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Homogeneous Catalytic Carbonylation of Nitroaromatics. 4. Preparation and Characterization of Ruthenium Radical Cations

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The neutral bis(phosphine) tricarbonyl complexes $Ru(PR_3)_2(CO)_3$ (R = phenyl, benzyl, p-tolyl, cyclohexyl) and M[1,2-bis(diphenylphosphino)ethane](CO)$_3$ (M = Ru, Fe) were found to undergo 1-electron oxidations giving the highly reactive 17-electron radical cations. The $E_{1/2}$ values for the reversible oxidations of $Ru(PR_3)_2(CO)_3$ were determined by using cyclic voltammetry and showed the expected dependence on phosphine basicity. Chemical oxidation of these complexes using ferrocenium salts generated species that were stable enough at -40 °C to characterize by using infrared and electron paramagnetic resonance spectroscopies. The infrared absorptions in the ν_{CO} region of a given cation appeared at least 100 cm^{-1} higher in energy compared to that of the neutral starting complex. The EPR spectra of the radical cations exhibited a broad 1:2:1 triplet with hyperfine coupling to phosphorus atoms of ≈20 G. Reagents such as organonitroso compounds, NO$_2$, triphenylmethane, tri-n-butyltin hydride, methylene chloride, tri-n-butyltin chloride, and chloranil were found to react with the radical cations. The presence of the chelating ligand 1,2-bis(diphenylphosphino)ethane (dppe) made the neutral complex of either iron or ruthenium easier to oxidize and the corresponding radical cation far more reactive than the bis(phosphine) complexes. Evidence was found supporting the formation of the dimer [Ru(dppe)(CO)$_3$]$_2$$^{2+}$.

Introduction

There has been much interest in organo-transition-metal carbonyl radicals because of their possible role in catalytic and stoichiometric transformations.[1-6] Numerous studies have been reported on their role in migratory insertion reactions, in electrocatalysis of ligand-substitution reactions, and as oxidizing and reducing agents. Synthetic routes to these interesting species involve irradiation or thermolysis of metal-metal bonded dimers, 1-electron oxidation or reduction of 18- and 16-electron compounds by electrochemical or chemical means, and radical chain initiation. Most of the metal carbonyl radicals investigated are short-lived. As a result, little structural information is known about them.

Among the more stable 17-electron species are the d^7 M-(PR$_3$)$_2$(CO)$_3$ complexes of manganese,[7,8] rhenium,[9,10] and iron.[11-15] Both the neutral Re and cationic Fe complexes can be isolated as solids, and a single-crystal X-ray crystallographic analysis of Re(PCy$_3$)$_2$(CO)$_3$ has been reported.[10]

We have been investigating the mechanism of the homogeneous catalytic carbonylation of nitroaromatics to carbamates.[16,17] One of the critical propositions is that activation of the nitroaromatic occurs by a single-electron-transfer reaction (eq 1). This reaction

$$Ru(dppe)(CO)_3 + ArNO_2 \rightarrow$$
$$[Ru(dppe)(CO)_3]^+ + [ArNO_2]^- \quad (1)$$
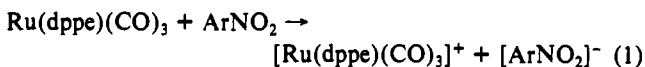
[dppe = 1,2-bis(diphenylphosphino)ethane] generates a cationic ruthenium-based radical about which nothing is known. This report describes our studies of the formation and reactivity of the radical cations $[Ru(PR_3)_2(CO)_3]^+$ and $[Ru(dppe)(CO)_3]^+$. In addition, we report some additional details on the iron cationic radical $[Fe(dppe)(CO)_3]^+$.

Experimental Section

The preparation, purification, and reactions described were performed under prepurified nitrogen. The following compounds were synthesized by reported procedures: $Ru(PR_3)_2(CO)_3$ [R = phenyl (**1a**), benzyl (**1b**), p-tolyl (**1c**), cyclohexyl (**1d**)],[18] $Ru(dppe)(CO)_3$ (**2**),[19] $Fe(PPh_3)_2(CO)_3$,[20] $Fe(dppe)(CO)_3$ (**3**),[21] $[Cp_2Fe][BF_4]$,[22] $[Cp_2Fe][PF_6]$[22] (Cp = η^5-C$_5$H$_5$), $[Ru(PPh_3)_2(CO)_2(o$-C$_6$H$_4$O$_2)][PF_6]$,[23] $[Ru(PPh_3)_2(CO)_2(NO)][PF_6]$,[24] and $[Ru(PPh_3)_2(CO)_3(X)][PF_6]$ (X = H,[24] Cl,[25] I[25]). The following compounds were obtained from Aldrich and used as received: AgBF$_4$, N(C$_6$H$_4$Br)$_3$, C$_6$Cl$_4$(O)$_2$, and NO$_2$. [NO][PF$_6$], [NO][BF$_4$], and Cp$_2$Fe were purchased from Alfa and used as obtained. Tetrahydrofuran (THF) and toluene were dried over sodium benzophenone ketyl. Methylene chloride was dried by refluxing over CaH$_2$ followed by distillation into a flask containing P$_2$O$_5$. Distillation from this vessel yielded dry CH$_2$Cl$_2$. Hexanes were dried by distillation from sodium benzophenone ketyl (tetraethylene glycol dimethyl ether (10%) was added to increase solubility).

Infrared spectra were recorded on a Mattson Cygnus 25 FTIR equipped with a HgCdTe detector. ^{1}H and ^{31}P NMR were obtained on an IBM AC-200 and a Varian VXR-300S spectrometer. Electron spin resonance spectra were recorded on a Bruker ESP 300 instrument and were calibrated against a solid sample of the diphenylpicrylhydrazyl radical. Mass spectra were obtained on a VG 7070E-HF instrument. Microanalyses were obtained from M-H-W laboratories.

Synthesis and Spectroscopy of the Radicals [Ru(PR$_3$)$_2$(CO)$_3$]$^+$ [R = Ph (1a$^+$), Bz (1b$^+$), p-Tol (1c$^+$), Cy (1d$^+$)] and [M(dppe)(CO)$_3$]$^+$ [M = Ru (2$^+$), Fe (3$^+$)]. The procedure was similar for each of phosphine complexes. Individual differences based on solubility or radical reactivity will be noted. The phosphine complex (typically 40 mg) was placed in a 3-neck flask and was dissolved in 2-5 mL of freshly distilled CH$_2$Cl$_2$ (for **1a-c, 2,** and **3**) or THF (for **1d**). This solution was then cooled to -43 °C (dry ice/acetonitrile slush bath) for **1a-d**, to -78 °C (dry ice/acetone) for **2**, and to 0 °C (ice bath) for **3**. After 10 min 1 equiv of solid

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Table I. Infrared and EPR Spectroscopic Data for Cation Radicals

compd	ν_{CO},^{a} cm^{-1}	$\langle g_{av} \rangle$ (temp, °C)^a	$\langle a(^{31}P) \rangle$, G
Ru(PPh₃)₂(CO)₃ (1a)	1897		
[Ru(PPh₃)₂(CO)₃][PF₆] (1a⁺)	2019	2.055 (−173)	22.6
Ru(PBz₃)₂(CO)₃ (1b)	1888		
[Ru(PBz₃)₂(CO)₃][PF₆] (1b⁺)	2004	2.053 (−73)	22.3
Ru(PTol₃)₂(CO)₃ (1c)	1887		
[Ru(PTol₃)₂(CO)₃][PF₆] (1c⁺)	2013	2.056 (−115)	22.1
Ru(PCy₃)₂(CO)₃ (1d)	1873 sh, 1853 vs		
[Ru(PCy₃)₂(CO)₃][PF₆] (1d⁺)	1991	2.060 (−173)	19.6
Ru(dppe)(CO)₃ (2)	2003 s, 1934 m, 1912 s		
[Ru(dppe)(CO)₃][PF₆] (2⁺)	b	2.052 (−173)	≈20^c
Fe(dppe)(CO)₃ (3)	1985 s, 1915 m, 1892 s		
[Fe(dppe)(CO)₃][PF₆] (3⁺)	2071 s, 2008 s, 1984 s	2.052 (−115)	21.4

^{a}Solvent = CH₂Cl₂. ^{b}The lifetime of the radical was too short to obtain a spectrum. ^{c}Very broad signals prohibited accurate measurement of coupling.

oxidant, usually very finely powdered [Cp₂Fe][PF₆], was added from an attached dip tube. An immediate color change from yellow to dark orange-brown was observed (green for 2⁺ and 3⁺). None of the radical cations were indefinitely stable at the reaction temperatures. For 1a⁺–c⁺ reaction with the solvent was complete within 10 min at −43 °C. Cation 1d⁺ was stable for approximately 5–10 min in THF at −43 °C. Cation 2⁺ was the least stable of all, completely reacting after 1–2 min. Compound 3⁺ was the most stable and was isolated by slow addition of hexanes (10 mL) to the CH₂Cl₂ solution. The green solid was collected, washed with toluene and hexanes, and then dried under an N₂ stream. The solid was air- and moisture-sensitive and was used immediately or stored under vacuum at 0 °C in the dark.

The oxidation procedure described above was also employed by using other oxidants, i.e. [Cp₂Fe][BF₄], [N(C₆H₄Br)₃][PF₆], and AgPF₆. However, when Ag⁺ was used as the oxidant, infrared spectroscopy indicated the presence of other species.

The infrared spectra for all of the radical cations (except 2⁺) were obtained by rapidly transferring a sample of the cold solution into a purged cell. Despite all attempts at rapid data collection, a varying amount of further reaction was usually evident in the infrared spectrum. The EPR spectra for all of the compounds were obtained by transfering a solution of the radical cation directly into a cold quartz tube that was purged with nitrogen. This was capped and frozen in liquid nitrogen during transportation to the EPR spectrometer. The tube was rapidly placed into the precooled EPR sample compartment and analyzed. A summary of the infrared and EPR spectral data of the radical cations is presented in Table I.

Halogen Abstraction Using [Ru(PPh₃)₂(CO)₃]⁺ (1a⁺). As a CH₂Cl₂ solution of 1a⁺ was allowed to warm to room temperature, the color of the solution changed to yellow and the infrared spectrum in CH₂Cl₂ contained two new strong peaks at 2082 and 2059 cm⁻¹, which were found to be identical with those reported for [Ru(PPh₃)₂(CO)₃(Cl)]⁺.[25] Reduction of the solvent and addition of 10 mL of hexane resulted in the precipitation of a yellow crystalline solid (62% yield). Use of [Cp₂Fe][BF₄] yielded the corresponding [BF₄]⁻ salt. Anal. Calcd for [Ru(PPh₃)₂(CO)₃(Cl)][BF₄]: C, 56.30; H, 3.64; Cl, 4.26. Found: C, 56.08; H, 3.80; Cl, 4.36. ¹H NMR (CD₂Cl₂): δ 7.92 (m, Ph), 7.71 (m, Ph), 7.59 (m, Ph), 7.35 (m, Ph). ³¹P NMR (CH₂Cl₂, relative to H₃PO₄): 18.3 ppm. Chlorine abstraction from Bu₃SnCl also yielded [Ru(PPh₃)₂(CO)₃Cl]⁺. Conducting the above procedure in CH₂I₂ yielded a yellow compound that had spectral properties identical with those of the known iodo cation [Ru(PPh₃)₂(CO)₃(I)]⁺.[25]

Isolation of [Ru(dppe)(CO)₃]₂[PF₆]₂. A CH₂Cl₂ solution of 2⁺ was warmed to room temperature, and the volume of the solvent was reduced to approximately 1 mL under vacuum. Addition of hexanes (10 mL) resulted in the precipitation of a yellow powder, which was recrystallized by slowly cooling a saturated THF solution (63% yield). Anal. Calcd for [Ru(dppe)(CO)₃]₂[PF₆]₂: C, 47.8; H, 3.4; Cl, 0.0. Found: C, 47.5; C, 3.8; Cl, 0.0. IR (THF): ν_{CO} 2102 w, 2062 m, 2039 vs, 1978 cm⁻¹ m. ¹H NMR (CD₂Cl₂): δ 7.67–7.55 (m, Ph), 3.13 (m, CH₂), 2.56 (m, CH₂). ³¹P NMR (CDCl₃, relative to H₃PO₄): 63.2 ppm.

Hydrogen Atom Abstraction Using [Ru(PPh₃)₂(CO)₃]⁺ (1a⁺) and [Ru(dppe)(CO)₃]⁺ (2⁺). 1a (43 mg, 0.06 mmol) and Bu₃SnH (17.5 mg, 0.06 mmol) were dissolved in freshly distilled CH₂Cl₂ (7 mL) in a 25-mL, 2-neck flask at 0 °C under a N₂ atmosphere. To this was added a CH₂Cl₂ solution (2 mL) of [Cp₂Fe][PF₆] (20.0 mg, 0.06 mmol). The light yellow starting solution turned bright yellow immediately upon addition of the oxidant. After the mixture was stirred for 5 min at 0 °C, the volatile material was removed by distillation under vacuum. The yellow residue was washed with 5 mL of toluene, 5 mL of Et₂O, and 5 mL of hexanes and then vacuum dried. The pale yellow solid was re-

crystallized from CH₂Cl₂/Et₂O, yielding an off-white solid (73% yield). IR (CH₂Cl₂): ν_{CO} 2122 vw, 2072 s, 2050 vs, 2010 cm⁻¹ w. ¹H NMR (CD₂Cl₂): δ 7.19 (m, Ph), 7.10 (m, Ph), −6.24 (t, $J_{P–H}$ = 14.9 Hz, Ru–H). ³¹P NMR (CD₂Cl₂, relative to H₃PO₄): 34.5 ppm. These data indicated the complex was the known cationic hydride [Ru(PPh₃)₂-(CO)₃(H)]⁺.[24] Substitution of Ph₃CH in place of Bu₃SnH gave lower yields of [Ru(PPh₃)₂(CO)₃H]⁺ with appreciable amounts of [Ru-(PPh₃)₂(CO)₃Cl]⁺.

The procedure for reacting 2⁺ with Bu₃SnH was the same as described for the preparation of [Ru(PPh₃)₂(CO)₃(H)][PF₆]. After recrystallization from CH₂Cl₂/Et₂O to remove [Ru(dppe)(CO)₃]₂²⁺, the infrared spectrum of the white salt was similar to that of the hydride compound, [Ru(dppe)(CO)₃(H)][BF₄], isolated by protonation of 2 with HBF₄·Et₂O. IR (CH₂Cl₂): ν_{CO} 2115 s, 2068 s, 2053 cm⁻¹ s. ¹H NMR (CD₂Cl₂): δ 7.20 (m, Ph), 2.64 (m, CH₂), 2.17 (m, CH₂), −7.63 (t, $J_{P–H}$ = 18.1 Hz, Ru–H). ³¹P NMR (CD₂Cl₂, relative to H₃PO₄): 64.2 ppm. FAB/MS (m/e): M⁺, 585; M − nCO (n = 1–3), 557, 529, 501. Anal. Calcd for [Ru(dppe)(CO)₃(H)][BF₄]: C, 49.8; H, 3.8. Found: C, 50.7; H, 4.2.

Reaction of [Ru(PPh₃)₂(CO)₃][PF₆] (1a⁺) with NO₂. The radical 1a⁺ (0.041 mmol) was prepared as previously described. A 1.15-mL aliquot of NO₂ was withdrawn from a flask purged with NO₂ at atmospheric pressure and room temperature. This corresponds to a 15% excess (0.047 mmol) of NO₂. This was added directly to the cold (−43 °C) solution of 1a⁺ resulting in a color change from dark brown to yellow. Upon warming of the solution to room temperature, the solvent was removed under vacuum, and the residue was washed with 5 mL of toluene, 5 mL of Et₂O, and 5 mL of hexanes. Recrystallization from CH₂Cl₂/Et₂O produced an orange solid in 27% yield. IR (CH₂Cl₂): ν_{CO} 2051 s, 2011 cm⁻¹ s; ν_{NO} 1763 cm⁻¹. A shoulder at 2069 cm⁻¹ was observed in the product from this reaction as well as in an authentic sample of [Ru-(PPh₃)₂(CO)₂(NO)][PF₆] prepared from Ru(PPh₃)₂(CO)₃ and [NO]-[PF₆]. We attribute this absorption to [Ru(PPh₃)₂(CO)₃H]⁺.[24] ¹H NMR (CD₂Cl₂): δ 7.51 (m, Ph), 7.39 (m, Ph). ³¹P NMR (CD₂Cl₂, relative to H₃PO₄): 17.8 ppm. These data proved the compound to be the known nitrosyl complex [Ru(PPh₃)₂(CO)₂(NO)][PF₆].

Reaction of [Ru(PPh₃)₂(CO)₃]⁺ (1a⁺) with Tetrachloro-o-quinone. To the dark brown solution of 1a⁺ was added 1 equiv of tetrachloro-o-quinone, resulting in a color change from brown to orange. After the solution warmed to room temperature, the solvent was removed under vacuum. The orange residue was washed with hexanes and toluene to extract a small amount (10% yield) of the netural species Ru(PPh₃)₂-(CO)₂(C₆Cl₄O₂), whose infrared spectrum was identical with that reported in the literature.[23] IR (CH₂Cl₂): ν_{CO} 2046 s, 1983 cm⁻¹ s. ¹H NMR (CD₂Cl₂): δ 7.50 (m, Ph), 7.44 (m, Ph). ³¹P NMR (CH₂Cl₂, relative to H₃PO₄): 6.0 ppm. The remaining residue was redissolved in CH₂Cl₂ (2 mL), the mixture was filtered, and hexanes (10 mL) were added to precipitate a brown solid (42% yield). The infrared and EPR spectra identified the compound as [Ru(PPh₃)₂(CO)₂(C₆Cl₄O₂)][PF₆], previously synthesized by a different method.[23] IR (CH₂Cl₂): ν_{CO} 2074 s, 2023 cm⁻¹ s. EPR (CH₂Cl₂, room temperature): $\langle g_{av} \rangle$ = 2.004; $\langle a(^{31}P) \rangle$ = 25.3 G (hyperfine coupling to ⁹⁹Ru and ¹⁰¹Ru was evident).

Reaction of [Ru(PR₃)₂(CO)₃]⁺ (1a⁺) with 2-Methyl-2-nitrosopropane and p-Chloronitrosobenzene. Freshly distilled CH₂Cl₂ (5 mL) was added to a 25-mL two-necked flask containing 1a (25 mg, 0.035 mmol) and 2-methyl-2-nitrosopropane (2.95 mg, 0.017 mmol). To this yellow-green solution was added [Cp₂Fe][PF₆] (11.6 mg, 0.035 mmol). An immediate color change to dark brown was observed. Infrared and EPR spectroscopic results of these solutions are summarized in Table II. We were unable to isolate the spin-trap adduct as a solid. The procedure described above was employed for the generation of [Ru(PR₃)₂(CO)₃-

Table II. Infrared and EPR Spectroscopic Data for Nitroso Adducts of Radicals

compd	$\nu_{CO},^a$ cm^{-1}	$\langle g_{av} \rangle$ (25 °C)	$\langle a_{iso} \rangle,^b$ G	$\langle a_{iso} \rangle,^c$ G
[Ru(PPh$_3$)$_2$(CO)$_3$(*t*-BuNO)]$^+$	*d*	2.006	18.0	2.9
[Ru(PBz$_3$)$_2$(CO)$_3$(*t*-BuNO)]$^+$	*d*	2.013	13.9	2.0
[Ru(PTol$_3$)$_2$(CO)$_3$(*t*-BuNO)]$^+$	*d*	2.008	18.0	2.2
[Ru(PCy$_3$)$_2$(CO)$_3$(*t*-BuNO)]$^+$	*d*	2.007 (-40 °C)^e	13.9	2.0
[Ru(dppe)(CO)$_3$(*t*-BuNO)]$^+$	2064 s, 1995 m, 1977 s	2.009	13.9	2.0
[Ru(PPh$_3$)$_2$(CO)$_3$(ClC$_6$H$_4$NO)]$^+$	2085 w, 2062 s, 2008 s	2.004	14.3	*f*
[Ru(dppe)(CO)$_3$(ClC$_6$H$_4$NO)]$^+$	2077 s, 2007 m, 1973 s	2.008	13.1	*f*

^{a}Solvent = CH$_2$Cl$_2$. ^{b}^{14}N hyperfine. ^{c}^{31}P hyperfine. ^{d}The lifetime of the radical was too short to obtain a spectrum. ^{e}Solvent = THF. ^{f}Very broad signals prohibited accurate measurement of smaller coupling.

Table III. Electrochemical Data for Ru(L)$_2$(CO)$_3$^{a}

ligand	$E_{1/2}^b$	ΔE_p	$i_{p,c}/i_{p,a}$	$E_{p,a}^c$	$E_{p,c}^d$
PPh$_3$	+0.255	0.118	1.0	+0.865	-0.950
PBz$_3$	+0.266	0.098	1.0	+0.567	-0.693
PTol$_3$	+0.200	0.124	1.0	+0.928	-1.120
PCy$_3$	-0.090	0.088	1.0	+0.982	-1.230
(dppe)$_{1/2}$				+0.171^e	-0.689

^{a}Measured in CH$_2$Cl$_2$/TBAH solution at 22 °C, $v = 0.1$ V/s. All potentials are reported in volts vs AgCl/Ag reference electrode as described in the text. ^{b}Half-wave potential of the quasi-reversible one-electron oxidation. ^{c}Anodic peak potential for the irreversible one-electron oxidative process. See text for details. ^{d}Cathodic peak potential for return reduction of irreversible oxidation. See text for details. ^{e}One irreversible oxidation is observed for this compound.

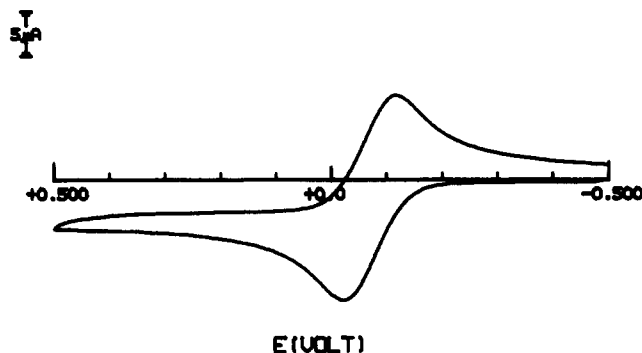(ClC$_6$H$_4$NO)][PF$_6$] except that precisely 1 equiv of ClC$_6$H$_4$NO was added.

Reaction of [Ru(dppe)(CO)$_3$]$^+$ (2$^+$) with *p*-Chloronitrosobenzene. To a 25-mL flask were added 2 (20 mg, 0.034 mmol), [Cp$_2$Fe][PF$_6$] (11.4 mg, 0.034 mmol), and ClC$_6$H$_4$NO (4.8 mg, 0.034 mmol). After placement under an atmosphere of nitrogen, freshly distilled CH$_2$Cl$_2$ was added. The color of the solution immediately turned an intense brown and was examined within 5 min by infrared and EPR spectroscopies. The product, presumed to be [Ru(dppe)(CO)$_3$(ClC$_6$H$_4$NO)][PF$_6$], was too reactive to allow its isolation as a solid. The above procedure was also employed for trapping the radical cation of iron, 3$^+$.

Electrochemical Studies. All electrochemical measurements were performed with a Bioanalytical Systems (BAS) Model 100 electrochemical analyzer. Electrochemical experiments were performed at 22 ± 2 °C with a normal three-electrode configuration consisting of a highly polished glassy-carbon-disk working electrode ($A = 0.07$ cm^2), a Pt-wire auxillary electrode, and a AgCl/Ag reference electrode containing 1.0 M KCl. The working compartment of the electrochemical cell was separated from the auxiliary compartment by a fritted-glass salt bridge and from the reference compartment by a modified Luggin capillary. All three compartments contained a 0.1 M solution of supporting electrolyte. Methylene chloride (Burdick and Jackson Laboratories, Inc.) and tetra-*n*-butylammonium hexafluorophosphate (Southwestern Analytical Chemicals, Inc.) were used without further purification. Electrolyte solutions were prepared and stored over 80–200-mesh activated alumina and 4-Å activated molecular sieves. Working solutions were deoxygenated with purified, solvent-saturated argon.

Table III contains a summary of the electrochemical data. Potentials are reported vs aqueous AgCl/Ag and are not corrected for the junction potential. No *iR* compensation was used in the electrochemical studies.[26] The $E^{o\prime}$ of the [Cp$_2$Fe]$^+$/Cp$_2$Fe couple was observed at +0.424 V.[27]

Results

Electrochemistry of Ru(PR$_3$)$_2$(CO)$_3$ and Ru(dppe)(CO)$_3$. Electrochemical studies were performed on the four phosphine complexes Ru(PR$_3$)$_2$(CO)$_3$ [R = Ph (1a), Bz (1b), *p*-Tol (1c), Cy (1d)]. The results of these studies are summarized in Table III, and the cyclic voltammogram of 1d is shown in Figure 1. Cyclic voltammetric studies revealed that each complex exhibits a quasi-reversible one-electron oxidation and an irreversible one-electron oxidation at higher potential. The first oxidation was designated a quasi-reversible one-electron process on the basis of the separation of anodic and cathodic peaks (0.088–0.124 V at

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E(VOLT)

**Figure 1.** Cyclic voltammogram of Ru(PCy$_3$)$_2$(CO)$_3$ in CH$_2$Cl$_2$.

a scan rate of 0.1 V/s), peak current ratios of unity ($i_{p,c}/i_{p,a} = 1$), the linear response of $i_{p,a}$ vs $n^{1/2}$ over the range of scan rates investigated, analysis of Anson plots prepared from double-step chronocoulometric experiments, and the similarity of these Ru complexes to an Fe complex previously reported. Controlled-potential electrolysis of the bis(phosphine) complexes failed to unambiguously identify the quasi-reversible oxidation as a 1-electron process due to instability of the 17-electron products at room temperature. $E_{1/2}$ values for the quasi-reversible oxidative process of compounds 1a–c are similar due to the comparable basicities of the phosphine ligands. The $E_{1/2}$ value observed for 1d was approximately 0.35 V lower in potential than was observed for the other phosphine ligands due to the greater electron-donating ability of tricyclohexylphosphine.

Under our experimental conditions, the previously reported[11,13,14] 1-electron oxidation of Fe(PPh$_3$)$_2$(CO)$_3$ (to produce the relatively stable 17-electron speices [Fe(PPh$_3$)$_2$(CO)$_3$]$^+$ was observed at +0.360 V compared to +0.255 V for 1a. The shift of $E_{1/2}$ was consistent with the change from a first-row to a second-row transition metal. The more electron-rich Ru center was oxidized more easily than the corresponding Fe center.

The second oxidations of 1a–d were irreversible under the scan rate conditions investigated. An irreversible return reduction coupled to the irreversible oxidation was observed at approximately −1 V for each of the compounds studied (Table III). Chronocoulometric experiments indicated that the second oxidation involved transfer of the same number of electrons as the quasi-reversiable process and was therefore assigned as a one-electron oxidation. The factors contributing to the lack of reversibility for this oxidation are unclear at this time.

The cyclic voltammetry of 2 showed only one electrochemically irreversible one-electron oxidative process at $E_{p,a} = +0.171$ V. When the scan rate was fast (~ 1 V/s or higher), some return reduction was observed at −0.689 V.

Chemical Oxidation of Ru(PR$_3$)$_2$(CO)$_3$ and M(dppe)(CO)$_3$ (M = Fe, Ru) and Spectroscopy of the Radicals. The 17-electron species [Ru(PR$_3$)$_2$(CO)$_3$][PF$_6$] [R = Ph (1a$^+$), Bz (1b$^+$), *p*-Tol (1c$^+$), Cy (1d$^+$)] were obtained by oxidation of the neutral compounds 1a–d, respectively, at low temperatures (−43 °C) (eq 2).
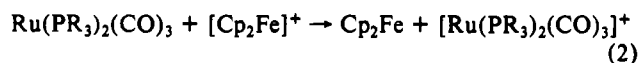
$$Ru(PR_3)_2(CO)_3 + [Cp_2Fe]^+ \rightarrow Cp_2Fe + [Ru(PR_3)_2(CO)_3]^+$$
$$(2)$$

Oxidants employed in this study were finely ground [Cp$_2$Fe][A] (A = BF$_4$, PF$_6$), [N(PhBr)$_3$][PF$_6$], or AgPF$_6$. The last, however,

Figure 4. EPR spectrum of {Ru(PCy$_3$)$_2$(CO)$_3$[N(O)-*t*-Bu]}[PF$_6$] in CH$_2$Cl$_2$ at room temperature.
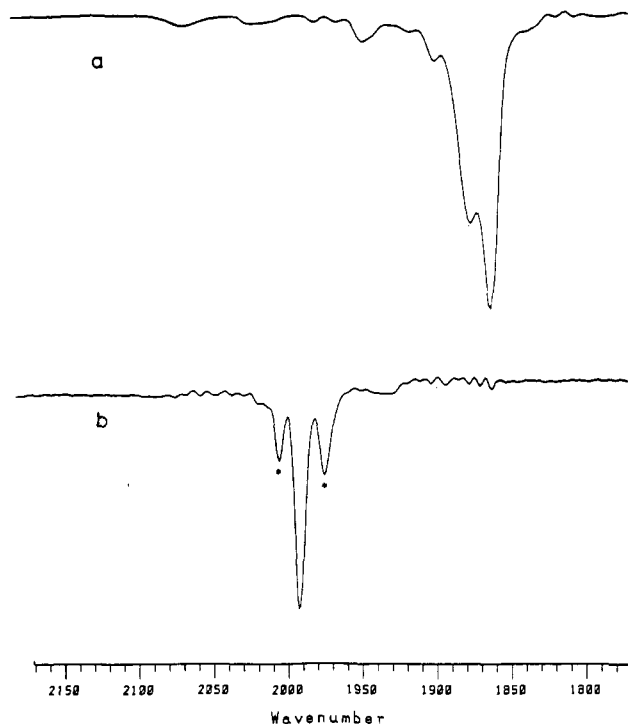
Figure 2. Infrared spectra in CH$_2$Cl$_2$ of (a) Ru(PCy$_3$)$_2$(CO)$_3$ and (b) [Ru(PCy$_3$)$_2$(CO)$_3$][PF$_6$]. The bands marked by asterisks continue to grow as the absorption at 1991 cm^{-1} disappears. They are assigned to an unknown decomposition product of the radical cation.
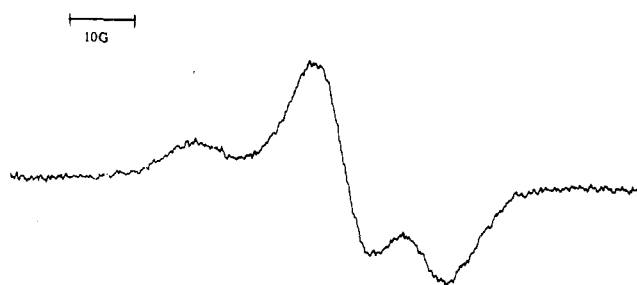

Figure 3. EPR spectrum of [Ru(PCy$_3$)$_2$(CO)$_3$][PF$_6$] in frozen THF at −173 °C.

also yielded other species, as judged by infrared spectroscopy. The radicals were very reactive and short-lived. Most of the reactions were performed in CH$_2$Cl$_2$ at −43 °C. When the oxidations were conducted in THF or CH$_3$CN, no dark color was observed and two CO stretches were found in the infrared spectrum instead of one. Only with the most stable of the radicals (R = Cy) could the oxidation be conducted in THF.

The radicals were dark brown in color and were characterized by infrared and EPR spectroscopies. Each radical exhibited one CO stretch in its infrared spectrum, which was shifted at least 100 cm^{-1} toward higher energy compared to the neutral compound. For example, [1d][PF$_6$] had a CO stretch at 1991 cm^{-1} (Figure 2) that was 130 cm^{-1} higher than that observed for the neutral compound. This shift compared well to that observed when the neutral iron complexes Fe(PR$_3$)$_2$(CO)$_3$ were oxidized to the corresponding cation.[11,14]

The EPR spectra of the radicals exhibited a 1:2:1 triplet due to coupling of the unpaired electron with two equivalent phosphorus atoms. For [Ru(PCy$_3$)$_2$(CO)$_3$][PF$_6$], which yielded the best spectrum, a 1:2:1 triplet was observed with g_{av} = 2.060 and a_{iso} = 19.6 G (see Figure 3). The spectrum was still broad, and the asymmetry suggested that a spectrum obtained at lower temperature could yield more information about the structure.

The dppe complexes of both iron and ruthenium were more reactive than the bis(phosphine) compounds. While the cation [Fe(dppe)(CO)$_3$]$^+$ (3$^+$) was reported previously,[11] it was found
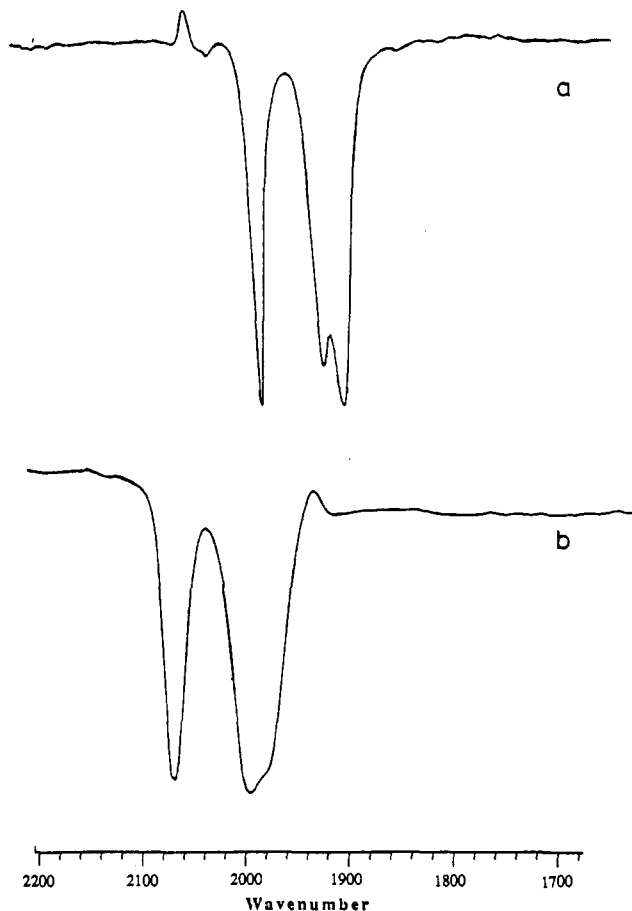
Figure 5. Infrared spectra of in CH$_2$Cl$_2$ of (a) Fe(dppe)(CO)$_3$ and (b) [Fe(dppe)(CO)$_3$][PF$_6$].

to be much less stable than [Fe(PR$_3$)$_2$(CO)$_3$]$^+$. We studied this iron cation along with the ruthenium complex in order to better characterize both compounds. Oxidation of yellow **3** by either [Cp$_2$Fe][A] (A = BF$_4$, PF$_6$) or [N(C$_6$H$_4$Br)$_3$][PF$_6$] yielded the dark green radical [3][PF$_6$] in CH$_2$Cl$_2$ at 0 °C. This complex was isolated as a dark green solid by addition of hexanes. As expected, it was very moisture and air sensitive and was used immediately. It could be stored briefly in the dark and had to be kept cold. Connelly and co-workers prepared[11] this compound by oxidation with AgPF$_6$; however, there were many species present in the reaction solution. The infrared spectrum of [3][PF$_6$] in CH$_2$Cl$_2$ (Figure 5) exhibited three CO stretches at 2071, 2001, and 1985 cm^{-1}. The three-band pattern resembled the three-band pattern observed in Fe(dppe)(CO)$_3$ with the absorptions shifted approximately 90 cm^{-1} toward higher energy. The EPR spectrum at room temperature in CH$_2$Cl$_2$ displayed a sharp 1:2:1 triplet with average g_{av} = 2.052 and coupling to phosphorus of 21.4 G. This suggested that the two phosphorus atoms were equivalent on the EPR time scale.

In contrast to [3][PF$_6$], the ruthenium analogue was very short-lived. Oxidation of a pale yellow CH$_2$Cl$_2$ solution of **2** with

Scheme I. Reactivity of $[Ru(PR_3)_2(CO)_3]^+$
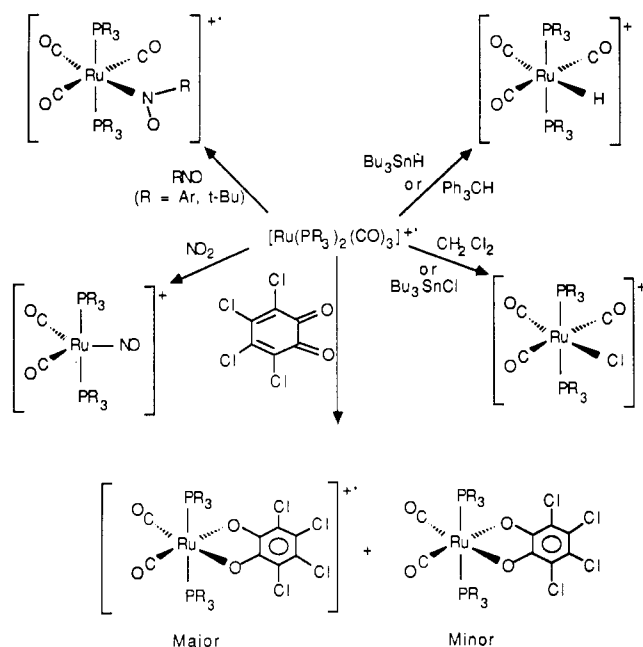
[Cp$_2$Fe][PF$_6$] at -78 °C yielded a dark green color. After a few seconds the color changed to a pale yellow. The EPR spectrum of the green compound, which was immediately frozen following the reaction, at -173 °C, showed a very broad 1:2:1 triplet presumably due to [2][PF$_6$]. The yellow compound was characterized partially and is believed to be [Ru(dppe)(CO)$_3$]$_2$[PF$_6$]$_2$.

Reactivity of the Radicals: Halogen and Hydrogen Abstractions. Halogen abstraction by metal-centered radicals has been well-studied.[6] Hydrogen abstraction is known but has not been studied quantitatively.[6] Following generation of the ruthenium radical [1a][PF$_6$] in CH$_2$Cl$_2$ at room temperature or in the presence of Bu$_3$SnCl, the yellow compound [Ru(PPh$_3$)$_2$(CO)$_3$(Cl)][PF$_6$] was isolated in 62% yield (eq 3). The compound was fully charac-

$$1a^+ + Bu_3SnCl\ (\text{or }CH_2Cl_2) \rightarrow$$
$$[Ru(PPh_3)_2(CO)_3(Cl)]^+ + Bu_3Sn^{\bullet}\ (\text{or }^{\bullet}CH_2Cl) \quad (3)$$
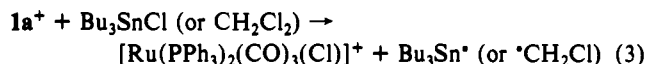
terized by IR and NMR (^{1}H and ^{31}P) spectroscopy and elemental analysis. The infrared spectrum was similar to that of [Ru(PPh$_3$)$_2$(CO)$_3$(Cl)][AlCl$_4$] prepared by Hieber and co-workers using a different route.[25] The observed infrared spectral pattern and the singlet in the ^{31}P NMR spectrum were consistent with a trans phosphine geometry with the carbonyl and chloride ligands in the equatorial plane. This was the observed geometry of the neutral isoelectronic complex Mn(PPh$_3$)$_2$(CO)$_3$Br, which was characterized by X-ray crystallography.[28] Oxidation of 1a in CH$_2$I$_2$ yielded the iodo derivative, [Ru(PPh$_3$)$_2$(CO)$_3$(I)][PF$_6$].

The ruthenium radical [1a][PF$_6$] abstracted a hydrogen atom from Ph$_3$CH or Bu$_3$SnH yielding the white salt [Ru(PPh$_3$)$_2$-(CO)$_3$(H)][PF$_6$] (eq 4). The infrared spectrum displayed three

$$1a^+ + Bu_3SnH \rightarrow [Ru(PPh_3)_2(CO)_3(H)]^+ + Bu_3Sn^{\bullet} \quad (4)$$
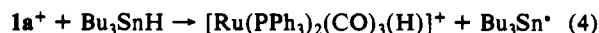
bands in the carbonyl region and was identical with the reported IR spectrum of [Ru(PPh$_3$)$_2$(CO)$_3$(H)][PF$_6$] prepared by protonation of 1a.[24] The presence of the hydride ligand was confirmed by ^{1}H NMR spectroscopy showing a triplet at -6.24 ppm ($^2J_{PH}$ = 14.9 Hz). A singlet was observed in the ^{31}P{^{1}H} NMR spectrum. The infrared spectrum in the CO region was similar to that of the chloro analogue [Ru(PPh$_3$)$_2$(CO)$_3$(Cl)][PF$_6$].[25] The spectroscopic data were consistent with the structure shown in Scheme I.

Reactivity of the Radicals: Radical-Trapping Reagents. Connelly and Manners reported the synthesis of [Ru(PPh$_3$)$_2$(CO)$_2$-

(C$_6$Cl$_4$O$_2$)][PF$_6$] by oxidation of Ru(PPh$_3$)$_2$(CO)$_2$(C$_6$Cl$_4$O$_2$) with [NO][PF$_6$] in toluene–methanol.[23] EPR spectroscopic studies suggested that the electron was removed from the organic ligand and the ruthenium remained in the 2+ oxidation state. The analogous paramagnetic iron derivative was synthesized by reaction of [Fe(PPh$_3$)$_2$(CO)$_3$][PF$_6$] with C$_6$Cl$_4$O$_2$.[12] The reaction of [1a][PF$_6$] with o-C$_6$Cl$_4$O$_2$ gave two ruthenium-containing products. The major species, isolated in 42% yield, was [Ru-(PPh$_3$)$_2$(CO)$_2$(o-C$_6$Cl$_4$O$_2$)][PF$_6$]. This product exhibited a 1:2:1 triplet in the EPR spectrum with hyperfine coupling of 25 G to the two equivalent phosphorus atoms. In the infrared spectrum two CO stretches of equal intensity were observed. These data were the same as those observed by Connelly and co-workers, and the structure of this compound is shown in Scheme I. A second product, identified as Ru(PPh$_3$)$_2$(CO)$_2$(o-C$_6$Cl$_4$O$_2$) by comparison to known spectra, was isolated in 10% yield.

Even at low temperature, reaction of [1a][PF$_6$] with NO$_2$ yielded a two-band pattern in the ν_{CO} region along with a new band at 1763 cm^{-1} due to the NO stretch. The product, isolated in low yield, was [Ru(PPh$_3$)$_2$(CO)$_2$(NO)][PF$_6$] (eq 5), and its

$$1a^+ + NO_2 \rightarrow [Ru(PPh_3)_2(CO)_2(NO)]^+ + CO_2 \quad (5)$$
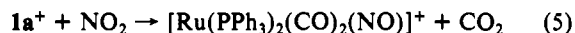
infrared spectrum was identical with the spectrum of an authentic sample prepared by reaction of Ru(PPh$_3$)$_2$(CO)$_3$ with [NO][P-F$_6$].[24] No intermediate nitro complex was observed in eq 5 as was found for the analogous reaction with the iron radical cations. With iron, CO$_2$ loss to give the nitrosyl complex required refluxing acetone.[12]

Organonitroso compounds have been used frequently as spin traps for both organic and organometallic radicals.[6] Connelly and co-workers reported that 2-methyl-2-nitrosopropane (t-BuNO) reacted with [Fe(PPh$_3$)$_2$(CO)$_3$]$^+$ to give the spin-trapped adduct [Fe(PPh$_3$)$_2$(CO)$_3$[N(O)-t-Bu]]$^+$.[12] The EPR spectrum of this adduct (g_{av} = 2.0027, $a_{iso}(^{31}$P) = 3.2 G, $a_{iso}(^{14}$N) = 19.1 G) established that the unpaired electron was localized more on the nitroso ligand than on the metal. It was of interest to examine the analogous reaction with the ruthenium cation radicals both to characterize further the reactivity of the 17-electron species and to explore the possible relationship between the spin-trapped adducts themselves and intermediates in the catalytic carbonylation of nitroaromatics.

Addition of [Cp$_2$Fe][PF$_6$] to a CH$_2$Cl$_2$ solution of 1a–d or 3 and t-BuNO resulted in an immediate color change from yellow to dark brown. The EPR spectrum of {Ru(PPh$_3$)$_2$(CO)$_3$[N-(O)-t-Bu]}[PF$_6$] exhibited a 1:1:1 triplet indicative of hyperfine coupling to ^{14}N (a_{iso} = 18.0 G). Further splitting of the signal into triplets was due to hyperfine coupling to the phosphorus atoms (a_{iso} = 2.9 G). Figure 4 shows the EPR spectrum of [Ru-(PCy$_3$)$_2$(CO)$_3$[N(O)-t-Bu]][PF$_6$] in THF at -40 °C, and Table III summarizes the data for these adducts. Replacing t-BuNO with p-chloronitrosobenzene resulted in EPR spectral signals that were less well resolved. This was attributed to the additional coupling from the two ortho hydrogens on the nitroso ligand. The magnitude of this hyperfine interaction was expected to be approximately 3 G,[29] similar to the value of the coupling to the phosphorus atoms.

The spectral data obtained were similar to those observed for {Fe(PPh$_3$)$_2$(CO)$_3$[N(O)-t-Bu]}[PF$_6$] and were consistent with an octahedral metal geometry with two trans-phosphine ligands and an equatorial arrangement of the carbonyl and organonitroso ligands (Scheme I). We were unable to isolate the spin-trapped compounds as solids.

Reactivity of [M(dppe)(CO)$_3$]$^+$ (2$^+$, 3$^+$). The reactivity of both the iron and ruthenium complexes containing dppe was greater than that found for the corresponding bis(phosphine) complexes. The most notable difference was the apparent propensity of 2$^+$ to dimerize. Oxidation of 2 in CH$_2$Cl$_2$ or THF in the presence of Bu$_3$SnCl yielded a yellow crystalline solid that did not contain chloride as determined by elemental analysis. The infrared

(28) Bond, A. M.; Colton, R.; McDonald, M. E. *Inorg. Chem.* **1978,** *17,* 2842.

(29) Russell, G. A.; Geels, E. J.; Smentowski, F. J.; Chang, K.-Y.; Reynolds, J.; Kaupp, G. *J. Am. Chem. Soc.* **1967,** *89,* 3821.

Scheme II. Reactivity of [Ru(dppe)(CO)₃]⁺
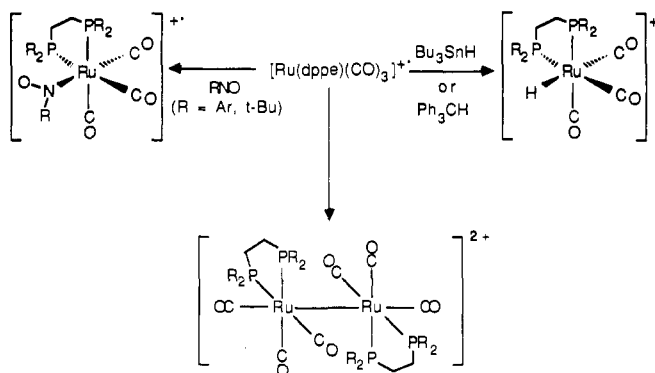
spectrum revealed four carbonyl bands at 2102, 2062, 2040, and 1978 cm⁻¹, and the ³¹P{¹H} NMR spectrum exhibited a singlet at 63.2 ppm. Elemental analysis was consistent with the formulation [2][BF₄]; however, its diamagnetic nature suggested that it was dimeric. A rapid dimerization of 2⁺ could explain the irreversibility observed in the cyclic voltammogram.

Although halogen abstraction was never observed by 2⁺, oxidation of 2 in the presence of Ph₃CH or Bu₃SnH resulted in hydrogen atom abstraction. The rate of hydrogen abstraction was faster with Bu₃SnH, resulting in higher yields of [Ru(dppe)-(CO)₃H]⁺. Some [Ru(dppe)(CO)₃]₂²⁺ was formed in both reactions. The infrared spectrum of the product exhibited three carbonyl stretches at 2115, 2068, and 2053 cm⁻¹ in a pattern similar to that observed for the neutral compound 2. The ³¹P{¹H} NMR spectrum displayed a singlet at 64.1 ppm, suggesting equivalent phosphorus atoms. A triplet was found at −7.63 ppm in the ¹H NMR spectrum with a coupling constant of 18.1 Hz. The proposed structure of the hydride is shown in Scheme II and is based upon a comparison to the isoelectronic compound Mn-(dppe)(CO)₃H. Darensbourg and co-workers established the structure of the manganese compound using infrared spectroscopy.[30] Protonation of 2 by HPF₆ or HBF₄ generated [Ru-(dppe)(CO)₃(H)]⁺ in good yields.

The reactions of organonitroso compounds with [2][PF₆] and [3][PF₆] were examined. The spin traps of these radicals were prepared by addition of CH₂Cl₂ to an equivalent amount of 2 or 3, ClC₆H₄NO (or *t*-BuNO), and [Cp₂Fe][PF₆]. The color changed immediately to dark brown. The infrared spectra for both the iron and ruthenium complexes showed three CO stretches in the same pattern as that observed for the neutral compounds. The stretches were shifted 80–90 cm⁻¹ toward higher frequencies. The EPR spectra for these species exhibited a 1:1:1 triplet due to coupling of the unpaired electron to ¹⁴N (15 G). This 1:1:1 triplet was split further into 1:2:1 triplets due to coupling to the two phosphorus atoms (2–3 G). The spin-trap adducts themselves were unstable.

Discussion

The neutral complexes having the formula Ru(PR₃)₂(CO)₃ where the phosphine ligands occupy axial positions undergo a reversible, one-electron oxidation. The radical cation that is produced has a limited lifetime at room temperature and must be kept cold (<−40 °C). Of the four phosphine ligands used in this study, three (PBz₃, PPh₃, and P(*p*-Tol)₃) have very similar donor properties, a fact reflected in the similar $E_{1/2}$ values of the corresponding ruthenium complexes (Table III). Tricyclohexylphosphine, however, is substantially more basic, and the corresponding ruthenium complex is easier to oxidize by 0.3 V. The analogous cations of iron have been extensively studied[11-14] and are more stable than the ruthenium radical cations. A direct comparison of $E_{1/2}$ values for 1a and Fe(PPh₃)₂(CO)₃ under identical conditions establishes that the ruthenium complex is easier to oxidize by 0.105 V.

The previous reports of isoelectronic radicals show that a common structure is not adopted by all five-coordinate d⁷ radicals. Therien and Trogler were able to show that the solution structure of [Fe(PR₃)₂(CO)₃]⁺ was trigonal bipyramidal with the phosphines in the axial positions.[14] The isoelectronic radicals of rhenium are also stable, and the recent X-ray crystallographic study of Re-(PCy₃)₂(CO)₃ (4) proved that it exists in the square-pyramidal

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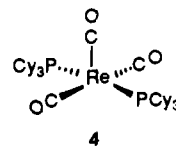
geometry in the solid state.[10] This was in agreement with earlier solution spectroscopic studies of the same Re radical.[9] Unfortunately both [Fe(PR₃)₂(CO)₃]⁺ and Re(PCy₃)₂(CO)₃ give one absorption in the carbonyl region of the infrared spectrum rendering infrared spectroscopy ineffective for differentiating between the two possible geometries of [Ru(PR₃)₂(CO)₃]⁺ (which also exhibits one carbonyl absorption). The broad lines in the EPR spectra of the ruthenium radicals are of little value in establishing the structure.

The differences in properties of the ruthenium complexes containing the chelating ligand, dppe, compared to the monodentate ligands are substantial. Cyclic voltammetry shows that the electrochemical oxidation is irreversible, unlike the corresponding iron complex. The latter, 3, exhibits a one-electron oxidation shifted 0.21 V to more negative potential relative to Fe(PPh₃)₂(CO)₃. The irreversible oxidation observed in the cyclic voltammogram for 2 apparently exhibits a similar shift relative to 1a, but the lack of a return cathodic wave prevents a comparison of $E_{1/2}$ values.

Proposing a structure of the one-electron oxidized product, 2⁺, is complicated further by the dppe ligand. While 2 has not been structurally characterized, 3 was found to have a structure between the trigonal-bipyramidal (3-tbp) and square-pyramidal (3-sp)
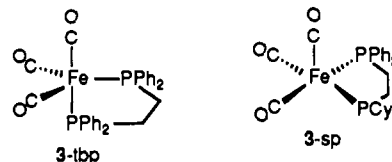
geometries.[31] The previous report describing the oxidation of 3 did not contain infrared spectral data due to impurities apparently caused by the Ag⁺.[11] Figure 5 shows that the radical cation, which can be generated cleanly by using ferrocenium cation, has a νCO pattern very similar to that found in 3, indicative of a similar structure.

The highly reactive nature of the radical 2⁺ prohibited us from obtaining its infrared spectrum. The EPR spectrum of 2⁺, obtained by quenching the reaction solution (1 + [Cp₂Fe]⁺ in CH₂Cl₂) from −78 °C to −173 °C, was very broad but appeared to show coupling to both phosphorus atoms. Unfortunately, the line width of the signal was too broad to establish whether or not the phosphorus atoms were equivalent.

Scheme I shows that all of the radicals reacted as expected on the basis of the previous studies of metal-based radicals. Particularly noteworthy are the differences observed between the complexes incorporating the chelating ligand, dppe, and those having monodentate phosphine ligands. As previously discussed, 2⁺ is much more reactive and is the only radical of the series that apparently forms a stable dimer. While the data are consistent with the formulation of the stable yellow product as a dimer, its characterization must be considered incomplete without a crystal structure. In studies of the isoelectronic manganese complex [Mn(depe)(CO)₃]₂ (depe = 1,2-bis(diethylphosphino)ethane), Tyler and Goldman reported an equilibrium between the dimer

(30) Darensbourg, D. J.; Froelich, J. A. *Inorg. Chem.* **1978**, *17*, 3300.

(31) Battaglia, L. P.; Delledonne, D.; Nardelli, M.; Pelizzi, C.; Predieri, G.; Chiusoli, G. P. *J. Organomet. Chem.* **1987**, *330*, 101.

and monomer.[32] No substantial evidence supporting the presence of **2**$^+$ in solutions of {[Ru(dppe)(CO)$_3$]$_2$}$^{2+}$ was obtained. The expected increase in metal–metal bond strength in going from the Mn to the Ru system apparently allows the dimer to form despite the larger size of the chelating ligand and the unfavorable electrostatic forces.

While the lifetime of **2**$^+$ is short, it is competitively trapped by using organonitroso compounds, Ph$_3$CH, or Bu$_3$SnH. The question as to why **2**$^+$ does not abstract halogens from CH$_2$Cl$_2$ or Bu$_3$SnCl remains unclear. Considering the ease of halogen abstraction by **1a** (eq 3), it would seem unlikely that thermodynamics alone could explain the inability of **2**$^+$ to abstract a halogen. Perhaps halogen atom abstraction is kinetically slower than hydrogen atom abstraction to such an extent that the former cannot compete with dimerization. Among the halogen donors CH$_2$Cl$_2$ has been shown to be the least reactive toward chlorine abstraction using transition metal-centered radicals.[8,33]

Relation to the Catalysis of Nitroaromatic Carbonylation. The neutral complexes **1** and **2** are known catalysts for the carbonylation of nitroaromatics in alcohols to give carbamates (eq 6).

$$ArNO_2 + 3CO + CH_3OH \rightarrow 2CO_2 + ArNHC(O)OCH_3 \quad (6)$$

Among these phosphine-substituted complexes, **2** was reported to have the fastest turnover rate.[34] In previous mechanistic studies of the catalysis of eq 6 by **2**, it was suggested that the first step involved the single electron transfer from **2** to ArNO$_2$.[16] This was followed by rapid CO$_2$ loss and CO addition to give the unusual, structurally characterized complex Ru(dppe)(CO)$_2$[C(O)N(Ar)O] (**5**) as the first isolable species.[17] Weak EPR signals were observed


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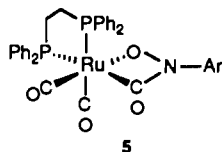
following the mixing of either the nitroaromatic or the corresponding nitrosoaromatic with **2** in the catalytic solutions at room temperature and atmospheric pressure of CO.[16] For *p*-chloronitrosobenzene, the signal appeared at *g* = 2.013 with two hyperfine couplings observable of 11.4 and 3.2 G. The larger value could be assigned unambiguously to the ^{14}N coupling because of

(32) Tyler, D. R.; Goldman, A. S. *J. Organomet. Chem.* **1986**, *311*, 349.
(33) Laine, R. M.; Ford, P. C. *Inorg. Chem.* **1977**, *16*, 388.
(34) Grate, J. H.; Hamm, D. H.; Valentine, D. H. U.S. Patent 4,603,216, 1986.

the 1:1:1 intensity pattern. The smaller coupling was originally assigned to coupling to the ortho hydrogens, and the structure of the active species **6** was proposed to result from the nitrosoarene

6
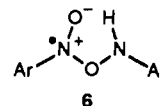
trapping of the protonated (from the methanol) radical anion of the nitrosoarene itself. Previous studies of the reactivity of nitrosoarene radical anions in basic media provided the basis for this suggestion.[29] The similarity of the spectral data reported here to those data from the previous study allow us to suggest that the spin-trapped radical cation {Ru(dppe)(CO)$_3$[N(O)Ar]}$^+$ is an alternative structure of the EPR-active species. Whatever the nature of the EPR-active species, it should noted that it probably forms only when the nascent radical pair (eq 1) separate and escape from the solvent cage.

Although the ruthenium radical cation does not appear to be involved in the rate-determining step of the catalysis, the single electron transfer event provides the mechanism by which the substrate interacts with the catalyst. The studies described in this paper provide a background of characterization and reactivity data that can be correlated directly with the studies involving the working catalyst.

Conclusions

The zerovalent ruthenium complexes Ru(PR$_3$)$_2$(CO)$_3$, where R = Ph, Cy, *p*-Tol, and Bz, and Ru(dppe)(CO)$_3$ have been found to undergo one-electron chemical and electrochemical oxidations giving the corresponding radical cations [Ru(PR$_3$)$_2$(CO)$_3$]$^+$ and [Ru(dppe)(CO)$_3$]$^+$. The stabilities of the radical cations depend on the nature of the phosphine ligand, and all are always less stable than the analogous iron complexes. The infrared and EPR spectra are consistent with a five-coordinate, low-spin d^7 complex but are unable to differentiate between a square-pyramidal and trigonal-bipyramidal structure. The radicals are able to abstract halogen atoms from organic halides and tri-*n*-butyltin chloride and hydrogen atoms from triphenylmethane and tri-*n*-butyltin hydride. The radicals can be trapped by using tetrachloro-*o*-quinone and organonitroso compounds. Evidence for radical dimerization was found only with the complex containing the chelating ligand, Ru(dppe)(CO)$_3$.

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Dihydrogen Complexes in Catalysis: Isotope Exchange Reactions

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Dihydrogen complexes [CpRu(CO)(PR$_3$)(η^2-H$_2$)]X (R = Ph (**1**), Cy (**2**); X = BF$_4^-$, CF$_3$SO$_3^-$), [Ru(dppe)$_2$H(η^2-H$_2$)]BF$_4$ (**3**), and [Ir(bq)(PPh$_3$)$_2$H(η^2-H$_2$)]SbF$_6$ (**5**) were tested as catalysts for H/D exchange between ROH and D$_2$. Complex **5** is the most efficient, while **3** is moderately active and **1** and **2** are essentially inactive. Maximum activity arises when an M–H group is cis to a coordination site capable of binding both H$_2$ and ROH. The relevance of these results to the mechanism of H/D exchange in hydrogenase is also discussed.

Introduction

Molecular hydrogen complexes$^{1-10}$ are of current interest largely in connection with the difficult structural and spectroscopic
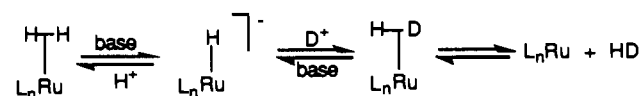
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Scheme I

problems they pose. Less attention has been given to their unusual reactivity patterns. They are often kinetically more efficient