Reduction–Oxidation Properties of Organotransition-metal Complexes. Part 23.[1] Pentaphenylcyclopentadienyl Carbonyl Complexes of Cobalt and Rhodium

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The reaction of $[Co_2(CO)_8]$ or $[\{RhCl(CO)_2\}_2]$ with C_5Ph_5Br and zinc dust in tetrahydrofuran (thf) gives $[M(CO)_2(\eta\text{-}C_5Ph_5)]$ (**1**, M = Co or Rh); in the case of rhodium, the intermediate $[RhBr(CO)_2(\eta\text{-}C_5Ph_5)][ZnCl_3]$ is isolable if the reaction is carried out in benzene. In the presence of $[Fe(\eta\text{-}C_5H_5)_2]^+$, (**1**, M = Rh) undergoes oxidatively-induced carbonyl substitution with ligands, L; for L = $P(OPh)_3$, the formation of $[M(CO)L(\eta\text{-}C_5Ph_5)]$ [**2**, M = Rh, L = $P(OPh)_3$] is catalytic in the oxidant. The complexes (**2**) are also prepared *via* (*a*) the substitution of $[RhBr(CO)_2(\eta\text{-}C_5Ph_5)][ZnCl_3]$ with PPh_3 or $AsPh_3$ and subsequent reduction by $[N(PPh_3)_2][Mn(CO)_5]$, (*b*) $[Co(\eta\text{-}C_5H_5)_2]$ reduction of $[MI_2(CO)(\eta\text{-}C_5Ph_5)]$ (**3**, M = Co) in the presence of $P(OMe)_3$ or $P(OPh)_3$, or (*c*) $[Co(\eta\text{-}C_5H_5)_2]$ reduction of $[RhBr_2\{P(OMe)_3\}(\eta\text{-}C_5Ph_5)]$ (**5**) in the presence of CO. Complexes (**3**, M = Co or Rh) are prepared from (**1**) and iodine in toluene–hexane at 0 °C; the rhodium complex (**3**, M = Rh) is reduced by $[Co(\eta\text{-}C_5H_5)_2]$ to give $[\{Rh(\mu\text{-}CO)(\eta\text{-}C_5Ph_5)\}_2]$. Compound (**5**) results from the addition of $P(OMe)_3$ to $[\{RhBr_2(\eta\text{-}C_5Ph_5)\}_2]$ (**4**), which is the product of the reaction between (**1**, M = Rh) and bromine in CH_2Cl_2. The compounds (**2**) undergo two one-electron oxidations at a platinum electrode in CH_2Cl_2; the first is reversible and the second is irreversible. The monocations [$\mathbf{2}^+$, M = Rh; L = PPh_3, $P(OPh)_3$, or $AsPh_3$] have been characterised in solution by i.r. and e.s.r. spectroscopy. Low-temperature e.s.r spectroscopy has shown that the radical cation $[Rh(CO)(PPh_3)(\eta\text{-}C_5Me_5)]^+$ is stable at −196 °C.

Remarkable differences are observed between analogous cyclopentadienyl and pentamethylcyclopentadienyl complexes of most of the transition metals.[2] It might be predicted, therefore, that perphenylation of the C_5 ring, with the resulting major changes in steric and electronic effects, would render the $\eta\text{-}C_5R_5$ ligand different again.

Surprisingly, little effort has been expended in exploiting this modification, even though there are ample synthetic pathways to $\eta\text{-}C_5Ph_5$ metal complexes. Thus, early studies showed that they could be prepared directly from C_5Ph_5Br {*e.g.* $[FeBr(CO)_2(\eta\text{-}C_5Ph_5)]$[3]} or the radical C_5Ph_5 {*e.g.* $[Ni(\eta\text{-}C_5Ph_5)]_2$[4]}, or indirectly from PhC_2Ph {*e.g.* $[Mo(\eta\text{-}C_5Ph_5)_2]$[5] and $[Pd_2(\mu\text{-}PhC_2Ph)(\eta\text{-}C_5Ph_5)_2]$[6]}. In addition, the recent synthesis of $[C_5Ph_5]^-$[7] has led to the isolation of the novel sandwich complex $[Sn(\eta\text{-}C_5Ph_5)_2]$[8] and to allyl derivatives such as $[Pd(\eta^3\text{-}C_3H_5)(\eta\text{-}C_5Ph_5)]$.[9]

Our interest[10,11] in these complexes derives primarily from the apparent ability of the $\eta\text{-}C_5Ph_5$ ligand to stabilise reactive organotransition metal radicals generated in one-electron transfer reactions. Whether the source of this stabilisation is steric or electronic in origin is, as yet, unknown. The greater thermal stability of $[Pd(\eta^4\text{-cod})(\eta\text{-}C_5Ph_5)]^Z$ (Z = 0 or 2, cod = cyclo-octa-1,5-diene), compared with the $\eta\text{-}C_5H_5$ analogues, is probably largely due to the bulky C_5-substituents. However, the electron-withdrawing nature of the phenyl groups also leads to a shift in redox potentials to more positive values such that, for example, the reduced complex $[Pd(\eta^4\text{-cod})(\eta\text{-}C_5Ph_5)]$ is more accessible, by 270 mV, than $[Pd(\eta^4\text{-cod})(\eta\text{-}C_5H_5)]$ (from the corresponding monocations).[10]

In this paper we describe the synthesis of a range of $\eta\text{-}C_5Ph_5$ complexes of cobalt and rhodium, largely derived from $[M(CO)_2(\eta\text{-}C_5Ph_5)]$ (**1**, M = Co or Rh).* Of particular note is the stability of the radical cations $[Rh(CO)L(\eta\text{-}C_5Ph_5)]^+$ [L = PPh_3, $P(OPh)_3$, or $AsPh_3$], the intermediacy of these species in the oxidatively induced substitution reactions of (**1**, M = Rh), and the catalytic formation of $[Rh(CO)\{P(OPh)_3\}(\eta\text{-}C_5Ph_5)]$. We will publish elsewhere the detailed electrochemical and e.s.r. spectroscopic studies which show[12] that the $[C_5Ph_5]^-$ ligand also stabilises the 19-electron radical anions $[M(CO)_2(\eta\text{-}C_5R_5)]^-$ (M = Co or Rh).

Results and Discussion

The complexes $[M(CO)_2(\eta\text{-}C_5Ph_5)]$ (**1**, M = Co or Rh), precursors to the compounds described herein, are not conveniently prepared by the methods used for $[M(CO)_2(\eta\text{-}C_5R_5)]$ (R = H or Me). For example, heating C_5Ph_5H and $[Co_2(CO)_8]$ in n-hexane for 18 h, or irradiating the mixture with u.v. light failed to give (**1**, M = Co), and $[\{RhCl(CO)_2\}_2]$ gave only trace quantities of (**1**, M = Rh) with $Na[C_5Ph_5]$ in tetrahydrofuran (thf). The desired dicarbonyl was prepared in *ca.* 30% yield from $[\{RhCl(CO)_2\}_2]$ and $Li[C_5Ph_5]$. However, the lithium salt is prepared from C_5Ph_5H, which is in turn made from C_5Ph_5Br, so that the overall yield does not compare favourably with that obtained directly from the bromide as described below.

The most convenient methods for the preparation of (**1**) involve somewhat different synthetic pathways. On adding zinc dust and $[Co_2(CO)_8]$ to C_5Ph_5Br an intense purple solution is initially formed, probably containing the radical C_5Ph_5.[13] After 1 h, however, the reaction mixture was dark brown, and good yields of brown crystals of (**1**, M = Co) were isolated by evaporation to dryness, extraction into CH_2Cl_2, and column chromatography on alumina. The solid complex slowly decomposes in air, but was readily characterised by elemental analysis, mass spectrometry, and the two intense absorptions in the i.r. carbonyl spectrum (Table 1).

The analogous rhodium complex (**1**, M = Rh) was prepared by the reaction of zinc dust with a mixture of C_5Ph_5Br and

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* A note reporting the synthesis of $[Co(CO)_2(\eta\text{-}C_5Ph_5)]$ has appeared since this work was submitted (W. Klaui and L. Ramacher, *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 97).

Table 1. Infrared spectroscopic and analytical data for pentaphenylcyclopentadienyl complexes of cobalt and rhodium

Complex	Colour	$(m/e)^a$	$\tilde{\nu}(CO)^b/cm^{-1}$	Analysis^c (%)	
				C	H
$[Co(CO)_2(\eta\text{-}C_5Ph_5)]$	Brown	560	2 016, 1 956	78.9 (79.3)	4.4 (4.5)
$[Rh(CO)_2(\eta\text{-}C_5Ph_5)]$	Orange	604	2 037, 1 973	73.4 (73.5)	4.0 (4.2)
$[CoI_2(CO)(\eta\text{-}C_5Ph_5)]$	Black		2 056	54.9 (55.0)	3.4 (3.2)
$[RhI_2(CO)(\eta\text{-}C_5Ph_5)]$	Black		2 072	52.3 (52.0)	3.0 (3.0)
$[Co(CO)\{P(OMe)_3\}(\eta\text{-}C_5Ph_5)]$	Brown		1 935	71.3 (71.3)	5.2 (5.2)
$[Co(CO)\{P(OPh)_3\}(\eta\text{-}C_5Ph_5)]$	Brown		1 948	74.3 (73.9)	4.4 (4.7)^d
$[Rh(CO)(PPh_3)(\eta\text{-}C_5Ph_5)]$	Red	836	1 946	76.8 (76.5)	5.8 (5.3)^e
$[Rh(CO)(AsPh_3)(\eta\text{-}C_5Ph_5)]$	Pink	882	1 940	70.5 (70.8)	4.1 (4.5)^f
$[Rh(CO)\{P(OMe)_3\}(\eta\text{-}C_5Ph_5)]$	Yellow	700	1 960	67.0 (66.9)	4.9 (4.9)
$[Rh(CO)\{P(OPh)_3\}(\eta\text{-}C_5Ph_5)]$	Yellow	886	1 971	72.6 (73.1)	4.4 (4.5)
$[\{RhBr_2(\eta\text{-}C_5Ph_5)\}_2]$	Red-purple			58.2 (58.1)	3.5 (3.5)^f
$[RhBr_2\{P(OMe)_3\}(\eta\text{-}C_5Ph_5)]$	Brown-purple			50.9 (51.0)	3.9 (3.9)^d

^{a} By mass spectrometry. ^{b} In CH_2Cl_2. ^{c} Calculated values in parentheses. ^{d} Analysed as a CH_2Cl_2 solvate. ^{e} Analysed as a thf solvate. ^{f} Analysed as a $0.5CH_2Cl_2$ solvate.

$[\{RhCl(CO)_2\}_2]$ in thf. Once again, a deep purple solution is initially formed, but after 4 h a green solution results which contains (1, M = Rh) and small quantitities of $[\{Rh(\mu\text{-}CO)(\eta\text{-}C_5Ph_5)\}_2]$. The two complexes are separable by column chromatography as orange and intense green air-stable solids, respectively. The latter is, however, better prepared by reacting $[RhI_2(CO)(\eta\text{-}C_5Ph_5)]$ (see below) and $[Co(\eta\text{-}C_5H_5)_2]$ in benzene, although even then it has defied complete purification. It has been characterised by analogy in that its colour and i.r. carbonyl spectrum [$\tilde{\nu}(CO)$ (CH_2Cl_2) = 1 767 cm^{-1}] are similar to those of $[\{M(\mu\text{-}CO)(\eta\text{-}C_5Me_5)\}_2]$ [M = Co, deep green, $\tilde{\nu}(CO)$ = 1 756 cm^{-1};[14] M = Rh, deep blue, $\tilde{\nu}(CO)$ = 1 732 cm^{-1} [15]]. In addition, preliminary studies show that it undergoes a reversible one-electron reduction to the anion $[\{Rh(\mu\text{-}CO)(\eta\text{-}C_5Ph_5)\}_2]^-$ ($E^\circ = -0.86$ V) which shows an anisotropic, frozen-solution (−196 °C) e.s.r. spectrum (g_1 = 2.001, g_2 = 2.083, g_3 = 2.186, g_{av} = 2.090) when generated with $[Co(\eta\text{-}C_5H_5)_2]$ (*cf.* $[\{Rh(\mu\text{-}CO)(\eta\text{-}C_5Me_5)\}_2]^-$, E° = −1.15 V *vs.* Ag–$AgNO_3$, in MeCN, g_{av} = 2.0704[16]).

Some indication of the route by which (1, M = Rh) is formed from $[\{RhCl(CO)_2\}_2]$, C_5Ph_5Br, and zinc is provided when the reaction is carried out in benzene rather than thf. On stirring the mixture at room temperature, a dark red-brown precipitate is formed which can be recrystallised from CH_2Cl_2–n-hexane as brick-red crystals. Although this complex has not been fully characterised, its method of preparation, insolubility in all but the more polar organic solvents, and elemental analysis (C and H only) all support the formulation $[RhBr(CO)_2(\eta C_5Ph_5)][ZnCl_3]$. In addition, the i.r. carbonyl spectrum shows two bands at 2 066 and 1 991 cm^{-1}, some 20—30 cm^{-1} to higher energy than those of (1, M = Rh) as expected for a more positively charged carbonyl complex.

On treatment with $[N(PPh_3)_2][Mn(CO)_5]$, $[RhBr(CO)_2(\eta\text{-}C_5Ph_5)][ZnCl_3]$ is converted to (1, M = Rh) in an overall yield similar to that obtained from the direct reaction between $[\{RhCl(CO)_2\}_2]$ and C_5Ph_5Br in thf.

The similar values of $\tilde{\nu}(CO)$ for (1) and $[M(CO)_2(\eta\text{-}C_5H_5)]$ [*e.g.* M = Co, $\tilde{\nu}(CO)$ (CH_2Cl_2) = 2 029, 1 963 cm^{-1}] imply similar M–CO bond strengths and perhaps, therefore, a similar susceptibility towards Lewis-base substitution of the carbonyl ligands. However, (1) does not readily undergo reactions with P- or As-donors. For example, (1, M = Co) and PPh_3 failed to react when irradiated (u.v. light) in toluene for 60 h or when treated with Me_3NO in acetone. Similarly, no reaction was observed when (1, M = Rh) and PPh_3 were heated under reflux in n-heptane for four days.

The mechanism of carbonyl substitution of $[M(CO)_2(\eta\text{-}C_5R_5)]$ (M = Co or Rh, R = Me) by Lewis bases is associative, involving a slippage of the $\eta\text{-}C_5R_5$ ligand to the η^3-bonding mode. Comparative kinetic studies of the substitution reactions of the cyclopentadienyl and pentamethylcyclopentadienyl complexes have shown that the methyl substituents in the latter lower the reaction rates markedly.[17] It seems likely, therefore, that steric rather than electronic factors lead to the substitutional inertness of (1).

The direct substitution of (1, M = Co or Rh) was successfully achieved *via* one-electron oxidation, as previously demonstrated[18] for $[Co(CO)_2(\eta\text{-}C_5R_5)]$ (R = H or Me). The oxidative substitution of (1, M = Rh) is readily demonstrated by cyclic voltammetry. Figure 1(*a*) shows the cyclic voltammogram of the dicarbonyl in CH_2Cl_2, with one irreversible oxidation wave (A) at *ca.* 1.03 V and a second (B) at a slightly more positive potential. A product wave (C) at *ca.* 0.18 V appears to be associated with the second oxidation in that wave C is absent if the initial scan is curtailed at 1.0 V, Figure 1(*b*).

On adding PPh_3 to the solution of (1, M = Rh), two oxidation waves are observed at 0.86 and 1.08 V together with a new product wave at 0.46 V, Figure 1(*c*). The last is associated with the *first* oxidation wave, as demonstrated by curtailing the initial voltage scan at 0.95 V, Figure 1(*d*), and is reversible, as shown by continuous scan cyclic voltammetry, Figure 1(*e*).

Further, detailed electrochemical studies on (1, M = Rh) are necessary to clarify the relationship between waves A, B, and C.* Nevertheless, in the presence of PPh_3 it is clear that the formation of $[Rh(CO)_2(\eta\text{-}C_5Ph_5)]^+$ is followed by rapid substitution to give $[M(CO)L(\eta\text{-}C_5Ph_5)]^+$ (2^+, M = Rh, L = PPh_3) which is reversibly reduced to $[M(CO)L(\eta\text{-}C_5Ph_5)]$ (2, M = Rh, L = PPh_3) at 0.46 V (see below). That this oxidative substitution is successful for rhodium is particularly noteworthy, and is dependent on the stability of the radical cation (2^+). By constrast, the oxidative substitution of $[Rh(CO)_2(\eta\text{-}C_5R_5)]$ (R = H or Me) is unsuccessful; the cations $[Rh(CO)L(\eta\text{-}C_5R_5)]^+$ (R = H[19] or Me[20]) are too unstable at room

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* Studies of the electrochemical properties of $[M(CO)_2(\eta\text{-}C_5R_5)]$ (M = Co or Rh; R = H, Me, or Ph) are in progress (W. E. Geiger and T. Gennett, personal communication).

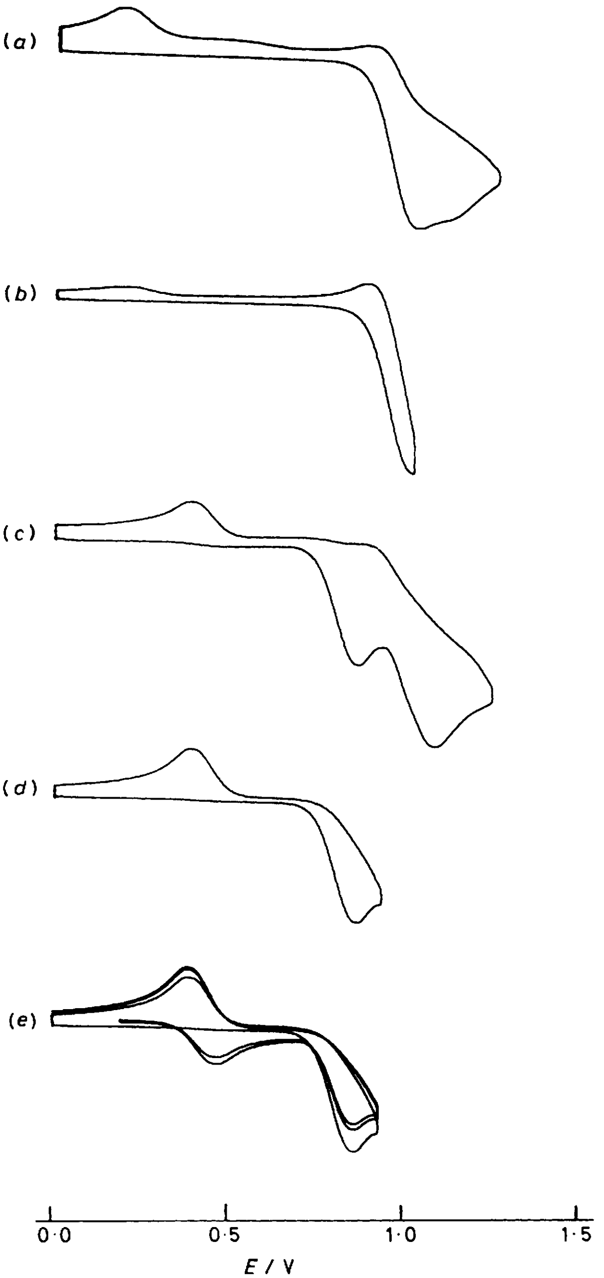

Figure 1. The cyclic voltammogram of $[Rh(CO)_2(\eta\text{-}C_5Ph_5)]$: (*a*) 0.0—1.25 V; (*b*) 0.0—1.0 V; (*c*) in the presence of PPh_3 (1:1), 0.0—1.25 V; (*d*) as (*c*) but 0.0—0.95 V; (*e*) as (*d*) but with continuous scanning

temperature to permit the subsequent reduction to $[Rh(CO)L(\eta\text{-}C_5R_5)]$ (R = H or Me).

The chemical synthesis of (**2**) *via* oxidative substitution is only completely successful for [**2**, M = Rh, L = $P(OPh)_3$], but then there is the bonus that the process is catalytic in oxidant. Thus, on adding a small quantity of $[Fe(\eta\text{-}C_5H_5)_2][PF_6]$ to (**1**, M = Rh) and an excess of $P(OPh)_3$ in CH_2Cl_2, CO is vigorously evolved and $[Rh(CO)\{P(OPh)_3\}(\eta\text{-}C_5Ph_5)]$ is readily isolable in high yield.

The overall substitution reaction can be expressed in terms of the steps (i)—(iv).

$$[Rh(CO)_2(\eta\text{-}C_5Ph_5)] - e^- \rightleftharpoons [Rh(CO)_2(\eta\text{-}C_5Ph_5)]^+ \quad \text{(i)}$$

$$[Rh(CO)_2(\eta\text{-}C_5Ph_5)]^+ + L \longrightarrow [Rh(CO)L(\eta\text{-}C_5Ph_5)]^+ + CO \quad \text{(ii)}$$

$$[Rh(CO)L(\eta\text{-}C_5Ph_5)]^+ + e^- \rightleftharpoons [Rh(CO)L(\eta\text{-}C_5Ph_5)] \quad \text{(iii)}$$

$$[Fe(\eta\text{-}C_5H_5)_2] - e^- \rightleftharpoons [Fe(\eta\text{-}C_5H_5)_2]^+ \quad \text{(iv)}$$

The catalytic cycle, observed when L = $P(OPh)_3$, depends on the relative potentials of the redox couples shown in steps (iii) and (iv). Despite the large, and unfavourable, difference between the potentials for the reduction of the ferrocenium ion (0.47 V) and the oxidation of (**1**, M = Rh) in the presence of L (*ca.* 1.0 V), the irreversibility of step (ii) allows oxidative substitution to occur. Once formed, [$\mathbf{2}^+$, M = Rh, L = $P(OPh)_3$] is a strong enough oxidant (E° = 0.67 V, see below) to regenerate $[Fe(\eta\text{-}C_5H_5)_2]^+$, renewing the catalytic cycle.

For phosphorus and arsenic ligands which are better donors than $P(OPh)_3$, the difference between the potentials for the couples (iii) and (iv) becomes less negative and, indeed, can become positive (*e.g.*, L = $AsPh_3$). Thus, the reaction between (**1**, M = Rh), $[Fe(\eta\text{-}C_5H_5)_2]^+$, and L leads to an inseparable, equilibrium mixture of (**2**), ($\mathbf{2}^+$), ferrocene, and the ferrocenium ion, and does not provide a practical route to (**2**).

The use of alternative, stronger oxidants such as (*a*) Ag^+, which gives an unstable adduct with (**1**, M = Rh), similar to that formed[19] with $[Rh(CO)(PPh_3)(\eta\text{-}C_5H_5)]$, (*b*) $[NO]^+$, which gives cationic nitrosyl complexes,[21] and (*c*) $[N(C_6H_4Br\text{-}p)_3]^+$ which causes extensive decomposition, was similarly unsuccessful. Alternative syntheses of (**2**) were therefore devised.

The salt formulated as $[RhBr(CO)_2(\eta\text{-}C_5Ph_5)][ZnCl_3]$ (see above) reacts with PPh_3 or $AsPh_3$ to give monocarbonyl complexes characterised only by i.r. spectroscopy as $[RhBr(CO)L(\eta\text{-}C_5Ph_5)][ZnCl_3]$ [L = PPh_3, $\tilde{\nu}$(CO) (CH_2Cl_2) = 1 979 cm^{-1}; L = $AsPh_3$, $\tilde{\nu}$(CO) (CH_2Cl_2) = 1 975 cm^{-1}]. On treating these complexes with $[N(PPh_3)_2][Mn(CO)_5]$, the neutral compounds (**2**, M = Rh, L = PPh_3 or $AsPh_3$) were isolated, after chromatography, as red, air-stable solids in moderate (L = PPh_3) or poor (L = $AsPh_3$) yields.

The third route to (**2**) also involves the reduction of halogeno complexes of Co^{III} or Rh^{III}. The halogenation of $[M(CO)_2(\eta\text{-}C_5R_5)]$ (R = H or Me) occurs as shown below, the final product depending on M, X, and R.

$$\begin{tikzcd}
{[M(CO)_2(\eta\text{-}C_5R_5)]} \arrow[r, "X_2"] & {[MX_2(CO)(\eta\text{-}C_5R_5)]} \arrow[dl, "-CO"'] \\
{[\{MX_2(\eta\text{-}C_5R_5)\}_2]} &
\end{tikzcd}$$

On monitoring the i.r. carbonyl spectrum of (**1**, M = Rh) in CH_2Cl_2 in the presence of iodine or bromine at room temperature, the band attributable to $[MX_2(CO)(\eta\text{-}C_5Ph_5)]$ (**3**, M = Co or Rh, X = Br or I) slowly disappeared and the final dimeric product was precipitated from the solution. The diiodomonocarbonyls (**3**, M = Co or Rh, X = I) were therefore isolated, in high yield, by reacting (**1**) with iodine in n-hexane–toluene (1:1) at 0 °C. The black solids were fully characterised by elemental analysis and by i.r. carbonyl bands at *ca.* 2 060 cm^{-1} (Table 1).

The dimeric bromide $[\{RhBr_2(\eta\text{-}C_5Ph_5)\}_2]$ (**4**) was best prepared by the dropwise addition of a dilute solution of bromine in CH_2Cl_2 to (**1**) in the same solvent. The precipitation of a near-quantitative yield of the red-purple product (Table 1) was completed by adding n-hexane to the reaction mixture.

Both (**3**) and (**4**) may be used in the synthesis of (**2**). Thus, the monocarbonyl (**3**, M = Co, X = I) in toluene was treated with

Table 2. Cyclic voltammetric data[a] for $[M(CO)L(\eta\text{-}C_5Ph_5)]$

M	L	$E_1{}^b$/V	$E_2{}^c$/V
Co	$P(OMe)_3$	0.43	0.95
Co	$P(OPh)_3$	0.55	1.44
Rh	PPh_3	0.46	1.29[d]
Rh	$AsPh_3$	0.42	1.12
Rh	$P(OMe)_3$	0.59	0.84
Rh	$P(OPh)_3$	0.67	1.18

[a] At a platinum-bead electrode in CH_2Cl_2, 5×10^{-4} mol dm^{-3} in complex and 0.1 mol dm^{-3} in $[NBu^n{}_4][PF_6]$ as supporting electrolyte. All potentials are quoted *vs.* the aqueous saturated calomel electrode. Under these conditions, the oxidation potentials of $[Fe(\eta\text{-}C_5H_5)_2]$ and $[Fe(\eta\text{-}C_5Me_5)_2]$ are 0.47 and −0.07 V respectively. [b] E_1 is the potential for the reversible one-electron oxidation of $[M(CO)L(\eta\text{-}C_5Ph_5)]$ to $[M(CO)L(\eta\text{-}C_5Ph_5)]^+$. [c] E_2 is the oxidation peak potential at a scan rate of 200 mV s^{-1}, for the irreversible one-electron oxidation of $[M(CO)L(\eta\text{-}C_5Ph_5)]^+$. [d] At a scan rate of 200 mV s^{-1} there is some evidence for reversibility ($i_{red}/i_{ox} = 0.7$); the corresponding reduction peak potential is 1.15 V.

$P(OMe)_3$ or $P(OPh)_3$ and then $[Co(\eta\text{-}C_5H_5)_2]$. The resulting brown solution was filtered to remove $[Co(\eta\text{-}C_5H_5)_2]I$, and then chromatographed to give brown crystals of [**2**, M = Co, L = $P(OMe)_3$ or $P(OPh)_3$] in *ca.* 50% yield. This method provides the only route to Lewis-base derivatives of (**1**, M = Co).

On reacting dimer (**4**) with $P(OMe)_3$, the mononuclear dibromide $[RhBr_2\{P(OMe)_3\}(\eta\text{-}C_5Ph_5)]$ (**5**) is formed as a brown-purple solid, characterised as a CH_2Cl_2 solvate by elemental analysis (Table 1) and ^1H n.m.r. spectroscopy {δ($CDCl_3$), 3.8 [9 H, d, *J*(MeP) 12 Hz, $P(OMe)_3$], 5.3 (2 H, s, CH_2Cl_2), 7.2 (25 H, m, C_5Ph_5)}. Treatment of (**5**) with $[Co(\eta\text{-}C_5H_5)_2]$ (1:2 ratio) in the presence of CO gas gave an orange solution from which a high yield of [**2**, M = Rh, L = $P(OMe)_3$] was isolated.

The One-Electron Oxidation of (**2**, M = Co *or* Rh).—The synthesis of (**2**), by the various routes described above, has allowed electrochemical and chemical studies of the formation of ($\mathbf{2}^+$) to be carried out.

Each of the complexes [**2**; M = Co, L = $P(OMe)_3$ or $P(OPh)_3$; M = Rh, L = PPh_3, $AsPh_3$, $P(OMe)_3$, or $P(OPh)_3$] undergoes a diffusion-controlled, reversible one-electron oxidation at a platinum bead electrode in CH_2Cl_2 (Table 2). The implied stability of the resulting radical cations ($\mathbf{2}^+$, M = Rh) contrasts with the high reactivity of $[Rh(CO)(PPh_3)(\eta\text{-}C_5H_5)]^+$ which rapidly yields[19] $[Rh_2(CO)_2(PPh_3)_2(\eta^5\text{:}\eta'^5\text{-}C_{10}H_8)]^{2+}$.

The potentials ($E°$) for the oxidation of (**2**) depend in the normal way on the donor abilities of the ligand L. Comparisons are difficult but the C_5Ph_5 ligand appears to shift $E°$ to slightly more positive potentials, in agreement with studies on $[Pd(\eta^4\text{-}cod)(\eta\text{-}C_5R_5)]^+$ (R = H or Ph).[10] Based on the electrochemical data for [**2**, M = Rh, L = PPh_3, $P(OMe)_3$, or $P(OPh)_3$] and [**2**, M = Co, L = $P(OMe)_3$ or $P(OPh)_3$] (Table 2), $E°$ for (**2**, M = Co, L = PPh_3) can be estimated at *ca.* 0.3 V which compares with a value of 0.17 V for $[Co(CO)(PPh_3)(\eta\text{-}C_5H_5)]$.[18]

Table 3. Infrared and e.s.r. spectroscopic data for $[Rh(CO)L(\eta\text{-}C_5Ph_5)]^+$ in CH_2Cl_2

L	$\tilde{\nu}$(CO)/cm^{-1}	g_{iso}	$A_{iso}{}^a$/G
PPh_3	2 041	2.059	15.0[b]
$AsPh_3$	2 039	2.060	17.0[c]
$P(OPh)_3$	2 060	2.049	17.0[b]

[a] Values from the computer-simulated spectra (G = 10^{-4} T). [b] Doublet, ^{31}P coupling. [c] Quartet, ^{75}As coupling.

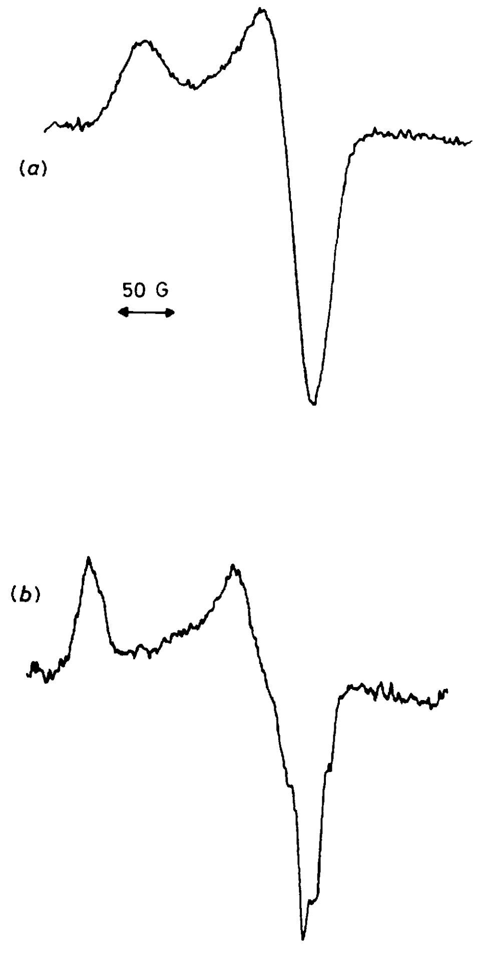

Figure 2. The frozen-solution (−196 °C, CH_2Cl_2) e.s.r. spectra of (*a*) $[Rh(CO)(PPh_3)(\eta\text{-}C_5Me_5)]^+$ and (*b*) $[Rh(CO)(PPh_3)(\eta\text{-}C_5Ph_5)]^+$

Although the cations ($\mathbf{2}^+$, M = Rh) have not been isolated they can be generated in solution and characterised by i.r. and e.s.r. spectroscopy (Table 3). As mentioned above, the redox potentials of the couples (**2**)–($\mathbf{2}^+$) and $[Fe(\eta\text{-}C_5H_5)_2]$–$[Fe(\eta\text{-}C_5H_5)_2]^+$ are such that the reactions between (**2**, M = Rh, L = PPh_3 or $AsPh_3$) and the ferrocenium ion lead to equilibrium mixtures of the four components. Nevertheless, the deep purple solutions containing ($\mathbf{2}^+$) show carbonyl stretching frequencies 90—100 cm^{-1} higher in energy than those of (**2**) (*cf.* $[Co(CO)\{P(C_6H_{11})_3\}(\eta\text{-}C_5H_5)]^Z$, Z = 0, $\tilde{\nu}$(CO) (hexane) = 1 920 cm^{-1};[22] Z = 1, $\tilde{\nu}$(CO) (CH_2Cl_2) = 2 045 cm^{-1}),[18] and the e.s.r. spectra show absorptions with *g* values at *ca.* 2.05—2.06 (Table 3) and hyperfine coupling to the P- or As-donor atoms of L is also observed.

The reaction between [**2**, M = Rh, L = $P(OPh)_3$] and $AgPF_6$ in CH_2Cl_2 similarly gave a deep purple solution, containing [$\mathbf{2}^+$, M = Rh, L = $P(OPh)_3$] (Table 3) but in this case decomposition to an orange, diamagnetic complex slowly occurred. This behaviour is probably due, in part, to the further oxidation of ($\mathbf{2}^+$); the cyclic voltammograms of (**2**) show second, irreversible oxidation waves at potentials accessible to Ag^+ salts in CH_2Cl_2 (Table 2).

The Radical Cations $[Rh(CO)(PPh_3)(\eta\text{-}C_5R_5)]^+$ (R = H *or* Me).—We have referred above to the instability at room temperature of the radical cations $[Rh(CO)(PPh_3)(\eta\text{-}C_5R_5)]^+$ (R = H[19] or Me[20]). The successful characterisation of ($\mathbf{2}^+$, M = Rh), however, has led us to reinvestigate the oxidation of $[Rh(CO)(PPh_3)(\eta\text{-}C_5R_5)]$, by low-temperature e.s.r. spectroscopy.

On adding CH_2Cl_2 to a solid mixture of $[Rh(CO)(PPh_3)(\eta\text{-}C_5Me_5)]$ and $[Fe(\eta\text{-}C_5H_5)_2][PF_6]$ in an e.s.r. tube, and immediate cooling to −196 °C, a crimson glass was formed which showed the axial spectrum in Figure 2 (*a*). The strong similarity between this spectrum [$g_1 = 2.115, g_2 = 2.025, g_{av} = (g_1 + 2g_2)/3 = 2.055$], and the frozen-solution spectrum, Figure 2 (*b*), of ($\mathbf{2}^+$, M = Rh, L = PPh_3) [$g_1 = 2.142$, $g_2 = 2.019$, $g_{av} = 2.060$ (*cf.* $g = 2.059$ for isotropic, solution spectrum)], is excellent evidence that $[Rh(CO)(PPh_3)(\eta\text{-}C_5Me_5)]^+$ exists at −196 °C; on warming the glass to the melting point, the colour of the cation was rapidly discharged.

Attempts were also made to generate $[Rh(CO)(PPh_3)(\eta\text{-}C_5H_5)]^+$ at low temperature. Although deeply coloured glasses were formed when $[Rh(CO)(PPh_3)(\eta\text{-}C_5H_5)]$ was reacted with $[Fe(\eta\text{-}C_5H_5)_2]^+$ (purple) or $[N_2C_6H_4F\text{-}p]^+$ (red-brown), no e.s.r. spectra could be detected at −196 °C.

Conclusions

The formation of ($\mathbf{2}^+$, M = Rh) at room temperature clearly demonstrates the ability of the C_5Ph_5 ligand to stabilise otherwise highly reactive radical cations. Further, detailed e.s.r. spectroscopic studies may help to shed light on the factors which influence such stabilisation, and in particular the role of delocalisation by the phenyl substituents on the C_5 ligand.

Experimental

The preparation, purification, and reactions of the complexes described were carried out under an atmosphere of dry nitrogen. Unless stated otherwise, the complexes are air-stable solids which dissolve in CH_2Cl_2 to give air-sensitive solutions. The compounds $[Co_2(CO)_8]$,[23] $[\{RhCl(CO)_2\}_2]$,[24] C_5Ph_5Br,[13] $[N(PPh_3)_2][Mn(CO)_5]$,[25] $[Fe(\eta\text{-}C_5H_5)_2][PF_6]$,[26] and $[Co(\eta\text{-}C_5H_5)_2]$[27] were prepared by published methods.

Cyclic voltammetry was carried out as previously described.[28] Infrared spectra were recorded on Nicolet MX5 FT or Perkin-Elmer PE 257 instruments. Spectra from the latter were calibrated against the absorption band of polystyrene at 1 601 cm^{-1}. Hydrogen-1 n.m.r. spectra were recorded on a JEOL PMX 60 instrument and calibrated against $SiMe_4$ as internal reference. Mass spectra were recorded on an AEI MX 902 spectrometer. E.s.r. spectra were recorded on a Varian Associates 4502/15 spectrometer with a solid sample of the diphenylpicrylhydrazyl radical as external reference. The e.s.r. spectra were simulated as previously described.[29] Microanalyses were by the staff of the Microanalytical Service of the School of Chemistry, University of Bristol.

Dicarbonyl(η*-pentaphenylcyclopentadienyl*)*cobalt*, $[Co(CO)_2(\eta\text{-}C_5Ph_5)]$.—To a solution of C_5Ph_5Br (1.54 g, 2.93 mmol) in thf (40 cm^3) was added zinc dust (0.20 g, 3.06 mmol) and $[Co_2(CO)_8]$ (0.50 g, 1.46 mmol). After stirring for 1 h the dark brown solution was evaporated to dryness, extracted into CH_2Cl_2, and chromatographed on an alumina–n-hexane column. Elution with CH_2Cl_2–n-hexane (1:5) gave the product as a brown solid which slowly decomposes in air, yield 1.06 g (65%).

Dicarbonyl(η*-pentaphenylcyclopentadienyl*)*rhodium*, $[Rh(CO)_2(\eta\text{-}C_5Ph_5)]$.—A mixture of $[\{RhCl(CO)_2\}_2]$ (0.10 g, 0.26 mmol), C_5Ph_5Br (0.30 g, 0.57 mmol), and zinc dust (0.04 g, 0.62 mmol), in thf (25 cm^3) was stirred for 4 h. The green solution was filtered, evaporated to dryness, and extracted with CH_2Cl_2. Chromatography on an alumina–n-hexane column gave an orange band which was eluted with CH_2Cl_2–n-hexane (1:6) to give an orange solution. Evaporation to dryness gave the product as an orange solid, yield 0.10 g (32%).

Further elution of the column, with CH_2Cl_2–n-hexane (1:3) gave a dark green band from which small quantities of $[\{Rh(\mu\text{-}CO)(\eta\text{-}C_5Ph_5)\}_2]$ were isolated by evaporation to dryness.

Bromodicarbonyl(η*-pentaphenylcyclopentadienyl*)*rhodium Trichlorozincate*, $[RhBr(CO)_2(\eta\text{-}C_5Ph_5)][ZnCl_3]$.—A mixture of $[\{RhCl(CO)_2\}_2]$ (0.50 g, 1.29 mmol), C_5Ph_5Br (1.35 g, 2.58 mmol), and zinc dust (0.17 g, 2.60 mmol) was stirred in benzene (25 cm^3) for 24 h. The dark red-brown precipitate was filtered off, washed with toluene, and recrystallised from CH_2Cl_2–n-hexane to give the product as brick-red crystals, yield 1.10 g (50%).

Carbonyldi-iodo(η*-pentaphenylcyclopentadienyl*)*cobalt*, $[CoI_2(CO)(\eta\text{-}C_5Ph_5)]$.—To a cooled (0 °C) solution of $[Co(CO)_2(\eta\text{-}C_5Ph_5)]$ (0.30 g, 0.53 mmol) in a mixture of toluene (40 cm^3) and n-hexane (40 cm^3) was added a solution of I_2 (0.14 g, 0.54 mmol) in toluene (10 cm^3). After 15 min the mother-liquors were decanted from the black crystalline product which was then washed with n-hexane and dried *in vacuo*, yield 0.32 g (80%).

The complex $[RhI_2(CO)(\eta\text{-}C_5Ph_5)]$ was prepared similarly in 85% yield.

Di-μ-carbonyl-bis(η*-pentaphenylcyclopentadienyl*)*dirhodium*, $[\{Rh(\mu\text{-}CO)(\eta\text{-}C_5Ph_5)\}_2]$.—To a stirred suspension of $[RhI_2(CO)(\eta\text{-}C_5Ph_5)]$ (0.42 g, 0.51 mmol) in benzene (50 cm^3) was added $[Co(\eta\text{-}C_5H_5)_2]$ (0.19 g, 1.00 mmol). The intense green solution was filtered, evaporated to low volume *in vacuo*, and then added to an alumina–n-hexane chromatography column. Elution with benzene gave a green solution which was evaporated to dryness to give the product as an impure dark green solid, yield 55 mg (19%).

Tetrabromobis(η*-pentaphenylcyclopentadienyl*)*dirhodium*, $[\{RhBr_2(\eta\text{-}C_5Ph_5)\}_2]$.—A dilute solution of bromine in CH_2Cl_2 (10 cm^3) was added dropwise to a stirred solution of $[Rh(CO)_2(\eta\text{-}C_5Ph_5)]$ (0.56 g, 0.93 mmol) in CH_2Cl_2 (20 cm^3), until the reaction was adjudged complete by i.r. spectroscopy. n-Hexane (10 cm^3) was then added to complete the precipitation of the red-purple product which was removed by filtration, washed with toluene (2 × 30 cm^3) and n-hexane (2 × 30 cm^3) and air-dried, yield 0.61 g (93%).

Dibromo(η*-pentaphenylcyclopentadienyl*)(*trimethyl phosphite*)*rhodium*, $[RhBr_2\{P(OMe)_3\}(\eta\text{-}C_5Ph_5)]$.—A suspension of $[\{RhBr_2(\eta\text{-}C_5Ph_5)\}_2]$ (0.61 g, 0.86 mmol) was stirred with $P(OMe)_3$ (0.12 cm^3, 0.96 mmol) in CH_2Cl_2 (20 cm^3) to give a brown solution. After filtration, the product was precipitated as a red-brown solid by the addition of n-hexane (40 cm^3), yield 0.63 g (88%).

Carbonyl(η*-pentaphenylcyclopentadienyl*)(*triphenyl phosphite*)*rhodium*, $[Rh(CO)\{P(OPh)_3\}(\eta\text{-}C_5Ph_5)]$.—On adding a catalytic amount of $[Fe(\eta\text{-}C_5H_5)_2][PF_6]$ (0.02 g, 0.06 mmol) to $[Rh(CO)_2(\eta\text{-}C_5Ph_5)]$ (0.50 g, 0.83 mmol) and $P(OPh)_3$ (0.3 cm^3, 1.10 mmol) in CH_2Cl_2 (25 cm^3), CO gas was vigorously evolved and the solution became yellow. The mixture was then evaporated to low volume and chromatographed on an alumina–n-hexane column. Elution with CH_2Cl_2–n-hexane (1:4) gave a yellow band which was partially evaporated to give the product as a bright yellow solid, yield 0.65 g (89%).

Carbonyl(η-pentaphenylcyclopentadienyl)(triphenylphosphine)rhodium, [Rh(CO)(PPh_3)(η-C_5Ph_5)].—A solution of [RhBr$(CO)_2$(η-C_5Ph_5)][$ZnCl_3$] (0.103 g, 0.123 mmol) and PPh_3 (0.035 g, 0.133 mmol) in CH_2Cl_2 (50 cm^3) was stirred for 20 min and then [N$(PPh_3)_2$][Mn$(CO)_5$] (0.116 g, 0.132 mmol) was added. The resulting green solution was evaporated to low volume *in vacuo*, and the residue was chromatographed on an alumina–n-hexane column. A yellow band containing [$Mn_2(CO)_{10}$] was eluted with n-hexane, and then a red band was eluted with CH_2Cl_2–n-hexane (1:1) to give the product as a red solid on evaporation to dryness, yield 34 mg (31%).

The complex [Rh(CO)($AsPh_3$)(η-C_5Ph_5)] was prepared similarly, in 8% yield.

Carbonyl(η-pentaphenylcyclopentadienyl)(trimethyl phosphite)cobalt, [Co(CO){P$(OMe)_3$}(η-C_5Ph_5)].—To a solution of P$(OMe)_3$ (0.11 cm^3, 0.87 mmol) in toluene was added [CoI_2(CO)(η-C_5Ph_5)] (0.32 g, 0.41 mmol) followed by [Co(η-C_5H_5)$_2$] (0.15 g, 0.82 mmol). The brown solution was filtered through Celite, to remove the green precipitate of [Co(η-C_5H_5)$_2$]I, and then evaporated to dryness. Chromatography of a CH_2Cl_2 extract of the residue on an alumina–n-hexane column gave two brown bands. The first, eluted with CH_2Cl_2–n-hexane (1:5) gave small quantities of [Co$(CO)_2$(η-C_5Ph_5)]; the second, eluted with CH_2Cl_2–n-hexane (1:3) gave the product as a light brown solid which slowly decomposes in air, yield 0.15 g (56%).

The complex [Co(CO){P$(OPh)_3$}(η-C_5Ph_5)] was prepared similarly, in 45% yield.

Carbonyl(η-pentaphenylcyclopentadienyl)(trimethyl phosphite)rhodium, [Rh(CO){P$(OMe)_3$}(η-C_5Ph_5)].—To a solution of [RhBr_2{P$(OMe)_3$}(η-C_5Ph_5)] (0.32 g, 0.38 mmol) in CH_2Cl_2 (40 cm^3), saturated with CO, was added [Co(η-C_5H_5)$_2$] (0.16 g, 0.85 mmol). The resulting orange solution was evaporated to dryness, extracted into toluene, and chromatographed on an alumina–n-hexane column. Elution with CH_2Cl_2–n-hexane (1:10) gave a yellow band containing a small quantity of [Rh$(CO)_2$(η-C_5Ph_5)]. Subsequent elution with CH_2Cl_2–n-hexane (1:3) gave a second yellow band from which the product was isolated as a yellow solid on partial evaporation *in vacuo*, yield 0.19 g (71%).

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References

1 Part 22, N. G. Connelly, M. J. Freeman, A. G. Orpen, J. B. Sheridan, A. N. D. Symonds, and M. W. Whiteley, *J. Chem. Soc., Dalton Trans.*, 1985, 1027.

2 See, for example, G. P. Pez and J. N. Armor, *Adv. Organomet. Chem.*, 1981, **19**, 1; P. T. Wolczanski and J. E. Bercaw, *Acc. Chem. Res.*, 1980, **13**, 121; P. M. Maitlis, *ibid.*, 1978, **11**, 301; R. B. King, *Coord. Chem. Rev.*, 1976, **20**, 155.

3 S. McVey and P. L. Pauson, *J. Chem. Soc.*, 1965, 4312.

4 A. Schott, H. Schott, G. Wilke, J. Brandt, H. Hoberg, and E. G. Hoffmann, *Liebigs Ann. Chem.*, 1973, 508.

5 W. Hübel and R. Merenyi, *J. Organomet. Chem.*, 1964, **2**, 213.

6 T. R. Jack, C. J. May, and J. Powell, *J. Am. Chem. Soc.*, 1977, **99**, 4709.

7 R. Zhang, M. Tsutsui, and D. E. Bergbreiter, *J. Organomet. Chem.*, 1982, **229**, 109.

8 M. J. Heeg, C. Janiak, and J. J. Zuckerman, *J. Am. Chem. Soc.*, 1984, **106**, 4259.

9 J. Powell and N. I. Dowling, *Organometallics*, 1983, **2**, 1742.

10 K. Broadley, G. A. Lane, N. G. Connelly, and W. E. Geiger, *J. Am. Chem. Soc.*, 1983, **105**, 2486.

11 K. Broadley, N. G. Connelly, G. A. Lane, and W. E. Geiger, *J. Chem. Soc., Dalton Trans.*, 1986, 373.

12 N. G. Connelly, W. E. Geiger, G. A. Lane, S. J. Raven, and P. H. Rieger, *J. Am. Chem. Soc.*, submitted.

13 K. Ziegler and B. Schnell, *Liebigs Ann. Chem.*, 1925, **445**, 266.

14 W. I. Bailey, jun., D. M. Collins, F. A. Cotton, J. C. Baldwin, and W. C. Kaska, *J. Organomet. Chem.*, 1979, **165**, 373.

15 A. Nutton and P. M. Maitlis, *J. Organomet. Chem.*, 1979, **166**, C21.

16 M. J. Krause and R. G. Bergman, *J. Am. Chem. Soc.*, 1985, **107**, 2973.

17 M. E. Rerek and F. Basolo, *Organometallics*, 1983, **2**, 372.

18 K. Broadley, N. G. Connelly, and W. E. Geiger, *J. Chem. Soc., Dalton Trans.*, 1983, 121.

19 N. G. Connelly, A. R. Lucy, J. D. Payne, A. M. R. Galas, and W. E. Geiger, *J. Chem. Soc., Dalton Trans.*, 1983, 1879.

20 N. G. Connelly and I. Manners, unpublished results.

21 N. G. Connelly, S. J. Raven, and W. E. Geiger, unpublished results.

22 A. J. Hart-Davis and W. A. G. Graham, *Inorg. Chem.*, 1970, **9**, 2658.

23 I. Wender, H. W. Sternburg, S. Metlin, and M. Orchin, *Inorg. Synth.*, 1957, **5**, 190.

24 J. A. McCleverty and G. Wilkinson, *Inorg. Synth.*, 1966, **8**, 211.

25 R. A. Faltynek and M. S. Wrighton, *J. Am. Chem. Soc.*, 1978, **100**, 2701.

26 J. C. Smart and B. L. Pinsky, *J. Am. Chem. Soc.*, 1980, **102**, 1009.

27 R. B. King and F. G. A. Stone, *Inorg. Synth.*, 1963, **7**, 99.

28 N. G. Connelly, M. J. Freeman, I. Manners, and A. G. Orpen, *J. Chem. Soc., Dalton Trans.*, 1984, 2703.

29 N. G. Connelly, I. Manners, J. R. C. Protheroe, and M. W. Whiteley, *J. Chem. Soc., Dalton Trans.*, 1984, 2713.

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