a solution of dimethylbis[(2,4,6-trimethylphenyl)tricarbonylchromium-C^l]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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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 com-

binations 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 $E_{1/2}{}^{rev}$). Substituent effects related to $E°$ or $E_{1/2}{}^{rev}$ 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 $E_{1/2}{}^{irr}$ 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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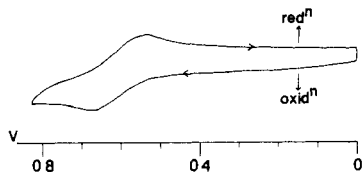(25) R. E. Dessy, T. J. Flautt, H. H. Jaffé, and G. F. Reynolds, *J. Chem. Phys.*, 30, 1422 (1959).

Figure 1. Cyclic voltammogram for oxidation of 5×10^{-4} M Cr-$(CO)_5P(m\text{-}CH_3C_6H_4)_3$ in CH_2Cl_2 (0.1 M Bu_4NClO_4) at -78 °C at a platinum electrode. Scan rate = 500 mV s^{-1}.

protons where present knowledge is relatively sparse. NMR measurements cannot normally be made on both oxidized and reduced species because one of the compounds is likely to be paramagnetic. In studies of phenomena such as exchange reactions[26] or solvent effects[27] the two techniques may be complimentary. In the area of substituent effects, if both linear and nonlinear free energy relationships indeed can be observed, *with the relationship being nucleus dependent*, then an additional approach to extending the understanding of chemical shifts may become available.

In the present report, electrochemical and NMR data have been obtained on a series of $Cr(CO)_5L$ (L = phosphine or nitrogen-based ligand) complexes in dichloromethane and the results compared. Electrochemical oxidations of the complexes are reversible at low temperature, or on short time scales at room temperature, to produce well-characterized 17-electron formally chromium(I) species

$$Cr(CO)_5L \underset{}{\overset{k_s,\, E^\circ}{\rightleftharpoons}} [Cr(CO)_5L]^+ + e^- \qquad (1)$$
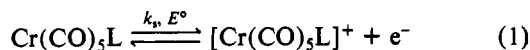
After computation of the heterogeneous charge-transfer rate constant, k_s, E° ($\sim E_{1/2}$) can be calculated from the electrochemical measurements. The molecules are rigid on the NMR time scale since separate carbonyl resonances cis and trans to L are observed. When L is a phosphorus donor, ^{31}P chemical shifts are readily obtained together with phosphorus–carbon coupling constants.

Experimental Section

Solvent. Analytical or spectroscopic grade dichloromethane was used without purification.

Syntheses. $Cr(CO)_6$ and the ligands L were all from commercial sources. The complexes were prepared by the method of Strohmeier[28-30] by irradiation of the carbonyl in THF followed by addition of the ligand. The complexes were usually recrystallized from dichloromethane by addition of hexane.

NMR Measurements. NMR spectra were recorded on a JEOL FX 100 spectrometer using an external ^7Li lock. Carbon-13 NMR spectra were recorded with spectral widths of 8000 Hz, 8192 data points, and a 2-s recycle delay in dichloromethane containing $Cr(acac)_3$ as a paramagnetic relaxant. Carbonyl chemical shifts (± 0.5 ppm) were referenced against Me_4Si. Phosphorus-31 NMR chemical shifts (± 0.25 ppm) were referenced against external 85% phosphoric acid. High-frequency positive convention was used to report the data.

Electrochemical Measurements. All electrochemical measurements were obtained at -78 °C (dry ice/acetone temperature) in dichloromethane (0.1 M Bu_4NClO_4) with a PAR Model 173 potentiostat/galvanostat in the three-electrode configuration with positive feedback circuitry to minimize the influence of the ohmic IR drop. The electrodes were Ag/AgCl (CH_2Cl_2 saturated LiCl) as the reference electrode, platinum wire as an auxiliary, and a platinum-disk working electrode. A PAR Model 175 Universal Programmer was used to provide the triangular voltage for the cyclic voltammetric experiments. Unless otherwise specified, data refer to a scan rate of 500 mV s^{-1} and a $Cr(CO)_5L$ concentration of 5×10^{-4} M.

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Table I. Electrochemical Data^a for Oxidation of $Cr(CO)_5L$ and ^{13}C NMR Chemical Shifts^b in Dichloromethane Solution

no.	compd	E°, V (vs. Ag/ AgCl)	$\delta(^{13}C)$ cis	trans	wtd av
1	$[Cr(CO)_5Br]^-$	0.40	216.6	223.1	217.9
2	$[Cr(CO)_5I]^-$	0.40	216.6	227.3	218.7
3	$Cr(CO)_5dam^c$	0.55	216.6	222.1	217.7
4	$Cr(CO)_5dpm^d$	0.65	216.7	221.7	217.7
5	$Cr(CO)_5P(p\text{-}MeOC_6H_4)_3$	0.55	216.6	221.4	217.6
6	$Cr(CO)_5P(OEt)_3$	0.75	215.8	220.0	216.6
7	$Cr(CO)_5P(OBu)_3$	0.90	215.2	219.6	216.1
8	$Cr(CO)_5P(OC_6H_5)_3$	1.25	214.0	217.6	214.7
9	$Cr(CO)_5P(C_6H_5)_3$	0.80	216.9	221.7	217.9
10	$Cr(CO)_5P(m\text{-}CH_3C_6H_4)_3$	0.65	217.4	222.3	218.4
11	$Cr(CO)_5NH_2CH_2C_6H_5$	1.35	214.4	219.5	215.4
12	$Cr(CO)_5CH_3CN$	1.35	213.9	219.1	214.9
13	$Cr(CO)_5C_5H_5N$	1.20	214.3	220.7	215.6
14	$Cr(CO)_6$	1.80	211.6	211.6	211.6

^{a} -78 °C. ^{b} 22 °C. ^{c} dam = $Ph_2AsCH_2AsPh_2$. ^{d} dpm = $Ph_2PCH_2PPh_2$.

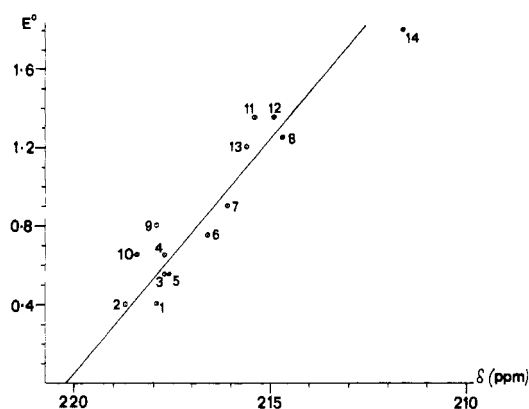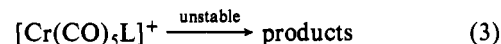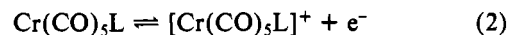**Figure 2.** Plot of E° (V (vs. Ag/AgCl)) for oxidation of $Cr(CO)_5L$ against $\delta(^{13}C)$(weighted average). Compounds are identified in Table I. Least-squares fit of $\delta(^{13}C)$ vs. E°: slope, 4.18 ± 0.38 ppm V^{-1}; intercept, 220 ± 0.7 ppm; variance, 0.357.

Results and Discussion

Preliminary experiments, at 20 °C, demonstrated that in dichloromethane (0.1 M Bu_4NClO_4) some of the formally chromium(I) 17-electron cations generated by the 1-electron oxidation of $Cr(CO)_5L$ were unstable (eq 2, 3). Consequently,

$$Cr(CO)_5L \rightleftharpoons [Cr(CO)_5L]^+ + e^- \qquad (2)$$

$$[Cr(CO)_5L]^+ \xrightarrow{\text{unstable}} \text{products} \qquad (3)$$

electrochemical data reported in Table I were obtained at -78 °C to discriminate against reaction 3. Figure 1 shows a typical cyclic voltammogram obtained at -78 °C for the first oxidation step of $Cr(CO)_5L$. The peak-to-peak separation is clearly greater than the Nernstian value expected for a diffusion-controlled (reversible) cyclic voltammogram. A digital simulation program based on the method of Feldberg[31] was used to generate theoretical cyclic voltammograms and hence to calculate E°. In these calculations, a diffusion coefficient of 10^{-6} cm^2 s^{-1} for both $Cr(CO)_5L$ and $Cr(CO)_5L^+$ and a value of 0.5 for the charge-transfer coefficient, α, was assumed. In computer simulations the heterogeneous charge-transfer rate constant, k_s, was varied until agreement between theoretical and experimental (peak-to-peak) separations was obtained for a scan rate of 500 mV s^{-1}. E° could then be calculated since

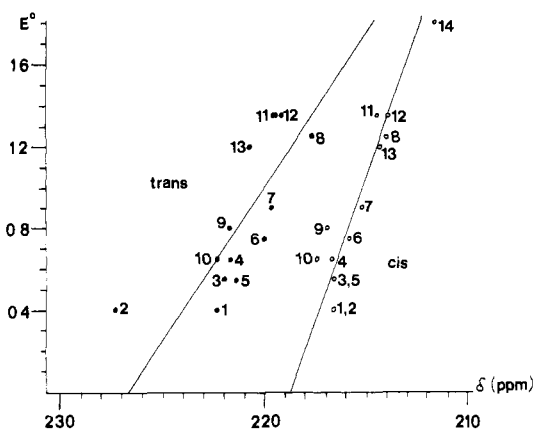(31) S. W. Feldberg in "Electroanalytical Chemistry", Vol. 3, A. J. Bard, Ed., Marcel Dekker, New York, pp 199-296.

Figure 3. Plot of $E°$ (V (vs. Ag/AgCl)) for oxidation of $Cr(CO)_5L$ against cis (O) and trans (●) carbonyl chemical shifts. Compounds are identified in Table I. Least-squares fit of $\delta(^{13}C)(cis)$ vs. $E°$: slope, 3.00 ± 0.35 ppm V^{-1}; intercept, 218.7 ● 0.7 ppm; variance, 0.313. $\delta(^{13}C)(trans)$ corresponding values: slope, 0.87 ± 1.08 ppm V^{-1}; intercept, 226.7 ± 2.0 ppm; variance, 2.94.

its value relative to the peaks is known in the theoretical calculations. Values of k_s were found to be in the range 10^{-2}–10^{-4} cm s^{-1} at −78 °C on platinum electrodes. For compounds oxidized at fairly positive potentials (more than +1.2 V vs. Ag/AgCl) evidence for surface reactions was sometimes encountered, but no correction was made for these phenomena. For some compounds, e.g. $[Cr(CO)_5I]^-$, second oxidation waves to produce formally Cr(II) species were observed,[32] but in this work only $E°$ data relating to eq 1 are used.

Figures 2 and 3 show plots of $E°$ for oxidation of $Cr(CO)_5L$ against $\delta(^{13}C)$. Several observations are readily made: the correlation between $E°$ and $\delta(^{13}C)$ (weighted average) is reasonable with a variance of 0.357 (Figure 2); however, the correlation with $\delta(^{13}C)(cis)$ is excellent (variance 0.313) while that with $\delta(^{13}C)(trans)$ is poor, with a variance of 2.94 (Figure 3).

The conclusion that follows from these data is that substituent effects influence cis and trans carbonyl chemical shifts in rather different manners. Statistical treatment of a plot of $\delta(^{13}C)(cis)$ vs. $\delta(^{13}C)(trans)$ produced the following data: slope 1.79 ± 0.32; intercept −164.6 ± −69.7 ppm; variance 3.63.

Bodner and co-workers[33-35] and others[34-39] have compared the carbon-13 carbonyl chemical shifts with infrared and other data for a number of group 6 metal compounds. They found correlations between carbon-13 shifts (particularly cis carbonyls) and (i) carbonyl stretching frequencies and (ii) metal–carbon bond lengths, and similar results have been reported for other systems[33-35,40-42] although whether a linear correlation exists with trans carbonyl groups is questionable.[35,42] In Cr-$(CO)_{6-n}L_n$ complexes the sequential replacement of carbonyl appears to be additive with respect to carbon-13 chemical

shifts. However, it should be noted that all of the correlations are within the 18-electron system whereas electrochemical data contain information on 17-electron systems.

Electrochemical data ($E°$) are governed by the ratio of terms of complexes in two oxidation states as defined by the Nernst equation. $E°$ is a free energy term obeying the usual thermodynamic relationships. On the other hand, the origin of carbon-13 chemical shifts is under continual debate and many factors contribute to the shielding. It is generally agreed that, although the diamagnetic term of the shielding equation is comparatively large, it is relatively invariant within a closely related series of compounds and that the shielding effects observed are due to charges in the paramagnetic term.[43-45] In the latter, it is the average excitation energy between ground and excited states (ΔE) that is considered to be influenced by π back-bonding in metal carbonyls.[41] Linear free energy relationships are observed for carbon chemical shifts when the shielding is controlled by electronic (resonance and inductive) effects via the paramagnetic term. Changes in stereochemistry within a series may result in deviations from linearity. A linear correlation with electrochemical data may thus occur when changes in both $E°$ and $\delta(^{13}C)$ arise from electronic effects, and this could be expected for a series of closely related ligands L in a series of $Cr(CO)_5L$ complexes where steric effects remain constant. In the present case L varies from an anion such as I^- to P and N donors to carbon monoxide, so steric effects may be significant.

The evidence available on $M(CO)_5L$ complexes clearly indicates that changes in electron density with varying L groups are important.[39,46] For example, a correlation has been established between the ionization potential of the free ligand, the stabilization energy of the lone pair on complexation, and the σ-donor capacity in a series of $Mo(CO)_5PX_3$ (X = F, Cl, Br, I) complexes.[47] In the Mo–P bond the π back-bonding more than compensates for the σ donation and causes a positive net charge on the molybdenum atom. Further results on $M(CO)_5PR_3$ complexes (M = Cr, Mo, W; R = C_6H_{11}, C_6H_5, O-i-C_3H_7, OC_6H_5) also using UV photoelectron spectroscopy[48] have made it possible to calculate the σ-donor/π-acceptor properties of the ligands. The carbonyl carbon-13 resonances correlated well with the σ-donor/π-acceptor properties of the ligand, whereas in nonaromatic PR_3 ligands the ligand carbon-13 resonance positions are related qualitatively to the reduction of electron density on complexation. Furthermore, when the ionization potential for the chromium d (b_2) orbital—a parameter for the electron density on the metal—is plotted against the cis carbonyl chemical shift, reasonable correlation for the various nitrogen and phosphorus ligands exists.[48-51] Correlation with the trans carbonyl chemical shift is less satisfactory.

It has already been noted from statistical data that $E°$ correlates in a linear fashion, far more satisfactorily with $\delta(^{13}C)(cis)$ than with $\delta(^{13}C)(trans)$. This result is entirely consistent with data from UV photoelectron[48] and infrared spectroscopy.[35] Since the $\delta(^{13}C)(cis)$ values for chromium are

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Table II. Comparison of $E°$ and ^{31}P and ^{13}C NMR Data for $Cr(CO)_5L$ Complexes in Dichloromethane[a]

no.	compd	$E°$, V (vs. Ag/AgCl)	$\delta(^{13}C)$ (cis)	$J(P,C)$, Hz	$\delta(^{13}C)$ (trans)	$J(P,C)$, Hz	$\delta(^{31}P)$	$\delta(^{31}P)$ (ligand)	$\Delta\delta(^{31}P)$
4	$Cr(CO)_5dpm^b$	0.65	216.7		221.7		46.6	−22.7	69.3
							−26.8		
5	$Cr(CO)_5P(p\text{-MeOC}_6H_4)_3$	0.55	216.6	14	221.4		68.4	−10.9	79.3
6	$Cr(CO)_5P(OEt)_3$	0.75	215.8	21	220.0	4	52.2	−29.9	82.1
7	$Cr(CO)_5P(OBu)_3$	0.90	215.2	17	219.6		−66.1	−139.0	72.9
8	$Cr(CO)_5P(OC_6H_5)_3$	1.25	214.0	20	217.6	38	−10.7	−70.9	60.2
9	$Cr(CO)_5P(C_6H_5)_3$	0.80	216.9	13	221.7	6	55.0	−5.3	60.3
10	$Cr(CO)_5P(m\text{-CH}_3C_6H_4)_3$	0.65	217.4	14	222.3	8	53.9	−5.2	59.1

^{a} Electrochemical data at −78 °C; NMR data at 22 °C. ^{b} dpm = $Ph_2PCH_2PPh_2$.

specifically known to be influenced by electronic charge (on the metal), the linear free energy relationship is consistent with this observation. Thus, $E°$, carbonyl stretching force constants and ionization potentials are all in agreement.

Linear free energy relationships require that substituent effects be additive. Timney[52] has used a simple empirical relationship based on ligand additivity to predict carbonyl stretching frequencies in a wide range of metal carbonyl complexes. Bodner and co-workers[53] have attempted to obtain empirical ligand parameters for the correlation of carbon-13 chemical shifts in metal carbonyl complexes. Pickett and co-workers[21,54] have suggested that additive relationships apply in electrochemistry while Treichel, Muek, and Bursten[55] proposed that the effects of the ligands in carbonyl complexes upon the energetics of principally 3d molecular orbitals obeyed a simple additivity relationship. Finally, Bursten[56] has used the ligand additivity model to explain the different oxidation potentials for the $M(CO)_n(CNR)_{6-n}$ series (M = Mn(I), Cr(0); R = CH_3, C_6H_5). This model should also be valid for photoelectron spectroscopy and permit prediction of ionization potentials.

These ligand additivity relationships generally all have an important limitation in that steric phenomena cause difficulties. For example, it has been well established that isomers of carbonyl complexes frequently have different $E°$ values.[57,58] The Bursten model, while encompassing some of these problems, still predicts that cis and trans $M(CO)_4L_2$ species will have the same $E°$ values, which is not strictly correct.[58] Mingos[59] has used extended Hückel molecular orbitals to show that the relative stabilities of geometrical isomers in 16-, 17-, and 18-electron octahedral complexes containing strong π-acid or π-donor ligands depend on the number of valence electrons and in a complimentary fashion on whether the ligands are acceptors or donors. Oxidation of formally Cr(0) to Cr(I) encompasses this situation, and it would appear that different steric and electronic interactions can apply to both halves of the redox couple. Since NMR data represent information from only half of the redox couple, correlation will not occur if structural factors involving both halves of the redox couple enter into the argument. Photochemical data[60,61] demonstrate these steric effects. For example, $Cr(CO)_5L$ complexes dissociate to $Cr(CO)_5$ or $Cr(CO)_4L$ depending on the wave-
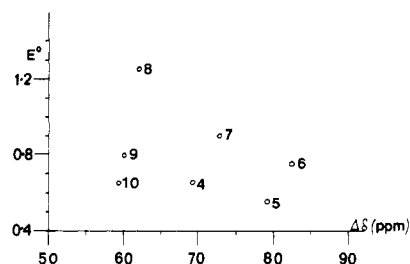

Figure 4. Plot of $E°$ (V (vs. Ag/AgCl)) for oxidation of $Cr(CO)_5L$ against phosphorus-31 coordination chemical shifts $\Delta\delta(^{31}P)$. Compounds are identified in Table II.

length.[60] With trans $W(CO)_4LL'$ (L = phosphine; L ≠ L') two distinct categories of photochemical behavior are observed,[61] depending on the nature of the phosphines, resulting in loss of either a phosphine or a carbonyl group.

All the above data lead us to the conclusion that linear free energy relationships between $E°$ and NMR (and many other parameters) will only occur under special conditions where steric factors are constant and charge effects (electronic) dominate. An example is the study of substituent effects on closely related nickel Schiff base complexes[62] where carbon-13 chemical shifts, electronic spectra, and polarographic measurements can all be related to electron density changes. Other studies of inorganic complexes or organic compounds where linear free energy relationships have been reported are in accordance with this conclusion.[5,63–66]

To emphasize the importance of steric terms, Table II and Figure 4 provide some data based on phosphorus-31 NMR spectra. Phosphorus-31 chemical shifts of the $(C_6H_5)_{3-n}PR_n$ and $(C_6H_5)_{3-n}PR_nCr(CO)_5$ derivatives (n = 0–3; R = H, CH_3, C_2H_5, $i\text{-}C_3H_7$, $i\text{-}C_4H_9$), in contrast to the carbon chemical shifts, are dominated by steric effects[67] although a small inductive effect is operative. The same authors have also discussed the NMR parameters of $Cr(CO)_5L$ (L = $(C_6H_5)_{3-n}PX_n$; n = 0–3; X = Cl, Br, I) complexes in terms of electronegativity and π-bonding effects.[68] Clearly no statistically significant linear correlation exists between $E°$ and $\delta(^{31}P)$ or carbon–phosphorus coupling constants. Importantly, as Figure 4 shows, no correlation exists even when $\Delta\delta(^{31}P)$ is used ($\Delta\delta(^{31}P)$ is the coordination chemical shift = δ(complex) − δ(free ligand)). Since in these complexes the phosphorus chemical shifts are known to be dominated by steric considerations,[67] this lack of correlation supports the hypothesis that, while electronic

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effects have parallels in both electrochemical and NMR data, steric effects do not. The lack of correlation between carbon-13 and phosphorus-31 in other $Cr(CO)_5L$ complexes[69] is also consistent with these ideas.

Registry No. **1**, 14911-72-9; **2**, 14911-71-8; **3**, 34818-93-4; **4**, 40545-00-4; **5**, 69021-33-6; **6**, 18461-32-0; **7**, 18461-33-1; **8**, 18461-39-7; **9**, 14917-12-5; **10**, 36491-08-4; **11**, 84051-19-4; **12**, 15228-38-3; **13**, 14740-77-3; **14**, 13007-92-6.

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Synthesis and X-ray Crystal Structure of Tris(di-*tert*-butylphosphido)tricarbonyltrirhodium(I)

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As part of a program[3] to investigate steric and electronic effects in transition-metal phosphido (R_2P^-) and phosphinidene (RP^{2-}) complexes, we have studied the reaction of [Rh(CO)$_2$Cl]$_2$ with *t*-Bu$_2$PLi in tetrahydrofuran.[4] From this reaction we have isolated and characterized several dinuclear complexes[4] and also the rhodium(I) trimer [Rh(μ-*t*-Bu$_2$P)CO]$_3$. We report here details of the isolation, characterization, and X-ray crystal structure of the trinuclear complex.

Experimental Section

All operations were performed under nitrogen or under vacuum. Microanalyses were by the Schwarzkopf Microanalytical Laboratory, Woodside, N.Y. Hexane and THF were dried over sodium and distilled from sodium/benzophenone under nitrogen before use. *t*-Bu$_2$PLi[5] and [Rh(CO)$_2$Cl]$_2$[6] were prepared by literature methods. NMR spectra were run on Varian EM-390 (^{1}H) (90 MHz), Varian FT-80 (^{31}P and ^{13}C at 32.384 and 20.0 MHz, respectively), Bruker WH-90 (^{31}P at -80 °C), and Nicolet FT-200 (^{31}P) instruments. IR spectra were run on a Perkin-Elmer 1330. Simulation of the ^{31}P{^{1}H} spectrum was done on a Nicolet NIC-80 using the Nicolet NMRCAL program.

[Rh(μ-*t*-Bu$_2$P)CO]$_3$. A solution of *t*-Bu$_2$PLi in THF (0.97 g, 6.4 mmol, in 7.0 mL) was slowly added to a solution of [Rh(CO)$_2$Cl]$_2$ (1.24 g, 3.20 mmol) in THF (40 mL) at -78 °C. The solution was allowed to warm slowly to -50 °C over a 1-h period. Volatile materials were then removed under vacuum at -50 °C. The residue was extracted into hexane (30 mL) at room temperature, and the resulting deep red solution was filtered. The solution was evaporated to 15 mL under vacuum and then transferred to a short column (3 × 10 cm) of 80–325 mesh chromatographic grade alumina. The column
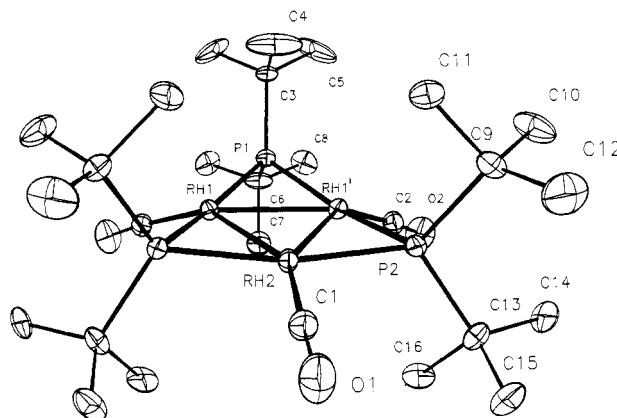
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Figure 1. Molecular structure of [Rh(μ-*t*-Bu$_2$P)CO]$_3$.

Table I. Bond Distances (Å) and Bond Angles (deg) in [Rh(μ-*t*-Bu$_2$P)CO]$_3$

	Distances		
Rh(1)–Rh(1)	2.638 (2)	Rh(1)–Rh(2)	2.659 (2)
Rh(1)–P(1)	2.273 (5)	Rh(1)–P(2)	2.295 (4)
Rh(1)–C(2)	1.85 (2)	Rh(2)–P(2)	2.273 (3)
Rh(2)–C(1)	1.82 (2)		

	Angles		
Rh(1)–Rh(1)–Rh(2)	60.26 (3)	Rh(1)–P(1)–Rh(1)	70.9 (2)
Rh(2)–Rh(1)–P(2)	54.02 (8)	Rh(2)–Rh(1)–P(1)	112.98 (9)
Rh(2)–Rh(1)–C(2)	143.9 (5)	P(1)–Rh(1)–P(2)	158.8 (2)
P(2)–Rh(1)–C(2)	98.4 (5)	P(1)–Rh(1)–C(2)	99.7 (5)
Rh(1)–Rh(2)–Rh(1)	59.48 (6)	Rh(1)–Rh(2)–P(2)	54.78 (9)
Rh(1)–Rh(2)–C(1)	149.8 (1)	P(2)–Rh(2)–C(1)	95.9 (1)

was eluted with hexane. Two dark red bands developed. The first contained the dinuclear complex [Rh(μ-*t*-Bu$_2$P)(CO)$_2$]$_2$[4] and the second [Rh(μ-*t*-Bu$_2$P)CO]$_3$. The fractions were collected, and that which contained the trimer was evaporated to ca. 15 mL and cooled at -40 °C for 12 h. The dark red-brown crystals were collected and dried under vacuum: yield 0.53 g, 30% based on [Rh(CO)$_2$Cl]$_2$; mp 223–225 °C dec; IR (Nujol mull, KBr plates) 1951 s, 1297 m, 1166 m, 1015 w, 801 w cm^{-1}; IR (hexane solution) (matched KBr cells) 1957 s, br, cm^{-1}; NMR ^{1}H δ 1.6 m (*t*-Bu) in C$_6$D$_6$ at ambient temperature referenced to external Me$_4$Si (δ 0.0), ^{31}P{^{1}H} δ 369.0 in C$_6$D$_6$ at ambient temperature referenced to external 85% H$_3$PO$_4$ (δ 0.0) (positive is downfield), ^{13}C{^{1}H} δ 47.11 s (*C*Me$_3$), 32.41 s (C*Me$_3$*) in C$_6$D$_6$ relative to Me$_4$Si. CO NMR resonances were not observed even with added Cr(acac)$_3$ and extended acquisition times.

X-ray Crystallography. The data crystal was sealed under nitrogen in a 0.5-mm o.d. Lindemann glass capillary. Data were collected on an Enraf-Nonius CAD-4 diffractometer using graphite-mono-chromated Mo Kα radiation. The diffracted intensities were collected by the ω–2θ scan technique in a manner similar to that previously described.[7] Crystal data: space group orthorhombic *Cmc*2$_1$ with $a = 19.563$ (8), $b = 15.633$ (7), and $c = 11.684$ (6) Å, mol wt 828.45, cell volume 3495.1 Å^3, $Z = 4$, calculated density 1.57 g cm^{-3}, crystal dimensions 0.20 × 0.30 × 0.35 mm. Calculated $\mu = 15.2$ cm^{-1}; least-squares refinement based on 998 observed reflections (1276 measured) ($2\theta \leq 44°$; $I \geq 3\sigma(I)$) gave $R = 0.036$ and $R_w = 0.043$. Hydrogen atoms were not located, and the non-hydrogen atoms were refined with anisotropic thermal parameters. The number of parameters varied was 172. Although the data to parameter ratio is low (5.8), the crystal scattered poorly at high angles. Further data are therefore unlikely to affect the key metal–metal, metal–phosphorus, or metal–carbonyl distances or angles. No absorption correction was applied since a χ-scan study revealed no problem. Systematic absences allowed the space group to be either *Cmcm* or *Cmc*2$_1$. However, with four molecules per unit cell, additional crystallographic considerations had to be taken into account. The point symmetry in *Cmcm* must be *mm*, while only a single mirror plane is required in *Cmc*2$_1$. The latter seemed more likely, and the correctness of the choice was borne out by the refinement. (In Figure 1, it can clearly be seen that the

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