(s), 1465 (s), 1450 (m), 1248 (m), 1185 (w), 1160 (m), 1148 (sh), 1100 (m), 1031 (m), 984 (m), 930 (m), 885 (m), 730 (m), 695 (s), 617 (s), and (m) 560 cm$^{-1}$. The ultraviolet spectrum of the complex in hexane shows a maximum at 230 m$\mu$ ($\epsilon$ 33,000) and a shoulder at 285 m$\mu$ ($\epsilon$ 12,500). The nmr spectrum of the complex in carbon tetrachloride, acetonitrile, and tetramethylsilane (60:35:5) mixture shows resonances at $\tau$ 3.00 (benzene ring, multiplet), 4.58 ($H_{4,5}$, pentet), 6.32 ($H_3$, pentet), 6.73 ($H_6$, septet), about 6.9 ($H_7$, multiplet), and 8.77 ($CH_3$, doublet) with respect to TMS. Relative intensities were 4:2:1:1:1:3.

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# Transition Metal Carbonyl Complexes of the Constrained Phosphite Esters: 4-Methyl-, 4-Ethyl-, and 4-Propyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane

By William E. Stanclift[1] and David G. Hendricker

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The mono- and disubstituted complexes of various metal carbonyls with $P(OCH_2)_3CR$, where R = $CH_3$ and $C_2H_5$, have been previously reported,[2,3] and the formation of *cis*-$Mo(CO)_3(P(OCH_2)_3CCH_3)_3$ has been observed in kinetic studies.[4] The strong $\pi$-bonding ability of the ligands[2] leads one to predict that trisubstituted complexes of the type $M(CO)_3L_3$, where M = Cr, Mo, or W and L = phosphite esters, should be readily obtainable.

The proton nmr spectra of the disubstituted compounds of the methyl and ethyl bicyclic phosphites display interesting features of phosphorus spin–spin coupling.[2,3] Previous reports in the literature[5,6] suggest that in disubstituted compounds such coupling is observed only when the phosphorus ligands are in the *trans* position. If such is the case, one would expect to observe proton absorptions having similar shapes for compounds of the types *cis*-$M(CO)_4L_2$ and *cis*-$M(CO)_3L_3$. The effect of the length of the alkyl chain on the coordination properties of ligands of the type $P(OCH_2)_3CR$ may be evaluated by comparing the properties of the compounds reported previously where R = $CH_3$ and $C_2H_5$ with those described herein where R = $C_3H_7$. The solubility in organic solvents of the complexes containing $P(OCH_2)_3CR$ ligands is enhanced by the larger $C_3H_7$ group, making their characterization in solution easier.

## Experimental Section

The infrared spectra were obtained in chloroform solutions and recorded on a Perkin-Elmer Model 21 double-beam spectrometer using sodium chloride optics. The proton nmr spectra were recorded for approximately 15% chloroform solutions on a Varian Associates Model A-60 spectrometer using tetramethylsilane as an internal standard. Carbon and hydrogen compositions were ascertained by combustion. Yields were calculated on the basis of the limiting reagent.

Iron pentacarbonyl was purchased from Antara Chemical Co., chromium hexacarbonyl was purchased from Pressure Chemical Co., and molybdenum and tungsten hexacarbonyls were gifts from Climax Molybdenum Co. The bicyclic phosphite ligands,[7,8] $C_7H_8Cr(CO)_3$[9] and $C_7H_8Mo(CO)_3$,[10] were prepared by methods described elsewhere.

A slightly greater mole ratio of ligand to metal carbonyl or $C_7H_8M(CO)_3$ than theoretically necessary to yield the di- and trisubstituted products was used while a slightly smaller ratio was used for the monosubstituted complexes. The trisubstituted chromium and molybdenum complexes were prepared from the appropriate cycloheptatriene compound. The solvent used in the preparation of all trisubstituted complexes of chromium, molybdenum, and tungsten was methylcyclohexane, diethyl ether, and toluene, respectively. Dioxane was used for $Fe(CO)_3L_2$, $W(CO)_4L_2$, and $W(CO)_5L$ while the remaining complexes were prepared with *n*-octane.

Two general methods were used in the preparation of the complexes listed in Table I. In method A, a mixture of metal carbonyl or cycloheptatriene metal carbonyl and ligand in approximately 30 ml of solvent was refluxed under a helium flush with magnetic stirring for the indicated time. Compounds were isolated by suction filtration and were washed on the filter with *n*-pentane, hexane, or anhydrous diethyl ether. In some cases, it was necessary to reduce the volume of the mixtures by vacuum evaporation in order to obtain a filterable product. After purification was effected according to the method listed in Table I, all compounds were dried under vacuum.

In method B, a mixture of metal carbonyl, ligand, and 50 ml of solvents was placed in a quartz flask. Irradiation with ultraviolet light (200-W Hanovia Model 654A-10) was carried out for the time indicated under a flush of helium with magnetic stirring. The mixtures were filtered by suction to remove solid decomposition products and then treated in the same manner given in method A. In the preparation of some compounds, mixtures of carbonyl complexes of varying degrees of substitution were obtained. By employing chromatography and/or fractional crystallization, it was possible to obtain pure compounds. As a result, both isomers of two complexes could be prepared using a single set of reaction conditions.

Preparative method A was employed for all of the reactions except for the tungsten complexes and the disubstituted iron complex for which method B was used. Analytical data for the compounds are presented in Table I.

Decomposition of the solid mono- and disubstituted complexes is observed after several days to weeks upon standing in air while solutions are usually stable for several hours or more. The colorless trisubstituted complexes appear to be less stable than the disubstituted complexes.

## Results and Discussion

The infrared spectra (Table II) confirm the expectation that compounds of the type $M(CO)_3L_3$ can be prepared. The number of observed bands in the CO stretching region, two of medium intensity, support the postulate that these compounds are the *cis* isomers.

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(1) NSF College Teacher Research Participant, Westminster College, New Wilmington, Pa.

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(3) D. G. Hendricker, Doctoral Dissertation, Iowa State University, Ames, Iowa, July 1965.

(4) J. R. Graham and R. J. Angelici, *J. Am. Chem. Soc.*, **87**, 5590 (1965).

(5) R. B. King, *Inorg. Chem.*, **2**, 936 (1963).

(6) J. M. Jenkins and B. L. Shaw, *Proc. Chem. Soc.*, 279 (1963).

(7) J. G. Verkade, T. J. Huttemann, M. K. Fung, and R. W. King, *Inorg. Chem.*, **4**, 83 (1965).

(8) D. G. Hendricker, *J. Heterocyclic Chem.*, **4**, 385 (1967).

(9) R. B. King, "Organometallic Syntheses," Vol. I, Academic Press Inc., New York, N. Y. 1965, p 123.

(10) See ref 9, p 125.

TABLE I

ANALYTICAL AND PREPARATIVE DATA FOR METAL CARBONYL COMPLEXES

| Compound | % carbon |  | % hydrogen |  | Reaction time, hr | Purification method | % yield |
|---|---|---|---|---|---|---|---|
|  | Calcd | Found | Calcd | Found |  |  |  |
| $Fe(CO)_4P(OCH_2)_3CC_3H_7$ | 38.4 | 38.3 | 3.8 | 4.0 | 17 | *a* | 31 |
| *trans*-$Fe(CO)_3(P(OCH_2)_3CC_3H_7)_2$ | 41.5 | 41.8 | 5.3 | 5.6 | 6 | *b* | 9 |
| $Cr(CO)_5P(OCH_2)_3CC_3H_7$ | 39.1 | 38.8 | 3.6 | 3.9 | 24 | *b* | 15 |
| *trans*-$Cr(CO)_4(P(OCH_2)_3CC_3H_7)_2$ | 41.9 | 41.9 | 5.1 | 5.0 | 24 | *c* | 20 |
| *cis*-$Cr(CO)_3(P(OCH_2)_3CCH_3)_3$ | 37.3 | 37.5 | 4.7 | 4.4 | 5 | *c* | 87 |
| *cis*-$Cr(CO)_3(P(OCH_2)_3CC_2H_5)_3$ | 40.5 | 40.5 | 5.3 | 5.4 | 1 | *c* | 85 |
| *cis*-$Cr(CO)_3(P(OCH_2)_3CC_3H_7)_3$ | 43.4 | 43.6 | 5.9 | 6.0 | 2 | *c* | 96 |
| $Mo(CO)_5P(OCH_2)_3CC_3H_7$ | 35.0 | 35.1 | 3.2 | 3.1 | 14 | *b* | 42 |
| *cis*-$Mo(CO)_4(P(OCH_2)_3CC_3H_7)_2$ | 38.6 | 38.9 | 4.7 | 4.6 | 9 | *c* | 10 |
| *trans*-$Mo(CO)_4(P(OCH_2)_3CC_3H_7)_2$ | 38.6 | 38.8 | 4.7 | 4.7 | 9 | *b* | 37 |
| *cis*-$Mo(CO)_3(P(OCH_2)_3CCH_3)_3$ | 34.6 | 34.5 | 4.3 | 4.3 | 3 | *d* | 97 |
| *cis*-$Mo(CO)_3(P(OCH_2)_3CC_2H_5)_3$ | 37.8 | 37.8 | 5.0 | 5.0 | 7 | *d* | 81 |
| *cis*-$Mo(CO)_3(P(OCH_2)_3CC_3H_7)_3$ | 40.8 | 40.7 | 5.6 | 5.7 | 6 | *d* | 66 |
| $W(CO)_5P(OCH_2)_3CC_3H_7$ | 24.0 | 24.1 | 2.2 | 2.4 | 2 | *b* | 40 |
| *cis*-$W(CO)_4(P(OCH_2)_3CC_3H_7)_2$ | 33.4 | 33.3 | 4.0 | 4.1 | 6 | *d* | 15 |
| *trans*-$W(CO)_4(P(OCH_2)_3CC_3H_7)_2$ | 33.4 | 33.4 | 4.0 | 4.1 | 6 | *d* | 32 |
| *cis*-$W(CO)_3(P(OCH_2)_3CCH_3)_3$ | 30.4 | 30.7 | 3.8 | 4.0 | 24 | *c* | 22 |
| *cis*-$W(CO)_3(P(OCH_2)_3CC_2H_5)_3$ | 33.4 | 33.2 | 4.4 | 4.4 | 17 | *d* | 28 |
| *cis*-$W(CO)_3(P(OCH_2)_3CC_3H_7)_3$ | 36.2 | 36.3 | 4.9 | 5.1 | 24 | *d* | 31 |

[a] Recrystallized from diethyl ether. [b] Precipitated from $CHCl_3$ using pentane or hexane. [c] Recrystallized from $CHCl_3$. [d] Chromatographed on Fisher A-540, 80–200 mesh alumina using $CHCl_3$–hexane.

TABLE II

INFRARED AND PROTON NMR SPECTRAL DATA FOR CARBONYL COMPLEXES AND LIGANDS[a]

| Compound | C–O stretching frequency, $cm^{-1}$ |  |  | $H_A(-OCH_2-)$ | $J_{POCH}$[b] |
|---|---|---|---|---|---|
| $P(OCH_2)_3CC_3H_7$ |  |  |  | 3.94[c] | 1.9 |
| $Fe(CO)_4P(OCH_2)_3CC_3H_7$ | 2067 s[d] | 1994 vs | 1968 vs | 4.47[c] | 6.4 |
| *trans*-$Fe(CO)_3(P(OCH_2)_3CC_3H_7)_2$ |  | 1936 vs |  | 4.29[e] | 5.2 |
| $Cr(CO)_5P(OCH_2)_3CC_3H_7$ | 2077 w | 1996 sh | 1962 vs | 4.21[c] | 4.2 |
| *trans*-$Cr(CO)_4(P(OCH_2)_3CC_3H_7)_2$ |  | 1928 vs |  | 4.17[e] | 4.4 |
| *cis*-$Cr(CO)_3(P(OCH_2)_3CC_3H_7)_3$ | 1992 m |  | 1914 m | 4.13[f] | 4.6 |
| $Mo(CO)_5P(OCH_2)_3CC_3H_7$ | 2084 w | 1987 sh | 1963 vs | 4.19[c] | 4.2 |
| *cis*-$Mo(CO)_4(P(OCH_2)_3CC_3H_7)_2$ | 2046 m | 1959 sh | 1939 vs | 4.16[e] | 4.3 |
| *trans*-$Mo(CO)_4(P(OCH_2)_3CC_3H_7)_2$ |  | 1939 vs |  | 4.17[e] | 4.3 |
| *cis*-$Mo(CO)_3(P(OCH_2)_3CC_3H_7)_3$ | 1998 m |  | 1922 m | 4.12[f] | 4.5 |
| $W(CO)_5P(OCH_2)_3CC_3H_7$ | 2085 w | 1998 sh | 1959 vs | 4.20[c] | 4.2 |
| *cis*-$W(CO)_4(P(OCH_2)_3CC_3H_7)_2$ | 2046 m | 1956 sh | 1933 vs | 4.17[e] | 4.4 |
| *trans*-$W(CO)_4(P(OCH_2)_3CC_3H_7)_2$ |  | 1931 vs |  | 4.17[e] | 4.3 |
| *cis*-$W(CO)_3(P(OCH_2)_3CC_3H_7)_3$ | 1996 m |  | 1918 m | 4.12[f] | 4.7 |
| $P(OCH_2)_3CC_2H_5$ |  |  |  | 3.96[c] | 1.6 |
| *cis*-$Cr(CO)_3(P(OCH_2)_3CC_2H_5)_3$ | 1992 m |  | 1912 m | 4.14[f] | 4.4 |
| *cis*-$Mo(CO)_3(P(OCH_2)_3CC_2H_5)_3$ | 1998 m |  | 1923 m | 4.13[f] | 4.3 |
| *cis*-$W(CO)_3(P(OCH_2)_3CC_2H_5)_3$ | 1995 m |  | 1916 m | 4.14[f] | 4.5 |
| $P(OCH_2)_3CCH_3$ |  |  |  | 3.93[c] | 1.8 |
| *cis*-$Cr(CO)_3(P(OCH_2)_3CCH_3)_3$ | 1991 m |  | 1913 m | 4.11[f] | 4.7 |
| *cis*-$Mo(CO)_3(P(OCH_2)_3CCH_3)_3$ | 1998 m |  | 1919 m | 4.09[f] | 4.5 |
| *cis*-$W(CO)_3(P(OCH_2)_3CCH_3)_3$ | 1996 m |  | 1918 m | 4.11[f] | 4.5 |

[a] Chemical shifts in ppm downfield with respect to tetramethylsilane; $J$ values in hertz; $CHCl_3$ used as solvent for all spectra. [b] Value taken as separation of two outer peaks. For compounds of the type $M(CO)_3L_3$ this value is a crude estimate owing to shape of resonance. [c] Doublet. [d] vs, very strong; s, strong; sh, shoulder; m, medium; w, weak. [e] Apparent triplet. [f] Multiplet.

The geometry proposed for these isolable compounds is in agreement with the assignment made by Angelici and Graham[4] for *cis*-$Mo(CO)_3(P(OCH_2)_3CCH_3)_3$ whose solution spectra were similar to those of the compounds reported in this paper. A comparison of the positions of the observed CO stretching modes with those reported for $M(CO)_3L_3$ compounds, where the L groups are different phosphorus-containing ligands, permits the inference that the $\pi$-acceptor ability of ligands of the type $P(OCH_2)_3CR$ is greater than that of alkylphosphines and alkyl phosphites but less than that of halophosphines.[11-13]

No appreciable differences are observed in CO stretching frequencies for a series of monosubstituted, *cis*- or *trans*-disubstituted, or *cis*-trisubstituted complexes containing various ligands of the type $P(OCH_2)_3CR$, where R = $CH_3$,[2,14] $C_2H_5$,[3] or $C_3H_7$ (Table II). Thus the prediction that extending the length of the R group would not be expected appreciably to affect coordination of the bridgehead phosphorus is verified.

The infrared spectra show that both the *cis* and *trans* isomers of the disubstituted complexes of molybdenum

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[11] R. Poilblanc and M. Bigorgne, *Bull. Soc. Chim. France*, 1301 (1962).

[12] F. A. Cotton, *Inorg. Chem.*, **3**, 702 (1964).

[13] R. J. Clark and P. I. Hoberman, *ibid.*, **4**, 1771 (1965).

[14] A. C. Vandenbroucke, D. G. Hendricker, R. E. McCarley, and J. G. Verkade, submitted for publication.

and tungsten carbonyl with $P(OCH_2)_3CC_3H_7$ have been isolated. The spectra we assign to the *cis* isomer exhibit two distinct bands, one of which is broad with a shoulder on the high-energy side similar to spectra reported for the *cis*-disubstituted metal carbonyl complexes of $As(OCH_2)_3CCH_3$,[14] $P(OCH_3)_3(CH_2)_3$,[14] $P(OCH_2)_3CCH_3$,[14] and $P(OCH_3)_3$.[11] A single, strong absorption in the CO stretching region was observed for all disubstituted complexes assigned as possessing the *trans* configuration. Only the *trans* form of the disubstituted chromium carbonyl complex was observed. A smaller, sterically hindered chromium atom may cause the *cis* isomer to be less stable than when the central metal is the larger molybdenum or tungsten atom. Although the *cis* isomers are easily prepared, difficulties in preparing *trans*-$M(CO)_4(P(OCH_2)_3CCH_3)_2$, where M = Mo and W, have been reported.[14] Our observation that analogous compounds with $P(OCH_2)_3CC_3H_7$ are easily prepared is attributed to the slightly bulkier character of the ligand imparting increased stability to the *trans* isomer.

The proton nmr spectra of the monosubstituted carbonyl complexes exhibit a doublet resonance assigned to the $-OCH_2-$ protons, hereafter referred to as $H_A$, and a multiplet of seven lines assigned to the $C_3H_7$ group. Because of the complexity of the seven-line group located at approximately 1.0 ppm, only the positions of the $H_A$ resonances are recorded in Table II. The $H_A$ doublets, which result from spin coupling with the phosphorus nucleus,[15,16] exhibit $J_{POCH}$ values of varying magnitude which appear to be a function of the geometry rather than of the metal atom in the complex.[2,3]

The expectation that the *trans*-disubstituted carbonyl complexes with $P(OCH_2)_3CC_3H_7$ would exhibit an apparent triplet resonance for the $H_A$ protons due to phosphorus–phosphorus coupling is confirmed. The complexity of this spectral pattern has been discussed elsewhere in detail.[15-17] It is noteworthy that the nmr spectra of the corresponding *cis* complexes also contain an apparent triplet $H_A$ signal. This behavior is unlike that of previous examples reported in the literature where no coupling was observed for *cis* isomers.[6] In some cases, the observance of phosphorus–phosphorus coupling has been taken as evidence that compounds were in the *trans* and not *cis* configuration.[8] Recently, however, Ogilvie, *et al.*,[19] have reported that such coupling is observed in the proton spectra of both *cis* and *trans* isomers of many complexes. For *cis*- and *trans*-$M(CO)_4(P(OCH_2)_3CC_3H_7)_2$, where M = Mo or W, the observed $H_A$ resonance shapes qualitatively indicate that the degree of coupling is greater for the *trans* isomer. Qualitative values for $J_{PP}$ in these complexes will be reported later.[20]

The proton nmr spectra of the trisubstituted carbonyl complexes are of considerable interest (Figure 1). In all cases, the signal for the $H_A$ protons appears to be a multiplet located downfield from the signal observed for the free ligand but upfield with respect to the resonance for the corresponding mono- and disubstituted compounds. Such an upfield shift on increased substitution has also been observed for the $Ni(CO)_{4-x}(P(OCH_2)_3CCH_3)_x$ system where $x = 1$–$4$.[2] In Figure 1, varying the ligand alkyl chain is found not to affect the shape of the $H_A$ resonance while changing the metal atom produces a difference in the degree of phosphorus–phosphorus coupling. From a theoretical analysis of spectra of the general type $X_nX'_n\ldots AA'\ldots$, the X part is found to exhibit a sharp outer pair of lines with a separation given by $J_{AX} + J_{A'X} + \ldots$ having a fractional intensity of $(1/2)^{r-1}$, where $r$ is the number of A-type nuclei.[16] Because the trisubstituted compounds are of the *cis* configuration and contain two groups of chemically equivalent nuclei, they may be denoted as $X_6X'_6X''_6AA'A''$, and hence one would expect the intensity of the outer doublet to be one-fourth that of the total. Assuming that coupling between protons on one ligand and phosphorus nuclei on the other ligands ($J_{A'X}$ and $J_{A''X}$) is zero, the separation of the outer doublet becomes $J_{POCH}$. Owing to the relative intensity of the outer doublet and the closeness of other lines, the $J_{POCH}$ values given in Table II for the tungsten and molybdenum complexes are crude estimates (Figure 1). No quantitative calculation of the magnitude of $J_{PP}$ for these complexes has been attempted, yet it is apparent that phosphorus–phosphorus coupling occurs

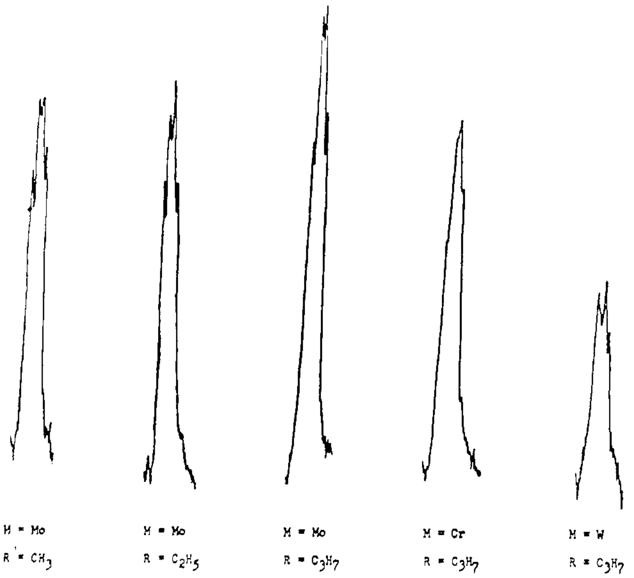

Figure 1.—Shapes of $H_A$ resonances observed for complexes of the type *cis*-$M(CO)_3(P(OCH_2)_3CR)_3$.

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[15] D. G. Hendricker, R. E. McCarley, R. W. King, and J. G. Verkade, *Inorg. Chem.*, **5**, 639 (1966).

[16] R. K. Harris, *ibid.*, **5**, 701 (1966).

[17] R. K. Harris, *Can. J. Chem.*, **42**, 2275 (1964).

[18] R. V. Lindsay, Jr., G. W. Parshall, and U. G. Stolberg, *J. Am. Chem. Soc.*, **87**, 658 (1965).

[19] F. Ogilvie, J. M. Jenkins, J. G. Verkade, and R. J. Clark, presented at 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1966.

[20] F. Ogilvie, J. M. Jenkins, R. J. Clark, and J. G. Verkade, submitted for publication.

in the trisubstituted as well as the disubstituted *cis* complexes.

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# The Nuclear Magnetic Resonance Spectra of Some Arenechromium Tricarbonyl Complexes Containing Trimethyl Group IVb Metal Substituents

BY THEODORE F. JULA[1] AND DIETMAR SEYFERTH

*Received December 29, 1967*

In a recent report[2] of the temperature dependence of the nmr spectra of the aromatic protons in several arenechromium tricarbonyl complexes containing bulky substituents it was postulated that the complexity of the aromatic resonance was due to a severe restriction of rotation about the chromium–arene bond. Thus for isopropylbenzenechromium tricarbonyl the aromatic protons were reported to appear as a singlet at +30° which broadened into a multiplet below −15°, while for *t*-butylbenzenechromium tricarbonyl the aromatic protons appeared as a multiplet which remained unchanged over the range +50 to −40°. This report suggested to us a method for measuring the relative steric effect of the trimethylmetal substituent in the chromium tricarbonyl complexes of the phenyltrimethyl derivatives of group IVb, and we report here concerning the question of restricted rotation in these complexes.

The nmr spectra of the chromium tricarbonyl complexes of phenyltrimethylsilicon, -germanium, and -tin[3] all showed a complex multiplet for the aromatic protons at $\tau$ *ca.* 4.5–5.0. However, the aromatic proton resonance of the uncomplexed arenes appeared as a very similar multiplet at $\tau$ *ca.* 2.6–3.0, so that it was not clear that the multiplet in the spectra of the complexes was due entirely to restricted rotation in the latter.

In order to examine this point further the chromium tricarbonyl complex of *p*-bis(trimethylsilyl)benzene was prepared, since the aromatic protons in the uncomplexed arene appear as a sharp singlet ($\tau$ 2.60). If restricted rotation about the chromium–arene bond were obtained in this case, the aromatic protons would no longer be equivalent (I). However, the aromatic proton resonance in the nmr spectrum of the complex remained a sharp singlet ($\tau$ 4.81). Similarly, the aromatic protons in the chromium tricarbonyl complexes of *p*-diisopropylbenzene and *p*-di-*t*-butylbenzene appeared as a sharp singlet (as in the uncomplexed arene). The physical data for the complexes used in this study are given in Table I, and the aromatic proton chemical shifts are summarized in Table II.

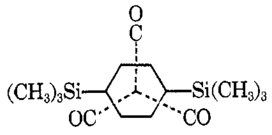

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TABLE I
PREPARATIVE DATA

| Compound | Yield, % | Mp, °C | Analyses, % Calcd C | Analyses, % Calcd H | Analyses, % Found C | Analyses, % Found H |
|---|---|---|---|---|---|---|
| *p*-$[(CH_3)_3Si]_2C_6H_4Cr(CO)_3$[a] | 70 | 123–124 | 50.11 | 6.20 | 50.38 | 6.19 |
| *p*-$[(CH_3)_3C]_2C_6H_4Cr(CO)_3$ | 23 | 140–141 | 62.56 | 6.80 | 62.45 | 6.76 |
| *p*-$[(CH_3)_2CH]_2C_6H_4Cr(CO)_3$ | 65 | 92–93 | 60.39 | 6.08 | 60.54 | 6.36 |
| $(CH_3)_2CHC_6H_5Cr(CO)_3$ | 69 | 61–62 | 56.27 | 4.97 | 56.24 | 4.72 |

[a] Prepared using $(CH_3CN)_3Cr(CO)_3$ (kindly supplied by Professor A. Davison).

TABLE II
$\tau$ VALUES

| Ligand | Aromatic protons in complex | Methyl protons in complex | Aromatic protons in free ligand | Methyl protons in free ligand |
|---|---|---|---|---|
| $(CH_3)_2CHC_6H_5$ | 4.88[a] | 8.79[b] | 2.90[a] | 8.79[b] |
| $(CH_3)_3SiC_6H_5$ | 4.5–5.0[c] | 9.69[a] | 2.5–2.9[c] | 9.74[a] |
| $(CH_3)_3GeC_6H_5$ | 4.5–4.9[c] | 9.58[a] | 2.6–2.9[c] | 9.65[a] |
| $(CH_3)_3SnC_6H_5$ | 4.8–5.0[d] | 9.68[a] | 2.6–3.0[c] | 9.75[a] |
| *p*-$[(CH_3)_2CH]_2C_6H_4$ | 4.90[a] | 8.80[b] | 3.00[a] | 8.79[b] |
| *p*-$[(CH_3)_3C]_2C_6H_4$ | 4.77[a] | 8.70[a] | 2.80[a] | 8.70[a] |
| *p*-$[(CH_3)_3Si]_2C_6H_4$ | 4.81[a] | 9.71[a] | 2.60[a] | 9.77[a] |

[a] Sharp singlet. [b] Doublet, $J$ = 6.5 cps. [c] Multiplet. [d] Broad single peak.

Finally, we have attempted to reproduce the results reported by Gracey and coworkers[2] for the temperature dependence of the nmr spectrum of isopropylbenzenechromium tricarbonyl (*ca.* 5% in deuteriochloroform). Although the aromatic proton resonance broadened somewhat at −37°, a similar broadening in the resonance due to the internal standard, tetramethylsilane, indicated that this was due to the increased viscosity of the sample near its freezing point (*ca.* −45°). Furthermore, no change was observed in the splitting pattern or chemical shift of the isopropyl group at lower temperatures, even though restricted rotation about the chromium–arene bond presumably would be concerted with a similar restriction of rotation about the carbon–arene bond. Magnetic nonequivalence of the $CH_3$ protons in sterically hindered isopropyl substituents has been observed.[4]

Thus we conclude that severe restriction of rotation

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