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Stabilization of Electrochemically Produced Cations of (Arene)tricarbonylchromium Complexes by Trifluoroacetic Acid

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Several studies of the electrochemical oxidation of (arene)tricarbonylchromium complexes have been carried out.[2-5] Previous workers[4,5] have used voltammetric techniques to show the one-electron nature of these oxidations. However, in longer time-scale experiments in the solvent employed, the oxidations are usually complicated by rapid follow-up reactions, which result in overall multielectron processes along with destruction of the complex. During our investigations of the electrochemistry of (arene)tricarbonylchromium complexes, we discovered that the oxidation products of these complexes could be made rather persistent under proper solvent conditions.[2,3] Nevertheless, even propylene carbonate (PC), which makes possible the rather good persistence of these cations,[2,3] is not entirely successfuel toward this end.

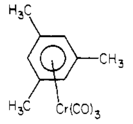
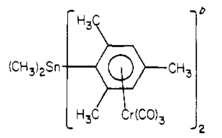
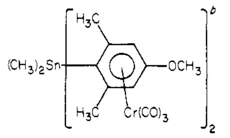
For this reason, we examined other solvent systems that might prove useful in further extending the lifetimes of (arene)tricarbonylchromium cations. Trifluoroacetic acid (TFAA) has been shown to be extremely useful in stabilizing cations of certain condensed aromatic compounds[6] and organometallic compounds[7] because of its low nucleophilicity. As a result of this low nucleophilicity, cations produced in TFAA are not as vigorously attacked. We wish to report in this note the extension of our studies of cations of (arene)tricarbonylchromium complexes. Our results show that oxidation of (arene)tricarbonylchromium complexes in TFAA media parallels previous accounts of successful use of TFAA as an electrochemical solvent[6,7] and gives cations that are extremely persistent even during very long-time-scale experiments.

Experimental Section

The complexes used in this study were either purchased from Strem Chemicals, Inc., or synthesized from $Cr(CO)_6$ by using standard procedures.[3,8] All synthesized compounds were characterized by IR, NMR, and mass spectroscopy. All work with solutions of the complexes was carried out under an atmosphere of prepurified argon. Dioxane and THF required as solvents for syntheses were freshly distilled from sodium–potassium alloy under argon. All other solvents were saturated with argon prior to use. Proton NMR spectra were recorded on a Perkin-Elmer 390 90-MHz spectrometer. Such spectra were taken in $CDCl_3$ with Me_4Si as the internal standard. Trifluoroacetic acid was syringed into the NMR tubes through a septum.

All electrochemical experiments were performed with use of 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 was Ag/AgCl, saturated NaCl(aq) buffered from the bulk TFAA solution by a bridge assembly containing PC. The junction potential at the TFAA/PC interface was considered negligible. The working electrode was a platinum disk. Coulometry was performed in a cell having four chambers, one for each electrode with a buffer chamber between the auxiliary and working chambers. The chambers are each separated from one another by glass frits.

Table I. Electrochemical Results

compd	$(E_{p,a} + E_{p,c})/2$,[a] V	ΔE_p, mV
$C_6H_6Cr(CO)_3$	+0.787	61
$(CH_3)_2Sn[C_6H_5Cr(CO)_3]_2$[b]	+0.783	61
$(CH_3)(C_6H_5)_2Sn[C_6H_5Cr(CO)_3]$[b]	+0.783	60
$(CH_3)(C_6H_5)Sn[C_6H_5Cr(CO)_3]_2$[b]	+0.784	61
$(CH_3)Sn[C_6H_5Cr(CO)_3]_3$[b]	+0.783	59
	+0.699	59
	+0.697	63
	+0.737	77[c]
$(C_6H_5{-}C_6H_5)Cr(CO)_3$	+0.786	69[c]

[a] Vs. the Ag/AgCl, saturated NaCl(aq) reference electrode. [b] Sn–aryl bonds cleaved by TFAA. [c] Without *iR* compensation.

TFAA was purchased from Aldrich Chemical Co. and used without further purification. Polarographic grade tetraethylammonium perchlorate was purchased from Eastman Chemical Co. and used without any further purification except for drying under vacuum at 70 °C for 1 h prior to use. The inert atmosphere for electrochemical experiments was argon of prepurified grade.

Cleavage of Dimethylbis[(2,4,6-trimethylphenyl)tricarbonylchromium-C^1]tin. In a 25-mL two-neck round-bottom flask containing a Schlenk filter apparatus and a rubber septum was placed the $Cr(CO)_3$ complex (0.395 g, 0.75 mmol). The flask was evacuated and filled with argon three times. A 50% hexane/50% $CHCl_3$ mixture (2 mL) was syringed in and stirred. TFAA (0.15 mL, 1.8 mmol) was then syringed in. After the mixture was stirred for a few more minutes, a white solid precipitated. The mixture was filtered, resulting in a clear, yellow solution. The solid, dimethylbis(trifluoroacetato)tin, was recrystallized three times from a 50% petroleum ether/50% CH_2Cl_2 mixture to give a melting point of 241–243 °C (lit.[9] mp 240–243 °C).

The yellow filtrate was subjected to vacuum (about 0.01 torr) to remove the solvents, unreacted TFAA, and mesitylene. The resulting yellow solid, (mesitylene)tricarbonylchromium, was obtained in 92% yield. This was recrystallized three times from hexane to give shiny yellow crystals: isolated sample mp 174–175 °C; authentic sample mp 174–175 °C. A mixture melting point experiment with an authentic sample exhibited no depression of the melting point. Isolated sample ^1H NMR ($CDCl_3$): δ 4.89 (s, 3 H, aromatic protons, complexed ring), 2.20 (s, 9 H, methyl protons, complexed ring). Authentic

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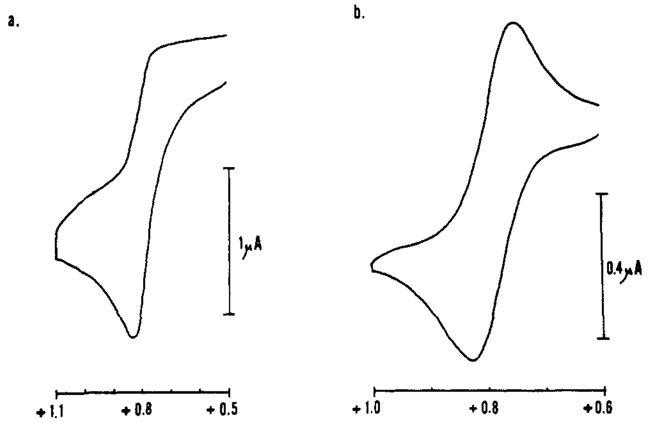

Figure 1. Cyclic voltammograms of (biphenyl)tricarbonylchromium (BPTC): (a) 1 mM BPTC in PC (0.25 M tetraethylammonium perchlorate, 0 °C, Pt-disk electrode, 200 mV/s; (b) 1 mM BPTC in TFAA (0.1 M tetraethylammonium perchlorate), 0 °C, Pt-disk electrode, 20 mV/s. Potentials are vs. the Ag/AgCl, saturated NaCl (aq) reference electrode.

sample ^1H NMR ($CDCl_3$): δ 4.89 (s, 3 H, aromatic protons, complexed ring), 2.20 (s, 9 H, methyl protons, complexed ring) (lit.[10] δ 4.884 and 2.194, respectively). Isolated sample IR (Nujol): 1969 (s), 1896 (s) cm^{-1}. Authentic sample IR (Nujol): 1969 (s), 1896 (s) cm^{-1}.

Results and Discussion

Cyclic voltammetric studies showed the oxidation process to be highly chemically reversible when performed in TFAA. It was demonstrated[2,3] that in propylene carbonate, complexes that do not have steric bulk around the ring exhibit poor chemical reversibility. For example, in PC the cyclic voltammogram of (biphenyl)tricarbonylchromium exhibits essentially no reduction peak on the reverse scan until scan rates approaching 1 V/s and higher are used. In contrast, cyclic voltammograms of (biphenyl)tricarbonylchromium taken in TFAA show that the cation possesses excellent chemical reversibility on the time scale of this experiment, exhibiting a ratio of cathodic to anodic current of unity even with scan rates as low as 20 mV/s. See Figure 1. Obviously, TFAA enhances the lifetime of the cation. Complexes with steric bulk around the ring such as (mesitylene)tricarbonylchromium also exhibited very persistant cations when oxidized.

Like the previous studies,[4,5] the features of the cyclic voltammogram indicate one-electron oxidation. Separation of the anodic and cathodic peaks is 60 mV. Diffusion control is indicated by a constant-current function and direct dependence of the current height on concentration.

In TFAA, cations such as the one produced from (mesitylene)tricarbonylchromium are persistent enough to perform Coulometric experiments, which require approximately 1 h to complete. The amount of charge passed proves the oxidation process to be one electron. The resulting cation can be reduced back to starting material with nearly the same amount of charge passed. Cycles of oxidation and subsequent reduction can be performed with only relatively minor degradation of the complex occurring. Solutions of the neutral complex are clear yellow while solutions of the cation are also clear but exhibit a deeper yellow color.

From these results, it is seen that 17-electron cations of these (arene)tricarbonylchromium compounds can be made to exist with half-lives on the order of hours in some cases.[11] All that is required is the judicious adjustment of conditions since these cations are susceptible to attack by nucleophiles. Trifluoroacetic acid possesses sufficiently low nucleophilicity so as to permit long-term persistence of the cation. In this respect, it supersedes previous solvents[2-5] used for electrochemical oxidation studies of (arene)tricarbonylchromium complexes. No longer is steric bulk around the ring required to stabilize the cations although this would still presumably be useful.

Because TFAA is a strong acid, a conceivable area of concern in using it as a solvent was the possibility it might react with the complexes, especially by protonation. It has been demonstrated[12] that certain arene–chromium organometallic compounds will protonate with TFAA, but such compounds have one or more phosphine ligands present. Protonation of (arene)tricarbonylchromium complexes by TFAA requires the presence of $BF_3{\cdot}H_2O$.[12] Thus the compounds studied here appear to be secure from such reaction. The hydrogen isotope exchange reaction was also studied[13] for (arene)tricarbonylchromium complexes. However, it, too, is of no consequence for the compound studied here since it leaves the compound unchanged.

The use of TFAA as a solvent did present one problem. Although it would have been of extreme value in our studies of the interaction of (arene)tricarbonylchromium groups,[2,3] it was not possible to use TFAA as a solvent for dimethyldiaryltin complexes. Tin–arene bonds are susceptible to scission by acids and electrophiles[14] including TFAA.[15] Ordinarily, the bond-rupture reaction is slowed by electron-withdrawing groups,[16] but we have found the process to be extremely facile even in the presence of the strong electron-withdrawing $Cr(CO)_3$ group. Steric acceleration[17] may be responsible. Nevertheless, the electrophilic aromatic substitution of H for Sn by TFAA appears to occur virtually instantaneously upon dissolution. An NMR spectrum of dimethylbis(phenyltricarbonylchromium-*C*^{1})tin, taken as rapidly as possible after dissolution in TFAA, is identical with that of (benzene)tricarbonylchromium in TFAA except for the $Sn{-}CH_3$ resonances of the former. Spectra taken in $CDCl_3$ are quite different as would be expected since the since the Sn–phenyl bond remains intact and does not form (benzene)tricarbonylchromium. In $CDCl_3$ a multiplet is found for dimethylbis(phenyltricarbonylchromium-*C*^{1})tin instead of a singlet as in TFAA.

Additional evidence for this $Sn{-}ArCr(CO)_3$ bond cleavage was seen in the NMR of dimethylbis[(2,4,6-trimethylphenyl)tricarbonylchromium-*C*^{1}]tin in the presence of TFAA. Integration of the NMR revealed three ring protons and nine methyl protons for both the complexed and uncomplexed rings. When cleaved by CF_3COOD instead, the integration ratio is 2 H:9 H. Furthermore, the $Sn{-}Ar_{H_{meta}}$ coupling constants observed in $CDCl_3$ disappear upon cleavage by TFAA. Clearly, even in the presence of a complexed tricarbonylchromium group, tin–arene bonds are readily cleaved by TFAA.

On the basis of the NMR results, experiments were performed to isolate the products of the cleavage reaction. When

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[11] Examination of cyclic voltammetric data indicates that the cations are infinitely persistent. Coulometric experiments show that a half-life between 1 and 1.5 h occurs in the worst examples and is probably directly attributable to residual oxygen or the migration of reduction products formed at the auxiliary electrode into the working chamber.

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a solution of dimethylbis[(2,4,6-trimethylphenyl)tricarbonylchromium-C^1]tin was treated with TFAA, (mesitylene)tricarbonylchromium and dimethylbis(trifluoroacetato)tin were isolated in greater than 90% yield (crude) and identified by using standard procedures. Uncomplexed mesitylene was also seen in the crude NMR of the liquid fraction after removal of the above two solids. The results confirmed the scission of the tin–arene bond and the substitution of H for Sn on the arene ring.

In conclusion, trifluoroacetic acid has been shown to be most effective in stabilizing (arene)tricarbonylchromium cations produced by one-electron oxidative electrolysis. Although not as easy to handle as other conventional electrochemical solvents due to its corrosive and toxic properties, these do not present any extraordinary problems.

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Registry No. $C_6H_6Cr(CO)_3$, 12082-08-5; $(CH_3)_2Sn[C_6H_5Cr(CO)_3]_2$, 31833-53-1; $(CH_3)(C_6H_5)_2Sn[C_6H_5Cr(CO)_3]$, 80031-89-6; $(CH_3)(C_6H_5)Sn[C_6H_5Cr(CO)_3]_2$, 80043-66-9; $(CH_3)Sn[C_6H_5Cr(CO)_3]_3$, 80031-87-4; $(C_6H_5–C_6H_5)Cr(CO)_3$, 12111-60-3; Sn, 7440-31-5; dimethylbis[(2,4,6-trimethylphenyl)tricarbonylchromium-C^1]tin, 80031-84-1; (mesitylene)tricarbonylchromium, 12129-67-8; dimethylbis[(2,6-dimethyl-4-methoxyphenyl)tricarbonylchromium-C^1]tin, 80031-96-5; dimethylbis(trifluoroacetato)tin, 650-22-6; TFAA, 76-05-1.

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Comparison of Carbon-13 and Phosphorus-31 Nuclear Magnetic Resonance Data and E° Values for a Series of Chromium Pentacarbonyl Complexes

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A common feature of many studies involving physical measurements of organic or inorganic compounds is the comparison of parameters obtained via one technique with those obtained from very different techniques. In many instances linear correlations are observed, usually in the form of free energy relationships, and these may be used in a variety of ways in the analysis of spectroscopic, thermodynamic, and kinetic data. The most widely used linear free energy relationship is probably associated with the correlation of a spectral, electrochemical, or other parameter with Hammett's substituent constants.[4,5]

Comparisons of electrochemical data, $E_{1/2}$ or E° (standard reduction potential), with almost every conceivable spectroscopic or other parameter and other permutations and combinations relevant to electrochemistry have been reported as perusal of ref 6–22 would indicate. However, with nuclear magnetic resonance, NMR, apart from some proton work where both the NMR $\delta(^1H)$ chemical shift and $E_{1/2}$ may correlate with acidity constants,[22] little is known. In fact for nuclei other than the proton, chemical shift changes are frequently not well understood.[23] For example, mercury-199 chemical shifts vary in a fashion that is certainly not always explained by the usual substituent inductive, mesomeric, or electronic effect.[24,25]

In electrochemical measurement, E° values reflect an energy difference between two oxidation states. This is a free energy term of thermodynamic significance, which may be either measured directly or calculated from polarographic or voltammetric measurements for reversible electrode processes (approximately equal to $E_{1/2}^{\mathrm{rev}}$). Substituent effects related to E° or $E_{1/2}^{\mathrm{rev}}$ may therefore be readily understood, as they have their origin in thermodynamic terms only. If the electrode processes are not diffusion controlled (Nernstian or reversible) and are governed by the rate of a chemical step or electron transfer, substituent effects related to $E_{1/2}^{\mathrm{irr}}$ are more difficult to interpret because kinetic as well as thermodynamic considerations apply.

In NMR spectroscopy chemical shifts may be influenced by inductive and mesomeric (acid–base) effects as is frequently the case with E° values. In such cases direct correlation between NMR and electrochemical measurements could be expected. However, steric as opposed to electronic effects may introduce additional complications. Since electrochemical measurements reflect energy differences between two oxidation states, the steric term may not be important with respect to a difference measurement if the two oxidation states are essentially isostructural. In contrast, the NMR data can be considered to originate from only half of the redox couple, so that steric effects may have a different influence on chemical shifts than on E° values. Correlation or lack of correlation could therefore provide a method for better understanding the origin of chemical shifts, particularly for nuclei other than

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