Journal of Organometallic Chemistry, 218 (1981) C25—C30
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary communication

THE ELECTROCHEMICAL GENERATION OF STABLE CATIONS OF ARENETRICARBONYLCHROMIUM COMPLEXES

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(Received April 23rd, 1981; in revised form July 27th, 1981)

Summary

The electrochemical oxidation of the mono- and bis-(tricarbonylchromium) complexes of dimethyldiphenyltin yield stable cations on the cyclic voltammetric time scale in contrast to usual arenetricarbonylchromium complexes. Oxidation of the mono-complex is a one-electron process yielding a stable cation while oxidation of the bis-complex is a two-electron process yielding a stable dication. 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. Similarly, the electrochemical oxidation of the tris-(tricarbonylchromium) complex of methyltriphenyltin is a three-electron process yielding a stable trication. All of the electrochemical data on the bis- and tris-complexes indicate that the arenetricarbonylchromium groups within each molecule are essentially noninteracting.

Results

Considerable interest has recently focused on the synthesis of organometallic mixed-valence compounds in the hope of producing new low dimensional highly conducting materials. We were interested in several new bis- and tris-(arenetricarbonylchromium) complexes in the hope that either oxidation or reduction might lead to new classes of mixed-valence species which might display high conductivity in the solid state. One convenient approach to the study of mixed-valence species and the determination of interaction or noninteraction between two identical moieties within a molecule appears to be a study of the molecule's redox properties. With this in mind, we examined the electrochemical redox properties of several mono- and bis-(tricarbonyl-

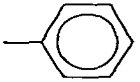
0022-328X/81/0000—0000/$ 02.50, © 1981, Elsevier Sequoia S.A.

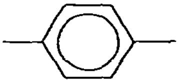
chromium) complexes of dimethyldiphenyltin and related derivatives as well as the mono-, bis-, and tris-complexes of methyltriphenyltin. These electrochemical studies indicate that the equivalent arenetricarbonylchromium groups in the bis- and tris-complexes are essentially noninteracting and do not yield mixed-valence compounds upon oxidation.

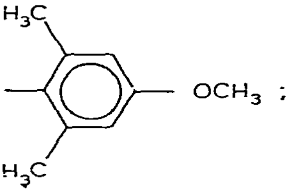
The electrochemical oxidations of arenetricarbonylchromium complexes have been previously reported and are characterized by a one-electron process [1,2]. However, these oxidations have usually been complicated by rapid follow-up reactions which result in overall multielectron processes along with destruction of the complex. We have found, however, that electrochemical oxidation of mono-, bis- and tris-(tricarbonylchromium) complexes (type I, type II, and type III, respectively) yield stable cations on the cyclic voltammetric time scale. Moreover, by appropriate substitution of the phenyl rings with electron-donating groups, the cations become much more persistent with half-lives over one hour under proper conditions of bulk electrolysis.

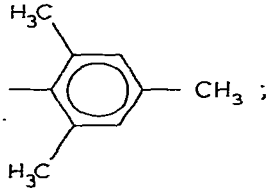
All the compounds [3] studied so far oxidize at approximately +0.8 V vs.

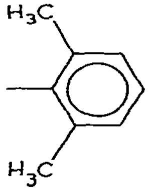
$(CH_3)_2Sn[ArCr(CO)_3]_2$

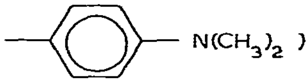
(IIa , Ar =  ;

IIb , Ar =  ;

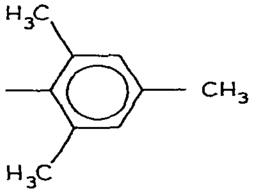
IIc , Ar =  ;

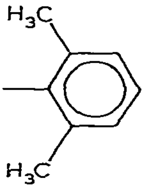
IId , Ar =  ;

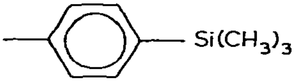
IIe , Ar =  ;

IIf , Ar = )

$(CH_3)_2Sn(Ar)[ArCr(CO)_3]$

(Ia , Ar =  ;

Ib , Ar =  ;

Ic , Ar = 

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

(IIIa , $n = 0$;
IIIb , $n = 1$;
IIIc , $n = 2$)

TABLE 1

Compound[a]	Temperature[b] (°C)	$(E_{p,a} + E_{p,c})/2$[c] (V)	ΔE_p (mv)	i_c/i_a	Scan rate (mV/sec)
Ia	0	+0.753	65	0.83	50
Ib	0	+0.747	70	0.61	50
Ic	0	+0.795	57	0.63	50
IIa	Amb.	+0.814	124	0.48	200
	0	+0.801	97	0.63	50
IIb	Amb.	+0.728	177	0.34	200
	0	+0.736	121	0.53	50
IIc	Amb.	+0.740	96	1.1	50
	0	+0.725	80	1.0	50
IId	Amb.	+0.780	97	1.0	50
	0	+0.769	79	1.0	50
IIe	Amb.	+0.793	150	0.53	50
	0	+0.787	98	0.91	50
IIf	Amb.	+0.572	105	0.40	50
	0	+0.565	95	0.56	50
IIIa	0	+0.825	143	0.56	50
IIIb	0	+0.830	139	0.61	50
IIIc	0	+0.833	77	0.63	50

[a] All compounds were at approximately 1 m*M* concentration in propylene carbonate with 0.25 *M* TEAP. [b] Amb is ambient temperature at 23 ± 2°C. [c] Potentials are vs. Ag/AgCl sat'd NaCl (aq.).

the Ag/AgCl reference electrode. The results are presented in Table 1. The corresponding free ligands (except the ligand corresponding to IIf which oxidizes at +0.76 V) show no oxidative electrochemistry out to the limits imposed by the solvents and supporting electrolytes (approximately +1.4 V in PC*). The first oxidation process of the complexes is diffusion controlled as demonstrated by the constant value of the current function and while another irreversible peak is observed, it is quite significant that this peak is 500 mV or more anodic of the first oxidation wave. This observation could be taken as indicating a single conjugated system. Such strongly interacting systems normally show two separate one-electron processes separated by 400 and 500 mV due to electron-electron repulsion and solvation effects [4—7], provided no chemical processes occur. However, noninteracting equivalent moieties within a molecule also show the same electrochemical features as the completely coupled system since each moiety exhibits the electrochemistry of the individual unit. Had the two phenyltricarbonylchromium groups been weakly interacting, a separation of perhaps only 100 mV between oxidation waves would have been expected. Noninteracting arenetricarbonylchromium groups are additionally supported by the fact that mono- and bis-complexes oxidize at essentially the same potential; however, the former is a one-electron process and the latter involves two electrons.

The anodic and cathodic peak separations in the cyclic voltammetric studies are considerably larger than expected for an electrochemically reversible one-electron oxidation, suggesting a quasireversible electrode process [8]. Despite the large peak separations, the oxidations exhibit the characteristics of a one-electron process. Coulometry experiments on Ia indicate a one-electron oxida-

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*PC = propylene carbonate;
TEAP = tetraethylammonium perchlorate.

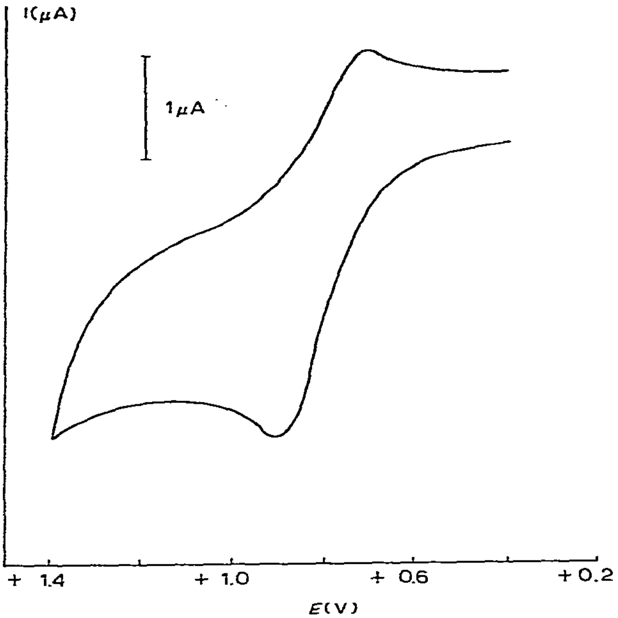

Fig. 1. Cyclic voltammogram of IIa, dimethylbis(phenyltricarbonylchromium)tin. 1 m*M* IIa in PC, 0.25 *M* TEAP, ambient temperature, 200 mV/sec, Pt disk.

tion. The extremely similar characteristics of the voltammograms of IIc made it also appear to be a one-electron process. However, the ratio of current heights for Ia to IIc is approximately 1/2 and coulometry of IId gives a two electron oxidation. This is all in accord with the model of Bard and Anson [12] for equivalent but noninteracting moieties in a molecule. The noninteraction is further demonstrated by calculation of an N_{bis} value, where N_{bis} is the number of electrons involved in the oxidation process. According to Bard and

$$N_{\text{bis}} = \frac{(i_{\text{bis}}/c_{\text{bis}})}{(i_{\text{mono}}/c_{\text{mono}})} \left(\frac{M_{\text{bis}}}{M_{\text{mono}}}\right)^{0.275} \tag{1}$$

Anson's model (eq. 1) where i is the anodic peak current, c the concentration and M the molecular weight. From data taken in PC, an N_{bis} value of 2.0 is calculated for complex IIc.

Likewise, the bis- and tris-complexes of methyltriphenyltin, IIIb and IIIa respectively, show voltammograms which appear to be one electron oxidations just as the mono-complex, IIIc, except that the current heights are double and triple that of the mono-complex. Calculations for N_{bis} gives a value of 2.0 and N_{tris} is calculated to be 3.0 from data taken in PC. It can be seen from the model of noninteracting equivalent moieties that the tris-complex has three such arenetricarbonylchromium groups.

Persistence of the cations is greatly affected by the temperature and solvent employed. The parent compound, IIa, shows only a small cathodic peak when cyclics are performed at ambient temperature in PC. Lowering the temperature to 0°C increases the lifetime of the cation. This same stabilization is seen for each of the compounds, although this is less dramatic for those complexes which have a ratio of i_c/i_a very close to unity already at ambient temperature.

However, the most effective way to increase the stability of the cations is by the presence and positioning of substituents on the phenyl rings. One well-known way to stabilize arene radical cations is to substitute the arene with methoxy groups. However, our attempt to stabilize our tricarbonylchromium cations by substituting the 4-position of the phenyl rings by an electron donating group, OCH_3, had no effect. Likewise, the even better stabilizing *N*,*N*-dimethylamino group did little to increase the lifetime of the cations although the peak potential of IIf is shifted approximately 250 mV cathodic of the parent complex. On the other hand, simultaneous substitution of the 2, 4 and 6 positions with donating groups produces a dramatic increase in the lifetime of the cations even at room temperature (Fig. 2). Notice that the ratio of cathodic to anodic currents is essentially unity (Table 1). It is interesting that substitution in only the 2 and 6 positions, compound IIe, causes little additional stability of the cation. We have therefore concluded that the persistence of the cation is a function of steric bulk around the phenyl ring which retards the attack of nucleophiles [13].

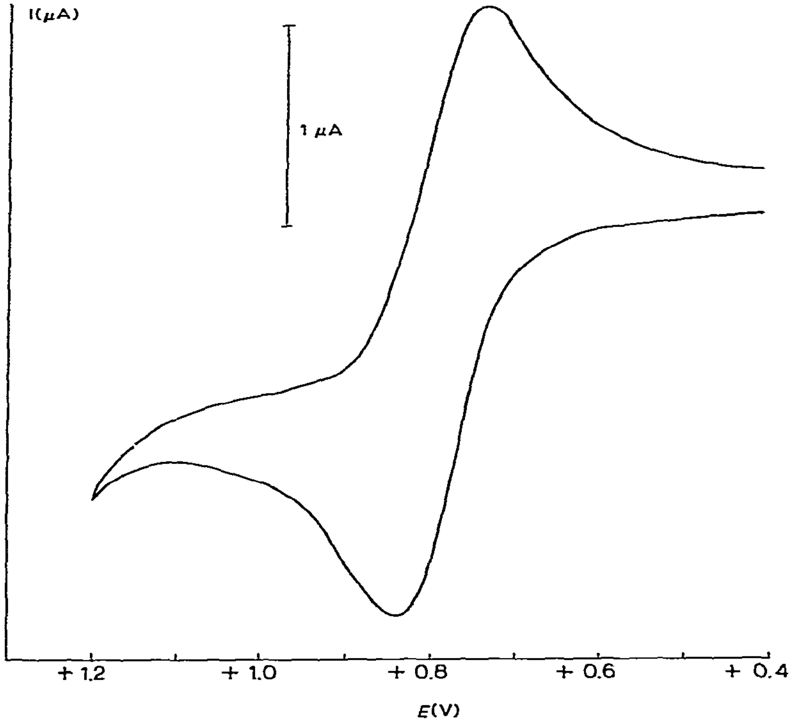

Fig. 2. Cyclic voltammogram of IId, dimethylbis(2,4,6-trimethylphenyltricarbonylchromium)tin. The conditions are 1 m*M* IId in PC, 0.25 *M* TEAP, ambient temperature, 50 mV/sec, Pt disk.

From the above data, it is clear that in the bis- and tris-complexes each arenetricarbonylchromium group is being oxidized to a cation with essentially no communication either conjugative or inductive with the other arenetricarbonylchromium groups in the molecule. Preliminary work on other

Group IVA analogs (Si, Ge, Pb) of complexes of type II show similar noninteraction between arenetricarbonylchromium groups. It would thus appear that attempts to prepare mixed-valence compounds employing arenetricarbonylchromium groups separated by one $(CH_3)_2M$ (M = Si, Ge, Sn, Pb) unit will fail. Electrochemical studies on other possible mixed-valence systems will be reported in the near future.

Acknowledgment. We gratefully acknowledge support of this work by the National Science Foundation, Grant No. CHE78-06661. We also would like to acknowledge a DuPont Fellowship to SNM.

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