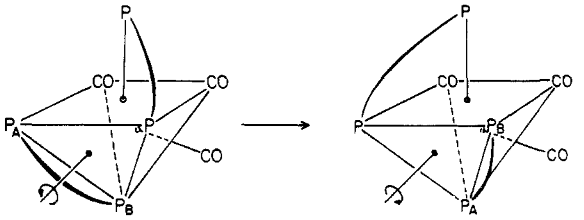

Figure 3. Proposed low-temperature process.

spectra were obtained at different times; however, the exchange parameters are again similar to those of the ^{31}P process (Table III).

We propose a mechanism for the low-temperature process involving a trigonal twist of either the P(4)-P(2)-P(3) or the P(1)-P(2)-P(3) face of 1. This concerted process simultaneously equilibrates two carbonyls and the ends of one dmpe ligand. Cyclic interchange P(4) → P(2) → P(3) produces the enantiomer of 1, where P(3)-P(4) and C(2)-C(3) have simultaneously equilibrated (Figure 3). Additionally, permutting P(2) → P(3) → P(1) exchanges P(1)-P(2) and C(2)-C(3). There is no physical basis for distinguishing between rotation of the upper or lower P-P-P face. Trigonal twists of the other six faces do not effect the required exchange. Other mechanisms may be possible, but the one described above represents the simplest conceivable intramolecular process. Dissociative arm on-arm off processes are unlikely as there is no uniquely long Ti-P bond.

We cannot distinguish between a large number of possible mechanisms for the high-temperature process.

Acknowledgment. The technical assistance of Louis F. Lardear and W. R. Reutter is gratefully acknowledged.

Registry No. 1, 81830-93-5; Ti(^{13}CO)$_3$(dmpe)$_2$, 81830-94-6.

Supplementary Material Available: A listing of all bond angles and distances (Table IV), atomic coordinates and thermal parameters (Table V), and structure amplitudes (Table VI) (24 pages). Ordering information is given on any current masthead page.

Electrochemical Generation of Stable Cations of (Arene)tricarbonylchromium Complexes. Studies on the Noninteraction of the Tricarbonylchromium Groups in Bis and Tris Complexes

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Complexes of the type $(CH_3)_2Sn[ArCr(CO)_3]_2$ were studied by cyclic voltammetry. The compounds can be made to undergo chemically reversible oxidation upon judicious choice of conditions and modification of Ar. The persistence of the cations seems to be a function of the steric bulk around the phenyl rings. Oxidation involves one electron per tricarbonylchromium group. The tricarbonylchromium moieties are essentially noninteracting and therefore adhere to the Bard-Anson-Saveant model. The same results are found for the bis and tris complexes of methyltriphenyltin where a dication and trication are formed, respectively. The structure of $(CH_3)_2Sn[2,4,6\text{-}(CH_3)_3C_6H_2Cr(CO)_3]_2$ was determined from 5287 observed diffractometer data and refined to an R value of 4.4%. The compound crystallizes in space group $P2_1/c$ with $Z = 4$ and lattice constants of $a = 15.514$ (2) Å, $b = 13.026$ (2) Å, $c = 15.709$ (2) Å, and $\beta = 119.51$ (1)°. The structure consists of a tin atom that is bonded to two methyl and two mesityl groups in a distorted tetrahedral geometry. Each mesityl group is also bonded to a $Cr(CO)_3$ moiety in a η^6 fashion. The average Sn-C(methyl) and Sn-C(mesityl) distances are 2.149 (4) and 2.182 (3) Å, respectively. When the Cr-CO bonds are projected onto the mesityl plane, they eclipse the methyl-substituted ring carbon atoms.

Introduction

A number of electrochemical studies have been carried out on various (arene)tricarbonylchromium complexes. Gubin has reported a one-electron reversible reduction of (acetophenone)tricarbonylchromium.[2,3] The EPR work of Ceccon[4,5] on radical anions of complexes such as (*tert*-butyl phenyl ketone)tricarbonylchromium has confirmed the speculation of Gubin that the lowest vacant orbital is primarily on the carbonyl portion of the organic ligand. In addition, work, by Dessey and co-workers,[6,7] had demonstrated a two-electron reduction of (benzene)tricarbonylchromium which was characterized as "ill-behaved". Reductive electrolysis resulted in a stable yellow

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(2) Khandkarova, V. S.; Gubin, S. P. *J. Organomet. Chem.* **1970**, *22*, 149.

(3) Gubin, S. P. *Pure* Appl. *Chem.* **1970**, *23*, 463.

(4) Ceccon, A.; Corvaja, C.; Giacometti, G.; Venzo, A. *J. Chim. Phys.* **1975**, *72*, 23.

(5) Ceccon, A.; Corvaja, C.; Giacometti, G.; Venzo, A. *J. Chem. Soc., Perkin Trans. 2* **1978**, 283.

(6) Dessey, R. E.; Stary, F. E.; King, R. B.; Waldrop, M. *J. Am. Chem. Soc.* **1966**, *88*, 471.

(7) Dessey, R. E.; King, R. B.; Waldrop, M. *J. Am. Chem. Soc.* **1966**, *88*, 5112.

0276-7333/82/2301-0938$01.25/0

solution which could be reoxidized with 100% recovery of starting complex. The potential of the reoxidation and number of electrons involved were not stated. Work in our labs on various substituted benzenes complexed with a tricarbonylchromium group indicates that the initial reduction product, that is the dianion, is not stable as judged by the reversibility of the cyclic voltammograms.[8] Instead, these dianions react with something in the bulk solution, presumably electrophiles, to give the stable product and/or products observed by Dessey. Furthermore, the potential required to oxidize such products is quite anodic of the reduction potential and apparently involves only one electron.[9] This same behavior is also observed in (naphthalene)tricarbonylchromium and some of its ring-substituted derivatives.[8] However, the naphthalene series exhibits a chemically reversible reduction showing all the characteristics of a two-electron, diffusion-controlled wave. Our present impression is that both the benzene series and the naphthalene series of dianion complexes undergo the same subsequent reactions but that the reactivity of the dianions is quite different in the two cases and manifests itself as a difference in the kinetics of the follow-up reaction and hence as a difference in cyclic voltammograms.

On the other hand, the oxidative electrochemistry of (arene)tricarbonylchromium complexes has been shown to proceed via a one-electron process.[10,11] Ordinarily, (arene)tricarbonylchromium complexes are very susceptible to oxidizing conditions. The complexes typically decompose with time in solutions exposed to air. Such oxidations are typically complicated by rapid subsequent reactions which result in overall multielectron processes along with destruction of the complex.

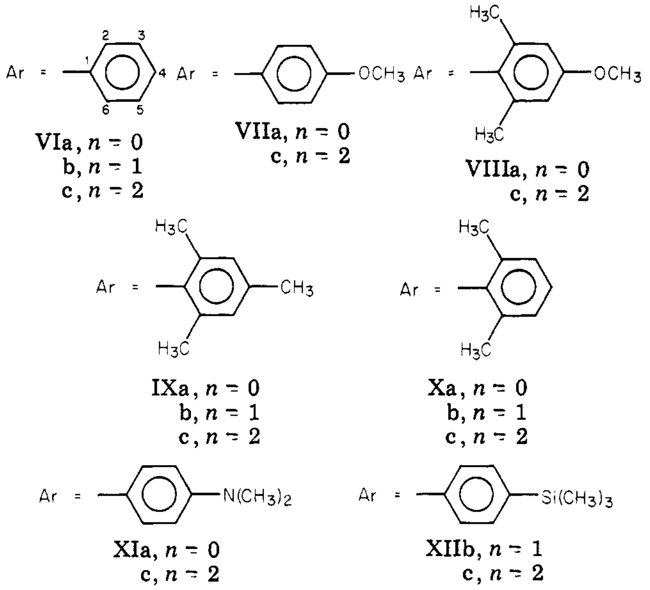
While seeking to produce a new class of mixed-valence complexes by reducing the bis(tricarbonylchromium) complex of dimethyldiphenyltin, VIa, we had occasion to study the oxidative electrochemistry also.[12] VIa exhibits cathodic electrochemistry which is very similar to other substituted benzene complexes. That is, VIa reduces at approximately −2.1 V vs. the Ag|AgCl reference electrode and is totally irreversible as seen by the cyclic voltammograms even at scan rates up to 10 V/s. However, with cyclic voltammetric experiments, the oxidation peak observed at +0.8 V on Pt showed a cathodic peak coupled to it at scan rates of 200 mV/s. Since it was conceivable that this unexpected stability of the cation was due to a mixed-valence interaction, we thoroughly studied the electrochemical behavior of VIa and related compounds and combined this with an X-ray cyrstal study. We now conclude that such a mixed-valence interaction does not exist. Furthermore, the oxidation products of bis(tricarbonylchromium) complexes of this type are actually dications, and there is essentially no interaction between the complexed arene portions. As compounds which contain equivalent but noninteracting moieties within the same molecule, they adhere to the Bard–Anson–Saveant model.[13]

Chart I

$(CH_3)E[C_6H_5Cr(CO)_3]_2$

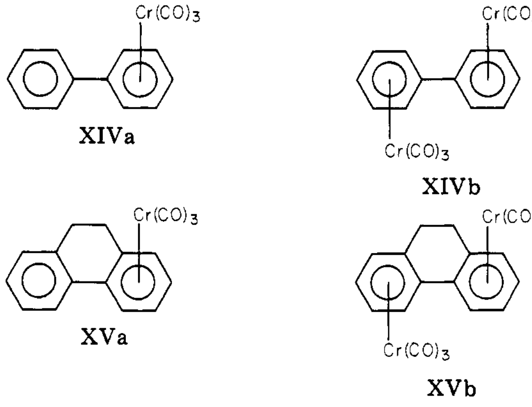
I, E = C
II, E = Si
III, E = Ge
IV, E = Sn
V, E = Pb

$(CH_3)_2(Ar)_nSn[ArCr(CO)_3]_{2-n}$



$(CH_3)(C_6H_5)_nSn[C_6H_5Cr(CO)_3]_{3-n}$

XIIIa, n = 0
b, n = 1
c, n = 2



Results and Discussion

The compounds comprising this study were η^6 tricarbonylchromium complexes of various arene systems in which more than one such π-bound aryl group can be placed on the same molecule. Among the various arene ligands used were those of the type $(CH_3)_2E(C_6H_5)_2$ where E = C, Si, Ge, Sn, and Pb. Particular attention was paid to compounds having the formulation $(CH_3)_2SnAr_2$ in which Ar is phenyl or substituted phenyl derivatives. A ligand somewhat related to the above is methyltriphenyltin, $CH_3Sn(C_6H_5)_3$. The bis- and tris(tricarbonylchromium) complexes were the focus of this study although whenever the mono complexes were available, they too were studied. Finally, the mono- and bis(tricarbonylchromium) complexes of biphenyl and 9,10-dihydrophenanthrene were also examined. These molecules remove any interposing feature such as $(CH_3)_2E$ from between the rings bearing the tricarbonylchromium groups. See Chart I.

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[8] Rieke, R. D.; Arney, J. S.; Rich, W. E.; Willeford, B. R.; Poliner, B. S. *J. Am. Chem. Soc.* **1975**, *97*, 5951.

[9] Arney, J. S. Ph.D. Thesis, University of North Carolina, Chapel Hill, NC 1975.

[10] Gubin, S. P.; Kandkarova, V. S. *J. Organomet. Chem.* **1970**, *22*, 449.

[11] Lloyd, M. K.; McCleverty, J. A.; Connor, J. A.; Jones, E. M. *J. Chem. Soc., Dalton Trans.* **1973**, 1768.

[12] Rieke, R. D.; Miligan, S. N.; Tucker, I.; Dowler, K. A.; Willeford, B. R. *J. Organomet. Chem.* **1981**, *218*, C25.

[13] Flanagan, J. B.; Margel, S.; Bard, A. J.; Anson, F. C. *J. Am. Chem. Soc.* **1978**, *100*, 4248. Ammar, F.; Saveant, J. M. *J. Electroanal. Interfacial Electrochem.* **1973**, *47*, 215.

Table I. Electrochemical Results

compd[a]	temp,[b] °C	$(E_{p,a} + E_{p,c})/2$,[c] V	ΔE_p, mV	i_c/i_a	scan rate, mV/s
I	0	+0.806	126	0.21	500
II	0	+0.835	134	0.43	200
III	0	+0.827	93	0.56	200
V	0	+0.786	108	0.55	200
VIa	amb	+0.816	129	0.48	200
	0	+0.810	116	0.63	50
VIIa	amb	+0.728	177	0.34	200
	0	+0.731	130	0.53	50
VIIIa	amb	+0.740	100	0.91	50
	0	+0.745	90	1.00	50
IXa	amb	+0.782	105	1.00	50
	0	+0.795	90	1.00	50
IXb	amb	+0.750	70	1.00	50
	0	+0.753	65	1.00	50
Xa	amb	+0.775	150	0.53	50
	0	+0.785	110	0.91	50
Xb	amb	+0.758	85	0.53	50
	0	+0.747	70	0.80	50
XIa	amb	+0.565	120	0.40	50
	0	+0.570	110	0.45	50
XIIb	0	+0.795	57	0.63	50
XIIIa	amb	+0.850	· · ·	· · ·	200
	0	+0.825	150	0.43	50
XIIIb	amb	+0.810	· · ·	· · ·	50
	0	+0.843	135	0.61	50
XIIIc	amb	+0.810	· · ·	· · ·	50
	0	+0.833	85	0.63	50
XIVa	0	+0.786	89	0.57	500
XIVb	0	+0.816	142	0.41	500
XVa	0	+0.787	97	0.50	500
XVb	0	+0.827	147	0.56	500

[a] All compounds were at approximately 1 mM concentration in PC with 0.25 M TEAP. [b] amb is the ambient temperature of 23 ± 2 °C. [c] Reference electrode[13] is Ag|AgCl, saturated NaCl(aq).

Table II. Atomic Coordinates[a]

atom	10^4x	10^4y	10^4z
Sn	2445.8 (2)	1064.6 (2)	2392.3 (2)
Cr_1	4630.7 (5)	7.6 (5)	1926.1 (5)
Cr_2	215.2 (6)	3149.4 (7)	1381.7 (5)
O_1	3206 (3)	−1669 (3)	817 (4)
O_2	5335 (5)	−1158 (4)	3785 (3)
O_3	6066 (3)	−1086 (4)	1499 (3)
O_4	−38 (6)	2461 (7)	3049 (5)
O_5	−336 (4)	4739 (5)	932 (4)
O_6	1690 (4)	4670 (4)	2770 (3)
C_1	3636 (3)	1198 (3)	2038 (3)
C_2	4636 (3)	1379 (3)	2767 (3)
C_3	5376 (4)	1494 (4)	2501 (4)
C_4	5153 (4)	1430 (4)	1510 (4)
C_5	4180 (4)	1229 (4)	803 (3)
C_6	3425 (3)	1092 (3)	1056 (3)
C_7	4954 (4)	1460 (5)	3843 (4)
C_8	5945 (5)	1581 (6)	1214 (6)
C_9	2391 (4)	846 (4)	228 (3)
C_{10}	3758 (4)	−1021 (4)	1257 (4)
C_{11}	5068 (4)	−716 (4)	3074 (4)
C_{12}	5519 (3)	−666 (4)	1678 (4)
C_{13}	1162 (3)	1887 (3)	1271 (3)
C_{14}	185 (3)	1515 (4)	965 (4)
C_{15}	−650 (4)	2010 (5)	207 (4)
C_{16}	−551 (4)	2890 (4)	−238 (3)
C_{17}	399 (3)	3290 (4)	78 (3)
C_{18}	1247 (3)	2809 (3)	835 (3)
C_{19}	15 (4)	545 (6)	1409 (5)
C_{20}	−1461 (4)	3411 (6)	−1059 (4)
C_{21}	2241 (4)	3318 (4)	1129 (4)
C_{22}	57 (5)	2703 (7)	2399 (5)
C_{23}	−739 (5)	4125 (5)	1111 (4)
C_{24}	1126 (5)	4076 (5)	2236 (4)
C_{25}	2718 (4)	1735 (5)	3747 (3)
C_{26}	2221 (5)	−571 (4)	2376 (5)
H_3	6071 (53)	1535 (55)	3211 (52)
H_5	3925 (55)	1005 (52)	−66 (55)
H_{15}	−1330 (52)	1692 (55)	−258 (51)
H_{17}	480 (55)	3971 (53)	−121 (55)

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

As far as oxidative electrochemistry is concerned, the compounds discussed here exhibit many similar characteristics to each other and to other benzenoid tricarbonylchromium complexes[11] as well. In general, these compounds oxidize at about +0.8 V vs. the Ag^0|AgCl, saturated NaCl(aq) reference electrode.[14] In the solvent system generally used for this study, propylene carbonate, PC, no further oxidation processes are observed before coming to solvent breakdown which is at approximately +1.4 V. In other solvents, such as methylene chloride in which one is able to observe more anodic regions, a second irreversible oxidation wave is detected. This wave is usually in the neighborhood of 500–600 mV anodic of the first wave and generally exists about where solvent breakdown for PC occurs. Table I lists the results of the cyclic voltammetric experiments. The main differences in the oxidative electrochemistry of these complexes is in the relative stability of the cations formed.

One major concern was that the oxidation process arises from a ligand-based orbital rather than one which included metal character. Hence the electrochemistry of the free ligands was investigated. With all of the free ligands except one, no oxidation processes were observed out to the limits imposed by PC. The single exception was dimethylbis(4-(*N*,*N*-dimethylamino)phenyl)tin, XIc. This ligand gives a single irreversible oxidation wave at approximately +0.76 V and furthermore exhibits two much less prominent cathodic processes on the reverse scan. This would seem to parallel other electrochemical oxidation studies[15–18] of different anilines including *N*,*N*-dimethylaniline which indicate a one-electron process to give what are generally unstable radical cations. These radical cations then proceed to give a variety of products. In fact, a published cyclic voltammogram[18] of *N*,*N*-dimethylaniline resembles quite closely the cyclic voltammogram of XIc.

However, upon complexation of the ligands with π-bound tricarbonylchromium groups, all of the compounds exhibit electrochemical oxidations as described above. Thus the metal carbonyl fragment is implicated as the chief reason that electrochemistry, and especially in the case at hand, oxidation occurs. Complexes containing one or more electron donating groups on the phenyl ring, such as VIIa possessing a 4-methoxy group, are slightly easier to oxidize than the parent complex VIa. The shifts are generally small, the largest shift occurring in XIa in which the oxidation potential is shifted 250 mV cathodic of the parent complex due to the presence of the *N*,*N*-dimethylamino group on the 4-position of the rings. The oxidation potential of XIa can be viewed as primarily determined by the metal carbonyl portion but modified by the inclusion of ligand character bearing the very good

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(14) The Ag|AgCl, saturated NaCl(aq) reference is about 40 mV anodic of SCE.

(15) Zweig, A.; Lancaster, J. E.; Neglia, M. T.; Jura, W. H. *J. Am. Chem. Soc.* **1964**, *86*, 4130.

(16) Seo, E. T.; Nelson, R. F.; Fritsch, J. M.; Marcoux, L. S.; Leedy, D. W.; Adams, R. N. *J. Am. Chem. Soc.* **1966**, *88*, 3498.

(17) Wawzonek, S.; McIntyre, T. W. *J. Electrochem. Soc.* **1967**, *114*, 1025.

(18) Hand, R.; Nelson, R. F. *J. Electrochem. Soc.* **1970**, *117*, 1353.

electron donor, *N,N*-dimethylamino, in the highest filled orbital. All of the shifts in the oxidation potential upon various group substitution about the ring can be taken to lend support to this interpretation. Shifts similar to those presented here have been previously reported.[11] The issue of whether the observed changes in oxidation potentials among the compounds studied here are a matter of direct conjugation or inductive effects or both remains unsolved. Either may operate in the highest occupied molecular orbital of (arene)tricarbonylchromium complexes giving rise to the shifts in oxidation potential observed. While these results may indicate a ligand π-orbital mixing with metal orbitals, they are not definitive. Indicative of a HOMO predominantly of metal 3d character but also including a significant π-ligand component is the photoelectron spectroscopy work and ab initio SCF MO calculation of Guest and co-workers.[19]

The alternative of viewing the highest occupied orbital as primarily π ligand is discounted for several reasons. First, the fact that all of these complexes oxidize at nearly the same potential is inconsistent with the large spread of oxidation potentials of the free ligands. Also, the relative amount of shift in the potentials from the parent complex VIa seem to be intuitively correct for the various electron donors in both type and additivity. For example, one would expect the 2,4,6-trimethyl-substituted complex IXa to be slightly more easily oxidized than the 2,6-dimethyl case Xa. The changes in potentials are rather small, but in each case they are as expected. Finally, the direction of shift would be the opposite of the observed shift if indeed a ligand-based orbital were primarily involved. The well-recognized character of the tricarbonylchromium moiety as an electron-withdrawing group [20-23] would make the complex more difficult to oxidize compared to the free ligand. In all cases presented here, the complex is always more easily oxidized than the free ligand.

Non-Nerstian behavior is also a general feature of the (arene)tricarbonylchromium complexes studied here. ΔE_p values which are greater than the theoretical value have been reported for other organometallic systems[6,7,24,25] and are generally interpreted as indicating that electron transfer is slow. Such systems are ordinarily, therefore, chemically reversible but electrochemically irreversible. The underlying cause of the greater peak separation may well be due to bond reorganization. Such changes could alter the geometry of the transition-metal complex cation away from that of the neutral molecule. If so, Marcus theory[26,27] indicates a larger free energy of activation. This manifests itself as a slow rate of electron transfer. The result is a cathodic peak to anodic peak separation which is somewhat greater than predicted for a couple which is both strictly electrochemically and chemically reversible. Small interaction of the (arene)tricarbonylchromium moieties may also account for this separation. This is dealt with later in the Results and Discussion.

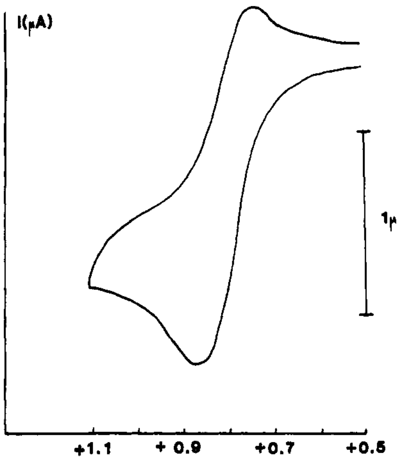

Figure 1. Cyclic voltammogram of VIa (1 mM in PC; 0 °C; 0.25 M TEAP; 50 mV/s; Pt disk).

Care was taken to ensure that this peak separation was not due to *iR* drop effects. Cyclic voltammetry using either a Luggin probe or *iR* feedback compensation in separate experiments were performed to determine that the peak separation is not an artifact of *iR* drop. Very little change occurred in the peak separation upon using either of the two aforementioned techniques as compared to not accounting for *iR* drop. While this strongly implicates slow electron transfer, no further attempts were made to isolate the precise cause of this peak separation.

It was the somewhat astonishing relative stability and persistence of the cations which led to the present study. It is well established that (arene)tricarbonylchromium complexes are sensitive to oxidants and oxidizing conditions. For example, a common means of accomplishing unusual chemistry on arene rings is to complex the ring with a tricarbonylchromium group, to perform the reactions of interest, and to remove the tricarbonylchromium portion with an oxidizing agent such as I_2, Ce^{IV}, or even air.[28] The result is an oxidized form of chromium and a modified arene ring which is no longer complexed.

In contrast, electrochemical experiments performed in PC show that the parent complex VIa is oxidized at a platinum disk electrode, giving a small cathodic peak upon reversing the scan in a cyclic voltammogram at moderate scan rates. This chemical reversibility suggested that perhaps under the proper conditions cations of extended lifetimes could be produced. Using cyclic voltammetry as the guide to indicate how stable the cations produced were, we made numerous modifications of both experimental conditions and the compounds themselves.

Perhaps the most obvious variable to change in order to stabilize the cations is to lower the temperature. This slows the rate of any chemical reaction following the oxidation process, presumably nucleophilic attack, which increases the lifetime of the cations. This is indeed exactly what is observed. While the cation of VIa shows evidence of being chemically reversible on the cyclic voltammetric time scale only at moderate scan rates (200 mV/s) at ambient temperature, the cyclics performed at 0 °C show a much more chemically reversible couple even at low scan rates (50 mV/s). The cation has considerably enhanced persistence at lower temperatures. See Figure 1.

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(19) Guest, M. F.; Hillier, I. H.; Higginson, B. R.; Lloyd, D. R. *Mol. Phys.* **1975**, *29*, 113.

(20) Nicholls, B.; Whiting, M. C. *J. Chem. Soc.* **1959**, 551.

(21) Carroll, D. G.; McGlynn, S. P. *Inorg. Chem.* **1968**, *7*, 1285.

(22) Brown, D. A.; Rawlinson, R. M. *J. Chem. Soc. A* **1969**, 1534.

(23) Bunnett, J. F.; Hermann, H. *J. Org. Chem.* **1971**, *36*, 4081.

(24) Lloyd, M. K.; McCleverty, J. A.; Orchard, D. G.; Connor, J. A.; Hall, M. B.; Hillier, I. M.: Jones, E. M.; McEwen, G. K. *J. Chem. Soc., Dalton Trans.* **1973**, 1743.

(25) Treichel, P. M.; Essenmacher, G. J. *Inorg. Chem.* **1976**, *15*, 146.

(26) Marcus, R. A. *Can. J. Chem.* **1959**, *37*, 155.

(27) Marcus, R. A. *J. Chem. Phys.* **1965**, *43*, 679 and previous papers in the series.

(28) For example: (a) Jackson, W. R.; Jennings, W. B. *J. Chem. Soc. B* **1969**, 1221. (b) Trahanovski, W. S.; Card, R. J. *J. Am. Chem. Soc.* **1972**, *94*, 2897. (c) Card, R. J.; Trahanovski, W. S. *Tetrahedron Lett.* **1973**, 3823. (d) Jaouen, G.; Meyer, A.; Simonneaux, G. *J. Chem. Soc., Chem. Commun.* **1975**, 813. (e) Semmelhack, M. F.; Hall, H. T.; Yoshifuji, M.; Clark, G. *J. Am. Chem. Soc.* **1975**, *97*, 1247. (f) Jaouen, G.; Meyer, A. *Tetrahedron Lett.* **1976**, 3547. (g) Semmelhack, M. F.; Thebtaranonth, Y.; Keller, L. *J. Am. Chem. Soc.* **1977**, *99*, 959. (h) Semmelhack, M. F.; Clark, G. *Ibid.* **1977**, *99*, 1675.

Even though it would be possible to continue to produce and study the cations using lower temperatures, this is less desirable in the solvent employed due to viscosity problems and other difficulties. A much more powerful way to stabilize these cations is to modify the molecules chemically. In this study, modification of the compounds was accomplished in two different ways.

The first alteration made was to change the central atom of the complex. This atom was changed to span the entire group 4A series, that is, carbon through lead. See Chart I. In addition the central atom with the attached methyl groups were removed altogether to give (biphenyl)bis(tricarbonylchromium) complex. The bis complex of 9,10-dihydrophenanthrene also removes the interposing group and was also tested.

In examining the group 4A series, stability of the cation as judged by the cyclic voltammogram appeared to increase somewhat in going down the series. While tin and lead showed rather equal stabilizing tendencies, the electrochemical oxidation wave of the dimethyldiphenyllead bis complex, V, was not as well-defined as the corresponding tin complex, IV. Using germanium as the central atom, III, also afforded a somewhat stable cation at moderate scan rates while the silicon, II, and carbon, I, analogues yielded cations possessing lifetimes long enough to be observed only at higher scan rates. Another feature of the oxidation of these group 4A analogues is the general trend toward easier oxidation as the central atom proceeds down the group. This is as expected with the decrease in electronegativity of each atom as one proceeds down the group as a substituent on the phenyl ring. The lone exception is the carbon-based compound I, which is out of sequence since it oxidizes nearly as easily as the tin analogue. Due to the various features of the tin-based complex such as good relative persistence of the cation and ready availability of synthetic precursors, complexes having a central tin atom were chosen for further study.

This further study involved the modification of the phenyl rings to increase the lifetimes of the cations. This approach to stabilizing the cations is actually much more flexible due to the great variety of substituents which can be placed on a phenyl ring as well as the great variety in positioning possible around the ring. Such variety allows for a multitude of factors to be included as compared to just changing the electronegativity of the central atom.

One well-known way to stabilize radical cations in polycyclic aromatic systems is to introduce a methoxy group as a substituent. This same concept was applied to the dimethyldiphenyltin complex first of all by placing a methoxy group in the 4-position of each phenyl ring giving VIIa. It came as something of a surprise that very little effect on the stability of this cation was observed as compared to the parent complex VIa. Consequently, other good electron donors were substituted in the 4- and 4′-positions. The presence of an *N,N*-dimethylamino group again did little to increase stability in the cation produced. The same is true of a trimethylsilyl group when placed at the 4- and 4′-positions. Apparent small degrees of extra persistence were noted in the sequence as $OCH_3 < N(CH_3)_2 < Si(CH_3)_3$ although no really astonishing stabilization occurred. The degree of persistence was judged according to the magnitude of the catodic current coupled to the oxidation process of the cyclic voltammograms. Such comparisons are of a more or less qualitative nature since non-Nernstian behavior complicates exact comparisons of current heights. Nevertheless, cyclic voltammetry reveals very clearly which systems are highly persistent and which systems are less so.

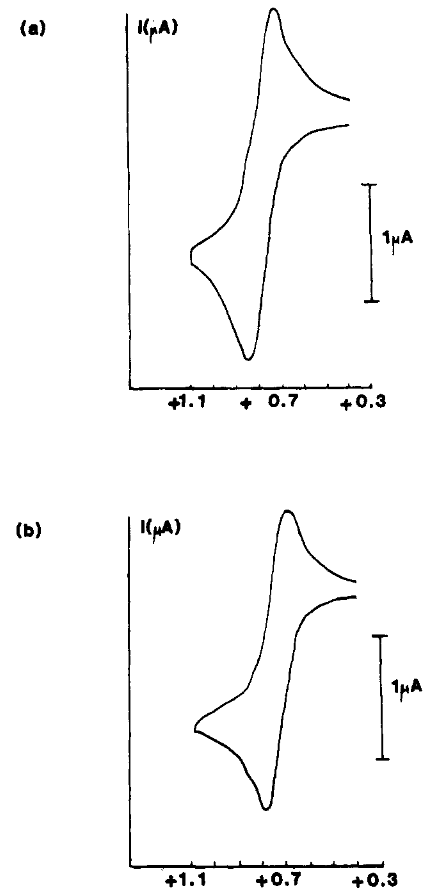

Figure 2. (a) Cyclic voltammogram of IXa (1 mM in PC; ambient temperature; 0.25 M TEAP; 50 mV/s; Pt disk). (b) Cyclic voltammogram of VIIIa (1 mM in PC; ambient temperature; 0.25 M TEAP; 50 mV/s; Pt disk).

While a single donating group seemed unpromising as a method of stabilizing the cations, the existence of more than one electron donor substituted on the ring did indeed enhance the lifetimes of the cations. This is most dramatically seen in those systems having the 2,4- and 6-positions simultaneously replaced with donor groups on each ring. Those complexes incorporating this feature, notably VIIIa and IXa, give cyclic voltammograms which are highly chemically reversible even at ambient temperatures. Half-lives of the cations of these two compounds are in the vicinity of 1 h. See Figure 2. Nevertheless, a compound such as Xa, having methyl groups only in the 2- and 6-positions, indicated a somewhat diminished persistence of the cation as compared to the trisubstituted cases VIIIa and IXa. As judged by the cyclic voltammograms, the cation Xa seems to be intermediate in stability between the single donor cases and the trisubstituted cases.

The most likely explanation involves the shielding of the cation by steric bulk. Steric considerations in the persistence of radicals have been previously discussed.[29] Such factors should presumably be important in warding off nucleophiles from the cation. Furthermore, this might well explain why there is an increase in the current height of the cathodic wave of the couple on the cyclic voltammograms with increasing steric bulk in the 4,4′-positions. The small but noticeable growth of the cathodic peak for the series 4,4′-OCH_3 < 4,4′-$N(CH_3)_2$ < 4,4′-$Si(CH_3)_3$ parallels the increase in steric hindrance at the para positions and indicates a relatively more persistent cation. Similar arguments could be made for the increase in the lifetime of

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(29) Griller, D.; Ingold, K. U. *Acc. Chem. Res.* **1976**, *9*, 13.

the cations as more positions around the phenyl rings are substituted. In like fashion, even the cations produced from the tricarbonylchromium complexes of benzene, toluene, and mesitylene show enhanced persistence. The cation of (mesitylene)tricarbonylchromium has a much greater half-life than the corresponding benzene complex as revealed by the cyclic voltammograms.[30]

From the beginning, the bis(tricarbonylchromium) complexes which were tested showed many of the characteristics of a one-electron oxidation. Although the peak separation of the cyclic voltammograms was nearly always greater than the theoretically expected value for a one-electron process, careful control of the *iR* drop loss indicated that this spreading of peaks was due to slow electron transfer.

It was never possible to get good coulometric data for compounds with two or fewer electron-donating groups substituted on the phenyl ring such as Xa or VIa. In the time frame of such an experiment, the cations were too unstable and gave three-electron oxidation per chromium atom and subsequent destruction of the complex. Nevertheless, once the much more stable cations of the 2,4,6-trisubstituted systems could be produced, coulometry experiments showed very convincingly that the oxidation process of these bis complexes involved two electrons, giving a dication. The mono(tricarbonylchromium) complexes, on the other hand, exhibited a one-electron oxidation to give a stable mono cation. It would appear that there is a one-electron oxidation for each tricarbonylchromium group present.

Furthermore, it can be inferred from the cyclic voltammetric data that the two (arene)tricarbonylchromium groups are essentially noninteractng. These compounds appear to follow the patterns described in the Bard–Anson–Saveant model.[13] Cyclic voltammograms of the bis complexes are rather like the cyclic voltammograms of the mono complexes especially in terms of peak separation. The major difference lies in the fact the current height of the bis complexes are approximately twice that of the mono complexes. This is in agreement with the Bard–Anson–Saveant model in which molecules with a number, *x*, of equivalent yet noninteracting moieties exhibit current heights which are *x* times that of the isolated moiety while still manifesting other characteristics of a one-electron process.

In addition, this model allows for a determination of the *n* value from the cyclic voltammograms for the electrochemical process in question when the moieties are noninteracting. Such a calculation is made by using eq 1. For

$$n_{\mathrm{bis}} = \frac{(i_{\mathrm{bis}}/c_{\mathrm{bis}})}{(i_{\mathrm{mono}}/c_{\mathrm{mono}})}\left[\frac{M_{\mathrm{bis}}}{M_{\mathrm{mono}}}\right]^{0.275} \qquad (1)$$

eq 1 as applied to the oxidation wave studied here, *i* is the anodic peak current of the cyclic, *c* is the bulk concentration, *M* is the molecular weight, and *n* is the number of electrons involved in the oxidation of the complex. The subscripts "mono" and "bis" refer to the mono(tricarbonylchromium) complexes and the corresponding bis(tricarbonylchromium) complexes, respectively.

The result of such a calculation from the cyclic voltammetric data of mono and bis complexes of the 2,4,6-trisubstituted type yields a value of 2.0 for n_{bis}. Similarly, the calculation of an n_{tris} value for complex XIIIa is accomplished by using the appropriate values for the tris complex and referencing it against (tricarbonylchromium)methyltriphenyltin XIIIc, data. Such a calculation gives an n_{tris} value of 3.0 while an n_{bis} value of 2.0 for XIIIb, bis(tricarbonylchromium)methyltriphenyltin is calculated. Just as for the derivatives of dimethyldiphenyltin, the mono, bis, and tris complexes of methyltriphenyltin exhibit rather similar cyclic voltammograms except that the current heights are in a ratio of 1:2:3, respectively. Again these molecules follow the Bard–Anson–Saveant model. They also exhibit a one-electron oxidation per tricarbonylchromium group and each of these groups is essentially noninteracting with any other such group within the molecule.

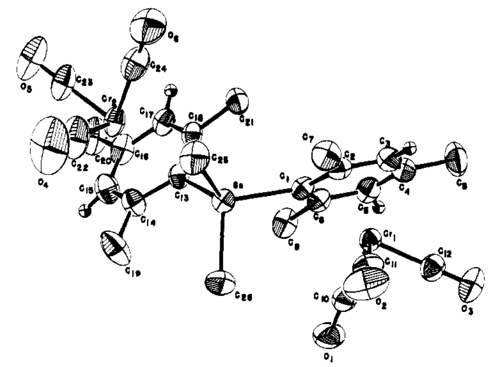

Figure 3. An ORTEP[30] drawing of one molecule of $(Ch_3)Sn[2,4,6-(Ch_3)_3C_6H_2Cr(CO)_3]_2$ at 50% probability. The aromatic hydrogen atoms have been reduced in size for clarity. The atomic numbering scheme is given except for aromatic hydrogen atoms which are numbered according to the attached carbon atom.

The greater than theoretical peak separation of the cyclic voltammograms could be attributed to small degrees of interaction between the tricarbonylchromium portions.[31] But because the electrochemical step is irreversible, as can be readily seen for mono complexes where interaction is impossible, little can really be said concerning bis complexes except that even if the peak separation is due to interaction, that interaction must be small. Since two "simultaneous" charge transfers must occur, each of which is irreversible, the actual separation due to interaction is difficult to judge but is almost certainly quite small and the system follows the Bard–Anson–Saveant model.

The existence of noninteraction among the (arene)tricarbonylchromium portions in the bis and tris complexes prompted an X-ray crystallographic study. The aims were in part to examine if any features of the trisubstituted complex enhanced stability of the cation and in part to look features preventing interaction. Since IXa gives a relatively stable dication upon oxidation, yet still exhibits noninteraction of the (arene)tricarbonylchromium groups, it was chosen for the X-ray study.

A drawing of one molecule of $(CH_3)_2Sn[(2,4,6-(CH_3)_3C_6H_2Cr(CO)_3]_2$ is shown in Figure 3 with the thermal ellipsoids in Table III represented at 50% probability.[32] The structure consists of a tin atom that is bonded to two methyl and two mesityl groups. Each mesityl group is also bonded to a $Cr(CO)_3$ moiety in a η^6 fashion. Individual bond distances are listed in Table IV, and angles are listed in Table V.

The geometry around the tin atom is distorted tetrahedral as indicated by the bond angles at the tin atom in Table V. The dihedral angle between the plane defined by Sn, C_{26}, C_{25} and the plane defined by Sn, C_{13}, C_1 is 82.4°, within ~8° of the tetrahedral value. The Sn–C_{26} and Sn–C_{25} distances are not unusual for Sn–C(methyl) distances. The Sn–C(mesityl) distances of 2.182 (3) Å appear

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[30] Rieke, R. D.; Milligan, S. N., unpublished results.

[31] Richardson, D. E.; Taube, H. *Inorg. Chem.* **1981**, *20*, 1278.

[32] Johnson, C. K. Report ORNL-3794; Oak Ridge National Laboratory: Oak Ridge, TN, 1965.

Table III. Anisotropic Thermal Parameters[a,b] (Å^2)

atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Sn	3.06 (1)	3.11 (1)	2.44 (1)	0.133 (9)	1.317 (8)	0.145 (8)
Cr_1	2.62 (2)	2.95 (2)	2.84 (2)	0.30 (2)	1.08 (2)	0.02 (2)
Cr_2	3.59 (3)	5.01 (4)	2.76 (3)	0.90 (3)	2.02 (2)	0.44 (2)
O_1	4.3 (2)	4.3 (2)	7.6 (3)	−0.6 (1)	1.2 (2)	−1.3 (2)
O_2	10.9 (4)	5.2 (2)	4.3 (2)	1.3 (2)	3.0 (2)	1.5 (2)
O_3	5.1 (2)	6.7 (2)	6.0 (2)	1.7 (2)	3.2 (2)	−0.3 (2)
O_4	13.6 (5)	16.6 (6)	7.5 (3)	3.5 (5)	8.3 (4)	5.0 (4)
O_5	8.3 (3)	9.4 (4)	7.2 (3)	4.5 (3)	5.1 (3)	1.4 (2)
O_6	7.4 (3)	8.2 (3)	4.9 (2)	−0.5 (2)	2.6 (2)	−2.5 (2)
C_1	3.1 (2)	2.9 (2)	2.8 (1)	0.5 (1)	1.3 (1)	0.1 (1)
C_2	3.5 (2)	2.9 (2)	3.3 (2)	0.0 (1)	1.3 (1)	−0.2 (1)
C_3	3.2 (2)	3.5 (2)	4.8 (2)	−0.2 (2)	1.7 (2)	−0.5 (2)
C_4	4.2 (2)	3.3 (2)	5.1 (2)	0.1 (2)	2.7 (2)	0.4 (2)
C_5	4.1 (2)	3.7 (2)	3.7 (2)	0.7 (2)	2.2 (2)	0.7 (1)
C_6	3.3 (3)	3.1 (2)	2.7 (1)	0.6 (1)	1.2 (1)	0.3 (1)
C_7	3.9 (2)	5.3 (3)	2.9 (2)	−0.2 (2)	0.8 (2)	−0.9 (2)
C_8	4.5 (3)	6.9 (4)	7.9 (4)	−0.0 (2)	4.3 (3)	0.6 (3)
C_9	3.3 (2)	5.5 (3)	2.5 (2)	0.7 (2)	0.8 (1)	−0.3 (2)
C_{10}	3.5 (2)	3.6 (2)	4.7 (2)	0.5 (2)	1.5 (2)	0.1 (2)
C_{11}	5.3 (3)	3.5 (2)	3.7 (2)	0.5 (2)	1.8 (2)	0.3 (2)
C_{12}	3.3 (2)	4.2 (2)	3.6 (2)	0.5 (2)	1.3 (2)	−0.2 (2)
C_{13}	2.6 (1)	3.7 (2)	2.6 (1)	0.0 (1)	1.4 (1)	0.0 (1)
C_{14}	3.1 (2)	4.5 (2)	3.7 (2)	−0.3 (2)	1.5 (2)	0.4 (2)
C_{15}	3.3 (2)	5.7 (3)	3.8 (2)	−0.3 (2)	1.5 (2)	0.3 (2)
C_{16}	3.4 (2)	5.6 (3)	2.7 (2)	1.0 (2)	1.2 (1)	0.2 (2)
C_{17}	3.9 (2)	4.1 (2)	2.7 (2)	0.7 (2)	2.1 (1)	0.4 (1)
C_{18}	3.2 (2)	3.6 (2)	2.6 (1)	0.1 (1)	1.8 (1)	−0.2 (1)
C_{19}	4.4 (3)	6.9 (4)	6.1 (3)	−1.2 (2)	2.2 (2)	2.3 (3)
C_{20}	4.0 (2)	8.0 (4)	3.8 (2)	2.1 (2)	1.2 (2)	1.8 (2)
C_{21}	3.5 (2)	3.9 (2)	4.6 (1)	−0.0 (2)	2.3 (2)	0.2 (2)
C_{22}	6.7 (3)	9.3 (5)	4.8 (3)	2.0 (3)	4.0 (3)	2.0 (3)
C_{23}	5.2 (3)	6.6 (3)	4.4 (2)	1.9 (2)	3.1 (2)	0.7 (2)
C_{24}	5.6 (3)	6.5 (3)	3.3 (2)	1.2 (2)	2.4 (2)	−0.4 (2)
C_{25}	5.1 (3)	6.5 (3)	2.6 (2)	0.0 (2)	1.9 (2)	−0.7 (2)
C_{26}	6.7 (3)	3.2 (2)	8.1 (4)	−0.3 (2)	4.7 (3)	0.4 (2)

[a] Estimated standard deviations are given in parentheses. $B_{ij} = 4\beta_{ij}/a_i{}^*a_j{}^*$, where β_{ij} are the unitless parameters used in refinement in the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [b] Isotropic thermal parameters of the aromatic H atoms were fixed at 7 Å^2.

Table IV. Bond Distances (Å)

Within the Coordination Spheres			
Sn-Cr_1	2.182 (3)	Cr_1-C_{11}	1.842 (4)
Sn-C_{13}	2.182 (3)	Cr_1-C_{12}	1.830 (3)
Sn-C_{25}	2.141 (3)	Cr_2-C_{13}	2.268 (3)
Sn-C_{26}	2.157 (4)	Cr_2-C_{14}	2.221 (4)
Cr_1-C_1	2.255 (3)	Cr_2-C_{15}	2.229 (4)
Cr_1-C_2	2.220 (3)	Cr_2-C_{16}	2.242 (3)
Cr_1-C_3	2.208 (4)	Cr_2-C_{17}	2.209 (3)
Cr_1-C_4	2.245 (4)	Cr_2-C_{18}	2.202 (3)
Cr_1-C_5	2.217 (3)	Cr_2-C_{22}	1.827 (4)
Cr_1-C_6	2.201 (3)	Cr_2-C_{23}	1.835 (4)
Cr_1-C_{10}	1.825 (4)	Cr_2-C_{24}	1.841 (5)
Within the Ligands			
C_1-C_2	1.423 (4)	C_{16}-C_{17}	1.402 (5)
C_2-C_3	1.410 (5)	C_{17}-C_{18}	1.413 (4)
C_3-C_4	1.421 (5)	C_{18}-C_{13}	1.421 (4)
C_4-C_5	1.388 (5)	C_{14}-C_{19}	1.527 (5)
C_5-C_6	1.422 (5)	C_{16}-C_{20}	1.525 (5)
C_6-C_1	1.418 (4)	C_{18}-C_{21}	1.527 (4)
C_2-C_7	1.513 (5)	C_{15}-H_{15}	1.03 (5)
C_4-C_8	1.527 (5)	C_{17}-H_{17}	0.97 (5)
C_6-C_9	1.520 (4)	C_{10}-O_1	1.158 (5)
C_3-H_3	1.11 (5)	C_{11}-O_2	1.138 (5)
C_5-H_5	1.25 (5)	C_{12}-O_3	1.155 (4)
C_{13}-C_{14}	1.430 (4)	C_{22}-O_4	1.145 (5)
C_{14}-C_{15}	1.412 (5)	C_{23}-O_5	1.148 (5)
C_{15}-C_{16}	1.390 (6)	C_{24}-O_6	1.159 (6)

Table V. Bond Angles (Deg)

C_1SnC_{13}	107.8 (1)	$C_5C_4C_8$	120.1 (4)
C_1SnC_{25}	116.3 (1)	$C_5C_6C_9$	117.1 (3)
C_1SnC_{26}	103.1 (1)	$C_1C_6C_9$	122.1 (3)
$C_{13}SnC_{25}$	104.9 (1)	$C_{14}C_{13}C_{18}$	117.3 (3)
$C_{13}SnC_{26}$	113.4 (2)	$C_{13}C_{14}C_{15}$	120.6 (3)
$C_{25}SnC_{26}$	111.5 (2)	$C_{13}C_{15}C_{16}$	121.2 (3)
$C_{10}Cr_1C_{11}$	90.0 (2)	$C_{15}C_{16}C_{17}$	119.0 (3)
$C_{10}Cr_1C_{12}$	87.0 (2)	$C_{16}C_{17}C_{18}$	120.9 (3)
$C_{11}Cr_1C_{12}$	90.6 (2)	$C_{17}C_{18}C_{13}$	120.7 (3)
$C_{22}Cr_2C_{23}$	89.0 (2)	$SnC_{13}C_{14}$	120.0 (2)
$C_{22}Cr_2C_{24}$	87.5 (2)	$SnC_{13}C_{18}$	122.6 (2)
$C_{23}Cr_2C_{24}$	87.5 (2)	$C_{13}C_{14}C_{19}$	121.3 (3)
$C_6C_1C_2$	117.9 (3)	$C_{15}C_{14}C_{19}$	118.0 (3)
$C_1C_2C_3$	120.2 (3)	$C_{15}C_{16}C_{20}$	120.4 (3)
$C_2C_3C_4$	121.6 (3)	$C_{17}C_{16}C_{20}$	120.5 (4)
$C_3C_4C_5$	118.0 (3)	$C_{17}C_{18}C_{21}$	116.4 (3)
$C_4C_5C_6$	121.4 (3)	$C_{13}C_{18}C_{21}$	122.8 (3)
$C_5C_6C_1$	120.8 (3)	$Cr_1C_{10}O_1$	178.7 (4)
SnC_1C_2	122.1 (2)	$Cr_1C_{11}O_2$	179.5 (4)
SnC_1C_6	119.9 (2)	$Cr_1C_{12}O_3$	178.5 (7)
$C_1C_2C_7$	122.5 (3)	$Cr_2C_{22}O_4$	177.4 (7)
$C_3C_2C_7$	117.3 (3)	$Cr_2C_{23}O_5$	179.2 (5)
$C_3C_4C_8$	121.9 (3)	$Cr_2C_{24}O_6$	179.0 (4)

slightly longer than the Sn–C(aryl) distances of 2.147 (6) Å reported in tetrakis(4-methylphenyl)tin.[33] This does not apparently result from the crowding of the two additional methyl groups adjacent to the σ-bonded carbon as the Sn–C(phenyl) bond of VIa is the same length as the Sn–C(mesityl) bond of IXa.[34] The orientation of the two mesityl planes can be described in terms of a rotation about the Sn–C_1 and Sn–C_{13} bonds by defining the plane containing Sn, C_1, and C_{13} as the reference plane. Accordingly, the mean plane of the mesityl ring A in Table VI is rotated 41.4° from the reference plane while the mean

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(33) Kariipides, A.; Wolfe, K. *Acta Crystallogr. Sec. B* **1975**, *B31*, 605.

(34) Schubert, U.; Willeford, B. R.; Zuckerman, J. J. *J. Organomet. Chem.* **1981**, *215*, 367.

Table VI. Mean-Plane Calculations and Deviations (Å) of Individual Atoms[a,b]

atom	dev	atom	dev
	Plane A		
*C_1	−0.020 (4)	Sn	−0.093
*C_2	0.006 (5)	Cr_1	1.717
*C_3	0.009 (5)	C_7	0.029
*C_4	−0.010 (5)	C_8	−0.044
*C_5	−0.003 (5)	C_9	0.063
*C_6	0.018 (4)		
	Plane B		
*C_{13}	−0.026 (4)	Sn	−0.102
*C_{14}	0.017 (5)	Cr_2	1.725
*C_{15}	0.001 (6)	C_{19}	0.012
*C_{16}	−0.010 (5)	C_{20}	−0.034
*C_{17}	0.001 (5)	C_{21}	0.046
*C_{18}	0.017 (4)		

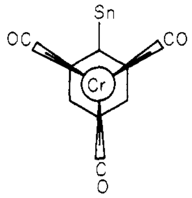
[a] The equations are derived from the equally weighted refinement of those atoms indicated by an asterisk and are based upon an orthonormal coordinate system where X, Y, and Z are in Å and their directions defined as $b' = b$, $c' = a \times b$, and $a' = b \times (a \times b)$. [b] Equations for the planes: A, $-0.141\,96X + 0.982\,79Y - 0.118\,22Z = 0.607\,50$; B, $0.469\,08X + -0.558\,36Y - 0.684\,24Z = 2.202\,99$.

plane of ring B is rotated 35.6° from the reference plane in the opposite direction of plane A.

A slight deviation of the ring carbon atoms from planarity is observed for the two mesityl rings (Table VI). It appears that the σ-bonded ring carbons (C_1 and C_{13}) move out of the plane by ~0.02 Å toward the tin while one adjacent carbon in ring A (C_6) and two adjacent carbons in ring B (C_{14} and C_{18}) move out of the plane away from the tin atom. These deviations are quite small, however, and do not lend themselves to a detailed analysis.

Bond parameters within the chromium coordination spheres are not unusual. The average C–C distances within the mesityl rings of 1.414 (5) Å (ring A) and 1.411 (5) Å (ring B) as well as the average Cr–C distances of 2.224 (4) Å (ring A) and 2.229 (4) Å (ring B) are in agreement with those reported in other (π-arene)$Cr(CO)_3$ complexes.[35,36] Similarly, the average bond parameters within the $Cr(CO)_3$ moieties are also in good agreement.[35,36]

The orientation of the Cr–CO bonds with respect to the mesityl plane is shown below. These Cr–CO bonds approximately eclipse the ring carbons bearing a CH_3 substituent. The average deviation from a perfectly eclipsed orientation is ~2° for ring A and ~1° for ring B. It was initially observed by Sim[37,38] that in the solid state the orientation of the Cr–CO vectors with respect to the arene plane in (π-arene)$Cr(CO)_3$ complexes is controlled by the nature of the ring substituents.



By considering an octahedral set of orbitals on chromium he concluded that the remaining three bonds from the $Cr(CO)_3$ moiety would point to the most electron-rich ring carbon atoms. These arguments are also consistent with the staggered orientation observed in unsubstituted (π-arene)$Cr(CO)_3$.[36] For a substituted π-arene, the electron-releasing or -donating properties of the substituent should determine which of the ring carbons are eclipsed by the Cr–CO vectors. A single CH_3 substituent would be expected to increase the negative charge of the carbon atoms ortho and para to the substituted carbon. The inclusion of two more CH_3 groups in the 3- and 5-positions would cause a cumulative buildup of negative charge of the three nonmethyl substituted carbons which then become the preferred sites of bonding to the chromium. With the assumption of an octahedral arrangement of orbitals on chromium, then the Cr–CO vectors should eclipse the CH_3-substituted ring carbons. Thus, the observed orientation fits nicely with this view.

Intermolecular interactions are within the range of normal van der Waals contact distances except for the $O_3 \cdots H_5{}^I$ interaction of 2.26 Å, where $I = 1 - x, -y, -z$. It is possible that a weak hydrogen bond occurs. No intermolecular interactions between aromatic rings occurs. The closest intermolecular contact between ring centers is 6.4 Å.

The crystal structure seems to lend support for a postulated sterically enhanced stability of the dication in that no locking of the molecule into a favorable orbital overlap situation appears to occur. In fact, the orientation of the molecule seems to be such that there are no favorable orbital interactions between the rings. Two possible models could have led to interaction between the π-bound organometallic portions. The first would involve interaction of the 5d tin orbitals and either phenyl or chromium 3d orbitals. It is extremely difficult to imagine how the tin orbitals could be interacting with both moieties due to rotation of the ring planes. It would appear that a single good overlap between tin and one arene ring would result in poor interaction with the second arene ring. Furthermore, a Mössbauer study of VIa indicates little or no interaction between tin and chromium.[39] Another conceivable means of (arene)tricarbonylchromium interaction is through the arene π orbitals mixing with the σ orbitals on the dimethyltin fragment as if those σ orbitals were a pseudo π orbital. However, the same rotation of the mesityl rings is such that this type of mixing is a remote possibility. So although there is greater stability of this dication with respect to other complexes in this series, the crystal structure does not suggest that the origin of this enhanced persistence is electronic in nature. In fact, steric factors seem to preclude orbital overlap of the two arene moieties. At this point, steric factors would appear to be the preferred explanation[29] for the longevity of this dication rather than any deocalization of charge.

Probably equally important in the noninteraction of these moieties is the distance between them. Saveant[40] has found that for compounds of the formula (p-$C_6H_4NO_2$)$(CH_2)_n$(p-$C_6H_4NO_2$) noninteraction of the reducible nitrophenyl groups occurs when $n = 2$ or greater, depending of course on solvent. When separated this far, these groups act independently as far as both internal factors and environmental factors are concerned. Distances between the phenyl ring atoms 1 and 1′ are about 4.0 and 5.3 Å for $n = 2$ and $n = 3$, respectively, in Saveant's compounds as judged from models. The 1 and 1′ distance in the tin complexes is about 3.6 Å. The Cr–Cr distance is much greater since they point away from each other.

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(35) Bailey, M. F.; Dahl, L. F. *Inorg. Chem.* **1965**, *4*, 1298.

(36) Rees, B.; Coppens, P. *Acta Crystallogr., Sect. B* **1973**, *29*, 2515.

(37) Sim, G. A. *Annu. Rev. Phys. Chem.* **1967**, *18*, 57–80.

(38) Carter, D. L.; McPhail, A. T.; Sim, G. A. *J. Chem. Soc. A*, **1966**, 822.

(39) Poeth, T. P.; Harrison, P. G.; Long, T. V.; Willeford, B. R.; Zuckerman, J. J. *Inorg. Chem.* **1971**, *10*, 522.

(40) Ammar, F.; Saveant, J. M. *J. Electroanal. Chem.* **1973**, *47*, 115.

Direct electronic interactions should be small at these distances and environmental factors apparently are involved only to a minimal extent.

In systems which have the capability of direct electronic interactions between the phenyl rings, such as XIVb and XVb, the Bard–Anson–Saveant model does not seem to hold. Calculations for n_{bis} are quite poor. The phenyl rings of XVb should be constrained to be coplanar by the saturated two-carbon bridge and a crystal structure of XIVb revealed[41,42] the two rings to be coplanar and the tricarbonylchromium moieties to be trans to each other. Thus the two phenyl rings should have at least some opportunity to engage in orbital overlap if the solution state matches the crystal state even slightly. Nevertheless, despite the possibility of orbital overlap and interaction, the cations are much less persistent than those of the dimethyldiaryltin complexes as judged by cyclic voltammetry. So while such a situation is much more favorable for electronic interactions to delocalize charge, apparently the dication is more subject to nucleophilic attack, having no other bulky shielding groups around the rings.

Conclusion

The electrochemical oxidation of the mono- and bis(tricarbonylchromium) complexes yield stable cations on the cyclic voltammetric time scale. The stability of the cations can be substantially increased by substitution of electron-donating groups simultaneously in the 2-, 4-, and 6-positions of the phenyl rings. The persistence of the cations in such cases are enhanced to a point that reasonable coulometric experiments could be carried out. These experiments showed that the mono complexes oxidize in a one-electron process to give a mono cation while oxidation of the bis complexes is a two-electron process, yielding a dication. Similarly, the electrochemical oxidation of methyltris(phenyltricarbonylchromium)tin is a three-electron process, giving a trication. All of the electrochemical data indicate that the (arene)tricarbonylchromium portions within each molecule are essentially noninteracting. It would thus appear that attempts to prepare mixed-valence compounds employing (arene)tricarbonylchromium groups separated by one $(CH_3)_2E$ (E = C, Si, Ge, Sn, Pb) unit will fail. Furthermore, the electrochemical studies strongly suggest that the HOMO involved in the oxidation of these compounds are mainly metallic in character and have, at best, only a small contribution from the phenyl π orbitals.

The enhanced persistence of the cations by substitution of the phenyl rings appears to be most satisfactorily explained in terms of steric effects. The X-ray structure seems to indicate that there is no reasonable possibility of delocalization of charge onto both rings. Instead, the cations seem to be stabilized by steric bulk about the rings, presumably by retarding nucleophilic attack.

Experimental Section

All starting materials were commercially available, were of reagent grade, and were used without further purification. The complexes for this study were prepared from either $Cr(CO)_6$ or $Cr(CO)_3(NH_3)_3$ using great care to exclude air and moisture. All work with solutions of the complexes was carried out under an atmosphere of prepurified nitrogen or argon. Dioxane and THF required as solvents in syntheses were freshly distilled from sodium–potassium alloy under argon or N_2. All other solvents were saturated with argon or N_2 prior to use. No attempts were made to optimize yields.

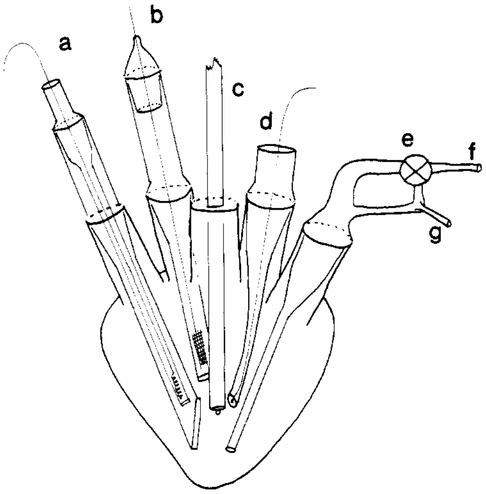

Figure 4. A schematic of cell A used for electrochemical experiments: (a) reference electrode bridge assembly; (b) auxiliary electrode (Pt guaze) bridge assembly; (c) DME; (d) working electrode (Pt disk); (e) bubbler with three-way stopcock; (f) argon inlet to bubbler; (g) argon outlet from cell.

Infrared spectra were obtained as Nujol mulls, cyclohexane solutions, or a neat liquid between KBr plates on a Perkin-Elmer 337 or 283 spectrophotometer. Proton NMR were recorded with a Varian A-60A or EM-360 or a Perkin-Elmer 390 90-MHz spectrometer. Such spectra were taken in $CDCl_3$ or CCl_4 solutions by using Me_4Si or, when more appropriate, residual $CHCl_3$, *p*-dioxane, or acetone as internal standards. Ultraviolet–visible spectra were acquired on a Hewlett-Packard 8450A spectrophotometer. Unless stated otherwise, melting points were taken on a Thomas Hoover capillary melting point apparatus and are corrected. All new compounds gave either satisfactory elemental analysis (performed by either MHW Laboratories, Phoenix, AZ, or Galbraith Laboratories, Knoxville, TN) or high-resolution mass spectra (performed by The Midwest Regional Center for Mass Spectrometry, University of Nebraska, Lincoln, NE).

Electrochemistry. All electrochemical experiments were performed using a PAR Model 173 potentiostat/galvanostat equipped with *iR* compensation in conjunction with a PAR Model 175 universal programmer and Model 179 digital coulometer. This system uses a conventional three-electrode configuration. The reference electrode[14] is Ag|AgCl, saturated NaCl(aq) buffered from the bulk solution by a bridge assembly while the working electrode is either a platinum disk for cell A or a platinum sphere for cell B. A schematic of cell A is shown in Figure 4. Cell B has been previously described.[43] Coulometry was performed in a cell having four chambers, one for each electrode with a buffer chamber between the auxiliary and working chembers. The chambers are each separated from one another by glass frits. Due to decomposition of the cations during the length of time of a coulometry experiment, *n* values were determined by plotting current vs. coulombs passed at the early stages of the oxidation and extrapolating to zero current.

Propylene carbonate, PC, was generally vaccum distilled once, discarding the first fraction as described by Adams,[44] and then stored over 4A molecular sieves. No particular advantage or changes were noted when using doubly distilled PC. Polarographic grade tetraethylammonium perchlorate, TEAP, was purchased from Eastman and used without any further purification except for drying in a vacuum at 70 °C for 1 h prior to use. The inert atmosphere was argon and prepurified grade (99.998%).

Syntheses. The preparation of compounds I, II, III, and V has already been described.[45] Likewise, compounds VIa (=IV), b, and c have also been previously reported.[39]

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[41] Ercoli, R.; Calderazzo, F.; Alberola, A. *Quad. Ing. Chim. Ital.* **1959**, 975.

[42] Corradini, P.; Allegra, G. *J. Am. Chem. Soc.* **1960**, *82*, 2075.

[43] Rieke, R. D.; Rich, W. E.; Ridgway, T. H. *J. Am. Chem. Soc.* **1971**, *93*, 1962.

[44] Nelson, R. F.; Adams, R. N. *J. Electroanal. Chem.* **1967**, *13*, 184.

[45] Nagelberg, S. B.; Reinhold, C. E.; Willeford, B. R.; Bigwood, M. P.; Molloy, D. C.; Zuckerman, J. J. *Organometallics*, submitted for publication.

Triamminetricarbonylchromium. This compound was used to synthesize the π tricarbonylchromium complexes and was prepared by the method of Hieber.[46] KOH (7.75 g) was dissolved in 95% ethanol (120 mL) by heating. After being cooled to ambient temperature, the solution was filtered into a pressure bottle reinforced with electrical tape. Hexacarbonylchromium (4.5 g, 20.5 mmol) was added, and the bottle and its contents were flushed with argon for 15 min. The bottle was then capped, covered with a cloth, and heated on a steam bath for 6 h. At the end of this time, the bottle was allowed to cool and finally placed in an ice/water bath to reduce internal pressure. The bottle was carefully opened, and the contents were poured into a 1-L round-bottom flask which had previously been evacuated and filled with argon three times. The bottle was washed with concentrated NH_4OH (150 mL), and this was added to the 1-L flask. The resulting orange solution was stirred under argon for two more hours by which time a bright yellow solid had formed. The mixture, being very air-sensitive, was filtered very quickly, collecting the solid on a glass frit. The solid was washed with ethyl alcohol to facilitate drying. The solid triamminetricarbonylchromium was then transferred to another flask and stored under an argon atmosphere. Since the compound decomposes slowly, it was freshly prepared for the syntheses of the complexes.

Dimethylbis(4-methoxyphenyl)tin (VIIc). Many of the free ligands were synthesized according to this basic procedure which parallels the method of Seyferth.[47] The reaction was carried out under an argon atmosphere in a three-neck 50-mL round-bottom flask equipped with a water condenser which is fitted with an argon inlet tube, a 25-mL addition funnel, and a rubber septum. Mg turnings (0.58 g, 0.024 mol) and a magnetic stirring bar were placed in the flask which was then evacuated and filled with argon three times. THF (5 mL) was introduced by syringe to cover the Mg turnings. This was followed by 4-bromoanisole (0.5 mL), also added by syringe, to start the reaction (no external heating was required). An additional amount of THF (7 mL) was added as the reaction began. The remainder of the 4-bromoanisole (2.5 mL, total 0.024 mol) was dissolved in THF (3 mL) in the addition funnel, and this solution added to the reaction solution at such a rate that gentle reflux was maintained. After the completion of the addition of this solution, the reaction mixture was refluxed for 0.5 h by external heating to ensure completion of the reaction. At the end of this time, the reaction mixture was cooled to ambient temperature while dimethyldichlorotin (1.99 g, 0.009 mol) was weighed and dissolved in THF (5 mL) under an argon atmosphere. This was added to the Grignard solution at such a rate that gentle reflux was maintained followed by heating to reflux for 2 h. Once again the reaction mixture was cooled to ambient temperature, filtered, and hydrolyzed by a saturated aqueous ammonium chloride solution (3 mL). The resulting clear organic layer was decanted from the solids formed. These solids were washed with ether, the washings were added to the organic layer, and the mixture was dried over $MgSO_4$. The oil obtained after stripping off the THF and ether was vacuum distilled (about 0.15 mmHg). The fraction distilling at about 155–160 °C solidified upon cooling, giving about 1.9 g, 60% yield: ^{1}H NMR ($CDCl_3$) δ 6.90 (m, 8 H, aromatic protons), 3.62 (s, 6 H, $ArOCH_3$), 0.44 (s, 6 H, $SnCH_3$), $J(^{117,119}Sn–CH_3)$ = 52.8 Hz; IR (Nujol) 1590 (s), 1496 (s), 1180 (s), 1078 (s), 1034 (m), 526 (ms), 512 (s), 465 (w) cm^{-1}, mass spectrum calcd for $C_{16}H_{20}O_2Sn$ 364.0492, found 364.0490.

Dimethylbis(4-methoxyphenyl)tricarbonylchromium)tin (VIIa). In a 50-mL two-neck round-bottom flask equipped with a water condenser, and argon inlet, magnetic stirring bar, and a rubber septum were placed dimethylbis(4-methoxyphenyl)tin (3.36 g, 9.27 mmol) and triamminetricarbonylchormium (3.62 g, 20.0 mmol). The assembly was evacuated and filled with argon three times before dioxane (25 mL) was added. Reflux was maintained for 3 h until the yellow slurry became brown-green. The reaction mixture was then cooled to ambient temperature and filtered by using standard Schlenk techniques. The flask and residue was washed with benzene. The benzene and dioxane were removed under vacuum, leaving a yellow oil which solidified upon addition of cold hexane and stirring. The crude product was dissolved in hot chloroform (25 mL) and filtered and hexane added (35 mL) following by cooling at ice/water temperatures. The precipitated crystals were collected on a frit, yielding 1.77 g, (30%) of bis complex (no mono complex was obtained with this ligand): mp 128 °C dec; ^{1}H NMR ($CDCl_3$) δ 5.5–5.13 (q, 8 H, aromatic protons), 3.58 (s, 6 H, $ArOCH_3$), 0.64 (s, 6 H, $Sn–CH_3$), $J(^{117,119}Sn–CH_3)$ = 55.5 Hz; IR (Nujol) 1975 (m), 1938 (s), 1892 (m), 1865 (s), 1848 (m), 675 (m), 625 (m), 532 (m), 526 (sh), 510 (mw); mass spectrum for $C_{22}H_{20}Cr_2O_8Sn$ calcd 635.8995, found 635.9005.

4-Chloro-3,5-dimethylanisole. Methanol (210 mL), dimethyl sulfate (140 mL, 1.48 mol), and 4-chloro-3,5-dimethylphenol (182.3 g, 1.16 mol) were placed in a large three-neck round-bottom flask equipped with a mechanical stirrer. The flask was fitted with an ice/water condenser and an addition funnel. The reaction solution was stirred rapidly and heated to reflux. A solution of KOH (138.5 g, 2.47 mol) in methanol (950 mL) was added via the addition funnel. The reaction solution was refluxed and stirred for 1 h. At the end of this time, the K_2SO_4 which formed was filtered off, washed with methanol, and finally dissolved in water. This aqueous solution was extracted with benzene, and both the benzene and methanol washings were combined with the reaction mixture and refluxed for one more hour. After being cooled, the reaction mixture was poured into a 10% aqueous NaOH solution. Attempts to extract with benzene were successful when the resulting emulsion problem was countered with saturating the aqueous layer with KCl. The benzene layer was separated and washed with a fresh portion of 10% NaOH solution. The benzene was removed, and what remained was vacuum distilled at 20–25 torr by using a Vigreux column, giving a clear, colorless liquid with a boiling point of 123–125 °C (lit.[48] bp 114–117 °C (20 torr); mp 21 °C). The melting point was very near ambient temperature, and the IR was quite free of any O–H stretch; yield 143 g, 72%.

Dimethylbis(2,6-dimethyl-4-methoxyphenyl)tin (VIIIc). This compound was prepared as VIIc above except that the Grignard reagent of 4-chloro-3,5-dimethylanisole was prepared by the Rieke method[49] of activation. The product was obtained by fractional distillation: bp 165–170 °C (0.2 torr); ^{1}H NMR ($CDCl_3$) δ 6.55 (s, 4H, aromatic protons), 3.73 (s, 6 H, $ArOCH_3$), 2.30 (s, 12 H, $ArCH_3$), 0.58 (s, 6 H, $SnCH_3$), $J(^{117,119}Sn–ArH_m)$ = 13.8 Hz, $J(^{117,119}Sn–CH_3)$ = 49.5 Hz; IR (Nujol) 1590 (s), 1378 (s), 1160 (s), 1080 (s), 828 (ms), 600 (m), 532 (m), 520 (s), 510 (s) cm^{-1}. Anal. Calcd for $C_{20}H_{28}O_2Sn$: C, 57.32; H, 6.69; Sn, 28.35. Found: C, 57.43; H, 6.75; Sn, 28.27.

Dimethylbis((2,6-dimethyl-4-methoxyphenyl)tricarbonylchromium)tin (VIIIa). Triamminetricarabonylchromium (3.74 g, 20.0 mmol), dimethylbis(2,6-dimethyl-4-methoxyphenyl)tin (3.88 g, 9.27 mmol), and dioxane (25 mL) were gently refluxed under argon for 2.5 h, cooled, filtered, and chromatographed on an inert atmosphere silica gel column, eluting with a 90% hexane/10% $CHCl_3$ mixture. After removal of the solvents under vacuum, the solid obtained was recrystallized from a chloroform/hexane mixture. No mono complex was obtained. The yield of purified bis complex was 25%: mp 192 °C dec; ^{1}H NMR ($CDCl_3$) δ 4.9 (s, 4 H, aromatic protons), 3.72 (s, 6 H, $ArOCH_3$), 2.25 (s, 12 H, $ArCH_3$), 0.85 (s, 6 H, $SnCH_3$), $J(^{117,119}Sn–ArH_m)$ = 9.0 Hz, $J(^{117,119}Sn–CH_3)$ = 54.6 Hz; IR (Nujol) 1948 (m), 1945 (s), 1880 (sh), 1862 (m, br), 1846 (m), 1376 (s), 675 (s), 665 (m), 628 (s), 540 (w), 523 (sh), 514 (ms), 504 (m), 475 (m) cm^{-1}; mass spectrum calcd for $C_{26}H_{28}Cr_2O_8Sn$ 691.9672; found 691.9649.

Dimethylbis(2,4,6-trimethylphenyl)tin (IXc). This compound has been previously prepared[50] by reacting mesityllithium with dichlorodimethyltin. The compound used for our work was prepared in 60% yield by reacting the Grignard product of mesityl bromide with dichlorodimethyltin in THF as for VIIc above: mp 101 °C (lit.[50] mp 101 °C); ^{1}H NMR ($CDCl_3$) δ 6.77 (s, 4 H, aromatic protons), 2.22 (s, 6 H, Ar-*p*-Ch_3), 2.28 (s, 12 H, Ar-*o*-CH_3), 0.58 (s, 6 H, $SnCH_3$), (lit.[50] δ 6.73, 2.22, 2.29, 0.59, respectively), $J(^{117,119}Sn–CH_3)$ = 51.0 Hz, $J(^{117,119}Sn–ArH_m)$ = 17.0 Hz (lit.[50] 51.25,

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[46] Hieber, V. W.; Abeck, W.; Platzer, H. K. *Z. Anorg. Allg. Chem.* **1955**, *280*, 252. Rausch, M. D.; Moser, G. A.; Zaiko, E. J.; Lipman, A. L. *J. Organomet. Chem.* **1970**, *23*, 185. Moses, G. A.; Rausch, M. D. *Synth. Inorg. Met-Org. Chem.* **1974**, *4*, 37.

[47] Seyferth, D. "Organic Syntheses"; Rabjohn, D, Ed.; Wiley: New York, 1963; Coll. Vol. 4, p258.

[48] Hoffmann, F. Neth. Patent 6 514 743, May 13, 1966; CA65:10597e.

[49] Rieke, R. D.; Bales, S. E. *J. Am. Chem. Soc.* **1974**, *96*, 1775.

[50] Kula, M. R.; Amberger, E.; Mayer, K. K. *Chem. Ber.* **1965**, *98*, 634.

16.0 Hz, respectively); IR (Nujol) 1597 (m), 1377 (s), 1180 (m), 844 (s), 750 (s), 574 (m), 550 (m), 536 (m), 512 (s), 504 (s) cm^{-1}.

Dimethyl(2,4,6-trimethylphenyl)((2,4,6-trimethylphenyl)tricarbonylchromium)tin (IXb). Athis compound was prepared by the same method as given for VIIIa. Chromatography of the crude product on an inert atmosphere silica gel column using 100% hexane as eluent resulted in the unreacted free ligand being removed followed by the mono complex. The mono complex was then recrystallized twice from hexane: yield 61%; mp 131–132 °C; ^{1}H NMR (CDCl$_3$) δ 6.83 (s, 2 H, aromatic protons, uncomplexed ring), 4.82 (s, 2 H, aromatic protons, complexed ring), 2.35–2.12 (m, 18 H, ArCH$_3$), 0.73 (s, 6 H, SnCH$_3$), $J(^{117,119}$Sn–ArH$_m$(uncomplexed)) = 18.0 Hz, $J(^{117,119}$Sn–ArH$_m$(complexed)) = 9.9 Hz, $J(^{117,119}$Sn–CH$_3$) = 59.5 Hz, 55.5 Hz; IR (Nujol) 1955 (s), 1897 (s), 1378 (s), 672 (sh), 667 (ms), 658 (m), 629 (s), 547 (mw), 535 (m), 522 (m), 507 (sh), 500 (m) cm^{-1}; mass spectrum calcd for $C_{23}H_{28}CrO_3Sn$ 524.0465; found 524.0465.

Dimethylbis((2,4,6-trimethylphenyl)tricarbonylchromium)tin (IXa). The bis complex was obtained by continuing to elute the same chromatography column of IXb with a 40% chloroform/60% hexane mixture. Beautiful yellow crystals were obtained after recrystallization from a chloroform/hexane mixture: yield 10%; mp 218 °C dec; ^{1}H NMR (CDCl$_3$) δ 4.80 (s, 4 H, aromatic protons), 2.16 (s, 18 H, ArCH$_3$), 0.9 (s, 6 H, SnCH$_3$), $J(^{117,119}$Sn–ArH$_m$) = 10.5 Hz, $J(^{117,119}$Sn–CH$_3$) = 55.5 Hz; IR (Nujol) 1959 (sh), 1943 (s), 1853 (s), 1378 (s), 671 (s), 626 (s), 535 (ms), 525 (ms), 503 (m) cm^{-1}; mass spectrum calcd for $C_{26}H_{28}Cr_2O_6Sn$ 657.9706; found 657.9709.

Dimethylbis(2,6-dimethylphenyl)tin (Xc). This compound was prepared in 65% yield by the same method as VIIc. The crude product was recrystallized three times from alcohol: mp 54 °C; ^{1}H NMR (CDCl$_3$) δ 7.18–6.84 (m, 6 H, aromatic protons), 2.32 (s, 12 H, ArCH$_3$), 0.62 (s, 6 H, SnCH$_3$), $J(^{117,119}$Sn–CH$_3$) = 52.5 Hz; IR (Nujol) 1563 (m), 1376 (s), 1024 (m), 713 (s), 546 (mw), 528 (ms, sh), 509 (s) 440 (m) cm^{-1}. Anal. Calcd for $C_{18}H_{24}Sn$: C, 60.22; H, 6.69; Sn, 33.09. Found: C, 60.39; H, 6.58; Sn, 32.94.

Dimethyl(2,6-dimethylphenyl)((2,6-dimethylphenyl)tricarbonylchromium)tin (Xb). This complex was prepared by the general method described for VIIIa, eluting the column with 100% hexane: yield 48%; mp 123 °C; ^{1}H NMR (CDCl$_3$) δ 7.03 (m, 3 H, aromatic protons, uncomplexed ring), 5.49 (t, 1:2:1, 1 H, aromatic proton, complexed ring), 4.86 (d, 2 H, aromatic protons, complexed ring), 2.36 (s, 6 H, ArCH$_3$), 2.12 (s, 6 H, ArCH$_3$), 0.80 (s, 6 H, SnCH$_3$), $J(^{117,119}$Sn–CH$_3$) = 55.5 Hz. IR (Nujol) 1950 (s), 1875 (s, br), 1860 (s, br), 1460 (s), 668 (s), 661 (s), 625 (s), 530 (s), 522 (s), 508 (s) cm^{-1}; mass spectrum calcd for $C_{21}H_{24}O_3CrSn$ 496.0173, found 496.0166.

Dimethylbis((2,6-dimethylphenyl)tricarbonylchromium)tin (Xa). The bis complex was isolated by continuing the chromatography column of Xb by eluting with a 30% chloroform/70% hexane mixture: yield 23%; mp 193 °C; ^{1}H NMR (CDCl$_3$) δ 5.56 (*t*, 1:2:1, 2 H, aromatic proton), 4.92 (d, 1:1, 4 H, aromatic protons), 2.2 (s, 12 H, ArCH$_3$), 0.92 (s, 6 H, SnCH$_3$), $J(^{117,119}$Sn–CH$_3$) = 54.90 Hz; IR (Nujol) 1968 (s), 1950 (s), 1895 (s, br), 1860 (s, br), 1378 (s), 1032 (s), 665 (sh), 660 (s), 620 (s), 526 (s), 518 (ms, sh), 473 (m) cm^{-1}; mass spectrum calcd for $C_{24}H_{24}O_6Cr_2Sn$ 631.9414, found 631.9409.

Dimethylbis(4-(*N*,*N*-dimethylamino)phenyl)tin (XIc). The same procedure as described for VIIc was followed and the product recrystallized three times from ethyl alcohol: yield 55%; mp 72 °C; ^{1}H NMR (CDCl$_3$) δ 7.34–6.60 (q, 8 H, aromatic protons), 3.8 (s, 12 H, ArNCH$_3$), 0.40 (s, 6 H, SnCH$_3$), $J(^{117,119}$Sn–CH$_3$) = 54.0 Hz; IR (Nujol) 1609 (s), 1359 (s), 1086 (s), 1021 (sh), 802 (s), 537 (m), 521 (s), 511 (s) cm^{-1}; mass spectrum calcd for $C_{18}H_{26}N_2Sn$ 388.1118, found 388.1116.

Dimethylbis((4-(*N*,*N*-dimethylamino)phenyl)tricarbonylchromium)tin (XIa). This complex was prepared in the manner of VIIIa and isolated by chromatographing on an inert atmosphere silica gel column using a 40% chloroform/60% hexane mixture. No mono complex was obtained: yield 15%; decomposes at 203–205 °C with only partial melting; ^{1}H NMR (CDCl$_3$) δ 5.53–4.73 (q, 8 H, aromatic protons), 2.85 (s, 12 H, ArNCH$_3$), 0.44 (s, 6 H, SnCH$_3$), $J(^{117,119}$Sn–CH$_3$) = 57.0 Hz; IR (Nujol) 1956 (s, br), 1892 (s, br), 1837 (s), 1372 (s), 677 (s), 671 (ms, sh), 632 (s), 622 (ms), 598 (s), 524 (m, sh), 517 (ms), 505 (ms) cm^{-1}; mass spectrum calcd for $C_{24}H_{26}Cr_2N_2O_6Sn$ 659.9622, found 659.9619.

Dimethylbis(4-(trimethylsilyl)phenyl)tin (XIIc). The starting material, 4-(trimethylsilyl)bromobenzene, was synthesized according to the method of Burkhard.[51] This was then reacted to form the corresponding Grignard reagent and the following reaction carried out as described above for VIIc. The solid obtained after removing THF at reduced pressure was recrystallized four times from ethyl alcohol: mp 77 °C; ^{1}H NMR (CDCl$_3$) δ 7.42 (s, 8 H, aromatic protons), 0.43 (s, 6 H, SnCH$_3$), 0.19 (s, 18 H, SiCH$_3$); IR (Nujol) 1405 (m), 1272 (s), 1030 (ms), 506 (s), 498 (m) cm^{-1}.

Dimethyl(4-(trimethylsilyl)phenyl)((4-(trimethylsilyl)phenyl)tricarbonylchromium)tin (XIIb). This complex was prepared by the same procedure as given for VIIIa. Chromatography was performed under an inert atmosphere on silica gel using 25% CHCl$_3$/75% hexane as eluent. This gave the mono complex which was recrystallized from hexane to give a yellow crystalline solid. No bis complex was isolated: mp 103 °C; ^{1}H NMR (CDCl$_3$) δ 7.42 (s, 4 H, aromatic protons, uncomplexed ring), 5.13 (q, 4 H, aromatic protons, complexed ring), 0.52 (s, 6 H, SnCH$_3$), 0.17 (d, 18 H, SiCH$_3$); mass spectrum calcd for $C_{23}H_{32}CrO_3SiSn$ 584.0314, found 584.0316.

Methyldiphenyl(phenyltricarbonylchromium)tin (XIIIc). Methyltriphenyltin (3.09 g, 8.47 mmol) and Cr(CO)$_3$(NH$_3$)$_3$ (1.58 g, 8.46 mmol) were reacted to give a crude product which was extracted with hot hexane. The extract was filtered and the filtrate cooled in ice. The yellow precipitate which formed was filtered, washed with cold hexane, and dried under N$_2$; yield 1.72 g, 41%. Recrystallization from hexane gave the analytical sample: mp(uncorr) 89–90 °C dec; ^{1}H NMR (CdCl$_3$) δ 7.47 (m, 10 H, aromatic protons, uncomplexed rings), 5.37 (m, 5 H, aromatic protons, complexed ring), 0.90 (s, 3 H, SnCH$_3$); IR (Nujol) 1980, 1970, 1905, 1880, 1865 cm^{-1}; mass spectrum calcd for $C_{22}H_{18}CrO_3Sn$ 501.9695, found 501.9658.

Methylphenylbis(phenyltricarbonylchromium)tin (XIIIb). Use of a larger excess of Cr(CO)$_3$(NH$_3$)$_3$ (3.547 g, 19.0 mmol) with methyltriphenyltin (2.307 g, 6.32 mmol) gave a crude product which, when treated as above, gave 1.08 g (34%) of the mono metal complex. The residue from the hexane extraction was extracted with CHCl$_3$ and filtered and the filtrate reduced in volume under vacuum. Addition of 1.5 vol of hexane, cooling in ice, and scratching the vessel with a glass stirring rod caused precipitation of the bissubstituted metal complex (1.54 g, 38%) which was filtered, washed with cold hexane, dried under N$_2$, and recrystallized from chloroform/hexane: mp(uncorr) 142–144 °C; ^{1}H NMR (CDCl$_3$) δ 7.53 (m, 5 H, aromatic protons, uncomplexed ring), 5.33 (m, 10 H, aromatic protons, complexed rings), 0.94 (s, 3 H, SnCH$_3$); IR (Nujol) 1975, 1965, 1920, 1890, 1870 cm^{-1}; mass spectrum calcd for $C_{25}H_{18}Cr_2O_6Sn$ 637.8936, found 637.8935.

Methyltris(phenyltricarbonylchromium)tin (XIIIa). Reaction of Cr(CO)$_3$(NH$_3$)$_3$ (6.87 g, 36.78 mmol) with methyltriphenyltin (2.23 g, 6.11 mmol) gave a product from which only a negligible amount was extractable with hexane. Treatment with CHCl$_3$ as above produced 1.76 g (45%) of the bis metal complex. The residue from the CHCl$_3$ extraction weighed 2.19 g (46%); this was extracted a second time with CHCl$_3$, and the residue dried under N$_2$: mp (uncorr) 224 °C dec; ^{1}H NMR (CDCl$_3$) δ 5.45 (m, 15 H, aromatic protons, complexed rings), 1.03 (s, 3 H, SnCH$_3$); IR (Nujol) 1980, 1970, 1925, 1905, 1880, 1870 cm^{-1}; mass spectrum calcd for $C_{28}H_{18}Cr_3O_9Sn$ 773.8188, found 773.8140.

(Biphenyl)tricarbonylchromium (XIVa). This complex has been described previously.[41,52] The synthetic method used here parallels the method of Nicholls and Whiting.[20,53] Biphenyl (1.60 g, 10 mmol) and hexacarbonylchromium (8.81 g, 40 mmol) were refluxed under inert atmosphere conditions in *n*-butyl ether (50 mL) and THF (6 mL) for 18 h. The resulting bright yellow solution was cooled rapidly to ambient temperature and the reaction mixture filtered by using standard Schlenk techniques. The unreacted hexacarbonylchromium was washed on the filter with two portions of methylene chloride. After the solvents were removed, the crude product was chromatographed on an inert

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(51) Burkhard, C. A. *J. Am. Chem. Soc.* **1946**, *68*, 2103.

(52) Fischer, E. O.; Kriebitzsch, N.; Fischer, R. D. *Chem. Ber.* **1959**, *92*, 3214.

(53) Fischer, E. O.; Ofele, K.; Essler, H.; Frolich, W.; Mortensen, J. P.; Semmlinger, W. *Chem. Ber.* **1958**, *91*, 2763.

atmosphere silica gel column eluting first with 100% hexane to remove unreacted biphenyl. Once the free ligand was removed, the solvent was switched to a 20% $CHCl_3$/80% hexane mixture until all the mono complex was eluted. The crude mono complex, 934 mg, was recrystallized from pentane. The total yield of pure product was 19%: mp 85.5–87 °C (lit.[41] 87–88); IR (cyclohexane) 1982 (s), 1916 (s) cm^{-1} (lit.[54] (cyclohexane) 1982, 1917 cm^{-1}); UV (cyclohexane) 241 nm (ϵ 3.6 × 10^4), 326 (9.6 × 10^3); ^1H NMR ($CDCl_3$) δ 7.42 (m, 5 H, uncomplexed ring), 5.48 (m, 5 H, complexed ring) (lit.[54] δ 7.42 (m, 5 H), 5.48 (m, 5 H)).

(Biphenyl)bis(tricarbonylchromium) (XIVb). The synthesis follows the procedure of Ercoli and co-workers.[41] Biphenyl (0.68 g, 4.4 mmol) and (benzene)tricarbonylchromium (3.79 g, 17.7 mmol) were placed in a 100-mL Schlenk tube and ground together with a glass rod. The tube was evacuated and filled with argon five times. At this point the tube was quickly immersed in an oil bath preheated to 165 ± 5 °C. Within minutes, an orange melt formed which became progressively more orange as the reaction proceeded. The reaction was carried out for 7 h under a slight positive argon pressure. Occasional gentle tapping of the sides of the Schlenk tube was performed to return sublimed (benzene)tricarbonylchromium to the melt. At the end of this time, the melt was allowed to cool slowly. When at ambient temperature, the sublimed material along the sides was scraped down and the solid which had formed at the bottom was cautiously broken up with a glass rod. A cold finger was inserted into the Schlenk tube, and sublimation at 0.06 torr and 40 °C for 2 h removed the unreacted biphenyl. Increasing the temperature to 70 ± 5 °C for 24 h removed the unreacted (benzene)tricarbonylchromium. The temperature was raised a final time to 95 ± 5 °C to remove any mono complex which had formed. The remaining solid was recrystallized under inert atmosphere conditions from a 1:1 heptane/acetone mixture (20 mL). Two crops were obtained, giving overall 25% yield: mp 212–213 °C (lit.[44] 215–216 °C); IR (THF) 1963 (s), 1899 (s) cm^{-1}; UV (THF) 232 nm (ϵ 2.8 × 10^4), 323 (1.6 × 10^4), 418 (4.9 × 10^3); ^1H NMR ($CDCl_3$) δ 5.48 (m, 10 H, complexed rings).

(9,10-Dihydrophenanthrene)tricarbonylchromium (XVa). This compound has been previously known, and an X-ray crystal study has been performed.[55] However no preparation or other properties are given. It was synthesized here by the same method as for XIVa above in 13% yield after recrystallization from hexane: mp 109.5–111.5 °C; ^1H NMR ($CDCl_3$) δ 7.60–7.07 (m, 4 H, aromatic protons, uncomplexed ring), 5.87–5.20 (m, 4 H, aromatic protons, complexed ring), 3.00–2.57 (m, 4 H, methylene protons); IR (cyclohexane) 1976 (s), 1914 (s), 1905 (s) cm^{-1}; mass spectrum calcd for $C_{17}H_{12}CrO_3$ 316.0182, found 316.0187.

(9,10-Dihydrophenanthrene)bis(tricarbonylchromium) (XVb). The same ligand exchange procedure as described for XIVb above was used. The residue remaining after sublimation to remove free ligand and mono complex was recrystallized under an inert atmosphere from a 1:1 mixture of acetone and hexane: yield 68%; mp 184 °C dec; ^1H NMR ($CDCl_3$) δ 5.60–5.23 (m, 8 H, aromatic protons, complexed rings), 3.08–2.50 (m, 4 H, methylene protons); IR (cyclohexane) 1975 (s), 1913 (s), 1904 (s) cm^{-1}; mass spectrum calcd for $C_{20}H_{12}Cr_2O_6$ 451.9444, found 451.9468.

X-ray Crystallography. Large yellow crystals of the compound were formed by recrystallization from a hexane solution that was initially 20% in chloroform. After 24 h more hexane was added, yielding an approximately 10% chloroform solution. The well-formed crystals were only moderately air-sensitive, decomposing to a green solid after several days exposure to air. The crystal selected for data collection was mounted in a 0.5-mm capillary under N_2 gas in a glovebag. This crystal had dimensions of 0.27 × 0.33 × 0.53 mm, and the largest dimensions was parallel to the capillary walls. A preliminary photographic examination led to the assignment of space group $P2_1/c$ (No. 14).[56] Final lattice constants of a = 15.514 (2) Å, b = 13.026 (2) Å, c = 15.709 (2) Å, and β = 119.51 (1)° along with Z = 4 provide a calculated density of 1.585 g/mL. Experimentally crystals of the compound would suspend nicely in spectroscopic grade carbon tetrachloride (d = 1.585 g/mL).

Intensity data were collected with the Picker FACS-1 diffractometer using Zr-filtered Mo Kα radiation to a limiting 2θ of 58.66° (1.2 Cu spheres). Each peak was scanned at the rate of 1.0 deg/min, and backgrounds were of 20-s duration. A set of three standard reflections was inserted every 100 data to check for instrument and crystal stability. These standards remained statistically constant through the collection of 7094 independent reflections. The data were corrected for absorption effects. Transmission factors ranged from 0.754 to 0.814. The intensity data were reduced to a set of $|F_o|$'s by application of Lorentz and polarization corrections (Lp). Standard deviations were calculated according to

$$\alpha_f = [((C + k^2B) + (0.02I)^2)/4|F_o|^2Lp^2]^{1/2}$$

where C and B are the counts of the scan and sum of the backgrounds, respectively, k is the ratio of the scan time to total background counting time, and I is the net intensity of the reflection. A total of 5287 reflections having $I > 3\sigma_I$ were taken as observed and utilized in the structure determination.

Direct methods[57] were used to locate the three heavy atoms while the remaining atoms were found by using Fourier techniques.[58] Full-matrix least-squares refinement[59] treating each of the nonhydrogen atoms isotropically produced R = 8.9% and WR = 9.4%.[60] Each nonhydrogen atom was then treated anisotropically in further block-diagonal refinement.[61] The addition of anomalous dispersion corrections[62] for the tin and two chromium atoms and the inclusion of aromatic hydrogen atoms with fixed thermal parameters converged with R = 4.5% and wR = 5.8%. All of these refinements were done by using unit weights. Empirical weights ($w = 1/\alpha^2$) were then calculated as described previously[32] and utilized in final cycles of block diagonal refinement which converged with R = 4.4% and wR = 6.2%. All shift-over errors were 3% or less, and the data to parameter ratio was 16:1. The resulting fractional coordinates from this final refinement are listed in Table II, and the associated thermal parameters are listed in Table III.

A final difference synthesis confirmed the correctness of the structure. The largest residual electron density of 1.07 e/Å^3 was in the region expected for methyl hydrogen atoms which were not included in refinement.

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Registry No. I, 75061-53-9; I cation, 81770-49-2; II, 75061-54-0; II cation, 81770-50-5; III, 75061-55-1; III cation, 81770-51-6; V, 75061-56-2; V cation, 81770-52-7; VIa, 31833-53-1; VIa cation, 80032-00-4; VIIa, 80031-95-4; VIIa cation, 80032-01-5; VIIc, 61726-36-1; VIIIa, 80031-96-5; VIIIa cation, 80032-02-6; VIIIc, 81769-36-0; IXa, 80031-84-1; IXa cation, 80032-03-7; IXb, 80031-92-1; IXb cation, 80031-97-6; IXc, 1091-36-7; Xa, 80031-85-2; Xa cation, 80032-04-8;

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[54] Brown, D. A.; Raju, J. R. *J. Chem. Soc. A* **1966**, 1617.

[55] Muir, K. W.; Ferguson, G.; Sim, G. A. *J. Chem. Soc., Chem. Commun.* **1966**, 465. Muir, K. W.; Ferguson, G. *J. Chem. Soc. B* **1968**, 476.

[56] Henry, N. F. M; Lonsdale, K., Eds. "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1952; Vol. I.

[57] A version of program FAME by P. F. Stokey, based upon the original version by R. Dewar and A. Stone, was used. Program REL by R. E. Long was also used.

[58] Atomic form factors from Cromer and Mann (Cromer, D. T.; Mann, J. L. *Acta Crystallogr., Sec. A* **1968**, *A24*, 321) and A. Zalkins Fourier program FORDAP were used.

[59] Busing, W. R.; Martin, K. O.; Levy, H. A. Report ORNL-TM-305; Oak Ridge National Laboratory: Oak Ridge, TN, 1962. The function minimized was $w(|F_o| - |F_c|)^2$.

[60] $R = \sum||F_o| - |F_c||/\sum F_o|$ and $wR = [\sum w(|F_o| - |F_c|)^2/w(F_o)^2]^{1/2}$, where w is the weighting factor.

[61] Program REFINE by J. J. Parks was used. The function minimized was $w(|F_o| - |F_c|)^2$.

[62] Cromer, D. T.; Libermann, D. *J. Chem. Phys.* **1970**, *53*, 1891.

Xb, 80031-93-2; Xb cation, 80031-98-7; Xc, 81769-37-1; XIa, 80031-86-3; XIa cation, 81770-46-9; XIc, 81769-38-2; XIIb, 80031-94-3; XIIb cation, 80031-99-8; XIIc, 81769-39-3; XIIIa, 80031-87-4; XIIIa cation, 80043-73-8; XIIIb, 80043-66-9; XIIIb cation, 80032-05-9; XIIIc, 80031-89-6; XIIIc cation, 80032-06-0; XIVa, 12111-60-3; XIVa cation, 81770-41-4; XIVb, 33010-84-3; XIVb cation, 81770-42-5; XVa, 12094-63-2; XVa cation, 81770-43-6; XVb, 81770-44-7; XVb cation, 81770-45-8; $Cr(CO)_6$, 13007-92-6; $Cr(CO)_3(NH_3)_3$, 14974-11-9; 4-bromoanisole, 104-92-7; 4-chloro-3,5-dimethylanisole, 6267-34-1; 4-chloro-3,5-dimethylphenol, 88-04-0.

Supplementary Material Available: A listing of the structure factor amplitudes (25 pages). Ordering information is given on any current masthead page.

Mechanism of Asymmetric Homogeneous Hydrogenation. Rhodium-Catalyzed Reductions with Deuterium and Hydrogen Deuteride

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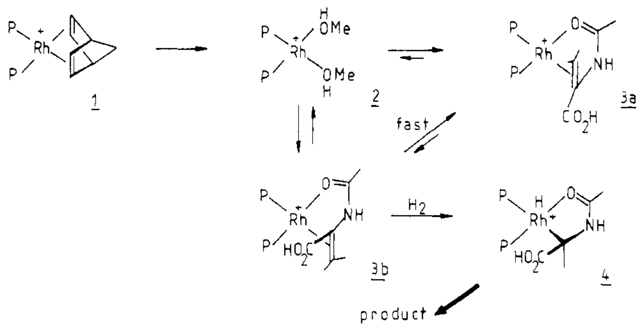
Propenoic acid, its tetramethylammonium salt, and *N*-vinylacetamide have been reduced with D_2 in methanol in the presence of a range of chiral rhodium bis(phosphine) ligands including (*RR*)-*trans*-4,5-bis((diphenylphosphino)methyl)-2,2-dimethyldioxolan ((*RR*)-diop), (*RR*)-1,2-bis((*o*-methoxyphenyl)-phenylphosphino)ethane ((*RR*)-dipamp), and (*SS*)-2,3-bis(diphenylphosphino)butane ((*SS*)-chiraphos). The optical purity of [2,3-$^2H_2$]propanoic acid was determined by ^2H NMR analysis of its (*S*)-methyl maldelate ester and that of *N*-[1,2-$^2H_2$]ethylacetamide by ^2H NMR analysis of *N*-ethylcamphanamide. In the former case, values of up to 60% were observed. Reduction of styrene with deuterium in the presence of ((*RR*)-diop)Rh complexes led to racemic product. Addition of HD to (*Z*)-acetamidocinnamic acid catalyzed by (diphos)-, (*RR*)-(dipamp)-, or (*RR*)-(diop)Rh complexes gave rise to a mixture of acetamido[2-^2H]- and acetamido[3-^2H]phenylalanine in which the former typically predominated by 1.35:1, whereas additions to octene, styrene, and *N*-vinylacetamide were not regioselective. The kinetic isotope effect (H_2 vs. D_2) for (diphos)Rh^+ catalyzed hydrogenation of (*Z*)-α-acetamidocinnamic acid is 1.22. Mechanistic implications are discussed.

Introduction

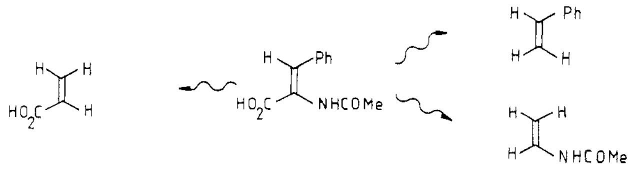
Recent research on asymmetric hydrogenation has been concerned with the preparation of new ligands,[1] reaction kinetics and X-ray identification of intermediates,[2] and the characterization of stable and transient species in solution by NMR.[3-5] The absolute configuration of intermediates may be inferred since the overall stereochemistry of hydrogenation is known,[6] and the mechanism shown in Scheme I is thus favored.

Speculations on the origin of stereoselectivity rely heavily on the numerous crystal structure determinations of chiral rhodium bis(phosphine) complexes[1c,e,2b,7] and the consistent conformational pattern first established by Knowles.[8] Opposed, C_2 related pairs of *P*-aryl rings are

Scheme I. Mechanism of Hydrogenation of Dehydroamino Acids by Chiral Rhodium Bis(phosphine) Complexes



Scheme II. "Dissection" of an Enamide into Component Monosubstituted Olefins



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(1) Inter alia; (a) MacNeil, P. R.; Roberts, N. K.; Bosnich, B. *J. Am. Chem. Soc.* 1981, *103*, 2273–80. (b) Meyer, D.; Poulin, J.-C.; Kagan, H. B.; Levine-Pinto, H.; Morgat, J. L.; Fromageot, P. *J. Org. Chem.* 1980, *45*, 4680. (c) Miyashita, A.; Yasuda, A.; Takaya, H.; Toriumi, K.; Ito, T.; Souchi, T.; Noyori, R. *J. Am. Chem. Soc.* 1980, *102*, 7932–4. (d) Samuel, O.; Couffingnal, R.; Laver, M.; Zhang, S. Y.; Kagan, H. B. *Nouv. J. Chim.* 1981, *5*, 15–21. (e) Ojima, I.; Kogure, T.; Yoda, N. *J. Org. Chem.* 1981, *45*, 4728–41. (f) Kashiwabara, K.; Hanoli, K.; Fujita, J. *Bull. Chem. Soc. Jpn.* 1980, *53*, 2275–80. (g) Valentine, D., Jr.; Sun, R. C.; Toth, K. *J. Org. Chem.* 1980, *45*, 3703–7; cf. preceding papers. (h) Koenig, K. E.; Bachman, G. L.; Vineyard, B. D. *Ibid.* 1980, *45*, 2362–5.

(2) (a) Chan, A. S. C.; Halpern, J. *J. Am. Chem. Soc.* 1980, *102*, 838–40. (b) Chan, A. S. C.; Pluth, J. J.; Halpern, J. *Ibid.* 1980, *102*, 5952–4.

(3) (a) Brown, J. M.; Chaloner, P. A. *J. Am. Chem. Soc.* 1980, *102*, 3040–8. (b) *J. Chem. Soc., Chem. Commun.* 1980, 344–6. (c) Brown, J. M.; Chaloner, P. A.; Parker, D.; Descotes, G.; Lafont, D.; Sinou, D. *Nouv. J. Chim.* 1981, *5*, 167–75.

(4) (a) Halpern, J.; Riley, D. P.; Chan, A. S. C.; Pluth, J. J. *J. Am. Chem. Soc.* 1977, *99*, 8056. (b) Brown, J. M.; Murrer, B. A. *Tetrahedron Lett.* 1979, 4859. (c) Brown, J. M.; Chaloner, P. A.; Kent, A. G.; Murrer, B. A.; Nicholson, P. N.; Parker, D.; Sidebottom, P. J. *J. Organomet. Chem.* 1981, *216*, 263. (d) Slack, D. A.; Greveling, I.; Baird, M. C. *Inorg. Chem.* 1979, *18*, 3125.

(5) Brown, J. M.; Chaloner, P. A.; Morris, G. E., in preparation.

(6) (a) Detellier, C.; Gelbard, G.; Kagan, H. B. *J. Am. Chem. Soc.* 1978, *100*, 7556. (b) Koenig, K. E.; Knowles, W. S. *Ibid.* 1978, *100*, 7561. (c) Kirby, G. W.; Michael, J. *J. Chem. Soc., Perkin Trans. 1* 1973, 115–20.

(7) (a) Knowles, W. S.; Vineyard, B. D.; Sabacky, M. J.; Stults, B. R. "Fundamental Research in Homogeneous Catalysis"; Tsutsui, M., Ed.; Plenum Press: New York 1980; p 523. (b) Ball, R. G.; Payne, N. C. *Inorg. Chem.* 1977, *16*, 1187. (c) Townsend, J. M.; Blount, J. F. *Ibid.* 1981, *20*, 269–71. (d) Cullen, W. R.; Einstein, F. W. B.; Huang, C. H.; Willis, A. C.; Yeh, E. S. *J. Am. Chem. Soc.* 1980, *102*, 988–93. (e) Ogha, Y.; Litaka, Y.; Achiwa, K. *Chem. Lett.* 1980, 861–4.

0276-7333/82/2301-0950$01.25/0