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

Acknowledgment.—Support of this research by Grant GY-2426 from the National Science Foundation is gratefully acknowledged. The authors also wish to thank Mrs. William Decker for performing the carbon and hydrogen analyses.

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

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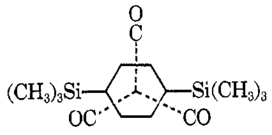
Received December 29, 1967

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 τ *ca.* 4.5–5.0. However, the aromatic proton resonance of the uncomplexed arenes appeared as a very similar multiplet at τ *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 (τ 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 (τ 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.



I

TABLE I

PREPARATIVE DATA

Compound	Yield, %	Mp, °C	Analyses, % Calcd C	Calcd H	Found C	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

τ 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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about the chromium–arene bond in these complexes is most likely not obtained and that the complexity of the aromatic proton resonance in such complexes is the result of differences in the magnetic environment already present in the free arene.

Experimental Section

Proton magnetic resonance spectra (Table II) were obtained with a Varian Associates A-60 spectrometer using *ca.* 5–10% solutions of the complex in carbon tetrachloride containing a small amount of tetramethylsilane as an internal standard in 5-mm o.d. Pyrex tubes sealed under nitrogen.

Elemental analyses were performed by Dr. S. M. Nagy, Microchemical Laboratory, MIT, and melting points are uncorrected. Chromium hexacarbonyl was vacuum sublimed before use. *p*-Bis(trimethylsilyl)benzene was prepared in these laboratories by D. R. Blank. *p*-Diisopropylbenzene and *p*-di-*t*-butylbenzene were purchased from Aldrich Chemical Co.

The complexes (Table I) of the *para*-disubstituted arenes were prepared by heating a mixture of chromium hexacarbonyl (10 mmol) with a slight excess of the arene in diglyme to reflux for 24–30 hr following the method of Nicholls and Whiting.[5] The yellow crystalline products were initially purified by recrystallization from diisopropyl ether under nitrogen, followed by vacuum sublimation (50–80° (0.07 mm)). The preparation of the complexes of the phenyltrimethyl group IVb derivatives has been reported previously.[3]

Acknowledgments.—The authors are grateful to the National Science Foundation for generous support of this work (Grant GP 6466X) and to Professors A. Davison and G. M. Whitesides for valuable discussions. This work was supported in part by Public Health Service Fellowship 5-F1-GM-21,803 (to T. F. J.).

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Magnetic Circular Dichroism of Charge-Transfer Transitions in $SbCl_6^-$ and $SnCl_6^{2-}$

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Received January 11, 1968

In recent articles[3–8] the value of magnetic circular dichroism (MCD) in the assignment of allowed transitions has been discussed and illustrated. Its application is most clear-cut when use is made only of the qualitative dispersion form or sign of the MCD; greater ambiguity exists when finer quantitative considerations are introduced. So far, assignments based on the sign of the MCD have been limited to cases where *C* terms—originating in ground-state angular momentum—are dominant, namely $Fe(CN)_6^{3-}$,[4,5] IrX_6^{2-} (X = Cl, Br),[7] and Tm^{2+}–CaF_2.[8] *A* terms—arising from both ground- and excited-state angular momentum—have been used, by their very existence, to prove excited-state degeneracy,[6] but no assignments have been made on the basis of their signs. We present here such an application in assigning the lowest charge-transfer transitions of $SbCl_6^-$ and $SnCl_6^{2-}$.

The molecular orbital diagram generally adopted for O_h metal hexachloride complexes is shown in Figure 1.[9] The approximate magnitudes of the $t_{1u}(\pi)$–t_{2g}, $t_{2u}(\pi)$–t_{2g}, $t_{1u}(\sigma)$–t_{2g}, and t_{2g}–e_g separations are known for several d^n ($0 \leqslant n \leqslant 6$) complexes from analyses of their spectra.[7,9–11] On the other hand, little is known about the unfilled orbitals immediately above e_g or about the molecular orbital energies in complexes with more than six d electrons. Even the ordering may there be different; thus, it is not impossible in d^{10} complexes for the $t_{1u}(\pi)$, $t_{2u}(\pi)$ levels to lie above t_{2g}.

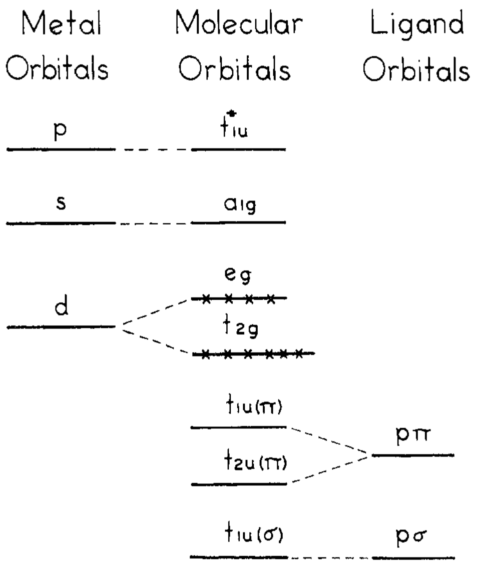

Figure 1.—Schematic molecular orbital diagram for O_h metal hexachloride complexes. Ligand g states are omitted since they are irrelevant to the present application. Crosses denote electrons in ground configuration of d^{10} complexes.

In the absence of spin–orbit coupling, the ground state of a d^{10} complex is $^1A_{1g}$ and allowed electric dipole transitions require a $^1T_{1u}$ upper state. The lowest energy one-electron excitations giving $^1T_{1u}$ levels are either $t_{1u}(\pi) \rightarrow a_{1g}$ or $e_g \rightarrow t_{1u}^*$, depending on the quantitative disposition of the energy levels. The $t_{2u}(\pi) \rightarrow a_{1g}$ transition is forbidden; hence the next allowed ligand to metal transition after $t_{1u}(\pi) \rightarrow a_{1g}$ is $t_{1u}(\sigma) \rightarrow a_{1g}$. If spin–orbit coupling is introduced, transitions become allowed to any T_{1u} spin–orbit

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