1904 *Organometallics* 1989, *8*, 1904-1909

Nucleophilic Attack on Carbon Monoxide in Carbonyl Phosphine Complexes of Rhodium(I) and Ruthenium(II): A Novel Route to Complexes of Rhodium(−I)

Gregory G. Johnston, Sven I. Hommeltoft, and Michael C. Baird*

Department of Chemistry, Queen's University, Kingston, Canada K7L 3N6

Received November 21, 1988

Reaction of [Rh(CO)$_2$(triphos)]PF$_6$ (triphos = MeC(CH$_2$PPh$_2$)$_3$) with sodium borohydride in CD$_2$Cl$_2$ results in the formation of the hydride RhH(CO)(triphos) and the formyl complex Rh(HCO)(CO)(triphos). In contrast, treatment of [Rh(CO)$_2$(triphos)]PF$_6$ with excess methyllithium in THF results in the formation of the rhodium(−I) complex Li[Rh(CO)(triphos)]. The mechanism of this unusual reaction appears to involve (i) nucleophilic attack of MeLi on a carbonyl carbon of [Rh(CO)$_2$(triphos)]PF$_6$ to yield the acetyl complex Rh(MeCO)(CO)(triphos), (ii) attack by a second mole of MeLi on the acetyl group to produce the complex Li[Rh(Me$_2$CO)(triphos)], and (iii) elimination of acetone to form product. In the presence of excess MeLi, the acetone reacts further to form *tert*-butoxide, which is also detected in the reaction mixture. The rhodium(−I) complex Li[Rh(CO)(triphos)] reacts with proton sources to yield the hydride RhH(CO)(triphos), with alkyl and acyl halides to form the alkyl complexes RhR(CO)(triphos) (R = Me, Et, Ph, MeCO), with trimethyltin chloride to form Rh(SnMe$_3$)(CO)(triphos), and with CO to form Li[Rh(CO)$_2$(η^2-triphos)], with a pendant phosphine. The complex [Ru(CO)$_3$(triphos)][AlCl$_4$]$_2$ can be synthesized by treating [RuCl(CO)$_2$(triphos)]Cl with AlCl$_3$ under an atmosphere of CO. The dicationic complex [Ru(CO)$_3$(triphos)]$^{2+}$ is very susceptible to nucleophilic attack at CO and reacts with ethanol, water, and NaBH$_3$CN to form the alkoxycarbonyl complex [Ru(CO$_2$Et)(CO)$_2$(triphos)]$^+$, the hydride complex [RuH(CO)$_2$(triphos)]$^+$ (presumably via [Ru(CO$_2$H)(CO)$_2$(triphos)]$^+$), and the formyl complex [Ru(HCO)(CO)$_2$(triphos)]$^+$, respectively.

We have previously reported details of the chemistry of ruthenium[1] and rhodium[2] complexes of the tridentate ligand 1,1,1-tris((diphenylphosphino)methyl)ethane, MeC(CH$_2$PPh$_2$)$_3$ (henceforth triphos). In the course of this work, we have observed several examples of nucleophilic attack on coordinated carbon monoxide, reactions which in most cases gave rise to interesting and in some cases novel products. We now report fully on reactions of various nucleophiles with the complexes [RhCl(CO)(triphos)],[2b] [Rh(CO)$_2$(triphos)]$^+$,[2b] and [Ru(CO)$_3$(triphos)]$^{2+}$.[1e] A preliminary communication concerning aspects of this research has appeared previously.[2a]

Experimental Section

Unless otherwise noted, all operations were performed at room temperature under an atmosphere of N$_2$ using standard vacuum line techniques. ^{1}H NMR, ^{2}H{^{1}H} NMR, ^{13}C{^{1}H} NMR, and ^{31}P{^{1}H} NMR spectra were obtained on a Bruker AM 400 spectrometer, operating at resonance frequencies of 400, 61.4, 100.9, and 162.0 MHz, respectively.

The complexes RhCl(CO)(triphos),[2b] [Rh(CO)$_2$(triphos)]PF$_6$,[2b] RhH(CO)(triphos),[2b,3] [Rh(CO)L(triphos)]PF$_6$ (L = PMe$_3$, P(OMe)$_3$),[2b] Rh(CO$_2$Me)(CO)(triphos),[4] RhR(CO)(triphos) (R = Me, Ph, MeCO, PhCO),[2b] and [RuCl(CO)$_2$(triphos)]PF$_6$[1c] were prepared by literature methods.

(i) Reactions of [Rh(CO)L(triphos)]PF$_6$ (L = CO, PMe$_3$, P(OMe)$_3$) with NaBH$_4$. (a) Excess NaBH$_4$ was added to solutions of 0.2 g of [Rh(CO)L(triphos)]PF$_6$ (L = CO, PMe$_3$, P(OMe)$_3$) in 20 mL of THF; after 20 min, the starting materials had been consumed (as assayed by IR spectroscopy). The volumes of the reaction mixtures were then doubled by the addition of equal amounts of ethanol, and the solutions were concentrated by removing the solvent under reduced pressure. When the volumes were reduced to approximately one-half, yellow precipitates of HRh(CO)(triphos) formed and were filtered, washed with ethanol, dried in vacuo, and identified by ^{1}H and ^{31}P NMR spectroscopy[2b,3] (yields 45–75%).

(b) The reaction of NaBH$_4$ with [Rh(CO)$_2$(triphos)]PF$_6$ was also monitored by low-temperature ^{1}H NMR spectroscopy. A CD$_2$Cl$_2$ solution of [Rh(CO)$_2$(triphos)]PF$_6$ was made up in an NMR tube, and the solution was cooled to −78 °C with a dry ice/acetone bath. Solid NaBH$_4$ was added to the NMR tube at −78 °C, and the sample was then placed into the spectrometer probe which was at a temperature of −80 °C. The ^{1}H NMR spectrum at this temperature showed no evidence for formation of either the hydride complex or any intermediates. Consequently, the temperature of the probe was raised to −50 °C and the reaction was monitored continuously for a period of 3 h. The resulting spectrum exhibited not only the resonance from RhH(CO)(triphos) but also two additional resonances. One of the latter was a weak multiplet at $\approx\delta$ 12 (J = 36 Hz), while the other was a triplet of doublets at δ −9.12 (^1J(Rh–H) = 11.5 Hz, ^2J(P–H) = 59 Hz).

(ii) Reactions of [Rh(CO)$_2$(triphos)]PF$_6$ with RLi (R = Me, *n*-Bu). (a) An excess (>3 equiv) of RLi was added to solutions of [Rh(CO)$_2$(triphos)]PF$_6$ (0.15–0.3 g) in THF (15 mL), the color of the solutions changing from yellow to deep red. When the additions of RLi were complete, ethanol was added to the mixtures to destroy any remaining RLi, and the solutions were concentrated under reduced pressure until there formed yellow precipitates of RhH(CO)(triphos), identified by ^{31}P NMR, ^{1}H NMR, and IR spectroscopy[2b,3] (yield 75%).

(b) Aliquots of MeLi were added to a solution of 0.2 g of [Rh(CO)$_2$(triphos)]PF$_6$ in 15 mL of THF, the reaction being monitored by ^{31}P NMR spectroscopy. After the addition of 0.5 equiv of MeLi, the only resonances in the spectrum were those of starting material (50%) and Rh(MeCO)(CO)(triphos)[2b] (50%). Addition of a second 0.5 equiv of MeLi to the sample resulted in a solution, the ^{31}P NMR spectrum of which exhibited three resonances, those of the starting complex (<5%), the above-mentioned acetyl species (85%), and RhH(CO)(triphos) (10%).

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0276-7333/89/2308-1904$01.50/0

After the addition of a second equivalent of MeLi to the reaction mixture, the ^{31}P NMR spectrum exhibited the resonance of RhH(CO)(triphos) and a doublet centered at δ 21.5 (^1J(Rh–P) = 155 Hz), assigned to a new species, A.

(c) In separate experiments, excess RLi (R = Me, *n*-Bu) was added to THF solutions of $[Rh(CO)_2(triphos)]PF_6$ and samples were withdrawn for ^{31}P NMR spectroscopy. Upon addition of the alkyllithium reagents, the solutions turned cherry-red and the ^{31}P NMR spectra of the reaction mixtures exhibited predominantly the resonance of A (>95%). Equivalent amounts of ethanol were added to the reaction mixtures, and the predominant resonance in the resulting ^{31}P NMR spectra was that of RhH(CO)(triphos) (90%).

These reactions were also carried out by using acetone-d_6 as the solvent, but only the resonance from RhH(CO)(triphos) was observed. The ^{31}P resonance of A was not observed in any spectra of the reaction mixtures.

(d) Solutions of 0.15 g of RhH(CO)(triphos) in 10 mL of THF were treated with excess (>3 equiv) of each of MeLi, lithium diethylamide (LDA), or LiOMe, the reactions being monitored by ^{31}P NMR spectroscopy. With MeLi, the resonance of the RhH(CO)(triphos) was partially (72%) replaced by that of A within 1 h; with LDA the reaction was 20% complete within 1 h. No reaction occurred with LiOMe.

(e) Excess MeLi (>3 equiv) was added to a solution of 0.25 g of $[Rh(CO)_2(triphos)]PF_6$ in 15 mL of THF under an atmosphere of CO. The ^{31}P NMR spectrum, obtained under a CO atmosphere, exhibited a pair of resonances assignable to a new complex, B, a doublet at δ 25.5 (^1J(Rh–P) = 156 Hz), and a singlet at δ −26, in the ratio 2:1. The resonance of A was absent. This experiment was then repeated under an atmosphere of N_2, the initial ^{31}P NMR spectrum now exhibiting only the resonance of A. Carbon monoxide was bubbled through the solution for ≈15 min, and the ^{31}P NMR spectrum (obtained under an atmosphere of CO) now exhibited the resonances of B.

(f) In an IR study, 3 equiv of MeLi was added to a dilute THF solution of $[Rh(CO)_2(triphos)]PF_6$; the IR spectrum showed that ν(CO) of the starting material had been replaced by a ν(CO) at 1695 cm^{-1}. Carbon monoxide was then bubbled through the solution for 10–15 min, and the resulting IR spectrum exhibited two ν(CO) at 1815 and 1870 cm^{-1}. One equivalent of ethanol per rhodium was then added to the reaction mixture, and the carbonyl region of this solution exhibited one ν(CO) at 1909 cm^{-1}, assignable to RhH(CO)(triphos).[2b,3]

(g) In an attempt to identify organic products from the reaction of excess MeLi with $[Rh(CO)_2(triphos)]PF_6$, a solution of 0.28 g of $[Rh(CO)_2(triphos)]PF_6$ in 20 mL of THF was treated with 1 mL of a 1.4 M ether solution of MeLi. No gas evolution was observed nor was any methane detected over the solution (GC). About 1 mL of ethanol was then added slowly, resulting in the rapid evolution of methane. In an attempt to detect and identify nongaseous organic products, 3 mL of a 1.4 M solution of MeLi was added to a 50-mL THF solution of 1.0 g of $[Rh(CO)_2(triphos)]PF_6$. The solvent was removed under reduced pressure, and the residual solid was placed under dynamic vacuum for 24 h. The stopper of the flask was then replaced with a septum, the flask was cooled in liquid N_2, and 1 mL of D_2O was added slowly. After the D_2O addition was complete, the flask was removed from the liquid N_2 bath and allowed to warm to room temperature. An additional 2 mL of D_2O was added to the reaction mixture, and the ^{1}H and ^{13}C NMR spectra were obtained. In the ^{13}C NMR spectrum, the only resonances that were not assignable to residual THF or ether were at δ 70.5 and 30.7, assignable to *tert*-butyl alcohol. In the ^{1}H NMR spectrum, the only resonance other than those of THF and ether was a singlet at δ 1.23. One drop of *t*-BuOH was added to the NMR tube, and the only change in the ^{1}H NMR spectrum was an increase in the relative intensity of the resonance at δ 1.23.

This experiment was repeated, except that CD_3Li was used in place of CH_3Li and the extraction step was performed with H_2O. The ^{2}H NMR spectrum of the extracted sample exhibited a signal at δ 0.96. Acetone-d_6 (10 μL) was then added to the NMR solution, and the ^{2}H NMR spectrum now exhibited a new signal at δ 1.9. In a separate NMR experiment, CD_3Li was added to acetone-d_6, and, in addition to the resonances of the acetone-d_6, the resulting ^{2}H NMR spectrum also exhibited a resonance at δ 0.96.

A 65% yield of *t*-BuOH (based on $[Rh(CO)_2(triphos)]PF_6$) was also detected by GC in the hydrolyzed reaction mixture.

(iii) Reactions of Rh(RCO)(CO)(triphos) (R = Me, Ph) with R′Li (R′ = Me, Ph, *n*-Bu). Solutions of the acyl complexes Rh(RCO)(CO)(triphos), formed by bubbling CO through solutions of 0.3 g of RhR(CO)(triphos)[2b] in 15 mL of THF, were treated under CO with 1–3 equiv of RLi, the reactions being monitored by ^{31}P NMR spectroscopy. The ^{31}P NMR spectra exhibited three resonances, that of RhH(CO)(triphos) and the doublet/singlet combination (ratio 2:1) of B. The relative amounts of RhH(CO)(triphos) and B depended upon the ratio of RLi:Rh(RCO)(CO)(triphos). As the ratio increased from 1 to 2, the relative yield of the RhH(CO)(triphos) decreased, while for ratios >2 there was essentially no RhH(CO)(triphos) formed. When acetone-d_6 was used as solvent, only RhH(CO)(triphos) was produced. The results of this experiment were independent of the R′Li and Rh(RCO)(CO)(triphos) (R = Me, Ph) used.

(iv) Chemistry and Properties of the Species A and B. (a) In a typical experiment, A was formed by adding 3 mL of a 1.4 M solution of MeLi to a solution of $[Rh(CO)_2(triphos)]PF_6$ in 40 mL of THF, ν(CO) of the starting material being replaced by a broad ν(CO) at 1695 cm^{-1} in the IR spectrum. Excess [PPN]Cl was added to the mixture, but there was no indication of a precipitate being formed, even on cooling to −78 °C. Carbon monoxide was bubbled through the above solution to form B (confirmed by ^{31}P NMR spectroscopy), but again, no solid precipitated from solution. Several variations on this approach also failed to yield crystalline materials.

(b) Solutions of A, prepared by the addition of 3.5 equiv of MeLi to solutions of 0.2 g of $[Rh(CO)_2(triphos)]PF_6$ in 15 mL of THF, were each treated with 1.1 equiv of RX (RX = MeI, EtI, Me_3SnCl, MeCOCl, Me_3SiCH_2Cl, *n*-BuCl, or PhBr). RhMe(CO)(triphos), RhPh(CO)(triphos), and Rh(MeCO)(CO)(triphos) were identified spectroscopically[2b] as the major products formed from the reactions of A with MeI, PhBr, and CH_3COCl, respectively. With EtI and Me_3SnCl, ethanol was added to the reaction mixtures when the IR spectra indicated that the reactions were complete. Concentrating the solutions by removing the solvent under reduced pressure resulted in the precipitation of yellow solids that were filtered, washed with ethanol, and dried in vacuo. The products were identified as RhEt(CO)(triphos) (30% yield) and $Rh(SnMe_3)(CO)(triphos)$ (65%) yield) on the basis of elemental analyses ($Rh(SnMe_3)(CO)(triphos)$ only) and their IR, ^{31}P NMR, ^{1}H NMR, and ^{13}C NMR ($Me_3SnRh(CO)(triphos)$ only) spectra. The complex RhEt(CO)(triphos) was contaminated with HRh(CO)(triphos) (10%) and a compound that exhibited a singlet in the ^{31}P NMR spectrum at δ 25: attempts to purify this alkyl complex by recrystallization from THF/ethanol or by column chromatography were not successful.

Spectral data for RhEt(CO)(triphos): IR ν(CO) = 1890 cm^{-1} (CH_2Cl_2); ^{1}H NMR (CD_2Cl_2) δ 1.00 (m, CH_2Me), 1.15 (m, CH_2*Me*), 1.58 (q, J = 3 Hz, Me), 2.34 (d, J = 7 Hz, $3CH_2$), 7.05–7.27 (m, Ph); ^{31}P NMR (CH_2Cl_2/CD_2Cl_2, 80:20 v/v) 9 (br, $\nu_{1/2}$ = 300 Hz). Spectral data for $Rh(SnMe_3)(CO)(triphos)$: IR (CH_2Cl_2) 1909 cm^{-1}; ^{1}H NMR (CD_2Cl_2) δ −0.39 (d, J = 42 Hz, $SnMe_3$), 1.61 (q, J = 4 Hz, Me), 2.99 (d, J = 8 Hz, $3CH_2$), 7.3–7.6 (m, Ph); ^{13}C NMR (CD_2Cl_2) δ −1.4 ($SnMe_3$), 37.0 (d, J = 19 Hz, CH_2), 39.1 (q, J = 12 Hz, Me), 38.4 (quaternary C), 128–136 (Ph); ^{31}P NMR (CH_2Cl_2/CD_2Cl_2, 80:20 v/v) δ 13.4 (d, J = 118 Hz, $^1J(^{117}$Sn–P = 245.8 Hz, $^1J(^{119}$Sn–P) = 255.2 Hz). Anal. Calcd for $Rh(SnMe_3)(CO)(triphos)$ (found): C, 58.79 (59.64); H, 5.26 (5.20).

There were no reactions with Me_3SiCH_2Cl and *n*-BuCl.

(v) Attempted Reactions of Rh(MeCO)(CO)(triphos) with LiOMe and LDA (Lithium Diethylamide). In two separate experiments, 30–45 mg of RhMe(CO)(triphos) were dissolved in THF and treated with CO to generate Rh(MeCO)(CO)(triphos). About 1 equiv of either LDA or LiOMe was then added to the reaction mixtures, and, after ≈10 min, samples were withdrawn and ^{31}P NMR spectra were obtained. There was no reaction with either LDA or LiOMe. In the case of LiOMe, a 10-fold excess of LiOMe was also added, but again there was no change in the ^{31}P NMR spectrum of the reaction mixture.

(vi) Reaction of $[Rh(CO)_2(triphos)]PF_6$ with LiOMe. A 3-fold excess of LiOMe in MeOH was added to a solution of 0.2 g of $[Rh(CO)_2(triphos)]PF_6$ in 15 mL of THF. The reaction mixture was stirred until the starting material had been consumed, and pentane was then added to produce a yellow precipitate containing RhH(CO)(triphos) (15%) and the known[4] complex $Rh(CO_2Me)(CO)$(triphos) (85% yield; ν(CO) = 1908 cm^{-1}, ν(C=O) = 1610 cm^{-1}, ν(C—O) = 1030 cm^{-1}; δ 6.7 (d, ^1J(Rh–P) = 104 Hz)).

(vii) Reaction of RhCl(CO)(triphos) with Lithium Alkoxides. Two equivalents of LiOMe was added to a suspension of 0.2 g of RhCl(CO)(triphos) in 15 mL of THF. ^{31}P NMR spectra of the reaction mixture run 15 and 90 min after the addition exhibited two sets of resonances, that of RhH(CO)(triphos) and a doublet at δ 6.9 (^1J(Rh–P) = 114 Hz). On the basis of the variation of relative intensities in the two spectra, the latter appeared to be the primary product and to convert to the hydride.

LiOEt was then added to a solution of 0.2 g of RhCl(CO)(triphos) in 15 mL of THF, the reaction mixture was stirred for 2 h, and a sample of the solution was drawn for GC analysis. In addition to ethanol and THF, acetaldehyde was also identified.

(viii) Synthesis and Reactions of $[Ru(CO)_3(triphos)]^{2+}$. A mixture of 1 g of $[RuCl(CO)_2(triphos)]^+$ and 2 g of freshly sublimed $AlCl_3$ in 10 mL of methylene chloride was treated with CO (1 atm). The reaction mixture was stirred for 10 min, and then an additional 0.5 g of $AlCl_3$ and 20 mL of CH_2Cl_2 were added and the mixture was stirred under CO for a further 20 min. At this point, an IR spectrum of the solution showed that the ν(CO) of the starting material (2089, 2049 cm^{-1})[1c] had been replaced with ν(CO) at 2141, 2099, and 2093 cm^{-1}, assigned to the tricarbonyl complex $[Ru(CO)_3(triphos)]^{2+}$ (see below). The solvent was evaporated, and the residue was dissolved in 40 mL of ethanol and treated with excess $NaPF_6$ to give a white precipitate, the IR spectrum (Nujol) of which exhibited, in addition to the ν(CO) of $[Ru(CO)_3(triphos)](PF_6)_2$, three new, weak ν(CO) at 2070, 2027, and 1635 cm^{-1}. The solid $[Ru(CO)_3(triphos)](PF_6)_2$ could not be obtained analytically pure.

The ^{31}P NMR spectrum of $[Ru(CO)_3(triphos)](PF_6)_2$ (CD_2Cl_2) exhibited a singlet at δ 3.6, while the ^{1}H NMR spectrum exhibited resonances at δ 2.10 (q, J(H–P) = 3 Hz, Me), 2.99 (m, 3 CH_2), and 7.2–7.6 (m, Ph). The ^{13}C NMR spectrum exhibited resonances at δ 29.4 (m, 3 CH_2), 38.0 (br s, quaternary C), 38.2 (q, J(P–C) = 10 Hz, Me), 184.9 (m, CO), 129–135 (m, Ph).

The complex giving rise to the ν(CO) at 2070, 2027, and 1635 cm^{-1} was extracted with CH_2Cl_2 and recrystallized from ethanol/ethyl ether. Analysis Calcd for $[Ru(CO_2Et)(CO)_2(triphos)]PF_6$ (Found): C, 55.24 (54.50); H, 4.44 (4.50). The ^{31}P NMR spectrum of $[Ru(CO_2Et)(CO)_2(triphos)]PF_6$ ($CDCl_3$) exhibited a triplet at δ 3.2 (1 P, J(P–P) = 29 Hz) and doublet at δ 3.9 (2 P). The ^{1}H NMR spectrum exhibited resonances at δ 1.83 (m, Me), 2.50 (m, CH_2), 2.68 (br d, J(H–P) = 10 Hz, CH_2), 2.78 (m, CH_2), 3.92 (q, J = 7 Hz, CH_2Me), δ 0.93 (t, J = 7 Hz, CH_2Me), and 7.0–7.7 (m, Ph). The ^{13}C NMR spectrum exhibited resonances at δ 31.4 (br d, J(C–P) = 23 Hz, CH_2), 32.5 (m, 2 CH_2), 37.3 (quaternary C), 37.8 (q, J(C–P) = 8 Hz, Me), 14.0 (CH_2Me), 60.2 (CH_2Me), and 128–133 (m, Ph). The two carbonyl resonances could not be detected.

In an IR experiment, water was added to a CH_2Cl_2 solution of $[Ru(CO)_3(triphos)]^{2+}$. After being stirred for 30 min, the solvent mixture was removed under reduced pressure and an IR spectrum of a CH_2Cl_2 solution of the residue was run. The sole product was $[RuH(CO)_2(triphos)]^+$.[1c]

To a slurry of 0.84 g of freshly prepared $[Ru(CO)_3(triphos)](PF_6)_2$ in 40 mL of THF was added 0.06 g of $NaBH_3CN$. After 40 min, the reaction mixture was filtered and the filtrate was concentrated to approximately 5 mL. After addition of 20 mL of ethanol and further concentration, a white precipitate of the formyl complex $[Ru(HCO)(CO)_2(triphos)]^+$ formed and was collected by filtration. The formyl complex exhibits ν(CO) at 2069, 2022, and 1632 cm^{-1} (CH_2Cl_2), while the ^{31}P NMR spectrum (CD_2Cl_2) exhibits resonances at δ −3.0 (t, 1 P, J(P–P) = 30 Hz) and 9.9 (d, 2 P). The ^{1}H NMR spectrum exhibits resonances at δ 1.87 (q, J(H–P) = 3 Hz, Me), 2.5–2.7 (m, 2 CH_2), 2.97 (m, CH_2), 12.67 (dt, J(H–P) = 44, 9 Hz, CHO), and 7.0–7.6 (m, Ph). The ^{13}C NMR spectrum exhibits resonances at δ 31.0 (br d, J(C–P) = 20 Hz, CH_2), 32.0 (m, 2 CH_2), 37.0 (br s, quaternary C), 38.2 (q, J(C–P) = 10 Hz, Me), 194.6 (m, CO), 251.3 (dt, J(C–P) = 50, 6 Hz, CHO), and 127–135 (m, Ph).

The formyl compound is unstable with respect to slow conversion to the hydride $[RuH(CO)_2(triphos)]^+$ and cannot be obtained analytically pure. This decomposition process takes many days in the solid state and several hours in solution at room temperature.

Results and Discussion

Rhodium Chemistry. Nucleophilic Attack on $[Rh(CO)_2(triphos)]^+$ by $NaBH_4$. The occurrence of attack by a nucleophile on coordinated CO ligands has been shown to be directly related to the force constant and hence to ν(CO) of the CO ligand, the higher the frequency of ν(CO), the more facile is an addition reaction.[5] As the complex $[Rh(CO)_2(triphos)]PF_6$ exhibits relatively high values of ν(CO) at 2060 and 1995 cm^{-1}, it was anticipated that the CO groups would be susceptible to nucleophilic attack. This was found to be so, as the reaction of $NaBH_4$ with $[Rh(CO)_2(triphos)]PF_6$ at low temperature resulted in the formation of an unstable species exhibiting a resonance at $\approx\delta$ 12 in the ^{1}H NMR spectrum. This complex is presumably the formyl complex Rh(HCO)(CO)(triphos),[6] but it is thermally very labile and decomposes on warming to give the hydride RhH(CO)(triphos). The proposed sequence of steps is given in eq 1.

$$[\mathrm{Rh(CO)_2(triphos)}]^+ + \mathrm{NaBH_4} \rightarrow \mathrm{Rh(HCO)(CO)(triphos)} \rightarrow \mathrm{RhH(CO)(triphos)} + \mathrm{CO} \quad (1)$$

The complexes $[RhL(CO)(triphos)]PF_6$ (L = $P(OMe)_3$, PMe_3) also reacted with $NaBH_4$ to form HRh(CO)(triphos).

Nucleophilic Attack on $[Rh(CO)_2(triphos)]^+$ by RLi (R = Me, *n*-Bu). Since the carbonyl ligands of $[Rh(CO)_2(triphos)]PF_6$ were attacked by $NaBH_4$, it was anticipated that the complex Rh(MeCO)(CO)(triphos) might be synthesized by nucleophilic attack of the methyl anion on CO. However, addition of excess MeLi to a solution of $[Rh(CO)_2(triphos)]PF_6$, followed by addition of ethanol (to destroy any remaining MeLi), resulted in the surprising formation of RhH(CO)(triphos). The reaction of excess *n*-BuLi with $[Rh(CO)_2(triphos)]PF_6$ also gave RhH(CO)(triphos). In both cases, the yield of RhH(CO)(triphos) was >80%, indicating that the hydride was in fact the major product of the reaction.

In an attempt to gain further information about this very interesting and novel process, the reaction of MeLi with $[Rh(CO)_2(triphos)]PF_6$ was monitored by ^{31}P NMR spectroscopy. Titration of a solution of $[Rh(CO)_2(triphos)]PF_6$ with MeLi showed that the initial reaction (ratio of MeLi:Rh = 1:1) involved the anticipated formation of the known[2b] acetyl compound Rh(MeCO)(CO)(triphos). After the formation of this compound was complete, subsequent addition of MeLi produced a mixture which contained some RhH(CO)(triphos), but which was comprised primarily of a species, A, which could not be isolated pure and hence was identified on the basis of its spectroscopic and chemical properties.

Addition of ethanol to a solution of A or forming A in acetone resulted in its complete conversion to RhH(CO)(triphos). Similar reactions involving *n*-BuLi and $[Rh(CO)_2(triphos)]PF_6$ proceeded in an identical manner.

Further evidence for the identity of A was found in its reactions with several electrophilic reagents RX (RX = MeI, EtI, PhBr, Me_3SnCl, and MeCOCl), which gave the corresponding rhodium(I) products (eq 2).

$$\mathrm{A} + \mathrm{RX} \rightarrow \mathrm{RhR(CO)(triphos)} \quad (2)$$

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The methyl, phenyl, and acetyl complexes are all known and were identified by ^{31}P NMR spectroscopy,[2b] while the products from the reactions of A with EtI and Me_3SnCl were isolated and identified as the new compounds RhEt(CO)(triphos) and $Rh(SnMe_3)$(CO)(triphos), respectively. For the latter two compounds, the ν(CO) are in the region expected for five-coordinate species of the type RhR(CO)(triphos),[2b] while the ^{1}H, ^{13}C, and ^{31}P NMR spectra of both complexes are completely compatible with the suggested formulations.[2b]

Since protonation of A yields the hydride RhH(CO)(triphos) while treatment with alkyl halides etc. proceeds as in eq 2, it would seem that A is best formulated as the rhodium(−I) species [Rh(CO)(triphos)]$^-$. Consistent with this hypothesis, the IR spectra of solutions of A exhibit a single ν(CO) at a very low frequency, 1695 cm^{-1}, indicative of significant negative charge on the metal atom. Furthermore, the ^{31}P NMR spectra of solutions of A exhibit a doublet resonance at δ 21.5 with ^1J(Rh–P) = 155 Hz, the latter about 50% greater than the corresponding ^1J(Rh–P) of complexes of the types [Rh(CO)L(triphos)]$^+$ and RhR(CO)(triphos).[2b] The considerable differences in the coupling constants suggest that the new complexes are of a type significantly different from the known rhodium(I) complexes, and a change from the five-coordination of the complexes [Rh(CO)L(triphos)]$^+$ and RhR(CO)(triphos) to four-coordination for the new, presumably tetrahedral species would be consistent with the increase in ^1J(Rh–P).[7]

Further support for the identification of A as the anionic rhodium(−I) complex [Rh(CO)(triphos)]$^-$ was obtained while attempting its synthesis in an atmosphere of CO. The addition of excess RLi (R = Me, *n*-Bu) to solutions of $[Rh(CO)_2(triphos)]PF_6$ under 1 atm of CO resulted in the formation of a second species, B, which was also formed by bubbling CO through a solution of [Rh(CO)(triphos)]$^-$. The IR spectrum of the new species exhibits two ν(CO) at 1815 and 1870 cm^{-1}, to considerably lower frequency than the ν(CO) of the rhodium(I) complex $[Rh(CO)_2(triphos)]PF_6$[2b] but comparable with the reported ν(CO) of the related complex $[Rh(CO)_2\{Ph_2P(CH_2)_2PPh_2\}]^-$ (1805, 1860 cm^{-1}).[8] In contrast to the ^{31}P NMR spectrum of $[Rh(CO)_2(triphos)]^-$ the ^{31}P NMR spectrum of B exhibits two phosphorus resonances, one of which has a chemical shift similar to that of free triphos (relative intensity 1P), suggesting a dangling triphos arm, while the other is a doublet at δ 25.5 (relative intensity 2P), with ^1J(Rh–P) almost equal to that of [Rh(CO)(triphos)]$^-$. Thus the best formulation of B would appear to be as the species $[Rh(CO)_2(\eta^2\text{-triphos})]^-$, formed by partial carbonylation of the electron-rich [Rh(CO)(triphos)]$^-$. The structures of both [Rh(CO)(triphos)]$^-$ and $[Rh(CO)_2(\eta^2\text{-triphos})]^-$ are expected to be pseudotetrahedral, and, since triphos spans mutually cis positions, it is able to coordinate either two or three positions in a tetrahedron.[9] Furthermore, for reasons discussed above, it is pertinent that δ_P and ^1J(Rh–P) of the two rhodium(−I) complexes are very similar.

Indirect support for the formulations also comes from the observations that the products from the reactions of various alkyllithium reagents with various acyl complexes were independent of the nature of both the alkyllithium and the acyl complex involved, the observed products being [Rh(CO)(triphos)]$^-$ and $[Rh(CO)_2(\eta^2\text{-triphos})]^-$, depending on whether CO is present or not. If the products contained residual alkyl fragments either from the alkyllithium reagents or from the acyl complexes Rh(RCO)(CO)(triphos), the nature of the products (and hence the ^{31}P NMR spectra) would vary as the alkyl and/or acyl groups were permuted.

Similiar anionic complexes of rhodium(−I) have been reported, although none has been isolated. The IR spectrum[8] of the complex $[Rh(dppe)(CO_2)]^-$ has been mentioned above. In addition, the complexes [Rh(CO)(triphos)]$^-$, $[Rh(CO)_2(PPh_3)_2]^-$, and $[Rh(CO)_2(dppe)]^-$ all exhibit similar reactions with alkyl and trialkyltin halides, giving σ-bonded alkyl- or trialkyltin–rhodium(I) complexes of the type $RhR(CO)_2L_2$ (R = trialkyltin, Me, C_6F_5; L = phosphorus donors).[8,10,11] Furthermore, as we have shown, [Rh(CO)(triphos)]$^-$ acts as a base, being able to deprotonate both ethanol and acetone to form RhH(CO)(triphos). As RhH(CO)(triphos) is the conjugate acid of [Rh(CO)(triphos)]$^-$, deprotonation of RhH(CO)(triphos) should generate [Rh(CO)(triphos)]$^-$, and it was indeed found that reaction of RhH(CO)(triphos) with MeLi or LDA does in fact result in the formation of [Rh(CO)(triphos)]$^-$. It should, however, be emphasized that the formation of [Rh(CO)(triphos)]$^-$ by deprotonation of RhH(CO)(triphos) occurs on a time scale which is much slower than required for the formation of [Rh(CO)(triphos)]$^-$ from the reaction of MeLi with $[Rh(CO)_2(triphos)]PF_6$. The relevance of this finding will become apparent below.

Finally, acyl complexes were confirmed as being intermediates in the reactions of $[Rh(CO)_2(triphos)]PF_6$ with alkyllithium reagents by the reactions shown in eq 3 and 4. Since the reactions were performed under an atmosphere of CO in order to stabilize the acyl complexes, [Rh(CO)(triphos)]$^-$ was not observed.

$$\mathrm{RhR(CO)(triphos) + CO \rightarrow Rh(RCO)(CO)(triphos) \xrightarrow{R'Li} [Rh(CO)_2(\eta^2\text{-triphos})]^-} \tag{3}$$

$$\mathrm{[Rh(CO)_2(\eta^2\text{-triphos})]^- \xrightarrow{EtOH} RhH(CO)(triphos)} \tag{4}$$

This type of reaction is quite general, applying to various combinations of alkyllithium reagents and acyl complexes.

Identification of Organic Products from the Reaction of Excess MeLi with $[Rh(CO)_2(triphos)]PF_6$. Having established that the metal-containing product from the reaction of excess MeLi with $[Rh(CO)_2(triphos)]PF_6$ is [Rh(CO)(triphos)]$^-$, it was necessary to determine the nature of the organic product(s). The possibility that gaseous organic products were formed during the reaction was examined by both volumetric and GC techniques. The results of both experiments indicated that there were no gaseous (in particular methane) products produced in the reaction of MeLi with $[Rh(CO)_2(triphos)]PF_6$. Furthermore, from the volumetric experiment, it was possible to determine an approximate stoichiometry of the reaction by destroying the remaining MeLi in both the blank and genuine runs; the difference in the amount of gas produced by the two runs was equal to the amount of MeLi consumed by the reaction with $[Rh(CO)_2(triphos)]PF_6$. On this basis, ~3 mol of MeLi were consumed per mole of rhodium complex.

The ^{13}C and ^{1}H NMR spectra of the hydrolyzed reaction mixtures exhibited the resonances of *t*-BuOH, suggesting that the reaction mixture originally contained *tert*-but-

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oxide. This conclusion was verified by the reaction of CD_3Li with $[Rh(CO)_2(triphos)]PF_6$, as the ^2H NMR spectrum of the hydrolyzed reaction mixture exhibited the resonance of *t*-BuOH-d_9. Confirming this assignment, the ^2H NMR spectrum of the reaction mixture containing CD_3Li and acetone-d_6 exhibited the resonance of *tert*-butoxide-d_9, the ^2H chemical shift of which was identical with that obtained from reaction of CD_3Li with $[Rh(CO)_2(triphos)]PF_6$. *tert*-Butyl alcohol was also detected in ≈65% yield in a hydrolyzed reaction mixture by GC, confirming that it is the major organic product of the chemistry under consideration here.

The formation of *t*-BuO^- as the product is consistent with stoichiometry of the reaction, as the reaction represents the removal of one CO molecule from $[Rh(CO)_2(triphos)]^+$ by 3 equiv of MeLi. Methane is not produced, and it seems reasonable the organic product is formed via successive attacks by Me^- at a carbonyl carbonyl atom. As demonstrated, the first step involves the formation of Rh(MeCO)(CO)(triphos) by nucleophilic attack on $[Rh(CO)_2(triphos)]PF_6$ (eq 5).

$$[Rh(CO)_2(triphos)]^+ + Me^- \rightarrow MeCORh(CO)(triphos) \quad (5)$$

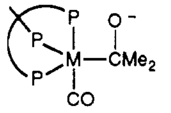
Reaction of Rh(MeCO)(CO)(triphos) with the second mole of MeLi must involve nucleophilic attack on the acetyl complex, although metal–acyl species generally react with bases through either deprotonation[12] (eq 6) or displacement[13] (eq 7) of the acyl group.

$$[M]\text{-}COCH_2R + B^- \rightarrow [[M]\text{-}COCHR]^- + BH \quad (6)$$

$$[M]\text{-}COR + B^- \rightarrow BCOR + \text{reduced metal species} \quad (7)$$

Deprotonation of the acyl group in complexes of the type η^5-$CpFe(CO)(PPh_3)(MeCO)$, as in eq 6, has been accomplished by *n*-BuLi and LDA (a strong but bulky base).[12] In the reaction of MeLi with Rh(MeCO)(CO)(triphos), deprotonation does not occur, since the product would be methane, which was not detected. Additionally, the strongly basic LDA does not react with Rh(MeCO)(CO)(triphos), seemingly in support of the suggestion that deprotonation is not a factor in the reactions under discussion here.

Although the site of attack of the second methyl group cannot be determined, we note that nucleophilic attack by Me^- on the acyl group could give a complex (C) which



C

could spontaneously eliminate acetone to yield the observed product Li[Rh(CO)(triphos)] (A). The acetone so formed would react rapidly with the third mole of MeLi which is consumed in the reaction, forming Li(*t*-BuO).

During the reactions of MeLi with Rh(MeCO)(CO)(triphos) and $[Rh(CO)_2(triphos)]PF_6$, the relative yields of RhH(CO)(triphos) and the anionic complexes depended upon the amount of MeLi used. As the ratio of MeLi:Rh(MeCO)(CO)(triphos) increased, the relative amount of RhH(CO)(triphos) decreased, and at ratios >2:1, there was essentially no RhH(CO)(triphos) formed. These observations can be rationalized on the basis of the formation of acetone during the reaction since, as already noted, $[Rh(CO)(triphos)]^-$ reacts with acetone to form HRh(CO)(triphos). Therefore there is a competition between $[Rh(CO)(triphos)]^-$ and Me^- for the liberated acetone. Obviously, the more Me^- present relative to $[Rh(CO)(triphos)]^-$, the smaller will be the ratio HRh(CO)(triphos):$[Rh(CO)(triphos)]^-$ formed.

There does not appear to be any other reasonable mechanism that is able to rationalize all of the observations discussed above. The possibility that Li[Rh(CO)(triphos)] is formed directly via deprotonation of RhH(CO)(triphos), formed via some other route, is precluded by the relative rates of the reactions; as noted above, deprotonation of RhH(CO)(triphos) occurs at a much slower rate than does the formation of $[Rh(CO)(triphos)]^-$. Likewise, any reaction scheme that requires the deprotonation of the intermediate acyl complex is precluded by the lack of methane formation. Furthermore, the possibility that adventitious RO^- was participating in the conversion of Rh(RCO)(CO)(triphos) to RhH(CO)(triphos) was precluded by the observation that Rh(MeCO)(CO)(triphos) does not react with a 10-fold excess of LiOMe, although it was found that $[Rh(CO)_2(triphos)]PF_6$ undergoes nucleophilic attack by MeO^-, as in eq 8.

$$[Rh(CO)_2(triphos)]^+ + LiOMe \rightarrow Rh(CO_2Me)(CO)(triphos) \quad (8)$$

$Rh(CO_2Me)(CO)(triphos)$ is a known compound, which has been prepared by other routes.[4]

Finally, we note that the fact that the second mole of MeLi does not deprotonate the acyl group is surprising. There have been few examples of complexes where a strong base will displace (or undergo nucleophilic attack on the coordinated acyl carbon of) an acyl group. In contrast, deprotonation of acyl groups by strong bases has been extensively observed and studied, particularly in complexes such as η^5-$CpFe(CO)(PPh_3)(MeCO)$ (L = CO, PPh_3).[13]

Ruthenium Chemistry. The cationic complex $[Ru(CO)_3(triphos)]^{2+}$ can be readily prepared by bubbling CO through CH_2Cl_2 solutions of the halo complexes $[RuX(CO)_2(triphos)]^+$ (X = Cl, Br, I) in the presence of excess $AlCl_3$ (eq 9). Although monitoring the reaction by IR spectroscopy suggested that the reaction proceeded rapidly and in high yield, it was not found possible to isolate the product, which was therefore characterized spectroscopically. Thus the high frequencies of the ν(CO) of the cation (2140, 2099, 2093 cm^{-1}) are consistent with a high positive charge. In the NMR spectra, the presence of a singlet in the ^{31}P NMR spectrum and the equivalence of the methylene group resonances in the ^1H and ^{13}C NMR spectra are also clearly consistent with the formulation.

$$[Ru(CO)_2Cl(triphos)]^+ + CO + AlCl_3 \rightarrow [Ru(CO)_3(triphos)]^{2+} + AlCl_4^- \quad (9)$$

As anticipated on the basis of the high values of ν(CO),[5] the cationic $[Ru(CO)_3(triphos)]^{2+}$ is susceptible to nucleophilic attack by ethanol, yielding the alkoxycarbonyl complex $[Ru(CO_2Et)(CO)_2(triphos)]^+$, which was isolated analytically pure. The IR spectrum of this complex exhibited ν(CO) at 2076 and 2032 cm^{-1}, in the region for ν(CO) of the analogous halo complexes,[1c] and ν(C=O) at 1636 cm^{-1}. The ^{31}P NMR spectrum exhibited two resonances in a 2:1 ratio, reflecting the anticipated nonequivalence of the phosphorus environments while the ^1H and the ^{13}C NMR spectra are also both consistent with none-

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quivalence of the methylene groups.

A number of alkoxycarbonyl complexes have been formed via nucleophilic attack on coordinated CO groups.[5c,14] The IR and NMR spectroscopic properties of the coordinated ethoxycarbonyl ligand reported here seem unexceptional.

The cationic [Ru(CO)$_3$(triphos)]$^{2+}$ reacted with water to give the known[1c] hydride, [RuH(CO)$_2$(triphos)]$^+$, presumably via the intermediacy of the metallocarboxylic acid [Ru(CO$_2$H)(CO)$_2$(triphos)]$^+$. The latter would be formed by nuclephilic attack on [Ru(CO)$_3$(triphos)]$^{2+}$ by water, as in eq 10. If D$_2$O were used, the corresponding ruthenium deuteride was formed.

$$[\mathrm{Ru(CO)_3(triphos)}]^{2+} + \mathrm{H_2O} \rightarrow [\mathrm{Ru(CO_2H)(CO)_2(triphos)}]^{+} \xrightarrow{-\mathrm{CO_2}} [\mathrm{RuH(CO)_2(triphos)}]^{2+} \quad (10)$$

Metallocarboxylic acids are believed to the intermediates in the conversion of a variety of carbonyl complexes by water and hydroxide ion to metal hydrides. Although the postulated intermediate could not be isolated in this ruthenium system, similar species have been isolated and/or characterized in other cases.[14a,15]

The cationic [Ru(CO)$_3$(triphos)]$^{2+}$ also underwent nucleophilic attack by a mild hydride donor, NaBH$_3$CN, to give a formyl complex (eq 11).

$$[\mathrm{Ru(CO)_3(triphos)}]^{2+} + \mathrm{H}^- \rightarrow [\mathrm{Ru(CHO)(CO)_2(triphos)}]^{2+} \quad (11)$$

Although this new complex was rather unstable and could not be obtained analytically pure, it was unambiguously characterized by its spectroscopic properties. Thus the IR spectrum exhibited ν(CO) at 2069 and 2022 cm^{-1} and ν(C=O) at 1632 cm^{-1}, all very similar to the abovementioned ethoxycarbonyl complex. The ^{31}P, ^{1}H, and ^{13}C NMR spectra were all consistent with the presence of phosphorus atoms and methylene groups being present in 2:1 ratios, and characteristic formyl hydrogen and carbon resonances were also observed.[6]

As noted elsewhere,[6,16] nucleophilic attack by hydride donors on coordinated CO ligands is a well-established process. However, in contrast with other formylruthenium compounds, such as [Ru(HCO)(CO)(diphosphine)$_2$]$^+$ salts, which decompose to the corresponding hydrides within minutes,[16] [Ru(CHO)(CO)$_2$(triphos)]$^{2+}$ is remarkably stable with respect to conversion to [RuH(CO)$_2$(triphos)]$^+$, taking hours in solution and days in the solid state (eq 12). The

$$[\mathrm{Ru(CHO)(CO)_2(triphos)}]^{2+} \rightarrow [\mathrm{RuH(CO)_2(triphos)}]^{+} + \mathrm{CO} \quad (12)$$

stability of the triphos system may reflect the greater stability of the tridentate ligand system to dissociation, as the chemistry of eq 12 is thought to involve prior dissociation of a phosphorus to form a coordinatively unsaturated species. The hydrogen can then migrate to the vacant site, followed by displacement of CO by the returning phosphorus atom.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council for support of this research by way of operating grants to M.C.B. and a graduate fellowship to G.G.J. We also thank Queen's University and the NATO Science Fellowship Program for fellowships to S.I.H. and Johnson Matthey and the International Nickel Company of Canada for loans of rhodium and ruthenium salts.

Registry No. [Rh(CO)$_2$(triphos)]PF$_6$, 75070-58-5; [Rh(CO)(PMe$_3$)(triphos)]PF$_6$, 121373-92-0; [Rh(CO)(ep(OMe)$_3$)(triphos)]PF$_6$, 121373-94-2; HRh(CO)(triphos), 101075-59-6; MeLi, 917-54-4; *n*-BuLi, 109-72-8; Rh(MeCO)(CO)(triphos), 110544-58-6; Li(A), 110544-60-0; Rh(PhCO)(CO)(triphos), 121373-95-3; PhLi, 591-51-5; Li[Rh(CO)$_2$($\#^2$-triphos)], 121373-96-4; Rh(Me)(CO)(triphos), 110544-59-7; Rh(Ph)(CO)(triphos), 121373-97-5; MeI, 74-88-4; PhBr, 108-86-1; MeCOCl, 75-36-5; Rh(Et)(CO)(triphos), 121373-98-6; Rh(SnMe$_3$)(CO)(triphos), 121373-99-7; EtI, 75-03-6; Me$_3$SnCl, 1066-45-1; Me$_3$SiCH$_2$Cl, 2344-80-1; *n*-BuCl, 109-69-3; Rh(CO$_2$Me)(CO)(triphos), 75070-63-2; RhCl(CO)(triphos), 34440-04-5; [Ru(CO)$_3$(triphos)]PF$_6$)$_2$, 121374-01-4; [RuCl(CO)$_2$(triphos)]$^+$, 47876-61-9; [Ru(CO$_2$Et)(CO)$_2$(triphos)]PF$_6$, 121393-27-9; [RuH(CO)$_2$(triphos)]$^+$, 99341-38-5; [RuCHCO)(CO)$_2$(triphos)]$^+$, 121374-02-5; CO, 630-08-0.

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