**2,5-Bis(trimethylstannyl)-1,2,5-triethyl-3,4-dimethyl-3-borolene (12).** To a solution of **6** (4.5 g, 15 mmol) in 40 mL of hexane was added **3** (3.0 g, 15 mmol). This mixture was heated at 60 °C for 12 h. The clear solution was cooled to −78 °C and kept at this temperature for 6 h. The colorless crystalline **12** was filtered off and washed twice with pentane at −78 °C: yield 4.75 g (63%); mp 45–48 °C. Anal. Calcd for $C_{18}H_{39}BSn_2$: C, 42.9; H, 7.8. Found: C, 42.5; H, 7.7.

Alternatively, fractional distillation of the reaction mixture after the hexane had been evaporated gave a yellowish oil (5.8 g), bp 95–115 °C ($10^{-3}$ torr) which crystallized after 5 days. $^1H$ NMR showed ca. 90% pure **12** to be present. Recrystallization from pentane at −78 °C yielded 3.8 g (50.4%) of pure **12**: mp 45–48 °C; IR (in hexane) $\nu_{C=C}$ 1682 (w), 1695 (w, sh), 1705 (w) $cm^{-1}$; mol wt in $C_6H_6$, 510 (calcd 503.7); MS (70 eV, 25 °C), *m/e* (relative intensities) 506 (M, 1.1), 491 (M − Me, 0.3), 341 (M − $Me_3Sn$, 41), 165 ($Me_3Sn$, 100).

**Acknowledgment.** Support of this work by the Deutsche Forschungsgemeinschaft and by the Fonds der Chemischen Industrie is gratefully acknowledged.

**Registry No. 2**, 87184-05-2; **3**, 1692-19-9; **6**, 87184-06-3; **12**, 87184-07-4; **14**, 87184-04-1.

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# Electrochemical, Chemical, and Spectroscopic Characterization of the *trans*-[Tetracarbonylbis(triphenylphosphine)chromium]$^{+/0}$ Redox Couple

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*Received March 25, 1983*

Electrochemical oxidation of *trans*-$Cr(CO)_4(PPh_3)_2$ at mercury, silver, or platinum electrodes or chemical oxidation with $AgClO_4$, $NOPF_6$ or $NOBF_4$ produces *trans*-$[Cr(CO)_4(PPh_3)_2]^+$. The 17-electron monomeric cation has been characterized by analysis and a wide variety of electrochemical (polarographic, voltammetric, and controlled potential electrolysis) and spectroscopic (infrared, electron spin resonance) techniques. *trans*-$[Cr(CO)_4(PPh_3)_2]^+$ is light and moisture sensitive and unlike *trans*-$Cr(CO)_4(PPh_3)_2$ reacts relatively rapidly with acetonitrile, acetone, iodide, and bromide as well as water. All reactions studied produce *trans*-$Cr(CO)_4(PPh_3)_2$ as a product, in some cases (bromide and iodide) by redox reactions and in others by disproportionation. Electron-transfer catalysis reactions initiated via the ligand, L, substitution reaction *trans*-$[Cr(CO)_4(PPh_3)_2]^+ + L \rightarrow$ *trans*-$[Cr(CO)_4PPh_3L]^+ + PPh_3$ do not appear to be favored, although the observation of $Cr(CO)_5PPh_3$ as a reaction product with CO in the presence of light suggests that this step may be light catalyzed. This reaction, if it occurs, is a slow step relative to other pathways, and the $[Cr(CO)_4(PPh_3)_2]^{+/0}$ redox couple is not a good candidate for electron-transfer catalysis.

## Introduction

Recently, much interest has been shown in the area of inorganic electron-transfer and catalysis.[3-10] Metal carbonyl complexes have attracted considerable attention in these studies. An example of a basis for catalysis is thought to be as follows: oxidation of a monomeric 18-electron carbonyl produces a relatively reactive 17-electron species (the catalyst). This species may react with the solvent or a deliberately added ligand to produce a new 17-electron complex that thermodynamically, at least, can react with the starting material in a homogeneous redox reaction to generate the final desired substituted 18-electron carbonyl complex and regenerate the catalyst. Equations 1–3 give

$$M(CO)_4P_2 \rightleftharpoons [M(CO)_4P_2]^+ + e \qquad (1)$$

$$[M(CO)_4P_2]^+ + L \rightleftharpoons [M(CO)_4PL]^+ + P \qquad (2)$$

$$[M(CO)_4PL]^+ + M(CO)_4P_2 \rightarrow M(CO)_4PL + [M(CO)_4P_2]^+ \qquad (3)$$

a typical scheme for a tetracarbonyl bis(phosphine) complex in a catalytic system (L = ligand, P = phosphine, M = metal). The thermodynamic requirement for this cycle to operate is that $E°$ for the $[M(CO)_4P_2]^{+/0}$ redox couple must be less positive than the $E°$ of the $[M(CO)_4PL]^{+/0}$ couple.

In the reported catalytic studies on carbonyl compounds it has been rare for the seventeen electron intermediate to be isolated and fully characterized, but for a detailed understanding of electron-transfer catalysis it is essential that the chemistry of the catalyst be known. In particular, detailed knowledge of alternative reaction pathways and methods for systematically minimizing their influence is a necessary prerequisite to achieving high catalytic activity.

Hershberger et al.[7] in a survey of carbonyl complexes briefly mentioned that the compound *trans*-$Cr(CO)_4(PPh_3)_2$ shows a chemically reversible oxidation cyclic

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voltammogram in acetonitrile, but the 17-electron complex was not characterized and the possibility of the use of this species in electron-transfer catalysis was not explored in any detail.

In this paper we report a detailed study of the redox couple

$$trans\text{-}Cr(CO)_4(PPh_3)_2 \rightleftharpoons trans\text{-}[Cr(CO)_4(PPh_3)_2]^+ + e^- \quad (4)$$

including isolation of *trans*-$[Cr(CO)_4(PPh_3)_2]^+$ and a study of its chemistry and reactivity in an endeavor to determine whether such a redox couple can be useful in the area of electron-transfer catalysis and to determine which factors aid or inhibit catalytic activity. Our previous studies[11-13] have indicated that pathways alternative to catalysis are available, but a systematic examination of this area has yet to be considered.

## Experimental Section

**Materials.** All solvents were of AR grade and were dried by using 4A molecular sieves. *trans*-$Cr(CO)_4(PPh_3)_2$ was prepared by the literature method.[14] *trans*-$[Cr(CO)_4(PPh_3)_2]^+$ was prepared by three methods: (a) slight excess of $AgClO_4$ was added to a solution of *trans*-$Cr(CO)_4(PPh_3)_2$ in dichloromethane under a nitrogen atmosphere in the absence of light. The yellow solution rapidly turned deep blue, and after 15 min the product, as its perchlorate salt, was precipitated by addition of *n*-hexane. It was recrystallized by dissolving it in dichloromethane and rapidly reprecipitating by addition of *n*-hexane. The solid was stored in the dark under refrigeration. (b) *trans*-$Cr(CO)_4(PPh_3)_2$ was oxidized by using $NOPF_6$. The reaction was slower, and the product was isolated as its $PF_6$ salt as described above. Use of $NOBF_4$ gave similar results. (c) Electrochemical oxidation of *trans*-$Cr(CO)_4(PPh_3)_2$ was carried out as described later in the text. Anal. Calcd for $[Cr(CO)_4(PPh_3)_2]ClO_4$: C, 60.9; H, 3.84; P, 7.86. Found: C, 60.1; H, 3.84; P, 7.90.

**Instrumentation. Electrochemical Measurements.** Polarograms and voltammograms were obtained with an E.G. and G. PAR Model 174A polarographic analyzer in a conventional three-electrode cell at 18 °C unless otherwise stated. The working electrode was either mercury (dropping or hanging drop) or platinum. For cyclic voltammetry, the platinum working electrode was used in the form of a disk or wire in a stationary mode. A vibrating platinum electrode was constructed by attaching the platinum wire working electrode to the arm of the polarographic drop knocker supplied with the PAR 174A polarographic analyzer. The wire electrode can be periodically displaced sideways in solution from its normal vertical position via the horizontal motion of the drop knocker arm. The displacement can be initiated by the electronic circuitry conventionally used to control the drop time in polarographic measurements. A steady-state response at platinum electrodes can be generated in this manner.

The reference electrode was Ag/AgCl (saturated LiCl; $CH_2Cl_2$). The auxiliary electrode was a platinum wire. Measurements were made in dichloromethane (0.1 M $Bu_4NClO_4$), acetone (0.1 M $Et_4NClO_4$), and acetonitrile (0.1 M $Et_4NClO_4$). All solutions were degassed with nitrogen and maintained under a nitrogen atmosphere throughout the measurements. Positive feed back circuitry was used to minimize ohmic *iR* drop losses.

Controlled potential electrolysis experiments were performed with a PAR Model 173 potentiostat/galvanostat. A three-electrode configuration was used with a platinum gauze working electrode. A potential of 1.0 V vs. the Ag/AgCl reference electrode was used. The auxiliary electrode was a platinum gauze separated from the bulk solution by a salt bridge containing a porous Vycor plug. Coulometric determination of the number of electrons involved in the oxidation was measured by a PAR Model 179 digital coulometer. For an *n* value of unity to be obtained, it was found to be essential to continuously purge the solution with nitrogen during the electrolysis and to rigorously exclude light by a combination of aluminium foil around the electrochemical cell and by working in the dark at night.

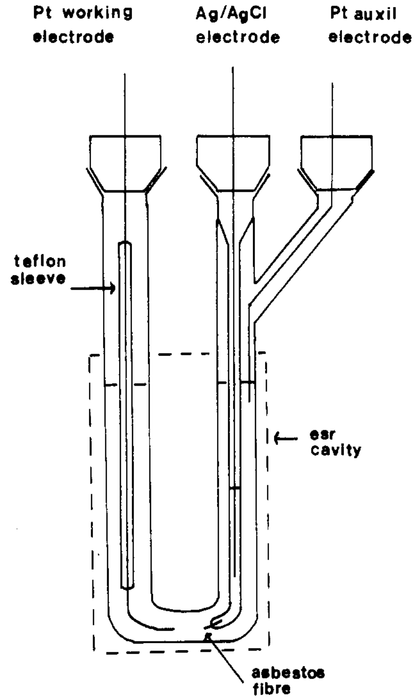

**Figure 1.** Diagrammatic sketch of the cell used for electrochemical measurements within the cavity of the ESR spectrometer. The diagram is broadened for clarity of the details. The actual cell is approximately 1 cm wide and 8 cm long.

**Spectroscopic Measurements.** Infrared spectra were recorded by using a Perkin-Elmer 457 spectrometer. NMR spectra were recorded on a JEOL FX 100 spectrometer using external $^7Li$ lock and a JEOL NM 5471 temperature controller calibrated against a platinum resistance thermometer. Phosphorus-31 NMR spectra were recorded at 40.26 MHz in dichloromethane solution and referenced against external 85% $H_3PO_4$. High-frequency positive convention is used. Magnetic moments in solution were measured by the Evans method[15] over a temperature range using the proton lines of both $CH_2Cl_2$ and $CH_3CN$ at 99.60 MHz.

ESR spectra were obtained with an X-band reflection type spectrometer employing phase-sensitive detection at 100 KHz.[16] A microprocessor interface was used for fast data acquisition and signal averaging. A cell was constructed for in situ generation of the 17-electron species and other electrochemical measurements within the cavity of the ESR spectrometer, and it is shown diagrammatically in Figure 1. The design of this cell is aimed at overcoming the problem of high ohmic *iR* drop, especially in solvents of low dielectric constant, even with high concentrations of supporting electrolyte. Platinum or silver working electrodes may be used. The electrode is covered with a Teflon sleeve exposing only the tip to the solution. The potential of the tip is monitored by a Ag/AgCl reference electrode isolated from the solution by a salt bridge with an asbestos fiber at a maximum of 2 mm from the tip surface. This minimizes inaccuracy in the potential measurement. The platinum auxiliary electrode may also be isolated by using a similar salt bridge if necessary. The cell requires a sample volume of less than 1 cm$^3$, and a good compromise between cavity Q and solution volume is achieved. High cell resistance still occurs but is mimimized by using positive feedback ohmic compensation. The cell can be operated under vacuum or under a nitrogen atmosphere, and variable-temperature

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Table I. Summary of Electrochemical Data for the *trans*-$[Cr(CO)_4(PPh_3)_2]^{+/0}$ Redox Couple at 18 °C

| compd | electrode | solv | $E_{1/2}$,[a] V | $(E_p)_{Ox}$,[b] V | $(E_p)_{Red}$,[c] V | $\Delta E$, mV |
|---|---|---|---|---|---|---|
| *trans*-$Cr(CO)_4(PPh_3)_2$ | Hg | $CH_2Cl_2$ | 0.65 | 0.72 | 0.62 | 100 |
| *trans*-$Cr(CO)_4(PPh_3)_2$ | Pt | $CH_2Cl_2$ | 0.66 | 0.74 | 0.57 | 170 |
| *trans*-$Cr(CO)_4(PPh_3)_2$ | Pt | $(CH_3)_2CO$ | 0.66 | 0.70 | 0.62 | 80 |
| *trans*-$Cr(CO)_4(PPh_3)_2$ | Pt | $CH_3CN$ | 0.66 | 0.71 | 0.60 | 110 |
| *trans*-$[Cr(CO)_4(PPh_3)_2]ClO_4$ | Hg | $CH_2Cl_2$ | (0.65) | (0.72) | (0.62) | 100 |
| *trans*-$[Cr(CO)_4(PPh_3)_2]PF_6$ | Hg | $CH_2Cl_2$ | (0.67) | (0.73) | (0.62) | 110 |
| *trans*-$[Cr(CO)_4(PPh_3)_2]PF_6$ | Pt | $CH_2Cl_2$ | (0.66) | (0.75) | (0.59) | 160 |

[a] $E_{1/2}$ for polarographic oxidation or reduction (parentheses) at dropping mercury electrode or vibrating platinum electrode. [b] $(E_p)_{Ox}$ is the oxidation peak potential under conditions of cyclic voltammetry at a scan rate of 500 mV $s^{-1}$. Parentheses indicate values obtained from reduction of *trans*-$[Cr(CO)_4(PPh_3)_2]^+$. [c] $(E_p)_{Red}$ is the reduction peak potential of cyclic voltammetry, other conditions as for footnote *b*.

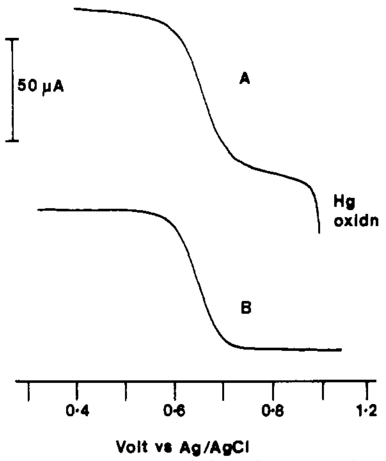

**Figure 2.** A. A current sampled dc polarogram for the oxidation of a $10^{-3}$ M solution of *trans*-$Cr(CO)_4(PPh_3)_2$ in dichloromethane (0.1 M $Bu_4NClO_4$) at 18 °C (drop time 0.5 s). B. A dc voltammogram at a vibrating platinum electrode for the oxidation of a similar solution.

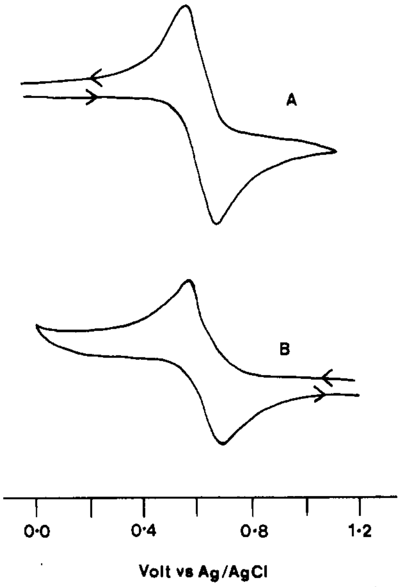

**Figure 3.** A. Cyclic voltammogram for the oxidation of a $10^{-3}$ M solution of *trans*-$Cr(CO)_4(PPh_3)_2$ in dichloromethane (0.1 M $Bu_4NClO_4$) at 18 °C at a platinum electrode (scan rate 500 mV $sc^{-1}$). B. Cyclic voltammogram for the reduction of a $10^{-3}$ M solution of *trans*-$[Cr(CO)_4(PPh_3)_2]^+$ under the same conditions.

measurements over the temperature range −150 to +40 °C are possible.

Controlled potential electrolysis to generate the 17-electron species may be carried out within the spectrometer cavity. Cyclic voltammetry and pulse voltammetry can be performed simultaneously with ESR monitoring.

## Results and Discussion

All studies were carried out in dichloromethane solution unless otherwise stated.

**(a) Polarography of *trans*-$Cr(CO)_4(PPh_3)_2$** Figure 2A is a current sampled dc polarogram for the oxidation of *trans*-$Cr(CO)_4(PPh_3)_2$ in dichloromethane which shows a single well-defined oxidation wave just prior to the oxidation of the mercury electrode. A plot of $E$ (potential) vs. log $(i_d - i)/i$ (where $i_d$ is the diffusion-controlled limiting current and $i$ is the current) is linear with a slope of −59 mV consistent with an electrochemically reversible one-electron oxidation. The $E_{1/2}$ value (half-wave potential) was found to be +0.65 V vs. Ag/AgCl at the dropping mercury electrode (dme). $E_{1/2}$ was essentially independent of drop time and concentration implying that the oxidation process is probably both chemically and electrochemically reversible. Polarographic data are summarized in Table I.

**(b) Direct Current Voltammetry at a Vibrating Platinum Electrode.** In previous work it has been shown[17-19] that oxidation of metal carbonyl complexes may occur via different mechanisms depending upon the identity of the metal electrode. Consequently oxidation of *trans*-$Cr(CO)_4(PPh_3)_2$ was investigated at a vibrating platinum electrode that mimics the dme with respect to electrochemical characteristics. The oxidation wave for *trans*-$Cr(CO)_4(PPh_3)_2$ in dichloromethane is shown in Figure 2B and is very similar, and with almost identical $E_{1/2}$, to that observed at the dme, implying that mercury has no thermodynamic effect on the oxidation.

**(c) Cyclic Voltammetry at Mercury and Platinum Electrodes.** The cyclic voltammograms for the oxidation of *trans*-$Cr(CO)_4(PPh_3)_2$ in dichloromethane at both platinum and mercury hanging drop electrodes are chemically reversible. Figure 3A shows the current–voltage curve at platinum, and numerical data are given in Table I. However, the peak to peak separations are greater than predicted for Nernstian behavior at the scan rates used. The heterogeneous charge-transfer rate constant at platinum is less than at mercury, but in both cases a quasi-reversible electron-transfer step is indicated on the time scale of these measurements.

Cyclic voltammograms at platinum for the oxidation of *trans*-$Cr(CO)_4(PPh_3)_2$ in acetone (0.1 M $NEt_4ClO_4$) and acetonitrile (0.1 M $NEt_4ClO_4$) were almost identical with respect to $E_{1/2}$ to that in dichloromethane (Table I), although the complex was only very sparingly soluble in these solvents (especially acetonitrile). Within the limits of experimental error the oxidations were chemically reversible on this time scale and the solvent does not appear to play a significant role in the reaction mechanism. The

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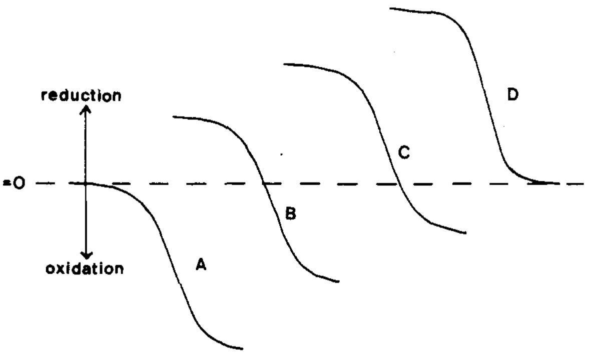

**Figure 4.** Polarographic monitoring between +0.4 and +0.85 V vs. Ag/AgCl during the course of oxidative electrolysis of a $10^{-3}$ M solution of *trans*-$Cr(CO)_4(PPh_3)_2$ in dichloromethane (0.1 M $Bu_4NClO_4$) at 18 °C at night: A, original solution; B and C, mixtures of *trans*-$Cr(CO)_4(PPh_3)_2$ and *trans*-$[Cr(CO)_4(PPh_3)_2]^+$; D, solution containing only *trans*-$[Cr(CO)_4(PPh_3)_2]^+$.

acetonitrile result is consistent with that reported earlier.[7]

**(d) Oxidative Controlled Potential Electrolysis.** Oxidative controlled potential electrolysis in the dark at a platinum electrode at 1.0 V vs. Ag/AgCl in dichloromethane (0.1 M $Bu_4NClO_4$ at 18 °C) gave an *n* value of 1.02 ± 0.02 electrons. However, if the experiment was not protected from light, apparent *n* values significantly greater than unity were obtained. During the course of the electrolysis the color of the solution changed from very pale yellow to deep blue.

Polarographic monitoring of the solution during the course of the oxidative electrolysis showed constant $E_{1/2}$ and a constant diffusion-controlled current, but the proportion of oxidative and reductive components gradually changed until at the Coulombic count corresponding to a complete one electron transfer, the polarogram was entirely reductive as shown in Figure 4.

**(e) Chemical Oxidation with $NOPF_6$ and $NOBF_4$.** Chemical oxidation of *trans*-$Cr(CO)_4(PPh_3)_2$ in dichloromethane with either $NOPF_6$ or $NOBF_4$ produced a deep blue color similar to that observed during the electrolysis experiments. Polarographic monitoring of the solution during the slow chemical oxidation produced a polarographic response essentially identical with that described for the electrolysis experiments, which indicates that the same product was formed and that NO is not coordinated to chromium when a nitrosyl salt is used.

**(f) Isolation and Characterization of the Oxidation Product.** After completion of the chemical oxidation of *trans*-$Cr(CO)_4(PPh_3)_2$ with $NOPF_6$, $NOBF_4$, or $AgClO_4$ the blue complex could be isolated as detailed in the Experimental Section. Analytical data for the perchlorate indicated the formula $[Cr(CO)_4(PPh_3)_2]ClO_4$ which is entirely consistent with the electrochemical data given above.

Although the observation of a chemically reversible redox couple is now recognized *not* to be conclusive proof of retention of stereochemistry,[20] in the present situation it does seem highly likely that the cation has the trans configuration because Mingos[21] has shown that trans isomers are electronically as well as sterically favored in 17-electron complexes. Thus, in this case, where the starting material is an 18-electron trans species, theoretical considerations support the expectation of a trans 17-electron complex. However, spectroscopic data are required to support this hypothesis.

The Nujol mull infrared spectrum of $[Cr(CO)_4(PPh_3)_2]^+$ shows a single carbonyl stretch at 1990 $cm^{-1}$ (cf. $Cr(CO)_4(PPh_3)_2$, $\nu_{CO}$ = 1880 $cm^{-1}$) which confirms the trans stereochemistry of the cation, and the difference in the stretching frequencies is as expected for the charge on the cation. However, infrared spectra in dichloromethane solution always show the presence of *trans*-$Cr(CO)_4(PPh_3)_2$ (and subsequently $Cr(CO)_5PPh_3$) as well as *trans*-$[Cr(CO)_4(PPh_3)_2]^+$. This is related to the light sensitivity of *trans*-$[Cr(CO)_4(PPh_3)_2]^+$ (and is unavoidable for infrared measurements) as solutions exposed to the light turned yellow within a few minutes. However, solutions kept in the dark show electrochemical and spectroscopic properties of *trans*-$[Cr(CO)_4(PPh_3)_2]^+$ (see below). Even solid *trans*-$[Cr(CO)_4(PPh_3)_2]^+$ in a Nujol mull shows decomposition to *trans*-$Cr(CO)_4(PPh_3)_2$ after deliberate exposure to sunlight. Thus solid *trans*-$[Cr(CO)_4(PPh_3)_2]^+$ salts should be stored in the dark under refrigeration, and they appear to be stable for at least some weeks under these conditions.

The reductive cyclic voltammogram of a dichloromethane solution of *trans*-$[Cr(CO)_4(PPh_3)_2]PF_6$ recorded in the dark is identical with the oxidation cyclic voltammogram of *trans*-$Cr(CO)_4(PPh_3)_2$, compare parts A and B of Figure 3 with respect to peak positions, and decomposition is slow compared with a similar solution exposed to an infrared beam.

Determination of the magnetic moment of *trans*-$[Cr(CO)_4(PPh_3)_2]^+$ in dichloromethane solution by the Evans method,[15] using the solvent proton resonance and a concentric narrow tube containing dichloromethane, gave a magnetic moment of 1.75 ± 0.03 $\mu_B$ over the temperature range +25 to −80 °C, thus confirming the monomeric nature of the cation.

**(g) Electron Spin Resonance.** In situ generation of $[Cr(CO)_4(PPh_3)_2]^+$ at 0 °C within the cavity of the ESR spectrometer as described in the Experimental Section at either platinum or silver electrodes gave a broad triplet with a *g* value of 2.027 and a hyperfine coupling constant of 18 ± 2 G arising from the two equivalent phosphorus atoms. Limited improvement in the signal resolution could be achieved by lowering the temperature. The reason for the broadness of the signal is not understood at this time. It could result from rapid spin–lattice relaxation or possibly by rapid electron transfer between *trans*-$[Cr(CO)_4(PPh_3)_2]^+$ and *trans*-$Cr(CO)_4(PPh_3)_2$ similar to that which has been shown unequivocally to occur in the corresponding *mer*-$[Cr(CO)_3P_3]^+$/*mer*-$Cr(CO)_3P_3$ system[22] (P = phosphine or phosphite) and in other organometallic systems.[23-25] Unfortunately, NMR line broadening experiments that might confirm this hypothesis were not possible due to the limited solubility of $Cr(CO)_4(PPh_3)_2$.

**(h) Chemical Reactions of *trans*-$[Cr(CO)_4(PPh_3)_2]^+$.** In general, 17-electron metal carbonyl systems have been shown to undergo three types of chemical change[11-13] that may occur in preference to electron-transfer catalysis. These are the following: (1) They undergo isomerism from cis to trans (or fac to mer) which is usually fast, but this is not relevant in this case as the 18-electron starting material is already trans. (2) They are oxidants and take part in redox reactions to regenerate the 18-electron complex, e.g., eq 5. (3) In coordinating solvents dispropor-

$$Cr(CO)_5I + PPh_3 \xrightarrow{\text{acetone}} [Cr(CO)_5I]^- + PPh_3O \quad (5)$$

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tionation occurs to give the stable 18-electron species and a higher oxidation state species. Loss of carbon monoxide also usually accompanies these reactions, e.g., eq 6.

$$2\mathrm{Cr(CO)_5I} \rightarrow [\mathrm{Cr(CO)_5I}]^- + \mathrm{Cr(II)} + 5\mathrm{CO} + \mathrm{I}^- \quad (6)$$

In this regard *trans*-$[\mathrm{Cr(CO)_4(PPh_3)_2}]^+$ is a typical well-behaved 17-electron system. Addition of $\mathrm{Bu_4NBr}$ or $\mathrm{Bu_4NI}$ to a solution of *trans*-$[\mathrm{Cr(CO)_4(PPh_3)_2}]^+$ in dichloromethane instantly discharged the deep blue color to give a yellowish orange solution. The $^{31}$P NMR spectrum showed only a single sharp line whose chemical shift ($\delta$ 74.2) was identical with that of a genuine sample of $\mathrm{Cr(CO)_4(PPh_3)_2}$. This result shows that no other phosphorus-containing species is present in the solution. The infrared spectrum of the solution showed *trans*-$\mathrm{Cr(CO)_4(PPh_3)_2}$ as the only carbonyl compound present. Thus a simple redox reaction occurs as shown in eq 7.

$$2trans\text{-}[\mathrm{Cr(CO)_4(PPh_3)_2}]^+ + 2\mathrm{X}^- \rightarrow 2trans\text{-}\mathrm{Cr(CO)_4(PPh_3)_2} + \mathrm{X_2} \quad (7)$$

The $\mathrm{Cr^I/Cr^0}$ redox couple ($E_{1/2} \approx E^\circ$) is not sufficiently positive to oxidize chloride ion, but addition of $\mathrm{Et_4NCl}$ (which is very difficult to dry rigorously) gave a slow reaction causing discharge of the deep blue color to leave a yellow solution. The $^{31}$P NMR spectrum showed three resonances assigned to *trans*-$\mathrm{Cr(CO)_4(PPh_3)_2}$, $\mathrm{PPh_3O}$ ($\delta$ 30.5), and $\mathrm{PPh_3}$ ($\delta$ −4.7), but this last signal was very weak. The two strong signals were significantly broadened and of approximately equal intensities. The presence of phosphine oxide is due to a side reaction with water introduced with the $\mathrm{NEt_4Cl}$, and the broadening is due to the presence of paramagnetic chromium(II) arising from the disproportionation reaction (eq 8). Monitoring of the reaction with deliberately added water leads to observation of the same products.

$$2[\mathrm{Cr(CO)_4(PPh_3)_2}]^+ \rightarrow \mathrm{Cr(CO)_4(PPh_3)_2} + \mathrm{Cr(II)} + 2\mathrm{PPh_3} + 4\mathrm{CO} \quad (8)$$

A solution of known concentration of *trans*-$[\mathrm{Cr(CO)_4(PPh_3)_2}]^+$ in an approximately 50/50 mixture of dichloromethane and acetonitrile slowly changed color from deep blue to yellow. The $^{31}$P NMR spectrum showed two broadened resonances of equal intensity due to *trans*-$\mathrm{Cr(CO)_4(PPh_3)_2}$ and $\mathrm{PPh_3}$, indicating that a disproportionation had occurred. A smaller bore (2-mm) NMR tube containing the mixed solvents was inserted into the 10-mm tube containing the reaction mixture, and the magnetic moment of the paramagnetic species in solution was determined by the Evans method[15] using the proton resonances of both dichloromethane and acetonitrile. However, the observed splitting of the two resonances was not equal ($\mathrm{CH_2Cl_2}$ 5.86 Hz; $\mathrm{CH_3CN}$ 4.64 Hz). In order to calculate a magnetic moment, it is necessary to make an assumption on the molecular weight (and hence the identity) of the paramagnetic species in solution. Possible species considered were $[\mathrm{Cr(CH_3CN)_6}]^{2+}$ and $[\mathrm{Cr(CH_3CN)_6}]^{3+}$, and only the former gave a sensible result for the magnetic moment, 2.90 $\mu_B$ based on the dichloromethane resonance splitting (2.60 $\mu_B$ based on the acetonitrile resonance splitting). The different splittings for the two components in the solvent mixture is also consistent with the presence of Cr(II) rather than Cr(III) in the solution. Chromium(II) is known to be labile so if this were the species present in solution, the position of the $\mathrm{CH_3CN}$ resonance would be the weighted exchange average between free and coordinated acetonitrile, rather than the position for free $\mathrm{CH_3CN}$ in the paramagnetic solution. On the other hand, if the chromium in solution was kinetically inert chromium(III), there is no obvious explanation for the different splittings observed in the resonances of the mixed solvents.

Thus the overall reaction scheme is thought to be

$$2trans\text{-}[\mathrm{Cr(CO)_4(PPh_3)_2}]^+ \xrightarrow{\mathrm{CH_3CN}} trans\text{-}\mathrm{Cr(CO)_4(PPh_3)_2} + \mathrm{Cr(II)} + 2\mathrm{PPh_3} + 4\mathrm{CO} \quad (9)$$

This scheme is not inconsistent with the observed reversibility of the $\mathrm{Cr^I/Cr^0}$ couple in acetonitrile because the electrochemical result was observed on a much shorter time scale.

Bubbling carbon monoxide through a dichloromethane solution of *trans*-$[\mathrm{Cr(CO)_4(PPh_3)_2}]^+$ in the dark in the presence or absence of deliberately added *trans*-$\mathrm{Cr(CO)_4(PPh_3)_2}$ produced no color change and no evidence of reaction by polarographic monitoring. However, reaction with carbon monoxide was rapid in sunlight to give both *trans*-$\mathrm{Cr(CO)_4(PPh_3)_2}$ and $\mathrm{Cr(CO)_5PPh_3}$ (identified by infrared spectroscopy). Addition of excess $\mathrm{P(OMe)_3}$ to a dichloromethane solution of *trans*-$[\mathrm{Cr(CO)_4(PPh_3)_2}]^+$ caused no immediate reaction, but the solution did slowly turn yellow. The $^{31}$P NMR spectrum showed the presence of *trans*-$\mathrm{Cr(CO)_4(PPh_3)_2}$ and $\mathrm{PPh_3O}$ together with unreacted $\mathrm{P(OMe)_3}$. There was no evidence at all for substitution of *trans*-$[\mathrm{Cr(CO)_4(PPh_3)_2}]^+$ by $\mathrm{P(OMe)_3}$.

Nuclear magnetic resonance turns out to be the generally ideal method for monitoring the reaction pathways of *trans*-$[\mathrm{Cr(CO)_4(PPh_3)_2}]^+$. Experiments can be conducted with relatively high concentrations of *trans*-$[\mathrm{Cr(CO)_4(PPh_3)_2}]^+$, and the influence of light- and/or water-induced pathways is minimized. Electrochemical monitoring of reactions of $10^{-3}$ M solutions with *trans*-$[\mathrm{Cr(CO)_4(PPh_3]_2}^+$ in $\mathrm{CH_2Cl_2}$ (0.1M $\mathrm{NBu_4ClO_4}$) confirm that *trans*-$\mathrm{Cr(CO)_4(PPh_3)_2}$ is a major product on reaction with bromide, iodide, acetonitrile, acetone, water, and light. However, the need to work with dilute solutions increased the problems associated with competitive reactions occurring between the deliberately added ligands and those occurring with light and/or water.

## General Conclusions

Chemical and light-initiated pathways associated with *trans*-$[\mathrm{Cr(CO)_4(PPh_3)_2}]^+$ appear to be dominated by reduction and disproportionation, both reactions leading to regeneration of *trans*-$\mathrm{Cr(CO)_4(PPh_3)_2}$. We could find no example where electron-transfer catalysis occurs in the experiments undertaken by addition of ligand to solutions containing mixtures of both *trans*-$[\mathrm{Cr(CO)_4(PPh_3)_2}]^+$ and *trans*-$\mathrm{Cr(CO)_4(PPh_3)_2}$. Potentially coordinating, but difficult to oxidize ligands, such as $\mathrm{CH_3CN}$ catalyze the disproportionation of *trans*-$[\mathrm{Cr(CO)_4(PPh_3)_2}]^+$ rather than initiate electron-transfer catalysis. Easily oxidized ligands such as iodide participate in the redox process consistent with reduction of *trans*-$[\mathrm{Cr(CO)_4(PPh_3)_2}]^+$ and oxidation of the ligand rather than the homogeneous redox reaction required for electron-transfer catalysis to occur.

In order that the general scheme representing a catalytic electron transfer summarized in eq 1–3 to work, it is necessary for the redox couple $[\mathrm{M(CO)_4PL}]^{+/0}$ to be more positive than the couple $[\mathrm{M(CO)_4P_2}]^{+/0}$. An excellent ligand to induce this catalysis might be expected to be carbon monoxide as it is known[26] that the redox couple $[\mathrm{M(CO)}_x\mathrm{L}_{6-x}]^{+/0}$ becomes less positive in the sequence $\mathrm{M(CO)_6}$, $\mathrm{M(CO)_5L}$, $\mathrm{M(CO)_4L_2}$, and $\mathrm{M(CO)_3L_3}$. Furthermore, in the 18-electron system reaction 10 does pro-

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[26] Bursten, B. E. *J. Am. Chem. Soc.* **1982**, *104*, 1299 and references cited therein.

*Organometallics* **1984**, *3*, 9–14

$$\textit{trans}\text{-}\mathrm{Cr(CO)_4(PPh_3)_2 + CO \rightarrow Cr(CO)_5PPh_3 + PPh_3} \quad (10)$$

ceed,[27,28] albeit slowly, and it seems that this would be accelerated in the 17-electron system to provide the possibility of a catalytic system as shown in eq 11–13.

$$\textit{trans}\text{-}\mathrm{Cr(CO)_4(PPh_3)_2} \rightleftharpoons \textit{trans}\text{-}\mathrm{[Cr(CO)_4(PPh_3)_2]^+ + e^-} \quad (11)$$

$$\textit{trans}\text{-}\mathrm{[Cr(CO)_4(PPh_3)_2]^+ + CO \rightarrow [Cr(CO)_5PPh_3]^+ + PPh_3} \quad (12)$$

$$\mathrm{[Cr(CO)_5PPh_3]^+} + \textit{trans}\text{-}\mathrm{Cr(CO)_4(PPh_3)_2 \rightarrow Cr(CO)_5PPh_3} + \textit{trans}\text{-}\mathrm{[Cr(CO)_4(PPh_3)_2]^+} \quad (13)$$

However, the presence of light is required in our experiments for generation of $\mathrm{Cr(CO)_5PPh_3}$, and no evidence of electron-transfer catalysis has been observed. This scheme is consistent with the light sensitivity of *trans*-$\mathrm{[Cr(CO)_4(PPh_3)_2]^+}$; in the presence of light both *trans*-$\mathrm{Cr(CO)_4(PPh_3)_2}$ and CO are produced, and as equation 12 would probably be light catalyzed, the catalytic cycle can commence. Alternatively, reaction of *trans*-$\mathrm{[Cr(CO)_4(PPh_3)_2}$ with deliberately added carbon monoxide at room temperature could give $\mathrm{Cr(CO)_5PPh_3}$ in the presence of light if $\mathrm{[Cr(CO)_5PPh_3]^+}$ disproportionates like other 17-electron systems to give $\mathrm{Cr(CO)_5PPh_3}$, Cr(II), and free CO.

It might be possible for addition of acetonitrile to lead to electron-transfer catalysis if the reaction proceeded via elimination of a phosphine

$$\textit{trans}\text{-}\mathrm{[Cr(CO)_4(PPh_3)_2]^+ + CH_3CN \rightarrow} \textit{trans}\text{-}\mathrm{[Cr(CO)_4(PPh_3)(CH_3CN)]^+ + PPh_3} \quad (14)$$

and the redox couple of *trans*-$\mathrm{[Cr(CO)_4(PPh_4)(CH_3CN)]^{+/0}}$ were more positive than the *trans*-$\mathrm{[Cr(CO)_4(PPh_3)_2]^{+/0}}$ couple, leading to the formation of *cis*- or *trans*-$\mathrm{Cr(CO)_4(PPh_3)(CH_3CN)}$. However, neither of these products are observed in the infrared or $^{31}$P NMR spectra. Alternatively, if acetonitrile reacted with *trans*-$\mathrm{[Cr(CO)_4(PPh_3)_2]^+}$ to give $\mathrm{[Cr(CO)_3(PPh_3)_2(CH_3CN)]^+}$, the new redox couple would almost certainly be less positive than the tetracarbonyl couple and the catalytic cycle cannot work under these circumstances.

The actual products of the reaction are observed to be *trans*-$\mathrm{Cr(CO)_4(PPh_3)_2}$, $\mathrm{PPh_3}$ and Cr(II), which indicates that neither of the substitution reactions described above are operating in the 17-electron system, and the observed products are fully consistent with a simple disproportionation reaction.

Addition of bromide or iodide to *trans*-$\mathrm{[Cr(CO)_4(PPh_3)_2]^+}$ results in simple redox reactions to give only *trans*-$\mathrm{Cr(CO)_4(PPh_3)_2}$ and free halogen; no halide substitution occurs. If, however, halide substitution did occur to give either $\mathrm{[Cr(CO)_3(PPh_3)_2X]^-}$ or $\mathrm{[Cr(CO)_4(PPh_3)X]^-}$, the redox couple for either species would be less positive than the $\mathrm{[Cr(CO)_4(PPh_3)_2]^{+/0}}$ couple since addition of a negative halide reduces the $E°$ substantially.[11] The proposed tricarbonyl species would have the added disadvantage of less carbonyl groups which also lowers the $E°$. Thus in neither case could a catalytic system operate.

Thus the conclusion is that compounds typified by *trans*-$\mathrm{Cr(CO)_4(PPh_3)_2}$ are not good candidates for catalytic electron-transfer reactions because there are too many competitive reactions that are frequently more favored both kinetically and thermodynamically.

**Acknowledgment.** J.E.K. thanks the Commonwealth Government for a Commonwealth Postgraduate Research Award.

**Registry No.** $\mathrm{Cr(CO)_5PPh_3}$, 14917-12-5; *trans*-$\mathrm{[Cr(CO)_4(PPh_3)_2]ClO_4}$, 87246-84-2; *trans*-$\mathrm{[Cr(CO)_4(PPh_3)_2]PF_6}$, 87246-85-3; *trans*-$\mathrm{Cr(CO)_4(PPh_3)_2}$, 38800-75-8; *trans*-$\mathrm{Cr(CO)_4(PPh_3)_2{}^+}$, 86475-63-0; CO, 630-08-0; $\mathrm{CH_3CN}$, 75-05-8; $\mathrm{(CH_3)_2CO}$, 67-64-1; $\mathrm{I^-}$, 20461-54-5; bromide, 24959-67-9; water, 7732-18-5.

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(27) Wovkulich, M. J.; Feinberg, S. J.; Atwood, J. D. *Inorg. Chem.* **1980**, *19*, 2609.

(28) Darensbourg, D. J.; Graves, A. H. *Inorg. Chem.* **1979**, *18*, 1257.

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# Macrocycles Containing Tin. Syntheses of Symmetrical Macrocycles Containing Two or Four Diphenylstanna Units

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*Received June 1, 1983*

The syntheses of macrocycles containing two diphenylstanna moieties, c-$\mathrm{[Ph_2Sn(CH_2)_n{-}]_2}$ (1, $n$ = 4, 5, 6, 8, 10, 12), and four diphenylstanna moieties, c-$\mathrm{[Ph_2Sn(CH_2)_n{-}]_4}$ (2, same $n$), are reported. $\alpha,\omega$-Bis(bromomagnesio)alkanes reacted with $\mathrm{Ph_3SnCl}$ to give $\alpha,\omega$-bis(triphenylstannyl)alkanes which upon treatment with HBr gave $\alpha,\omega$-bis(bromodiphenylstannyl)alkanes 4. Compounds 4 reacted with the corresponding chain length $\alpha,\omega$-bis(bromomagnesio)alkanes to give 1 and 2. Alternatively, good yields of 1 ($n$ = 4, 5, 6, 8) were obtained by converting 4 to dilithium reagents 7 which were allowed to react with $\alpha,\omega$-dibromoalkanes. Good yields of 2 ($n$ = 4–6) were obtained by first treating 4 with $\mathrm{Cl(CH_2)_nMgBr}$ to give dichlorides which were then allowed to react with 7 in a second step. Purifications of the macrocycles and several synthetic intermediates were effected by preparative reverse-phase chromatography. The macrocyclic products were characterized by NMR spectroscopy, molecular weight determinations, and elemental analyses.

Macrocyclic and macrobicyclic compounds containing the basic atoms oxygen, nitrogen, and sulfur have been widely exploited in cation coordination chemistry during the past decade. In various applications including solubilization of salts in organic media, chromatographic separations, and catalysis, the dominant features of this chemistry are the size of the cavities formed by the basic atoms of the host compounds and the fit of cationic guests

0276-7333/84/2303-0009$01.50/0