1975

I. Hindered rotation studies in bis(tricarbonylchromium) complexes of diarylmethanes and mono(tricarbonylmetal) complexes of alkyl biphenyls, II. The synthesis of triisocynaide ligands and their metal complexes

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I. HINDERED ROTATION STUDIES IN BIS(TRICARBONYLCHROMIUM) COMPLEXES OF DIARYLMETHANES AND MONO(TRICARBONYLMETAL) COMPLEXES OF ALKYL BIPHENYLS. II. THE SYNTHESIS OF TRIISOCYANIDE LIGANDS AND THEIR METAL COMPLEXES.

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Chemistry, organic

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I. Hindered rotation studies in bis(tricarbonylchromium) complexes of diarylmethanes and mono(tricarbonylmetal) complexes of alkyl biphenyls. II. The synthesis of triisocyanide ligands and their metal complexes

by

David Joseph Kowalski

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Iowa State University
Ames, Iowa

1975

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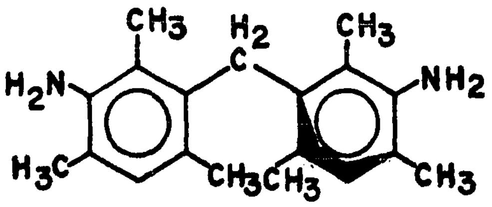
HINDERED ROTATION STUDIES IN BIS(TRICARBONYLCHROMIUM) COMPLEXES OF DIARYLMETHANES

Historical

Maclean and Adams (1) synthesized 3,3'-diaminodimesitylmethane (1) and diaminodimesityl ketone (2) in an attempt to demonstrate the presence of enantiomorphs in the diamino compounds. Being unable to resolve these compounds, they suggested a distortion of the tetrahedral structure in the methane, and a distortion of the trigonal structure in the ketone to a degree that permitted free rotation of the mesityl groups. They also raised the idea that a synchronization of the rings was taking place during rotation or a combination of these effects.



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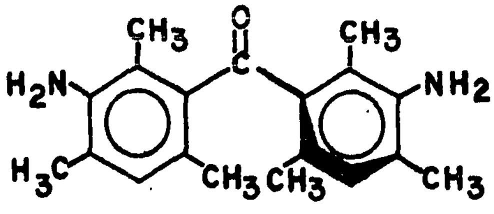

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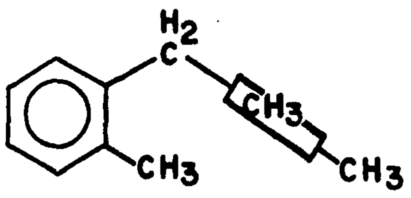
O'Shaughnessy and Rodebush (2) examined the ultraviolet spectrum of dimesityl ketone and interpreted the spectrum to indicate that only one of the mesityl rings was in conjugation with the carbonyl group. Following up on this work, Rekker and Nauta (3) calculated an angle of 68 degrees between the planes of the carbonyl group and the mesityl ring for dimesityl ketone.

Kwart and Alekman (4) examined the temperature dependence of dimesityl carbonium ions and their respective precursors by nuclear magnetic resonance spectroscopy. Even at -60° the o-methyl groups were capable of ready exchange of their environments. They postulated intramolecular rotation involving the coordinated motion of the two mesityl rings where it was assumed that both rings rotate with the same angular velocity and the arrangement of the rings was such that their planes were perpendicular. They referred to this type of rotational mechanism as a "Cogwheel Effect".

Montaudo, Caccamese and Finocchiaro (5) have looked at the conformational equilibrium in molecules containing substituted diarylmethane units. Their results indicate that, depending on the substitution pattern at the four ortho positions, different conformational preferences can arise. Two low energy conformations (3 and 4) can be drawn for mesityl-o-tolylmethane. In the two rapidly interconverting conformers the ortho-methyl group will be shielded (3) or deshielded (4) by the ring current of the adjacent aromatic nucleus, and the field position of the NMR signal will reflect the relative populations of the two forms.



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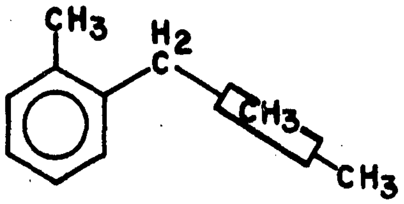
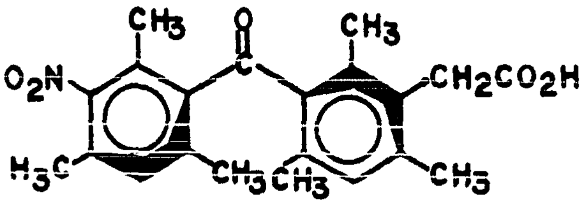


4

In mesityl-o-tolylmethane the o-tolyl methyl absorbs at 2.58 δ, while the o-methyls of the mesityl ring absorb at 2.3 δ. They designated conformer 4 as existing predominately. This effect is seen whenever three of the four ortho positions are occupied.

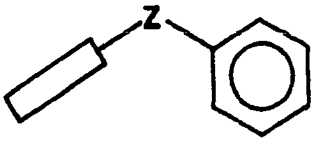
Narayanan, Selvarajan and Swaminathan (6) successfully demonstrated the existence of optical isomerism in suitably substituted benzophenones by resolving 5. The asymmetry in 5 is caused by a non planar configuration re-



5

sulting from steric interactions involving the *o*- and *o*'-methyl groups; nonidentity of the two substituted benzene rings; and the absence of a vertical plane of symmetry in each of the rings.

Recently Gust and Mislow analyzed the conformations of diarylmethanes, related compounds and their interconversions (7). The two most stable conformations are termed the perpendicular (6) and the helical (7) conformations.



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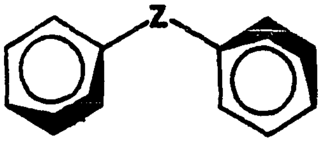
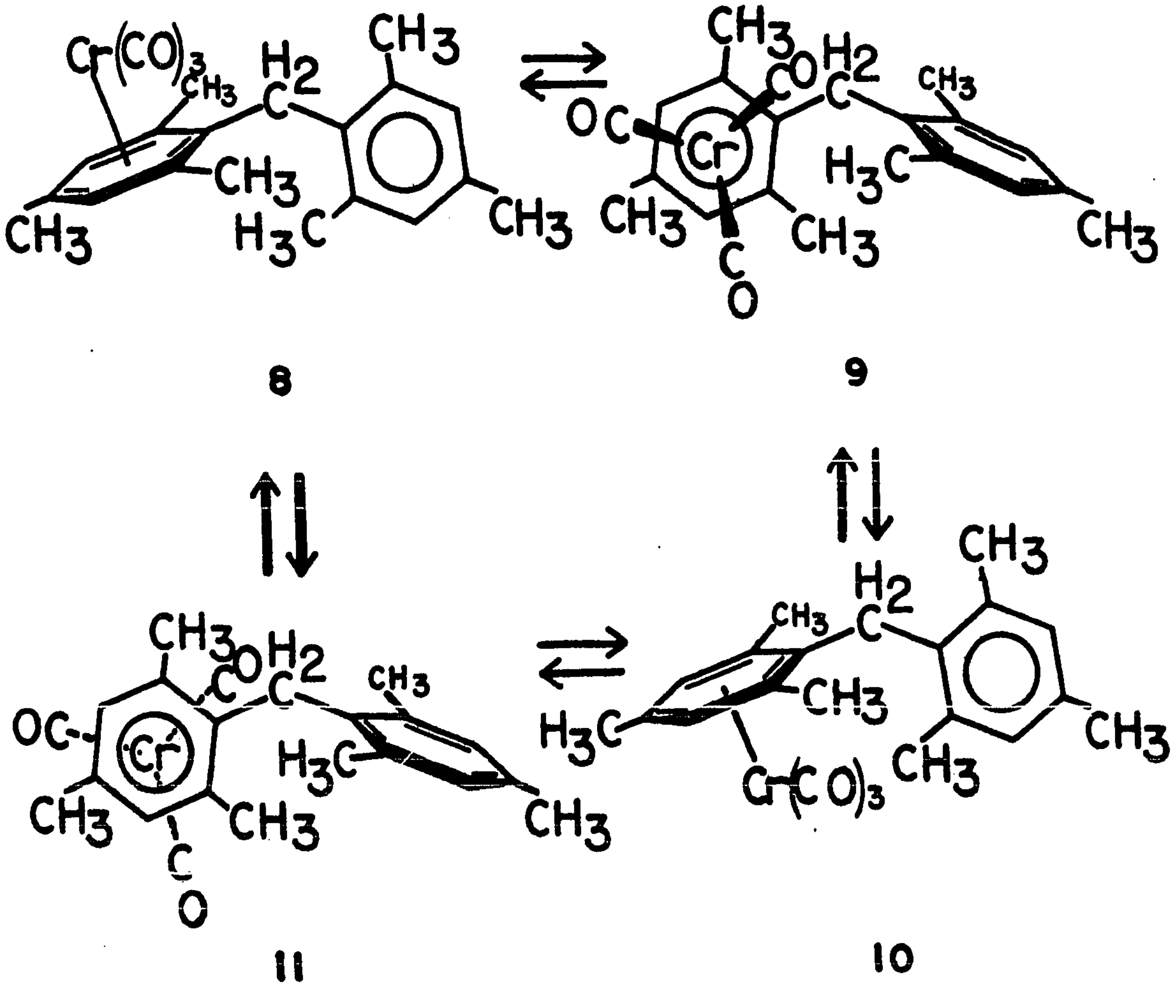


7

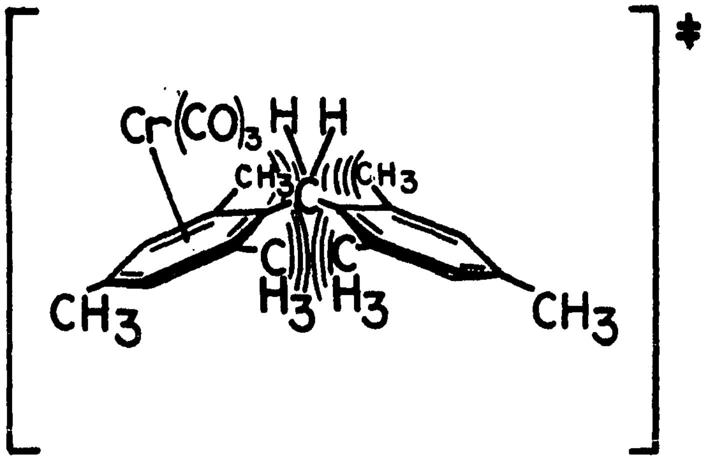
Trahanovsky, Kowalski and Avery (8) studied the hindered rotations in the monotricarbonylchromium complexes of dimesitylmethane, dimesityl ketone and 1,1-dimesitylethene. In each of these three compounds a low temperature NMR spectrum exhibits five methyl singlets, where one signal is twice the intensity of each of the other four. This signal was ascribed to the *o*-methyls of the complexed ring. The *p*-methyls of the uncomplexed and complexed rings give rise to separate signals. The *o*-methyl signals of the uncomplexed ring are temperature dependent and collapse to a singlet at high temperature. The cogwheel mechanism for ((mesityl)tricarbonylchromium)mesitylmethane is shown in Scheme 1. The existence of conformation 10 is very unlikely since models indicate severe steric interactions between the tricarbonylchromium group and an o-methyl of the uncomplexed ring. The presence of the tricarbonylchromium moiety prevents the cogwheel mechanism from operating so in order to equilibrate the o-methyl signals of the uncomplexed ring, a transition state involving the tetra-o-methyl interaction (12) was invoked.

The barrier energies for the methane and ethene complexes were nearly the same while the ketone complex had an increased barrier energy of 5 kcal/mole. This was rationalized by saying that the ground state of the ketone complex was stabilized by a resonance interaction between the keto group and the uncomplexed ring.

A di(tricarbonylchromium) complex that exhibits molecular dissymmetry has been reported by Kowalski (9). Di((mesityl)tricarbonylchromium) ketone (13) exhibits three sharp singlets in the methyl region of the NMR and two peaks for the mesityl protons of the complexed rings. Enantiomeric conformations (14 and 15) exist for the molecule.



Scheme 1. The cogwheel mechanism for ((mesityl)tricarbonylchromium)mesitylmethane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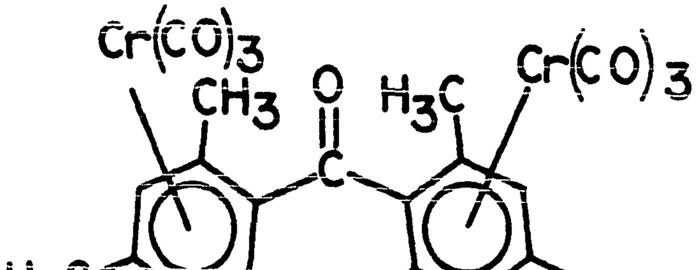
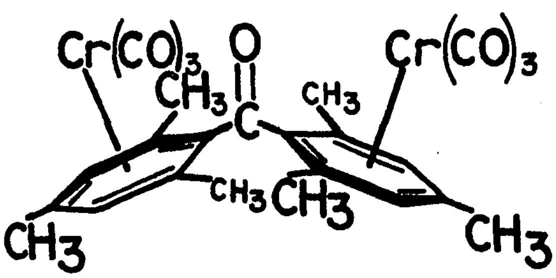
H
H
CH3
C
CH3
C
C
H3
H3
CH3
CH3
‡

12


Cr(CO)3
CH3
O
C
H3C
Cr(CO)3
H3C
CH3
CH3
CH3

13



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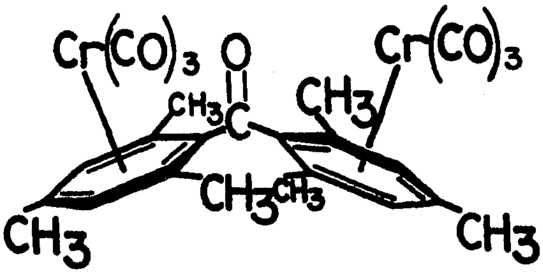


15

Ercoli, Calderazzo and Alberola (10) have been successful in preparing ditricarbonylchromium complexes of a variety of diarenes including biphenyl, diphenylmethane and stilbene. They utilized a ligand exchange reaction between the diarene and excess benzenetricarbonylchromium in a melt at 160°.

Results

The fact that a small amount of the bis(tricarbonylchromium) complex of dimesityl ketone had been isolated and that it possessed an interesting NMR spectrum prompted us to continue working in this area. The idea was to see how the free energy of activation for rotation of the mono(tricarbonylchromium) complexes compared to the bis(tricarbonylchromium) complexes of various diaryl compounds.

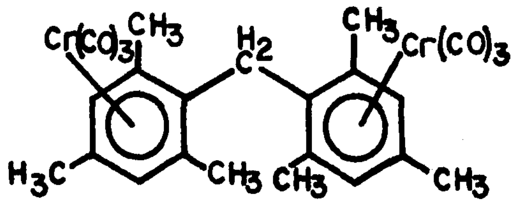
Di((mesityl)tricarbonylchromium) ketone (<u>13</u>) had been prepared in a very small yield by complexation of dimesityl ketone with hexacarbonylchromium in glyme solvent (9). The reactions conditions were varied so as to favor the formation of the bis complex, however, suitable conditions for increasing the yield starting with hexacarbonylchromium were not found. Various attempts to prepare even small quantities of the dicomplex of dimesitylmethane starting with hexacarbonylchromium met with failure. The dicomplexes were successfully prepared in moderate yields by the method of Ercoli, Calderazzo and Alberola (10). The oil bath temperature for this work was 185° and the reactions were terminated when the melt solidified.

In the three dicomplexes studied, that of dimesityl ketone, dimesitylmethane and 1,1-dimesitylethene, the NMR spectra could be interpreted as arising from hindered rotation. The free energies of activation for rotation for these complexes are reported in Table 1, at the end of this section.

Di((mesityl)tricarbonylchromium) ketone (13) was dissolved in o-dichlorobenzene and its spectrum was run on the 100 MHz NMR. At ambient temperature the methyl region consists of three sharp equally intense singlets at 1.79 δ, 2.06 δ and 2.25 δ. The mesityl ring proton signals occur as singlets at 4.55 δ and 4.62 δ. As the temperature is raised coalescence of the mesityl ring proton signals occurs at 92°. The methyl signals at 1.79 δ and 2.25 δ are seen to broaden as the temperature is raised and coalescence for the o-methyl signals occurs at 117° ± 5°. As the temperature was further increased a broadened singlet at 2.10 δ was observed to emerge. A single crystal x-ray diffraction study of the ketone dicomplex (11) confirms the helical conformation in the solid state.

The 100 MHz NMR spectrum for di((mesityl)tricarbonylchromium)methane (16) at -43° in deuterochloroform exhibited three methyl singlets of equal intensity occurring at 1.87 δ, 2.16 δ and 2.43 δ. The complexed mesityl ring proton signals occur as broadened singlets at 4.95 δ and 5.07 δ. The methane proton signals occur as a singlet at 3.77 δ. Raising the temperature results in the coalescence of the mesityl ring proton signals at 10° in deuterochloroform. The methyl signals at 1.87 δ and 2.43 δ are seen to collapse as the temperature is raised and coalescence for these o-methyl signals occur at +37 ± 5° in deuterochloroform. A 100 MHz NMR spectrum in o-dichlorobenzene at +104° shows that the o-methyl signal has emerged at 2.04 δ while the resonance due to the p-methyls remains a singlet now at 1.99 δ. The mesityl ring proton signals now absorb as a singlet at 4.79 δ as do the methane proton signals at 3.81 δ.

A 100 MHz NMR spectrum for 1,1-di((mesityl)tricarbonylchromium)ethene (17) at +98° in o-dichlorobenzene is shown in Figure 1 and a spectrum at -49° in deuterochloroform is



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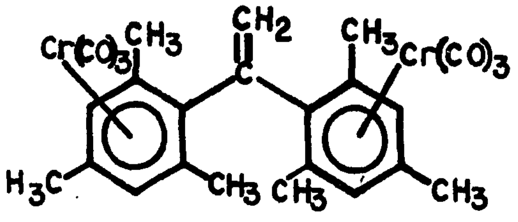


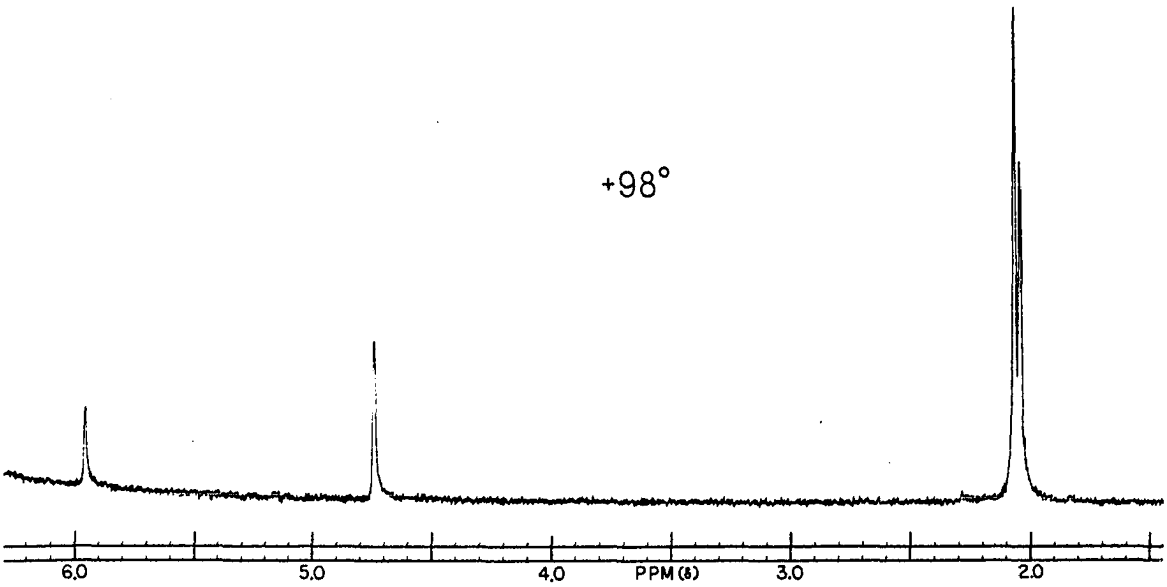
17

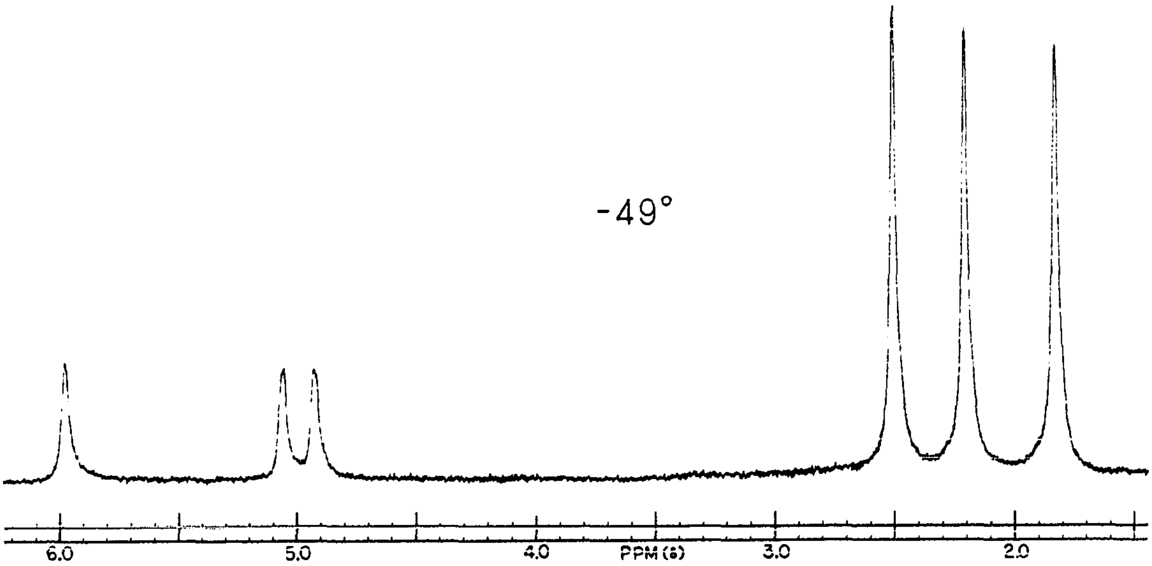
shown in Figure 2. In the low temperature spectrum three methyl singlets of equal intensity occur at 1.83 δ, 2.21 δ and 2.50 δ. The complexed ring proton signals occur as broadened singlets at 4.93 δ and 5.06 δ, and the ethene proton signals occur as a singlet at 5.98 δ. Upon raising the temperature the mesityl proton signals coalesce at -3° in deuterochloroform and coalescence of the o-methyl signals at 1.83 δ and 2.50 δ occurs at +24° ± 5° in deuterochloroform. The high temperature spectrum in o-dichlorobenzene exhibits singlets at 2.04 δ, 2.06 δ, 4.74 δ and 5.96 δ with an integration ratio of 6:12:4:2 for the p-methyl, o-methyl, mesityl ring proton signals and ethene proton signals respectfully.

The coalescing methyl region for the three dicomplexes has a range of temperature connected with it because the coalescing peaks were the outermost peaks in the methyl spectra and happened to coalesce beneath the p-methyl peak.

Figure 1. HA-100 NMR spectrum of 1,1-di((mesityl)tricarbonylchromium)ethene (17) in o-dichlorobenzene at +98°

Figure 2. HA-100 NMR spectrum of 1,1-di((mesityl)tricarbonylchromium)ethene (17) in deuterochloroform at -49°


+98°
6.0
5.0
4.0
PPM (δ)
3.0
2.0


-49°
6.0
5.0
4.0
PPM (δ)
3.0
2.0

Direct observation of the flat topped coalescent peak is not possible and only by comparing many scans at various temperatures can one reliably place the coalescent temperature. It is felt that the coalescent temperature is within ± 5° of the actual temperature.

Table 1. The activation free energies for rotation for the bis(tricarbonylchromium) complexes of dimesityl ketone (<u>13</u>), dimesitylmethane (<u>16</u>) and 1,1-dimesitylethene (<u>17</u>)[a]

Compound (Solvent)	T_c[b]	T_c[c]	ν_{AB}[d]	$\Delta G^{*}_{T_c}$[e]
<u>13</u> (o-$C_6H_4Cl_2$)	92	-	7	19.5
	-	117	46	19.5
<u>16</u> ($CDCl_3$)	10	-	12	14.7
	-	37	56	15.2
<u>17</u> ($CDCl_3$)	-3	-	13	13.9
	-	24	67	14.4

[a] See <u>experimental</u> for an explanation of how the samples were prepared for NMR analysis. T_c obtained on the 100 MHz NMR.

[b] The coalescence temperature in °C for the mesityl ring protons. Error is ± 2° C.

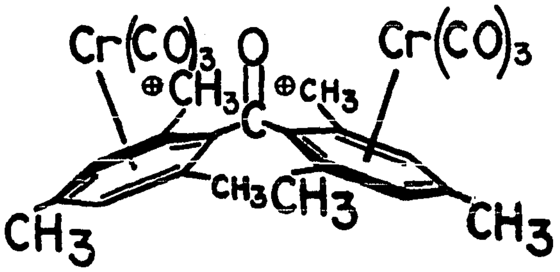
[c] The coalescence temperature in °C for the <u>o</u>-methyls. Error is ± 5° C.

[d] This is the separation in Hz of the two coalescing peaks well below the coalescence temperature.

[e] The free energy of activation for rotation at the coalescence temperature is kcal/mole. Estimated error is ± 0.5 kcal/mole.

Discussion

The NMR spectrum for di(mesityl)tricarbonylchromium ketone is interpreted to indicate the presence of a dicomplex where the barrier to rotation is large so that the molecule exists in molecularly disymmetric enantiomers (14 and 15).



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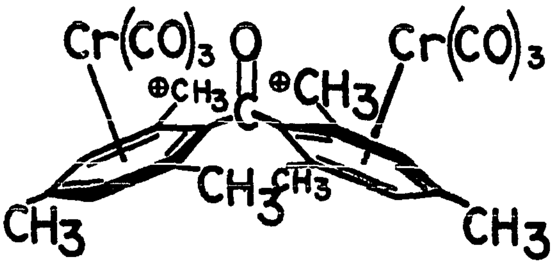

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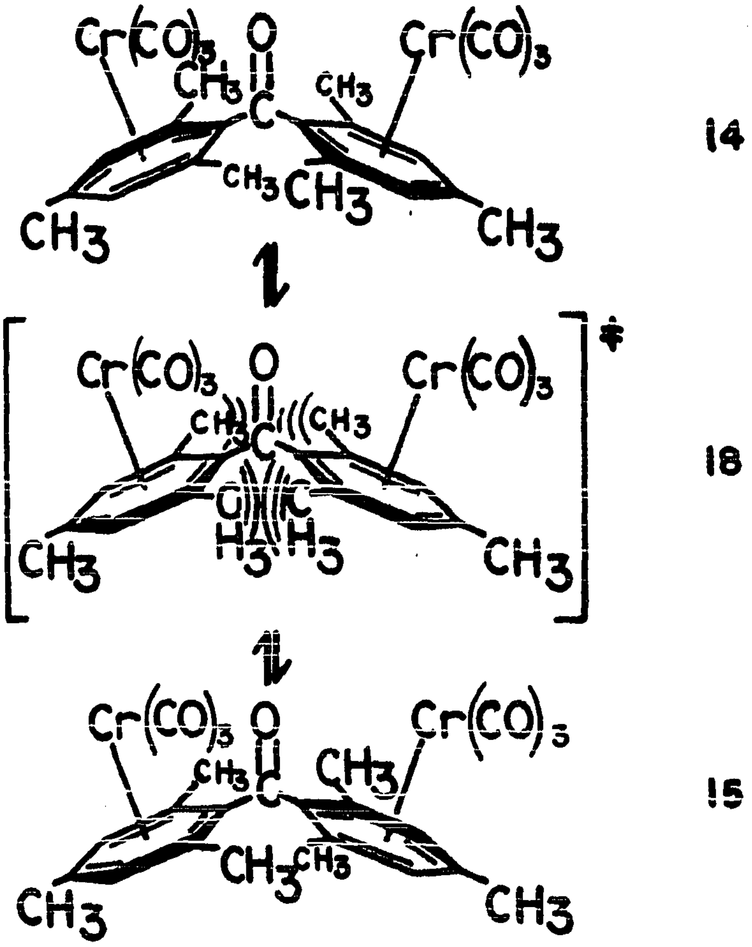
Each enantiomer exists in a helical conformation (7). The unlabelled o-methyl group from each mesityl ring lies in the bottom face of the opposite mesityl ring and constitutes the highest field peak since it is the most shielded. The labelled o-methyl from each ring is in the most deshielded environment. The mesityl ring protons are also in different magnetic environments and give rise to separate signals. A single crystal x-ray diffraction study of the ketone dicomplex (11) has been completed and the helical conformation was confirmed for the solid state. The low temperature NMR spectra for the methane dicomplex

(16) and the ethene dicomplex (17) are similar to that of the ketone dicomplex (13) and indicate that 16 and 17 also exist in helical conformations.

A mechanism that accounts for the equilibration of the o-methyls and the mesityl ring protons at high temperature is shown in Scheme 2. This mechanism also allows for the interconversion of the enantiomeric conformations. The mechanism as shown involves the tetra-o-methyl interaction



Scheme 2. Mechanism for the interconversion of the enantiomeric conformations of dicomplexed dimesityl compounds

(18) as the transition state where the plane of each mesityl ring is perpendicular to the aryl-central carbon-aryl plane. A similar transition state was proposed for the equilibration of the *o*-methyls of the uncomplexed ring in the monotricarbonylchromium complexed diaryl compounds (8,9). The major difference between the transition state for the mono- and di-complexes is, of course, the presence of the additional tricarbonylchromium moiety in the dicomplexes.

The barrier energies for the mono- and di-tricarbonylchromium complexes within a given dimesityl compound are very similar. For the ketone complexes and the ethene complexes the barrier energies are the same within experimental error. A 1 kcal/mole difference exists between the methane monocomplex and its dicomplex. This small difference could easily arise from the different solvent system used for the temperature study. As in the monocomplexes the barrier energy for the ketone dicomplex is again about 5 kcal/mole greater than the methane or ethene dicomplexes.

The steric strains in the transition state that both mono- and di-complexes experience must be similar. Since the barrier energies for both the mono- and di-complex of the ethene are the same, this indicates that the ground state energies are the same and furthermore that there are no additional steric strains present in the ground state of the ethene dicomplex that do not already exist in the ground state of the ethene monocomplex. The same can be said for the methane system, namely that the similarity of the barrier energies for the two complexes indicates that the ground state for the two complexes are the same.

In the ketone mono- and di-complexes neither ring is conjugated with the carbonyl in the transition state. For the ketone monocomplex the very high barrier was attributed to a resonance interaction between the carbonyl group and the uncomplexed ring (8,9). This interaction would stabilize the ground state and consequently the barrier energy would be larger. It was pointed out, however, that the carbonyl group could be partially or fully conjugated with a complexed ring (8). If this was operant then the results would indicate that the delocalization of electrons between carbonyl groups or carbon-carbon double bonds and phenyl rings is not greatly affected by the presence of a tricarbonylchromium moiety on the phenyl ring. Evidence for this comes from the ketone dicomplex where the ground state involves partial conjugation of two complexed phenyl rings with the carbonyl and the net stabilization of about 5 kcal/mole is the same as the stabilization that results from full conjugation of a carbonyl group with an uncomplexed ring. The results indicate that the delocalization of π electrons is similar for both uncomplexed phenyl rings and tricarbonylchromium complexed phenyl rings.

Experimental

Equipment, methods and materials

Nuclear magnetic resonance spectra were run on a Varian Associates HA-100 Nuclear Magnetic Resonance Spectrometer; variable temperature work employed the V-6040 variable temperature controller and the V-4333 probe.

Melting points were taken on a Thomas Hoover Capillary Melting Point Apparatus. All melting points are uncorrected.

The dicomplexes were prepared by the method of Ercoli, Calderazzo and Alberola (10).

Elemental analyses were carried out by Spang Microanalytical Laboratory (Ann Arbor, Michigan).

Methylene chloride, pentane and benzene were obtained from J. T. Baker Co., glyme was obtained from Aldrich, deuterochloroform from Mallinckrodt, and *o*-dichlorobenzene from Matheson, Coleman and Bell.

Prepared compounds

Di((mesityl)tricarbonylchromium) ketone (**13**) Benzenetricarbonylchromium (12) (1.0 g, 4.67 mmol) and dimesityl ketone (8) (0.62 g, 2.44 mmol) were placed in a five ml tear drop shaped 14/20 flask and the contents were mixed together. A male standard taper joint was attached to the flask and to this was attached a nitrogen inlet. The system was purged with nitrogen for fifteen minutes. The flask was then immersed in an oil bath that had been preheated to 160°, and within five minutes the solid contents had melted, and the solution color was deep red. In about thirty minutes a liquid began to coat the inside of the standard taper shaft. The benzene which slowly condensed was removed by increasing the nitrogen flow and opening the system at the top of the shaft until the shaft was visibly dry. No noticeable change was observed when the temperature of the oil bath was increased to 200°, except that the benzenetricarbonylchromium sublimed out of solution at a faster rate. By tapping the flask it could be returned to the melt. After fluctuating the temperature for nearly four hours, it was finally set at 185° for three hours. The system was cooled and kept under nitrogen overnight. The next day an additional 0.5 g (2.34 mmol) of benzenetricarbonylchromium was added and the flask was immersed in the oil bath now set at 185°. Within six hours the melt solidified at that temperature. The cooled material was broken up, dissolved in methylene chloride and chromatographed on a 175 g silica gel column using a solvent system of 30% methylene chloride and 70% pentane. The deep red final band was collected and recrystallized from methylene chloride-pentane to give 0.75 g

(60%) of the desired dicomplex. The mp was 226-229°, lit. (9) mp 226-227°; NMR ($CDCl_3$) δ 4.90 (d, J = 2 Hz, 2), 4.74 (d, J = 2 Hz, 2), 2.42 (s, 6), 2.23 (s, 6), and 1.91 ppm (s, 6). The elemental analysis was performed on a sample that had been obtained in low yield from the direct complexation of the ketone and hexacarbonylchromium. The mp and NMR spectrum of this sample agree very well with the material obtained by the method reported above. Anal. Calcd. for $C_{25}H_{22}Cr_2O_7$: C, 55.77; H, 4.12. Found: C, 55.90; H, 4.32.

Di((mesityl)tricarbonylchromium)methane (16)

Benzenetricarbonylchromium (12) (1.5 g, 7.0 mmol) and dimesitylmethane (8) (0.60 g, 2.34 mmol) were placed in a small flask and the solids were thoroughly mixed. After purging the system with nitrogen for 15 minutes, the flask was immersed in a preheated oil bath (185°) and maintained there until the melt went solid (8 hr). Periodically the flask was tapped to return the benzenetricarbonylchromium to the melt and likewise periodically the formed benzene was removed with a nitrogen stream. After cooling, the solid was broken up, dissolved in methylene chloride and chromatographed down a silica gel column using a solvent system of 20% benzene and 80% pentane. The last band was removed, recrystallized from methylene chloride-pentane and sublimed

(170° at 0.01 mm), mp 228-232° with decomposition; NMR ($CDCl_3$) δ 4.95 (broad s, 4), 3.79 (s, 2), and 2.69-1.49 (broad peak with superimposed s at 2.13, 18). Anal. Calcd. for $C_{25}H_{24}Cr_2O_6$: C, 57.26; H, 4.61. Found: C, 57.27; H, 4.58.

1,1-Di((mesityl)tricarbonylchromium)ethene (17) Benzenetricarbonylchromium (12) (1.5 g, 7.0 mmol) and dimesityl ethene (8) (0.62 g, 2.33 mmol) were placed in a small flask. After mixing the solids thoroughly, the system was purged with nitrogen for 15 minutes and then the flask was immersed in a preheated oil bath (185°) and maintained there until the melt solidified (9-1/2 hr). Periodically the flask was tapped to return the benzenetricarbonylchromium to the melt and likewise periodically the formed benzene was removed with a nitrogen stream. After cooling, the solid was broken up, dissolved in methylene chloride and chromatographed on a silica gel column using a solvent system of 20% methylene chlorine and 80% pentane. The last band was removed and recrystallized from methylene chloride-pentane after a sublimation (170° at 0.01 mm) to give yellow needles (0.4 g, 32%); mp (in a sealed tube under N_2) 255-256°; NMR ($CDCl_3$) δ 5.99 (s, 2), 4.92 (s, 4), and 2.70-1.60 ppm (broad peak with a superimposed singlet at 2.17, 18). Anal. Calcd. for $C_{26}H_{24}Cr_2O_6$: C, 58.21; H, 4.51. Found: C, 58.10; H, 4.40.

Nuclear magnetic resonance technique

A given dicomplex was dissolved in a suitable solvent and the solution was filtered through a pad of activated charcoal in a sintered glass frit into the NMR tube. The activated charcoal aids in removing trace impurities and paramagnetic metal species.

Either before or after a variable temperature study, the range under investigation was calibrated by using the methanol standard for low temperature or the ethylene glycol standard for high temperature. The chemical shift difference versus the observed dial temperature was obtained for the standard sample at various points covering the range studied. These points were then plotted on the graph that contained the true curve for the standard. A smooth line was drawn connecting the points. The actual temperature was obtained from the point on the true curve which possessed the same chemical shift difference as the point on the plotted curve at the observed temperature.

Tetramethylsilane was the internal standard and the source for lock.

The free energy of activation, $\Delta G^{\ddagger}_{T_c}$, at the coalescence temperature, T_c, the temperature at which the two peaks become a single peak with a flat top, is given by the equation $\Delta G^{\ddagger}_{T_c} = 4.580 \times 10^{-3} \times T_c \times (9.976 + \log (T_c/\nu_{AB}))$ where

ν_{AB} is the width of the peak at its half height (13). The ν_{AB} was determined by measuring the separation of the two peaks well below the coalescence temperature (14, 15).

HINDERED ROTATION STUDIES IN MONO(TRICARBONYLMETAL) COMPLEXES OF ALKYL BIPHENYLS

Historical

Biphenyl and its substituted derivatives have interested chemists for about seventy years (16, 17). After having elucidated the structure of biphenyl, chemists became interested in the physical property of hindered rotation that biphenyls exhibit (18). Over the years the work dealt primarily with hindered rotation in tri- and tetra-ortho substituted biphenyls, because these could easily be studied by polarimetry utilizing the racemization of one of the pure optical antipodes provided the substituents were sufficiently large. Results were obtained for diortho substituted biphenyls, but the substituents had to be very large and racemization occurred with moderate rates at room temperature (19, 20). Monoortho substituted biphenyls have been studied the least (21).

With the arrival of Nuclear Magnetic Resonance (NMR), interest again arose in studying those biphenyls that were not easily studied by racemization techniques. Polarimetry measures barriers that are in excess of 18 kcal/mole, while NMR techniques measure barriers in the range of 5 to 26 kcal/mole. It has even been confirmed that the process which is observed by polarimetry is the same as the process that is studied by NMR (22, 23).

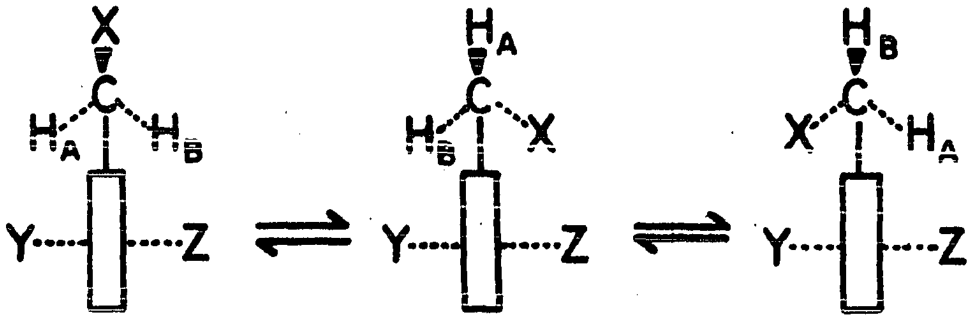
NMR investigations have also revealed that a solvent effect on the internal rotation in biphenyls (unbridged (24), singly bridged (25) and doubly bridged (22)) is very small, if present at all. However, a small solvent effect (1 kcal/mole) has been observed for the bridged biphenyl, 1-hydroxy-5,7-dihydro(c,e)oxepin (26), and for variously substituted 2-isopropyl-2'-hydroxybiphenyls (27).

Biphenyl itself has been the subject of experimental determinations and theoretical calculations. The experimental barriers range between 0.3 - 4 kcal/mole (28, 29, 30), while the theoretical calculations have a spread of values not exceeding 5 kcal/mole (31). In the case where the calculated barrier was 3.1 kcal/mole, the angle between the two rings in the ground state was calculated to be 40° (31). This contrasts slightly with some other work where the angle of twist was calculated to be 30° (32). These authors also calculated the angle of twist for various methyl substituted biphenyls, bipyridyls and phenylpyridines. An angle of twist of 70° was calculated for both 2,6-dimethylbiphenyl and 2,2'-dimethylbiphenyl.

Optically active 2,2'-diamino-6,6'-dimethylbiphenyl has been converted into optically active 2,2'-dimethylbiphenyl at low temperature (33). The barrier to rotation in the latter biphenyl was experimentally determined to be

17.4 kcal/mole at -35°. The barrier energy was determined by polarimetry where the racemization occurred at -32° with a half life of seven minutes.

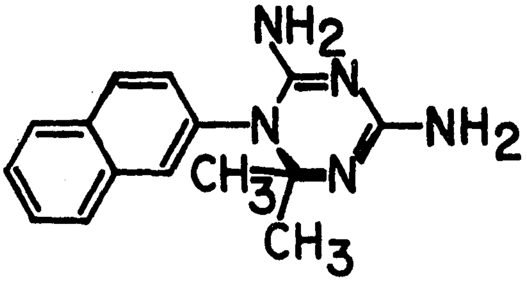
The rates of rotation of asymmetric biphenyls have also been studied by NMR (34). The two aromatic rings of an *o*-substituted biphenyl may not be coplanar because of the steric requirements of the *o*-substituents. An *o*-substituent on one ring then lies above the plane of the second (19) and if the second ring bears different *o*-groups (Y and Z), the substituent on the first ring is in an asymmetric environ-



19 20 21

ment. If the substituent is a substituted methyl group, the two protons are not necessarily magnetically equivalent. Rotation about the phenyl-substituent bond does not render the protons equivalent (19, 20, 21). That this can indeed be the case is clearly seen from the NMR spectrum of dl-2,2'-bis(acetoxymethyl)biphenyl in which the CH_2O proton resonance appears as an AB quartet. Upon warming, the quarter collapses eventually to a single line. The free energy of activation for rotation for 2,2'-bis(bromomethyl)-biphenyl and its acetate derivative has been determined by NMR to be 22.2 ± 0.1 and 21.7 ± 0.1 kcal/mole respectively (35). In several bridged diphenyls (36, 37, 38) non-equivalent o-methylene protons have been observed, but in these systems the methylene groups are part of a ring and thus are not free to rotate.

Hindered rotation has been observed by NMR for 1-(β-naphthyl)-1,2-dihydro-2,2-dimethyl-4,6-diamino-s-triazine (22), where the asymmetric shielding of the naphthyl group is sufficient to cause chemical shift differences between the diastereotopic methyl groups (39). The asymmetric shielding of the naphthyl group is also able to cause chemical shift differences between diastereomeric rotational isomers. The NMR spectrum for 23 exhibits



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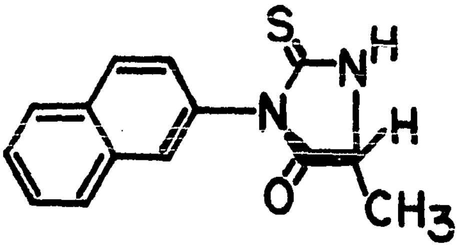
overlapping quartets for the 5-methine proton, one quartet for each diastereomeric rotational isomer (39). The NMR spectrum for 24 exhibits overlapping doublets for the 5-methyl group, one doublet for each diastereomeric rotational isomer (40).



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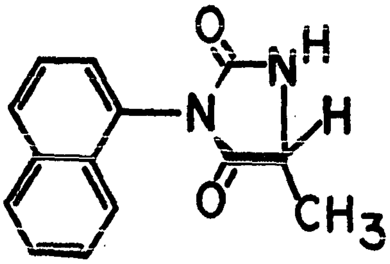

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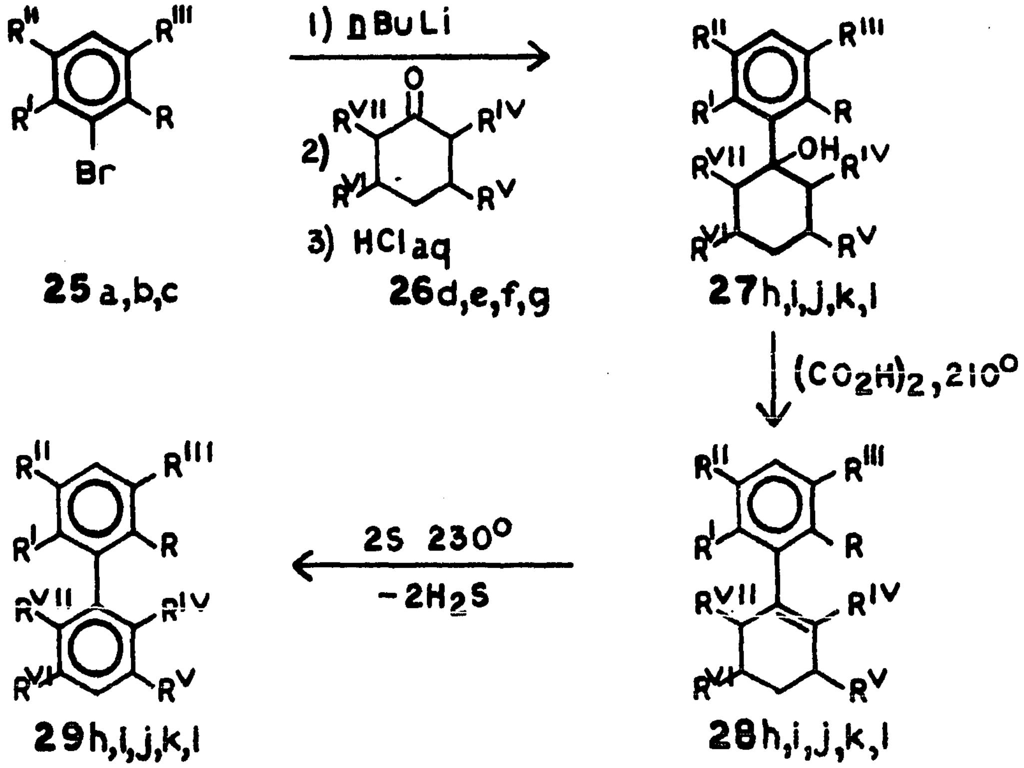
Results

The alkyl biphenyls needed for this investigation were synthesized as shown in Scheme 3.



a $R=R^{I}=H$; $R^{II}=R^{III}=CH_3$

b $R=R^{I}=R^{II}$; $R^{III}=CH_3$

c $R=CH_3$; $R^{I}=R^{II}=R^{III}=H$

d $R^{IV}=R^{VII}=CH_3$; $R^{V}=R^{VI}=H$

e $R^{IV}=CH_2CH_3$; $R^{V}=R^{VI}=R^{VII}=H$

f $R^{IV}=R^{VII}=CH_2CH_3$; $R^{V}=R^{VI}=H$

g $R^{V}=R^{VI}=CH_3$; $R^{V}=R^{VI}=H$

h $R=R^{I}=R^{V}=R^{VI}=H$; $R^{II}=R^{III}=R^{IV}=R^{VII}=CH_3$

i $R^{I}=R^{II}=R^{III}=R^{IV}=R^{VII}=H$; $R=R^{V}=R^{VI}=CH_3$

j $R=R^{I}=R^{II}=R^{V}=R^{VI}=H$; $R^{III}=R^{IV}=R^{VIII}=CH_3$

k $R=R^{I}=R^{V}=R^{VI}=H$; $R^{II}=R^{III}=CH_3$; $R^{IV}=R^{VII}=CH_2CH_3$

l $R=R^{I}=R^{V}=R^{VI}=R^{VII}=H$; $R^{II}=R^{III}=CH_3$; $R^{IV}=CH_2CH_3$

Scheme 3. Synthetic scheme for the preparation of various alkyl substituted biphenyls

2,6-Diethylcyclohexanone (26f) was prepared according to the literature procedure. This involves the coupling of two equivalents of diethyl ethylmalonate with 1,3-dibromopropane to give ethyl 3,3,7,7-nonanetetracarboxylate (41). Subsequent hydrolysis and decarboxylation yield 2,6-diethylpimelic acid (41), and this diacid was cyclized with barium hydroxide at high temperature to give the product 2,6-diethylcyclohexanone (42). No attempt was made to separate or even determine the cis- to trans-ratio for the 2,6-diethylcyclohexanone.

A sizeable quantity of 3,5-dimethylbromobenzene was required. Unfortunately the Sandmeyer reaction on 3,5-dimethylaniline even with modifications gave low yields. 2,6-Dimethylaniline is commercially available and it seemed attractive to apply to this amine the reactions that had successfully converted p-toluidine to m-bromotoluene (43, 44). The reaction details differed in that the intermediate 2,6-dimethyl-4-bromoacetamide was not stable in the acidic aqueous workup and hydrolyzed. The bromoaniline precipitates as the solution is made more basic. The bromoaniline was converted to the bromobenzene by diazotizing the amino group followed by the addition of hypophosphorous acid. The overall yield from the 2,6-dimethylaniline to the 3,5-dimethylbromobenzene was 47%. The sequence is easily carried out on 100 gm quantities of the aniline.

The aryl bromides (25a-c) were allowed to react with n-butyl lithium in ether solution at room temperature, thus converting them into the corresponding aryl lithium compounds. Reaction of these with the various cyclohexanones (26 d-f) resulted in the formation of the phenyl substituted cyclohexanols (27h-l). These compounds could easily be dehydrated to the corresponding olefins (28h-l) using anhydrous oxalic acid at a temperature around 210° (45). The yields of the olefins were nearly quantitative. Compound 28h reacts very slowly with potassium permanganate in aqueous acetone solution and with bromine in carbon tetrachloride, slow decolorization is accompanied by the evolution of hydrogen bromide. The olefins were aromatized to the corresponding biphenyls (29h-l) by using the stoichiometric amount of sulfur at 230° (46). Each biphenyl was contaminated by a small amount of its corresponding olefin. The biphenyl can be separated from the olefin by thick layer chromatography.

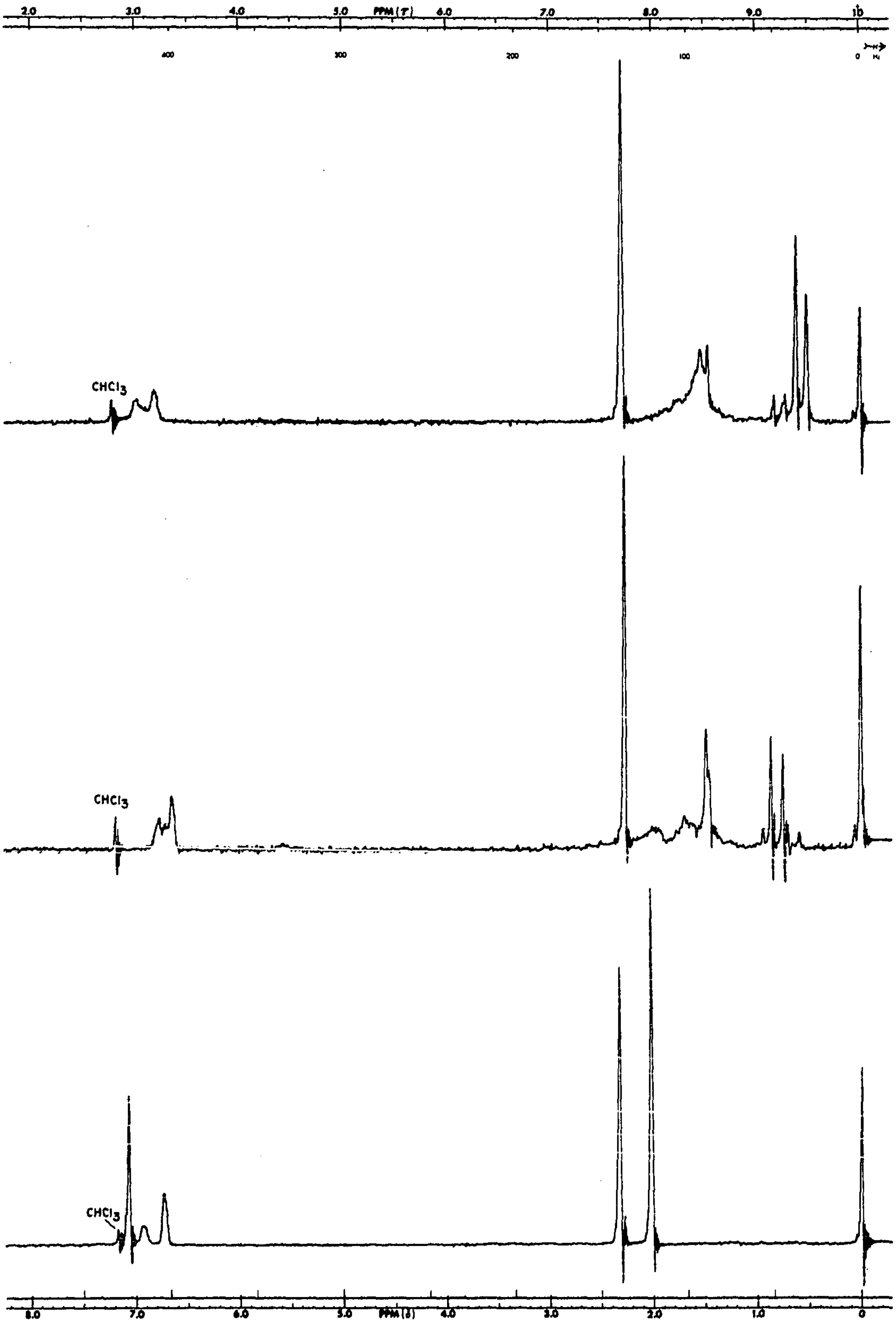
In Figure 3 is shown the NMR spectrum for 1-(3,5-dimethylphenyl)-2,6-dimethylcyclohexanol (27h). In Figure 4 is shown the NMR spectrum for the corresponding olefin (28h), while the NMR spectrum in Figure 5 is that of the corresponding tetramethylbiphenyl (29h).

The tetramethylbiphenyl in deuterochloroform exhibits

Figure 3. A-60 NMR spectrum of 1-(3,5-dimethylphenyl)-2,6-dimethylcyclohexanol (27h) in deuterochloroform at ambient temperature

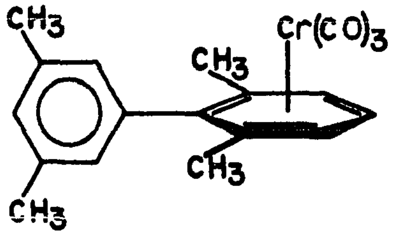
Figure 4. A-60 NMR spectrum of 1-(3,5-dimethylphenyl)-2,6-dimethylcyclohex-1-ene (28h) in deuterochloroform at ambient temperature

Figure 5. A-60 NMR spectrum of 2,3',5',6-tetramethylbiphenyl (29h) in deuterochloroform at ambient temperature


2.0
3.0
4.0
5.0
PPM (τ)
6.0
7.0
8.0
9.0
10
400
300
200
100
0 Hz
CHCl₃
CHCl₃
CHCl₃
8.0
7.0
6.0
5.0
PPM (δ)
4.0
3.0
2.0
1.0
0

singlets in the NMR at 7.06 δ, 6.93 δ, 6.73 δ, 2.33 δ, and 2.02 δ with an integration ratio of 3:1:2:6:6 respectively. The signal at 2.33 δ is assigned to the methyl groups at the 3'- and 5'-positions of the biphenyl, and this is reasonable considering the position of the methyl signal of the intermediates leading to the biphenyl. The various singlets for the tetramethylbiphenyl in deuterochloroform were expanded on the HA-100 MHz NMR, and the singlets at 7.06 δ and 2.02 δ are only broadened with little fine structure. The protons that give rise to these singlets are all attributable to the 2,6-dimethylphenyl ring. The broad singlets at 6.93 δ and 6.73 δ appear as poorly resolved octets while the signal at 2.33 δ is clearly a quartet with the two outer peaks being much reduced in intensity and the spacing between any two adjacent peaks is 0.62 Hz. Coupling between the aromatic protons and the methyl group accounts for the observed multiplicity (47).

The tetramethylbiphenyl (<u>29h</u>) was allowed to react with hexacarbonylchromium in glyme solvent at reflux for 32 hr. The complex could also be prepared by utilizing the ligand transfer reaction (10) between benzenetricarbonylchromium and the biphenyl in a melt at 180°. The isolated complex was dissolved in deuterochloroform and exhibits the NMR spectrum shown in Figure 6. Broad singlets at 7.0 δ and 6.73 δ account for the aromatic protons of the uncomplexed ring. By analogy to the parent biphenyl the resonances at 2.39 δ and 2.32 δ arise from the methyl groups on the uncomplexed ring. The complexed aromatic proton signals appear as a triplet and doublet centered at 5.53 δ and 4.99 δ respectively, while the methyl signals of the complexed ring appear as a singlet at 1.93 δ. Both the NMR spectrum and its integration are consistent with structure 30 for the complex where the tricarbonylchromium group is bound to the ring bearing the methyl groups at the 2- and 6-positions.



30

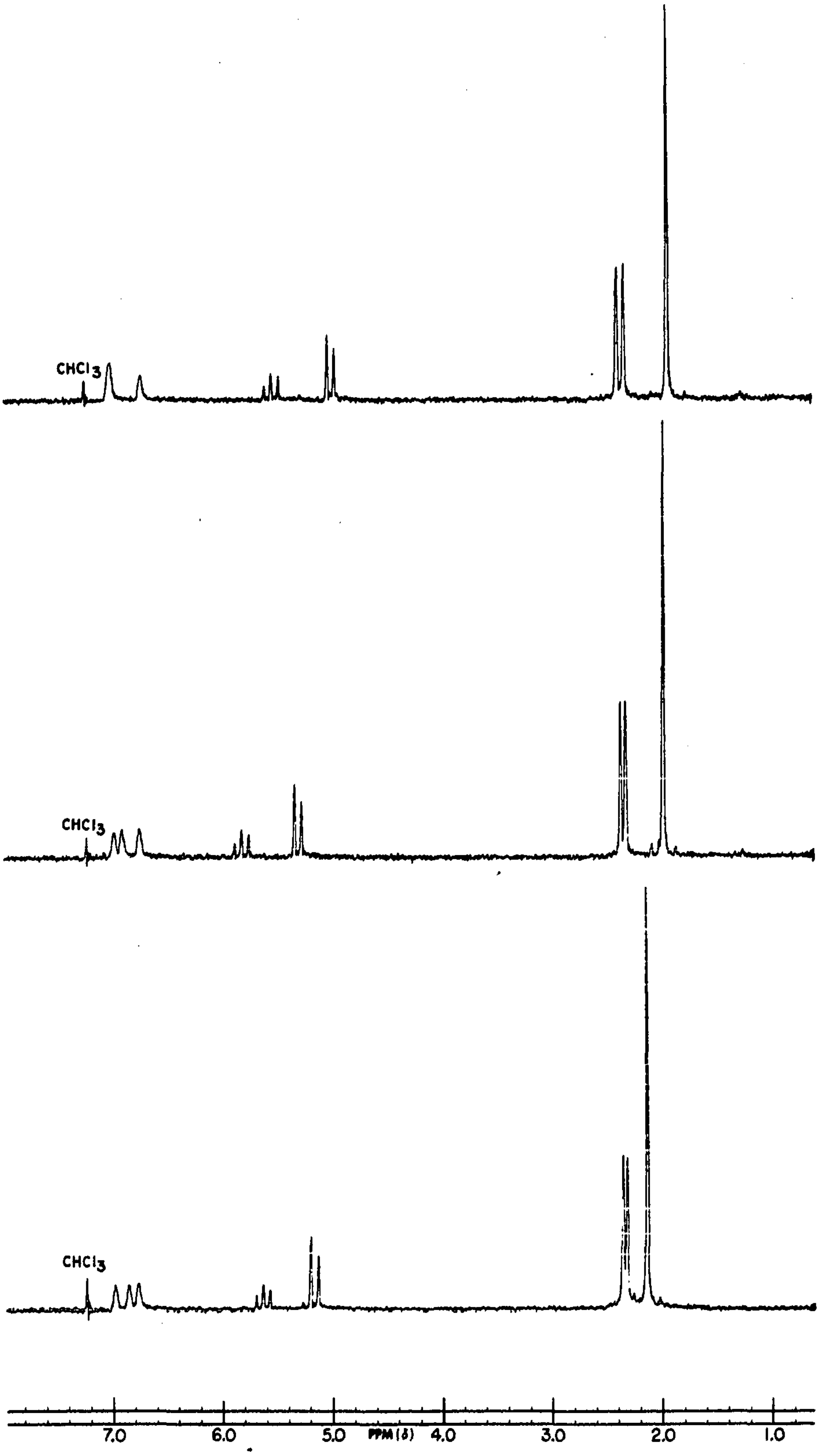
In o-dichlorobenzene as solvent at ambient temperature the complexed aromatic proton signals appear as a triplet and doublet centered at 5.3 δ and 4.74 δ respectively while the methyl signals of the uncomplexed ring occur at 2.23 δ and 2.20 δ. The methyl signals of the complexed ring occur as a singlet at 1.79 δ.

A similar NMR spectrum is shown in Figure 7 for the product complex in deuterochloroform that resulted when 29h was allowed to react with hexacarbonylmolybdenum in glyme

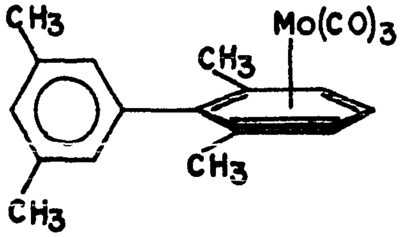
Figure 6. HA-100 NMR spectrum of 1-(3,5-dimethylphenyl)-2,6-dimethylphenyltricarbonylchromium (<u>30</u>) in deuterochloroform at ambient temperature

Figure 7. HA-100 NMR spectrum of 1-(3,5-dimethylphenyl)-2,6-dimethylphenyltricarbonylmolybdenum (<u>31</u>) in deuterochloroform at ambient temperature

Figure 8. HA-100 NMR spectrum of 1-(3,5-dimethylphenyl)-2,6-dimethylphenyltricarbonyltungsten (<u>32</u>) in deuterochloroform at ambient temperature


CHCl3
CHCl3
CHCl3
7.0
6.0
5.0
PPM (δ)
4.0
3.0
2.0
1.0

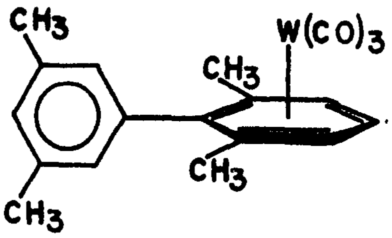
solvent. The uncomplexed ring proton signals occur as broadened singlets at 6.98 δ, 6.90 δ and 6.74 δ while the complexed ring proton signals occur as a triplet and doublet at 5.81 δ and 5.30 δ respectively. The methyl signals of the uncomplexed ring appear as a pair of singlets at 2.36 δ and 2.32 δ, while the methyl signals of the complexed ring constitute the singlet at 1.97 δ. Both the NMR spectrum and its integration are consistent with structure 31 for the complex where the tricarbonylmolybdenum moiety is bound to the ring bearing the methyl groups at the 2- and 6-positions. In o-dichlorobenzene as solvent at ambient temperature the complexed ring proton signals appear as a triplet and doublet centered at



31

5.57 δ and 5.04 δ respectively while the methyl signals of the uncomplexed ring occur at 2.24 δ and 2.18 δ. The methyl signals of the complexed ring occur as a singlet at 1.84 δ.

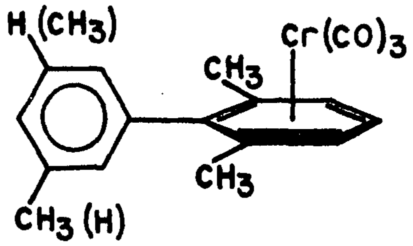
It is always nice to have a complete series but the known synthetic approaches to the preparation of arenetricarbonyltungsten complexes failed when applied to the tetramethylbiphenyl 29h. The preparation of arenetricarbonyltungsten complexes by a variety of methods have with few exceptions resulted in poor yields (48, 49, 50, 51). The ligand transfer reaction of arenetricarbonylmetals (Cr, Mo, W) have been studied but only to elucidate the mechanism(s) (52, 53, 54). Only in the case of chromium has the reaction been used synthetically (10). The desired tungsten complex was prepared in 42% yield by a ligand exchange reaction between toluenetricarbonyltungsten and 29h. The two reactants were mixed and heated to 130° for 16-1/2 hr. The NMR spectrum of the resulting complex in deuterochloroform is shown in Figure 8 and its similarity to the molybdenum (31) and chromium (30) complexes is readily noticed. The uncomplexed ring proton signals occur as broadened singlets at 6.98 δ, 6.86 δ and 6.77 δ while the complexed ring proton signals occur as a triplet and doublet at 5.63 δ and 5.16 δ respectively. The methyl signals of the uncomplexed ring appear as a pair of singlets at 2.35 δ and 2.32 δ while the methyl signals of the complexed ring constitute the singlet at 2.13 δ. Structure 32 seems reasonable from the NMR spectrum



32

and its integration. In o-dichlorobenzene as solvent at ambient temperature the complexed aromatic proton signals appear as a triplet and doublet centered at 5.38 δ and 4.90 δ respectively while the methyl signals of the uncomplexed ring occur at 2.24 δ and 2.17 δ. The methyl signals of the complexed ring occur as a singlet at 2.00 δ.

The NMR spectrum of biphenyl 29j in deuterochloroform exhibits two singlets for the methyl signals, the m-methyl occuring at 2.37 δ and the o-methyls signal at 2.02 δ. The biphenyl was allowed to react with hexacarbonylchromium in glyme solvent and the resulting tricarbonylchromium complex in deuterochloroform exhibits three methyl singlets in the NMR spectrum at 2.44 δ, 2.37 δ and 1.94 δ with an integration of 1.5:1.5:6 respectively. The integration of the complexed to uncomplexed ring protons is three to four.



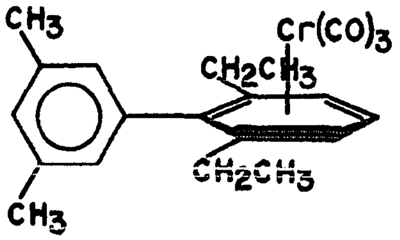
33

The NMR spectrum and its integration are consistent with the complex having structure 33. In tetrachloroethane 33 exhibits two m-methyl signals of very nearly the same intensity. The presence of two m-methyl signals requires the presence of two compounds, one that has the m-methyl group *syn* to the metal moiety and one that has the m-methyl group *anti* to the metal moiety.

Biphenyl 29k exhibits an aromatic methyl singlet at 2.33 δ in the NMR spectrum in deuterochloroform. Complexation of this biphenyl was accomplished by utilizing the ligand transfer reaction (10) between benzenetricarbonylchromium and the biphenyl in a melt at 180°. The NMR spectrum of the complex in deuterochloroform exhibits two methyl singlets at 2.37 δ and 2.31 δ, and the triplet and doublet for the complexed ring proton signals at 5.61 δ and

5.03 δ. The NMR spectrum is consistent with structure 34 for the complex.

Biphenyl 29i exhibits two singlets in the NMR spectrum; the m-methyl occuring at 2.34 δ and the o-methyl at 2.25 δ. The corresponding tricarbonylchromium complex prepared from the interaction of the biphenyl with hexacarbonylchromium exhibits two methyl singlets in the NMR spectrum; the m-methyl occurring at 2.34 δ and the o-methyl at 2.10 δ. The integration of complexed aromatic protons to uncomplexed aromatic protons is four to three. The following structure (35) is consistent with the NMR spectrum and the integration.



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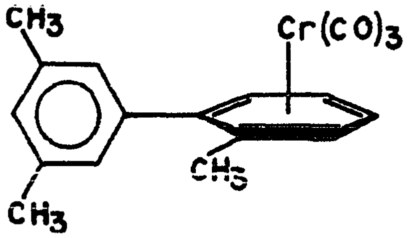
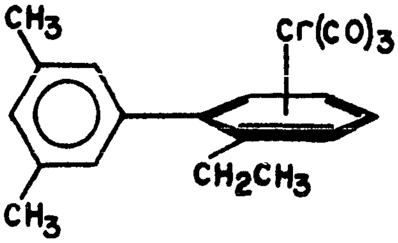


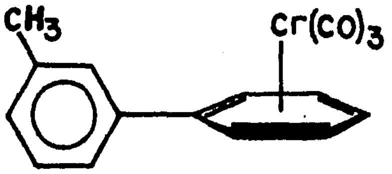
35

Biphenyl 29-1 exhibits an aromatic methyl singlet at 2.33 δ in the NMR spectrum in deuterochloroform. Complexation of this biphenyl was accomplished with hexacarbonylchromium in glyme solvent. The resulting complex exhibited a single methyl resonance in the NMR spectrum ($CDCl_3$) at 2.34 δ. The integration of the complexed to uncomplexed ring protons is four to three. The following structure (36) is consistent with the data. The ligand transfer reaction (10) between benzenetricarbonylchromium and the biphenyl 29-1 in a melt at 180° gave a material that was separated into two yellow fractions by column chromatography. The NMR spectrum of the first fraction was interpreted as arising from a mixture of mono complexes, while the NMR of the second fraction is consistent with a dicomplex structure.



36

3-Phenyltoluene exhibits a methyl singlet at 2.38 δ in the NMR spectrum ($CDCl_3$). Upon complexation with hexacarbonylchromium, the NMR spectrum in deuterochloroform exhibits two methyl singlets of unequal intensity at 2.38 δ and 2.28 δ. The melting point range for the recrystallized material is very large. This fact and the integration of the NMR spectrum are consistent with the material as being a mixture of the two possible mono complexes (37 and 38).



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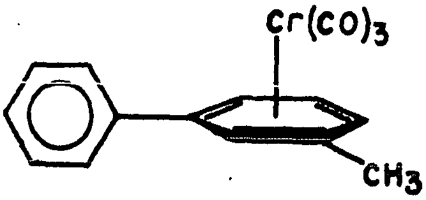


38

Satisfactory exact masses were obtained for the complexes as well as for parent biphenyls by double focusing mass spectrometry.

Temperature dependent NMR spectra were not observed for compounds 35, 36, and 37, whereas temperature dependent spectra were observed for complexes 30-34. The results from the variable temperature NMR study are presented in Table 2 at the end of this section.

1,1,2,2-Tetrachloroethane was initially chosen as the high temperature solvent but it proved to be unsatisfactory since only the tricarbonylchromium complexes exhibited moderate stability at very high temperature. Tetrachloroethane was used as the solvent for the temperature study of compounds 30 and 34. A far better solvent for these complexes is o-dichlorobenzene. All of the complexes studied in this solvent were stable at high temperature for hours. The most labile complex is the molybdenum one, 31, and its half life for decomposition at 130° was estimated to be on the order of 3-4 hours. Any decomposition that does occur seems to have very little, if any, effect on the resolution. A sample of 31 was kept at 130° long enough to observe the formation of the o-methyl peak for the free biphenyl. The resolution of the ambient spectrum for the cooled sample was as good as it was prior to warming, the only difference being the small peak due to starting material. The color of the solution was, however, very dark and some sediment was present. o-Dichlorobenzene was used as the solvent for the temperature study for complexes 30, 31, 32 and 34. The use of solvents that contained protons prevented the observation of the uncomplexed ring protons.

The NMR spectra for the variable temperature study of compound 30 are shown in Figures 9 to 11. At -20° (Figure 10) the methyl signals of the uncomplexed ring in o-dichlorobenzene occur at 2.23 δ and 2.16 δ. As the temperature is raised the two signals are seen to broaden and collapse (Figure 11). At +125° (Figure 9) a singlet has emerged at 2.25 δ. It is of lower intensity than the o-methyl signal because of coupling with the aromatic protons. The coupling gives rise to a quartet for the m-methyl signal and the quartet can be seen in Figure 11 at 125°. The complexed ring proton signals at +125° occur as a triplet and doublet at 5.29 δ and 4.78 δ (Figure 9). Complexes 31, 32, 33 and 34 have similar variable temperature NMR spectra although only in the case of 30 was the final quartet so nicely resolved. The signals that coalesced for these complexes were in all cases singlets and not quartets so a complete line shape analysis is not considered necessary.

A ^{13}C Fourier transform NMR was obtained for complex 30 in deuterochloroform. Interestingly all of the carbon signals for the uncomplexed ring occur at different field values. Tentative assignments based on chemical shifts and gated decoupling are given. The carbonyl carbon signal occurs at 233.8 ppm, the 3'- and 5'-quaternary carbon signals occur at 138.5 and 137.9 ppm while the 1'-quaternary carbon signal

Figure 9. HA-100 NMR spectrum of 1-(3,5-dimethylphenyl)-2,6-dimethylphenyltricarbonylchromium (30) in o-dichlorobenzene at +125°

Figure 10. HA-100 NMR spectrum of 1-(3,5-dimethylphenyl)-2,6-dimethylphenyltricarbonylchromium (30) in o-dichlorobenzene at -20°

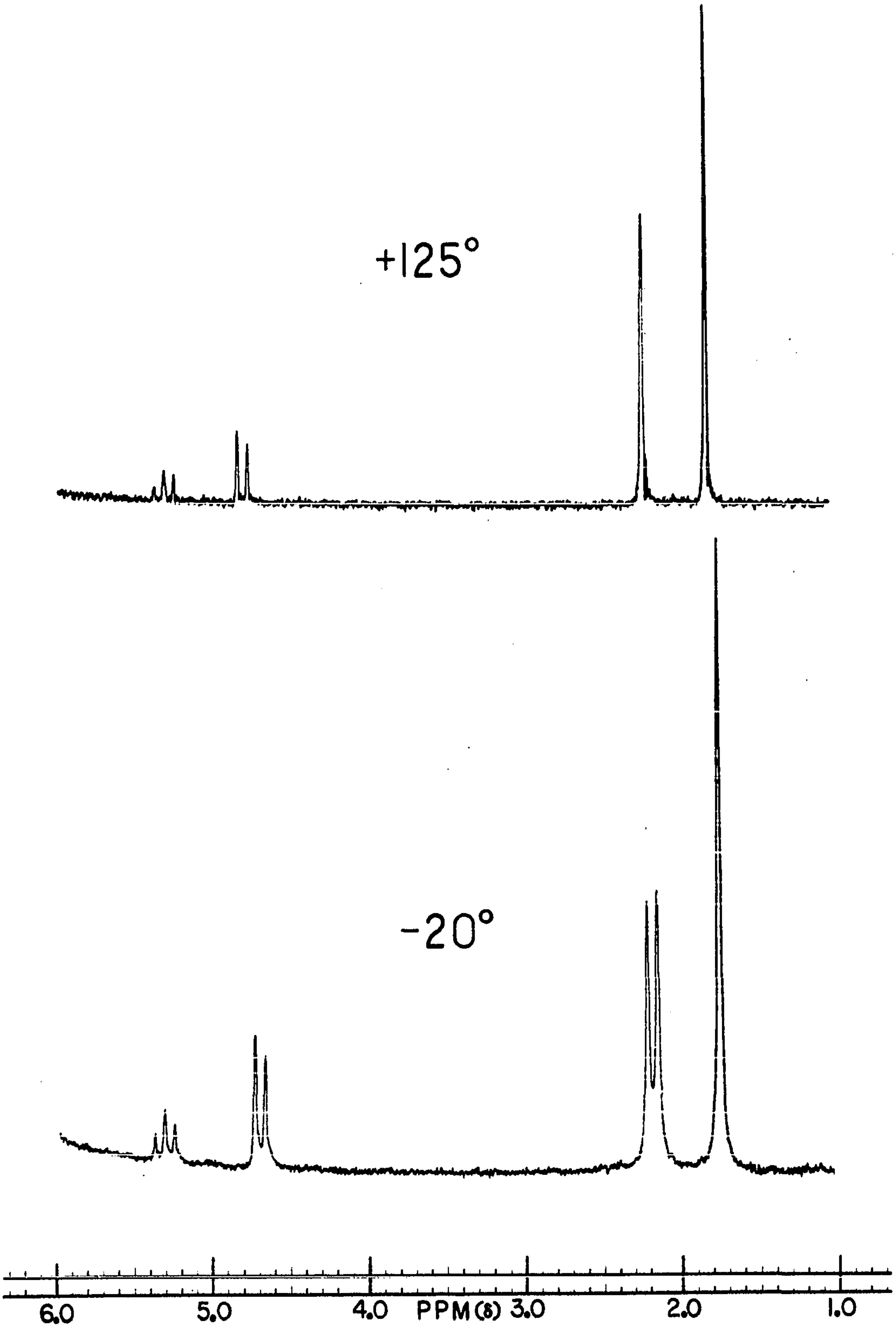
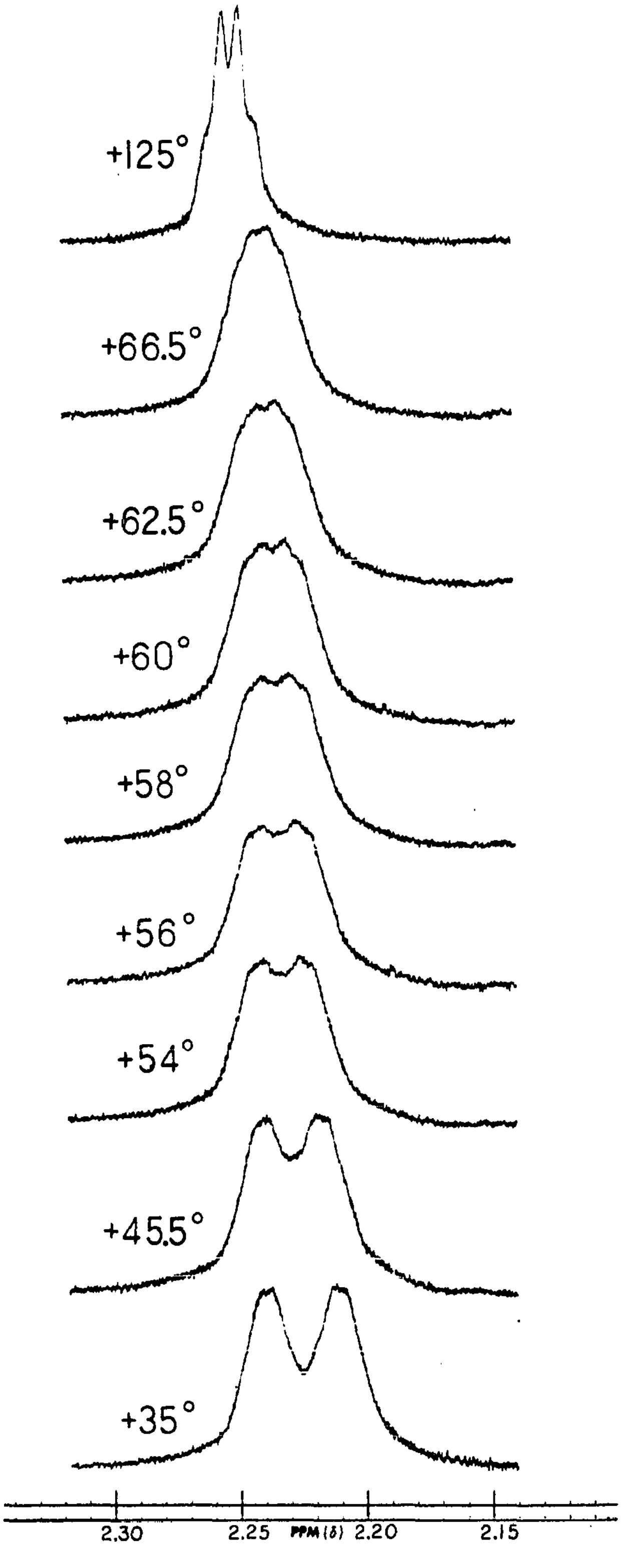

+125°
-20°
6.0
5.0
4.0
PPM(δ)
3.0
2.0
1.0

Figure 11. HA-100 NMR spectra of the expanded methyl region of the uncomplexed ring of 1-(3,5-dimethylphenyl)-2,6-dimethylphenyltricarbonylchromium (<u>30</u>) in <u>o</u>-dichlorobenzene at various temperatures


+125°
+66.5°
+62.5°
+60°
+58°
+56°
+54°
+45.5°
+35°
2.30
2.25
PPM (δ)
2.20
2.15

occurs at 135.1 ppm. The 2'-, 4'- and 6'-carbon signals occur at 130.1, 129.7 and 127.2 ppm. The quaternary carbon signals of the complexed ring occur at 115.2 and 111.6 ppm while the 3- and 5-carbon signal and the 4-carbon signal occur at 96.0 and 88.9 ppm. The m-methyl carbon signals occur at 21.4 and 21.2 ppm while the o-methyl carbon signal occurs at 20.3 ppm.

Table 2. The activation free energies for rotation for the mono(tricarbonylmetal) complexes of alkyl biphenyls[a]

Compounds	Solvent	T_c [b]	ν_{AB} [c]	$\Delta G^{\ddagger}_{T_c}$ [d]
30[e]	o-$C_6H_4Cl_2$	58	6.5	17.7
31[f]	o-$C_6H_4Cl_2$	95	7.0	19.7
32[g]	o-$C_6H_4Cl_2$	109	7.3	20.5

[a] See experimental for an explanation of how the samples were prepared for analysis. T_c obtained on the 100 HMz.

[b] The coalescence temperature in °C for the methyl resonances of the uncomplexed phenyl ring. Error is ± 2°C.

[c] This is the separation in Hz of the two coalescing peaks well below the coalescence temperature.

[d] The free energy of activation for rotation at the coalescence temperature, in kcal/mole. Estimated error is ± 0.2 kcal/mole.

[e] 1-(3,5-Dimethylphenyl)-2,6-dimethylphenyltricarbonylchromium.

[f] 1-(3,5-Dimethylphenyl)-2,6-dimethylphenyltricarbonylmolybdenum.

[g] 1-(3,5-Dimethylphenyl)-2,6-dimethylphenyltricarbonyltungsten.

Table 2 (Continued)

Compounds	Solvent	T_c[b]	ν_{AB}[c]	$\Delta G^{*}_{T_c}$[d]
34[h]	o-$C_6H_4Cl_2$	62	6.5	17.9
30	$CHCl_2CHCl_2$	111	6.2	20.7
33[i]	$CHCl_2CHCl_2$	110	6.1	20.7
35[j]	CS_2/CD_2Cl_2	-	-	<9
36[k]	CS_2/CD_2Cl_2	-	-	<9
37[l]	CS_2	-	-	<10

[h] 1-(3,5-Dimethylphenyl)-2,6-diethylphenyltricarbonyl chromium.

[i] 1-(3-methylphenyl)-2,6-dimethylphenyltricarbonylchromium.

[j] 1-(3,5-Dimethylphenyl)-2-methylphenyltricarbonylchromium.

[k] 1-(3,5-Dimethylphenyl)-2-ethylphenyltricarbonylchromium.

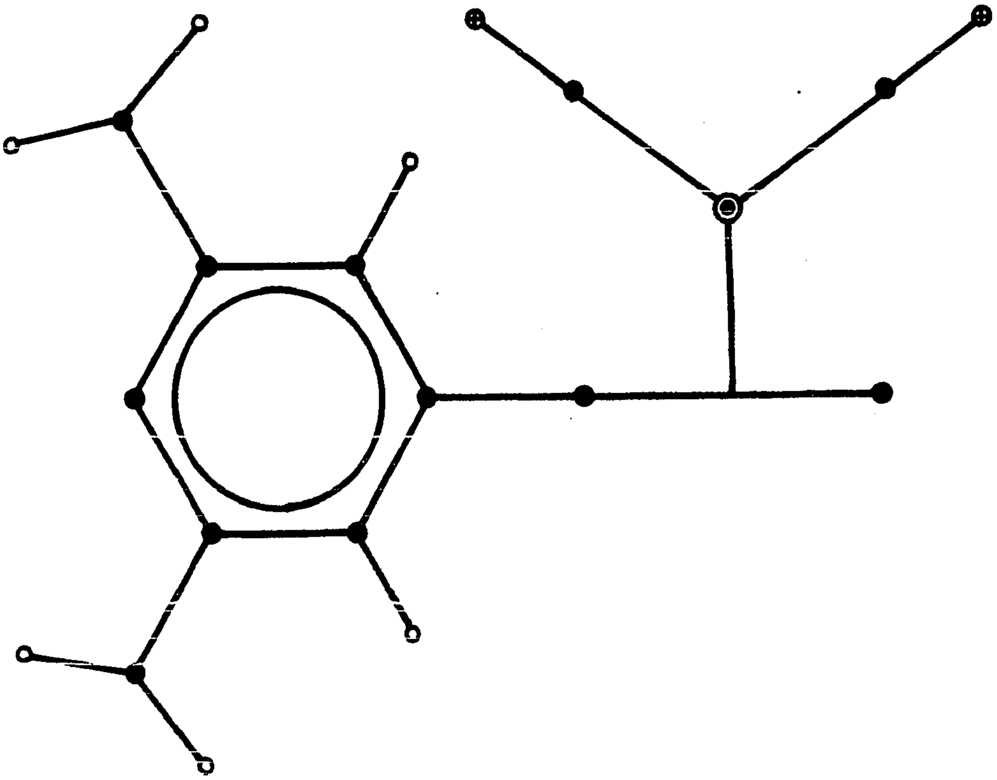
[l] 1-(3-methylphenyl)phenyltricarbonylchromium.

Discussion

The synthesis of the tricarbonylchromium complexes were easily prepared from hexacarbonylchromium. In all cases the mono- or di-o-substituted ring was preferentially complexed. In the ligand transfer reaction the di-o-substituted ring was preferentially complexed but in the case of a mono-o-substituted biphenyl, a mixture of the two possible mono complexes result in addition to the bis complex.

A scale drawing of complex 30 is shown in Figure 12. The bond lengths and angles used for the tricarbonylchromium complexed ring are the same as those found for benzenetricarbonylchromium (55). The bond lengths for the uncomplexed ring and other bonds were obtained from a compilation of such data (56). In Figure 12 the molecule is treated as rigid, with the two phenyl rings being mutually perpendicular and no bond angle or length distortions. The rotation about the methyl-aryl bond results in the generation of a cone by the methyl hydrogens and it is the extent of that cone that is shown in Figure 12. Likewise for the freely rotating tricarbonylmetal group, it is the extent of the carbonyl cone that is shown in Figure 12. In the rigid molecule the *syn*-*o*-hydrogens distance to the oxygen of the carbonyl is measured to be 1.47 Å. At this distance the van der Waals radii for the hydrogen and the oxygen are overlapping. To relieve this interaction the tricarbonylchromium group could move toward the *p*-carbon of the complexed ring or the cone that the carbonyls generate could tip away from the *syn*-*o*-hydrogen. The *syn*-*o*-hydrogen could bend back toward the methyl group or the angle between the two rings could decrease. The angle has been calculated to be 70° (32). The uncomplexed ring could bend down away from the tricarbonylchromium and an

Figure 12. A scale drawing of 1-(3,5-dimethylphenyl)-2,6-dimethylphenyltricarbonylchromium (30) (some groups omitted for clarity) where ● equals carbon, O equals hydrogen, ◐ equals chromium and ⊕ equals oxygen



1cm=0.7Å

angle of 10° made by the 4 carbon-midpoint of the aryl aryl bond-4' carbon would increase the hydrogen-oxygen distance to 1.85 Å. Most likely all of these effects and others are involved.

The conditions for the ligand transfer reaction make it a less selective reagent than hexacarbonylchromium with respect to steric effects. From Figure 12 it is easy to see that if a methyl group replaces the *syn*-*o*-hydrogen, a large steric crowding would exist between itself and the tricarbonylchromium group. However, in biphenyl **29-l** where only one *o*-substituent is present, it is possible to complex the dimethylphenyl ring, provided the *o*-substituent is *anti* to the metal moiety. When two *o*-substituents are present, the one *o*-substituent must be *syn* to the metal moiety on the adjacent ring and the steric interaction is so severe that the complex cannot be prepared. The distortions that relieve the steric crowding for the *syn*-*o*-hydrogen case apparently are not sufficient to decrease the steric crowding when larger substitutes are present.

The synthesis of **32** by a ligand transfer reaction demonstrates the important synthetic application of this reaction for the preparation of arenetricarbonyltungsten complexes.

Hindered rotation is observed in complexed **30**-**34**. Hindered rotation is not observed in **29h** by NMR because of the symmetry of the molecule, yet literature data (33, 35) indicate that a sizeable barrier should exist, considering the *o*-substituents. Complexation of a phenyl ring greatly changes the magnetic environment for the one side of the complexed ring and this effect is large enough to be felt at the meta positions of the uncomplexed ring. The magnetic environment on the other side of the complexed ring is probably not very different from an uncomplexed ring. This environmental difference results in the *syn*-*m*-methyl absorbing at a different field value than the *anti*-*m*-methyl in the NMR spectrum, provided the rotation is slow enough so averaging of the signals does not occur. Also the *syn*-*o*-hydrogen absorbs at a different field value than the *anti*-*o*-hydrogen.

The parent biphenyl (**29h**) is viewed as having two equal *m*-methyl-adjacent phenyl ring π interactions, while the complexed (**30**-**32**) are viewed as having only one *m*-methyl-(*anti*)-adjacent phenyl ring π interaction. This is accounted for nicely by the *m*-methyl signal at 2.32 ± 0.01 δ that is common to **29h** and the complexed **30**-**32**. The downfield shift of the *syn*-*m*-methyl absorption with respect to the *anti*-*m*-methyl absorption varies with the metal and the observed order is Cr(2.39) > Mo(2.37) > W(2.35). From Figure 12 it is not possible to predict whether the effect of the carbonyl cone is one of shielding or deshielding. The metal is however involved magnetically, since shifts are noted for all three metals even though the bond distance of 2.01 Å is the same for both the cyclopentadienyl-molybdenum bond (57) and the cyclopentadienyl-tungsten bond (57) which is greater than the cyclopentadienyl-chromium bond distance of 1.84 Å (58). No crystal structure data could be found for a benzenoid metal (Cr, Mo, W) series.

From Figure 12 it appears that the tricarbonylmetal can affect the field position for the syn-o-hydrogen. In biphenyl 29h the two o-hydrogens are equivalent and upfield of the p-hydrogen. In the complexes the position for the anti-o-hydrogen would not be expected to move greatly from that found for the parent biphenyl. This is indeed the case for an o-hydrogen signal appears at 6.75 ± 0.02 δ that is common to 29h and complexes 30-32. In the complexes an aromatic proton signal at 6.99 ± 0.01 δ is attributed to the p-hydrogen of the uncomplexed ring. The downfield shift of the syn-o-hydrogen absorption with respect to the anti-o-hydrogen varies with the metal and the order is Cr(7.0) > Mo(6.91) > W(6.86).

From the NMR spectra of 30-32, it is observed that the degree of upfield shift of the aromatic proton resonances upon complexation follows the nonperiodic trend of Cr > W > Mo while the degree of upfield shift of the aromatic methyl resonance upon complexation follows the periodic trend Cr > Mo > W. This is in agreement with the NMR studies that have been done on methyl substituted arenetricarbonylmetal complexes (50), where the former order was partially attributed to differing electron withdrawing effects among the metals.

The transition state for the equilibration of the *m*-methyls of complexes 30, 32, 34 and for the equilibration of the *m*-methyls of complex 33 involves the coplanar arrangement of the two rings. It seems reasonable to assume that the tricarbonylmetal moiety will have little steric effect on the transition state. The electronic effect of the tricarbonylmetal moiety on the transition state will be discussed later.

The two signals for the *m*-methyl of complex 33 are of nearly equal intensity in tetrachloroethane, deuterochloroform and *o*-dichlorobenzene and this indicates that there are no severe steric interactions between the *syn*-*m*-methyl group and the tricarbonylchromium group. In addition to the fact that the barrier energies for complexes 33 and 30 in tetrachloroethane are nearly the same indicates that any buttressing effect by the *m*-methyl group on the *o*-hydrogen must be very small.

A large decrease in the barrier energy for complex 30 results when *o*-dichlorobenzene is used as the solvent instead of tetrachloroethane. This decrease is attributed to a solvent effect. Comparing the NMR spectra of 30 in deuterochloroform and *o*-dichlorobenzene, the doublet for the complexed aromatic protons in the latter solvent is shifted upfield 25 Hz. This is taken as evidence that the bottom side of the complexed ring is in turn complexed with an *o*-dichlorobenzene molecule. This aromatic solvent induced shift has been observed for other arenetricarbonylchromium complexes and has even been used as a means of determining the structure for some complexes (59). The aromatic solvent bound to the bottom face of the complexed ring can by a steric interaction with the *anti*-*o*-hydrogen cause the uncomplexed ring to become more coplanar with the complexed ring. This would destabilize the ground state for the biphenyl complex and provided the transition state would be similar for both solvents (tetrachloroethane and *o*-dichlorobenzene) the net effect would be a lower barrier energy for the molecule in the aromatic solvent. It is also possible that the transition state could be stabilized by the *o*-dichlorobenzene since it can now be complexed to the extended π system of the biphenyl. Regardless of the per cent importance of the two effects, the net result is a lower barrier energy for the complexed biphenyl in *o*-dichlorobenzene.

This solvent effect is indeed beneficial. The temperature range studied for **30** in *o*-dichlorobenzene is lower than that required for **30** in tetrachloroethane. Finding a very high temperature solvent for **31** proved fruitless.

Even in tridecane at 130° 31 readily decomposed. In o-dichlorobenzene the temperature range needed for 31 was readily accessible. As for 31 a solvent effect was noted in going from deuterochloroform to o-dichlorobenzene. The upfield shift for the doublet of the complexed aromatic protons was 26 Hz. This is very close to the value for 30 and indicates that the amount of π complexation of the o-dichlorobenzene to the back side of the complexed molybdenum ring is nearly the same as for the complexed chromium ring. A solvent effect was also noted for 32 in going from deuterochloroform to o-dichlorobenzene. In this case the shift was 26 Hz and indicates that the amount of π complexation by o-dichlorobenzene to the back side of the complexed tungsten ring is nearly the same as for 31 and 30. Upfield shifts were also noted for the triplet of the complexed aromatic protons and the complexed ring methyls.

If the amount of π complexation by the solvent is similar for all three complexes, then the large difference in barrier energies must arise not from variable amounts of π complexation by solvent but from some other effect.

The ground states for the three complexes could be different by the amount of resonance stabilization between the uncomplexed and complexed rings, the difference arising from the different metals. The amount of resonance stabilization in the ground state is expected to be small because of the large angle between the two rings. The transition state for all three complexes involves coplanar rings. The tricarbonylmetal moiety can have its greatest stabilizing effect at the transition state, where the demand for resonance stabilization is the greatest. From the results one can conclude that the tricarbonylchromium moiety is much more able to stabilize the transition state than corresponding tricarbonylmolybdenum moiety which in turn is better than the tricarbonyltungsten moiety, in other words the resonance effect follows the periodic order Cr > Mo > W.

The barriers for 30 and 34 are the same within experimental error and this is rationalized by saying that in the transition state the ethyl group has adopted a conformation that will minimize the steric interactions. The conformation most likely has the methyl group of the ethyl moiety bent back alongside the complexed ring. The steric interaction then resembles a methyl group.

Even at -100° there was no evidence for hindered rotation for the mono-*o*-substituted complexes (34 and 36). The inability to find hindered rotation indicates that the dimethylphenyl ring bends away from the *o*-methyl group as the two rings approach the coplanar transition state. Decreasing the methyl-hydrogen interaction lowers the barrier energy and this far outweighs the increase to the barrier energy from the increased hydrogen-hydrogen interaction and the bending motion of the rings. Stabilization of the transition state by the tricarbonylchromium group will also lower the barrier energy. Consequently the barrier energy will be less than expected. For 36 the methyl group of the ethyl moiety may align itself along the side of the complexed ring as is the case for 34. The barrier energy for 36 would then be similar to that for 35.

No hindrance to rotation was found for 37 at -80°. The complex was prepared before it was realized that the barrier to rotation in biphenyl was so small.

Experimental

Equipment

Nuclear magnetic spectra were run on a Varian Associates HA-100 Nuclear Magnetic Resonance Spectrometer; variable temperature work employed the V-6040 variable temperature controller and the V-4333 probe.

Nuclear magnetic spectra were also run on a Varian Associates A-60 Nuclear Magnetic Resonance Spectrometer.

Melting points were taken on a Thomas Hoover Capillary Melting Point Apparatus.

The apparatus used in the preparation of most of the tricarbonylchromium complexes was constructed according to the instructions of Strohmeier (60).

The source of commercial compounds is shown in Table 3.

Table 3. Source of commercial compounds for the mono(tricarbonylmetal) complex project

Compound	Source
2,6-Dimethylaniline	Aldrich
Acetic acid	Baker
Bromine	Baker
n-Butyl lithium	Foote
Oxalic acid	Baker
Glyme	Aldrich
m-Bromotoluene	Baker
o-Bromotoluene	Baker
Sulfur	Baker
Hexacarbonylchromium	Strem
Hexacarbonylmolybdenum	Pressure Chemical
Hexacarbonyltungsten	Strem
2-Ethylcyclohexanone	Pfaltz and Bauer
2,6-Dimethylcyclohexanone	Aldrich
3,5-Dimethylcyclohexanone	Chemical Samples Co.
Diethyl ethylmalonate	Aldrich
1,3-Dibromopropane	Aldrich
Barium hydroxide	Baker
Sodium hydride	Alfa-Ventron
Lithium aluminum hybride	Baker
3-Phenyltoluene	Aldrich

Prepared compounds

All melting points are uncorrected.

All new compounds were analyzed by double focussing mass spectrometry using an Associated Electronics MS-902 at an ionization potential of 70 eV.

2,6-Dimethyl-4-bromoaniline 2,6-Dimethylaniline (91 g, 0.752 mol) and glacial acetic acid (300 ml) were mixed and brought to reflux for 2-1/2 hr. The solution was cooled to 40° and 122 g (0.762 mol) of bromine was slowly added so that the temperature would not exceed 50° while the solution was rapidly stirred. About 3/4 of the bromine was added when a solid formed which did not redissolve when the rest of the bromine was added. The mixture was warmed on a water bath for 3/4 hr after all the bromine was added. The mixture was poured slowly into 3.75 l. of water with vigorous stirring and sodium bisulfite was added until the bromine color was discharged. The solution was filtered to remove solid waste and the filtrate was neutralized slowly with solid sodium bicarbonate until the pH reaches seven. Sodium hydroxide (solid) was then added until the pH reached 10 and the resulting solid was filtered. The solid was washed with water and dried. The crude material (113 g, 75.5%) had a brown color and a mp of 47-50°, lit. (61) mp 50-51°; NMR ($CDCl_3$) δ 7.02 (s, 2), 3.24 (s (broad), 2) and

2.11 ppm (s, 6).

3,5-Dimethylbromobenzene (25a) This compound was prepared using the analogous procedure of Snyder and coworkers (62). Starting with 100 g (0.5 mol) of crude 2,6-dimethyl-4-bromoaniline, 58 g of the desired product was formed (62.7%); bp 86-88° (11 mm), lit. (63) bp 84-87° (14 mm); NMR ($CDCl_3$) δ 7.08 (s, 2), 6.85 (s, 1) and 2.26 ppm (s, 6).

1-(3,5-Dimethylphenyl)-2,6-dimethylcyclohexanol (27h) 3,5-Dimethylbromobenzene (10 g, 0.054 mol) was allowed to react with 24 ml (3.5 g, 0.054 mol) of n-butyl lithium in 50 ml of anhydrous ether for 40 min at room temperature. A solution of 6.8 g (0.054 mol) of 2,6-dimethylcyclohexanone in 25 ml of anhydrous ether was then added over a period of 15 min. The mixture was kept at reflux for several hr. The mixture was then poured into 100 ml of 10% hydrochloric acid (HCl) and the ether solution was washed with water and dried over anhydrous magnesium sulfate ($MgSO_4$). Removal of the ether gave an oil which was distilled to yield the desired material (7.1 g, 56.8%); bp 108-111° (0.85 mm); NMR ($CDCl_3$) δ 7.1-6.7 (m, 3) 2.3 (s, 6), ((2.0-1.2 (m)) integration of 8), 1.47 (s, 1) and ((0.78 ppm (d, J = 6 Hz), 0.56 ppm (d, J = 6 Hz)) integration of 6); high resolution mass spec m/e 232,1828 (calcd. for $C_{16}H_{24}O$, 232.1827).

1-(3,5-Dimethylphenyl-2,6-dimethylcyclohex-1-ene (28h) The alcohol 27h (6 g, 0.025 mol) was heated in the presence of 3.8 g (0.042 mol) of anhydrous oxalic acid for 1/2 hr at 210°. At the end of the 1/2 hr another 1.0 g (0.012 mol) of anhydrous oxalic acid was added and the temperature was maintained at 210° for an additional 1/2 hr. The cooled mixture was taken up in a mixture of 100 ml of ether-50 ml of water. The ether solution was washed three times with 10% sodium hydroxide (NaOH) solution and once with water and then dried ($MgSO_4$). Removal of the ether gave an oil which was distilled to yield the desired material (5 g, 90.5%); bp 112-114° (1.2 mm); NMR ($CDCl_3$) δ 6.85-6.6 (m, 3), 2.26 (s, 6). ((2.2-1.2 (m)) integration of 7), 1.47 (d, J = 1 Hz, 3) and 0.81 ppm (d, J = 6.5 Hz, 3); high resolution mass spec m/e 214.1724 (calcd. for $C_{16}H_{22}$, 214.1722).

2,3',5',6-Tetramethylbiphenyl (29h) The olefin 28h (4.9 g, 0.023 mol) and 1.5 g (0.046 mol) of sulfur were heated together for 2 hr at 230°. The mixture was distilled under reduced pressure and the yellow distillate was chromatographed on a 50 g alumina column using pentane as the eluting solvent. The biphenyl came off the column in the first 250 ml of pentane. The solvent was removed and the oil was distilled to yield the desired material (3.14 g, 68%); bp 88-92° (0.6 mm); NMR ($CDCl_3$) δ 7.06 (s, 3), 6.93 (s broad), 1), 6.73 (s broad), 2), 2.33 (s, 6) and 2.02 ppm (s, 6); high resolution mass spec m/e 210.1406 (calcd. for $C_{16}H_{18}$, 210.1408).

1-(3,5-Dimethylphenyl)-2,6-dimethylphenyltricarbonylchromium (30) 2,3',5',6-Tetramethylbiphenyl (1.5 g, 7.0 mmol) and hexacarbonylchromium (1.6 g, 7.0 mmol) were placed in a 50 ml round bottom flask equipped with a side arm. Freshly distilled glyme (from lithium aluminum hydride (LAH)) was added (20 ml) and the flask was connected to the Strohmeier apparatus. The mixture was kept at reflux for 32 hr under nitrogen. The cooled reaction was taken up in ether, filtered through a bed of Celite, washed with water and dried ($MgSO_4$). The solvent was removed leaving a yellow semi-solid. Pentane (10 ml) was added to the semi-solid and it was filtered through a glass filtering frit. The yellow solid was washed with pentane and then recrystallized from a mixture of methylene chloride-pentane to give 285 mg of product, mp 168-171°; NMR ($CDCl_3$) δ 7.0 (s (broad), 2), 6.73 (s (broad), 1), 5.53 (t, J = 6 Hz, 1), 4.99 (d, J = 6 Hz, 2), 2.39 (s, 3), 2.32 (s, 3) and 1.93 ppm (s, 6); high resolution mass spec m/e 346.0660 (calcd. for $C_{19}H_{18}CrO_3$, 346.0661).

1-(3-Methylphenyl)-2,6-dimethylcyclohexanol (27j) n-Butyl lithium (26 ml, 3.74 g, 0.058 mol) was added under nitrogen to a solution of m-bromotoluene (10 g, 0.058 mol) in

50 ml of anhydrous ether at room temperature. The solution was stirred for about 15 min. Then slowly a solution of 2,6-dimethylcyclohexanone (7.3 g, 0.058 mol) in 25 ml anhydrous ether was added over a period of 10 min. The milky solution was kept under reflux for several hr. The cooled solution was poured into 100 ml of 10% HCl and the ether solution was washed once with water, dried over $MgSO_4$ and the ether was removed. The liquid that remained was distilled to yield the desired material (8.9 g, 70%); bp 105-112° (0.6 mm); NMR ($CDCl_3$) δ 7.3-6.9 (m, 4), 2.33 (s, 3), ((2.1 - 0.9 (m)) integration of 9) and ((0.78 ppm (d, J = 6 Hz), 0.56 ppm (d, J = 6 Hz)) integration of 6); high resolution mass spec <u>m/e</u> 218.1670 (calcd. for $C_{15}H_{22}O$, 218.1671).

<u>1-(3-Methylphenyl)-2,6-dimethylcyclohex-1-ene (28j)</u>

The title compound was prepared by the analogous procedure used in the preparation of <u>28h</u>. Starting with 5.4 g (0.06 mol) of anhydrous oxalic acid and 8 g (0.037 mol) of <u>27j</u> followed by an additional 1.6 g (0.017 mol) of anhydrous oxalic acid, 4.8 g (64%) of the desired olefin was obtained; bp 99-103° (1.1 mm); NMR ($CDCl_3$) δ (7.1-6.7 (m)) integration of 4), 2.33 (s, 3), ((1.2-2.2 (m)) integration of 7), 1.45 (quartet, J = 1 Hz, 3) and ((0.8 ppm (d, J = 7 Hz), 0.65 ppm (d, J = 7 Hz) integration of 3).

<u>2,3',6-Trimethylbiphenyl (29j)</u> The title compound was prepared by the analogous procedure used in the preparation of <u>29h</u>. Starting with 4.8 g (0.024 mol) of <u>28j</u> and 1.6 g (0.05 mol) of sulfur, 2.9 g (61.5%) was isolated; bp 79-80° (0.45 mm); NMR ($CDCl_3$) δ ((7.2-6.8 (m)) integration of 7), 2.37 (s, 3) and 2.03 ppm (s, 6); high resolution mass spec <u>m/e</u> 196.1252 (calcd. for $C_{15}H_{16}$, 196.1252).

<u>1-(3-Methylphenyl)-2,6-dimethylphenyltricarbonylchromium (33)</u> The title compound was prepared by the analogous procedure used in the preparation of <u>30</u>. Starting with 1.5 g (7.6 mmol) of <u>29j</u> and 1.7 g (7.7 mmol) of hexacarbonylchromium with a reflux time of 19 hr, 188 mg of the desired complex was isolated; mp 143-144°; NMR ($CDCl_3$) δ ((7.41-6.81 (m) integration of 4), 5.55 (t, J = 6 Hz, 1), 5.0 (d, J = 6 Hz, 2), 2.44 (s, 1.5), 2.37 (s, 1.5) and 1.94 ppm (s, 6); high resolution mass spec <u>m/e</u> 332.0492 (calcd. for $C_{18}H_{16}CrO_3$, 332.0505).

<u>1-(2-Methylphenyl)-3,5-dimethylcyclohexanol (27i)</u> The title compound was prepared by the analogous procedure used in the preparation of <u>27j</u>. Starting with 7.75 g (0.045 mol) of <u>o</u>-bromotoluene, 20 ml (2.92 g, 0.045 mol) of <u>n</u>-butyl lithium and 5.72 g (0.045 mol) of 3,5-dimethylcyclohexanone, 4 g (37%) was obtained after distillation; bp 110-111° (0.3 mm);

NMR ($CDCl_3$) δ 7.5-6.9 (m, 4), ((2.59 (s), 2.58 (s)) integration of 3), and ((0.93 ppm (d, J = 6 Hz), 0.91 ppm (d, J = 6 Hz)) integration of 6).

1-(2-Methylphenyl)-3,5-dimethylcyclohex-1-ene (28i) The olefin 28i was prepared by the analogous procedure used in the preparation of 28h. Starting with 2.5 g (0.027 mol) of anhydrous oxalic acid and 4 g (0.018 mol) of 27i, followed by an additional 0.85 g (9 mmol) of anhydrous oxalic acid, 2.8 g (76%) of the desired olefin was obtained, NMR ($CDCl_3$) δ 7.06 (s, 4), 5.33 (s (broad), 1), 2.25 (s, 3), 1.2-2.2 (m, 6) and 1.0 ppm (m, 6).

2,3',5'-Trimethylbiphenyl (29i) The crude olefin 28i (2.8 g, 0.014 mol) and 0.9 g (0.028 mol) of sulfur were heated together for 1-1/2 hr. The mixture was cooled and taken up in pentane and chromatographed on a 50 g alumina column. The biphenyl came off the column in the first 250 ml of pentane. The remaining colorless liquid after removing the solvent was distilled to give 1.85 g (67.5%) of the desired product; bp 120-124° (0.9 mm); NMR ($CDCl_3$) δ 6.18 (s, 4), 6.92 (s (broad), 3), 2.33 (s, 6) and 2.25 (s, 3); high resolution mass spec m/e 196.1253 (calcd. for $C_{15}H_{16}$, 196.1252.

1-(3,5-Dimethylphenyl)-2-methylphenyltricarbonylchromium (35) The complex 35 was prepared by the analogous procedure used in the preparation of 30. Starting with 1.5 g (7.6 mmol) of 29i and 1.7 g (7.6 mmol) of hexacarbonylchromium with a reflux time of 20 hr, 166 mg of the desired complex was isolated; mp 105-106°; NMR ($CDCl_3$) δ 6.98 (s, 3), 5.48 (m, 2), 5.15 (m, 2), 2.35 (s, 6) and 2.11 ppm (s, 3); high resolution mass spec *m/e* 332.0492 (calcd. for $C_{18}H_{16}CrO_3$, 332.0505).

1-(3,5-dimethylphenyl)-2-ethylcyclohexanol (27-1) The title compound was prepared by the analogous procedure used in the preparation of 27j. Starting with 14.7 g (0.079 mol) of 3,5-dimethylbromobenzene, 35 ml (5.1 g, 0.087 mol) of *n*-butyl lithium and 10 g (0.079 mol) of 3-ethylcyclohexanone, 11.4 g (62%) was obtained after distillation; bp 112° (0.25 mm); NMR ($CDCl_3$) δ 7.05 (s (broad), 2), 6.86 (s (broad), 1), 2.31 (s, 6), and 2.1-0.5 ppm (m, 15); high resolution mass spec *m/e* 232.1828 (calcd. for $C_{16}H_{24}O$, 242.1827).

1-(3,5-dimethylphenyl-2-ethylcyclohex-1-ene (28-1) The title compound was prepared by the analogous procedure used in the preparation of 28h. Starting with 11 g (0.047 mol) of 27-1 and 7 g (0.077 mol) of anhydrous oxalic acid, followed by an additional 1.8 g (0.02 mol) of anhydrous oxalic acid, 9.7 g (95.5% crude yield) of the olefin was obtained. NMR ($CDCl_3$) δ 6.76 (m, 3), 5.97 (m, 0.6), 2.8-0.6 ppm (m, superimposed singlet at 2.27 ppm), 19).

1-(3,5-dimethylphenyl)-2-ethylbenzene (29-1) The crude styrene mixture (28-1) (9,6 g, 0.044 mol) and 2.9 g (0.090 mol) of sulfur were heated together for two hrs at 230 ± 5°. After cooling, the mixture was taken up in pentane and chromatographed on a 100 g silica gel column. After collecting 400 ml of solution, the pentane was removed on a rotary evaporator leaving 7 g of crude material; NMR ($CDCl_3$) δ 7.16 (m, 3), 6.87 (s (broad), 2), 6.73 (s (broad), 1), 2.56 (q, J = 7.5 Hz, 2), 2.33 (s, 6), and 1.08 ppm (t, J = 7.5 Hz, 3); high resolution mass spec m/e 210.1404 (calcd. for $C_{16}H_{18}$, 210.1408).

1-(3,5-dimethylphenyl)-2-ethylphenyltricarbonylchromium (36) The complex was prepared by the analogous procedure used in the preparation of 30. Starting with 1 g (4.7 mmol) of 29-1 and 1 g (4.55 mol) of hexacarbonylchromium, with a reflux time of 20 hr, 1 g (63%) of the desired complex was obtained; mp 107-108°; NMR ($CDCl_3$) δ 7.0 (s, 3), 4.46 (m, 2), 4.17 (m, 2), 2.7-2.06 (m, (superimposed singlet at 2.34), 8), and 1.06 ppm (t, J = 7.5 Hz, 3); high resolution mass spec m/e 346.0669 (calcd. for $C_{19}H_{18}CrO_3$, 346.0661).

Ethyl 3,3,7,7-nonanetetracarboxylate Sodium hydride (4.8 g, 0.2 mol) was added to a flask containing dry glyme. Diethyl ethylmalonate (40 g, 0.212 mol) in glyme solvent was slowly added over a period of 1 hr to the rapidly stirred sodium hydride-glyme slurry. The solution became clear once all the malonate was added and the system was brought to reflux at which point 20.2 g (0.199 mol) of 1,3-dibromopropane was added over a 1 hr period. The mixture was allowed to reflux for four hr and let to cool and stand overnight. Ether-water was added and the ethereal solution was washed once with 10% HCl, five times with 100 ml portions of water and once with saturated sodium chloride solution. The ether solution was dried ($MgSO_4$) and the ether was removed under reduced pressure leaving a viscous oil which was distilled to give the desired product (38.3 g, 92.5%); bp 166-169° (0.45 mm), lit. (41) bp 247° (30 mm); NMR ($CDCl_3$) δ 4.18 (q, J = 7 Hz, 8), 2.2-1.5 (m, 8), 1.25 (t, J = 7 Hz, 12), and 0.80 ppm (t, J = 7.5 Hz, 8).

3,3,7,7-Nonanetetracarboxylic acid The tetra acid was prepared by the procedure of Perkin and Prentice (41). Starting with 115 g (0.276 mol) of ethyl 3,3,7,7-nonanetetracarboxylate, 61.8 g of the tetra acid (73.8%) was formed; NMR (DMSO-d_6) δ 11.2 (s (broad), 2), (2.1-1.4 (m), 1.3-0.5 ppm (m), total integration of 8).

α,α-Diethylpimelic acid Heating the solid 3,3,7,7-nonanetetracarboxylic acid (60.3 g, 0.198 mol) in a flask to 190° (oil bath) resulted in its liquefaction and the evolution of a gas. The temperature was finally raised to 227° until no more gas was given off. Upon cooling the desired material (39.5 g, 92% crude yield) became semi-solid; NMR ($CDCl_3$) δ 11.6 (s, 1), (2.25 (m), and 0.93 ppm (t, J = 7 Hz), total integration of 9); lit. mp (41) 96-97°.

2,6-Diethylcyclohexanone (26f) The crude α,α-diethylpimelic acid (39.4 g, 0.182 mol) and 2.5 g of barium hydroxide (($Ba(OH)_2 \cdot 8\ H_2O$), 1.35 g ($Ba(OH)_2$, 7.9 mmol) were placed in a large test tube that was equipped for distillation. The test tube was immersed in an open air bath and the temperature of the bath was raised until an internal temperature of 345 ± 5° was reached. At this temperature a material slowly distilled over. The temperature was maintained for 5-1/2 hrs at which time the bath temperature was slowly increased until a temperature of 390° was reached 3-1/2 hr later. The distilled material was taken up in an ether-water mixture and the ether solution was washed twice with 10% NaOH, once with water, once with saturated sodium chloride solution and dried over $MgSO_4$. The ether was removed and the liquid was distilled to yield the desired product (18.4 g, 65.5%); bp 85-87° (10.5 mm), lit. (42)

bp 205-207° (767 mm); NMR ($CDCl_3$) δ 2.5-1.1 (m, 12), and 0.85 ppm (t, J = 7 Hz, 6).

1-(3,5-Dimethylphenyl)-2,6-diethylcyclohexanol (27k)

The title alcohol was prepared by the analogous procedure used in the preparation of 27j. Starting with 12 g (0.0648 mol) of 3,5-dimethylbromobenzene, 41 ml (0.058 mol) of *n*-butyl lithium and 10 g (0.0648 mol) of 2,6-diethylcyclohexanone, 10 g (59.2%) of the desired carbinol was obtained; bp 127-136° (0.25 mm); NMR ($CDCl_3$) δ 6.92 and 6.77 (broad singlets, 3), 2.29 (s, 6), and 2.1-0.4 ppm (m, 19); high resolution mass spec *m/e* 260.2129 (calcd. for $C_{18}H_{28}O$, 260.2140).

1-(3,5-Dimethylphenyl)-2,6-diethylcyclohex-1-ene (28k)

The title olefin was prepared by the analogous procedure used in the preparation of 28h. Starting with 5.7 g (0.063 mol) of anhydrous oxalic acid and 10 g (0.038 mol) of 27k followed by an additional 1.5 g (0.016 mol) of anhydrous oxalic acid, 7.4 g (79.5%) of the desired olefin was obtained; bp 100-103° (0.07 mm); NMR ($CDCl_3$) δ 6.71 and 6.61 (broad singlets, 3), 2.26 (s, 6) and 2.26-0.5 ppm (m, 17). There is an olefin absorption at 5.54 with a relative integration of 0.4.

1-(3,5-Dimethylphenyl)-2,6-diethylbenzene (29k) The title compound was prepared by the analogous procedure used in the preparation of 29h. Starting with 7.4 g (0.030 mol) of 28k and 2 g (0.062 mol) of sulfur, 5 g (68%) of the biphenyl was obtained. NMR ($CDCl_3$) δ 7.08 (m, 3), 6.88 (broad singlet, 1), 6.7 (broad singlet, 2), 2.3 (q, J = 7 Hz, 4), 2.3 (s, 6) and 1.1 ppm (t, J = 7 Hz, 6); high resolution mass spec m/e 238.1715 (calcd. for $C_{18}H_{22}$, 238.1722).

1-(3,5-Dimethylphenyl)-2,6-diethylphenyltricarbonylchromium (34) Benzenetricarbonylchromium (1.2 g, 4.7 mmol) and 29k (0.75 g, 3.1 mmol) were mixed in a small flask. After purging the system with nitrogen for 15 minutes, the flask was immersed in a preheated oil bath (180°) and maintained there for 20 hr. Periodically the flask was tapped to return the benzenetricarbonylchromium to the melt and likewise periodically the formed benzene was removed with a nitrogen stream. After cooling the solid was broken up and placed in a sublimation apparatus and excess benzene complex was sublimed out at 90° at 0.1 mm. The remaining residue was recrystallized from methylene chloride-pentane to give 0.7 g (60.5%) of nice yellow crystals; mp 152-155°; NMR ($CDCl_3$) δ 7.03 (s (broad), 2), 6.80 (s (broad), 1), 5.61 (t, J = 6 Hz, 1), 5.03 (d, J = 6 Hz, 2), 2.37 (s, 3), 2.31 (s, 3), 2.17 (q, J = 7.5 Hz, 4) and 1.02 ppm (t, J = 7.5 Hz, 6); high resolution mass spec m/e 374.0959 (calcd. for $C_{21}H_{22}CrO_3$, 374.0974).

1-(3,5-Dimethylphenyl)-2,6-dimethylphenyltricarbonylmolybdenum (31) Into a 50 ml round bottom flask was placed 29h (1 g, 4.7 mmol) and 1.26 g (4.7 mmol) of hexacarbonylmolybdenum. Glyme (21 ml freshly distilled from LAH) was added and the flask was connected to the Strohmeier apparatus. After purging the system with nitrogen, the system was brought to reflux and maintained there for 33 hr. At this time another 1 g (3.7 mmol) of hexacarbonylmolybdenum was added and reflux was continued for an additional 6 hr. After cooling, ether was added and the solution was filtered through a bed of Celite. The dingy yellow ether solution was washed five times with water, once with saturated sodium chloride solution and dried ($MgSO_4$). The ether was removed leaving a black solid, which was dissolved in methylene chloride and filtered through a pad of activated charcoal. The clear yellow solution was concentrated on a rotary evaporator and again filtered through a pad of activated charcoal. To the clear yellow solution was added pentane and the solution was stored in a refrigerator. Yellow crystals (0.5 g) of the desired complex soon formed; mp 183.5-184° (under nitrogen in a sealed tube); NMR ($CDCl_3$) δ 6.98 (s, 1), 6.90 (s, 1), 6.74 (s, 1), 5.81 (t, J = 6 Hz, 1), 5.30 (d, J = 6 Hz, 2), 2.36 (s, 3), 2.32 (s, 3) and 1.97 ppm (s, 6); high resolution mass spec *m/e* 386.0337 (calcd. for $C_{19}H_{18}MoO_3$, 386.0324).

1-(3,5-Dimethylphenyl)-2,6-dimethylphenyltricarbonyltungsten (*32*) Toluenetricarbonyltungsten (48) (90.7 mg, 0.25 mmol) were mixed in a 10 x 75 mm culture test tube. A nitrogen inlet was constructed from a pipette and a needle which pierced the capped tube. After flushing the system with nitrogen the test tube was immersed in an oil bath at 130° and maintained there for 16-1/2 hr at which time the solution solidified. A nitrogen flow continually removed toluene from the reaction mixture. The cooled solid was dissolved in methylene chloride and filtered through a pipette which contained a plug of nonabsorbent cotton. To the clear yellow solution was added pentane and the solution was stored in a refrigerator. Yellow crystals of the desired complex were obtained (52.5 mg, 44%); mp 202-204° (decomp); NMR ($CDCl_3$) δ 6.98 (s, 1), 6.86 (s, 1), 6.77 (s, 1) 5.63 (6, J = 6 Hz, 1), 5.16 (d, J = 6 Hz, 2), 2.35 (s, 3), 2.32 (s, 3), and 2.13 ppm (s, 6); high resolution mass spec *m/e* 476.0748 (calcd. for $C_{19}H_{18}WO_3$, 476.0738).

1-(3-Methylphenyl)phenyltricarbonylchromium (37) and 3-phenyltoluenetricarbonylchromium (38) 3-Phenyltoluene (5 g, 0.029 mol) and hexacarbonylchromium (3.3 g, 0.015 mol) were placed in a 50 ml round bottom flask equipped with a side arm. Freshly distilled diglyme (LAH) was added (20 ml) and the flask was connected to the Strohmeier apparatus. After flushing the system with nitrogen, the mixture was brought to reflux for 3 hr. The cooled reaction was taken up in ether, filtered through a bed of Celite, washed with water and dried over $MgSO_4$. The ether was removed on a rotary evaporator and the residue was chromatographed on a silica gel column using benzene-hexane as the eluant. The first yellow band was collected (2 g) and the NMR spectrum revealed it to be a mixture of monocomplexes; mp 50-80°; NMP ($CDCl_3$) δ 7.5-7.15 (m, 5.1), 5.6-5.1 (m, 3.9), 2.38 (s, 1.3), and 2.28 (s, 1.6); high resolution mass spec m/e 304.0193 (calcd. for $C_{16}H_{12}CrO_3$, 304.0192).

Nuclear magnetic resonance technique

Refer to the Experimental part of the previous project (HINDERED ROTATION STUDIES IN BIS(TRICARBONYLCHROMIUM) COMPLEXES OF DIARYLMETHANES) in this dissertation for a description of the NMR technique that was used for the present project also.

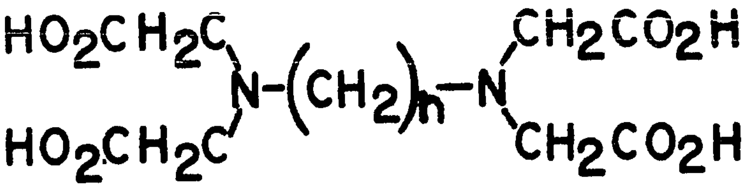
PART II. THE SYNTHESIS OF TRIISOCYANIDE LIGANDS AND THEIR METAL COMPLEXES

THE SYNTHESIS OF TRIISOCYANIDE LIGANDS AND THEIR METAL COMPLEXES

Historical

Few areas of chemistry can be covered in their entirety, comprehensively and in a unified manner. Isocyanide chemistry is one of these rarities. All of the known chemistry of isocyanides from its beginnings, around the middle of the last century to 1970, were compiled in a book of less than 300 pages (64). The principle reason for the relatively small volume of publications on the subject is that convenient and generally applicable methods for the preparation of isocyanides became available only in the 1960's, when isocyanide syntheses by dehydration of N-monosubstituted formamides were developed. A review article on the synthesis of isocyanides giving some representative experimental procedures recently appeared (65). The area of α-metallated isocyanides is readily being explored because of its tremendous synthetic importance (66).

The design of a compound for eventual metal complexation must take into account the factors affecting the stability of metal complexes and also the geometrical consideration of molecular construction (67). The design of ligands is usually directed towards the production of stable metal complexes (67), however the formation and dissociation of relatively weak metal complexes is relevant to the chemistry of metal enzyme systems (68). Small chelate rings are by far the most common and are in general the most stable (67). Medium and large chelate rings have been postulated in a variety of compounds (69). It has even been shown that the stability constants of metal complexes derived from the tetracarboxylic acid (39) decrease along the series n = 2>3>4>5 (70). The cobalt complex vitamin B_{12} contains a nineteen membered ring (71) in addition to the highly stable porphyrin structure. Another example involves just a heme unit and a twelve membered chelate ring (72).



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In tridentate chelating agents the donor atom can be arranged in linear or branched (bifurcated) patterns (67). Patterns 42 and 43 are special examples of the linear pattern 40 and pattern 44 is an example of both the linear 40 and the bifurcated pattern 41. Of the five patterns 43 and 44 have not been reported (67). A few

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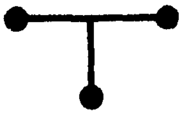

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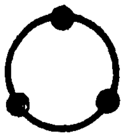

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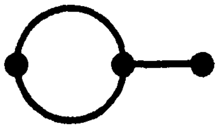

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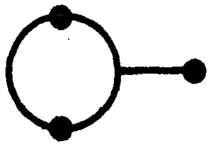

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examples of pattern 42 are reported (73, 74). The linear pattern 40 is by far the most common and may reflect the ease of synthesis. Some examples are: 2,6-bis(α-pyridyl)-pyridine (75), 1,7-diamino-4-azaheptane (76), 3-thiapentane-1,5-dithiol (77) and bis(dimethylphosphinomethyl)phenylphosphine (78). Examples of 41 include 1,1,1-tris(diphenylphosphinomethyl)ethane (79), *cis*, *cis*, 1,3,5-triaminocyclohexane (80, 81) and tri(N-pyrazoyl)methane (82).

Isocyanides can be prepared from the corresponding primary amine. Primary amines are commonly prepared by a number of methods. The Gabriel synthesis with some modifications (83) now gives good yields of the primary amines. They can also be formed readily by the reduction of amides, nitriles, nitro compounds and oximes (84). The Hofmann reaction on primary amides leads to primary amines with one less carbon atom (85), while the related molecular rearrangements of carboxylic acid derivatives, namely carbonyl azides (Curtius (86) and Schmidt (87) rearrangements) and hydroxamic acids (Lossen (88) rearrangement) also lead to primary amines. A sequence for the conversion of hydroxyl groups to amino groups has recently been applied to the synthesis of amine ligands (89). The sequence involves conversion of an alcohol to its benzenesulfonate which is converted to the azide by nucleophilic displacement; the azide is then reduced (90) to the amine by lithium aluminum hydride.

The area of transition metal complexes of isocyanides has developed as slowly as the development of the isocyanides themselves. Interestingly the beginnings of the metal complexes and the beginnings of the isocyanides occurred simultaneously for it was the alkylation of silver cyanide with allyl iodide (91) that gave rise to the first isocyanide. The interest in both the isocyanides and their metal complexes increased after suitable preparative methods for the isocyanides were found in the 1960's. Several excellent reviews (92, 93, 94) have recently appeared in an attempt to keep pace with the rapidly growing area of metal isocyanide complexes.

The mono-, bis-, tris- and hexakis-isocyanide complexes of chromium (95, 96), molybdenum (95, 97) and tungsten (98, 99) are known. Recently the tetrakisisocyanide complexes of chromium (100), molybdenum (101), and tungsten (101) have been reported. There is also evidence for the formation of the pentakisisocyanidecarbonylchromium (102). With the exception of the hexakis complexes, the majority of the other complexes are prepared by displacement reactions.

A generally accepted view has been that carbon monoxide is a better π acceptor and a weaker σ donor than a substituted isocyanide group (103). Evidence for this came from the fact that $(Ag(CNR)_4)^+$, $(Fe(CNR)_6)^{2+}$ and $(Mn(CNR)_6)^{2+}$ are known where π bonding is of relatively little importance; derivatives of this type are not known for carbon monoxide (104). Further evidence came from the case of oxidation of $(Mn(CO)_x(CNCH_3)_{6-x})^+$ with x = 1-5, where a decrease was noted as the number of carbonyls increased (105). Whereas molecular orbital calculations agree with the results, the calculations indicate that the existence of $(Mn(CNCH_3)_6)^{2+}$ and nonexistence of $(Mn(CO)_6)^{2+}$ is not a consequence of reduced σ donating ability of the carbonyl but rather is a result of greater stabilization of the highest occupied molecular orbital in the carbonyl parent species with a resultant increased difficulty of oxidation.

In the case where both carbon monoxide and isocyanide are bonded to the same metal, it was concluded that the main part of back bonding was done by carbon monoxide and not by the isocyanide group (106). However, it has been shown that the stretching frequency of the isocyano group in metal complexes is completely unsuitable as a means to obtain detailed information on the electronic distribution within the isocyano group (94). The molecular orbital calculation indicates that σ donation to the metal may increase the bond strength of the isocyano group and raise the frequency enough so that even fairly extensive back bonding may not lower the frequency to below that of the free ligand (103). The two carbon-nitrogen stretching frequencies observed in $Mn(CO)_3(CNCH_3)_2Br$ occur at 2220 and 2202 cm^{-1}. Both the crystal structure data and the molecular orbital results indicate that π back bonding is definitely taking place to the methyl isocyanide ligands (107).

Recently there has been a lot of interest in the reaction of tripod ligands with transition metal to form complexes. The tripod ligands that have been synthesized are of three types. One type is derived from the readily available $CH_3C(CH_2P(C_6H_5)_2)_3$ (PPP) and some of its reactions are shown below. The second type of tripod ligand is derived from the readily available $N(CH_2CH_2OH)_3$ where again the hydroxyl moiety is easily converted into other donor groups. Many ligands (NX_3) have been prepared but they do not bond to metals as tripod ligands. Rather they bond through the donor atom at the termini of two legs of the tripod and the apical nitrogen and the third leg with its donor atom

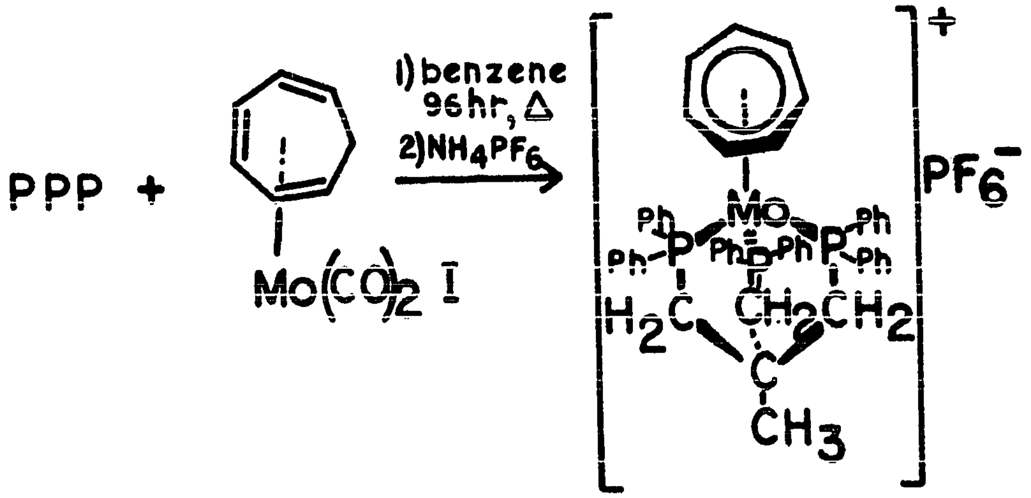
$$\mathrm{PPP + Mo(CO)_3C_7H_8 \xrightarrow[5hr,\,\Delta]{CH_2Cl_2} PPPMo(CO)_3} \qquad (108)$$

$$\mathrm{PPP + Cr(CO)_6 \xrightarrow[50hr]{150^\circ} PPPCr(CO)_3} \qquad (109)$$

$$\mathrm{PPP + W(CO)_6 \xrightarrow[50hr]{150^\circ} PPPW(CO)_3} \qquad (109)$$

$$\mathrm{PPP + Ru_3(CO)_{12} \xrightarrow[4hr,\,\Delta]{toluene} Ru(CO)_2\,PPP} \qquad (110)$$

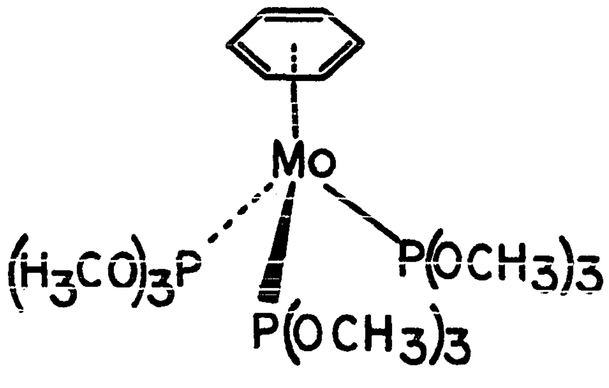
$$\mathrm{PPP + CoCl_2 \xrightarrow{NaBH_4} PPPCo^+Cl^-} \qquad (111)$$



(112)

dangles off the side of the molecule (113). The third type of tripod ligand is the tris- or tetrakis-pyrazolylborate $((C_3H_3N_2)_nBH_{4-n})^-$ (n = 3 or 4). This ligand has been shown to form extensive series of stable complexes with transition metals, their carbonyls and their cyclopentadienyls (114, 115, 116).

The area of arenetricarbonylmetal complexes is firmly established (117). A new area that involves an arene ring complexed to a metal with the remaining coordination sites being completely occupied by ligands other than carbonyl seems to be emerging. Two examples are 45 (118) and 46 (119). No examples that contain isocyanides and benzene or its derivatives have been reported but several have been reported where the arene ring is cyclopentadienyl and they



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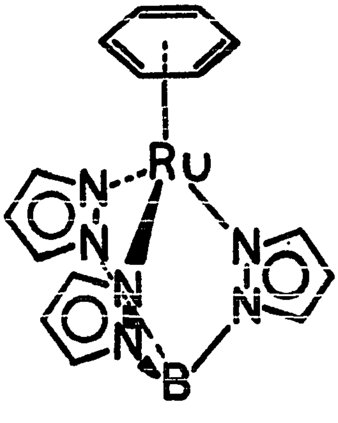

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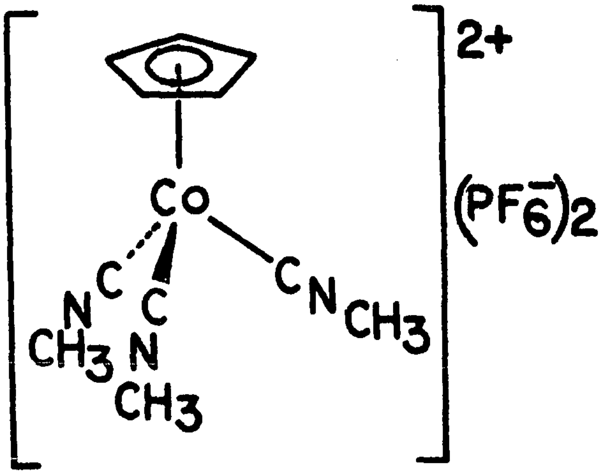

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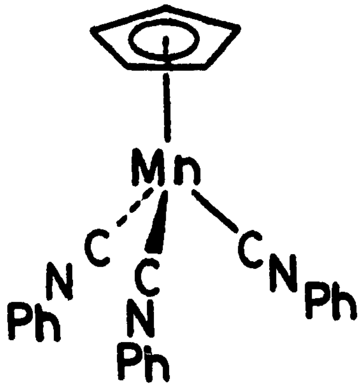

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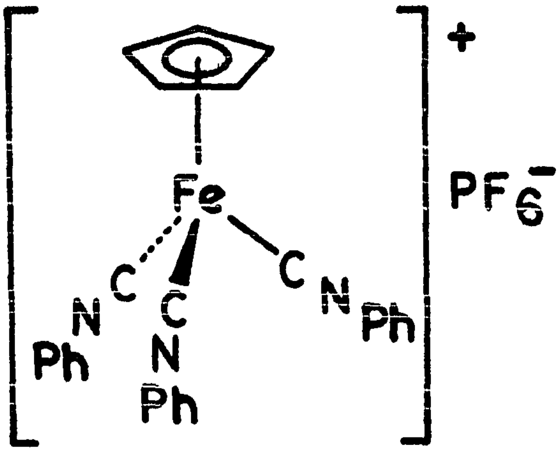
are 47 (120), 48 (121) and 49 (122).



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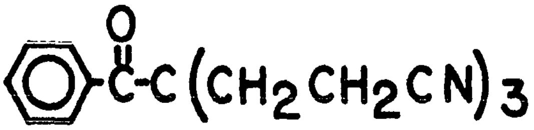
No reports could be found for the existence of a tri-isocyanidemetal complex where the isocyanide ligands were joined at some point to essentially generate a bicyclic cage structure, where the metal occupies an apical site. Currently the preparation of transition metal complexes possessing new and novel structures is of interest because of their catalytic potential.

Results

Synthesis of 1,1,1-tris(γ-isocyanopropyl)-2-phenylethane

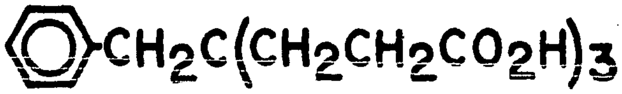
The reaction between acrylonitrile and acetophenone under basic conditions gave as reported (123) the tris-cyanoethylation product, 1,1,1-tris(β-cyanoethyl) acetophenone (50). A high pressure, high temperature hydrogeneration over Ra/Ni in tetrahydrofuran in the presence of ammonia are the conditions that were used to reduce tris(β-cyanoethyl)amine to its tetramine (124). The conditions used for 50 were very similar and indeed reaction had occurred but no readily identifiable product could be separated from the complex mixture. Likewise the low pressure hydrogenation (50 psi) of 50 over 10% Pd/C in acetic acid yielded only starting material as did the low pressure hydrogenation over Ra/Ni (W-2) in a mixture of sodium acetate and acetic anhydride (125).



50

Reduction (126) of 50 with a one to one mixture of lithium aluminum hydride and aluminum trichloride resulted in total loss of all the organic material. Extraction of the aqueous solution at different pH's with various solvents failed to produce any organic material. Diborane is known to reduce nitriles (127) and the reduction of 50 resulted in a gelatinous reaction mixture from which no organic material was isolated.

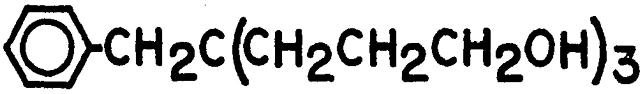
Since acetophenone derivatives are known to react with isocyanides (128), the focus now centered on reducing the carbonyl group. The keto trinitrile (50) was subjected to a Wolff-Kishner reduction using the Huang-Minlon modification (129). The NMR spectra of the crystallized product was consistent with the methylene triacid (51). The carbonyl was reduced to the hydrocarbon and the nitrile had undergone hydrolysis to the acid.



51

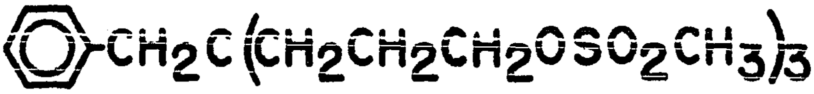
Further evidence for the carbonyl reduction came from the mass spectrum of 51 where the largest peak is 91, attributable to the benzyl group, whereas in 50 the largest peak occurs at 105, attributable to the benzoyl group.

Reactions now centered around the conversion of the triacid to the triisocyanide. Reduction of triacid 51 in tetrahydrofuran with diborane successfully converted it into the trialcohol (52) in good yield. Subsequently 52 was

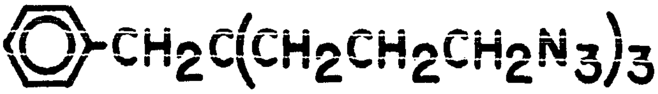


52

converted to its trimesylate (53) by reaction with mesyl chloride in pyridine at 0° for one day. Reaction of trimesylate 53 with sodium azide in diethylene glycol at 135° for 15 hr gave after workup triazide 54. This triazide was easily purified on silica gel using 70/30 methylene



53

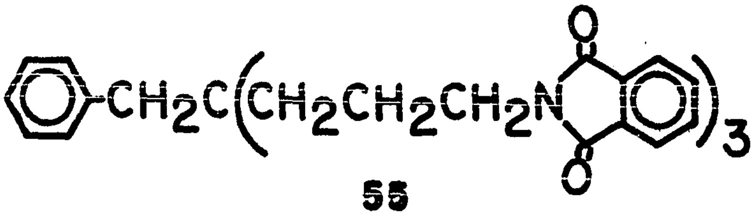


54

chloride/hexane.

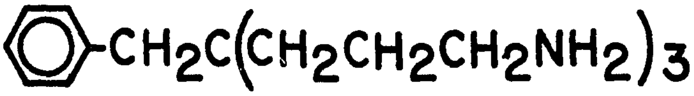
The azide group can be reduced by lithium aluminum hydride to the corresponding amine (90). However, based on one experiment, triazide 54 was not reduced after 18 hr at reflux in tetrahydrofuran. Triazide 54 undergoes reaction with diborane in tetrahydrofuran but no product was isolated from the gelatinous precipitate that formed. Of the catalytic reductions that were attempted the best one was Pd/C with hydrazine hydrate in ethanol solvent for about 6 hr, however this approach was not pursued further.

The trimesylate (53) had been allowed to interact with potassium phthalimide (130) in dimethylformamide at 95° for 2 hr (83). The corresponding triphthalimide (55) was purified by chromatography on silica gel using 50/50 methylene chloride/chloroform. Triphthalimide 55 was easily converted to the amine hydrochloride by allowing it to react with hydrazine in ethanol at reflux for 2 days. The solvent was removed leaving a colorless water soluble solid. After acidification of an aqueous solution and filtering, the solvent was removed leaving the semi-solid amine hydro-

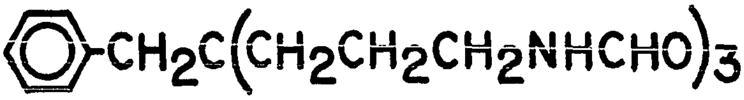


55

chloride. This material was stored as the hydrochloride salt and was converted to triamine 56 as needed, since there are indications that polyamines react with atmospheric carbon



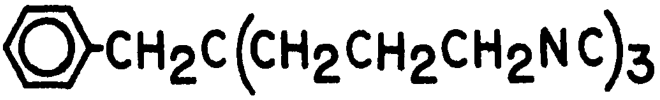
56



57

dioxide (131, 132). The hydrochloride salt was converted to the amine by neutralizing an aqueous solution of the salt and extracting it with chloroform. The triamine was converted to formamide 57 by dissolving it in a large excess of ethyl formate and maintaining a gentle reflux for 10 hr. Removal of the solvent leaves a very viscous oil. The oil was dissolved in pyridine and *p*-toluenesulfonyl chloride was added. Workup of the reaction gave a brown crystalline material. The triisocyanide (58) was purified by column chromatography on silica gel using ethyl acetate. The isocyanide band occurs at 2160 cm^{-1} in the IR spectrum. In

Scheme 4 is shown the sequence of reactions that lead to the



58

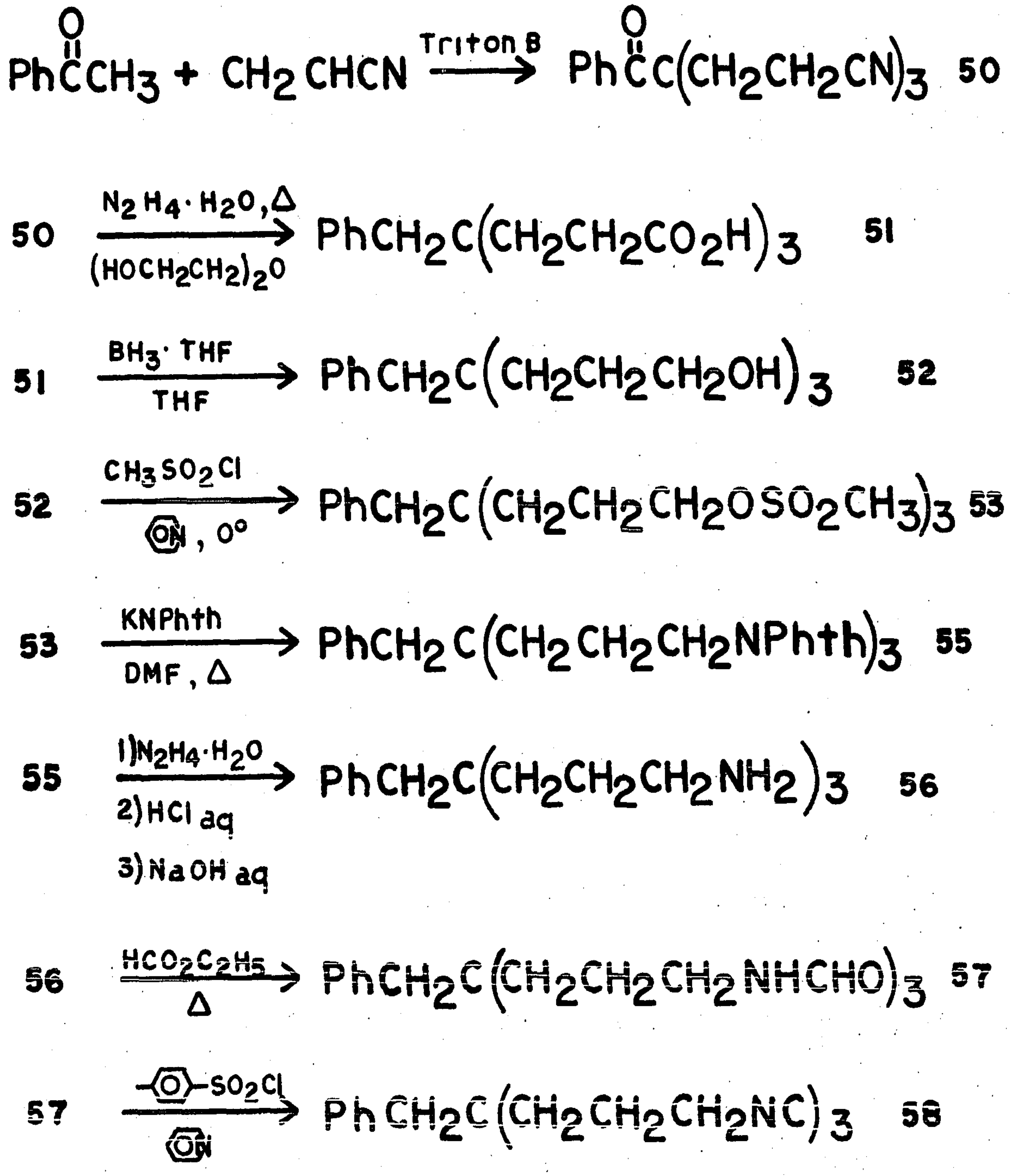
preparation of 58.

Synthesis of tris(β-isocyanoethyl)methane

The trialcohol (59) has been reported in the literature (133). Ethyl β-hydroxyglutarate was converted to its chloride using phosphorus pentachloride (134). The chloride was allowed to condense with the anion of diethyl malonate giving ethyl ω-carboxymethanetriacetate (134) which was hydrolyzed and decarboxylated with 20% hydrochloric acid (135). The methanetriacetic acid was converted to its methyl ester and reduced using lithium aluminum hydride (133) to give 59.

$$HC(CH_2CH_2OH)_3$$

59



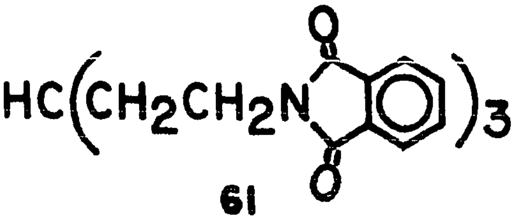
Scheme 4. Synthetic scheme for the preparation of 1,1,1-tris(γ-isocyanopropyl)-2-phenylethane

The reactions that converted 52 to 58 were now applied to trialcohol 59. It was found that the yield for the mesylation reaction could be increased from 50% to 96% by using triethylamine instead of pyridine. Trimesylate 60

$$HC(CH_2CH_2OSO_2CH_3)_3$$

60

was successfully converted to triphthalimide 61 by warming a solution of 60 and potassium phthalimide in dimethylformamide.



61

Hydrazinolysis of 61 followed by acidification of the aqueous solution and filtration gave a solution from which the amine hydrochloride was obtained when the solvent was removed. The amine hydrochloride was dissolved in water and neutralized with base, but because triamine 62 is so water soluble it cannot be extracted out of the aqueous solution. Removal of the water under reduced pressure left the amine and the salt. The amine was then taken up in methylene chloride and

$$HC(CH_2CH_2NH_2)_3$$

62

filtered from the solid. Removal of the solvent left the triamine which was allowed to react with ethyl formate. Triformamide 63 initially separates as an oil, which eventually solidifies. The formamide was only slightly

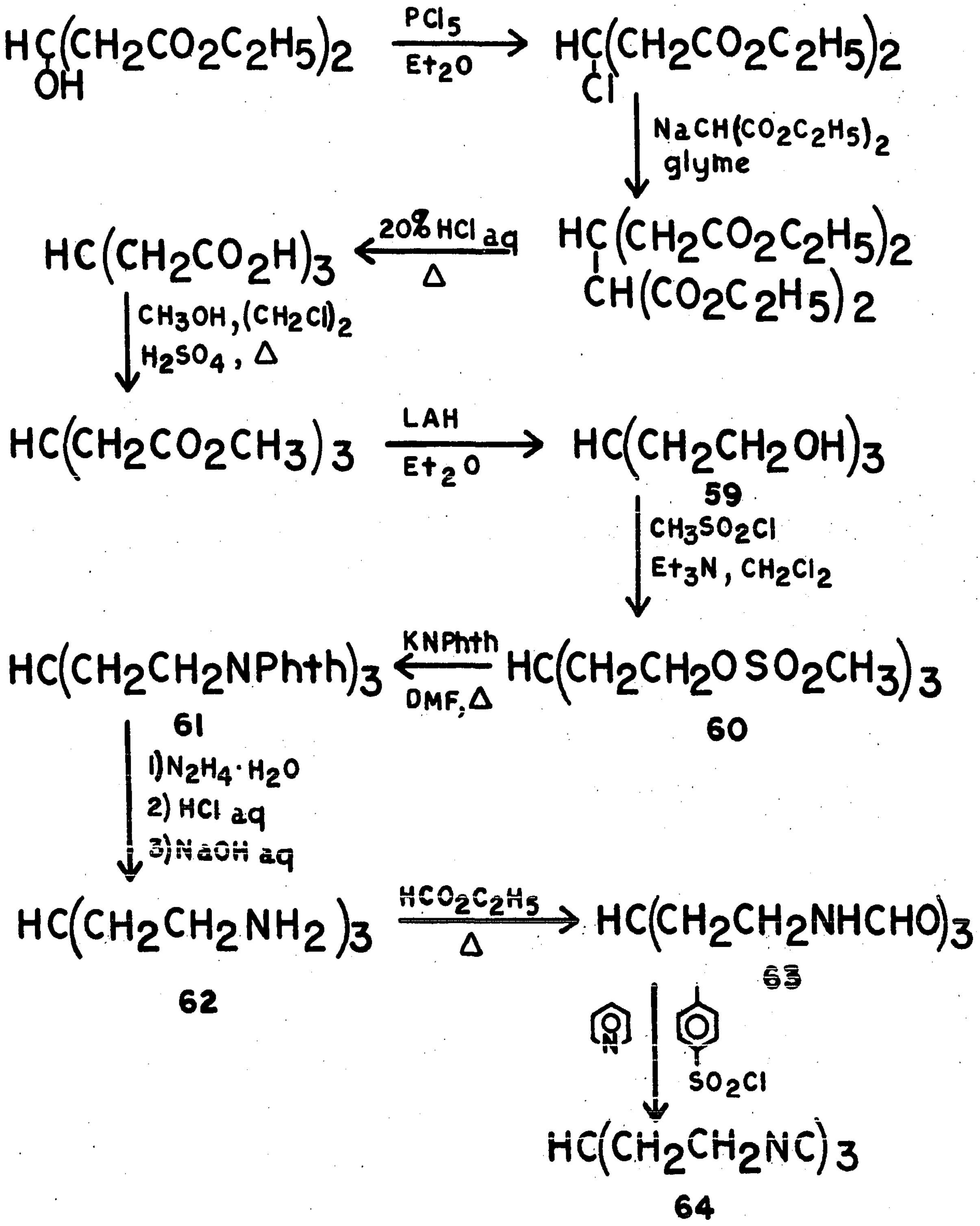
$$HC(CH_2CH_2NHCHO)_3$$

63

soluble in pyridine but nevertheless readily went into solution once the toluenesulfonyl chloride was added. Upon workup triisocyanide 64 was obtained. In Scheme 5 is shown the sequence of reactions that lead to the preparation of 64.

$$HC(CH_2CH_2NC)_3$$

64



Scheme 5. Synthetic scheme for the preparation of tris(β-isocyanoethyl)methane

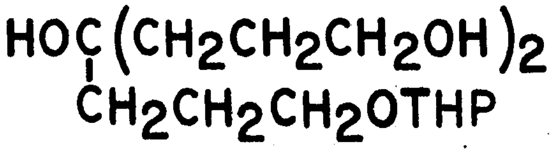
Alternate synthetic approaches to triisocyanides

Having on hand a large quantity of 51, it seemed attractive to try and degrade the triacid to a derivative with one less carbon atom in each chain that could lead to the isocyanide functional group. A modified Curtius reaction (136) eventually resulted in a solid which was insoluble in aqueous and organic media. The reaction conditions used to convert undecyl chloride to undecyl isocyanate (137) were applied to 51. An IR spectrum of the material in benzene after heating did exhibit an isocyanate band. Concentrated hydrochloric acid was added to the solution and as a gas evolved a precipitate formed, presumably the amine hydrochloride. However, upon basification of an aqueous solution of the amine hydrochloride a precipitate formed accounting for the majority of the material; the precipitate being insoluble in common organic solvents. A modified Curtius using diphenylphosphoryl azide in t-butyl alcohol converts an acid to a urethan (138); the t-butyl urethane being easily converted to an amine. Applying the reaction to 51 resulted in a material whose spectra indicated the presence of a dicarbamate mono isocyanate. Upon bubbling dry hydrogen chloride through the benzene solution a water soluble solid was obtained. Basification of the aqueous solution with either sodium hydroxide or tetraethylammonium hydroxide resulted in the formation of a precipitate accounting for the majority of the material as above. The diphenylphosphoryl azide reaction was rerun on 51 using the less hindered ethanol but as before the spectra of the isolated material indicated a dicarbamate mono isocyanate.

A series of Hunsdieker type reactions were attempted on 51. When 51 was heated in a mixture of bromotrichloromethane and bromobenzene with mercuric oxide and bromine (139), a small yield (5%) of a mixture of brominated products was formed. Spectra indicate the presence of the anticipated bromide and a tetrabromide where the fourth bromine was at the para position of the phenyl ring. If the reaction was carried out with only bromotrichloromethane as solvent, 51 was reisolated.

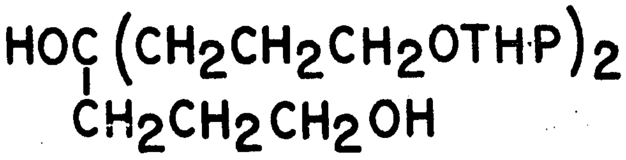
The silver salt of 51 was prepared and when dropped into a solution of bromine in carbon tetrachloride at reflux, the silver salt coagulated; the bromine was not consumed and very little gas was evolved. Thallium salts are reported (140) to give better yields of aliphatic bromides than the corresponding silver salts (141). The thallium salt of 51 was prepared from the acid and thallous ethoxide. However neither the addition of the dry acid salt to a solution of bromine in carbon tetrachloride with subsequent warming to reflux or the slow addition of the dry acid salt to a solution of bromine in carbon tetrachloride at reflux led to product. In both cases the salt coagulated, the bromine was not consumed and very little carbon dioxide was evolved.

Another sequence of reactions that could lead to triisocyanides was initiated but was not pursued to the final stage because trialcohol 52 was successfully prepared about the same time. 3-Chloropropanol was allowed to react with dihydropyran following a literature procedure (142) to give 2-(γ-chloropropoxy)-tetrahydropyran (143). Attempts to prepare its Grignard reagent from magnesium turnings in either ether or tetrahydrofuran met with failure. The use of activated magnesium (144) did give rise to the Grignard reagent. One third of an equivalent of diethyl carbonate was added and after workup with excess saturated ammonium chloride solution, the product mixture was separated on a silica gel column using ether as the solvent. The major, minor and desired products are 65, 66, and 67 respectively. Subsequent to the formation of the desired product 67, the tertiary alcohol group would be protected. The tetrahydropyranyl ethers would be cleaved and the resulting trialcohol would be converted to its triisocyanide.



$$\begin{array}{l}\mathrm{HO\underset{|}{C}(CH_2CH_2CH_2OH)_2}\\ \quad\mathrm{CH_2CH_2CH_2OTHP}\end{array}$$

65



$$\begin{array}{l}\mathrm{HO\underset{|}{C}(CH_2CH_2CH_2OTHP)_2}\\ \quad\mathrm{CH_2CH_2CH_2OH}\end{array}$$

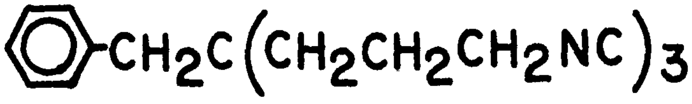
66

$\mathrm{HOC(CH_2CH_2CH_2OTHP)_3}$

67

Synthesis of triisocyanidemetal complexes

The interaction of triisocyanide 58 with various metal complexes led to workable product only when high dilution conditions were employed. The interaction of triisocyanide 64 with various metal complexes led to labile materials.

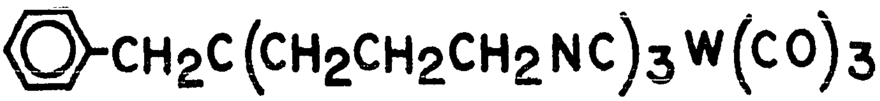


58

$$HC(CH_2CH_2NC)_3$$

64

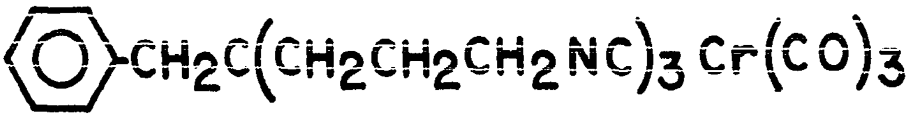
Toluenetricarbonyltungsten was allowed to interact with 58 for 18 hr at reflux in toluene under high dilution conditions. Thick layer chromatography using methylene chloride-pentane effected a separation between any remaining starting tungsten complex and a series of slower moving bands. The second band with an R_f of about 0.45 on a thin layer slide was collected and recrystallized from chloroform-pentane. Its ability to be recrystallized seems to favor a non or small polymer formulation. The presence of two carbonyl bands at 1942 and 1875 cm^{-1} and two isocyanide bands at 2160 and 2118 cm^{-1} in the IR spectrum in methylene chloride is indicative of a tricarbonyltriisocyanidemetal complex. The α-methylene protons of the isocyano moiety in the NMR spectrum of the complex show a downfield shift and this is consistent with the formation of a metal isocyanide bond. The β- and γ-methylene protons are also observed to be shifted downfield and the absence of signals in the region for uncomplexed 58 indicates that all of the chains are bound to metals. The phenyl ring protons are not shifted upfield discounting any possible π arene complex formulation. A value of 599 was found for the molecular weight by osmometric molecular weight determination. This compares nicely with the calculated value of 575 and indicates that a monomeric complex has indeed been formed. The complex does not have a melting point but rather a decomposition point (170°) where the solid changes color only from white to black; the crystals remain intact. No mass spectra could be obtained for this complex or any of the other complexes reported in this section. The results indicate that a monomeric structure 68 exists for the complex. In Figure 13 is shown



68

the NMR spectrum for 58 in deuterochloroform while the spectrum for 68 in deuterochloroform is shown in Figure 14. In Figure 14 the phenyl region is partially obscured by the chloroform impurity in the deuterated solvent.

When cycloheptatrienetricarbonylchromium was allowed to interact with 58 in toluene at reflux, a material was isolated after thick layer chromotography whose spectra are very similar to those for 68. The major difference is that the R_f for the chromium complex is about 0.8 on a thin layer slide, much faster than for 68. The NMR spectrum again shows the absence of uncomplexed isocyanide and the noncomplexed nature of the phenyl ring. The IR spectrum in methylene chloride exhibits two isocyanide bands at 2160 and 2119 cm^{-1} and two carbonyl bands at 1942 and 1878 cm^{-1}. The similarity of the spectral properties indicates that a monomeric structure exists for the chromium complex 69. In Figure 15 is shown the NMR spectrum for complex 69 in deuterochloroform, where again the phenyl region is partially obscured by the chloroform impurity in the deuterated solvent.

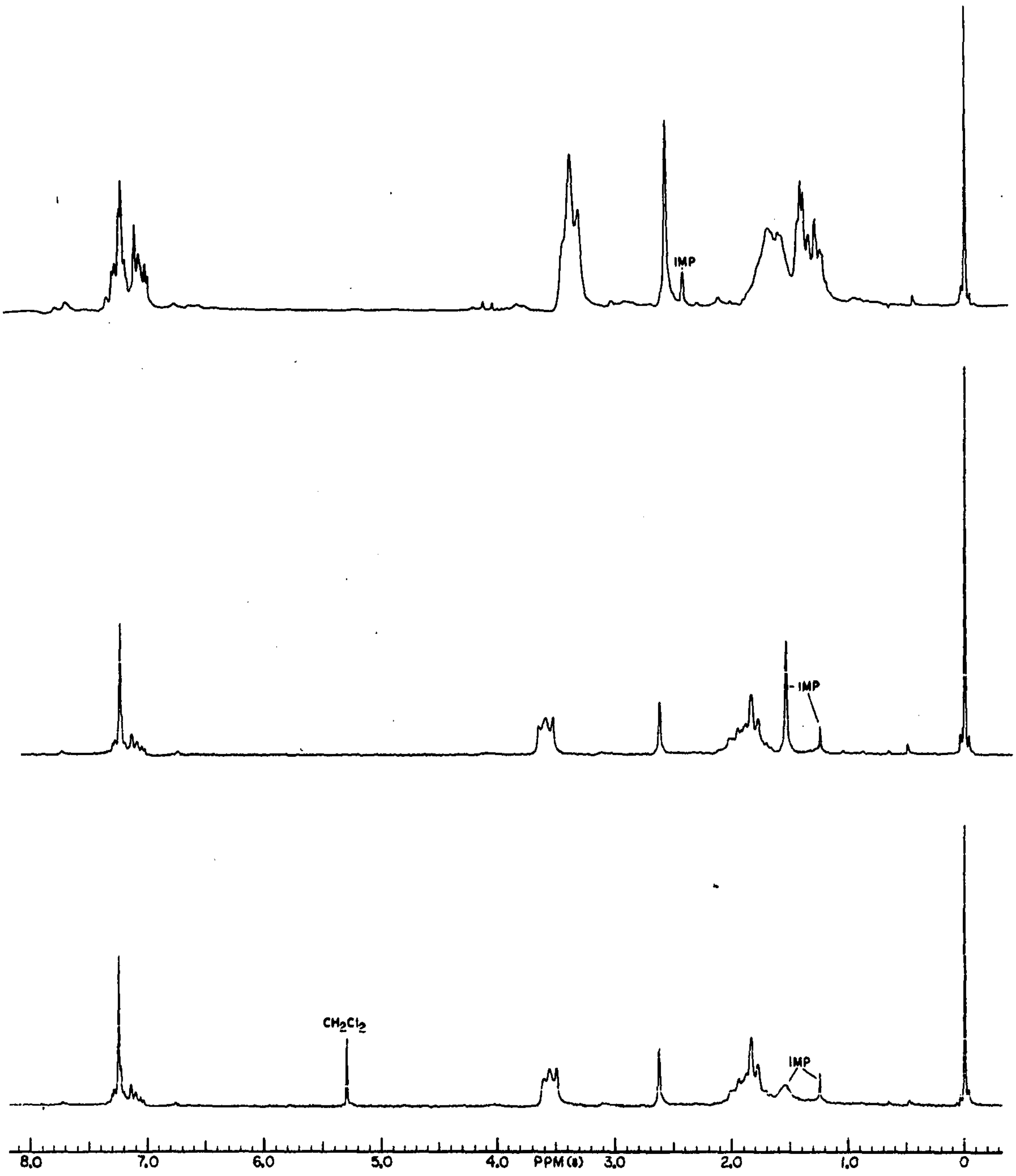


69

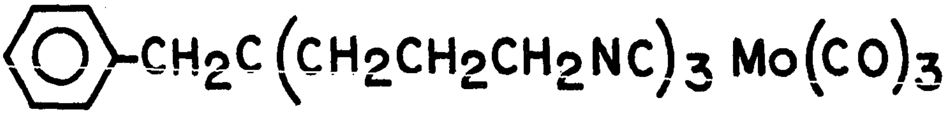
Figure 13. HX-90 proton NMR spectrum of 1,1,1-tris-(γ-isocyanopropyl)-2-phenylethane (58) in deuterochloroform at ambient temperature

Figure 14. HX-90 proton NMR spectrum of tricarbonyl-(1,1,1-tris(γ-isocyanopropyl)-2-phenylethane)tungsten (68) in deuterochloroform at ambient temperature

Figure 15. HX-90 proton NMR spectrum of tricarbonyl-(1,1,1-tris(γ-isocyanopropyl)-2-phenylethane)-chromium (69) in deuterochloroform at ambient temperature


IMP
IMP
CH2Cl2
IMP
8.0
7.0
6.0
5.0
4.0
PPM (δ)
3.0
2.0
1.0
0

When cycloheptatrienetricarbonylmolybdenum was allowed to interact with 58 in benzene solvent at room temperature, a somewhat labile material was isolated after thick layer chromatography. Again the spectral properties are very similar to those of 68 and 69. Two isocyanide bands at 2151 and 2110 cm^{-1} and two carbonyl bands at 1945 and 1874 cm^{-1} in the IR spectrum in methylene chloride are observed. The NMR spectrum is very similar to that for 68 and 69 and again indicates no π arene complex and the lack of free isocyanide. The R_f value for the molybdenum complex is about 0.65 on a thin layer slide. A monomeric structure 70 seems to be consistent with the individual data especially when it is compared to the data of 68 and 69.



70

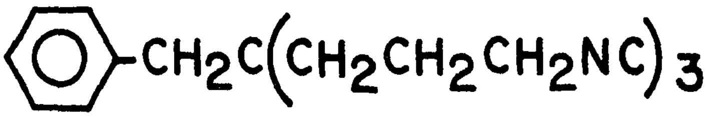
The interaction of 58 with pentacarbonylmanganese bromide under high dilution conditions in tetrahydrofuran resulted in the loss of starting material but no discernable product has as yet been isolated. No reaction occurred when 58 was allowed to react with hexacarbonylchromium in glyme solvent at reflux for several days nor was any reaction observed when 58 was allowed to react with benzenetricarbonylchromium in glyme solvent at reflux.

The interaction of triisocyanide 64 with the various reagents, toluenetricarbonyltungsten, cycloheptatrienetricarbonylchromium and cycloheptatrienetricarbonylmolybdenum under high dilution conditions appear to give complexes of rather low molecular weight (fast moving on thin layer chromatography) but these materials seem to be labile and cannot be chromatographed using thick layer methods. Liquid chromatography was applied to the separation of the tungsten complexes and also the chromium complexes. Separation does occur on a microstyragel column using THF as the solvent and subsequent IR analysis of the various fractions from either system exhibit both carbonyl bands and isocyanide bands. The complexes however alter upon standing even at 0° to give materials that are insoluble in common organic solvents.

Discussion

Present results

There were no reports in the literature of a bis- or tris-isocyanidemetal complex in which the isocyanide chains are tied together. Triisocyanides 58 and 64 were synthesized to see if stable monomeric metal complexes could be made from them. The decision to synthesize the compounds with three methylene units and two methylene units in each chain was arrived by inspection of potential complexes using Drieding models. It was assumed that the triisocyanide would use its carbon lone pairs for bonding. The present results



58

$$HC(CH_2CH_2NC)_3$$

64

indicate that the first stable triisocyanidemetal complexes of this type have been prepared.

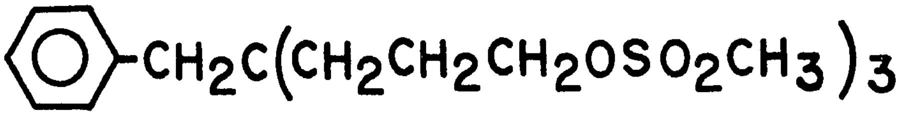
The tricarbonyltriisocyanidemetal complexes that were prepared from the bifurcated ligand <u>58</u> have properties that are both similar and different from the unbridged tricarbonyltriisocyanidemetal complexes. The bridged complexes are very light colored, cream, similar to those reported. The bridged complexes (Cr, W) are stable; the molybdenum is somewhat labile when left open to the air; however a sample of the tungsten complex was exposed to the air for several months with no change in spectral or chromatographic behavior. The IR spectra for the two types of compound are very similar. In the NMR spectrum of an unbridged complex the deshielding effect on the protons decreases upon going from the α- to the β-carbon, when compared to the starting isocyanide (95). In the bridged complexes the overall deshielding effect on the protons on the β- and γ-carbons (0.66 ppm) is greater than on the α-carbon (0.19 ppm) (see Figures 13 to 15). A slight deshielding effect is also noted on the benzyl protons in going from the parent triisocyanide to the complexes (0.04 ppm). Mass spectra have been obtained for the unbridged tricarbonyltriisocyanidemetal complexes although the authors report that difficulty was experienced because of degradation at temperatures necessary for volatilization (95). No mass spectral data could be obtained for the bridged complexes. Comparing melting point behavior, there is again a difference because the unbridged complexes do have melting points (95) but the bridged complexes have wide decomposition points during which the complex turns black; the crystals, through black, retain their original appearance.

The strongest evidence for the monomeric nature of the bridged complexes is the acceptable molecular weight determination for the tungsten complex (68). The chromatographic behavior is also indicative of a monomeric complex, since the complexes (68, 69 and 70) move almost as fast as the starting monomeric organometallic reagent. The NMR spectrum is also indicative of a structure where a degree of order must be present to have that great of an overall deshielding effect on the protons at the β- and γ-carbons (0.66 ppm). A slight deshielding effect is also noted on the benzyl protons (0.04 ppm). One would not expect to see this effect if an unbridged structure was formulated.

In conclusion the results indicate that a monomeric structure best accounts for the data. The present work is then important because it shows that a bridged triisocyanide-metal complex can be formed and further that three methylene units in each chain is an acceptable number for the preparation of these complexes.

Prospective synthesis of triisocyanides

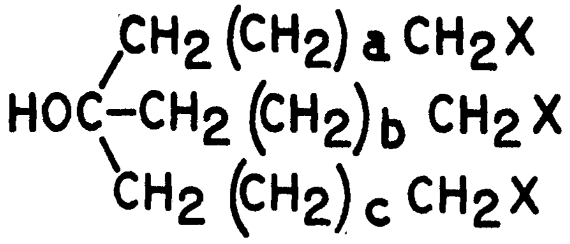
It is good to consider the potential of the various synthetic schemes that were investigated. The cyanoethylation reaction is very convenient for the incorporation of three chains each having three carbon atoms. The results also show that the cyano group can be converted to the isocyano group with the original carbon skeleton intact. The results further show that degradation reactions leading to derivatives with one less carbon in each chain does offer problems. The cyanoethylation reaction is of wide scope (145) and can be applied to a variety of *p*-substituted acetophenones as well as acetone, nitromethane and 2-furylmethyl ketone to give triscyanoethylated products. One then possesses some control of the nature of the fourth group on the apical carbon atom. If homologs of 53 were desired the synthetic method for homologation of primary halides



53

(146) could be used to increase each chain length by one carbon atom whereas the use of diethylmalonate could increase each chain by two carbon atoms.

The cyanoethylation reaction suffers in that all three chains will, of course, be the same length. It may be desirable to prepare triisocyanide ligands where two or none of the chains have the same length. A suitable reaction sequence that may allow for the construction of molecules with variable chain length was investigated but only superficially, and in the case where all the chains had the same length. Chloroalcohols can be converted to their tetrahydropyranyl ethers and by using activated magnesium the corresponding Grignard reagent can be prepared. By the addition of a Grignard reagent prepared from a chlorotetrahydropyranyl ether, $ClCH_2(CH_2)_cCH_2OTHP$, to $THPOCH_2(CH_2)_bCH_2COCH_2(CH_2)_aCH_2OTHP$ it is possible to generate molecules (71) with variable chain lengths. The hydroxyl moiety on the apical carbon atom allows one to have control over the functionality at

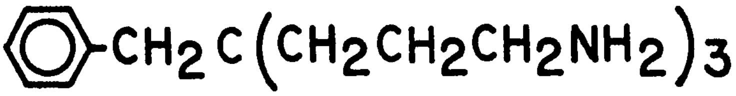


71

that site. The tetrahydropyranyl ether can easily be removed and the alcohol can then be converted to the isocyano group by the reported procedure.

If altering the tertiary alcohol group was not possible because of the presence of the tetrahydropyranyl ether, the benzyl protecting group could then be utilized. The Grignard reagent from γ-bromopropylbenzyl ether has been prepared without difficulty (147). The benzyl group can then be removed by hydrogenolysis (148) leaving the trialcohol.

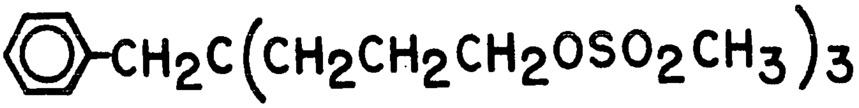
Whereas the present work deals with the synthesis of triisocyanides as ligands, various intermediates could in fact be used as ligands themselves, such as <u>54</u> and <u>62</u>, the triamines. Also it is possible to prepare substituted phosphines and arsines from <u>53</u> and <u>61</u>, the trimesylates.



54

$HC(CH_2CH_2NH_2)_3$

62



53

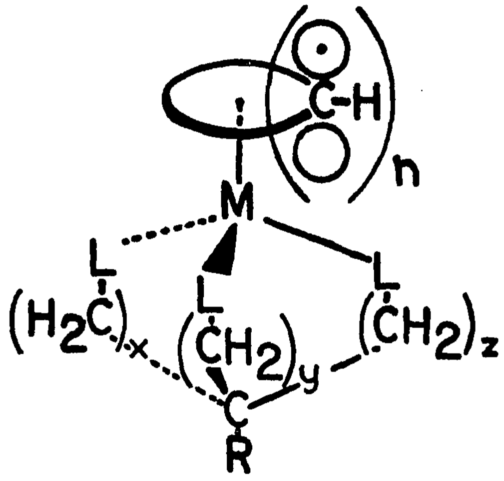
$HC(CH_2CH_2OSO_2CH_3)_3$

61

Prospective work on triisocyanidemetal complexes

The tricarbonyltriisocyanidemetal complexes (68 to 70) that have been prepared may be examined to determine their capacity as catalysts. It is known that the hexakis(arylisocyanide)chromium complexes when allowed to react with trialkylaluminum produce an effective catalyst for obtaining isotactic 1,2-polybutadiene (92). The analogous molybdenum and tungsten complexes are effective in initiating the polymerization of methyl methacrylate in the presence of organic halides, such as carbon tetrachloride (92). The olefin metathesis reaction is readily being explored (149) and the catalyst systems used are binary and ternary metal systems where the transition metal most often used is tungsten (150). Complex 68 as well as 69 and 70 could be tested to determine if they are olefin metathesis catalysts. If inactive by themselves, the addition of an equivalent of dichloroethylaluminum could result in the generation of activity since the aluminum reagent is one of the common coordination catalysts for olefin metathesis.

A final goal of the project may be to synthesize a member or members of a relatively new class of compound (72) and to study the physical and chemical properties of these complexes. Analyzing 72, it is realized that L must be able to donate a pair of electrons to the metal and it would seem advantageous for L to be able to accept electron density from



72

the metal. Carbon monoxide fits the electronic requirement very nicely but it is a terminal ligand. Non-terminal ligands are plentiful and those whose electronic requirements are suitable are phosphines, arsines and isocyanides. Strohmeier investigated the π acceptor strengths of ligands in the complexes (Arene(Cr(CO)$_2$L) and placed them in the following order: CO > PR$_3$ ∿ isocyanide > nitrile (151, 152).

If the eighteen electron rule is to be followed, then the choice of the metal will determine the value for n in 72 and correspondingly choosing a certain ring size will determine what metal can be used. This can easily be seen in Table 4, where the relationship of n to M is shown for the formation of neutral complexes and for the formation of

Table 4. Relationship of n to M for the formation of neutral complexes and for the formation of positively charged complexes (+1)

value for n	2	3	4	5	6	7
metal (M)	Ni	Co	Fe	Mn	Cr Mo W	V
metal (M) when complex has a positive charge		Ni	Co	Fe Mo	Mn	Cr Mo W

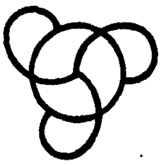
positively charged complexes (+1) that would exist as salts.

The value of x, y and z will be determined by the steric constraints imposed on the system when all three ligands bond to the metal. For example, if one were to make L equal to isocyanide and x = y = z = o, it would be very difficult to bond the three carbon lone pairs to the same metal and have a stable complex.

The fourth group on the apical carbon atom, R, can be any functional group so long as it does not interfere with the triisocyanide ligand or the resulting complex.

The complexes whose physical and chemical properties may warrant investigation possess the following specifications: n = 6, M = Cr, Mo or W, L = isonitrile, x = y = z = 3 and R is any noninterfering group. The carbonyls of benzenetricarbonylchromium make an angle of about 90° with respect to each other (55). In order for the isocyanide to form 90° angles with respect to each other, the chains must be three methylene units long. This of course assumes that the isonitrile bonds with its lone pair. The value of three was arrived at by inspection of the molecule using Dreiding models. A value of two resulted in somewhat strained metal isocyanide bonds and may account for the lability of the metal complexes derived from 64. A value of three results in a good fit and stable tricarbonyltriisocyanide complexes are now known. A value of four resulted (models) in a very loose and flexible complex but may be useful for metals whose bound ligands form an angle approaching the tetrahedral angle. An x-ray crystal structure may be performed on one of the complexes, possibly the tungsten (68) to see if the metal isocyano group is linear or bent. The crystal structure will confirm the monomeric nature of the complex and give an idea of the spacial requirement for the organic portion of the molecule.

Constructing a Framework model of a tricarbonyltriisocyanidemetal complex reveals two interesting aspects. One is that the chains spiral to a small extent as they connect the apical carbon to the metal. This gives rise to clockwise (73), counterclockwise (74), or mixed twist (75) conformations, when viewed from the apical carbon to the metal. The methylene protons of the benzyl group on the apical carbon atom in theory are in different magnetic environments. Since a singlet is observed in the NMR spectra for the complexes (68 to 70), a rapid equilibrium



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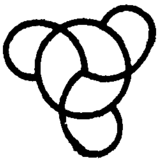

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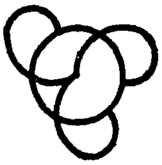
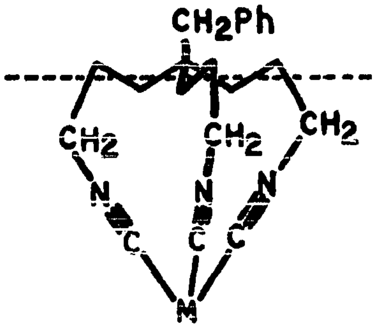


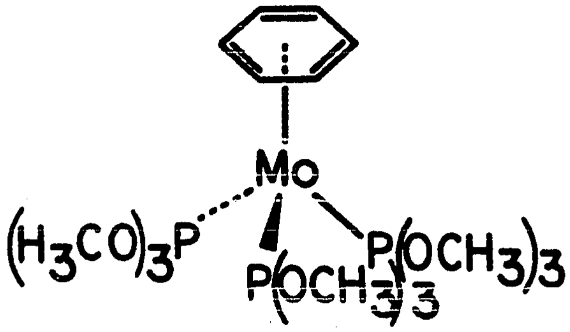
75

between the enantiomers 73 and 74 could exist and account for the results or else the environmental magnetic difference is very slight and the protons are not affected enough to be observed as different. Secondly, the midpoints of the β-γ and γ-δ carbon-carbon bonds seem to form a plane; the net effect being a flat topped molecule (76), were it not for the benzyl group.



76

It seems very likely that the bonding constraints around the metal and the isocyano groups in the tricarbonyltriisocyanidemetal complexes would be very similar to those in the arenetriisocyanidemetal complexes. Finding a way of replacing the carbonyls with an arene ring would be one approach to the formation of the desired complexes. It is felt that the arenetriisocyanidechromium complexes must arise from a non-carbonyl precursor. Recently 45 was prepared from bisbenzenemolybdenum with excess trimethylphosphite in the absence of solvent at about 110° (118). The reaction of bisbenzenemolybdenum with 58 could yield the corresponding arenetriisocyanidemolybdenum complex 77. Some of the arenephosphitemolybdenum complexes decompose readily in air. In 77 the chelate effect could give the molecule very enhanced stability.



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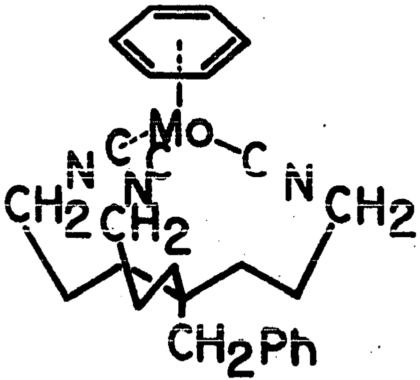

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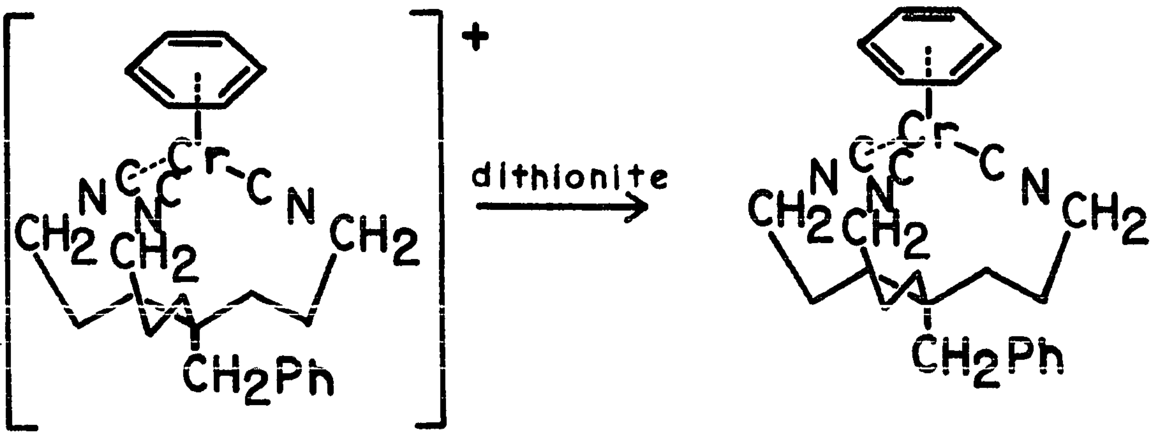
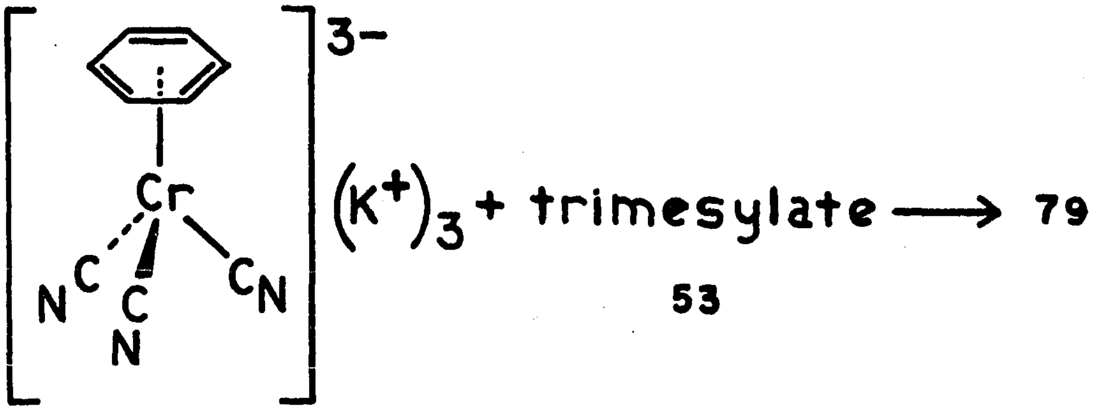
Starting with bisbenzenechromium, it may be possible to prepare the corresponding chromium complex however it is known that bisbenzenechromium is displaced by carbon monoxide under forcing conditions to give hexacarbonylchromium and no benzenetricarbonylchromium was isolated (117). It is known that arene ligand exchange occurs from the cationic bisbenzenechromium (117), so it may be possible to displace one of the arene rings from the cationic specie by 58 to give 78; a mild reducing agent such as dithionite could then convert 78 to neutral 79.



78 79

The reduction of $K_3(Cr^{+3}(CN)_6)$ in liquid ammonia with potassium gives $K_6(Cr^{\circ}(CN)_6)$ (153), perhaps a suitable starting point for the preparation of 79 and some of its derivatives. Displacement of three of the cyanides with an aromatic ring would give rise to 80. Alkylation of 80 with a trismethanesulfonate such as 53 under high dilution



80

conditions could give 79. The alkylation reaction of metal cyanides to give metal complexed isocyanides is well known (92).

When complexes of the type 79 are prepared then it would be interesting to see if ligand exchange reactions analogous to those for the arenetricarbonylchromium complexes could be performed on these complexes. This would then allow for the formation of a wide assortment of arenetriisocyanidechromium complexes.

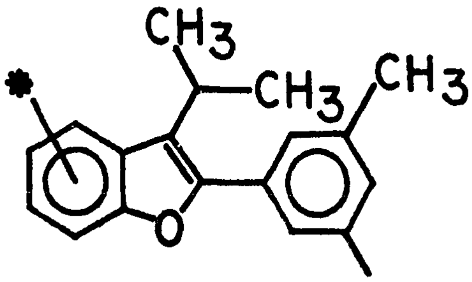
The preparation of complex 79 where the π arene ring is toluene could be interesting. The reactions of this complex could then be investigated. One reaction of special interest would be the oxidation of the complex to give mono cation

78. Whereas it is not possible to oxidize the corresponding arenetricarbonylchromium system to its isolable mono cation, it seems likely that with isocyanides present such an oxidation reaction could lead to a stable mono cation that could be isolated as the salt. Isocyanides are known to stabilize metals with positive oxidation states (102). The tying back of the isocyanides can again give the molecule added stability (chelate effect). The cation lacks one electron needed for the closed shell so the complex is paramagnetic. Now it is known that arenetricarbonylmetal complexes form complexes with an aromatic solvent (59), so it seems likely that a complex would also form between an aromatic ring and the backside of the complexed ring in 78. Since the complexed ring in 78 is toluene the aromatic ring would not be symmetrically displaced. The paramagnetic nature of the complex could cause the aromatic protons of the uncomplexed ring to shift from their normal field position in the NMR spectrum. In effect mono cation 78 could act as a paramagnetic shift reagent for the protons of an aromatic ring and for the carbons of the aromatic ring. This in turn could be highly useful for structure elucidation.

The neutral, mono cation and dication (stabilized by the isocyanides) complexes could also be tested for their catalytic properties.

The possibility exists that complexes having structure 79 could be unusually stable. The hexakis(arylisocyanide)-chromium complexes are quite stable to air, heat and alkali (90). These complexes are also very highly colored ranging from yellow to red with green or metallic reflectances. It is thought that perhaps the arenetriisocyanide complexes would also exhibit similar properties. If the properties were very similar, then the R group on the triisocyanide could be converted into a polymerizable functional group. The arenetriisocyanide complex could then be copolymerized with other monomers to give highly colored polymers where the color is part of the polymer and not a dye additive.

The triisocyanide moiety of a complex must occupy more space than the tricarbonyls of the analogous complex. The magnetic environment of the tricarbonylmetal moiety bound to one ring of a biphenyl can be felt at the *syn*-meta position of the other ring. Refer to the Results and Discussion parts of the (HINDERED ROTATION STUDIES IN MONO(TRICARBONYLMETAL) COMPLEXES OF ALKYL BIPHENYLS) project reported in this dissertation. The effect however is small and if the distance were made much larger it would not be observed. The triisocyanide moiety allows one to expand the sphere of influence to study processes such as hindered rotation at points far removed from the actual metal complex. Such complexes whose hindered rotation properties could not be studied with the tricarbonyl moiety are 81 through 83, where the metal moiety would be at the starred position. Replacing the tricarbonylmetal moiety with the much larger



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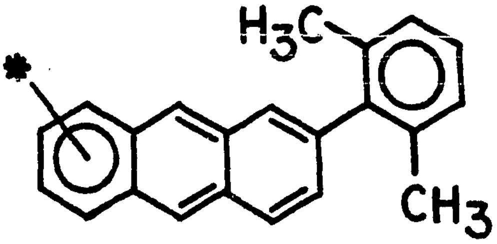

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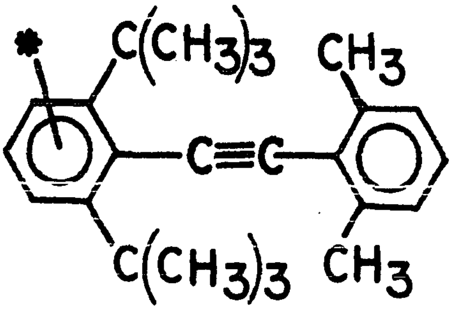
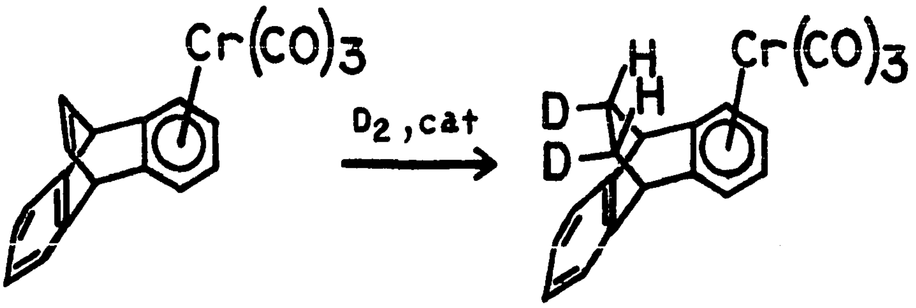


83

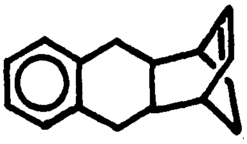
triisocyanidemetal moiety could enable one to study these systems.

The triisocyanide ligand is flexible and its sphere of influence can be controlled by the functional groups on the α-methylene carbon. Considering structure 76 the α-methylene protons form a plane that is parallel to the arene ring. By replacing those protons with other R groups the sphere of influence is spread out in a plane parallel to the aromatic ring. The much larger group may be able to determine the stereochemistry of reactions at sites far removed from the metal center. For example 84 is known to be catalytically deuterated to give only 85, because the tricarbonylchromium group serves as a blocking group to shield one face of the carbon-carbon double bond (154). It is



84 **85**

unlikely that the tricarbonylchromium group would be able to control the stereochemistry in 86 where the double bond is far removed from the metal moiety. However, a suitable substituted triisocyanidemetal complex could control the stereochemistry. The same can be said about the reduction of the ketone in 87.



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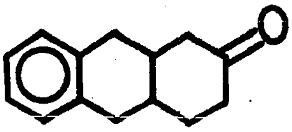

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As one can see the project is in its infancy and can evolve in many directions, of which only some have been mentioned. The possibilities become staggering when the implications of Table 5, which itself is incomplete are considered. The present work is important because it shows that a triisocyanidemetal complex can be formed and further that three methylene units in each chain is an acceptable number for the preparation of these complexes.

Experimental

Equipment, methods and materials

Nuclear magnetic spectra were run on a Varian Associate A-60 Nuclear Magnetic Resonance Spectrometer.

Proton magnetic resonance spectra were run on a Bruker HX-90 spectrometer with a Nicolet 1089 computer using the Fourier Transform mode.

IR spectra were recorded on a Beckman IR 12, a Beckman IR 18A and a Beckman IR 2450 using NaCl cells. The instruments were calibrated with respect to the 1601 cm^{-1} band for polystyrene.

Melting points were taken on a Thomas Hoover Capillary Melting Point Apparatus.

Molecular weight determination and elemental analysis were carried out by Spang Microanalytical Laboratory (Ann Arbor, Michigan).

Thick layer chromatography plates were obtained from Brinkmann Instruments, Inc.

The source of commercial compounds is shown in Table 5.

Prepared compounds

All melting points are uncorrected.

Compounds were analyzed by double focussing mass spectrometry using an Associated Electronics Industries MS-902

Table 5. Source of commercial compounds for the triisocyanide ligands and their metal complexes project

Compound	Source
Acetophenone	Matheson Coleman and Bell
Acrylonitrile	Aldrich
Triton B.	Eastman Organic
Hydrazine hydrate	Baker
Diethylene glycol	Baker
Borane in tetrahydrofuran	Alfa-Ventron
Mesyl chloride	Baker
Potassium carbonate	Baker
Sodium azide	Baker
Phthalimide	Eastman
Dimethylformamide	Fischer
Ethyl formate	Baker
Pyridine	Baker
p-Toluenesulfonyl chloride	Baker
Ethyl β-hydroxyglutarate	Aldrich
Sodium hydride	Alfa-Ventron
Diethylmalonate	Baker
Ethylene dichloride	Baker
Triethylamine	Mallinckrodt
Deuterochloroform	Stohler Isotope Chemical
Acetone-d_6	Stohler Isotope Chemical

Table 5 (Continued)

Compound	Source
Pyridine-d_5	Stohler Isotope Chemical
Pentane	Baker
Methylene chloride	Baker
Toluene	Baker
Cycloheptatrienetricarbonylchromium	Pressure Chemical
Cycloheptatrienetricarbonylmolybdenum	Pressure Chemical

at an ionization potential of 70 eV.

1,1,1-Tris(β-cyanoethyl) acetophenone (50) The title compound was prepared according to the procedure of Bruson and Reiner (123). Starting with 60 g (0.5 mol) of acetophenone and 79.5 g (1.5 mol) of acrylonitrile, 41 g of recrystallized material was isolated; mp 126-128°, lit. (123) mp 128-129°; NMR ($CDCl_3$) δ 7.5 (m, 5) and 2.27 ppm (s, 12); IR ($CHCl_3$) 2265, 1678 and 1601 cm^{-1}; high resolution mass spec m/e 279.1374 (calcd. for $C_{17}H_{17}N_3O$, 279.1372).

1,1,1-Tris(β-carboxyethyl)-2-phenylethane (51) Compound 51 was prepared according to the procedure of Fieser and Fieser (129). Starting with 14.8 g (0.053 mol) of 50, 12 g of potassium hydroxide, 7.5 ml of 85% hydrazine and 75 ml of diethylene glycol, 7 g of crude material was isolated. Isolation involved water dilution of the reaction mixture followed by acidification with hydrochloric acid until a homogenous solution again resulted. The solution was extracted with ether; the ethereal solution was washed with water, saturated sodium chloride solution and dried over anhydrous magnesium sulfate ($MgSO_4$) and removal of the ether gave the product. Once the material solidifies it dissolves in ether only with difficulty. The material was recrystallized from acetone, filtered and washed with ether; mp 168-172°; NMR (acetone-d_6) δ 7.28 (s, 5), 5.9 (broad singlet, OH), 2.66 (s, 2), 2.6-2.2 (m, 6) and 1.8-1.4 ppm (m, 6). The acid protons are concentration dependent and water is believed to be present in the sample. High resolution mass spec _m/e_ 322.1422 (calcd. for $C_{17}H_{22}O_6$, 322.1416).

1,1,1-Tris(γ-hydroxypropyl)-2-phenylethane (52) To a rapidly stirred solution of 16.1 g (0.05 mol) of _51_ in 200 ml of tetrahydrofuran was added 225 ml of a 1 M solution of borane in tetrahydrofuran over a 2 hr period. Almost immediately a precipitate started to form as the borane solution was added. The reaction mixture was brought to gentle reflux at which time most of the precipitate dissolved. What did not dissolve, slowly changed from a grainy type of precipitate to a gelatinous precipitate during the two days of reflux. To the cooled solution was added water followed by ether. After separating the layers the aqueous layer was extracted several times with ether. The combined ethereal solution was washed several times with water to which had been added some saturated sodium chloride solution; without the sodium chloride emulsions are a problem. The ether solution was washed twice with saturated sodium chloride, dried ($MgSO_4$) and the ether was removed on a rotary evaporator leaving a sticky gum (13.3 g, 95%) which eventually solidified. Once the material solidifies it is difficult to redissolve it in ether. A small sample was recrystallized from chloroform and the crystals were washed with ether and dried; mp 91.5-93.5°; NMR ($CDCl_3$) δ 7.16 (m, 5), 3.56 (m, 6), 2.8 (broad singlet, 3), 2.53 (s, 2), and 2.0-0.8 ppm (m, 12); IR ($CHCl_3$) 3625, 3400, 2940, 2875, 1340, 1060 and 1025 cm^{-1}; high resolution mass spec *m/e* 189.1492 base peak (calcd. for $C_{10}H_{21}O_3$ (molecular ion minus $PhCH_2$), 189.1491).

1,1,1-Tris(γ-methanesulfanatopropyl)-2-phenylethane (**53**)

A solution of 2.3 g (8.2 mmol) of crude **52** in 75 ml of pyridine in a 125 ml glass stoppered Erlenmeyer flask was cooled to 0° and treated with 6 ml (9 g, 0.079 mol) of freshly distilled mesyl chloride. The flask was stoppered and kept in the refrigerator for a period of two days. The solution was poured into 400 ml of ice-water. A yellow oil formed that was not soluble in ether but did dissolve in a mixture of methylene chloride/ether, 25/75 v/v. Using pure methylene chloride as the organic solvent, one encounters emulsions. The aqueous solution was extracted several times with the mixed solvent system. The organic solution was washed twice with water, twice with cold 20% hydrochloric acid, once with water and twice with saturated sodium chloride solution. The organic layer was dried ($MgSO_4$-K_2CO_3) and the solvents were removed under reduced pressure at room temperature, giving rise to a yellow-brown oil (2.45 g); NMR ($CDCl_3$) δ 7.2 (m, 5), 4.18 (triplet, J = 6 Hz, 6), 2.98 (s, 9), 2.56 (s, 2), and 2.1-0.9 ppm (m, 12); IR ($CDCl_3$) 2950, 2875, 1360, 1340, 1180 and 975 cm^{-1}.

1,1,1-Tris(γ-azidopropyl)-2-phenylethane (54) Compound 54 was prepared according to the procedure of Fleischer and coworkers (89). Starting with 2.45 g (4.76 mmol) of crude 53, 2.3 g (0.035 mol) of sodium azide and 14 ml of diethylene glycol 1.4 g of crude material was isolated as a yellow-brown oil. This oil was chromatographed on silica gel using 70/30 v/v methylene chloride/hexane. Removal of the solvent gave 1.0 g of 54; NMR (CCl_4) δ 7.3-6.8 (m, 5), 3.25 (triplet, J = 6 Hz, 6), 2.53 (s, 2), and 1.9-0.8 ppm (m, 12); IR ($CHCl_3$) 2950, 2870, 2108 cm^{-1}.

1,1,1-Tris(γ-phthalimidopropyl)-2-phenylethane (55)

To a solution of 1 g (1.9 mmol) of 53 in 2.6 ml of dimethylformamide was added 1.1 g (5.93 mmol) of potassium phthalimide. The syrupy solution became very gooey when the flask was immersed in an oil bath at 95 ± 5°. Another 10 ml of dimethylformamide was added and the flask was maintained in the oil bath for two hr. The cooled reaction mixture was taken up in chloroform and poured into water. The layers were separated and the aqueous layer was extracted three times with chloroform. The combined chloroform extracts were washed twice with water, twice with cold 3% sodium hydroxide solution, once with water and twice with saturated sodium chloride solution. The chloroform layer was dried ($MgSO_4$) and the solvent was removed on a rotary evaporator giving a yellow oil which soon crystallized. The material was chromatographed on silica gel using 50/50 v/v methylene chloride/chloroform and the product (0.9 g, 60%) is the second band to come off the column, mp 189-202°; NMR ($CDCl_3$) δ 8.0-7.5 (m, 12), 6.98 (s, 5), 3.63 (triplet, J = 6.5 Hz, 6), 2.46 (s, 2), and 2.1-0.8 ppm (m, 12); IR ($CDCl_3$) 2945, 2865, 1755, 1715, 1625, 1450, 1405 and 1370 cm^{-1}; high resolution mass spec m/e 576.2120 (calcd. for $C_{34}H_{30}N_3O_6$ (molecular ion minus $PhCH_2$), 576.2135).

<u>1,1,1-Tris(γ-aminopropyl)-2-phenylethane (56)</u> A mixture of <u>55</u> (13.5 g crude material, 0.021 mol) and 15 g of hydrazine hydrate in 1 liter of 95% ethanol were heated under reflux for 42 hr. The solvent was removed on a rotary evaporator leaving a white solid mass which was dissolved in 500 ml of water and the solution was made acidic (pH = 3) by the addition of dilute hydrochloric acid. After cooling in an ice bath and filtering, the filtrate was concentrated to dryness under reduced pressure and the thick viscous oil that resulted eventually solidified. The weight of this mixture (11 g) exceeds the theoretical weight for the triamine-trihydrochloride (7.7 g). The salt mixture (2.2 g) was dissolved in 25 ml of water and the solution was made basic (pH = 12) by the addition of 10% sodium hydroxide, then 10 ml of saturated sodium chloride solution was added. The homogeneous solution was extracted with chloroform several times and these extracts were combined and washed twice with saturated sodium chloride solution. The organic layer was dried ($MgSO_4$) and the solvent was removed leaving 0.85 g (77%) of the triamine as an almost colorless oil; NMR ($CDCl_3$) δ 7.25 (m, 5), 2.7 (triplet, J = 6 Hz), 2.58 (s), (combined integration of the peaks at 2.7 and 2.58 is 8), and 1.8-1.0 ppm (m, 18); IR ($CHCl_3$) 3100 (very broad), 2950, 2880 and 1610 cm^{-1}; high resolution mass spec <u>m/e</u> 277.2532 (calcd. for $C_{17}H_{31}N_3$, 277.2518). The above procedure is

similar to that used for the hydrolysis of phthaloyl-L-phenylalanylglycine anilide (155).

1,1,1-Tris(γ-formamidopropyl)-2-phenylethane (57)

The crude triamine 56 (0.85 g, 3.06 mmol) was dissolved in 20 ml of freshly distilled ethyl formate and the solution was kept at reflux for 22 hr. The solvent was then removed leaving a very viscous material. The reaction was quantitative although the NMR spectrum exhibits signals due to the presence of small amounts of ethyl alcohol and ethyl formate; (NMR-pyridine-d_5) δ 8.64 (s, very broad at its base, 6), 7.35 (s, 5), 3.45 (m, 6), 2.52 (s, 2) and 2.0-1.0 ppm (m, 12); IR (thin film) 3270 (broad), 3040, 2930, 2860, 1720, 1535 and 1380 cm^{-1}; high resolution mass spec m/e 361.2378 (calcd. for $C_{20}H_{31}N_3O_3$, 361.2366).

1,1,1-Tris(γ-isocyanopropyl)-2-phenylethane (58) The crude triformamide 57 (110 mg, 0.304 mmol) was dissolved in 2.5 ml of pyridine and to this was added p-toluenesulfonyl chloride (232 mg, 1.21 mmol). The color changed from pale yellow to green-yellow almost immediately. The solution was stirred at room temperature for one hr before ice was added to it and the solution was then poured into water. The aqueous solution was extracted three times with 50% methylene chloride 50% ether. The organic layer was washed twice with saturated sodium chloride solution, dried ($MgSO_4$) and the solvent was removed on a rotary evaporator leaving 73.4 mg (78%) of product; mp 80-86°; NMR ($CDCl_3$) δ 7.4-7.0 (m, 5), 3.6-3.2 (m, 6), 2.59 (s, 2), and 1.9-1.2 ppm (m, 12); IR (thin film) 2960, 2880, 2160, 1460, 1360 and 1180 cm^{-1}; high resolution mass spec m/e 306.1964 (calcd. for $C_{20}H_{24}N_3$ (molecular ion minus a hydrogen atom), 306.1970).

Ethyl β-chloroglutarate The title compound was prepared by the procedure of Dreifuss and Ingold (134). Starting with 29 g (0.142 mol) of ethyl β-hydroxyglutarate and 30 g (0.144 mol) of phosphorous pentachloride, 28.7 g (91.3%) of the product was isolated; NMR ($CDCl_3$) δ 4.56 (quin, J = 7 Hz, 1), 4.18 (q, J = 7 Hz, 4), 2.84 (d, J = 7 Hz, 4) and 1.27 ppm (t, J = 7 Hz, 6).

Ethyl ω-carboxymethanetriacetate The title compound was prepared by a modification of the procedure used by Dreifuss and Ingold (134). To a slurry of sodium hydride (3.6 g, 0.15 mol) in glyme was added a glyme solution of diethyl malonate (24 g, 0.15 mol) over a period of 3/4 hr. The solution was allowed to stir for an hour and a glyme solution of ethyl β-chloroglutarate (32.3 g, 0.145 mol) was then added over an hour period. The mixture was stirred for four hr and let stand overnight. About half of the glyme solvent was removed under reduced pressure. The remaining solution was poured into dilute hydrochloric acid and was extracted several times with ether. The ethereal extracts were combined and successively washed with aqueous sodium carbonate solution, water and saturated sodium chloride solution. The ether solution was dried ($MgSO_4$) and the solvent was removed under reduced pressure leaving an oil which was distilled to give the desired product (25.2 g, 50.3%); bp 146-161° (0.07 mm), lit (134) bp 200-205° (12 mm); NMR ($CDCl_3$) δ ((4.18 (q, J = 7 Hz), 4.12 (q, J = 7 Hz)), combined integration of 8), 3.71 (m, 1), 2.56 (d, J = 6 Hz, 4) and 1.26 ppm (t, J = 7 Hz, 13).

Methanetriacetic acid The triacid was prepared by the procedure of Lukes and Syhora (135). Starting with 25 g (0.072 mol) of ethyl ω-carboxymethanetriacetate and 75 ml of 20% aqueous hydrochloric acid, 14 g (102%) of crude material was isolated; NMR (acetone-d_6) δ 2.51 ppm (m). Any remaining water and hydrochloric acid would cause rapid exchange of the acid protons.

Methyl methanetriacetate The triacid was esterified by dissolving 13.75 g (0.072 mol) of the crude methanetriacetic acid in a mixture of 22 g of methyl alcohol and 67 ml of ethylene dichloride. To this solution was added 0.6 ml of concentrated sulfuric acid and the solution was kept at reflux for 15 hr. Once cool the reaction mixture was poured into water and washed successively with water, aqueous sodium bicarbonate solution and saturated sodium chloride solution. The organic layer was dried ($MgSO_4$) and the solvent was removed leaving an oil which was distilled to give the desired product (12.3 g, 73.5% overall from ethyl ω-carboxymethanetriacetate); bp 99-102° (0.07 mm), lit. (135) 117-120° (1 mm); NMR ($CDCl_3$) δ 3.66 (s, 9) and 2.51 ppm (m, 7); IR (thin film) 2960, 1745, 1440, 1215, 1165 and 1000 cm^{-1}; high resolution mass spec m/e 232.0949 (calcd. for $C_{10}H_{16}O_6$, 232.0947).

3-(2-Hydroxyethyl)pentanediol (59) Trialcohol 59 was prepared by the procedure of Lukes, Strouf and Ferles (133). Starting with 12.5 g (0.053 mol) of methyl methanetriacetate, 5.5 g (69%) of product was isolated; bp 173-176° (0.04 mm), lit. (133) bp 190-192° (2 mm); NMR (acetone-d_6) δ 3.61 (m, 9) and 1.56 ppm (broad triplet, J = 5 Hz, 7); IR (thin film) 3340, 2940, 2880, 1055 and 1023 cm^{-1}.

Tris(β-methanesulfonatoethyl)methane (60) The title compound was prepared by applying the procedure of Crossland and Serves (156) to 59. Starting with 2.5 g of 59, 6.2 g (96%) of product was obtained. A small quantity was recrystallized from ether-methylene chloride at 0° to give a mp of 74.5-75.5°; NMR ($CDCl_3$) δ 4.27 (broad triplet, J = 6 Hz, 6), 3.03 (s, 9) and 1.84 ppm (m, 7).

Tris(β-phthalimidoethyl)methane (61) To a solution of 2.4 g (6.28 mmol) of crude 60 in 75 ml of dimethylformamide was added 3.5 g (18.9 mmol) of potassium phthalimide. The solution was heated (oil bath at 95°) and stirred for three hr. The cooled reaction mixture was poured into water and extracted with chloroform three times. The chloroform extracts were combined and washed with water, and saturated sodium chloride solution. The organic layer was dried ($MgSO_4$) and the solvent was removed leaving 3.2 g (95%) of crude product. NMR ($CDCl_3$) δ 7.6 (broad singlet, 12), 3.72 (t, J = 6.5 Hz, 6) and 1.80 ppm (m, 7); mp 168-170° (methylene chloride-ether).

Tris(β-aminoethyl)methane (62) To a solution of 61 (3 g, 5.6 mmol) in 200 ml of 95% ethanol was added 1.5 g (30 mmol) of hydrazine hydrate. The solution was kept at reflux for 19 hr. The solvent was removed under reduced pressure leaving a white solid which was dissolved in water and the solution was acidified. After filtering, the filtrate was concentrated to dryness under reduced pressure leaving a second white solid (amine hydrochloride, 1.6 g). The amine hydrochloride was dissolved in 5 ml of water and a large excess of 25% sodium hydroxide solution was added. The water was removed on a rotary evaporator leaving an oil. If the oil did not dissolve in methylene chloride the neutralization was repeated. The methylene chloride solution was dried ($MgSO_4$) and the solvent was removed on a rotary evaporator leaving an oil; NMR ($CDCl_3$) δ 2.70 (t, J = 7 Hz, 6) and 1.40 ppm (m, 13).

Tris(β-formamidoethyl)methane (63) To the crude amine 62 (145 mg, 1 mmol) was added 10 ml of ethyl formate. A cloudiness developed that does not dissolve as reflux is reached. Reflux was maintained for 14 hrs at which time an insoluble oil was present. The excess ethyl formate was removed under reduced pressure leaving 210 mg of product; mp 111-116°; NMR (pyridine-d_5) δ 8.45 (broad singlet, 6), 3.46 (q, J = 6 Hz, 6) and 1.64 ppm (t, J = 6 Hz, 7); IR (thin film) 3500, 3290, 3060, 2940, 2880, 1665, 1540, 1390 and 1252 cm^{-1}; high resolution mass spec m/e 229.1431 (calcd. for $C_{10}H_{19}N_3O_3$, 299.1426).

Tris(β-isocyanoethyl)methane (64) Triformamide 63 (114.3 mg, 0.5 mmol) was dissolved in 4 ml of pyridine and to this was added 325.2 mg (1.71 mmol) of p-toluenesulfonyl chloride. After one hr of stirring at room temperature, a few chips of ice were added to the solution and the solution was poured into water. The aqueous solution was extracted several times with methylene chloride and the extracts were combined and washed with water and saturated sodium chloride solution. The organic layer was dried ($MgSO_4$) and the solvent was removed leaving 67.3 mg (77% crude yield) of a brown oil; NMR ($CDCl_3$) δ 3.47 (broad triplet, 5.8) and 1.78 ppm (broad singlet, 7.2); IR (thin film) 2950 and 2160 cm^{-1}; high resolution mass spec m/e 174.1034 (calcd. for $C_{10}H_{12}N_3$ (molecular ion minus a hydrogen atom), 174.1031).

Tricarbonyl(1,1,1-tris(γ-isocyanopropyl)-2-phenylethane)-tungsten (68) A solution of toluenetricarbonyltungsten (48) (94.9 mg, 0.263 mmol) in 90 ml of toluene and a solution of 1,1,1-tris(γ-isocyanopropyl)-2-phenylethane (58) (80.8 mg, 0.263 mmol) in 90 ml of toluene were simultaneously added to 400 ml of toluene at reflux over a 5 hr period. Reflux was continued for a total time of 18 hr. The cooled solution was filtered and the solvent was removed on a rotary evaporator leaving a solid which was taken up in methylene chloride and the solution was filtered to remove any solid and the solvent was again removed. The residue was dissolved in a minimum volume of methylene chloride and spotted on a thick layer chromatography plate which was developed using 70/30 methylene chloride/pentane. The second band was removed and crystallized from chloroform-pentane to give 28.7 mg (19%) of off-white flat needles; NMR ($CDCl_3$) δ 7.3-6.9 (m, 5), 3.60 (m, 6), 2.63 (s, 2) and 2.0-1.6 (m, 12); IR (CH_2Cl_2) 2160, 2118, 1942 and 1875 cm^{-1}. Molecular weight (osmometric in acetone) 599; calcd. 575; Anal. calcd. for $C_{23}H_{25}N_3O_3W$: C, 48.02%; H, 4.38%;

N, 7.30%. Found: C, 48.36%; H, 4.26%, N, 6.72%.

Tricarbonyl(1,1,1-tris(γ-isocyanopropyl)-2-phenylethane) chromium (69) A solution of cycloheptatrienetricarbonylchromium (56.7 mg, 0.247 mmol) in 75 ml of toluene and a solution of 1,1,1-tris(γ-isocyanopropyl)-2-phenylethane (58) (77.4 mg, 0.252 mmol) in 75 ml of toluene were simultaneously added to 400 ml of toluene at reflux over a 4-1/2 hr period. Reflux was maintained for an additional 15-1/2 hr and the solvent was removed on a rotary evaporator leaving a yellow orange solid. The solid was taken up in a minimum volume of methylene chloride and spotted on a thick layer chromatography slide. The plate was developed using 70/30 methylene chloride/pentane and the second band was removed using methylene chloride (23 mg, 21%). The material was crystallized from methylene chloride-pentane to give off-white plates; NMR ($CDCl_3$) δ 7.3-7.0 (m, 5), 3.57 (m, 6), 2.63 (s, 2) and 1.95-1.65 ppm (m, 12); IR (CH_2Cl_2) 2160, 2119, 1942 and 1878 cm^{-1}.

Tricarbonyl(1,1,1-tris(γ-isocyanopropyl)-2-phenylethane) molybdenum (70) A solution of cycloheptatrienetricarbonylmolybdenum (68 mg, 0.25 mmol) in 75 ml of benzene and a solution of 1,1,1-tris(γ-isocyanopropyl)-2-phenylethane (77 mg, 0.25 mmol) in 75 ml of benzene were simultaneously added to 400 ml of benzene at room temperature over a 6 hr period.

After an additional 2 hr the solvent was removed under reduced pressure and the resulting solid was dissolved in methylene chloride and filtered. The solution was concentrated and spotted on a thick layer chromatography slide. The slide was developed using 70/30 methylene chloride/pentane. The second band was removed using methylene chloride (6 mg, 5%); NMR ($CDCl_3$) δ 7.3-7.0 (m, 5), 3.56 (m, 6), 2.63 (s, 2) and 2.0-1.65 ppm (m, 12); IR (CH_2Cl_2) 2151, 2110, 1945, and 1874 cm^{-1}.

SUMMARY

Bis(tricarbonylchromium) complexes of dimesitylmethane, dimesityl ketone and 1,1-dimesitylethene have been prepared. By NMR spectroscopy the molecules appear to be in a helical conformation thereby giving rise to separate signals for the o-methyls. Variable temperature NMR was performed on the complexes and the barrier energy for the ketone dicomplex is about 5 kcal/mole greater than either the methane or ethene dicomplexes. This is rationalized in terms of stabilization of the ground state.

Various alkyl substituted (2,3',5',6-tetramethyl, 2,3',6-trimethyl, 2,3',5'-trimethyl, 2-ethyl-3',5'-dimethyl and 2,6-diethyl-3',5'-dimethyl) biphenyls and their corresponding ortho substituted arene tricarbonylmetal complexes were prepared. The NMR spectrum for the tetramethylbiphenyl chromium complex exhibited three methyl signals. The 2- and 6-methyls of the complexed ring are equivalent whereas the 3'- and 5'-methyls of the uncomplexed ring are nonequivalent. All of the signals for the carbon atoms of the uncomplexed ring occur at different frequencies in the ^{13}C NMR spectrum. The tricarbonylmetal moiety is used as a means of inducing dissymmetry, allowing one to observe hindered rotation that could not be observed otherwise for the uncomplexed biphenyls. Variable temperature NMR was performed

on the tricarbonylmetal complexes (Cr, Mo, W) of 2,3',5',6-tetramethylbiphenyl and it was found that the barrier energy for rotation about the biphenyl bond increased as the metal is changed from chromium to molybdenum to tungsten. This is rationalized in terms of differing amounts of stabilization of the transition state by the different tricarbonylmetal moieties.

The tripodal isocyanide ligand $PhCH_2C(CH_2CH_2CH_2NC)_3$ was synthesized using the following sequence $PhCOC(CH_2CH_2CN)_3 \rightarrow PhCH_2C(CH_2CH_2CO_2H)_3 \rightarrow PhCH_2C(CH_2CH_2CH_2OH)_3 \rightarrow PhCH_2C(CH_2CH_2CH_2OSO_2CH_3)_3 \rightarrow PhCH_2C(CH_2CH_2CH_2NPhth)_3 \rightarrow PhCH_2C(CH_2CH_2CH_2NH_2)_3 \rightarrow PhCH_2C(CH_2CH_2CH_2NHCHO)_3 \rightarrow PhCH_2C(CH_2CH_2CH_2NC)_3$. The synthesis of the tripodal isocyanide ligand $HC(CH_2CH_2NC)_3$ was accomplished in eleven steps. The synthesis of the trialcohol, $HC(CH_2CH_2OH)_3$, is known and the sequence of reactions that converted it into its respective triisocyanide were the same that successfully converted $PhCH_2C(CH_2CH_2CH_2OH)_3$ to its triisocyanide.

The triisocyanide, $PhCH_2(CH_2CH_2CH_2NC)_3$, when allowed to react with toluenetricarbonyltungsten, cycloheptatrienetricarbonylchromium and cycloheptatrienetricarbonylmolybdenum under high dilution conditions gave the respective stable monomeric tricarbonyltriisocyanidemetal complexes. The other triisocyanide when subjected to similar conditions gave products that were more labile and were not sufficiently characterized. Three methylene units in each chain is an acceptable number for the formation of bicyclic triisocyanide-metal complexes in which the metal bonds to ligands in an octahedral manner.

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