Homo- and Heterobimetallic Complexes of Rhodium, Iridium, Palladium, and Platinum Containing a Dimetalated Olefin

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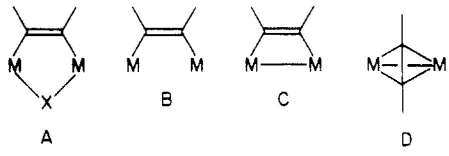
Received August 26, 1985

Reaction of $[Rh_2Cl_2(\mu\text{-}CO)(Ph_2Ppy)_2]$ with electrophilic acetylenes gives the dimetalated olefin derivatives $[Rh_2Cl_2(\mu\text{-}RC{=}CR')(Ph_2Ppy)_2]$ ($R = R' = CO_2Me, CF_3$; $R = CO_2Me, R' = H$). These add carbon monoxide in terminal sites to form $[Rh_2Cl_2(CO)_2(\mu\text{-}RC{=}CR')(Ph_2Ppy)_2]$. Chloride abstraction from $[Rh_2Cl_2(\mu\text{-}CO)(Ph_2Ppy)_2]$ by silver perchlorate yields $[Rh_2Cl(\mu\text{-}CO)(Ph_2Ppy)_2]ClO_4$ which adds carbon monoxide to give $[Rh_2(CO)_2(\mu\text{-}Cl)(Ph_2Ppy)_2]ClO_4$. Dimethyl acetylenedicarboxylate (DMAD) also forms the dimetalated olefin complex $[Pd_2Cl_2(\mu\text{-}DMAD)(Ph_2Ppy)_2]$ with $[Pd_2Cl_2(Ph_2Ppy)_2]$ while $[PtBr_2(Ph_2Ppy)_2]$ adds to $[IrBr_2(CO)_2)]^-$ to give $[PtIrBr_3(CO)(Ph_2Ppy)_2]$. Heterobimetallic, dimetalated olefin complexes $[IrRhCl_2(CO)(\mu\text{-}CO)(\mu\text{-}RC{=}CR)(DPM)_2]$ ($R = CO_2Me, CF_3$) are formed from the appropriate acetylene and $[IrRh(CO)_2(\mu\text{-}Cl)(DPM)_2]Cl$. Isomers with the terminal carbonyl bound to iridium and to rhodium are both formed. Loss of one carbonyl ligand occurs at reflux under nitrogen to form the metal–metal bonded complexes $[IrRhCl_2(CO)(\mu\text{-}RC{=}CR)(DPM)_2]$ ($R = CO_2Me, CF_3$). Chloride abstraction from $[IrRhCl_2(CO)(\mu\text{-}CO)(\mu\text{-}DMAD)(DPM)_2]$ by silver perchlorate under carbon monoxide yields $[IrRh(CO)_2Cl(\mu\text{-}CO)(\mu\text{-}DMAD)(DPM)_2]ClO_4$ in which the terminal carbonyls are both bound to rhodium. This is readily and reversibly decarbonylated to $[IrRhCl(CO)_2(\mu\text{-}DMAD)(DPM)_2]ClO_4$ which contains a metal–metal bond and in which the carbonyl groups are now bound to iridium. The reverse process occurs by initial attack of carbon monoxide at rhodium. The mononuclear complexes $[Ir(CO)X(Ph_2Ppy)_2]$ ($X = Cl, Br$) are readily formed, but diiridium complexes bridged by 2-pyridyldiphenylphosphine could be obtained only with difficulty and attempts to form related rhodium–iridium dimers failed. The infrared and ^{13}C and ^{31}P NMR spectra of the new complexes are discussed as are possible mechanisms for the interconversions of $[IrRhCl(CO)_2(\mu\text{-}CO)(\mu\text{-}DMAD)(DPM)_2]ClO_4$ and $[IrRhCl(CO)_2(\mu\text{-}DMAD)(DPM)_2]ClO_4$.

Introduction

Considerable interest has been shown in recent years in the reactivity of unsaturated molecules toward binuclear metal complexes stabilized by "short bite" ligands such as bis(diphenylphosphino)methane (DPM) and bis(diphenylarsino)methane (DAM). Previous papers from our laboratories have described the syntheses of cationic binuclear rhodium and iridium complexes of these ligands which contain dimetalated olefin moieties derived from electronegatively substituted acetylenes.[1–4] In these, the acetylene is attached parallel to the metal–metal axis (A–C) rather than perpendicular to it (D) as has heretofore



been the more common mode of attachment. Concurrent with our work a considerable number of related complexes of rhodium,[5] iridium,[6] palladium,[7] and platinum[8] have been reported.

Our continuing interest in acetylene complexes has led us to inquire what effects the use of unsymmetrical ligands and the presence of two different metals in this class of binuclear complexes might have on their reactions with acetylenes. We report here on the results of this study.

Experimental Section

All solvents were appropriately dried and distilled prior to use and were stored under dinitrogen. All syntheses were performed under atmospheres of dinitrogen or carbon monoxide as appropriate by using standard Schlenk techniques although the final products generally proved not to be significantly sensitive to air or moisture. Hydrated iridium(III) chloride was purchased from the Aesar Group while hydrated rhodium(III) chloride was obtained from Alfa Inorganics and bis(diphenylphosphino)methane (DPM) from Strem Chemicals. Dimethyl acetylenedicarboxylate (DMAD) and hexafluorobut-2-yne (HFB) were obtained from Aldrich and PCR/SCM Specialty Chemicals, respectively. Published procedures were used to prepare $[RhCl(COD)]_2$[9] (COD = cycloocta-1,5-diene), $[RhCl(CO)_2]_2$,[10] $[IrCl(c\text{-}C_8H_{14})_2]_2$,[11] $[Ir(CO)_2Cl(p\text{-}CH_3C_6H_4NH_2)]$,[12] $[Rh_2Cl_2(\mu\text{-}CO)(Ph_2Ppy)_2]$[13] ($Ph_2Ppy$ = 2-pyridyldiphenylphosphine), $[Pd_2Cl_2(Ph_2Ppy)_2]$,[14] $[IrRh(CO)_2(\mu\text{-}CO)(\mu\text{-}Cl)(DPM)_2]Cl$,[15] $[PtX_2(Ph_2Ppy)_2]$ ($X = Cl, Br$),[16]

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and 2-pyridyldiphenylphosphine.[14] Carbon monoxide was Matheson CP grade while ^{13}CO (98% isotopic purity) was obtained from Cambridge Isotope Laboratories. Infrared spectra were obtained on a Perkin-Elmer 683 spectrometer as Nujol mulls unless otherwise specified. Proton NMR spectra were obtained at 90 MHz on a Varian EM-390 spectrometer with chemical shifts referred to internal tetramethylsilane (δ 0.0). Noise-decoupled phosphorus-31 NMR spectra were obtained on JEOL FX-60 and IBM/Brucker AF-200 spectrometers at 24.15 and 81.02 MHz, respectively, using a 45° pulse and a 4-s repetition rate. Carbon-13 NMR spectra were obtained at 50.32 MHz on the AF-200 spectrometer using a 30° pulse and a 6-s repetition rate. Phosphorus and carbon chemical shifts are referred to external 85% H_3PO_4 (δ 0.0) and external tetramethylsilane (δ 0.0), respectively, using the high-frequency-positive convention. All spectra were obtained at ambient probe temperature (ca. 30 °C) unless otherwise specified. Spectral simulations were performed with a local version of the LAOCOON-3 program of Bothner-By and Castellano.[17,18] Analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

$[Rh_2Cl_2(\mu\text{-}H_3CO_2CC{=}CCO_2CH_3)((C_6H_5)_2P(C_5H_4N))_2]$ (1). To a benzene suspension of $[Rh_2Cl_2(\mu\text{-}CO)(Ph_2Ppy)_2]$ (0.2 g, 0.24 mmol) was added an excess of dimethyl acetylenedicarboxylate. The solid soon dissolved to give a dark red solution which was then stirred under reflux for 3 h. Concentration of the cooled solution to ca. 10 mL followed by dilution with diethyl ether afforded a purple solid which was filtered off and recrystallized from dichloromethane–diethyl ether to give the product as dark reddish purple crystals in essentially quantitative yield. Anal. Calcd for $C_{40}H_{34}O_4P_2N_2Cl_2Rh_2$: C, 50.81; H, 3.63; Cl, 7.50; N, 2.96. Found: C, 50.7; H, 3.6; Cl, 7.7; N, 2.8. IR: 1638 (w) cm^{-1} ($\nu_{C{=}C}$).[20] ^1H NMR ($CDCl_3$): δ 3.57 (s, 6 H, CO_2CH_3).[21] $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 35.6 (AA′XX′, $^1J_{Rh-P}$ = 150.0, $^2J_{Rh'-P}$ = −6.6, $^3J_{P-P'}$ = 14.7, $^1J_{Rh-Rh'}$ = 13.6 Hz).

$[Rh_2Cl_2(\mu\text{-}F_3CC{=}CCF_3)((C_6H_5)_2P(C_5H_4N))_2]\cdot C_6H_6$ (2). A solution of $[Rh_2Cl_2(\mu\text{-}CO)(Ph_2Ppy)_2]$ (0.20 g, 0.24 mmol) in 20 mL of a 1:1 (v:v) mixture of benzene and tetrahydrofuran was prepared in a serum-capped flask and the flask partially evacuated and repressurized with hexafluorobut-2-yne. After the solution was stirred for 5 hours concentration of the initial reaction mixture under reduced pressure produced a brownish purple solid in virtually quantitative yield. Recrystallization could be accomplished from dichloromethane on dilution with diethyl ether. Anal. Calcd for $C_{44}H_{34}F_6P_2N_2Cl_2Rh_2$: C, 50.64; H, 3.29; F, 10.93; Cl, 6.80. Found: C, 50.3; H, 3.3; F, 10.6; Cl, 6.8. IR: 1670 (m) cm^{-1} ($\nu_{C{=}C}$). ^1H NMR (CD_2Cl_2): δ 7.22 (s) (benzene). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 35.3 (AA′XX′, $^1J_{Rh-P}$ = 147.8, $^2J_{Rh'-P}$ = −5.8, $^3J_{P-P'}$ = 14.6, $^1J_{Rh-Rh'}$ = 12.4 Hz).

$[Rh_2Cl_2(\mu\text{-}HC{=}CCO_2CH_3)((C_6H_5)_2P(C_5H_4N))_2]$ (3). A suspension of $[Rh_2Cl_2(\mu\text{-}CO)(Ph_2Ppy)_2]$ in acetone/benzene (2:1, v/v, 30 mL total volume) containing an excess of methyl propiolate was refluxed for 2 h. The reaction mixture was filtered hot to remove unreacted $[Rh_2Cl_2(\mu\text{-}CO)(Ph_2Ppy)_2]$ and other insoluble material. (Longer reaction times increase the yield of this insoluble yellow powder at the expense of 3. The insolubility of the yellow material prevented adequate purification or characterization.) The purple filtrate was diluted with diethyl ether to precipitate a purple solid. This was collected and chromatographed on a silica gel column. Elution with benzene/tetrahydrofuran (5:1, v/v) removed a purple band. Dilution of this fraction with diethyl ether afforded the product as dark, wine-red crystals in 42% yield. Anal. Calcd for $C_{38}H_{32}O_2P_2N_2Cl_2Rh_2$: C, 51.43, H, 3.64; Cl, 7.99. Found: C, 52.0; H, 3.8; Cl, 7.7. IR: 1556 (m) cm^{-1} ($\nu_{C{=}C}$). ^1H NMR (CD_2Cl_2): δ 3.62 (s, 3 H, CO_2CH_3), 5.23 (br, 1 H, =CH). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 38.7, 39.5 (ABXY, $^1J_{Rh-P}$ = 148.2, 147.8, $^2J_{Rh-P}$ = −6.6, −7.4, $^3J_{P-P}$ = 16.2, $^1J_{Rh-Rh}$ = 13 Hz).

$[Rh_2Cl_2(CO)_2(\mu\text{-}H_3CO_2CC{=}CCO_2CH_3)((C_6H_5)_2P(C_5H_4N))_2]$ (4). A solution of 1 in 10 mL of dichloromethane was purged with carbon monoxide until the original purple color had changed to bright orange (ca. 2 min). Addition of diethyl ether while the flow of carbon monoxide was maintained precipitated the product as orange crystals in virtually quantitative yield. These were filtered under pressure of carbon monoxide, washed with diethyl ether, and dried in a stream of carbon monoxide. Anal. Calcd for $C_{42}H_{34}O_6P_2N_2Cl_2Rh_2$: C, 50.37; H, 3.34; Cl, 7.08. Found: C, 49.9; H, 3.5; Cl, 7.2. IR: 2060 (vs), 2037 (s) cm^{-1} ($\nu_{C{\equiv}O}$); 1563 (m) cm^{-1} ($\nu_{C{=}C}$). ^1H NMR ($CDCl_3$, −40 °C): δ 3.64 (s, 3 H), 3.55 (s, 3 H, CO_2CH_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −58 °C): δ 26.4, 27.2 (ABXY, $^1J_{Rh-P}$ = 124.7, 129.6, $^2J_{Rh-P}$ = −3.6, −2.6, $^3J_{P-P}$ = 15.6, $^1J_{Rh-Rh}$ = 8.0 Hz). ^{13}C NMR (CD_2Cl_2, −50 °C): δ 188.8 (dd, $^1J_{Rh-C}$ = 54.2, $^2J_{P-C}$ = 12.0 Hz), 171.9 (dm, $^1J_{Rh-C}$ = 58.4 Hz).

$[Rh_2Cl_2(CO)_2(\mu\text{-}F_3CC{=}CCF_3)((C_6H_5)_2P(C_5H_4N))_2]$ (5). This was prepared from 2 in a manner analogous to that used for 4 and was obtained as orange yellow crystals in nearly quantitative yield. Anal. Calcd for $C_{40}H_{28}F_6O_2P_2N_2Cl_2Rh_2$: C, 46.76; H, 3.34; Cl, 6.90; N, 2.73. Found: C, 46.6; H, 2.9; Cl, 6.9; N, 2.7. IR: 2075 (vs), 2048 (s) cm^{-1} ($\nu_{C{\equiv}O}$); 1598 (m) cm^{-1} ($\nu_{C{=}C}$). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −33 °C): δ 25.3 (m). ^{13}C NMR (CD_2Cl_2, −39 °C): δ 189 (dm, $^1J_{Rh-C}$ = 58 Hz), 170 (dm, $^1J_{Rh-C}$ = 57 Hz).

$[Rh_2Cl(CO)((C_6H_5)_2P(C_5H_4N))_2]ClO_4$ (6). A solution of $[Rh_2Cl_2(\mu\text{-}CO)(Ph_2Ppy)_2]$ (0.30 g, 0.36 mmol) in 40 mL of a mixture of acetone and dichloromethane (3:1, v/v) was treated with 0.075 g (0.36 mmol) of silver perchlorate. After being stirred for 3 h while protected from light the dark red solution was filtered through a pad of diatomaceous earth to remove precipitated silver chloride. Concentration of the filtrate under reduced pressure followed by addition of diethyl ether afforded the product as brick-red crystals in near quantitative yield. Anal. Calcd for $C_{35}H_{28}O_5Cl_2P_2N_2Rh_2$: C, 46.95; H, 3.16; Cl, 7.92. Found: C, 46.0; H, 3.6; Cl, 8.0. IR: 1826 (s) cm^{-1} (ν_{CO}).

$[Rh_2(CO)_2(\mu\text{-}Cl)((C_6H_5)_2P(C_5H_4N))_2]ClO_4\cdot(CH_3)_2CO$ (7). Purging a suspension of 6 in acetone with carbon monoxide caused the solid to dissolve with the formation of an orange solution. Dilution with diethyl ether precipitated the product as burnt orange crystals in near quantitative yield. These were filtered off and recrystallized from acetone/diethyl ether under a carbon monoxide atmosphere. The same complex could also be obtained directly from $[Rh_2Cl_2(\mu\text{-}CO)(Ph_2Ppy)_2]$ and silver perchlorate under a carbon monoxide atmosphere. Anal. Calcd for $C_{39}H_{34}P_2N_2O_7Cl_2Rh_2$: C, 47.73; H, 3.50; Cl, 7.22. Found: C, 47.3; H, 3.6; Cl, 6.8. IR: 2012 (s), 1997 (vs) cm^{-1} ($\nu_{C{\equiv}O}$). $^{31}P\{^1H\}$ NMR ($(CD_3)_2CO$, −33 °C): δ 35.8 (AA′XX′, $^1J_{Rh-P}$ = 132.7, $^2J_{Rh-P'}$ = −3.3, $^3J_{P-P'}$ = 6.22, $^1J_{Rh-Rh'}$ = 5.5 Hz). ^{13}C NMR (CD_2Cl_2, −39 °C): δ 183.7 (ddd, $^1J_{Rh-C}$ = 83.4, $^2J_{P-C}$ = 16.0, $^4J_{P'-C}$ = 2.0 Hz).

$[Pd_2Cl_2(\mu\text{-}H_3CO_2CC{=}CCO_2CH_3)((C_6H_5)_2P(C_5H_4N))_2]$ (8). To a dichloromethane solution of $[Pd_2Cl_2(Ph_2Ppy)_2]$ (0.20 g, 0.25 mmol) was added an excess of dimethyl acetylenedicarboxylate whereupon the dark red solution rapidly became orange. After being stirred for 1 h, the solution was diluted with diethyl ether and hexane to precipitate the product as dark orange crystals in 90% yield. An analytical sample was obtained by recrystallization from dichloromethane–diethyl ether. Anal. Calcd for $C_{40}H_{34}O_4P_2N_2Cl_2Pd_2$: C, 50.44; H, 3.64; N, 2.94; Cl, 7.44. Found: C, 50.1; H, 3.7; N, 2.9; Cl, 7.2. IR: 1583 (m) cm^{-1} ($\nu_{C{=}C}$). ^1H NMR (CD_2Cl_2): δ 3.30 (s, 6 H, CO_2CH_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 33.9 (s).

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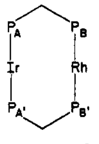
(18) In the simulation of the 24.15-MHz AA′BB′X (A = B = P; X = Rh) the following notation is used:



With the exception of complexes **11** and **13** the large number of degeneracies or near degeneracies observed in the spectra made it impossible to satisfactorily refine values for $^2J_{P(A)-P(A')}$ and $^2J_{P(B)-P(B')}$. Hence these values were fixed at 350 Hz which allowed for satisfactory simulations and are comparable to those determined for **11** and **13** and to those determined previously for related systems.[4,19]

(19) Pregosin, P. S.; King, R. W. "^{31}P and ^{13}C NMR of Transition Metal Phosphine Complexes"; Springer-Verlag: New York, 1979; Tables 18b, 19, 21.

(20) Key to infrared absorption intensities: vs, very strong; s, strong; m, medium; w, weak; br, broad.

(21) Key to NMR peak multiplicities: s, singlet; d, doublet; dd, doublet of doublets; dt, doublet of triplets; dq, doublet of quintets; dm, doublet of multiplets; ddd, double doublet of doublets; dtt, double triplet of triplets; t, triplet; m, multiplet.

[$PtIr(CO)Br_3((C_6H_5)_2P(C_5H_4N))_2$] (9). To a solution of 0.352 g (0.398 mmol) of [$PtBr_2(Ph_2Ppy)_2$] in 20 mL of dichloromethane was added a dichloromethane solution (5 mL) of Bu_4N[$Ir(CO)_2Br_2$]. Gas evolution occurred, and the solution became bright yellow. Following a 5-h reflux the solution had become orange. It was cooled, diluted with diethyl ether, and left to stand at room temperature for several days during which time a mixture of orange and yellow solids precipitated. The solvent was removed under reduced pressure, the residue taken up in 20 mL of THF, and the mixture refluxed for 4 h. The yellow solid present was filtered off from the orange solution and recrystallized from dichloromethane–diethyl ether to finally yield the product as orange-yellow crystals in 62% yield. Anal. Calcd for $C_{35}H_{28}Br_3P_2N_2OIrPt$: C, 35.57; H, 2.39. Found: C, 35.4; H, 2.6. IR: 2022 (vs) cm^{-1} ($\nu_{C\equiv O}$). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ −2.7 (d), −20.5 (d, $J_{P-P'}$ = 16.5, $^1J_{Pt-P}$ = 4034, $^2J_{Pt-P'}$ = 129.1 Hz).

[$RhIr(CO)(\mu$-$CO)Cl_2(\mu$-$H_3CO_2CC{=}CCO_2CH_3)((C_6H_5)_2PCH_2P(C_6H_5)_2)_2$]·$0.5CH_2Cl_2$ (10). To a suspension of [$RhIr(CO)_2(\mu$-$CO)Cl(DPM)_2$]Cl (0.20 g, 0.164 mmol) in CO-saturated dichloromethane (25 mL) was added an excess of dimethyl acetylenedicarboxylate. The flask was stoppered, and the contents were stirred under a static atmosphere of carbon monoxide for 1 h by which time most of the solid has dissolved to give a cloudy, pale yellow solution. Filtration through a pad of diatomaceous earth followed by dilution of the filtrate with hexane afforded the product as a pale yellow powder in 78% yield. Recrystallization was accomplished from dichloromethane–diethyl ether. The spectroscopic data indicated the presence of two isomers in both the crude and recrystallized products. Anal. Calcd for $C_{58.5}H_{51}P_4O_6Cl_3RhIr$: C, 51.08; H, 3.74; Cl, 7.73. Found: C, 51.1; H, 3.9; Cl, 7.3. Isomer **10a**: IR 2050 (vs), 1647 (s) cm^{-1} (ν_{CO}); 1562 (m) cm^{-1} ($\nu_{C=C}$); ^1H NMR (CD_2Cl_2) δ 1.81 (s, 3 H), 3.15 (s, 3 H) (CO_2CH_3); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) $\delta(P_A)$ −13.5, $\delta(P_B)$ 7.6 (AA′BB′X, $^2J_{P_A-P_{A'}} = {}^2J_{P_B-P_{B'}}$ = 350, $^2J_{P_A-P_B}$ = 8.6, $^1J_{Rh-P_B}$ = 141.0, $J_{P_A-P_{B'}}$ = 5.2, J_{Rh-P_A} = 5.5 Hz); ^{13}C NMR (CD_2Cl_2) $\delta(CO_t)$ 170.3 (t, $^2J_{P-C}$ = 7.7 Hz), $\delta(CO_{br})$ 198.4 (dq, $^1J_{Rh-C}$ = 27.3, $^2J_{P-C}$ = 6.4 Hz). Isomer **10b**: IR 2073 (vs), 1679 (s) cm^{-1} (ν_{CO}); 1562 (m) cm^{-1} ($\nu_{C=C}$); ^1H NMR (CD_2Cl_2) δ 1.88 (s, 3 H), 3.21 (s, 3 H, CO_2CH_3); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) $\delta(P_A)$ −25.6, $\delta(P_B)$ 8.8 (AA′BB′X, $^2J_{P_A-P_{A'}} = {}^2J_{P_B-P_{B'}}$ = 350, $^2J_{P_A-P_B}$ = 13.3, $^1J_{Rh-P_B}$ = 143.5, $J_{P_A-P_{B'}}$ = 7.3, J_{Rh-P_A} = 5.9 Hz); ^{13}C NMR (CD_2Cl_2) $\delta(CO_t)$ 164.9 (dm, $^1J_{Rh-C}$ = 42.0 Hz), $\delta(CO_{br})$ 224.1 (m).

[$RhIr(CO)Cl_2(\mu$-$H_3CO_2CC{=}CCO_2CH_3)((C_6H_5)_2PCH_2P(C_6H_5)_2)_2$] (11). A suspension of **10** in 15 mL of tetrahydrofuran was refluxed under a slow nitrogen purge for 15 h to yield a suspension of coral colored needles in a dark yellow solution. The solid was filtered off, washed with tetrahydrofuran and diethyl ether, and dried in vacuo to give an analytically pure product in 75% yield. Anal. Calcd for $C_{57}H_{50}P_4O_5Cl_2RhIr$: C, 52.46; H, 3.87; Cl, 5.43. Found: C, 52.7; H, 4.1; Cl, 5.1. IR: 2009 (vs) cm^{-1} ($\nu_{C\equiv O}$), 1562 (m) cm^{-1} ($\nu_{C=C}$). ^1H NMR (CD_2Cl_2): δ 2.24 (s, 3 H), 2.69 (s, 3 H) (CO_2CH_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): $\delta(P_A)$ −24.4, $\delta(P_B)$ 10.8 (AA′BB′X, $^2J_{P_A-P_{A'}}$, $^2J_{P_B-P_{B'}}$ = 374.2, 360.5, $^2J_{P_A-P_B}$ = 59.1, $^1J_{Rh-P_B}$ = 124.3, $J_{P_A-P_{B'}}$ = 16.6, J_{Rh-P_A} = 3.0 Hz). ^{13}C NMR (CD_2Cl_2): $\delta(CO_t)$ 152.0 (dtt, $^2J_{P-C}$ = 10, $^2J_{Rh-C}$ = 7, $^3J_{P'-C}$ = 3 Hz).

[$RhIr(CO)Cl_2(\mu$-$F_3CC{=}CCF_3)((C_6H_5)_2PCH_2P(C_6H_5)_2)_2$]·$1.5CHCl_3$ (12). A suspension of [$RhIr(CO)_2(\mu$-$CO)Cl(DPM)_2$]Cl (0.20 g, 0.164 mmol) was prepared in CO-saturated dichloromethane–tetrahydrofuran (3:1, v/v, 40 mL) in a serum-capped flask. The flask was partially evacuated and successively pressured to ca. 1 atm with carbon monoxide and hexafluorobut-2-yne. The mixture was stirred for 0.5 h by which time a cloudy orange solution had formed. This was filtered through a pad of diatomaceous earth and the filtrate diluted with diethyl ether to yield a yellow powder. The solid was collected by filtration and suspended in 35 mL of tetrahydrofuran and the mixture refluxed under a slow nitrogen purge for 5 h. The resulting cloudy, burgundy solution was filtered while hot through a pad of diatomaceous earth and its volume reduced to ca. 10 mL under reduced pressure. Dilution with hexane afforded a purplish red solid which was collected and recrystallized from chloroform–diethyl ether to give the product as purplish pink flakes in 62% yield. Anal. Calcd for $C_{56.25}H_{45.25}P_4F_6OCl_{5.75}RhIr$: C, 45.83; H, 3.10; Cl, 13.83. Found: C, 45.8; H, 3.2; Cl, 13.4. IR: 2009 (vs) cm^{-1} ($\nu_{C\equiv O}$); 1587 (m) cm^{-1} ($\nu_{C=C}$). $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta(P_A)$ −28.1 (m), $\delta(P_B)$ 7.9 (m, $^1J_{Rh-P_B}$ = 120 Hz).

[$RhIr(CO)_2(\mu$-$CO)Cl(\mu$-$H_3CO_2CC{=}CCO_2CH_3)((C_6H_5)_2PCH_2P(C_6H_5)_2)_2$]$ClO_4$·$0.5CH_2Cl_2$ (13). To a suspension of **10** (0.462 g, 0.347 mmol) in 20 mL of dichloromethane was added $AgClO_4$ (0.073 g, 0.347 mmol), and the mixture was stirred for 2 h while a slow stream of carbon monoxide was bubbled through it. The resulting cloudy pale yellow solution was filtered through a pad of diatomaceous earth under pressure of carbon monoxide, and the filtrate was diluted with diethyl ether and hexane to afford the product as yellow microcrystals. These were filtered off, washed with diethyl ether, and dried in a stream of carbon monoxide (yield 80%). Anal. Calcd for $C_{59.5}H_{51}P_4O_{11}Cl_3RhIr$: C, 48.70; H, 3.51; Cl, 7.25. Found: C, 48.0; H, 4.1; Cl, 7.4. IR: 2098 (vs), 2042 (vs), 1747 (s) cm^{-1} (ν_{CO}); 1575 (m) cm^{-1} ($\nu_{C=C}$). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −53 °C): $\delta(P_A)$ −28.0, $\delta(P_B)$ 17.1 (AA′BB′X, $^2J_{P_A-P_{A'}}$, $^2J_{P_B-P_{B'}}$ = 373.5, 358.7, $^2J_{P_A-P_B}$ = 19.2, $^1J_{Rh-P_B}$ = 138.2, $J_{P_A-P_{B'}}$ = 1.1, J_{Rh-P_A} = 5.1 Hz). ^{13}C NMR (CD_2Cl_2, −53 °C): $\delta(CO_{br})$ 204.7 (m), $\delta(CO_t)$ 189.2 (dt, $^1J_{Rh-C}$ = 54.0, $^2J_{P-C}$ = 10.2 Hz), 158.9 (dt, $^1J_{Rh-C}$ = 48.0, $^2J_{P-C}$ = 6.3 Hz).

[$RhIr(CO)_2Cl(\mu$-$H_3CO_2CC{=}CCO_2CH_3)((C_6H_5)_2PCH_2P(C_6H_5)_2)_2$]$ClO_4$·$0.5CH_2Cl_2$ (14). Complex **13** was dissolved in 15 mL of dichloromethane to give a purplish brown solution. Purging with a stream of nitrogen for 1 h caused the color of the solution to change to dark red. Dilution with diethyl ether afforded the product as red-violet crystals in 85% yield. Anal. Calcd for $C_{58.5}H_{51}P_4O_{10}Cl_3RhIr$: C, 48.81; H, 3.58; Cl, 7.39. Found: C, 48.4; H, 4.0; Cl, 7.9. IR: 2092 (s), 2051 (vs) cm^{-1} ($\nu_{C\equiv O}$) 1580 (m) cm^{-1} ($\nu_{C=C}$). ^1H NMR (CD_2Cl_2): δ 2.93 (s, 3 H), 2.49 (s, 3 H, CO_2CH_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): $\delta(P_A)$ −23.5, $\delta(P_B)$ 10.0 (AA′BB′X; $^2J_{P_A-P_{A'}} = {}^2J_{P_B-P_{B'}}$ = 350, $^2J_{P_A-P_B}$ = 37.9, $^1J_{Rh-P_B}$ = 111.2, $J_{P_A-P_{B'}}$ = 29.9, J_{Rh-P_A} = 2.4 Hz). ^{13}C NMR (CD_2Cl_2): $\delta(CO_t)$ 172.8 (t) ($^2J_{P-C}$ = 5.4 Hz), 145.6 (m).

[$RhIr(CO)(\mu$-$CO)Cl_2(\mu$-$F_3CC{=}CCF_3)((C_6H_5)_2PCH_2P(C_6H_5)_2)_2$]·$3CHCl_3$ (16). A chloroform solution of **12** was purged with carbon monoxide whereupon the color of the solution rapidly changed from burgundy to bright yellow. On standing the product soon precipitated as bright yellow crystals in quantitative yield. These were collected, washed with diethyl ether, and dried in vacuo. Anal. Calcd for $C_{59}H_{47}P_4F_6O_2Cl_{11}RhIr$: C, 41.41; H, 2.83; Cl, 22.79. Found: C, 41.6; H, 3.0; Cl, 23.0.

[$Ir(CO)Cl((C_6H_5)_2P(C_5H_4N))_2$] (17). A solution of 0.200 g (0.512 mmol) of [$Ir(CO)_2Cl(p$-toluidine)] in 5 mL of tetrahydrofuran was added to one of 0.271 g (1.023 mmol) of 2-pyridyldiphenylphosphine in 10 mL of tetrahydrofuran. The resulting brownish yellow solution was stirred briefly under reduced pressure and diluted with diethyl ether to afford yellow crystals of the product in 75% yield. Anal. Calcd for $C_{35}H_{28}P_2N_2OClIr$: C, 53.74; H, 3.62. Found: C, 53.1; H, 3.7. IR: 1957 (vs) cm^{-1} ($\nu_{C\equiv O}$). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 23.3 (s).

Results and Discussion

Reaction of [$Rh_2Cl_2(\mu$-$CO)(Ph_2Ppy)_2$] with the electrophilic acetylenes DMAD, HFB, and methyl propiolate readily forms dark brownish purple or red-violet complexes analyzing as [$Rh_2Cl_2(DMAD)(Ph_2Ppy)_2$] (**1**), [$Rh_2Cl_2(HFB)(Ph_2Ppy)_2$]·$C_6H_6$ (**2**), and [$Rh_2Cl_2(HC_2CO_2CH_3)(Ph_2Ppy)_2$] (**3**). From their ^{31}P NMR spectra which are symmetric, have virtually the same appearance at 24.15 and 81.02 MHz, and closely resemble that of [$Rh_2Cl_2(\mu$-$CO)(Ph_2Ppy)_2$][13] and from the proton NMR spectrum of **1**, both **1** and **2** are symmetrical molecules. The infrared absorptions at 1638 and 1670 cm^{-1} in **1** and **2**, respectively, are observed at identical energies in samples of **1** and **2** prepared from [$Rh_2Cl_2(\mu$-$^{13}CO)(Ph_2Ppy)_2$][22] confirming that these are not due to "ketonic" bridging carbonyl ligands. Despite the fact that these bands appear at noticeably higher energies than many of those previously attributed to $\nu_{C=C}$ of these acetylenes when bound as dimetalated olefins[1,4] we feel that this is the only reasonable

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[22] This was prepared by stirring [$RhCl(COD)$]$_2$ under an atmosphere of ^{13}CO in dichloromethane to give [$RhCl(^{13}CO)_2$]$_2$ followed by slow addition of this solution to one containing the ligand. The ^{13}C NMR spectrum (CD_2Cl_2 solution) in the carbonyl region consisted of a triplet of triplets centered at 228.6 ppm ($^1J_{Rh-C}$ = 45.6; $^2J_{P-C}$ = 9.8 Hz).

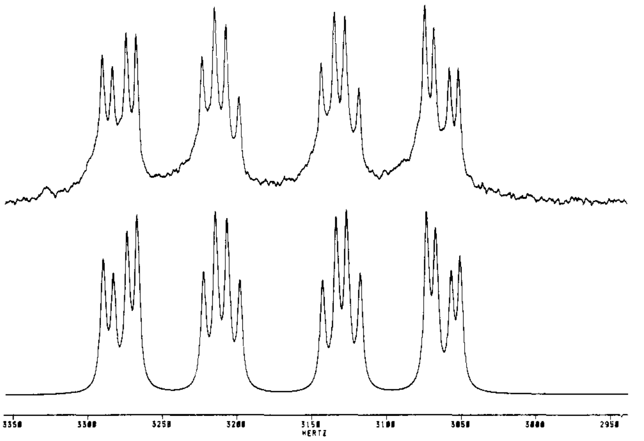
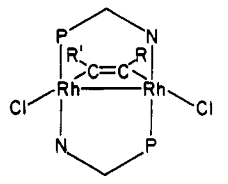


Figure 1. Observed (top) and calculated (bottom) 81.02-MHz, $^{31}P\{^1H\}$ NMR spectrum of $[Rh_2Cl_2(\mu\text{-}HC{=}CCO_2Me)(Ph_2Ppy)_2]$ (3).

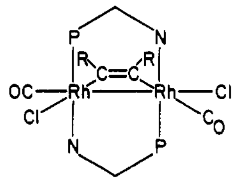
assignment and note that $\nu_{C=C}$ has been observed at 1638 and 1653 cm^{-1} in $[Rh_2Cl_2(\mu\text{-}HFB)(DPM)_2]$[5a] and in $[Cp_2Rh_2(CO)_2(\mu\text{-}HFB)]$,[23] respectively. The infrared spectrum of 3 shows a band attributable to $\nu_{C=C}$ while the proton NMR spectrum contains a resonance in the vinylic region indicating that 3 also contains a dimetalated olefin. As this moiety is unsymmetrical, the two phosphorus atoms should occur at slightly different chemical shifts and this is seen in the 81.02-MHz ^{31}P NMR spectrum which is quite different from those of 1 and 2 and has been satisfactorily simulated as the AB portion of an ABXY spin system (Figure 1). The data thus indicate that 1–3 have a structure analogous to that found for $[Rh_2Cl_2(\mu\text{-}HFB)(DPM)_2]$.[5a]



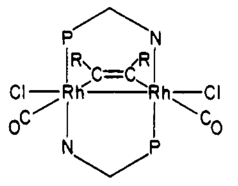
1, $R = R' = CO_2Me$
2, $R = R' = CF_3$
3, $R = H$; $R' = CO_2Me$

The behavior of $[Rh_2Cl_2(\mu\text{-}CO)(Ph_2Ppy)_2]$ toward electrophilic acetylenes contrasts with that observed for $[Rh_2Cl_2(\mu\text{-}CO)(DPM)_2]$[5a] in that the products no longer contain carbonyl ligands. Also, while 1 and 2 add carbon monoxide, these adducts are quite labile and contain only terminal carbonyl ligands (vide infra) while $[Rh_2Cl_2(\mu\text{-}HFB)(DPM)_2]$ forms the stable adduct $[Rh_2Cl_2(\mu\text{-}CO)(\mu\text{-}HFB)(DPM)_2]$.[5a,b] In this and the closely related complexes $[Rh_2Cl_2(\mu\text{-}CO)(\mu\text{-}DMAD)(DPM)_2]$[5b] and $[Rh_2(CO)(O_2CMe)(\mu\text{-}CO)(\mu\text{-}DMAD)(DPM)_2]PF_6$[1] the bridging carbonyl has been characterized as "ketonic" (formally CO^{2-}).[24] In the theoretical treatment of these species the presence of the bridging carbonyl obviates the necessity for a metal–metal bond,[24] and indeed the metal–metal separations (ca. 3.35 Å) clearly indicate its absence. By analogy with these DPM systems it is likely that were 1–3 to retain a bridging carbonyl, it would also be "ketonic" and no metal–metal bonding should be present. The ready loss of the carbonyl ligand from $[Rh_2Cl_2(\mu\text{-}CO)(Ph_2Ppy)_2]$ on formation of 1–3 suggests that this is not favored presumably because the smaller bite and decreased flexibility of 2-pyridyldiphenylphosphine as compared to DPM prevent the metals from attaining a nonbonding separation. Instead, with retention of the metal–metal bond favored, attack of the acetylene on $[Rh_2Cl_2(\mu\text{-}CO)(Ph_2Ppy)_2]$ may result in movement of the carbonyl ligand to a terminal position from which it can be readily lost.

Carbonylation of dichloromethane solutions of 1 and 2 leads to the formation of yellow-orange, crystalline solids analyzing as $[Rh_2Cl_2(CO)_2(DMAD)(Ph_2Ppy)_2]$ (4) and $[Rh_2Cl_2(CO)_2(\mu\text{-}HFB)(Ph_2Ppy)_2]$ (5), respectively, which are stable in a carbon monoxide atmosphere. Slow reversion to 1 and 2 occurs in the absence of carbon monoxide. The spectroscopic data indicate retention of the dimetalated olefin and the presence of only terminal carbonyl ligands. In 4, the chemical shift and coupling constants associated with the downfield ^{13}C NMR resonance are comparable to those for the terminal carbonyl ligand in $[Rh_2(CO)(O_2CMe)(\mu\text{-}CO)(\mu\text{-}DMAD)(DPM)_2]PF_6$,[1] suggesting a similar disposition of this ligand. The successful simulation of the 81.02-MHz ^{31}P NMR spectrum as the AB portion of an ABXY spin system indicates the two ends of the molecule are not identical, and therefore the most reasonable disposition of the second carbonyl ligand is approximately collinear with the metal–metal axis. This is also consistent with the larger number of couplings evident in the ^{13}C NMR resonance for this ligand since, as it is likely that the metal–metal bond is retained, this carbonyl could also be coupled to the second rhodium atom and/or the remote phosphorus atom as appears to occur with 11 (vide infra). The spectroscopic data for 5 are similar to those for 4, indicating it has the same structure. The NMR spectra of 4 and 5 also contain resonances consistent with the presence of a small quantity of a symmetrical isomer (**4b** and **5b**) with both carbonyl ligands trans to the dimetalated olefin.[25] Electronically 4 and 5 are analogous to $[Ir_2(CO)_2Cl_2(\mu\text{-}DMAD)_2(DPM)_2]$,[4,6a] which has been found to have the structure assigned to isomer **a**[6a] and to contain a metal–metal bond. It is thus reasonable that 4 and 5 should also contain a metal–metal bond.



4a, $R = CO_2Me$
5a, $R = CF_3$



4b, $R = CO_2Me$
5b, $R = CF_3$

Abstraction of one chloride ligand from $[Rh_2Cl_2(\mu\text{-}CO)(Ph_2Ppy)_2]$ by silver perchlorate occurs readily to yield a red, crystalline product analyzing as $[Rh_2Cl(CO)(Ph_2Ppy)]ClO_4$ (6). The infrared spectrum shows that the bridging carbonyl ligand is retained, and the shift to higher energy is consistent with formulation of 6 as a cationic species. This is also suggested by the lack of significant splitting in the ν_3 band of the perchlorate ion (~1100 cm^{-1}) which indicates that this ion is not strongly coordinated.[26] Unfortunately the low solubility prevented a reliable measurement of the solution conductance to confirm this point. The ^{31}P NMR spectrum shows a weak, asymmetric doublet centered at 41.6 ppm which is invariant down to −60 °C. The peak separation is ca. 135 Hz which is com-

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[23] Dickson, R. S.; Kirsch, H. P. *Aust. J. Chem.* **1972**, *25*, 2535.

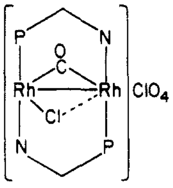
[24] (a) Hoffman, D. M.; Hoffmann, R. *Inorg. Chem.* **1981**, *20*, 3543. (b) Hoffman, D. M.; Hoffmann, R.; Fisel, C. R. *J. Am. Chem. Soc.* **1982**, *104*, 3858.

[25] For 4 these additional resonances are δ(CO) 190 (dm) and δ(P) 27.2 (br d, $J = 125.6$ Hz).

[26] Nakamoto, K. "Infrared and Raman Spectra of Inorganic and Coordination Compounds", 3rd ed., Wiley: New York, 1978; p 242.

parable to that found for $[Rh_2Cl_2(\mu\text{-}CO)(Ph_2Ppy)_2]$,[13] and the asymmetry suggests that the two sides of the molecule are not equivalent. One structure consistent with the data is that shown in which the remaining chloride ligand asymmetrically bridges the two metals. An alternative which cannot be excluded, despite the indication of the infrared spectrum, is one analogous to $[Rh_2Cl_2(\mu\text{-}CO)(Ph_2Ppy)_2]$ with a weakly coordinated perchlorate ion in place of one chloride.

Complex **6** readily adds carbon monoxide to form an orange, crystalline product analyzing as $[Rh_2(CO)_2Cl(Ph_2Ppy)_2]ClO_4{\cdot}Me_2CO$ (**7**). The ^{13}C and ^{31}P NMR spectra are invariant with temperature and indicate a symmetrical species. The chemical shifts and coupling constants in the former spectrum compare favorably with those in $[Rh_2(CO)_2(\mu\text{-}Cl)(DPM)_2]BPh_4$[27] and with the remaining spectroscopic data indicate that **7** is an "A-frame" complex. Addition of carbon monoxide to a solution of **7** results in rapid exchange of free and bound carbon monoxide as indicated by the loss of all rhodium- and phosphorus-carbon couplings. A gradual broadening of the singlet carbonyl resonance occurs on cooling to −50 °C, and further cooling to the limit of the deuterodichloromethane solvent (ca. −80 °C) caused the resonance to broaden significantly, but no rhodium-carbon coupling was evident. Thus the CO exchange is still rapid at this temperature, a situation analogous to that found for $[Rh_2(CO)_2(\mu\text{-}O_2CMe)(DAM)_2]PF_6$.[1] It is probable that the exchange process involves the formation of $[Rh_2(CO)_2(\mu\text{-}CO)(\mu\text{-}Cl)(Ph_2Ppy)_2]ClO_4$ as an intermediate as occurs for the DPM and DAM analogues, but this is evidently too unstable to be isolated.



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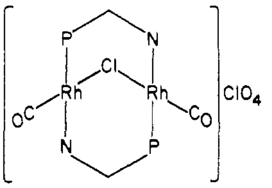
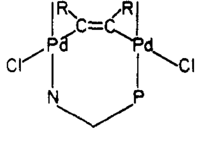


7

It has been stated that $[Pd_2Cl_2(Ph_2Ppy)_2]$ does not show the reactivity of the Pd–Pd bond exhibited by $[Pd_2Cl_2(DPM)_2]$.[14] We have not explored this in detail but do find that $[Pd_2Cl_2(Ph_2Ppy)_2]$ readily reacts with DMAD to form a dark orange, crystalline product which analyzes as $[Pd_2Cl_2(DMAD)(Ph_2Ppy)_2]$ (**8**) and in which the DMAD also appears to be bound as a dimetalated olefin.



8, R = CO_2Me

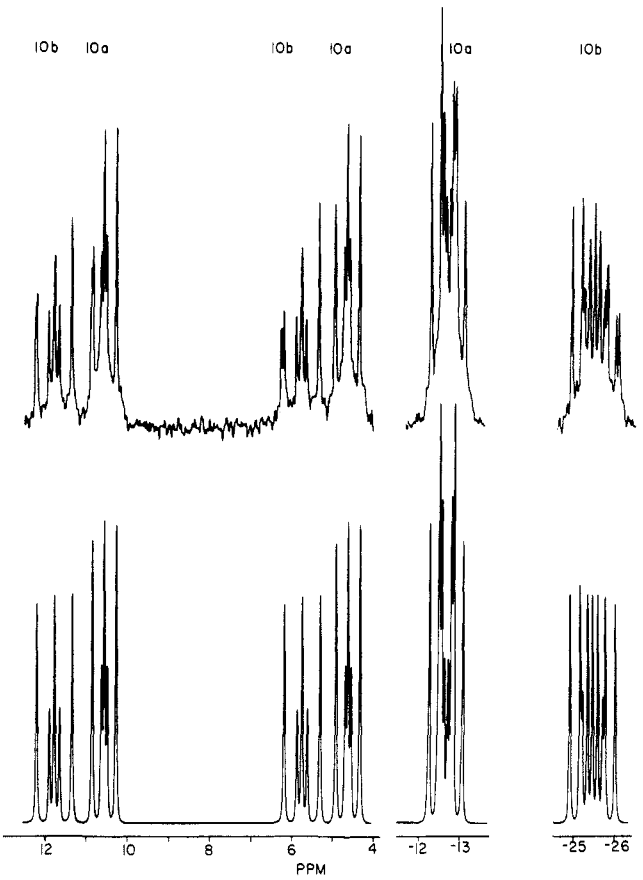
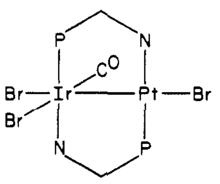


Figure 2. Observed (top) and calculated (bottom) 24.15-MHz, $^{31}P\{^1H\}$ NMR spectrum of a mixture of isomers **a** and **b** of $[IrRhCl_2(CO)(\mu\text{-}CO)(\mu\text{-}DMAD)(DPM)_2]$ (**10a** and **10b**).

The orange-yellow product **9** from the reaction of $[PtBr_2(Ph_2Ppy)_2]$ with $Bu_4N[IrBr_2(CO)_2]$ analyzes as $[PtIr(CO)Br_3(Ph_2Ppy)_2]$. The ^{31}P NMR spectrum consists of two doublet resonances each flanked by pairs of satellites, also doublets, due to ^{195}Pt ($I = {}^1/_2$, 33.4% natural abundance), indicating a head-to-tail arrangement of the 2-pyridyldiphenylphosphine ligands. The coupling constants obtained agree well with those for $[PtRh(CO)X_3(Ph_2Ppy)_2]$ (X = Cl, Br)[16] and with the remaining spectroscopic data suggest an analogous structure for **9**.



9

The heterobimetallic complex $[IrRh(CO)_2(\mu\text{-}CO)(\mu\text{-}Cl)(DPM)_2]Cl$[15] as a suspension in dichloromethane under carbon monoxide readily reacts with DMAD to form an adduct which analyzes as the hemisolvate $[IrRh(CO)_2Cl_2(DMAD)(DPM)_2]{\cdot}0.5CH_2Cl_2$ (**10**) when isolated as described in the Experimental Section. The spectroscopic data indicate that the DMAD is bound as a dimetalated olefin and that **10** is formed as a mixture of two isomers. The successful simulation of the 24.15-MHz ^{31}P NMR spectra as AA′BB′X (A, B = P; X = Rh) spin systems (Figure 2) indicates that the $\{Ir(\mu\text{-}DPM)_2Rh\}$ core is retained in both. By contrast, reaction of DMAD with $[IrRh(CO)_2(\mu\text{-}Cl)(DPM)_2]Cl$[15] under nitrogen produces a single isomer of **10**, hereafter designated as isomer **a**, thereby permitting the identification of the spectroscopic parameters associated with each isomer. A sample of **10a**

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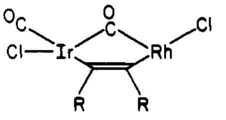
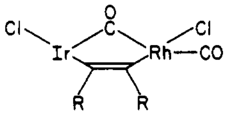
[27] IR: **10a**, $\nu(^{12}CO)$ 2050 (m), 1647 (m) cm^{-1}, $\nu(^{13}CO)$ 2000 (s), 1608 (s) cm^{-1}; **10b**, $\nu(^{12}CO)$ 2073 (m), 1679 (m) cm^{-1}; $\nu(^{13}CO)$ 2024 (s), 1641 (s) cm^{-1}.

ca. 75% enriched in ^{13}CO was prepared analogously from labeled precursors[27] for a determination of the ^{13}C NMR spectrum. This clearly shows that the terminal carbonyl ligand is bound to iridium, and the lack of observable coupling with the bridging carbonyl ligand suggests that these ligands are approximately cis to one another. A similar situation obtains in the closely related complexes $[Rh_2(CO)(O_2CMe)(\mu\text{-}CO)(\mu\text{-}DMAD)(L_2)_2]PF_6$ (L_2 = DPM, DAM)[1] where the terminal and bridging carbonyl ligands are approximately cis and no coupling between them could be observed. This contrasts with what is observed in $[Rh_2(CO)_2(\mu\text{-}CO)(\mu\text{-}Cl)(DPM)_2]BPh_4$,[28] in which the terminal carbonyls are cis to the bridging carbonyl and in $[Ir_2(CO)_2(\mu\text{-}CO)(\mu\text{-}Cl)(DPM)_2]BPh_4$,[29] which presumably has the same structure, where $^2J_{C_t-C_b}$ is 13.7 and 12.2 Hz, respectively. While this indicates that $^2J_{C_t-C_b}$ is insensitive to changes in the metal from rhodium to iridium, both these complexes contain formally univalent metals while **10a** and $[Rh_2(CO)(O_2CMe)(\mu\text{-}CO)(\mu\text{-}DMAD)(L_2)_2]PF_6$ all contain formally trivalent metals. It thus appears that $^2J_{C_t-C_b}$ between cis carbonyl ligands is diminished below the limit of detectability when the formal oxidation state of the metal is raised from I to III. The data are thus in accord with **10a** having the structure shown (DPM ligands in **10**–**15** omitted for clarity).



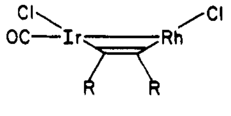
10a, R = CO_2Me

Decarbonylation of the labeled sample of **10a** in refluxing tetrahydrofuran afforded a substantially enriched sample of **11** (vide infra) which was recarbonylated by using 98% ^{13}CO directly in the NMR tube. The ^{31}P NMR spectrum again showed the presence of **10a** and **10b** with the latter now predominating.[27] It might be noted that despite the presence of excess carbon monoxide, no evidence for rapid exchange of free and bound carbon monoxide or any other sort of fluxional process was apparent in either the ^{31}P or ^{13}C NMR spectra. In the ^{13}C NMR spectrum resonances attributable to **10a** were evident, and, in addition, two more intense signals attributable to terminal and bridging carbonyl ligands in **10b** were seen which are dramatically different in appearance from those for **10a**. The former appears as a doublet of septets which is only consistent with this ligand being bound to rhodium. The value of $^1J_{Rh-C_t}$ is only slightly smaller than that found for the terminal carbonyl ligand in $[Rh_2(CO)(O_2CMe)(\mu\text{-}CO)(\mu\text{-}DMAD)(DPM)_2]PF_6$,[1] and the upfield shift of this resonance compared with that for the dirhodium complex is consistent with the attached rhodium being neutral rather than cationic. The seven-line pattern in each each half of this resonance can be reasonably well simulated by assuming it to be a superimposition of a triplet arising from the isotopomer with ^{12}CO in the bridging site ($^2J_{P-C_t}$ = 6.0 Hz), and a four-line pattern (overlapping triplet of doublets) arising from the isotopomer with ^{13}CO in the bridging site ($^2J_{P-C_t}$ = 6.0, $^2J_{C_t-C_{br}}$ = 5.6 Hz). The bridging carbonyl resonance consists of a large number of closely spaced lines with no obvious splitting pattern, and attempts to simulate it have been unsuccessful. However, as it is evident from the infrared spectrum that ^{13}CO incorporation in the terminal position is incomplete, this resonance will also be a superimposition of two multiplet patterns. Adding to the complexity of this resonance is the possibility that the bridging carbonyl may be coupled to a different extent to the two sets of phosphorus atoms as was found in $[Rh_2(CO)(O_2CMe)(\mu\text{-}CO)(\mu\text{-}DMAD)(DPM)_2]PF_6$.[1] Despite the uncertainty in the details of the couplings associated with the bridging carbonyl, it is clear that **10b** has the terminal carbonyl attached to rhodium rather than to iridium, and with an observable value for $^2J_{C_b-C_t}$ it is likely that the terminal carbonyl is trans to the bridging carbonyl.



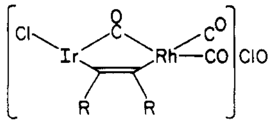
10b, R = CO_2Me

As mentioned earlier, either **10a** or a mixture of **10a** and **10b**, when refluxed in tetrahydrofuran, converts to a coral colored complex which analyzes as $[IrRh(CO)Cl_2(DMAD)(DPM)_2]$ (**11**). The infrared spectrum indicates that the dimetalated olefin moiety is retained and that a single terminal carbonyl ligand is present. The ^{31}P NMR spectrum is similar to those of **10a** and **10b** and has been similarly analyzed. The single carbonyl resonance in the ^{13}C NMR spectrum is clearly different from that observed for the terminal carbonyl ligand in **10a**, and while it must be due to a terminal carbonyl ligand attached to iridium,[30] it indicates a different environment for this ligand. A hexafluorobut-2-yne analogue (**12**) was also prepared and shows similar infrared and ^{31}P NMR spectra, indicating that **11** and **12** have the same structure. The fact that $\nu_{C\equiv O}$ is identical in both suggests that the carbonyl ligand is approximately collinear with the metal–metal axis. In the absence of a bridging carbonyl, a significant metal–metal interaction is required to produce the observed diamagnetism. Such an interaction would also be consistent with the observation that the carbonyl ligand appears to be coupled to the rhodium. Thus **11** and **12** are best considered to be analogues of $[Rh_2Cl_2(\mu\text{-}RC{=}CR)(DPM)_2]$[5a] (R = CO_2Me, CF_3) and to have a related structure.



11, R = CO_2Me
12, R = CF_3

The ionic complex $[IrRh(CO)_3Cl(DMAD)(DPM)_2]ClO_4{\cdot}0.5CH_2Cl_2$ (**13**) is readily prepared from **10** and silver perchlorate in the presence of carbon monoxide. The spectroscopic data indicate the maintenance of the $\{IrRh(\mu\text{-}DMAD)(\mu\text{-}DPM)_2\}$ core and the presence of one bridging and two terminal carbonyl ligands. The ^{13}C NMR spectrum of an enriched sample indicates that both terminal carbonyl ligands are bound to rhodium with the lower field resonance attributable to one approximately cis to the bridging carbonyl since its chemical shift and coupling constants compare favorably with those for the terminal carbonyl ligand in $[Rh_2(CO)(O_2CMe)(\mu\text{-}CO)(\mu\text{-}DMAD)(DPM)_2]PF_6$.[1] The data are therefore in accord



13, R = CO_2Me

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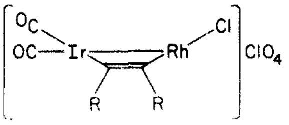
[28] Mague, J. T.; Sanger, A. R. *Inorg. Chem.* **1979**, *18*, 2060.

[29] Mague, J. T.; DeVries, S. H. *Inorg. Chem.* **1980**, *19*, 3743.

[30] This resonance is a poorly resolved quartet with a maximum line separation of 10 Hz. An approximate simulation as an overlapping triplet of doublet of triplets indicated coupling to the two adjacent phosphorus atoms, the rhodium atom, and the two remote phosphorus atoms.

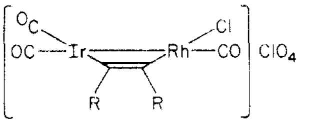
with the formulation $[IrRh(CO)_2Cl(\mu\text{-}CO)(\mu\text{-}DMAD)(DPM)_2]ClO_4$.

Red-violet crystals analyzing as $[IrRh(CO)_2Cl(DMAD)(DPM)_2]ClO_4{\cdot}0.5CH_2Cl_2$ (**14**) are obtained from solutions of **13** on purging with dinitrogen. The infrared and ^{31}P NMR spectra of **14** are quite similar to those of **13** except that no bridging carbonyl absorption is present. The ^{13}C NMR spectrum of an enriched sample of **14** shows, however, that *both carbonyl ligands are now attached to iridium.* The 145.6 ppm resonance is very similar to that observed for **11**, and the apparent long-range coupling to rhodium, together with the absence of a bridging carbonyl, suggests the existence of significant metal–metal interaction.

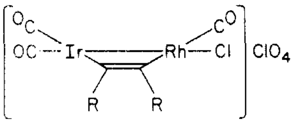


14, R = CO_2Me

Complex **14** can be reconverted to **13** on treatment with carbon monoxide in dichloromethane solution at room temperature. Some insight into the mechanism of this conversion is obtained by carrying out the reaction at low temperature. Thus when ^{13}CO is added to an enriched sample of **14** at −78 °C in an NMR tube and the sample placed directly into the precooled probe (−58 °C), the ^{13}C NMR spectrum shows the presence of a new species (**15**) with three signals at 176.1, 175.5, and 156.0 ppm, indicating that *only terminal carbonyl ligands are present.* On standing overnight at room temperature, the ^{13}C and ^{31}P NMR spectra show that only traces of **15** remain and the major species now present is **13**. The two higher field ^{13}C resonances for **15** are similar in appearance to those for **14** and do not differ greatly from them in chemical shift, suggesting that **15** still retains two terminal carbonyl ligands bound to iridium. The resonance at 176.1 ppm is partially obscured by the one at 175.5 ppm but appears to be a doublet of triplets with coupling constants of ca. 54 and 10 Hz. This is consistent with a terminal carbonyl ligand bound to rhodium. The ^{31}P NMR spectrum of **15** at 81.02 MHz is quite similar to those of **13** and **14** at this frequency,[31] indicating that the major structural features of **15** are the same as in the other two complexes. Two structures, **15a** and **15b**, are consistent with the spectroscopic data, and we are inclined to prefer **15a**. It is the one which would be the more obvious result of carbon monoxide addition to **14** since it is likely that in **14** the chloride is approximately trans to the carbon atom of the dimetalated olefin. Also, the ^{13}C resonance for the carbonyl ligand on rhodium shows some indication of fine structure which could be due to coupling with either the remote phosphorus atoms or with the carbonyl ligand on iridium which is along the metal–metal axis. Finally this is also the structure determined for the stable isomer of the closely related complex $[Ir_2(CO)_3Cl(\mu\text{-}DMAD)(DPM)_2]PF_6$.[4]



15a, R = CO_2Me



15b, R = CO_2Me

Pertinent to the discussion of the interconversions of **13** and **14** is the observation (^{13}C and ^{31}P NMR) that **13**, presumably as its chloride salt,[32] is the major species formed initially at low temperature (≤−58 °C) when **11** is treated with ^{13}CO. On warming to room temperature, **10a** and **10b** rapidly form with the latter predominating, and on standing in solution the proportion of **10a** increases at the expense of **10b**. These results suggest that the chloride ligand on rhodium is relatively labile, but the fact that **10a** and **10b** are readily formed from **13** when free chloride is present indicates that the interconversions of **13** and **14** probably do not involve complete removal of their chloride ligand since no evidence of **10a** and **10b** is seen in these systems. The carbonylation of **14** to **13** could easily occur by addition of CO to rhodium with an intramolecular transfer of the chloride to iridium. Loss of a carbonyl ligand from iridium and further addition of CO at rhodium would complete the process. An intramolecular chloride transfer via a chloro-bridged intermediate has been proposed for the fluxional behavior of $[Ir_2(CO)_2Cl(\mu\text{-}DMAD)(DPM)_2]A$ (A = PF_6, ClO_4)[4] while ready interconversions of bridging and terminal carbonyl ligands occur in $[Rh_2(CO)_2(\mu\text{-}Cl)(DPM)_2]BPh_4$[27] in the presence of carbon monoxide. However, the stable isomer of $[Ir_2(CO)_3Cl(\mu\text{-}DMAD)(DPM)_2]A$ (A = PF_6, ClO_4), which has the same structure as proposed for **15**, does not exchange with free carbon monoxide and is not fluxional at room temperature, indicating that loss of a carbonyl ligand from the positively charged metal or its displacement by the chloride ligand in the formation of a chloride-bridged intermediate is not a facile process there. Indeed elevated temperatures are required to decarbonylate the diiridium complex.[4] It may be, however, that replacement of iridium on the other side of the molecule by rhodium increases the lability of the carbonyl groups on the positively charged iridium, and, in fact, the room-temperature ^{13}C NMR spectrum of the solution of **13** prepared by the carbonylation of **14** suggests that the 156.0 ppm resonance of the residual **15** is broadened. As this is the resonance assigned to the carbonyl trans to rhodium, it appears that this ligand is undergoing exchange.

A more difficult process to rationalize is the conversion of **13** and **14** which occurs with reasonable facility on flushing a solution of the former with nitrogen. As noted earlier, this occurs within about 1 h. If the nitrogen purge is stopped after about 20 min, the ^{31}P and ^{13}C NMR spectra (−58 °C) of the solution show only **13** and **14** in approximately equal amounts. The first step appears to be loss of the carbonyl ligand which is attached to rhodium and is cis to the bridging carbonyl since the ^{13}C NMR spectrum of **13** in the presence of ^{13}CO at room temperature shows that the resonance assigned to this ligand is extensively broadened, indicating that it is undergoing exchange with free carbon monoxide. The other two ^{13}C resonances are not markedly different than at low temperature. From this point, since **14** is a dicarbonyl, no more carbonyl ligands can be displaced or they would get flushed from the solution. Also, the absence of any **10a** or **10b**

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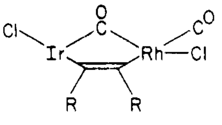
(31) The 81.02-MHz ^{31}P NMR spectrum of **15** consists of a double triplet of doublets at 1.1 ppm and an approximate triplet at −25.8 ppm while that of **14** consists of a doublet of triplets at low field and a triplet at high field. Although both appear to be first order, the 24.15-MHz spectrum of the latter has been simulated as an AA′BB′X spin system, and with the parameters obtained from this analysis, it is evident that the "triplet" splitting observed at 81.02 MHz does not correspond to $^2J_{P_A-P_B}$ but rather is a combination of this with one of the minor couplings. Thus the spectrum of **15** should also be properly considered as an AA′BB′X pattern, and the only coupling constant which can be obtained directly is $^1J_{Rh-P}$ (94 Hz).

(32) Further evidence for the displacement of chloride in this initial step is the observation that on carbonylation of a dichloromethane solution of **11** at room temperature a momentary increase in the conductance occurs.

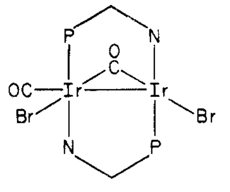
argues that complete dissociation of chloride or intermolecular chloride transfer in unlikely. A possible route might be the migration of one carbonyl group from rhodium to iridium to put the chloride trans to the metal–metal bond, followed by dissociation of chloride to form a tight ion pair. Migration of the second carbonyl to iridium in like fashion followed by coordination of the chloride to rhodium would then complete the process. Support for this proposal comes from our earlier observation that in dichloromethane solution the isomer of $[Ir_2(CO)_3Cl(\mu\text{-DMAD})(DPM)_2]BPh_4$ with the chloride trans to the metal–metal bond slowly converts to the isomer having the chloride trans to the carbon atom of the dimetalated olefin.[4]

Reaction of HFB with a dichloromethane solution containing predominantly $[IrRh(CO)_2(\mu\text{-Cl})(DPM)_2]Cl$ yields a rather insoluble yellow powder whose infrared spectrum shows carbonyl absorptions at 2084, 1693, 2074, and 1655 cm^{-1} and a band attributable to $\nu_{C{=}C}$ at 1560 cm^{-1}. The analytical data for this material were unsatisfactory, and the low solubility prevented adequate purification. The infrared spectrum suggests that analogues of **10a** and **10b** ($R = CF_3$) were formed, and this is supported by the ready conversion of this material to **12**. The reported ^{31}P NMR spectrum was obtained by using a dichloromethane extract of the crude material, and on the basis of a comparison of the infrared spectra of the insoluble residue and the original solid, it appears the ^{31}P NMR spectrum is that of the HFB analogue of **10a**. Carbonylation of a chloroform solution of **12** readily affords yellow crystals analyzing as $[IrRh(CO)_2Cl_2(HFB)(DPM)_2]\cdot 3CHCl_3$ (**16**). The presence of chloroform was confirmed by the presence of a strong band at 758 cm^{-1} (ν_5). Complex **16** was also quite insoluble in most solvents, and a saturated solution in dichloromethane showed a poor quality ^{31}P NMR spectrum which appeared to be the same as that just described. The infrared spectrum in the carbonyl region was noticeably different however. The band at 1655 cm^{-1} was now very weak, suggesting that very little of the isomer of **16** corresponding to **10a** is present. Considering that **16** precipitates rather rapidly, this is consistent with the results of the carbonylation of **11** which indicate that the major initial product at room temperature is **10b**. The remainder of the carbonyl absorptions appear at 2102 (s), 2084 (m), 2074 (m), and 1690 (s) cm^{-1}. Of particular note is the strong band at 2102 cm^{-1} which is absent from the spectrum of the product obtained directly from $[IrRh(CO)_2(\mu\text{-Cl})(DPM)_2]Cl$. Comparison of the spectrum of this product with that for **16** suggests that a third species is present, in addition to HFB analogue of **10a** and **10b**, which has ν_{CO} at 2102, 1690, and possibly 2074 cm^{-1}. We suggest that this may be the isomer **16c**.

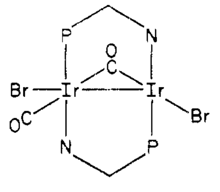


16c, $R = CF_3$

Several attempts to prepare binuclear diiridium and iridium–rhodium complexes bridged by 2-pyridyldiphenylphosphine met with little success. Only monomeric species appeared to result when equivalent amounts of the ligand were reacted with $[IrCl(CO)_2(p\text{-toluidine})]$ or with $[Ir_2Cl_2(c\text{-}C_8H_{14})_4]$ plus carbon monoxide. Monomeric species were also the major products of the reactions of $[IrX(CO)(Ph_2Ppy)_2]$ (X = Cl (**17**), Br (**18**))[33] with $[IrCl(CO)_2(p\text{-toluidine})]$ in tetrahydrofuran or with $Bu_4N[IrBr_2(CO)_2]$ in dichloromethane, respectively. However, among the variety of singlet resonances evidently due to the monomeric complexes[34] in the ^{31}P NMR spectrum (−80 °C) of each reaction mixture was a pair of doublet resonances (δ 17.8, −9.9 (J = 16.5 Hz; X = Cl), δ 18.3, −10.2 (J = 17.5 Hz; X = Br)) which showed evidence for fluxional behavior at higher temperatures. Since the coupling constants are very close to the value of $^3J_{P-P}$ observed for **9** and for $[Rh_2Cl_2(\mu\text{-CO})(Ph_2Ppy)_2]$,[13] the spectra are consistent with an unsymmetrical diiridium complex with two 2-pyridyldiphenylphosphine ligands bridging in a head-to-tail fashion, but with the small quantity present attempts to isolate it failed. Pursuing this route, equivalent amounts of $Bu_4N[IrBr_2(CO)_2]$ and 2-pyridyldiphenylphosphine were refluxed for 21 h in dichloromethane with a slow nitrogen purge. The powdery yellow product did not give a satisfactory elemental analysis but appears to have the approximate composition $[IrBr(CO)(Ph_2Ppy)]$. The infrared spectrum shows carbonyl absorptions at 2018, 1934, and 1776 cm^{-1} while the ^{31}P NMR spectrum (−58 °C) consists of two pairs of doublet resonances (δ 18.4, −9.2 (J = 16.5 Hz), δ 18.0, −10.1 (J = 16.4 Hz)). The ^{31}P NMR data and particularly the indication from the infrared spectrum that a bridging carbonyl is present suggest formation of dimeric species. Presumably one of these is that discussed above while the other evidently has a closely related structure. We suggest that these may be E and F.



E



F

All attempts to synthesize mixed rhodium–iridium dimers with 2-pyridyldiphenylphosphine, including reaction of $[RhCl(CO)(Ph_2Ppy)_2]$ with $[Ir(CO)_2Cl(p\text{-toluidine})]$ or with $[Ir_2Cl_2(c\text{-}C_8H_{14})_4]$ plus carbon monoxide as well as that of **17** with $[Rh_2Cl_2(CO)_4]$, were unsuccessful. In all cases the only identifiable product was $[Rh_2Cl_2(\mu\text{-CO})(Ph_2Ppy)_2]$ which formed in substantial quantities, indicating a significant lability of the 2-pyridyldiphenylphosphine in these systems. It is possible that the lack of success here is due to the smaller bite and greater rigidity of 2-pyridyldiphenylphosphine as compared with DPM which is suggested by the fact that the rhodium–rhodium distance in $[Rh_2Cl_2(\mu\text{-CO})(Ph_2Ppy)_2]$ is 2.612 (1) Å[13] while in $[Rh_2Br_2(\mu\text{-CO})(DPM)_2]$ it is 2.7566 (7) Å.[37] However, 2-pyridyldiphenylphosphine has also been shown to span a metal–metal separation of 2.845 (1) Å in $[PtMoCl_2(\mu\text{-CO})(Ph_2Ppy)_2]$,[38] and there is no consistent pattern of metal–metal distances in the structurally characterized dirhodium and diiridium complexes of DPM to suggest that the iridium–iridium or particularly the rhodium–iridium distance in the desired 2-pyridyldiphenylphosphine-bridged dimers would necessarily have to be too

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[33] $[Ir(CO)Br(Ph_2Ppy)_2]$ was characterized spectroscopically ($\nu_{C{=}O}$ 1958 cm^{-1}; δ(P) (CD_2Cl_2) 22.6 (s)).

[34] Those which could be identified were $[Ir(CO)_2X(Ph_2Ppy)_2]$ (X = Cl (δ(P) 9.7 (s)); X = Br (δ(P) 8.8 (s)), $[Ir(O_2)(CO)X(Ph_2Ppy)_2]$ (X = Cl (δ(P) 2.4 (s)); X = Br (δ(P) 6.6 (s)), and $[Ir(CO)_3(Ph_2Ppy)_2]X$ (δ(P) 2.3 (s)) by comparison with authentic samples prepared as reported for the triphenylphosphine analogues.[35,36]

[35] Payne, N. C.; Ibers, J. A. *Inorg. Chem.* **1969**, *8* 2714.

[36] Church, M. J.; Mays, M. J.; Simpson, R. N. F.; Stefanini, F. P. *J. Chem. Soc. A* **1970**, 2909.

[37] Cowie, M.; Dwight, S. K. *Inorg. Chem.* **1980**, *19*, 2508.

[38] Farr, J. P.; Olmstead, M. M.; Rutherford, N. M.; Wood, F. E.; Balch, A. L. *Organometallics* **1983**, *2*, 1758.

large to be comfortably spanned by this ligand.

Conclusions

The use of 2-pyridyldiphenylphosphine as a bridging ligand in binuclear rhodium complexes containing a dimetalated olefin results in addition of carbon monoxide in terminal positions rather than in eventual insertion into the metal-metal bond to form a carbonyl-bridged species as occurs in the analogous DPM-bridged species. This is attributed to the shorter bite and greater rigidity of 2-pyridyldiphenylphosphine which prevents the rhodium atoms from separating enough to accommodate a bridging carbonyl ligand. Attempts to form iridium dimers bridged by this ligand appeared to succeed but were difficult, and the nature of the product could not be confirmed with certainty. Mixed rhodium-iridium dimers could not be prepared, presumably due to the greater stability of the dirhodium complex. The proposed structures and chemistry of DPM-bridged rhodium-iridium dimers containing a dimetalated olefin are a combination of those found previously for the homometallic counterparts. Interestingly, they show a much greater mobility of the carbonyl ligands than do either of these counterparts.

Acknowledgment. This research was primarily supported by the Chemistry Department of Tulane University. Partial support by the Gulf Oil Foundation is also gratefully acknowledged. We thank Professor Max Roundhill for helpful discussion and suggestions.

Registry No. **1**, 100815-00-7; **2**, 100815-01-8; **3**, 100815-02-9; **4a**, 100815-03-0; **4b**, 101141-33-7; **5a**, 100815-04-1; **5b**, 101053-44-5; **6**, 100815-06-3; **7**, 100815-08-5; **8**, 100815-09-6; **9**, 100815-10-9; **10a**, 100815-11-0; **10b**, 100896-61-5; **11**, 100815-12-1; **12**, 100857-91-8; **13**, 100815-14-3; **14**, 100815-16-5; **16a**, 100815-17-6; **16b**, 100896-62-6; **16c**, 100815-18-7; $Rh_2Cl_2(\mu\text{-}CO)(Ph_2Ppy)_2$, 75361-61-4; $Pd_2Cl_2(Ph_2Ppy)_2$, 78055-58-0; $PtBr_2(Ph_2Ppy)_2$, 84074-40-8; $Bu_4N[Ir(CO)_2Br_2]$, 73190-78-0; $[RhIr(CO)_2(\mu\text{-}CO)Cl(DPM)_2]Cl$, 87482-56-2; $Ir(CO)_2Cl$(*p*-toluidine), 14243-22-2; $Ir_2Cl_2(c\text{-}C_8H_{14})_4$, 12246-51-4; Rh, 7440-16-6; Ir, 7439-88-5; Pt, 7440-06-4; dimethyl acetylenedicarboxylate, 762-42-5; heafluorobut-2-yne, 692-50-2; methyl propiolate, 922-67-8.

Reduction of Metal Carbonyls via Electron Transfer. Formation and Chain Decomposition of Formylmetal Intermediates

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Received July 30, 1985

Electron transfer to metal carbonyls such as $Cr(CO)_6$ and $Fe(CO)_5$ affords the corresponding 19-electron anion radicals which undergo facile hydrogen atom transfer with trialkyltin hydrides. The yields of the resultant formylmetal carbonyls are limited by a radical-chain decomposition, the mechanism of which is established by a detailed study of the formyldirhenate complex $(OC)_5ReRe(CO)_4CHO^-Bu_4N^+$ (IV). The chain process in Scheme I leading to the hydridodirhenate V is induced either thermally by azo initiator or photochemically with light of $\lambda > 400$ nm. High kinetic chain lengths and quantum yields of >300 are measured. Reductive methods involving initiation at an electrode surface or with sodium anthracene also promote the chain decomposition, but the turnover numbers are limited. Detailed kinetics analysis of the cyclic voltammetric data reveals the presence of two mechanistic pathways—one involving a radical-chain process (Scheme I) and the other an electron-transfer process (Scheme II). The radical-chain process for the decomposition of formylmetals is retarded by hydrogen atom donors. The latter is shown by the unusual stabilization of a variety of formylmetal species that are otherwise quite transient. Synthesis and decomposition of formylmetals by homolytic mechanisms involving facile hydrogen atom transfers are thus microscopically related processes.

Introduction

Current interest in metal carbonyls derives from their critical involvement in the industrially important catalytic reduction of carbon monoxide.[2,3] As part of our interest in organometallic electrochemistry, we recently found a series of facile homolytic reactions accompanying the one-electron oxidation and reduction of metal carbonyls.[4,5] Indeed the possibility of paramagnetic carbonylmetals participating as reactive intermediates in the catalytic CO reduction and Fischer-Tropsch synthesis has intrigued us for some time.[6] Since metal catalysis of carbon monoxide fixation has recently centered around formylmetal complexes as one of the prime intermediates along the reaction pathways,[7-9] we wish to focus on the production of this

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