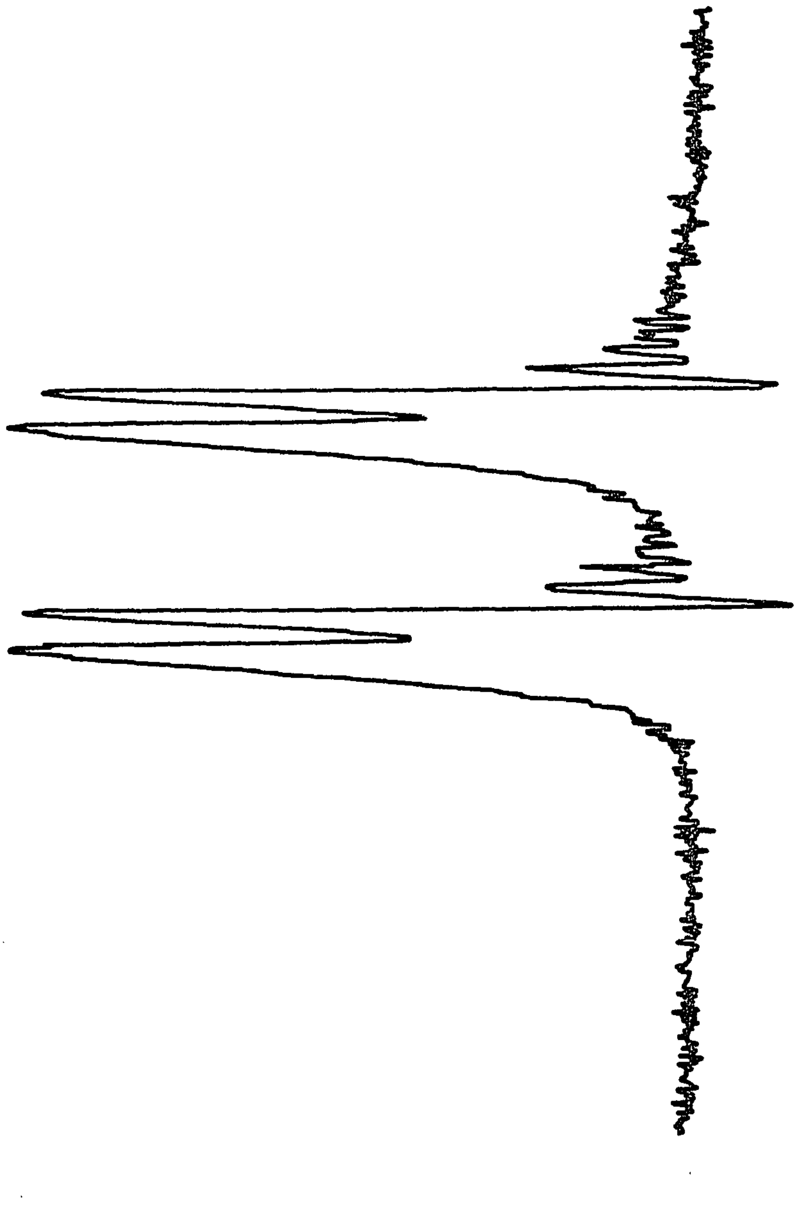


Figure 10. ^1H nmr spectrum of <u>trans</u>-$(OC)_3Fe[P(OCH_2)_3P][P(CH_2O)_3P]$. $^2J_{PH}$ and $^3J_{PH}$ are +8.7 and +6.2 Hz, respectively, for the phosphite coordinated ligand, and 0.9 and 2.8 Hz, respectively, for the phosphine coordinated ligand

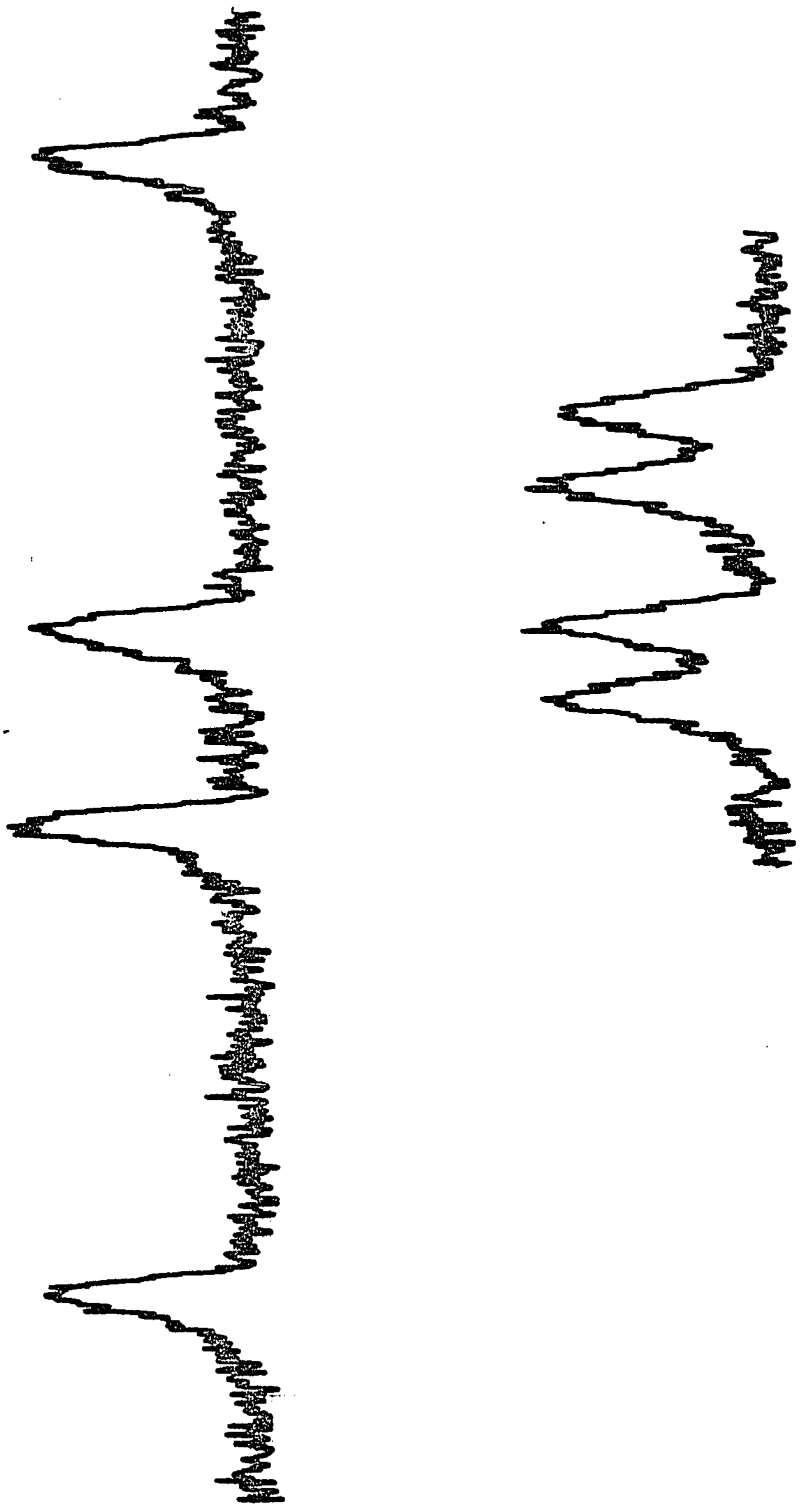


Figure 11. The nmr schematic of *cis*-$(OC)_4Mo[P(OCH_2)_3P][P(CH_2O)_3P]$. The upper schematic is of the ^{31}P spectrum while the lower one is of the ^{1}H spectrum. All J values are in Hz. $\delta^{31}P$ values are in ppm with respect to external 85% phosphoric acid and $\delta^{1}H$ values are in ppm with respect to internal tetramethylsilane. Each line in the ^{31}P schematic represents a septet

^{31}P SCHEMATIC: EACH LINE REPRESENTS A SEPTET

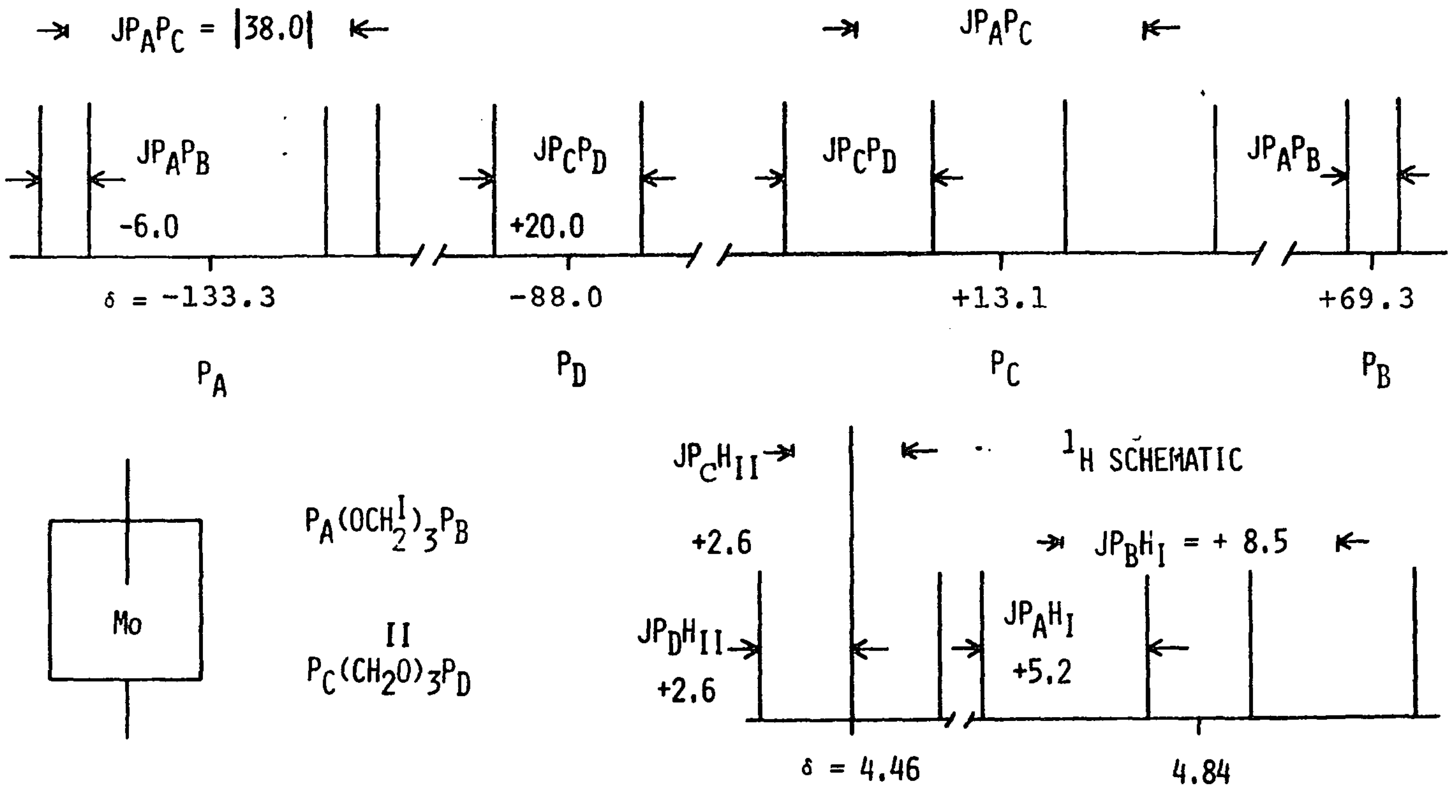
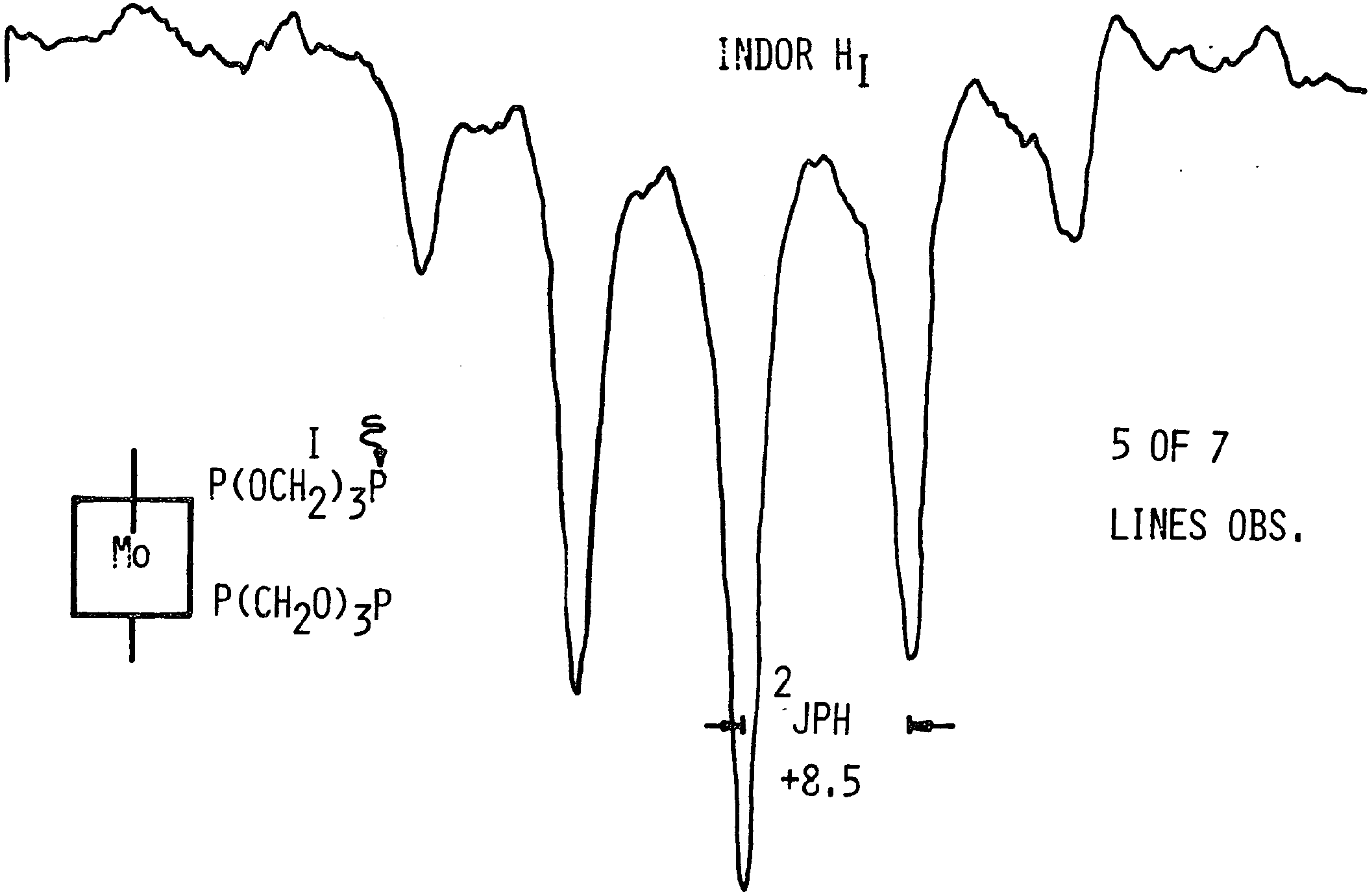


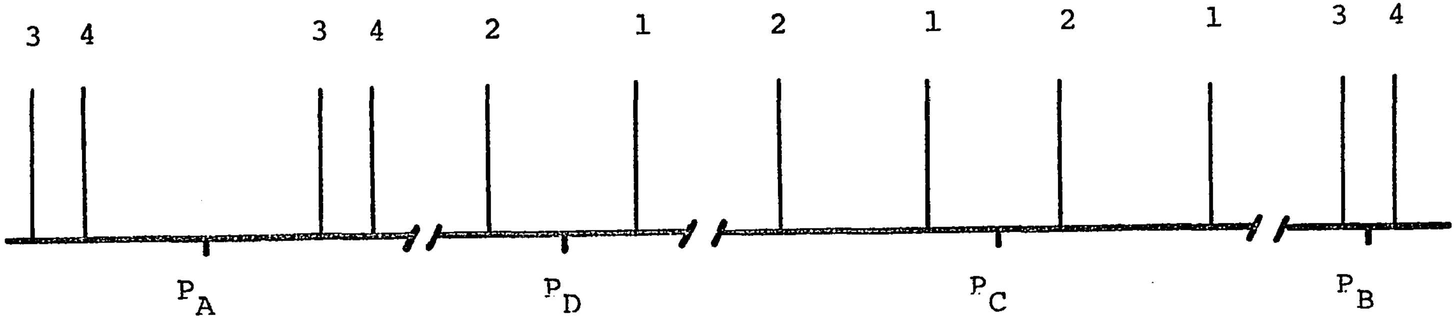
Figure 12. The ^{31}P INDOR spectrum of one of the twelve peaks in cis-$(OC)_4MO[P(OCH_2)_3P][P(CH_2O)_3P]$. See Figure 11. Five of the 7 lines are observed in this spectrum of the indicated phosphorus nucleus

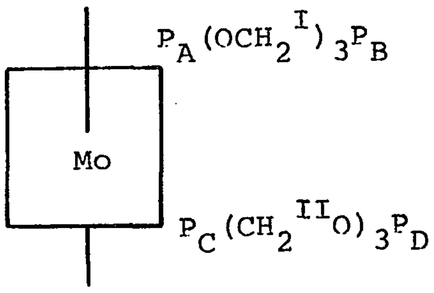

INDOR H_I
I
$P(OCH_2)_3P$
Mo
$P(CH_2O)_3P$
$^2J_{PH}$
+8.5
5 OF 7
LINES OBS.

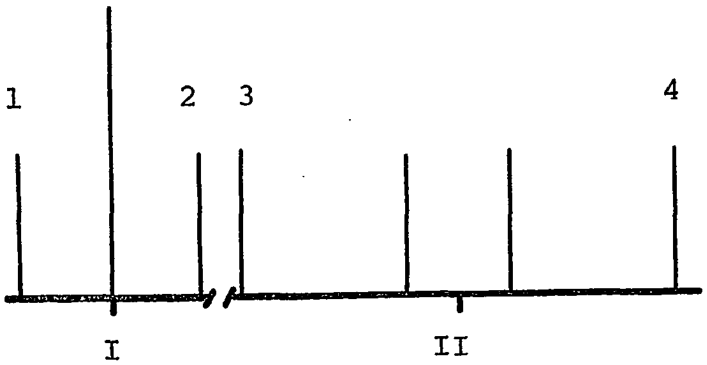
The spectrum consists of two doublets and two doublet of doublets. The doublets arise from the non-coordinated phosphorus atoms which are coupled to the nearest coordinated phosphorus nuclei ($^3J_{PP}$). Each coordinated phosphorus is coupled to two chemically different phosphorus atoms; a situation analogous to the protons in the ligand itself. If any long-range $^5J_{PP}$ coupling occurs it would be revealed as additional fine structure in each resonance. As Figure 12 shows, the only splitting observed is due to $^2J_{PH}$ and so $^5J_{PP}$ is undoubtedly less than one Hz. It is interesting to note that if the phosphorus spectrum had been observed directly, many of the peaks could not have been observed since J_{PH} is of the same magnitude as $^3J_{PP}$ for the phosphite coordinated ligand and since direct observation gives poorer resolution than that obtained with the INDOR technique. Thus, determining J_{PH} would have been extremely difficult and a reasonable estimate of $^5J_{PP}$ would have been impossible.

The iron complex should have the same nmr features as the molybdenum complex. Since $^3J_{PP}$ is larger in the iron complexes, it was thought $^5J_{PP}$ would more likely exist in the disubstituted iron than in the disubstituted molybdenum complex. Unfortunately, the solubility of the iron complex is much less than that of the molybdenum. Although an INDOR spectrum of the phosphite coordinated ligand was obtained,

Figure 13. The nmr schematic of <u>cis</u>-$(OC)_4Mo[P(OCH_2)_3P][P(CH_2O)_3P]$ showing the associated ^{1}H and ^{31}P peaks. The ^{31}P peaks observed when performing ^{31}P INDOR experiments on ^{1}H peaks 1-4 are labeled 1-4 respectively


3
4
3
4
2
1
2
1
2
1
3
4
P_A
P_D
P_C
P_B


$P_A(OCH_2^{I})_3P_B$
Mo
$P_C(CH_2^{II}O)_3P_D$

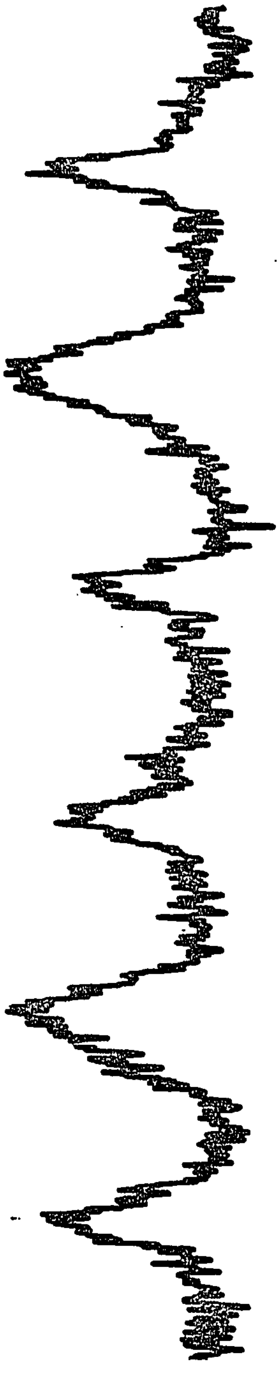

1
2
3
4
I
II

the resolution was too poor to resolve the $^3J_{PH}$ splitting of the coordinated phosphorus atom. Moreover, it was not possible to locate the resonances of the phosphine coordinated ligand due to the difficulty of irradiating only one of two proton peaks separated by less than one Hz under the instrumental conditions necessary for such low solubility.

The $^2J_{PP}$ value obtained from the molybdenum and iron complexes is comparable with those reported for other iron and molybden complexes (63, 64). It should be noted that when $^2J_{PH}={}^3J_{PH}$, the inside two lines of the doublet of doublets overlap giving rise to the 1:2:1 triplet observed for the phosphine ligand as indicated in Figure 11.

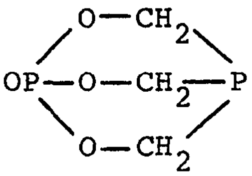
The third disubstituted complex, cis-$(OC)_4Cr[P(OCH_2)_3P]_2$, is spectrally more complex than the first two. Chemically there are only two different phosphorus atoms instead of four as in the other complexes. However, the two coordinated phosphite-phosphorus atoms are magnetically nonequivalent and if appreciable $^2J_{PP}$ coupling occurs, second-order effects in the nmr spectrum are observed. This "virtual coupling" results in the appearance of an envelope of lines between the proton doublet whose separation is equal to $^3J_{PH}$ + $^5J_{PH}$ and not $^3J_{PH}$ as is the case when second-order effects are absent. The value of $^5J_{PH}$ can be assumed to equal zero (65, 66). The phosphorus nmr spectrum

Figure 14. ^1H nmr spectrum of <u>cis</u>-$(OC)_4Cr[P(OCH_2)_3P]_2$. The broad center peak of each doublet arises from second order effects

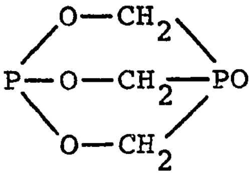


shows only the doublet of doublets seen in a monosubstituted complex. While in theory $^{2}J_{PP}$ could be determined from the ^{31}P spectrum, it is not feasible in the vast majority of cases (67). A discussion of the nmr parameters in Tables 5 and 6 will be deferred until later.

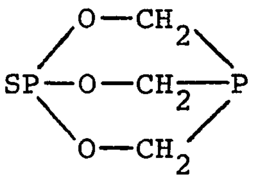
The study of the chemistry of $P(OCH_2)_3P$ reveals the rather surprising tendency of this ligand to coordinate the phosphite-phosphorus atom in preference to the phosphine-phosphorus atom for a variety of acceptor species. In general phosphines and phosphites are easily oxidized to their oxides and sulfides. The lone-pair of electrons on phosphorus also donate readily to carbonium ions to form phosphonium salts, to boron compounds such as diborane to form adducts, and to metals to form coordination compounds. Although L also undergoes these reactions, there occur several unusual exceptions which will now be discussed. When all the possible oxide and sulfide combinations of L are considered, eight compounds are possible (Figure 15). Seven of these have now been prepared (IX-XV) and preliminary results indicate that the eighth, $OP(OCH_2)_3PS$, can also be prepared. Peroxides invariably oxidize both phosphorus atoms of L even in the presence of an excess of L (68). When milder oxidizing agents were used, the same results occurred (68). The oxidation of phosphites during the reduction of metals is not unique with copper(II) salts



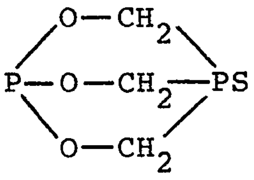
IX



X



XI



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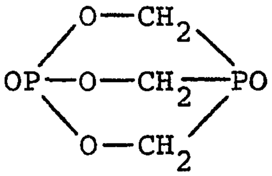
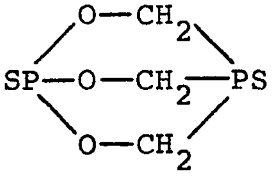
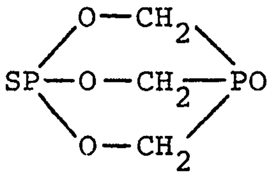


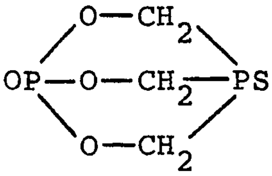
XIII



XIV



XV



XVI

Figure 15. The eight possible oxides and sulfides of $P(OCH_2)_3P$

inasmuch as nickel halides are also known to oxidize phosphites with reduction of the nickel to nickel(0) (53). In the copper reduction below, however, only the phosphite-phosphorus is oxidized:

$$Cu(BF_4)_2 + P(OCH_2)_3P \rightarrow [Cu_xL_y][BF_4]_x + OP(OCH_2)_3P \quad (1)$$

The nickel reaction is thought to involve water:

$$NiX_2 + 5P(OR)_3 + 2NR_3 + H_2O \rightarrow Ni[P(OR)_3]_4$$

$$+ 2[HNR_3]x + OP(OR)_3 \quad . \quad (2)$$

Whether the reaction involving cupric tetrafluoroborate described in the experimental section (Equation 1) follows the same type of mechanism is not known, although it seems likely that it does. If the cupric nitrate reaction also follows the same mechanism as the tetrafluoroborate salt, there is at least a competing reaction because some nitric oxide is evolved. The presence of the nitric oxide was detected when the stopper of the reaction vessel was removed after the reaction had been going several minutes. Exposure of the reaction to the air resulted in immediate formation of a gas with characteristic color and odor of nitrogen dioxide.

Whatever the mechanism(s), $OP(OCH_2)_3P$ is preferentially formed over its linkage isomer and the dioxide. Traces of the latter two compounds are seen in the nmr spectra of the reaction mixture, but the amount of both is less than five percent of the phosphate mono-oxide of L. Since peroxides give only the dioxide of L even in the presence of excess L, it appears that the oxidation of one phosphorus atom enhances the oxidation susceptibility of the other. This fact implies that an entirely different oxidation mechanism occurs in the metal reduction reaction. Possibly the intermediate is a metal-L complex, and the specific oxidation of L derives from coordination of L in the intermediate. Additional studies are necessary before further speculations become possible.

To prepare the phosphine mono-oxide of L, $P(OCH_2)_3PO$, it was thought necessary to find a blocking agent for the phosphite moiety which could be removed once the phosphine-phosphorus had been oxidized. Subsequent isomerization to $OP(OCH_2)_3P$ seemed unlikely since the dioxide is stable in the presence of excess L. The borane group was felt to be the easiest group to remove after the oxidation and benzoyl peroxide was chosen over hydrogen peroxide for the oxidizing agent since water present in hydrogen peroxide will hydrolyze the borane adduct. The removal of the borane by benzoyl peroxide was unexpected

$$H_3BP(OCH_2)_3P + (C_6H_5CO_2)_2 \rightarrow P(OCH_2)_3PO \qquad (3)$$

and is not understood. After more than six hours of refluxing in acetonitrile, the ratio of $H_3BP(OCH_2)_3P$ to $P(OCH_2)_3PO$ did not change from the ratio observed after two and one-half hours. However, when double the molar quantity of benzoyl peroxide was added, only a small broad peak was observed in the nmr and the presence of bicyclic compounds could not be detected. At present, it is not obvious why one equivalent of peroxide is not sufficient to oxidize all the phosphine-phosphorus, nor is it clear what happened to the borane moiety. One possibility is the direct attack on the boron by the peroxide to give a boron ester and hydrogen gas.

The reaction of sulfur with L in refluxing toluene produces only the monosulfides, but not in equal amounts.

$$S + P(OCH_2)_3P \rightarrow SP(OCH_2)_3P + P(OCH_2)_3PS \qquad (4)$$

This is in contrast to the reaction of L with sulfur at 110° in the absence of a solvent in which $SP(OCH_2)_3P$ is the sole product (1). In neither case was the formation of any disulfide observed. Inasmuch as both isomers of the monosulfide are formed, the lack of disulfide formation can not be ascribed to the inertness of either phosphorus atom. Furthermore, since the disulfide has been synthesized (see later), its failure to form in refluxing toluene can not be due to instability of the disulfide product.

Since the reaction is homogeneous, insolubility of the monosulfides is not a factor. The possibility that the oxidation of one phosphorus atom increases the difficulty of oxidizing the other is rendered tenuous by the observation that L easily oxidizes to the dioxide. Possibly a higher temperature is needed, and that the use of a higher boiling solvent will give the disulfide.

The production of the disulfide of L from H_2S and a copper(I) complex of L

$$H_2S + [Cu_xL_y][BF_4]_x \rightarrow SP(OCH_2)_3PS \qquad (5)$$

seems surprising in view of the above discussion. The cuprous complex of L is insoluble in acetonitrile, although possibly not as insoluble as the copper sulfides and so the reaction could be controlled by their relative solubilities. If the reaction of H_2S with the copper complex is stopped before ninety minutes,the monosulfide isomers are found in addition to the disulfide. The relative amounts appear to depend on the amount of hydrogen sulfide used. When an analogous reaction is run using free ligand rather than the cuprous complex, only a trace of the monosulfides is found and no disulfide. When a suspension of the cuprous complex and sodium sulfide is stirred together, only the free ligand is recovered. Since monosulfide can be found uncomplexed in solution during the reaction, with none being present at the end of the reaction, the ligand molecules apparently need not be constantly coordinated. The rapid appearance of a dark solid in the reaction appears to preclude the possibility of the cuprous complex acting as a catalyst, although it is possible the copper sulfide may be a catalyst. The evolution of hydrogen seems likely, but attempts to detect it were not successful. The large amount of hydrogen sulfide present make the detection of a small amount of hydrogen difficult and the failure to find the gas can not be construed as evidence for its absence.

The one mixed chalconide derivative characterized was synthesized by reacting $SP(OCH_2)_3P$ with hydrogen peroxide (1). The linkage isomer, $OP(OCH_2)_3PS$, was shown to form by this method when $P(OCH_2)_3PS$ is used.

The sulfide, $P(OCH_2)_3PS$, is moisture sensitive and soon hydrolyzes when exposed to the air. The ligand L also is moisture sensitive. Whether the sulfur has any effect on the hydrolysis rate of the phosphite moiety is not known.

The infrared bands for $\nu P{=}O$ and $\nu P{=}S$ of the chalconide derivatives of L are listed in Table 7. The bands are in the region in which similar molecules absorb (69, 70).

In the reaction of L with trimethyloxonium tetrafluoroborate

$$[(CH_3)_3O]BF_4 + P(OCH_2)_3P \rightarrow [P(OCH_2)_3PCH_3]BF_4$$

$$\rightarrow [CH_3P(OCH_2)_3P]BF_4 \qquad (6)$$

a distinct difference in the chemistry of the phosphite- and phosphine-phosphorus atoms is observed. When the reaction between equimolar quantities of the reactants is monitored _via_ nmr spectroscopy within five minutes of mixing the reactants together, the phosphine monophosphonium salt isomer $[P(OCH_2)_3PMe]^+$ comprises 80-90 percent of the product. Rapid cooling of the reaction mixture at this point permits easy isolation of the phosphine monophosphonium salt isomer as crystals. However, when the reaction

Table 7. Infrared frequencies of chalconide derivatives of L[a]

Compound	P=O		P=S	
	phosphite	phosphine	phosphite	phosphine
$OP(OCH_2)_3P$	1300			
$OP(OCH_2)_3PO$[b]	1325	1220		
$SP(OCH_2)_3P$[b]			807	
$P(OCH_2)_3PS$				705
$SP(OCH_2)_3PS$			834	737
$SP(OCH_2)_3PO$[b]		1215	807	

[a] Values are in cm^{-1}. All spectra were obtained in KBr.

[b] See reference 68.

is allowed to remain at room temperature for a longer period of time, the phosphite isomer increases in amount at the expense of the phosphine isomer. No free ligand is observed at any time. This isomerization has not been observed to go to completion, but approximately 90% of the compound as the phosphite isomer is formed after five minutes at 70°. It appears, therefore, that the phosphine reaction is kinetically favored over the phosphite but the phosphite isomer appears to be thermodynamically more stable as is suggested by the ready isomerization of the phosphine isomer in the reaction mixture.

Attempts to prepare the diphosphonium salt by using three moles of oxonium salt to one mole of ligand were unsuccessful and only gave the $[CH_3P(OCH_2)_3P]BF_4$ compound. Since the bicyclic compounds I and II both form diphosphonium salts, the absence of a diphosphonium salt of L is somewhat surprising. Coskran reported the synthesis of the triphenylmethyl diphosphonium salt based mainly on the proton nmr spectrum (68). The large downfield shift of the ligand protons in the phosphonium salt was comparable to that observed for the dioxide compound. However, the characterization of a greater variety of compounds in the present work indicates that this is a poor criterion (vide infra). Moreover the chemical shift of the ligand protons in $[CH_3P(OCH_2)_3P]BF_4$ is comparable to that of the triphenylmethyl phosphonium salt. Possibly a much larger excess of the oxonium salt than was used would be sufficient to generate the diphosphonium salt.

Once $[P(OCH_2)_3PCH_3]BF_4$ was isolated as a crystalline compound, it was found to be quite stable with respect to isomerization. When the compound is redissolved in acetonitrile, no trace of the phosphite isomer was observed even after several hours. Addition of L to a solution of pure phosphine monophosphonium salt also resulted in no detectable changes. Apparently either some of the linkage isomer or the oxonium salt is necessary for the isomerization to occur. Further studies on this interesting phenomenon are in order.

It should be mentioned that if the oxonium salt is responsible, a possible mechanism would involve a diphosphonium salt as an unstable intermediate which rapidly loses the methyl carbonium ion from the phosphine-phosphorus. Such a situation would prohibit isolation of the diphosphonium salt as a pure compound. However, the characterization of $[(OC)_5WP(OCH_2)_3PCH_3]BF_4$ in this work suggests that isolation or detection of the diphosphonium salt is worthy of further efforts.

Diborane reactions of L likewise show some

$$P(OCH_2)_3P + 1/2\ B_2H_6$$

$$\rightarrow H_3BP(OCH_2)_3P \xrightarrow{1/2\ B_2H_6} H_3BP(OCH_2)_3PBH_3 \quad (7)$$

interesting differences in the chemistry of the two phosphorus atoms. The phosphite borane monoadduct is easily prepared, while no evidence of the existence of the phosphine borane monoadduct has been found. Under the conditions of the reaction, it is impossible to determine if borane is first coordinated to the phosphine-phosphorus and then rapidly isomerizes to the phosphite-phosphorus or if the phosphite borane monoadduct is formed immediately.

The diborane adduct $H_3BP(OCH_2)_3PBH_3$ undergoes two very interesting reactions. First, the di-adduct will react immediately with water to give the phosphite borane monoadduct. This

$$H_3BP(OCH_2)_3PBH_3 + H_2O \rightarrow H_3BP(OCH_2)_3P \quad (8)$$

compound is also attacked by water, but the hydrolysis is much slower. When L is added to a solution of the diadduct, the phosphite-phosphorus of L quickly abstracts the borane moiety from the phosphine-phosphorus atom of the di-adduct to give only the phosphite borane

$$H_3BP(OCH_2)_3PBH_3 + P(OCH_2)_3P \rightarrow 2H_3BP(OCH_2)_3P \quad (9)$$

monoadduct. These two reactions and the reaction of L with diborane clearly show that the phosphine-phosphorus-boron bond is more labile than the phosphite-phosphorus-boron bond. Also the latter bond is thermodynamically more stable than the former.

The conclusion to be drawn from the phosphonium salt and diborane chemistry of L is that the phosphite-phosphorus is a better coordination site than the phosphine-phosphorus. This contrasts with previous results which show that trialkyl phosphines are better ligands toward BH_3 than trialkyl phosphites (71). Furthermore, ligation of phosphorus compounds has been found to decrease as the electronegativity of the group on phosphorus decreases: $H_3BP(CH_3)_3$, $H_3BP[N(CH_3)_2]_3 > H_3BP(OR)_3 > H_3BP(OCH_2)_3CCH_3 >> H_3BPF_3$ (71-75). From this ligation series it was expected that the phosphine-phosphorus would be at least as strong a ligand if not stronger than the phosphite-phosphorus in L.

Two effects have been proposed which may be responsible, in part, for the weaker ligation of the phosphine-phosphorus. Burg and Wagner (76) postulated a weak B-H bonding electron flow to the phosphorus 3d orbitals to explain the greater stability of phosphine-borane adducts over the corresponding amine adducts. That this interaction is weak, however, is demonstrated by the above ligation series since the more electronegative atoms on phosphorus apparently decrease the availability of the phosphorus lone pair even though the 3d orbitals are energetically made more favorable for π-bonding. The similar ligand strengths of $P(CH_3)_3$ and $P[N(CH_3)_2]_3$ in the above series may be due to a balancing of these two effects by the inductive effect of the two methyl groups in the $N(CH_3)_2$ moiety, while the more electronegative OR groups decrease the availability of the lone pair more than can be compensated for by an increase in π-bonding. Compton et al. observed that $P(CH_2O)_3CCH_3$ does not form a stable $B(CH_3)_3$ adduct or a phosphonium salt (2). They note that the 1.52D moment is oriented in the molecule such that the phosphine-phosphorus atom is at the positive end of the dipole and they suggested that this reduced the attractiveness of the phosphorus lone pair to an electrophilic moiety. This reasoning is supported by the observation that the adamantane like phosphite, $P(OCH)_3(CH_2)_3$, is a stronger ligand then $P(OCH_2)_3CCH_3$ toward $B(CH_3)_3$ since the former compound has a moment of 4.51D compared to 4.15D for the latter phosphite (62).

A series of displacement reactions was studied in an attempt to better understand the nature of the boron-phosphorus bonds in $H_3BP(OCH_2)_3PBH_3$:

$$H_3BP(OCH_2)_3P + P(n\text{-}C_4H_9)_3 \rightarrow P(OCH_2)_3P + H_3BP(n\text{-}C_4H_9)_3 \tag{10}$$

$$H_3BP(CH_2Cl)_3 + P(OCH_2)_3P \rightleftarrows P(CH_2Cl)_3 + H_3BP(OCH_2)_3P \tag{11}$$

$$H_3BP(OCH_2)_3PBH_3 + P(CH_2O)_3CCH_3 \rightarrow H_3BP(OCH_2)_3P + H_3BP(CH_2O)_3CCH_3 \tag{12}$$

$$H_3BP(OCH_2)_3PBH_3 + P(CH_2O)_3As \rightarrow H_3BP(OCH_2)_3P + H_3BP(CH_2O)_3As \tag{13}$$

Conclusions drawn from equilibrium experiments concerning relative donor-acceptor bond enthalpies are invalid if entropy effects are substantially dissimilar. It is assumed here, particularly among the caged ligands, that entropy effects are not dominant. Reaction 10 was observed to go completely to the right upon heating at 90°C for two hours although no reaction was observed at room temperature. The equilibrium of reaction 11 was found to be about 75% in favor of $H_3BP(OCH_2)_3P$, thus showing the ligand strength of the phosphite-phosphorus in L to be greater than that of $P(CH_2Cl)_3$ ($H_3BP(CH_2Cl)_3$: $^2J_{PH}=3.8$ Hz, $\delta CH_2=4.15$ ppm). The reaction proceeded rapidly to the right at room temperature but proceeded to the left only upon heating to 90°C.

Reactions 12 and 13 proceed completely to the right at room temperature ($H_3BP(CH_2O)_3As$: $^2J_{PH}$=0.0 Hz, δCH_2=4.75 ppm). The phosphine-phosphorus in $P(OCH_2)_3P$, $P(CH_2O)_3CCH_3$, and $P(CH_2O)_3As$ are all at the positive end of the dipole where μ=3.10D (49), 1.52D (2) and 1.58D (49), respectively. Although μ is not known for $H_3BP(OCH_2)_3P$, it is certainly greater than for the latter two compounds and directionally the same. It seems likely that the relative ligand strengths of the phosphines is due to the difference in dipole moments and that the greater moment, the weaker the ligation of the phosphorus at the positive end of the dipole. The bicyclic phosphines are all weaker bases than the phosphite which is at the negative end of the dipole. The moment of $P(CH_2Cl)_3$ is not known but should be near zero since it probably lies between that of $P(CH_2O)_3CCH_3$ (1.52D) and $P(CH_3)_3$ (1.19D, (77)) whose moments lie in opposite directions. The dipole moment is not the only factor, however, since tri-n-butylphosphine is a better ligand than the phosphite-phosphorus of L in spite of its lower μ value of 2.2D (77) compared to 3.1D for L. The oxygens on the phosphorus apparently reduce the donating ability of the phosphite-phosphorus. On this consideration alone, it would be expected that compounds with a highly electronegative atom in the β position would fall between the phosphite-phosphorus of L and tri-n-butylphosphine in ligand strength. Since the phosphite-phosphorus of L is a better ligand than $P(CH_2Cl)_3$, some other factor must be operating. The difference in steric requirements may be important as well as a difference in π-bonding ability. Both considerations would tend to favor L over $P(CH_2Cl)_3$ since L certainly has the less sterically hindered lone pair and since the 3d orbitals will be lowered in energy more by α oxygen atoms than by β chlorine atoms. The amount of π-bonding will be small in BH_3 adducts as indicated above, but it may become important when the basicities are similar.

These considerations of dipole moment and π-bonding ability could also be important in determining the relative ligation properties of the phosphorus atoms of L toward carbonium ions although insufficient data are available to draw any firm conclusions.

The carbonyl complex chemistry of L varies slightly with the metal. With chromium, molybdenum and tungsten three different methods were used to prepare the complexes. Ultraviolet irradiation was used for chromium, heat was utilized for molybdenum, and a simple replacement reaction provided the best results for tungsten. Any one method could be used with any of the metal carbonyls, with only the yields varying. In the case of molybdenum, an amine replacement reaction has been reported (78). This reaction was tried and does indeed give results comparable to the method reported in the experimental section.

For all three metal carbonyls, monodentate phosphite coordinated complexes of L have been characterized as well as bridging bidentate complexes. As was pointed out earlier, the phenomenon of exchange in the compounds is unlikely. Not only do the proton nmr spectra of the pure compounds and mixtures of the complexes and free ligand have the same chemical shift, but addition of L to the bridged complexes does not result in the formation of the monodentate complex at the expense of the bidentate complex.

The isolation of bidentate complexes of L indicates that the phosphine-phosphorus is certainly capable of bonding to the metal carbonyl groups. The failure to detect any monodentate phosphine coordinated complexes of L is thus somewhat surprising. Possibly this is due to the inability of the phosphine-phosphorus to compete with the phosphite-phosphorus under the conditions of the reactions. Sufficiently mild conditions would perhaps lead to a mixture of phosphite and phosphine monodentate complexes. This explanation is supported by the reaction of L with $(OC)_5Mo(C_5H_{11}N)$. The nmr spectrum of the reaction mixture indicated the presence of some phosphine monodentate L complex as well as phosphite monodentate and the bridged bidentate complexes. Two attempts were made to separate these complexes with column chromatography but no separation was obtained. The reaction of L with the analogous aniline complex of tungsten did not produce any phosphine monodentate complex, even though aniline is a weaker base than piperidine. The disubstituted metal tetracarbonyl complexes are also prepared by replacement reactions. For the chromium complex, an olefin is the ligand being displaced by L and the only complex isolated was the bis-(phosphite monodentate) system. A similar reaction with the molybdenum olefin also gives only the bis-(phosphite monodentate) complex. A mixture of the bis-(phosphite monodentate) and the phosphite-phosphine monodentate molybdenum tetracarbonyl complexes is obtained when the displaced ligand is N, N, N', N'-tetramethyl-1,3-propane diamine (79). The diamine complex is expected to be replaced more easily than the olefin. With the appropriate choice of starting material, it will probably be possible to prepare phosphine monodentate complexes of the group VIB metal carbonyls.

The phosphine moiety seems to be a better competitor with the phosphite moiety in iron(O) carbonyl complexes. The complex $(OC)_4FeP(CH_2O)_3P$ is readily isolated, although the yield is poorer than that of the linkage isomer. Again the bidentate complex of L is also found. All of these compounds are prepared using irradiation. A disubstituted phosphite-phosphine monodentate iron complex is also formed readily. The surprising observation in iron(O) carbonyl chemistry is the failure to detect either of the other two disubstituted isomers. Regardless of which monosubstitued iron complex is the starting material for forming the disubstituted complex, at least a small amount of one or the other isomers would be expected to form. The dipole moment of the complex isolated would be approximately 6.2D (based on L=3.1D), while the moment of the other two isomers would be nearly zero. The formation of complexes of low dipole moment would normally be expected to be favored in the nonpolar solvent used, and indeed the complexes $(OC)_3FeL_2$ for $L=P(OCH_2)_3CCH_3$ and $P(CH_2O)_3CCH_3$ are easily prepared (54, 2). It is possible that a head to tail arrangement of dipoles is favored whenever feasible. If the isolated disubstituted complex is formed from only one of the two $(OC)_4FeL$ isomers, it may be possible to form one of the other two isomers from the appropriate $(OC)_4FeL$ complex and excess L.

The iron complexes are more sensitive to air and water than those of the group VIB metals and the iron complexes are all sensitive to light. A greater amount of polymerization appears to occur with iron than with the group VIB metals, and with nickel tetracarbonyl only polymer was obtained in reactions with L. This tendency toward increased polymerization as the right side of the periodic table is approached may be explained in two ways. The carbonyls are more readily replaced by other ligands in progressing from chromium to nickel (80). Also, it appears the competitive ability of the phosphine moiety increases from chromium to nickel. Monomeric nickel carbonyl complexes can possibly be made in the presence of a large excess of L.

Monodentate ligands generally give simple axially substituted trigonal bipyramidal structures with $Fe(CO)_5$ and equatorial CO groups are replaced only after the axial CO groups have been substituted (81). Two important exceptions occur for complexes of the type $Fe(CO)_4L$ when L=olefin or PF_3. Although the olefin bond has been found to be in the equatorial plane (82, 83), these complexes involve an iron atom with six nearest neighbors and the distinction between a distorted trigonal bypyramidal and a distorted octahedral geometry becomes somewhat problematic. Spectroscopic studies of the $(OC)_{5-n}Fe(PF_3)_n$ system indicate that a mixture of axial and equatorial trigonal bypyramidal isomers is present (81b, 84-86). Attempts to isolate the isomers have thus far proven to be unsuccessful because of equilibria involving facile intramolecular exchange of the CO and PF_3 ligands.

The system $(OC)_4FeP(OCH_2)_3P$ was believed to also have geometric isomers (45), however, further work indicates this is not the case. In the chromatography of the $Fe(CO)_5$ and L reaction described in the experimental section, one fraction of the elutant contained, in addition to a large amount of L (ca. 60%), two compounds in unequal amounts with nearly identical ^1H nmr spectral parameters corresponding to $(OC)_4FeP(OCH_2)_3P$. The proton chemical shifts differed by 3.6 Hz permitting complete resolution of the eight peaks. The preceding fraction contained only one $(OC)_4FeP(OCH_2)_3P$ complex with a small amount of L (ca. 10%), and was easily purified and shown to be axial-$(OC)_4FeP(OCH_2)_3P$ from the observation of three νCO bands expected for C_{3v} symmetry (87a) and a parent ion peak of 320. The following fraction also contained only one $(OC)_4FeP(OCH_2)_3P$ complex in addition to a large amount of L (ca. 90%). The ir of the latter fraction showed one very strong band with two shoulders and one weak band. Four bands are expected from an equatorially substituted $(OC)_4FeL$ complex (81). Attempts to separate the small amount of complex from L were unsuccessful, and ^{31}P INDOR experiments were performed on both the pure axial isomer and the "non-axial" complex in the mixture. The results were similar, but not within experimental error (45). A mass spectrum was obtained of the mixture and the highest peak observed was 320.

A search for a better method of preparation of the "non-axial $(OC)_4FeP(OCH_2)_3P$" was unsuccessful, but the complex trans-$(OC)_3Fe[P(OCH_2)_3P][P(CH_2O)_3P]$ was isolated and characterized. The ^1H nmr spectrum of this compound was described earlier, but it should be pointed out that the peaks of the phosphine coordinated L overlap with the two downfield peaks of L when both compounds are present in solution. The νCO values for the three compounds are: ax-$(OC)_4FeP(OCH_2)_3P$, 2068 (s), 1991 (s), 1954 (vs); trans-$(OC)_3Fe[P(OCH_2)_3P][P(CH_2O)_3P]$, 1927; "non-axial-$(OC)_4FeP(OCH_2)_3P$", 2071 (w), 1996 (sh), 1955 (sh), 1927 (s). If the disubstituted complex has a small impurity of axial-$(OC)_4FeP(OCH_2)_3P$, a spectrum similar to the "non-axial $(OC)_4FeP(OCH_2)_3P$" may be seen and a large amount of L would hide the phosphine peaks in the ^1H nmr spectrum. A ^{31}P INDOR experiment on the disubstituted complex was performed as described earlier. The observed frequencies for the disubstituted compound and the "non-axial-$(OC)_4FeP(OCH_2)_3P$" are given in Table 8, and it can be seen that they are within experimental error. The second half of each doublet in the phosphite-phosphorus region was not observed in the latter compound possibly due to the combination of low-intensity peaks arising from the low solubility and the 77 Hz separation. The mass spectrum of the "non-axial" compound apparently resulted from the small amount of axial-$(OC)_4FeP(OCH_2)_3P$ present as an impurity which is more volatile than the disubstituted complex.

Table 8. Frequency of ^{31}P peaks from ^{31}P INDOR of $YP(OCH_2)_3P^a$

	trans- $(OC)_3Fe[P(OCH_2)_3P][P(CH_2O)_3P]$	"non-axial $(OC)_4FeP(OCH_2)_3P$"
$YP(OCH_2)_3\underline{P}$	24, 287, 569	24, 287, 565.6
	24, 287, 576	24, 287, 573.2
$Y\underline{P}(OCH_2)_3P$	24, 293, 186	
	24, 293, 109	24, 293, 109.7
	24, 293, 175	
	24, 293, 098	24, 293, 098.3

[a] The spectrometer is locked on CH_3CN. Values are in Hz.

The conclusion from nmr data that $(OC)_3FeL_2$ contains L coordinated through a phosphite- and a phosphine-phosphorus is confirmed in the structure determination. The bond distances and angles are listed in Tables 9, 10 and 11. Figure 16 shows a perspective view of the molecule.

The crystal was found to contain acetonitrile molecules. The best fit appears to be 0.4 molecule per asymmetric unit, and the structure was refined to an R factor of 0.089 with this number. This particular number for solvent molecules probably represents a partial loss of the solvent of crystallization during the selecting and mounting of the crystal. The solvent molecule was not

Table 9. Bond distances in *trans*-$(OC)_3Fe[P(OCH_2)_3P]$ $[P(CH_2O)_3P]$

Fe-P(1)	2.116(4)	Fe-C(3)	1.81(1)
Fe-P(3)	2.190(4)	Fe-C(6)	1.78(2)
P(3)-C(1)	1.82(1)	C(3)-O(3)	1.15(1)
P(3)-C(2)	1.80(1)	C(6)-O(6)	1.15(2)
P(2)-C(4)	1.86(2)		
P(2)-C(5)	1.85(1)	N-C(7)	1.14(2)
		C(7)-C(8)	1.43(3)
P(4)-O(1)	1.60(2)		
P(4)-O(2)	1.642(8)		
P(1)-O(4)	1.568(9)		
P(1)-O(5)	1.590(7)		
C(1)-O(1)	1.50(2)		
C(2)-O(2)	1.42(1)		
C(4)-O(4)	1.46(2)		
C(5)-O(5)	1.46(1)		

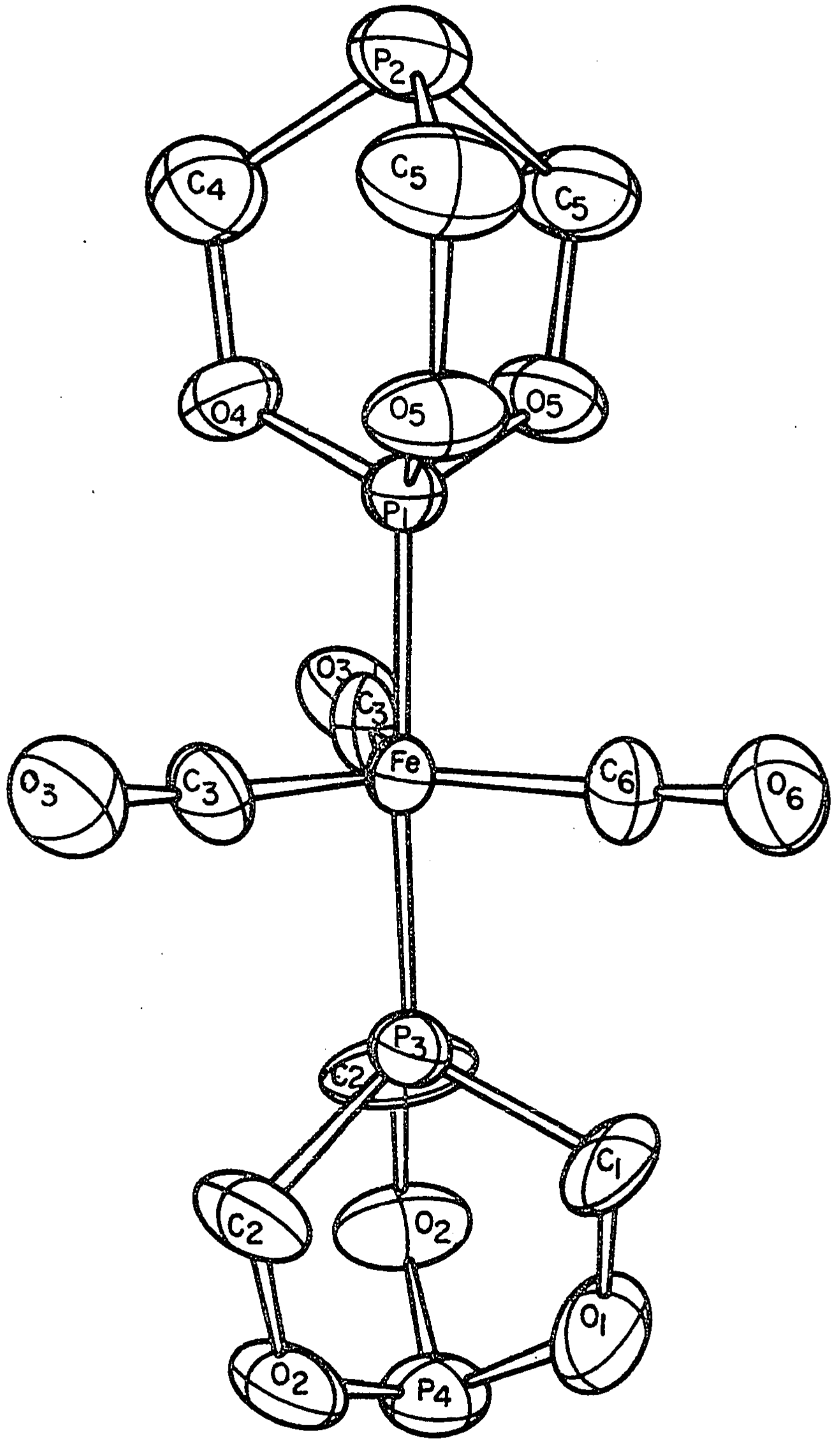
Table 10. Nonbonded distances in trans-$(OC)_3Fe[P(OCH_2)_3P][P(CH_2O)_3P]$

P(1)-P(2)	3.025(5)
P(3)-P(4)	3.022(5)
C(1)-C(2)	2.79(2)
C(4)-C(5)	2.78(2)
O(1)-O(2)	2.50(1)
O(4)-O(5)	2.49(1)
O(3)-N	3.61(3)
O(3)-C(7)	3.33(2)
O(3)-C(8)	3.55(2)
C(6)-C(1)	3.25(1)
C(6)-O(5)	3.18(1)
C(6)-C(3)	3.09(2)
C(3)-O(4)	3.19(1)
C(3)-C(2)	>4

Table 11. Selected bond angles in *trans*-$(OC)_3Fe[P(OCH_2)_3P][P(CH_2O)_3P]$

P(1)-Fe-P(3)	176.4(2)	Fe-C(3)-O(3)	176.7(8)
P(1)-Fe-C(3)	88.4(3)	Fe-C(6)-O(6)	175 (1)
P(1)-Fe-C(6)	88.5(4)	N-C(7)-C(8)	177 (2)
P(3)-Fe-C(3)	89.8(3)		
P(3)-Fe-C(6)	95.2(5)		
C(3)-Fe-C(6)	118.4(3)		
C(1)-P(3)-C(2)	100.6(5)		
C(4)-P(2)-C(5)	97.1(5)		
O(4)-P(1)-O(5)	104.2(4)		
O(1)-P(4)-O(2)	101.0(4)		
P(2)-C(4)-O(4)	113.6(9)		
P(2)-C(5)-O(5)	114.0(7)		
P(3)-C(2)-O(2)	114.4(7)		
P(3)-C(1)-O(1)	108 (1)		
P(1)-O(4)-C(4)	120.8(9)		
P(1)-O(5)-C(5)	120.2(6)		
P(4)-O(2)-C(2)	121.2(6)		
P(4)-O(1)-C(1)	125.4(9)		

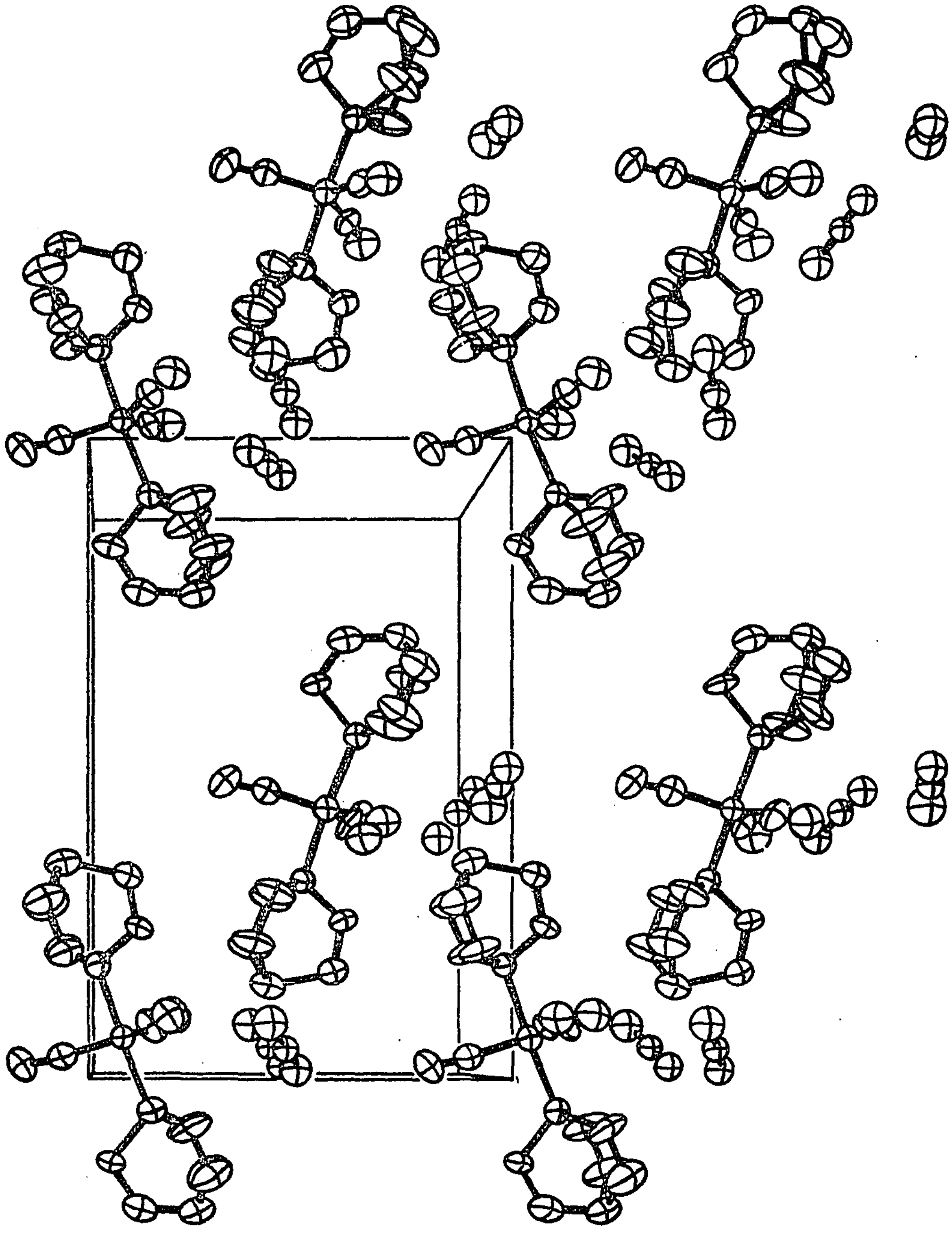
Figure 16. Perspective drawing of the molecule *trans*-$(OC)_3Fe[P(OCH_2)_3P][P(CH_2O)_3P]$ indicating the atom-labeling scheme. Hydrogen atoms are not shown


P2
C4
C5
C5
O4
O5
O5
P1
O3
C3
O3
C3
Fe
C6
O6
P3
C2
C1
C2
O2
O1
O2
P4

included in Figure 16 for clarity. The solvent molecules have been included in Figure 17, and their relationship to the iron complex can be seen. The solvent molecule contains some disorder. When the methyl carbon and the nitrogen are interchanged, no effect is noticed in the R factor. Furthermore, none of the atoms lie on the mirror plane in which many of the atoms of the complex lie, nor is the solvent molecule parallel to the mirror plane.

The mirror plane contains the C_3 axis of the complex. The iron and the four phosphorus atoms, therefore, are in the mirror plane. Of necessity, two of the OCH_2 groups of each bicyclic system are mirrored through this plane, while the third OCH_2 group lies in the plane. The same arrangement occurs for the carbonyl groups. Only two possible ways of arranging the two phosphorus ligands on iron are available because of the mirror plane. The two ligands may be either eclipsed or staggered. The carbonyls would probably be staggered in the former position but must be eclipsed to one ligand in the latter conformation. The phosphorus ligands are found to be staggered with respect to one another and the carbonyls are eclipsed with respect to the phosphine coordinated ligand. The geometry around iron is a trigonal bypyramid with the carbonyls in the equatorial positions and slightly bent (*ca.* 1°) toward the phosphite coordinated ligand. The two phosphorus ligands

Figure 17. View of the unit cell down the b axis of one layer of complex and solvent molecules



are bent about 3° from linearity. These differences from an idealized trigonal bypyramid are probably within experimental error. The eclipsing of the carbonyls and the phosphine coordinated ligand is the most favorable conformation sterically, since a model shows more room for the carbonyls between the protons on one methylene group than between the protons on different methylenes.

A comparison of the bond parameters of the complex leads to four observations: a) a significant difference in the metal-phosphorus bond length exists in the two ligands; b) a significant change occurs in the bridgehead angles upon coordination; c) the phosphorus-phosphorus distance in the two ligands is constant; d) the carbon-oxygen parameters are essentially constant within experimental error. The iron-carbon and carbon-oxygen bond lengths of the carbonyl groups are the same as in compounds IV-VII.

The iron-phosphorus bonds found in compounds IV-VIII are listed in Table 12. The iron-phosphorus bond length in the phosphite coordinated ligand is 0.03A shorter than the distance of the lone iron phosphite complex listed (VIII). Metal-phosphorus bond lengths are believed to remain constant as oxidation states are changed (34), and this trend probably holds for iron also. The difference in bond length could well be due to steric interactions. The much bulkier triphenylphosphite may not be able to get

Table 12. Iron-phosphorus bond lengths

Compound	Fe-P distance (A)	
IV	2.260(5)	
V	2.293(6)	2.312(6)
VI	2.25	
VII	2.24(2)	
VIII	2.15(2)	
trans-$(OC)_3Fe$ $P(CH_2O)_3P$	2.190(4)	
$P(OCH_2)_3P$	2.116(4)	

as close as the more compact $P(OCH_2)_3P$.

The metal-phosphorus bond length of the coordinated phosphine-phosphorus is 0.05A shorter than the shortest metal-phosphine bond listed. Again, steric considerations are probably important, although it is very surprising that complex V has the longest metal-phosphorus distance. Even considering that steric interactions are involved, it is unlikely that they can account for all of the difference. The phosphine-phosphorus of L must be able to form a stronger bond to the metal than the other phosphine-phosphorus atoms. The oxygen atoms bonded to the carbons would increase the π accepting ability of the phosphorus in L, even as the donating ability of L is lowered compared to the normal phosphines. Recent structure determinations of PF_3 complexes in which the metal-phosphorus bond has been found to be shorter than in other phosphorus complexes lend support to the metal-phosphorus double bond character increasing with the electronegativity of the groups on phosphorus (87b).

Another very important factor in comparing bond lengths is the nature of the other ligands. When a phosphorus atom is trans to a carbonyl group, it must compete with a very good π acceptor for the metal's electron density. When the phosphorus is trans to another phosphorus or an even weaker π acceptor, it will gain a greater share of the metal's electron density. In the complex with the two L ligands, the phosphorus atoms are trans and the iron-phosphorus bond should be shorter than in those complexes with carbonyls trans to the phosphorus. A more informative comparison will involve Fe-P(1) and Fe-P(3). The phosphine bond (Fe-P(3)) is significantly longer than the phosphite bond (Fe-P(1)) and this difference is certainly more than expected from the small difference in steric requirements. The phosphite bond is then the stronger bond and this would normally be explained in terms of increased π-bonding ability of the phosphite-phosphorus over the phosphine-phosphorus (38). However, the results of the borane and phosphonium chemistry of L indicate that the phosphite is the better ligand of the two phosphorus atoms and the difference in bond lengths would be expected if the phosphite were the stronger ligand. However, the difference in the ligation of the two phosphorus atoms toward BH_3 was tentatively ascribed to a dipole effect and possible differences in π-bonding ability. Since phosphorus-metal π-bonding will involve 3d orbitals on the metal rather than B-H bonding orbitals, multiple bonding in the metal-phosphorus bond is likely to be a more important factor than in the boron-phosphorus bond. Furthermore, any difference in π-bonding ability of the two phosphorus atoms in L will also be more important in metal complexes. However, the dipole moment effect can not be neglected when comparing the relative strength of the two phosphorus bonds to metals. A series of structure determinations of complexes in which the dipole moment of L varies greatly for compounds of similar inductive effect is needed to elucidate the dipolar effect. The earlier observation that the phosphine-phosphorus becomes a better competitor with the phosphite-phosphorus for a metal as the lability of the displaced CO increases would appear to indicate that any dipole moment effect here may be dominated by the higher nucleophilicity of the phosphine-phosphorus as observed in the phosphonium salt chemistry. The resultant complex containing a phosphine-phosphorus link to the metal may be kinetically favored and stabilized under mild conditions. Thermodynamically, however, the phosphite-phosphorus to metal bond may be more stable owing to either the π-bonding or dipolar effect or a combination of both factors.

The rigid nature of the bicyclic system is expected to limit the changes in bond parameters of the cage when the phosphorous atoms change from three to four coordinate atoms. The observation of a three degree change upon coordination is then thought to be significant. Bent has observed that the greater the electronegativity of a substituent, the less s character the substituent bond will have (88). From this it would be expected that the lone pair will gain in p character upon coordination. A gain in s character in the phosphorus-carbon and phosphorus-oxygen bonds will cause an increase in the bridgehead angle. This is observed, but it is surprising that the change is the same for both bridgehead angles. Further, strictly on Bent's rule, the phosphite bridgehead should have a smaller angle than the phosphine bridgehead but steric requirements apparently prohibit this from happening. It is probable then that steric considerations are the main factor in the angle change of the bridgehead upon phosphorus coordination.

The phosphorus-phosphorus distance is the same in both ligands. This could be related to the fact that the angle change at each phosphorus is the same upon coordination or it could be a parameter that is constant in L and its derivatives. The former would seem to be more likely. If the angle change at the bridgehead is the same in all derivatives, it may well be that the phosphorus-phosphorus distance has only three values: one in $P(OCH_2)_3P$; one in all monodentate compounds; and a third in all bidentate compounds.

The bond parameters for the rest of the molecule are essentially constant within experimental error. The smaller carbon and oxygen atoms are not refined as well as the iron and phosphorus atoms. The angle around C(1) has a particularly large value, along with the C(1)-O(1) bond length. Although apparently some distortion occurs here, it is not felt to affect the measurement of the bridgehead angle, since the most important atom is the phosphorus which is well-behaved.

The phosphorus-phosphorus length of 3.024 (± 0.005) is approximately halfway between a phosphorus-phosphorus single bond of 2.23A and a calculated non-bonded distance of 3.8A (89). This compares with the phosphorus-phosphorus non-bonded distance of 2.884 (± 0.007) in compound V. Davies <u>et</u> <u>al</u>. have discussed this short distance in terms of a non-bonded interaction of the 3s orbitals (41). They invoke the interaction argument because of the following observations. First, the X-ray crystal structure of

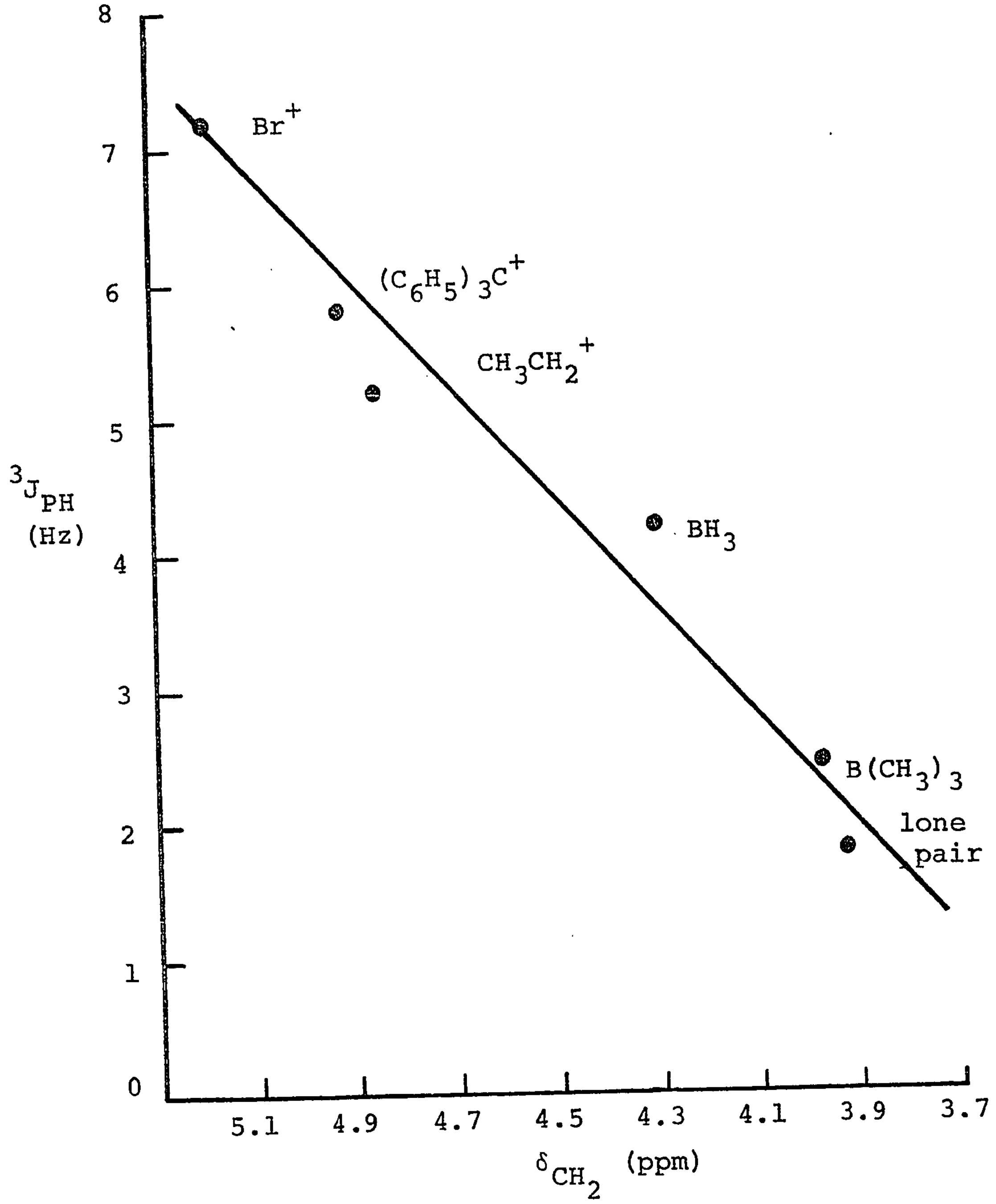
$(CH_3CH_2)_3P(OC)_3Mo(P(CH_3)_2)_2Mo(CO)_3P(CH_2CH_3)_3$ shows that the bridging phosphorus-phosphorus non-bonded distance is 3.80A. This is the calculated distance from the Van der Waals radii of two adjacent non-bonded phosphorus atoms. Second, the proton nmr of $(OC)_4Mo(P(CH_3)_2)_2Mo(CO)_4$ consists of a doublet. This is the expected spectrum for a simple $(AX_6)_2$ system. The structure of this complex is assumed to be very similar to the former disubstituted complex. Third, the nmr of V consists of a 1:2:1 triplet. This "virtual coupling" is indicative of significant phosphorus-phosphorus coupling. Calculated overlap integrals for phosphorus 3s orbitals for phosphorus-phosphorus distances of 2.88 and 3.80A are 0.083 and 0.018 respectively. The value for a bonding distance of 2.23 is 0.210. They conclude that there is a correlation between the size of J_{PP} and the degree of overlap of the phosphorus 3s orbitals.

The existence of $^2J_{PP}$ coupling through the metal does not seem to have been considered in their discussion. A recent study (64) of $^2J_{PP}$ values has shown a dependence of $^2J_{PP}$ on (a) the stereochemistry of the complex, (b) the metal atom, (c) the ligands other than phosphorus in the complex, and (d) the nature of the phosphorus ligand. Thus factors (b) and (c) are important in comparing the magnitude of $^2J_{PP}$ in the above compounds. It has also been pointed out that apparent triplets are possible even when ${}^2J_{PP}$ is small if J_{PH} is also small. Hence it is not obvious from the observations of Davies et al. that a correlation between the size of J_{PP} and the degree of overlap of the phosphorus 3s orbitals exists.

The question of "through-space" coupling is interesting, however, and where phosphorus atoms are possibly close enough to interact it should be considered. Derivatives of L certainly afford an excellent opportunity to investigate the existence of a through-space mechanism. A large number of ${}^3J_{PP}$ values were obtained and structural parameters are known for two differently bonded L ligands. It will be helpful to examine the values of ${}^2J_{PH}$ and ${}^3J_{PH}$ first, since more is known about these values.

Verkade et al. found a correlation between ${}^3J_{PH}$ and $\delta_{{}^1H}$ for $P(OCH_2)_3CCH_3$ and a number of its derivatives (90) and this correlation has been recently extended by McEwen (91) (Figure 18). The correlation is explained in terms of an increase in s character of the three phosphorus-oxygen bonds with increasing electronegativity of the acceptor group. The increase in electronegativity of the groups follows in the order: a lone pair of electrons $< B(CH_3)_3 < BH_3 < CH_3CH_2^+ < (C_6H_5)_3C^+ < Br^+$. Ogilvie et al. (64) observed that a similar correlation exists with the oxide and sulfide derivatives and the Cr, Mo, W, Fe and Ni carbonyl complexes of $P(OCH_2)_3CCH_3$, but that this correlation has a different

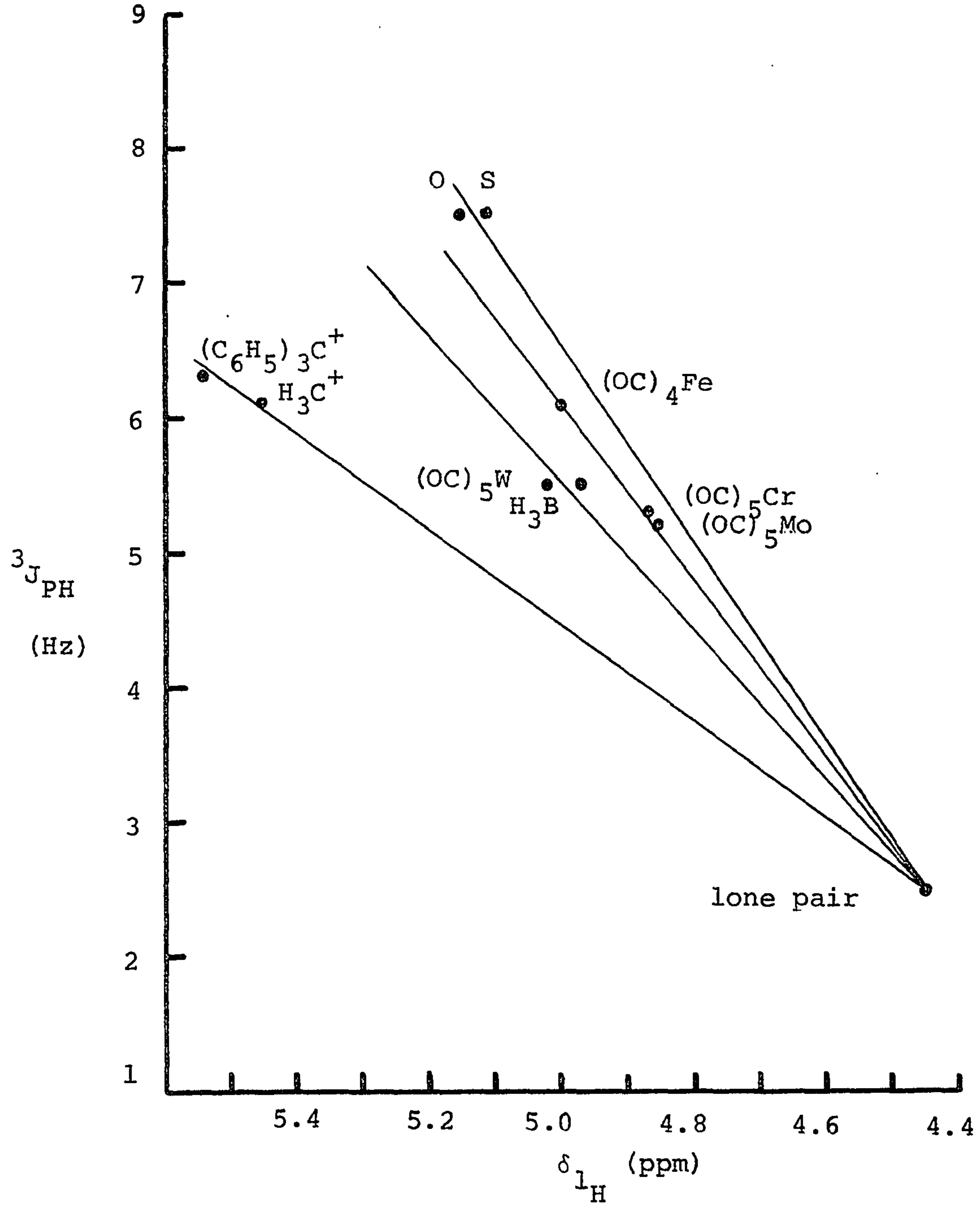
Figure 18. Plot of $^3J_{PH}$ vs. δ_{CH_2} for derivatives of $P(OCH_2)_3CCH_3$. A correlation coefficient of 0.98 confirms the linear relationship


8
7
6
5
4
3
2
1
0
$^3J_{PH}$ (Hz)
Br^+
$(C_6H_5)_3C^+$
$CH_3CH_2^+$
BH_3
$B(CH_3)_3$
lone pair
5.1
4.9
4.7
4.5
4.3
4.1
3.9
3.7
δ_{CH_2} (ppm)

slope than the former correlation. It was suggested that the difference in slopes might be due to some degree of double bond character in the latter group as opposed to only single bond character in the former group. It should be noted that this interpretation implies no π-bonding exists with BH_3. A similar plot for $YP(OCH_2)_3P$ compounds where Y is a lone pair of electrons, BH_3, CH_3^+, $M(CO)_5$(M=Cr, Mo and W), $Fe(CO)_4$, O and S does not produce a linear correlation (Figure 19). The group $Y=(C_6H_5)_3C^+$ from reference 68 was also plotted and found to be next to the CH_3^+ point. Four different lines can be drawn through the plotted data. One interpretation for the four slopes is differences in the degree of double bond character in the phosphorus-acceptor bond. This implies at least a little π-bonding in the BH_3 adduct since BH_3 and $W(CO)_5$ lie on the same line but on a different line than the phosphonium salts.

An alternate interpretation is one of no correlation particularly since two of the lines consist of two closely spaced points at one end and one point at the other end of the line. If no correlation exists, the difference in behavior between $P(OCH_2)_3P$ and $P(OCH_2)_3CCH_3$ must be explained. The former system may well be a more complicated one than the latter and not explainable by an argument concerned with only one end of the molecule. Possibly the other phosphorus atom bridgehead undergoes slight rehybridization when the phosphite-phosphorus atom becomes

Figure 19. Plot of $^{3}J_{PH}$ <u>vs</u>. $\delta_{^{1}H}$ for $YP(OCH_2)_3P$ compounds

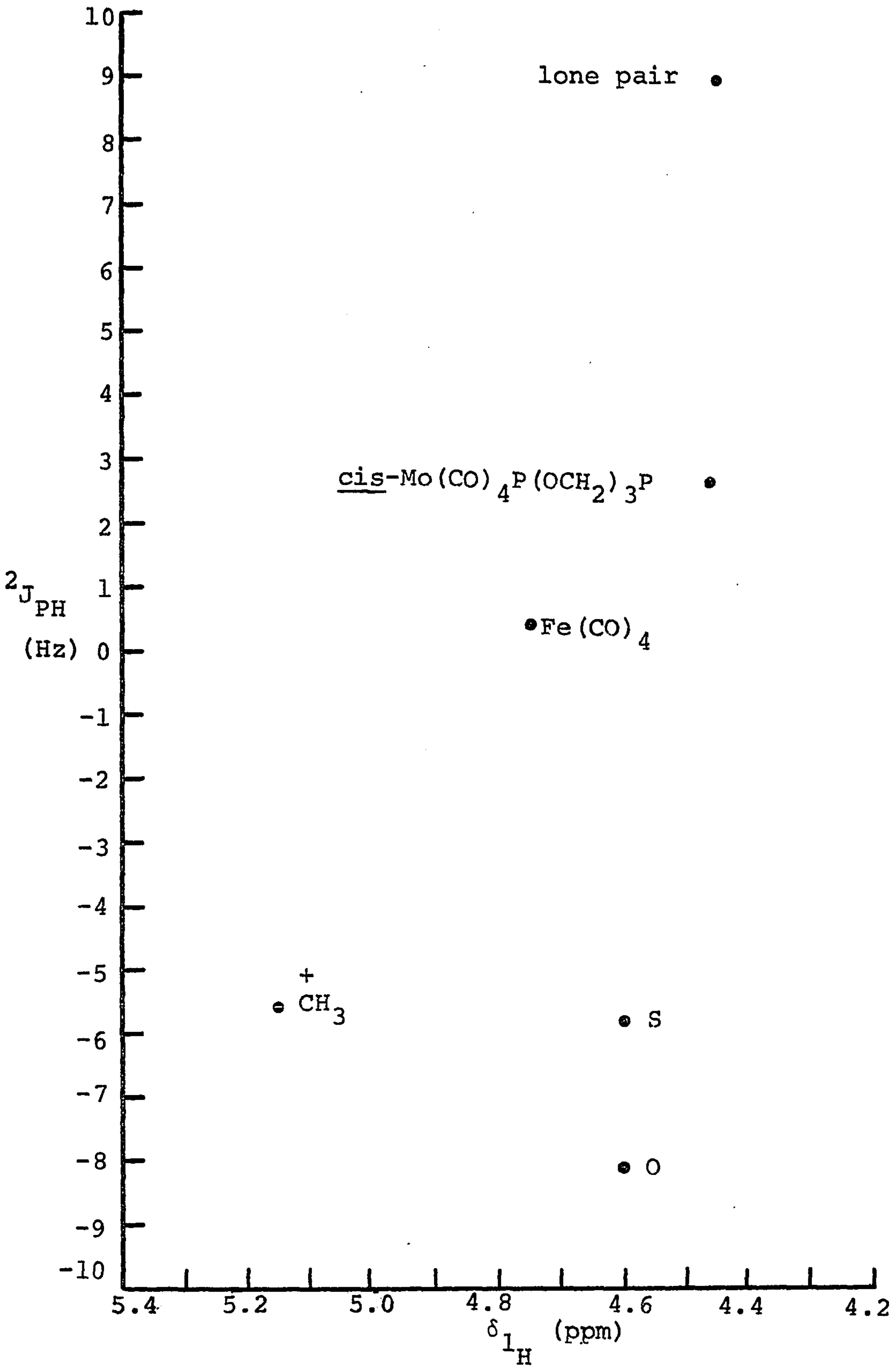

O
S
$(C_6H_5)_3C^+$
H_3C^+
$(OC)_4Fe$
$(OC)_5W$
H_3B
$(OC)_5Cr$
$(OC)_5Mo$
lone pair
$^3J_{PH}$
(Hz)
9
8
7
6
5
4
3
2
1
5.4
5.2
5.0
4.8
4.6
4.4
$\delta_{^1H}$ (ppm)

coordinated,thus acting somewhat like a hinge.

If a similar treatment is used for $^{2}J_{PH}$ for $P(OCH_2)_3PY$ complexes, no correlation with $\delta_{^{1}H}$ is apparent (Figure 20). It is observed that $^{2}J_{PH}$ becomes increasingly more negative as the Lewis acidity of Y increases and two earlier studies had predicted such a change. For the series of compounds $P(CH_2O)_3CCH_3$ to $(OC)_4FeP(CH_2O)_3CCH_3$ to $OP(CH_2O)_3CCH_3$, Boros et al. cited nmr data that strongly indicated a change in sign but they were unable to determine the absolute signs (2). Manatt and co-workers (92) discussed sign data obtained on other phosphine derivatives, which indicated that the s character in the phosphorus-carbon bonds increases due to increasing electronegativity of the Y group on phosphorus. Thus PCH coupling ($^{2}J_{PH}$) should become less positive or more negative. The data for $P(OCH_2)_3PY$ certainly agree with the change in sign postulated, but again, there does not appear to be a simple relationship with just the one end of the molecule.

The values for $^{3}J_{PP}$ range from -37 to +151 Hz for the compounds listed in Tables 5 and 6. While this study was in progress, McFarlane (93) reported that $^{3}J_{PP}$ in L was -38.1 ± 0.4 Hz , which agrees well with the value in Table 5. Two trends should be mentioned. First, $^{3}J_{PP}$ increases markedly from negative to positive values as the Lewis acidity of the Y group increases in the order electron pair <

Figure 20. Plot of ${}^{2}J_{PH}$ vs. $\delta_{{}^{1}H}$ for $P(OCH_2)_3PY$ compounds


10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
-4
-5
-6
-7
-8
-9
-10
$^2J_{PH}$
(Hz)
lone pair
cis-Mo(CO)$_4$P(OCH$_2$)$_3$P
Fe(CO)$_4$
$\overset{+}{\text{CH}_3}$
S
O
5.4
5.2
5.0
4.8
4.6
4.4
4.2
$\delta_{^1H}$ (ppm)

metal carbonyl fragment < methyl < chalconide for $YP(OCH_2)_3P$, $P(OCH_2)_3PY$ and $YP(OCH_2)_3PY$ compounds. Second, $^3J_{PP}$ is more sensitive to coordination of the phosphine-phosphorus than the phosphite-phosphorus.

The increase in $^3J_{PP}$ parallels the rise in $^3J_{PH}$ and the decrease in $^2J_{PH}$ for the same groups. It is likely that the same reasons for the J_{PH} trends are true for the $^3J_{PP}$ trend.

Why $^3J_{PP}$ should be more dependent on the phosphine-phosphorus than on the phosphite-phosphorus is not obvious. The reason does not appear to be dependent on the change in the bridgehead angle. Although $^3J_{PP}$ could not be measured on the phosphine coordinated ligand of $(OC)_3Fe[P(OCH_2)_3P][P(CH_2O)_3P]$, the value of $^3J_{PP}$ for the phosphite ligand (+ 9.0 Hz) is comparable to $^3J_{PP}$ for $(OC)_4FeP(OCH_2)_3P$ (+ 8.6 Hz). The value for $^3J_{PP}$ in $(OC)_4FeP(CH_2O)_3P$ (47.1 Hz) is thus likely to be comparable to the value of $^3J_{PP}$ in the phosphine coordinated ligand of the disubstituted complex. It is obvious then that although the bridgehead angle changes by the same amount upon coordination of either phosphorus, the change in $^3J_{PP}$ varies from one phosphorus to the other by a factor of two. A possible factor may well be the rigid bicyclic system's inability to reflect changes in hybridization accurately. It may well be that in L the phosphorus-carbon bonds contain more s character than do the phosphorus-oxygen bonds, but steric restrictions necessitate that the CPC angle be smaller than the OCO angle. That is, many of the bonds in L may be "bent" bonds, and the per cent s character in them is not measurable by determining bond parameters. Since carbon is less electronegative than oxygen, the s character in the phosphorus-carbon bonds will be more affected by the Y group than the s character in the phosphorus-oxygen bonds. The observation that the FPF angle is the same in PF_3 and PF_3 complexes (87b) appears to support this idea since the s character in a phosphorus-fluorine bond would be expected to change very little upon coordination of the phosphorus. Hence the greater effect of the phosphine-phosphorus on $^3J_{PP}$ than the phosphite-phosphorus.

The idea of bent bonds is substantiated by the findings of Schleyer et al. (94) that the adamantane and [2.2.2] bicyclooctane molecules are strained. Adamantane has previously been considered to be strain free, but their calculations show 6.48 kcal/mole of strain while [2.2.2] bicyclooctane has 11.01 kcal/mole of strain. Whether $P(OCH_2)_3P$ has more or less strain than the hydrocarbon analog is not certain, for one of the main reasons for the strain in the bicyclic hydrocarbons is the inability of the C-C-C angles to expand to "normal" 112 degrees found in open-chain hydrocarbons. The angles around oxygen and carbon in

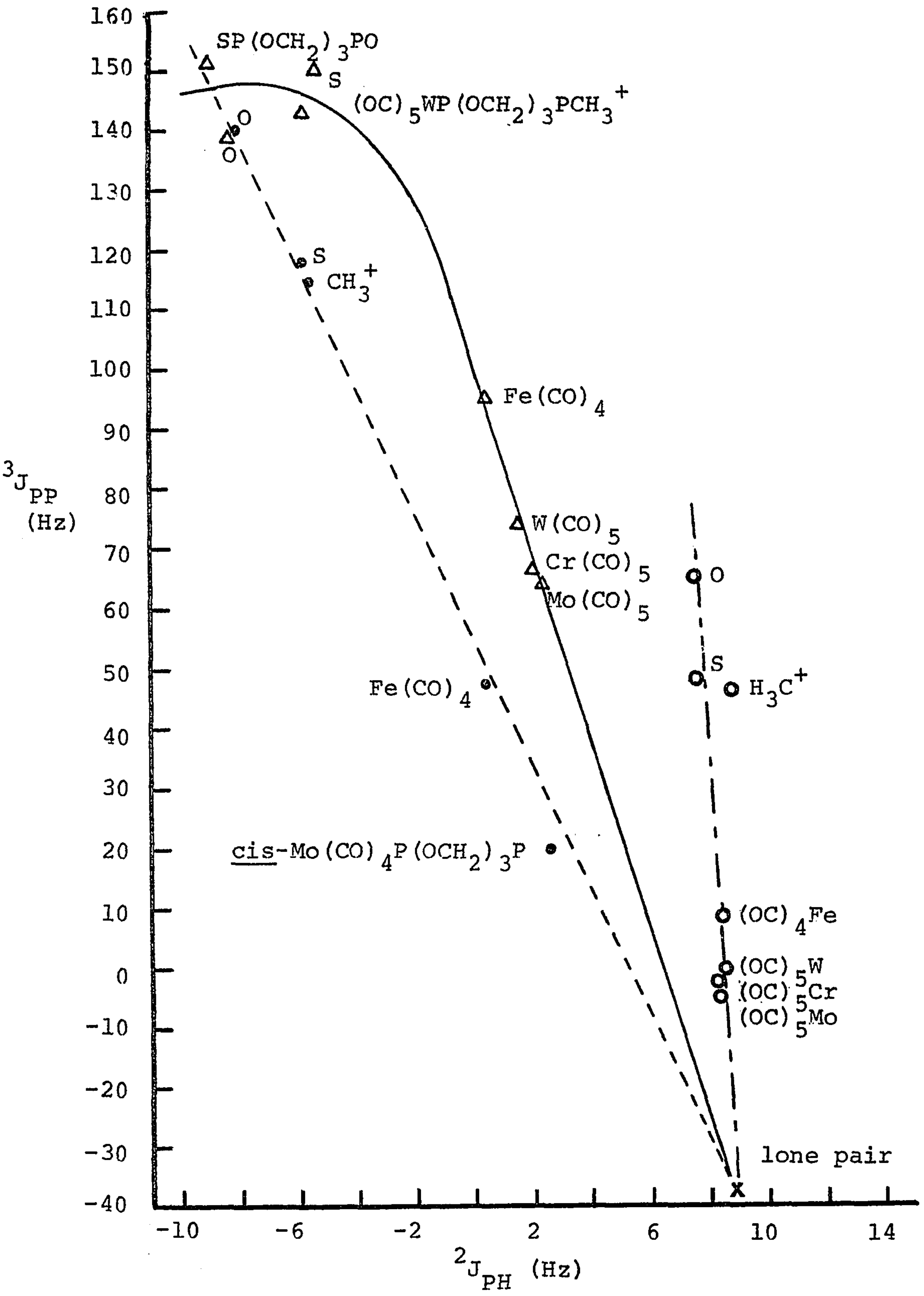
L are very near to favorable values, but as pointed out the bridgehead angles are not and significant strain may well be present.

From what has been said, it is expected that $^3J_{PP}$ for $YP(OCH_2)_3PY$ compounds should be larger than for either $YP(OCH_2)_3P$ or $P(OCH_2)_3PY$. This is the case for all of the compounds except one. In fact, the value for $^3J_{PP}$ appears to be additive for the metal carbonyl complexes. Hence, $^3J_{PP}$ for $(OC)_4FeP(OCH_2)_3P$ is +8.6 Hz, an increase of 45.8 Hz from the value for $P(OCH_2)_3P$. For the linkage isomer, $(OC)_4FeP(CH_2O)_3P$, $^3J_{PP}$ is +47.1 Hz for an increase of 84.3 Hz over L. The bridged complex has a $^3J_{PP}$ value of +95.3 Hz, an increase of 132.5 Hz over L. The sum of the increases in $^3J_{PP}$ for the two linkage isomers is 130.1 Hz which is very good agreement with the experimental value. A similar calculation of the increase in $^3J_{PP}$ for $(OC)_5WP(OCH_2)_3PCH_3$ gives a value of 188.6 Hz compared to the experimental value of 180.4 Hz. The molybdenum system, using the $^3J_{PP}$ value from the phosphine coordinated ligand in the <u>cis</u>-$(OC)_4MoL_2$ complex, gives an experimental value of 89.8 Hz compared to a calculated value of 100.9 Hz. The agreement is not unreasonable although more data are needed to firmly substantiate the additivity principle in complexes. The additive nature of $^3J_{PP}$ does not hold for the chalconide compounds of L. Although $^3J_{PP}$ for the disulfide is larger than either of the monosulfides, it is far from being equal to their sum (187 Hz measured, 240 Hz calculated). In the oxides, $P(OCH_2)_3PO$ is one Hz larger than the dioxide and only eleven Hz smaller than $SP(OCH_2)_3PO$. This non-additive nature of $^3J_{PP}$ in the chalconides is not understood and a further study of $^3J_{PP}$ in other derivatives of L may lead to a better explanation of the phenomenon.

Figures 21 and 22 show the variation of $^3J_{PP}$ with $^2J_{PH}$ and $^3J_{PH}$, respectively, for the three types of L derivatives: $YP(OCH_2)_3P$, $P(OCH_2)_3PY$ and $YP(OCH_2)_3PY$. If the hybridization of the non-coordinated phosphorus atom in the $YP(OCH_2)_3P$ and $P(OCH_2)_3PY$ compounds has changed slightly from $P(OCH_2)_3P$, $^3J_{PP}$ would be expected to correlate with $^2J_{PH}$ and $^3J_{PH}$, and support for this postulate stems from Figures 21 and 22. Furthermore, the correlation of $^3J_{PP}$ with $^2J_{PH}$ and $^3J_{PH}$ for the $YP(OCH_2)_3PY$ compounds indicates that the hinge effect of the bridgehead atoms is operating in addition to the changes incurred on phosphorus coordination.

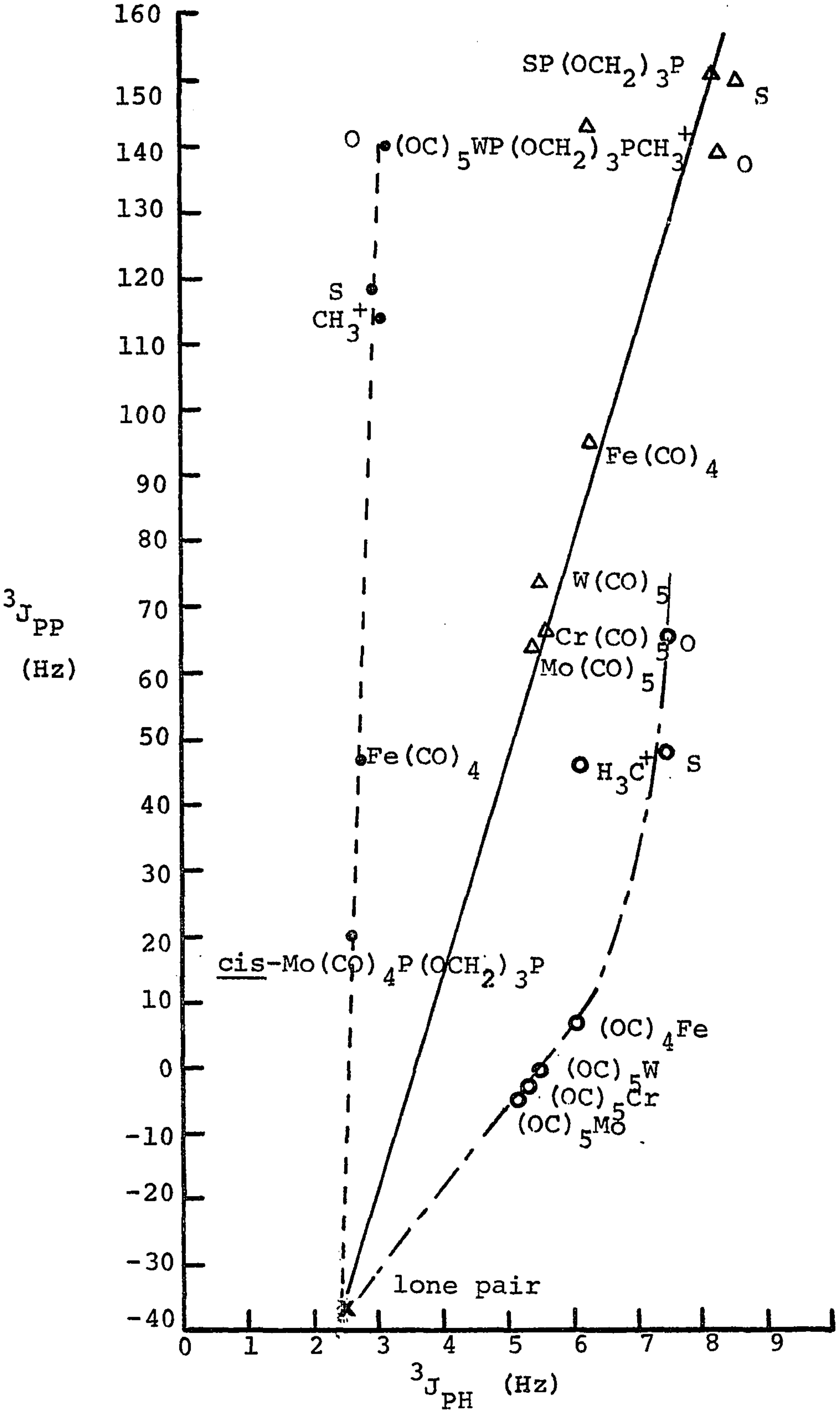
The correlations of $^3J_{PP}$ with $^2J_{PH}$ and $^3J_{PH}$ point strongly to a through bond mechanism in $^3J_{PP}$. If through-space coupling were occurring, it is difficult to see how $^3J_{PP}$ could rise positively with the increasing Lewis acidity of Y as observed inasmuch as the phosphorus non-bonding hybrid lobe(s) would be expected to lose s character. It is also interesting to note the results of photo-

Figure 21. Plot of $^{2}J_{PH}$ *versus* $^{3}J_{PP}$ for $YP(OCH_2)_3P$ (— — —), $P(OCH_2)_3PY$ (- - - - -), and $YP(OCH_2)_3PY$ (———), where the Y groups are those indicated adjacent to each point



$^3J_{PP}$ (Hz)
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
$SP(OCH_2)_3PO$
S
$(OC)_5WP(OCH_2)_3PCH_3^+$
O
O
S
CH_3^+
$Fe(CO)_4$
$W(CO)_5$
$Cr(CO)_5$
$Mo(CO)_5$
$Fe(CO)_4$
cis-$Mo(CO)_4P(OCH_2)_3P$
O
S
H_3C^+
$(OC)_4Fe$
$(OC)_5W$
$(OC)_5Cr$
$(OC)_5Mo$
lone pair
-10
-6
-2
2
6
10
14
$^2J_{PH}$ (Hz)

Figure 22. Plot of $^{3}J_{PH}$ <u>versus</u> $^{3}J_{PP}$ for $YP(OCH_2)_3P$ (—— - ——), $P(OCH_2)_3PY$ (- - - - - -), and $YP(OCH_2)_3PY$ (————), where the Y groups are those indicated adjacent to each point


SP(OCH$_2$)$_3$P
S
O
(OC)$_5$WP(OCH$_2$)$_3$PCH$_3^+$
O
S
CH$_3^+$
Fe(CO)$_4$
W(CO)$_5$
Cr(CO)$_5$
Mo(CO)$_5$
O
Fe(CO)$_4$
H$_3$C$^+$
S
cis-Mo(CO)$_4$P(OCH$_2$)$_3$P
(OC)$_4$Fe
(OC)$_5$W
(OC)$_5$Cr
(OC)$_5$Mo
lone pair
$^3J_{PP}$
(Hz)
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
0
1
2
3
4
5
6
7
8
9
$^3J_{PH}$ (Hz)

electron studies on a number of bicyclic compounds. For the compound $N(CH_2CH_2)_3N$ a strong interaction of the nitrogen lone pair atomic orbitals was found (95-97). The mechanism is shown to be a through-bond coupling involving the p components of the carbon-carbon σ bond and the nitrogen lone pair atomic orbitals. Lone pair coupling and nuclear coupling are transmitted by different components of the orbitals (p _versus_ s components), but it seems reasonable that bond pathways are used in both cases and that if p orbital coupling is not through-space, s orbital coupling need not be either.

SUGGESTIONS FOR FUTURE WORK

The synthesis of a number of compounds of the type $YP(OCH_2)_3PX$ and $XP(OCH_2)_3PY$ where X and Y are BH_3, CH_3^+, O, S, and metal carbonyl groups will give a better understanding of the limits of the additive nature of $^3J_{PP}$ in derivatives of L. Such a study will further test the proposed mechanism for $^3J_{PP}$ coupling, and it may provide an explanation for the deviation of the chalconides from the pattern of the other derivatives.

A series of structure determinations on a number of L derivatives would show whether L is a strained molecule. The most likely compounds would include $P(OCH_2)_3P$, $YP(OCH_2)_3P$, $P(OCH_2)_3PY$, and $YP(OCH_2)_3PY$ where Y is S[1], CH_3^+ and a metal carbonyl group. This study will show whether the bond parameters depend on the Y group or are dictated by steric requirements.

Further information on the interactions of the atoms in L can be gained by performing photoelectron spectroscopy studies on Y and its derivatives. A comparison of the photoelectron spectrum of L with $P(CH_2O)_3CCH_3$ and $P(OCH_2)_3CCH_3$ will show if the phosphorus-phosphorus coupling affects the energy of the phosphorus orbitals significantly (as seems likely). A series of L derivatives will indicate if a correlation can be found between $^3J_{PP}$ and orbital energy.

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[1] This study with Y=S is presently being done.

The chemistry of L should be further investigated to gain more knowledge of the effect of the dipole moment on basicity. The effect of the dipole moment on the basicity of the phosphorus atoms toward carbonium ions is of interest. Also, determination of the relative basicities of $SP(OCH_2)_3P$ and $P(OCH_2)_3PS$ to other phosphines and phosphites will be useful in understanding the dipole moment effect. Determination of the rates of hydrolysis of L, $P(OCH_2)_3PO$ and $P(OCH_2)_3PS$ will indicate whether coordination of the phosphine-phosphorus by various groups affects the chemistry of the phosphite-phosphorus.

More information about the phosphonium salt chemistry of L would be useful. The isomerization mechanism of $[P(OCH_2)_3PCH_3]BF_4$ is of interest particularly since it is possible that the coordination of one phosphorus is affecting the coordination properties of the other phosphorus. The preparation of the diphosphonium salt is also of interest in this respect.

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