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Dialkyl and Trialkyl Heterobinuclear Complexes of Rhodium and Iridium: Models for Adjacent-Metal Involvement in Bimetallic Catalysts

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The heterobinuclear dialkyl complexes [RhIr(R)$_2$(μ-CO)(dppm)$_2$] (dppm = μ-Ph$_2$PCH$_2$PPh$_2$; R = CH$_3$ (**2**), CH$_2$Ph (**3**)) have been prepared. Both A-frame-like compounds have one alkyl group terminally bound to each metal and a bridging carbonyl ligand. Some subsequent reactivity studies of **2** are reported. Reaction of **2** with CO yields [RhIr(CO)$_3$(dppm)$_2$] and acetone. If this reaction is monitored at low temperature by NMR spectroscopy, the dicarbonyl species [RhIr(CH$_3$)$_2$(CO)$_2$(dppm)$_2$] (**4**) is first observed, followed by [RhIr(CH$_3$)$_2$(CO)$_3$(dppm)$_2$] (**5**). In both products, both methyl groups are bound to Ir. Warming to ambient temperature under CO yields acetone and [RhIr(CO)$_3$(dppm)$_2$]. Crossover experiments suggest that acetone arises primarily from an intramolecular process. We propose that migratory insertion of a CO and a methyl group occurs on Ir; presumably reductive elimination also occurs from this metal. Compound **2** reacts with H$_2$ at −78 °C to yield [RhIrH(CH$_3$)$_2$(μ-H)(μ-CO)(dppm)$_2$] (**6**), in which one methyl group is bound to Rh while the other, together with a hydride ligand, is terminally bound to Ir. This latter species reacts with CO at 0 °C to yield [RhIrH-(C(O)CH$_3$)(CH$_3$)(μ-H)(μ-CO)(dppm)$_2$] (**7**), in which migratory insertion involving CO and the Rh-bound methyl group has yielded a Rh-bound acetyl group. At ambient temperature, under an atmosphere of CO, [RhIr(CO)$_3$(dppm)$_2$] is formed, together with acetaldehyde and methane. Crossover experiments support a predominantly intramolecular process for acetaldehyde formation but are equivocal on the formation of methane. Compound **2** oxidatively adds CH$_3$I or n-C$_4$H$_9$I, yielding [RhIr(CH$_3$)$_2$(R)(μ-I)(μ-CO)(dppm)$_2$] (R = CH$_3$, n-C$_4$H$_9$), in which the added alkyl group in each case is bound to Ir. The n-butyl product reacts with CO to yield [RhIr(n-C$_4$H$_9$)(CH$_3$)$_2$(μ-CO)$_2$(dppm)$_2$][I], in which the n-butyl group has migrated to Rh. A similar product, [RhIr(CH$_3$)$_3$(μ-CO)$_2$(dppm)$_2$][CF$_3$SO$_3$], is obtained in the reaction of **2** with methyl triflate in the presence of CO.

Introduction

Small cluster complexes, containing two or more adjacent metals, have attracted considerable attention, both as models for processes occurring at adjacent metal sites on the surfaces of heterogeneous catalysts[1] and because such complexes may display novel reactivity in their own right, on the expectation that adjacent metals can act in a cooperative manner in the activation of substrate molecules.[2] The utility of discrete clusters as models for surface reactivity is based on the premise that processes occurring on metal surfaces do not differ in any fundamental way from those taking place in simple homogeneous systems,[3] yet these latter systems are much easier to study. With the increasing emphasis on bimetallic catalysts,[4] in which two *different* metals are involved, an obvious extension of the modeling studies is to mixed-metal clusters containing two different metal types.[5] Although small, well-defined cluster complexes cannot be expected to effectively model all aspects of surface reactivity, they can yield valuable information relating to substrate binding and the

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subsequent transformations of the bound substrates, since these clusters can support both terminal and bridging coordination modes that also appear on metal surfaces.[1g]

In considering the effects of metal–metal cooperativity in substrate activation, the incorporation of different adjacent metals clearly expands the scope of metal-promoted activation through the wide range of metal combinations that can be used. Furthermore, when studying the reactivity of such systems, it is of interest to establish the metal at which different processes arise and the roles of the different metals in promoting the transformations of interest.

We maintain that the prototype cluster—the binuclear complex, containing only two adjacent metals—is a key species in establishing the roles of adjacent metals in substrate activation. Not only do binuclear systems have the ability to support substrate binding in either bridging or terminal coordination modes, but the lack of unnecessary complexity in these two-metal systems makes them ideal for establishing the natures of metal–metal and metal–substrate interactions and in establishing the intimate details of how the substrate transformations occur.[6]

In this study we extend our previous investigations on homo-[7] and heterobinuclear complexes[7a–c,8] containing a single methyl ligand to complexes involving the Rh/Ir combination of metals which include two and three alkyl groups. Alkyl complexes of the late transition metals are of relevance in a variety of catalytic processes such as olefin hydrogenation, hydrosilation, and hydroformylation,[9] Fischer–Tropsch chemistry,[10] and methanol carbonylation.[11] Complexes containing two or more alkyl groups can yield additional information about C–C bond-formation processes. In our heterobinuclear complexes we are attempting to establish the preference of molecular fragments that are relevant in catalytic transformations (e.g., CH$_3$, H, CO) to occupy the different metal sites and to establish the tendencies of the different metals toward important processes such as oxidative addition, migratory insertion, and reductive elimination. Although a number of related dialkyl homobinuclear, late-metal complexes have been reported for a number of metals.[12–18] similar reports involving heterobinuclear species are much fewer.[5a,19] Our ultimate goal is to obtain an improved understanding about the roles of the different metals in bimetallic systems.

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Experimental Section

General Comments. All solvents were appropriately deoxygenated and dried by distillation over the appropriate drying agents prior to use and were stored under dinitrogen. Deuterated solvents used for NMR experiments were degassed and stored under dinitrogen over molecular sieves. Reactions were carried out routinely at room temperature (unless otherwise stated) and under standard Schlenk conditions; compounds that were isolated as solids were purified by recrystallization. Hydrated rhodium trichloride was purchased from Engelhard Scientific, whereas methyl triflate ($CH_3OSO_2CF_3$), benzylmagnesium chloride (2 M in THF), methyllithium (1 M solution in THF/cumene), methyllithium-d_3·lithium iodide complex (0.5 M solution in diethyl ether), and methyl iodide were obtained from Aldrich and were used as received. Hydrogen was purchased from Linde, and carbon monoxide was purchased from Matheson. ^{13}CO was supplied by Isotec Inc. All gases were used as received. The compound *trans*-[RhIr(Cl)$_2$(CO)$_2$(dppm)$_2$][20] (dppm = μ-$Ph_2PCH_2PPh_2$; **1**) was prepared as previously reported.

All routine NMR experiments were conducted on a Bruker AM-400 spectrometer, whereas the ^{13}C{^{31}P} experiments were conducted on a Bruker AM-200 spectrometer operating at 50.3 MHz, or the AM-400 spectrometer operating at 100.6 MHz. ^{1}H−^{1}H COSY experiments were performed on the AM-400 spectrometer. Infrared spectra were obtained on a Nicolet 7199 Fourier transform or a Perkin-Elmer 883 IR spectrometer, either as Nujol mulls on KBr plates or as solutions in KCl cells with 0.5 mm window path lengths. Elemental analyses were performed by the microanalytical service within our department. Spectroscopic data for all compounds are given in Table 1.

Preparation of Compounds. (a) [RhIr(CH$_3$)$_2$(μ-CO)(dppm)$_2$] (2). [RhIrCl$_2$(CO)$_2$(dppm)$_2$] (**1**) (200 mg, 0.17 mmol) was dissolved in 150 mL of freshly distilled THF, and the resulting yellow solution was cooled to −78 °C in a dry ice/acetone bath. Ten molar equivalents of methyllithium (1.68 mL, 1.0 M solution in THF) was added via a gastight syringe, causing the solution to darken slightly. After removing the dry ice/acetone bath to allow the reaction mixture to warm to ambient temperature, the mixture was stirred vigorously for 3 h, during which time the solution changed from yellow to red. The mixture was then transferred through a cannula to a second vessel containing ca. 75 g of thoroughly deoxygenated Florisil under argon, and the resulting red slurry was transferred through a cannula to a filter frit tube containing a 5 cm layer of deoxygenated Celite. The supernatant was drawn through the Celite into a 250 mL collection flask filled with Ar by applying a partial vacuum. The solution volume was reduced to ca. 5 mL under dynamic vacuum, the flask was backfilled with Ar, and 40 mL of freshly distilled, scrupulously deoxygenated pentane was added, causing the precipitation of a brick-red solid. The solid was washed with 2 × 20 mL of the aforementioned pentane and then dried overnight in vacuo. Mass of compound **2** isolated: 0.119 g (yield 62%). A satisfactory elemental analysis could not be obtained for compound **2** because of its extreme air sensitivity (the brick-red solid turned yellow instantly upon exposure to air). Attempts to obtain high-resolution mass spectra also failed. ^{31}P{^{1}H} and ^{1}H NMR spectra of **2** are shown in Figures S1 and S2 in the Supporting Information. Samples of **2** containing ^{13}CO were prepared as described above starting with [RhIrCl$_2$(^{13}CO)$_2$(dppm)$_2$].

(b) [RhIr(^{13}CH$_3$)$_2$(μ-^{13}CO)(dppm)$_2$] (2a). Neat ^{13}CH$_3$I (0.500 mL, 1.14 g, 7.98 mmol) was added by syringe to a rapidly stirring 5.00 mL sample of 1.6 M n-BuLi in hexanes inside a centrifuge tube that had been cooled to 0 °C in a water/ice bath. The water/ice bath was removed, and the mixture was allowed to achieve ambient temperature. About 5 min after ambient temperature had been reached, a white solid began to precipitate from solution. The mixture was centrifuged for 20 min, and the colorless supernatant above the compacted white solid in the bottom of the tube was removed by syringe. Pentane (5 mL, freshly distilled) was added and the tube was shaken, producing a milky-white suspension. The tube was centrifuged a second time for 20 min, and the pentane supernatant was discarded. Diethyl ether (10 mL) was added, affording a white suspension, which was transferred through a cannula to a rapidly stirring orange solution of 0.100 g (0.084 mmol) of [RhIrCl$_2$(^{13}CO)$_2$(dppm)$_2$] in 100 mL of freshly distilled THF at −78 °C. The dry ice/acetone bath was removed, and the mixture was allowed to gradually warm to room temperature. Once the solution reached about 0 °C, it changed color from yellow to orange-red. The solution was stirred for 3 h, and then the mixture was transferred to a flask containing ca. 50 g of thoroughly dried and deoxygenated Florisil. The mixture was stirred over the Florisil for 30 min and then filtered through a layer of Celite into another flask. The solvent volume was reduced to ca. 5 mL under vacuum, and 40 mL of pentane was added, causing the immediate precipitation of a red solid. The solid was washed twice with 10 mL of pentane, then dried overnight under vacuum. Mass of red solid isolated: 0.045 g (48% yield).

(c) [RhIr(CH$_2$Ph)$_2$(μ-CO)(dppm)$_2$] (3). The procedure is the same as described above except that 100 mg (0.084 mmol) of [RhIrCl$_2$(CO)$_2$(dppm)$_2$], benzylmagnesium chloride (420 μL, 2 M solution in THF), and 50 mL of dry THF were used and the mixture was stirred for 4 h at room temperature. The volume was reduced by one-half and the solution was filtered through a frit followed by the addition of 50 mL of *n*-pentane, causing the precipitation of a dull yellow solid. The extremely air-sensitive solid was recrystallized from benzene/*n*-pentane and dried under N_2. Satisfactory microanalyses could not be obtained due to its extreme air and moisture sensitivity.

(d) [RhIr(CH$_3$)$_2$(CO)$_2$(dppm)$_2$] (4). Carbon monoxide gas (1.0 mL, 0.041 mmol) was injected by gastight syringe into a red solution of 0.033 g (0.030 mmol) of compound **2** in 1.0 mL of CD_2Cl_2 that had been cooled to −78 °C in a dry ice/acetone bath. The mixture was warmed to −40 °C and then stirred vigorously for 15 min. During this time the solution changed color from red to orange. The ^{1}P{^{1}H}, ^{1}H, and ^{13}C{^{1}H} NMR spectra for the orange solution showed that the starting organometallic compound **2** had been essentially completely converted to [RhIr(CH$_3$)$_2$(CO)$_2$(dppm)$_2$] (**4**). However, the product could not be isolated pure, decomposing within hours, so was characterized by spectroscopic techniques.

(e) [RhIr(CH$_3$)$_2$(CO)$_3$(dppm)$_2$] (5). A sample of **4**, prepared as described in part (d), was maintained at −40 °C, and carbon monoxide was passed through the solution to replace the dinitrogen atmosphere above the solution. ^{31}P{^{1}H} NMR spectroscopy established that compound **5** was generated in approximately 65% yield together with **4** (25%) and several unidentified species. Removal of the CO atmosphere resulted in conversion of **5** to **4**, while the unidentified products remained. Warming the temperature to ambient under the CO atmosphere resulted in the slow conversion to the known species [RhIr(CO)$_3$(dppm)$_2$][21] in approximately 30% yield of the phosphorus-containing products together with unidentified

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Table 1. Spectroscopic Parameters for the Compounds

compound	IR,[a,b] $\mathrm{cm^{-1}}$	NMR[c,d] $\delta(^{31}P\{^1H\})$	$\delta(^1H)$	$\delta(^{13}C\{^1H\})$
$[RhIr(CH_3)_2(\mu\text{-}CO)(dppm)_2]$ (**2**)	1715 (ms)	31.9 (dm, $^1J_{RhP}$ = 154 Hz), 21.5 (m)[e]	3.86 (m, 2H), 3.53 (m, 2H), −0.35 (td, $^3J_{PH}$ = 7.4 Hz, $^2J_{RhH}$ = 2.0 Hz, 3H), 0.22 (t, $^3J_{PH}$ = 7.7 Hz, 3H)	230.8 (dm, $^1J_{RhC}$ = 29 Hz), 4.81 (dt, $^2J_{PC}$ = 9.1 Hz, $^1J_{CC}$ = 11.5 Hz), 2.78 (ddt, $^2J_{PC}$ = 9.1 Hz, $^2J_{CC}$ = 8.7 Hz, $^1J_{RhC}$ = 22.8 Hz)
$[RhIr(CH_2Ph)_2(\mu\text{-}CO)(dppm)_2]$ (**3**)	1713 (ms)	29.3 (dm, $^1J_{RhP}$ = 161Hz), 18.1 (m)	3.62 (m, 2H), 3.38 (m, 2H), 2.57 (t, 2H), 1.82 (td, 2H)	230.1 (dm, $^1J_{RhC}$ = 30.5 Hz)
$[RhIr(CH_3)_2(CO)_2(dppm)_2]$ (**4**)[f]	1984 (m), 1944 (bs)	10.0 (dm, $^1J_{RhP}$ = 152 Hz), −16.4 (m)	5.41 (m, 2H), 5.22 (m, 2H), −0.23 (t, $^3J_{PH}$ = 7.6 Hz, 3H), −1.39 (m, 3H)	185.7 (t), 182.6 (dt, $^1J_{RhC}$ = 67.8 Hz)
$[RhIr(CH_3)_2(CO)_3(dppm)_2]$ (**5**)[g]		6.9 (dm, $^1J_{RhP}$ = 153 Hz), −7.8 (m)	4.97 (m, 2H), 4.64 (m, 2H), 0.40 (b, 3H), −1.18 (b, 3H)	204.8 (dt, $^1J_{RhC}$ = 77.4 Hz), 190.2 (dt, $^1J_{RhC}$ = 60.2 Hz), 184.3 (t), −7.7 (t, $^2J_{PC}$ = 6.2 Hz), −9.0 (t, $^2J_{PC}$ = 6.9 Hz)
$[RhIrH(CH_3)_2(\mu\text{-}H)(CO)(dppm)_2]$ (**6**)	1815 (m)	36.0 (dm, $^1J_{RhP}$ = 148 Hz), 9.4 (m)	3.64 (m, 2H), 3.23 (m, 2H), −0.86 (t, $^3J_{PH}$ = 5.0 Hz, 3H), −0.26 (td, $^3J_{PH}$ = 6.6 Hz, $^2J_{RhH}$ = 2.0 Hz, 3H), −10. 65 (dm, $^1J_{RhH}$ = 14.0 Hz, 1H), −13.36 (t, $^2J_{PH}$ = 19 Hz, 1H)	233.3 (dm, $^1J_{RhC}$ = 23 Hz)
$[RhIrH(COCH_3)(CH_3)(\mu\text{-}H)(CO)(dppm)_2]$ (**7**)[f]	1742 (ss), 1626 (m)	24.6 (dm, $^1J_{RhP}$ = 166 Hz), 10.5 (m)	3.63 (m, 2H), 3.18 (m, 2H), 0.97 (s, 3H), −1.02 (t, 3H), −11.83 (dm, $^1J_{RhH}$ = 20.1 Hz, $^2J_{P(Ir)H}$ = 13.8 Hz, $^2J_{P(Rh)H}$ = 18.2 Hz, 1H), −13.58 (t, $^2J_{PH}$ = 20 Hz, 1H)	277.5 (dm, $^1J_{RhC}$ = 29.0 Hz, $^2J_{CC}$ = 9.8 Hz), 227.2 (dm, $^1J_{RhC}$ = 24.4 Hz)
$[RhIr(CH_3)_3(\mu\text{-}I)(\mu\text{-}CO)(dppm)_2]$ (**8**)	1709 (ms)	27.7 (dm, $^1J_{RhP}$ = 154 Hz), −11.4 (m)	4.42 (m, 2H), 3.58 (m, 2H), 0.85 (t, $^3J_{PH}$ = 6 Hz, 3H) −0.17 (t, $^3J_{PH}$ = 6.4 Hz, 3H), −0.23 (td, $^3J_{PH}$ = 8 Hz, $^2J_{RhH}$ = 2.0 Hz)	220.4 (dq, $^1J_{RhC}$ = 38 Hz, $^2J_{PC}$ = 5.4 Hz), −11.6 (t, $^2J_{PC}$ = 5.6 Hz)[h]
$[RhIr(CH_3)_2(n\text{-}C_4H_9)(\mu\text{-}I)(\mu\text{-}CO)(dppm)_2]$ (**9**)		26.3 (dm, $^1J_{RhP}$ = 152 Hz), −12.9 (m)	4.56 (m, 2H), 3.54 (m, 2H), 2.14 (m, 2H), 1.01 (m, 2H), 0.85 (m, 2H), 0.39 (t, $^3J_{HH}$ = 6 Hz, 3H), −0.22 (t, $^3J_{PH}$ = 7.2 Hz, 3H), −0.24 (td, $^2J_{RhH}$ = 2.3 Hz, $^3J_{PH}$ = 8 Hz, 3H)	222.6 (dq, $^2J_{PC}$ = 6.0 Hz, $^1J_{RhC}$ = 37 Hz)
$[RhIr(n\text{-}C_4H_9)(CH_3)_2(\mu\text{-}CO)_2(dppm)_2][I]$ (**10**)	1776 (ss)	28.7 (dm, $^1J_{RhP}$ = 149 Hz), −1.4 (m)	3.34 (q, $^2J_{PH}$ = 4.2 Hz, 4H), 1.78 (m, 2H), 0.88 (m, 2H), 0.59 (m, 2H), 0.02 (t, $^3J_{HH}$ = 6.8 Hz, 3H), −0.19 (t, $^3J_{PH}$ = 6.5 Hz, 6H)	215.4 (dm, $^1J_{RhC}$ = 40 Hz) −9.81 (t, $^2J_{PC}$ = 6 Hz)
$[RhIr(CH_3)_3(CO)_2(dppm)_2][CF_3SO_3]$ (**11**)	1783 (bs)	29.8 (dm, $^1J_{RhP}$ = 140 Hz), −2.5 (m)	3.33 (m, 4H), 0.82 (td, 3H), −0.13 (t, 6H)	214.8 (dm, $^1J_{RhC}$ = 20.3 Hz, 1C), 24.1 (dt, $^1J_{RhC}$ = 22.8 Hz, 1C), −9.6 (t, $^2J_{PC}$ = 6 Hz, 2C)

[a] IR abbreviations: ss = strong sharp, bs = broad strong, ms = medium sharp, m = medium. [b] Nujol mull except as indicated. Values quoted are ν(CO) except as indicated. [c] NMR abbreviations: t = triplet, dt = doublet of triplets, ddt = doublet of doublets of triplets, dm = doublet of multiplets, td = triplet of doublets, b = broad, m = multiplet, dq = doublet of quintets. [d] $^{31}P\{^1H\}$ chemical shifts are referenced vs external 85% H_3PO_4, while ^1H and $^{13}C\{^1H\}$ are referenced vs TMS, CD_2Cl_2 solution. Chemical shifts for the phenyl hydrogens are not given in the ^1H NMR data. [e] The AA′BB′X spin system gives rise to a multiplet (m) and a doublet of multiplets (dm) owing to coupling to ^{103}Rh in the latter. [f] 0 °C. [g] −40 °C. [h] Obtained on a sample prepared by the reaction of **2** with $^{13}CH_3I$.

products. Characterization of **5** was by $^{31}P\{^1H\}$, $^{13}C\{^1H\}$, and ^1H NMR spectroscopy at −40 °C.

(f) [RhIr(H)(CH$_3$)$_2$(*μ*-H)(*μ*-CO)(dppm)$_2$] (6). Compound **2** (90 mg, 0.080 mmol) was dissolved in 15 mL of THF, and the resulting red solution was cooled to −78 °C in a dry ice/acetone bath. Hydrogen gas was slowly passed through the solution at ca. 0.1 mL s^{-1} for a period of 5 min. The solution was then slowly warmed to room temperature under an H_2 purge and stirred until the deep red color turned pale yellow (~10 min). Dichloromethane (20 mL) was added, the small quantity of white suspended particles (assumed to be residual LiCl) was allowed to settle, the clear yellow supernatant was transferred to another vessel, and the solvent volume was reduced to ca. 5 mL under vacuum. Carefully degassed pentane (40 mL) was added, affording a yellow solid. The supernatant was discarded, and the solid was washed with 2 × 10 mL of pentane and then dried under dynamic vacuum for 3 h. Mass of compound **6** isolated: 0.043 g (48% yield). A satisfactory elemental analysis for this compound could not be obtained owing to decomposition of the solid over a several-hour period, presumably initiated by methane loss. The isotopomer **[RhIr(^{13}CH$_3$)$_2$(D)(*μ*-D)(*μ*-^{13}CO)(dppm)$_2$] (6a)** was prepared in an analogous fashion starting with [RhIr(^{13}CH$_3$)$_2$(*μ*-^{13}CO)(dppm)$_2$] and using D_2 in place of H_2. The $^{31}P\{^1H\}$ and ^1H NMR spectra of a ^{13}CO-enriched sample of **6** are given in Figures S3 and S4 in the Supporting Information.

(g) [RhIr(H)(COCH$_3$)(CH$_3$)(*μ*-H)(*μ*-CO)(dppm)$_2$] (7). The procedure described above for **6** was repeated. Once the pale yellow solution was obtained, the sample was transferred via a syringe to an NMR tube. The tube was then immersed in a dry ice/acetone bath to bring the sample temperature to −78 °C, and CO gas was passed through the solution briefly. NMR data (^1H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$) collected at 0 °C after allowing the solution to stand at this temperature for 2 h showed **7** as the major product in addition to variable amounts of **6** and the known tricarbonyl species [RhIr(CO)$_3$(dppm)$_2$].[21] Upon warming to room temperature, compound **7** reacted further with CO to form [RhIr(CO)$_3$(dppm)$_2$], between 40 and 45% yield together with equivalent amounts of acetaldehyde and methane. The presence of methane and acetaldehyde was confirmed by their resonances in the ^1H NMR spectrum.

(h) [RhIr(CH$_3$)$_3$(*μ*-I)(*μ*-CO)(dppm)$_2$] (8). Neat CH_3I (11 *μ*L, 0.18 mmol) was added by microliter syringe to a solution of compound **2** (0.200 g, 0.178 mmol) in 8 mL of THF at room temperature. The solution changed immediately from cherry-red to orange-brown. The mixture was stirred for 1 h, and the solvent was stripped off in vacuo, affording an orange solid. Recrystallization of the solid from CH_2Cl_2/Et_2O at 22 °C gave [RhIr(CH$_3$)$_3$(*μ*-I)(*μ*-CO)(dppm)$_2$] (**8**) (0.081 g, 36%) as yellow crystals. Anal. Calcd for $C_{54}H_{53}P_4ORhIrI$: C, 51.23; H, 4.22. Found: C, 51.32; H, 4.14.

(i) [RhIr(CH$_3$)$_2$(*n*-Bu)(*μ*-I)(*μ*-CO)(dppm)$_2$] (9). Neat *n*-BuI (10 *μ*L, 0.088 mmol) was added by microliter syringe to a solution of compound **2** (0.100 g, 0.089 mmol) in 20 mL of THF at 22 °C. The solution was stirred for 6 h, during which time the solution gradually changed from red to orange-brown. The solvent volume was reduced to ca. 2 mL in vacuo, and 15 mL of diethyl ether was added, causing the immediate formation of a yellow precipitate. The supernatant was discarded and the solid washed with 10 mL of diethyl ether. Recrystallization from CH_2Cl_2/Et_2O (1:1) at ambient temperature afforded [RhIr(CH$_3$)$_2$(*n*-Bu)(*μ*-I)(*μ*-CO)(dppm)$_2$]·2CH$_2$Cl$_2$ (**9**) (0.037 g, 0.025 mmol, 29%) as yellow crystals. Anal. Calcd for $C_{59}H_{63}Cl_4IP_4ORhIr$: C, 48.01; H, 4.30. Found: C, 48.18; H, 3.85.

(j) [RhIr(CH$_3$)$_2$(*n*-Bu)(*μ*-CO)$_2$(dppm)$_2$][I] (10). A colorless solution of *n*-BuI (10 *μ*L, 0.088 mmol) in 20 mL of CH_2Cl_2 was added through a cannula to a rapidly stirring solution of [RhIr(CH$_3$)$_2$(CO)$_2$(dppm)$_2$] (**4**) (ca. 0.105 g, ca. 0.091 mmol) in 20 mL of CH_2Cl_2 at −78 °C. (NOTE: compound **4** was prepared in situ via the reaction of a sample of compound **2** with a stoichiometric amount of CO gas.) The dry ice/acetone bath was removed, ambient temperature was achieved after 15 min, and stirring was continued for 3 h. Gradually, the solution changed from orange to yellow. The solvent was removed under vacuum, affording a yellow-brown residue. Recrystallization of the solid from CH_2Cl_2/hexane (1:1) afforded yellow-brown crystals of [RhIr(CH$_3$)$_2$(*n*-Bu)(*μ*-CO)$_2$(dppm)$_2$][I]·2CH$_2$Cl$_2$ (**10**) (0.027 g, 20%). Anal. Calcd for $C_{60}H_{63}Cl_4IP_4O_2RhIr$: C, 47.92; H, 4.22. Found: C, 47.80; H, 4.59. Compound **10** was also prepared inadvertently as the product from the reaction of *n*-BuI-contaminated $^{13}CH_3Li$ with [RhIrCl$_2$(^{13}CO)$_2$(dppm)$_2$], during an early attempt to prepare [RhIr(^{13}CH$_3$)$_2$(*μ*-^{13}CO)(dppm)$_2$].

(k) [RhIr(CH$_3$)$_3$(CO)$_2$(dppm)$_2$][CF$_3$SO$_3$] (11). Compound **2** (50 mg, 0.045 mmol) was dissolved in 2 mL of CH_2Cl_2 at −78 °C. One equivalent of methyl triflate (5 *μ*L, 0.044 mmol) was added via a syringe. This was stirred for 5 min, and an atmosphere of CO was then placed over the solution. The reaction mixture was stirred for 0.5 h and then taken to ambient temperature over a 15 min period. The orange product was precipitated and washed twice with 5 mL of ether and dried under dinitrogen gas stream and then in vacuo. Yield: 35 mg, 61%. Anal. Calcd for $IrRhSP_4O_5F_3C_{56}H_{53}$: C, 51.18; H, 4.07. Found: C, 51.41; H, 4.08.

Low-Temperature Intermediates in the Reaction of Compound 2 with CO. The procedure for preparing compound **4** was repeated except that 1 mL of CO gas was added at −78 °C and the NMR analysis was carried out at −40 °C. The major species in solution, in approximately 65% yield, was [RhIr(CH$_3$)$_2$(CO)$_3$(dppm)$_2$] (**5**) together with several unidentified minor species. Compound **5** can also be obtained by cooling a solution of **4** to −40 °C and adding 1 mL of CO gas at this temperature.

Crossover Experiments Involving Compound 6. A solution containing 0.061 g of compound **6** in 0.50 mL of C_6D_6 was combined with a solution containing approximately 0.02 g of compound **6a** in 0.50 mL of C_6D_6 in a 5 mm NMR tube. The mixture was cooled to 0 °C in an ice bath, and 5.0 mL of ^{13}CO gas was injected into the solution via a gastight syringe. The mixture was warmed to room temperature and then stirred for 20 min. The NMR spectra for the sample showed that the expected ^{13}CO-insertion products, [RhIr(H)(^{13}C(O)CH$_3$)(CH$_3$)(^{13}CO)(*μ*-H)(dppm)$_2$] and [RhIr(D)(^{13}C(O)^{13}CH$_3$)(^{13}CH$_3$)(^{13}CO)(*μ*-D)(dppm)$_2$], had been formed and that some free ^{13}CO was present in solution. The NMR tube containing the insertion products and free ^{13}CO was kept under Ar overnight at 23 °C. An NMR spectroscopic analysis of the reaction mixture the following morning revealed the presence of $CH_3{}^{13}C(O)H$, $^{13}CH_3{}^{13}C(O)D$, $^{13}CH_3{}^{13}C(O)H$, and $CH_3{}^{13}C(O)D$ in an approximate 16.6:4.2:1.0:0.75 ratio based on integration of the ^{13}C-carbonyl signals in the $^{13}C\{^1H\}$ NMR spectrum. The ^1H NMR spectrum showed the presence of $^{13}CH_4$, $^{13}CH_3D$, CH_4, and CH_3D in an approximate 1:1.6:6.0:1.1 ratio. Integration of the resonances for the methane isotopomers was not accurate owing to substantial overlap of the signals. The $^{31}P\{^1H\}$ and ^1H NMR spectra revealed the presence of the known compound [RhIr(CO)$_3$(dppm)$_3$][21] as approximately 45% of the products observed. Three other unidentified RhIr(dppm)$_2$-containing products, in comparable proportions, accounted for the remaining phosphorus-containing species. No effort was made to identify these unknowns beyond attempted comparisons of their spectra with those of known species.

***T_1* Measurements.** To determine the possible influence of deuterium substitution at the acyl carbon on the integration of this carbon in the ^{13}C NMR experiments, a determination of the T_1 values for acetaldehyde and acetaldehyde-d_1 was carried out. T_1 measurements were carried out on a Varian Unity 500 MHz instrument using the inversion recovery method (180−*τ*−90−aq). Owing to the low boiling point of the compounds (21 °C), the T_1 measurements were carried out at

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[21] McDonald, R.; Cowie, M. *Inorg. Chem.* **1990**, *29*, 1564.

Table 2. Crystallographic Data for Compounds 8 and 10

	$[RhIr(CH_3)_3(\mu\text{-}I)(\mu\text{-}CO)(dppm)_2]$ (**8**)·$2CH_2Cl_2$	$[RhIr(CH_3)(n\text{-}C_4H_9)(\mu\text{-}CO)_2(dppm)_2][I]$ (**10**)·$2CH_2Cl_2$
formula	$C_{56}H_{57}Cl_4IIrOP_4Rh$	$C_{60}H_{63}Cl_4IIrO_2P_4Rh$
fw	1433.71	1503.79
cryst dimens, mm	0.36 × 0.10 × 0.09	0.41 × 0.19 × 0.14
cryst syst	monoclinic	monoclinic
space group	$P2_1/n$ (alternate setting of $P2_1/c$ (No. 14))	$C2/c$ (No. 15)
a, Å	20.098(2)[a]	48.012(3)[b]
b, Å	12.289(1)	11.0171(7)
c, Å	22.645(2)	23.225(2)
β, deg	90.942(2)	102.734(1)
V, Å^3	5592.1(9)	11983(1)
Z	4	8
ρ_{calcd}, g cm^{-3}	1.703	1.667
μ, mm	3.568	3.336
radiation (λ, Å)	graphite-monochromated Mo Kα (0.71073)	
T, °C	−80	−80
scan type	ω scans (0.2°) (25 s exposure)	ω scans (0.2°) (20 s exposure)
2θ(max), deg	52.80	52.76
total data collected	27 226 ($-25 \leq h \leq 20$, $-14 \leq k \leq 15$, $-25 \leq l \leq 28$)	32 913 ($-58 \leq h \leq 60$, $-13 \leq k \leq 13$, $-21 \leq l \leq 29$)
no. of unique rflns	11423 ($R_{int} = 0.0622$)	12250 ($R_{int} = 0.0360$)
no. of observns	7786 ($F_o^2 \geq 2\sigma(F_o^2)$)	9996 ($F_o^2 \geq 2\sigma(F_o^2)$)
range of transmn factors	0.7395−0.3599	0.6524−0.3417
no. of data/restraints/params	11 423 ($F_o^2 \geq 3\sigma(F_o^2)$)/12[c]/512	12 250 ($F_o^2 \geq 3\sigma(F_o^2)$)/0/658
residual density, e/Å^3	8.313 to −1.530	1.765 to −1.005
R_1 ($F_o^2 \geq 2\sigma(F_o^2)$)[d]	0.0694	0.0356
wR_2 ($F_o^2 \geq -3\sigma(F_o^2)$)	0.1958	0.0949
GOF (S)[e]	1.022 ($F_o^2 \geq -3\sigma(F_o^2)$)	1.038 ($F_o^2 \geq -3\sigma(F_o^2)$)

[a] Cell parameters obtained from least-squares refinement of 6253 centered reflections. [b] Cell parameters obtained from least-squares refinement of 6637 centered reflections. [c] Distances within the disordered solvent molecule (CH_2Cl_2) were assigned fixed idealized values ($d(Cl{-}C) = 1.80$ Å; $d(Cl\cdots Cl) = 2.95$ Å). [d] $R_1 = \sum||F_o| - |F_c||/|F_o|$; $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^4)]^{1/2}$. [e] $S = [\sum w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$ (n = number of data, p = number of parameters varied; $w = [\sigma^2(F_o^2) + (a_oP)^2 + a_1P]^{-1}$, where $P = [\max(F_o^2, 0) = 2F_c^2]/3$. For **8**, $a_o = 0.1183$ and $a_1 = 7.9278$. For **10**, $a_o = 0.0498$ and $a_1 = 28.9800$.

4.5 °C. The temperature inside the probe was calibrated against a standard methanol sample provided by Varian and maintained at ± 0.1 °C during the experiments. Prior to all T_1 measurements the pulse width was calibrated at 4.5 °C. During the inversion recovery experiments, composite pulse ^{1}H decoupling (Waltz) was applied at all times using a minimum of decoupling power to minimize sample heating during the measurements. In addition, to ensure that resonance offset effects were not a problem, the transmitter was positioned adjacent to the resonance of the carbonyl carbon. The T_1 for this carbon was initially assumed to be as long as 90 s for the deuterated compound, and the relaxation delay for all measurements was set to be 5 times this value. A total of nine different τ values were used (1, 2, 4, 10, 25, 50, 100, 200, and 500 s), and a total of eight scans were acquired for each value of τ. All spectra were processed using 0.5 Hz line broadening. The data were then fit to an exponential equation using VNMR 6.1C. An excellent fit was obtained showing spin lattice relaxation times for the carbonyl carbons of acetaldehyde and acetaldehyde-d_1 were 14 and 18 s, respectively. The closeness of these T_1 values indicated that under the conditions of our $^{13}C\{^1H\}$ NMR data acquisition to determine the concentrations of the acetaldehyde isotopomers, only minor differences (ca. 3%) in the integrations would result from these T_1 differences.

X-ray Data Collection, Structure Solution, and Refinement. (a) Orange crystals of $[RhIr(CH_3)_3(\mu\text{-}I)(\mu\text{-}CO)(dppm)_2]$ (**8**)·$2CH_2Cl_2$ were obtained via slow evaporation of a dichloromethane/chloroform solution of the compound. Data were collected on a Bruker PLATFORM/SMART 1000 CCD diffractometer[22] using Mo Kα radiation at −80 °C. Unit cell parameters were obtained from a least-squares refinement of the setting angles of 6253 reflections from the data collection. The space group was determined to be $P2_1/n$ (an alternate setting of $P2_1/c$ [No. 14]). The data were corrected for absorption through use of the SADABS procedure. See Table 2 for a summary of crystal data and X-ray data collection information. The structure of **8** was solved using the Patterson location of heavy atoms and structure expansion routines as implemented in the DIRDIF-99[23] program system. Refinement was completed using the program SHELXL-93.[24] Hydrogen atoms were assigned positions based on the geometries of their attached carbon atoms and were given thermal parameters 20% greater than those of the attached carbons. The dppm phenyl rings attached to P(2) were found to be disordered; each was refined as two sets of regular hexagons ($d(C{-}C) = 1.39$Å), each with an occupancy factor of 50% and with a common isotropic displacement parameter. Both solvent dichloromethane molecules were found to be disordered; each was split into two sets of two chlorine and one carbon (and two hydrogen) atom, which were refined with an occupancy factor of 50%, a common isotropic displacement parameter, and fixed idealized Cl−C (1.80 Å) and Cl···Cl (2.95 Å) distances. The final model for **8** was refined to values of $R_1(F) = 0.0694$ (for 7786 data with $F_o^2 \geq 2\sigma(F_o^2)$) and $wR_2(F^2) = 0.1958$ (for all 11 423 independent data). The high residuals in the final electron density maps were located in the vicinities of the phenyl rings that did not show obvious disorder in earlier maps. Attempts to obtain better models by incorporating crystal twinning were unsuccessful.

(b) Orange crystals of $[RhIr(CH_3)_2(C_4H_9)(\mu\text{-}CO)_2(dppm)_2][I]$ (**10**)·$2CH_2Cl_2$ were obtained via slow diffusion of diethyl ether into a dichloromethane solution of the compound. Data were collected and corrected for absorption as for compound **8** above (see Table 2). Unit cell parameters were obtained from a least-squares refinement of the setting angles of 6637 reflections from the data collection, and the space group was determined to be $C2/c$ (No. 15). The structure of **10** was solved using the direct-methods program SIR-97,[25] and refinement was com-

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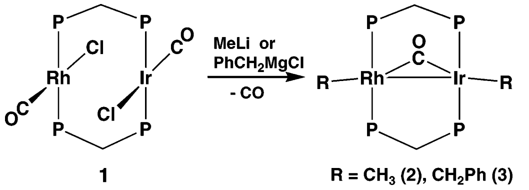
[22] Programs for diffractometer operation, data collection, data reduction, and absorption correction were those supplied by Bruker.

[23] Beurskens, P. T.; Beurskens, G.; de Gelder, R.; Garcia-Granda, S.; Israel, R.; Gould, R. O.; Smits, J. M. M. The *DIRDIF-99* program system; Crystallography Laboratory, University of Nijmegen: The Netherlands, 1999.

[24] Sheldrick G. M. *SHELXL-93*, Program for crystal structure determination; University of Göttingen: Germany, 1993.

Scheme 1



pleted using the program SHELXL-93, during which the hydrogen atoms were treated as for **8**. The final model for **10** was refined to values of $R_1(F) = 0.0356$ (for 9996 data with $F_o^2 \geq 2\sigma(F_o^2)$) and $wR_2(F^2) = 0.0949$ (for all 12 250 independent data).

Results and Compound Characterization

(a) Dimethyl and Related Species. Reaction of $[RhIrCl_2(CO)_2(dppm)_2]$ (**1**, dppm = μ-$Ph_2PCH_2PPh_2$) with an excess of MeLi at −78 °C yields the dimethyl monocarbonyl product $[RhIr(CH_3)_2(\mu\text{-}CO)(dppm)_2]$ (**2**) as outlined in Scheme 1. This species is exceedingly air sensitive, decomposing instantly in solution upon exposure to air and within seconds as a solid, so characterization is based upon its spectroscopy and upon the characterization of a number of its subsequent reaction products. The $^{31}P\{^1H\}$ NMR spectrum of **2** displays a pattern that is typical of an AA′BB′X spin system (X = ^{103}Rh) in such A-frame species in which the Ir-bound phosphorus nuclei appear as a multiplet at δ 21.5 (AA′ portion of the spectrum) and the Rh-bound nuclei appear as a doublet of multiplets at δ 31.9 (BB′ portion of the spectrum), having additional coupling to Rh of 154 Hz (see Figure S1 in the Supporting Information). All subsequent compounds display a qualitatively similar pattern, so these spectral features will be discussed only if they are unusual. In the ^{1}H NMR spectrum the dppm methylene protons appear as two multiplets at δ 3.86 and 3.53, consistent with the "front/back" asymmetry of the compound, and the methyl resonances appear as a triplet of doublets at δ −0.35 and a triplet at δ 0.22. In both cases the triplet pattern results from coupling to a pair of adjacent ^{31}P nuclei, whereas the doublet in the high-field signal results from coupling to Rh, suggesting that this methyl group is bound to this metal. This assignment is further supported by selective ^{31}P-decoupling experiments, which clearly establish the phosphorus nuclei to which the different protons are coupled, and is confirmed by the $^{13}C\{^1H\}$ NMR spectrum of a $^{13}CH_3$- and ^{13}CO-enriched sample of **2** in which the Rh-bound methyl group appears as a doublet of doublets of triplets at δ 2.78 displaying 22.8 Hz coupling to Rh as well as coupling to a pair of phosphorus atoms and to the sole carbonyl ligand, while the Ir-bound methyl group, at δ 4.81, displays coupling to only a pair of ^{31}P nuclei and the carbonyl group. The carbonyl resonance in the same sample appears as a complex multiplet at δ 230.8, but on broad-band ^{31}P decoupling, simplifies to a doublet of doublets of doublets, retaining 29 Hz coupling to Rh and coupling to the ^{13}C nuclei in the two methyl groups. In the IR spectrum the carbonyl stretch of a nonisotopically enriched sample appears at 1715 cm^{-1}, similar to the values reported for the related compounds $[Rh_2X_2(\mu\text{-}CO)(dppm)_2]$ (X = CH_3, Cl, Br);[15a,26] compound **2** is presumed to have a structure similar to these analogues.

The dibenzyl compound $[RhIr(CH_2Ph)_2(\mu\text{-}CO)(dppm)_2]$ (**3**) is prepared by the reaction of **1** with benzylmagnesium chloride and has spectral parameters very similar to those of **2**. In particular, the ^{1}H NMR spectrum displays the benzyl methylene resonances as a triplet of doublets at δ 1.82, in which 1.5 Hz coupling to Rh is observed, and as a triplet at δ 2.57. The carbonyl ligand is clearly bridging, as seen by the IR stretch at 1713 cm^{-1} and the ^{13}CO resonance in the NMR spectrum at δ 230.1, displaying 30.5 Hz coupling to Rh. Compound **2** can also be prepared by the reaction of **1** with MeMgCl, parallel to the preparation of **3**; however this route proved to be more troublesome, giving a number of unidentified impurities. Although the successful syntheses of compounds **2** and **3** suggest the possibility of generating a series of related dialkyl or possibly diaryl compounds, no other analogues have been prepared at this time. In addition, the subsequent chemistry of **3**, similar to that described below for **2**, has not been investigated.

At ambient temperature compound **2** reacts with carbon monoxide to yield the known tricarbonyl complex $[RhIr(CO)_3(dppm)_2]$[21] and acetone as the major products, each in about 30% yield, together with unidentified decomposition products (the relative amounts of species present were established by integration of the $^{31}P\{^1H\}$ and ^{1}H NMR spectra; in particular integration of the dppm methylene signal and that of acetone gave the relative amounts of the two products). If ^{13}CO is used in the reaction with unenriched **2**, an additional doublet ($^2J_{CH}$ = 9 Hz) flanking the acetone resonance at δ 2.07 appears in the ^{1}H NMR spectrum, due to coupling of the acetone protons with the ^{13}C label. Acetone was also observed in the carbonylation of the dirhodium analogue $[Rh_2(CH_3)_2(\mu\text{-}CO)(dppm)_2]$.[15a]

In an attempt to identify possible intermediates in the formation of acetone from **2** the addition of CO was carried out at low temperatures and the solution was monitored by multinuclear NMR spectroscopy. At −78 °C compound **2** reacts with carbon monoxide to yield the dicarbonyl dimethyl product $[RhIr(CH_3)_2(CO)_2(dppm)_2]$ (**4**) as shown in Scheme 2. Two carbonyl resonances of equal intensity appear for **4** in the $^{13}C\{^1H\}$ NMR spectrum, at δ 185.7 and 182.6, and the 68 Hz coupling to Rh of the latter and the absence of Rh coupling in the former indicate that one carbonyl is bound to each metal. The IR spectrum confirms the terminal binding mode of both carbonyls. In the ^{1}H NMR spectrum the methyl groups appear as triplets at δ −0.23 and −1.39, and the absence of Rh coupling indicates that both are bound to Ir. This assignment is confirmed by selective ^{31}P decoupling experiments, which establish that the protons of both methyl groups couple to only the Ir-bound ^{31}P nuclei. The similarities of the spectral parameters for **4** with those of the methyl hydrido and methyl cyano analogues $[RhIrX(CH_3)(CO)_2(dppm)_2]$ (X = H, CN) previously described[8e] support a

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(25) Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G. L.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R. *J. Appl. Crystallogr.* **1999**, *32*, 115−119.

(26) (a) Cowie, M.; Dwight, S. K. *Inorg. Chem.* **1980**, *19*, 2500. (b) Cowie, M.; Dwight, S. K. *Inorg. Chem.* **1980**, *19*, 2508. (c) Gelmini, L.; Loeb, S. J.; Stephan, D. W. *Inorg. Chim. Acta* **1985**, *98*, L3.

Scheme 2

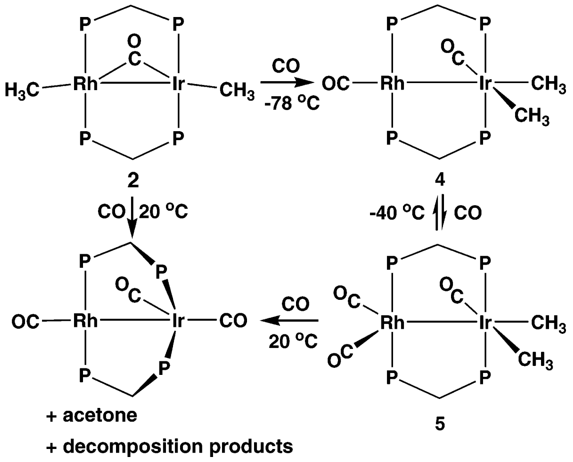
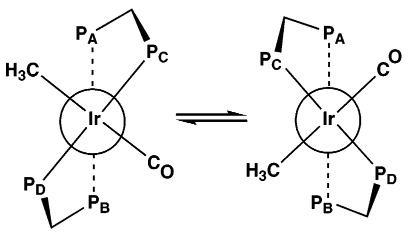


Chart 1

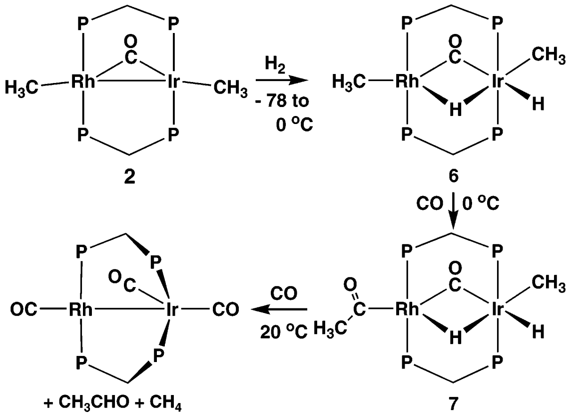


similar structural assignment, which has also been observed in the X-ray structural determination of the related cationic species $[RhIr(CH_3)(PMe_3)(CO)_2(dppm)_2]^+$.[8e]

Warming a sample of **4** to ambient temperature in the absence of CO does not regenerate **2**; compound **4** is stable for several hours under these conditions but decomposes to unidentified products after this time.

Whereas the ambient-temperature $^{31}P\{^1H\}$ NMR spectrum of **4** is characteristic of an AA′BB′X spin system, as noted for **2**, at −80 °C it transforms to a more complex pattern characteristic of an ABCDX ($X = {}^{103}Rh$) spin system, with the four ^{31}P resonances centered at approximately δ 14.7, 5.9, −14.1, and −24.1, indicating that all phosphorus nuclei are chemically inequivalent. As is commonly observed in Rh/Ir systems, the lower-field resonances correspond to the Rh-bound ^{31}P nuclei, and this is confirmed by the additional Rh coupling observed for these signals. The $^{31}P\{^1H\}$ NMR spectra of **4** at 0, −40, and −80 °C are given in Figure S5 in the Supporting Information. In contrast, the $^{13}C\{^1H\}$ NMR resonances for the carbonyl and the ^1H resonances for the methyl groups remain invariant over this temperature range, indicating that no exchange involving these groups is occurring. We suggest that the fluxional process being observed in the $^{31}P\{^1H\}$ NMR spectrum results from twisting of the complex about the Rh−Ir bond as outlined in Chart 1. In either extreme (**A** or **B**) the phosphorus nuclei on Rh (P_A and P_B) are inequivalent, being adjacent to either an Ir-bound CH_3 or CO group. At higher temperature rapid libration about the Rh−Ir bond exchanges these two ^{31}P environments, yielding an average signal for the two. A similar fluxional process has been observed for the related hydrido-alkynyl species $[RhIrH(CO)_2(\mu\text{-}C_2Ph)(dppm)_2]$.[27]

Scheme 3



In the reaction of **2** or **4** with excess CO at −40 °C the major species present (in approximately 65% yield by NMR), along with **4** and other unidentified compounds, is the dimethyl tricarbonyl species $[RhIr(CH_3)_2(CO)_3(dppm)_2]$ (**5**), shown in Scheme 2. The $^{13}C\{^1H\}$ NMR spectrum of this species is consistent with two carbonyls being terminally bound to Rh (δ 204.8, 190.2) having coupling to this metal of 77.4 and 60.2 Hz, respectively, and the third (δ 184.3) bound to Ir. As was the case for **4**, the methyl groups are inequivalent and both are bound to Ir, as indicated by the lack of Rh coupling in both the ^1H and ^{13}C NMR spectra and by the ^{31}P-decoupling experiments. Removal of the atmosphere of CO at 0 °C results in facile loss of the carbonyl, regenerating **4**. Warming **5** to ambient temperature under CO generates acetone, $[RhIr(CO)_3(dppm)_2]$, and unidentified decomposition products. Although no acetyl-containing complex could be unequivocally identified between 0 and 20 °C, owing to overlapping resonances of the other minor products in the ^1H and ^{31}P NMR spectra, one acyl carbonyl resonance was observed in the $^{13}C\{^1H\}$ NMR spectrum (δ 279). This signal displayed no coupling to Rh, so was clearly bound to iridium, suggesting that one of the two Ir-bound methyl groups had undergone migratory insertion.

To establish whether the generation of acetone from **2** occurred by an intra- or intermolecular pathway, crossover experiments were carried out using equimolar amounts of **2** and $[RhIr(CD_3)_2(\mu\text{-}CO)(dppm)_2]$ (**2−CD₃**), and the organic products were analyzed by GC/MS. Carbonylation of this mixture at between 300 and 600 Torr produced only $(CH_3)_2CO$ and $(CD_3)_2CO$, with no evidence of the crossover product $(CH_3)C(O)CD_3$, supporting an intramolecular pathway. If the reaction is carried out at slightly higher pressures (between 760 and 800 Torr), the crossover product is detected as approximately 4% of the total acetone produced. Also at higher pressures, carbonylation in the presence of an excess of the hydrogen atom source, tris(trimethylsilyl)silane (20 μL), produced trace amounts of acetaldehyde and methane in addition to mainly acetone (by NMR), suggesting the presence of small amounts of acetyl and methyl radicals. These observations are consistent with the onset of a radical pathway at higher pressures, consistent with earlier findings on the related dirhodium analogue.[15]

(b) Reaction of 2 with H₂. The reaction of **2** with H_2 shown in Scheme 3 proceeds readily at −78 °C,

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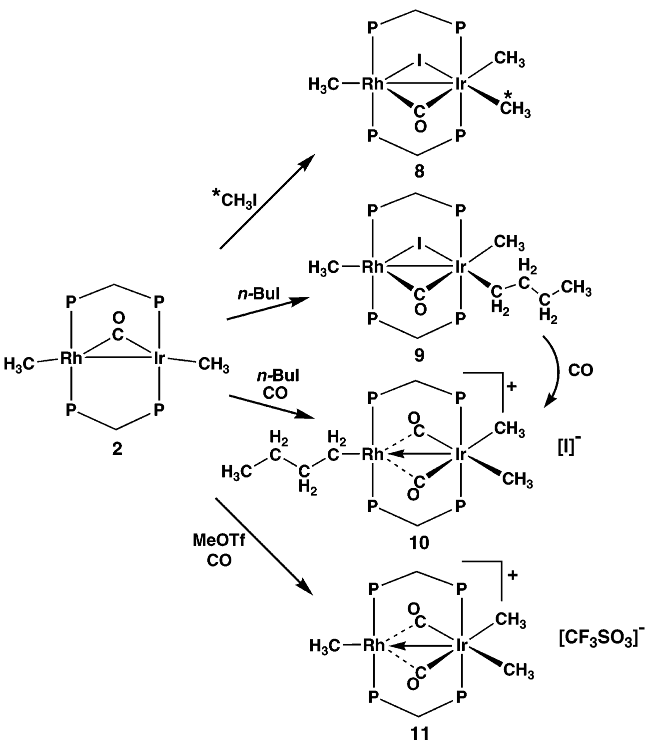
[27] George, D. S. A.; McDonald, R.; Cowie, M. *Organometallics* **1998**, *17*, 2553.

yielding the oxidative-addition product, the dihydride [RhIrH$(CH_3)_2$(μ-H)(μ-CO)$(dppm)_2$] (**6**). In the ^{1}H NMR spectrum the Ir-bound methyl group appears at δ −0.86 and shows coupling to only the adjacent pair of phosphorus atoms, while the Rh-bound methyl group, at δ −0.26, shows additional 2.0 Hz coupling to Rh. One hydride resonance appears as a doublet of multiplets at δ −10.65 and has coupling of 14 Hz to Rh, while the other appears as a triplet at −13.36, with coupling to only the Ir-bound phosphorus atoms. These resonances correspond to a hydride that bridges both metals and to one that is terminally bound to Ir, respectively. In the $^{13}C\{^1H\}$ NMR spectrum the bridging carbonyl appears at δ 233.3 and displays 23 Hz coupling to Rh. The hydride ligands are assumed to have a mutually *cis* arrangement as shown, on the basis of an assumption of H_2 attack in the A-frame "pocket", as has been reported for similar species.[27,28] Support for this arrangement is seen in the ^{1}H NMR spectrum of a ^{13}CO-enriched sample of **6** in which the high-field triplet of the terminal Ir-bound hydride displays additional *trans* coupling to the carbonyl ligand of 36 Hz. In addition, in a sample that is ^{13}CO and $^{13}CH_3$ enriched, no coupling is observed between the carbonyl and the Ir-bound methyl group, suggesting a mutually *cis* arrangement of these groups, as shown in Scheme 3. Compound **6** is stable for brief periods in solution under an atmosphere of H_2, after which it decomposes. It also slowly decomposes in the solid state, either under N_2 or vacuum, presumably by methane loss.

Compound **6** reacts with CO at 0 °C to give the acetyl-methyl-dihydride species [RhIrH(C(O)CH_3)(CH_3)(μ-H)$(dppm)_2$] (**7**). At temperatures below 0 °C the reaction is slow, with unreacted starting material being the major species after several hours. The ^{1}H NMR spectrum of **7** shows the Ir-bound methyl group as a triplet with coupling to the Ir-bound phosphorus nuclei, the bridging hydride at δ −11.83 with 20 Hz coupling to Rh and coupling to all phosphorus nuclei, and the terminal Ir-bound hydride at δ −13.58 with coupling to only the Ir-bound phosphorus nuclei. The acetyl methyl protons appear as a singlet at δ 0.97. In the $^{13}C\{^1H\}$ NMR spectrum the bridging carbonyl appears at δ 227.2 with 24 Hz coupling to Rh and the acyl carbonyl appears at δ 277.5 with 29 Hz coupling to Rh. The presence of the bridging and acyl carbonyls is supported by the IR spectrum, which shows stretches for these groups at 1742 and 1626 cm^{-1}, respectively. When an atmosphere of ^{13}CO gas is placed over a sample of unlabeled **6** at 0 °C, the $^{13}C\{^1H\}$ NMR spectrum taken immediately shows ^{13}CO incorporation only in the metal-bridged position, suggesting that migratory insertion precedes carbonyl addition. Compound **7** could not be isolated since it decomposes upon workup. Upon warming to room temperature under an atmosphere of CO, **7** transforms into [RhIr$(CO)_3(dppm)_2$],[21] together with methane and acetaldehyde, as established by NMR.

To determine whether the formation of acetaldehyde and methane occurs by intra- or intermolecular processes, a mixture of two isotopomers of **6**, namely, [RhIrD$(^{13}CH_3)_2$(μ-D)(μ-^{13}CO)$(dppm)_2$] and [RhIrH$(CH_3)_2$(μ-H)(μ-^{13}CO)$(dppm)_2$], were reacted with ^{13}CO and the products were analyzed by NMR (^{1}H and ^{13}C). The major isotopomers of acetaldehyde detected were $CH_3{}^{13}C(O)H$ and $^{13}CH_3{}^{13}C(O)D$, in an approximate 4:1 ratio, while a small amount of both $^{13}CH_3{}^{13}C(O)H$ and $CH_3{}^{13}C(O)D$ (each approximately 5−6% of the major isotopomer) was also observed. Because the isotopomer of **6** containing deuterium was present in about one-third the initial concentration of that containing hydrogen, the above ratio of the two major acetaldehyde isotopomers is not exactly as expected. However integration of all signals was difficult owing to overlap of the resonances. In addition, a small part of the discrepancy in the somewhat lower than expected amount of $^{13}CH_3{}^{13}C(O)D$ detected by $^{13}C\{^1H\}$ NMR spectroscopy may result from the differences in ^{13}C relaxation times of the acyl carbonyl bound to hydrogen or deuterium (see Experimental Section).[29] In the case of methane, the major products were CH_4 and $^{13}CH_3D$; however, significant amounts of the crossover products $^{13}CH_4$ and CH_3D were also observed.

Scheme 4



(c) Trialkyl Species. Compound **2** reacts with methyl iodide to yield the trimethyl product [RhIr$(CH_3)_3$(μ-I)(μ-CO)$(dppm)_2$] (**8**), shown in Scheme 4. In the ^{1}H NMR spectrum the Rh-bound methyl group, at δ −0.23, displays 2.0 Hz coupling to Rh, as well as coupling to the Rh-bound phosphorus nuclei, while the two others, at δ 0.85 and −0.17, are bound to Ir, as shown by their coupling to the Ir-bound phosphorus nuclei. When $^{13}CH_3I$ is used, exclusive $^{13}CH_3$ incorporation into one of the Ir-bound sites is observed, corresponding to the ^{1}H resonance at δ 0.85, which in this case displays coupling to ^{13}C of 132 Hz; the $^{13}C\{^1H\}$ resonance for this group appears at δ −11.6. The resonance for the bridging carbonyl appears at δ 220.4, with coupling of

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(28) Vaartstra, B. A.; Cowie, M. *Inorg. Chem.* **1989**, *28*, 3138.

(29) (a) Gust, D.; Pearson, H.; Armitage, I. M.; Roberts, J. D. *J. Am. Chem. Soc.* **1976**, *98*, 2723. (b) Lickfield, G. C.; Savitsky, G. B.; Beyerlein, A. L.; Spencer, H. G. *Macromolecules* **1983**, *16*, 396.

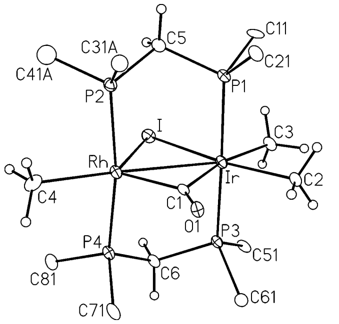


Figure 1. Perspective view of [RhIr$(CH_3)_3(\mu$-I$)(\mu$-CO$)$(dppm$)_2$] (**8**) showing the atom-labeling scheme. Nonhydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level. Hydrogens on the dppm methylene groups and the methyl ligands are drawn artificially small. Only the ipso carbons of the phenyl rings are shown.

Table 3. Selected Distances and Angles for [RhIr$(CH_3)_3(\mu$-I$)(\mu$-CO$)$(dppm$)_2$] (8)

Distances (Å)			
Ir−Rh	2.9152(8)	Rh−I	3.092(1)
Ir−I	2.8008(8)	Rh−C(1)	1.935(9)
Ir−C(1)	2.152(9)	Rh−C(4)	2.20(1)
Ir−C(2)	2.15(1)	P(1)−P(2)[a]	3.049(4)
Ir−C(3)	2.16(1)	P(3)−P(4)[a]	3.071(3)

Angles (deg)			
I−Ir−C(3)	85.9(3)	Rh−I−Ir	59.06(2)
C(1)−Ir−C(2)	86.9(4)	Rh−C(1)−Ir	90.8(4)
C(2)−Ir−C(3)	80.2(4)	Ir−C(1)−O(1)	135.4(7)
I−Rh−C(4)	129.5(3)	Rh−C(1)−O(1)	133.7(7)
C(1)−Rh−C(4)	127.5(4)		

[a] Nonbonded contacts.

38 Hz to Rh. If $^{13}CH_3I$ is added to ^{13}CO-enriched **2**, the ^{13}C resonances for the added methyl group and the ^{13}CO group do not show mutual coupling, suggesting that they have a mutually *cis* arrangement. This implies that the $^{13}CH_3$ and I fragments have a *trans* arrangement, as diagrammed in Scheme 4. The structure of **8** has been confirmed by an X-ray structure determination, shown in Figure 1, with selected bond lengths and angles given in Table 3. Although the crystal used in this determination was of poor quality (as were all crystals of this compound investigated), the data are certainly good enough to unambiguously establish the connectivity within the molecule. In particular, the iodo group is shown to be bridging both metals. The Rh−Ir separation (2.9152(8) Å) is intermediate between a normal single bond and a nonbonded separation, but is significantly shorter than the nonbonded, intraligand P−P separations (3.049(4), 3.071(3) Å), indicating compression along the Rh−Ir vector, suggesting a weak bonding interaction. The carbonyl ligand is symmetrically bridging, as shown by the similarity of the Ir−C(1)−O(1) and Rh−C(1)−O(1) angles. On Ir, the pair of methyl groups occupy the sites opposite the bridging I and CO groups, while on Rh the lone methyl group is opposite the Rh−Ir bond. All metal−methyl bonds appear normal.

Compound **2** also reacts readily with *n*-BuI to give a product, [RhIr$(CH_3)_2(n$-$C_4H_9)(\mu$-I$)(\mu$-CO$)$(dppm$)_2$] (**9**), that closely resembles the trimethyl species (**8**) in all spectroscopic parameters, so is assumed to have a similar structure. Only the methyl signal at δ −0.24 in the ^{1}H NMR spectrum displays coupling to Rh, so clearly this group is bound to Rh. The *n*-Bu and the other methyl group are bound to Ir, as shown in Scheme 4. In the ^{1}H NMR spectrum the resonances for the *n*-Bu group appear at δ 2.14, 1.01, 0.85, and 0.39 in a 2:2:2:3 ratio and the Ir-bound methyl group appears at δ −0.22. The ^{13}C resonance of the carbonyl group is very close to that observed for **8**, and its low-field chemical shift (δ 222.6) together with its 37 Hz coupling to Rh clearly establish its bridging geometry. Although the location of the iodo ligand cannot be established spectroscopically, it is assumed to bridge the metals, as determined for **8**, on the basis of the close similarity of the spectral parameters in the two compounds. Isotopic labeling on compound **9** was not carried out, so the relative positions of the Ir-bound *n*-butyl and methyl groups were not established. They are assigned the positions shown on the basis of analogy with the closely related compound **8**.

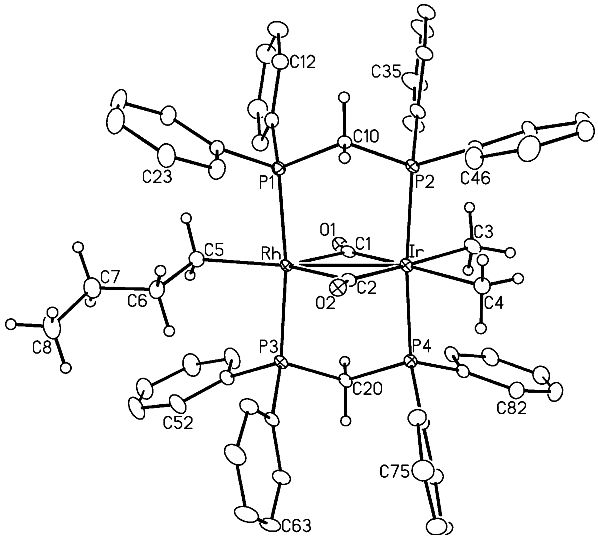


Figure 2. Perspective view of the complex cation of [RhIr$(n$-$C_4H_9)(CH_3)_2(\mu$-CO$)_2$(dppm$)_2$][I] (**10**). Thermal parameters as described for Figure 1.

Under a CO atmosphere compound **9** transforms to [RhIr$(CH_3)_2(n$-$C_4H_9)(\mu$-CO$)_2$(dppm$)_2$][I] (**10**), and this product can also be obtained in the reaction of **4** with *n*-BuI. Compound **10** displays only one resonance in the ^{13}C{^{1}H} NMR spectrum at δ 215.4, corresponding to both bridging carbonyl ligands, with typical coupling to Rh of 40 Hz. The IR spectrum confirms the bridging arrangement, displaying a band at 1776 cm^{-1}. In the ^{1}H NMR spectrum only one signal (integrating as six protons) at δ −0.19 is observed for the pair of methyl ligands, showing that they are chemically equivalent on the NMR time scale, and the resulting symmetry on either side of the RhIrP$_4$ plane is further shown by the appearance of only one resonance for the four dppm methylene protons. The methyl ligand resonance displays coupling to only the Ir-bound phosphines. The resonances for the *n*-butyl group appear at δ 0.02 (t), 0.59 (m), 1.78 (m), and 0.88 (m), integrating as 3:2:2:2. No Rh coupling is evident in any of the methylene signals; nevertheless the symmetry of the compound, as indicated by the other spectral data, make it clear that this group is bound to Rh. This has been confirmed by the X-ray structure determination of **10**, and a representation of the cationic complex is shown in Figure 2. Selected bond lengths and angles are given

Table 4. Selected Distances and Angles for [RhIr(n-C_4H_9)$(CH_3)_2$(μ-CO)$_2$(dppm)$_2$][I] (10)

Distances (Å)			
Ir−Rh	2.7916(4)	Rh−C(5)	2.122(5)
Ir−C(1)	2.031(5)	C(5)−C(6)	1.512(7)
Ir−C(2)	2.028(4)	C(6)−C(7)	1.537(8)
Ir−C(3)	2.144(5)	C(7)−C(8)	1.525(8)
Ir−C(4)	2.155(5)	P(1)−P(2)[a]	3.048(2)
Rh−C(1)	2.091(5)	P(3)−P(4)[a]	3.051(2)
Rh−C(2)	2.116(5)		
Angles (deg)			
C(1)−Ir−C(3)	90.9(2)	Ir−C(1)−O(1)	148.4(4)
C(2)−Ir−C(4)	91.0(2)	Ir−C(2)−O(2)	150.6(4)
C(3)−Ir−C(4)	81.2(2)	Rh−C(1)−O(1)	126.1(4)
C(1)−Rh−C(5)	126.0(2)	Rh−C(2)−O(2)	124.4(4)
C(2)−Rh−C(5)	141.1(2)	Rh−C(5)−C(6)	114.8(3)

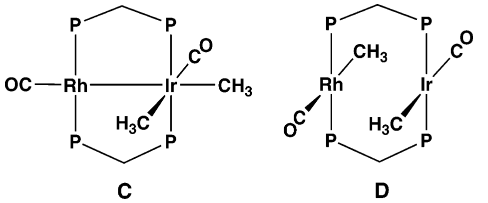
in Table 4. The Rh−Ir separation (2.7916(4)Å) is consistent with a single bond. Although the nature of the metal−metal bond is equivocal, we prefer to consider this interaction as a dative bond between a coordinatively saturated Ir(+3) center and an unsaturated Rh(+1) center; this dative bond is necessary to give Rh a favorable 16e configuration. Ignoring, for the moment, the metal−metal bond, the Ir center has an octahedral geometry in which the mutually *cis* methyl groups are opposite the semibridging carbonyls. These carbonyls are primarily bonded to Ir (Ir−C = 2.031(5), 2.028(4) Å) while involved in a somewhat weaker interaction with Rh (2.091(5), 2.116(5) Å). The angles at these carbonyl carbons are consistent with this description in which the Ir−C−O angles (148.4(4)°, 150.6(4)°) are more linear than the corresponding Rh−C−O angles (126.1(4)°, 124.4(4)°). The metal−alkyl distances are normal, as are the parameters within the *n*-butyl group.

If the reaction of **2** with methyl triflate is carried out at −78 °C, a trimethyl monocarbonyl species is formed, which upon warming rearranges to what appears to be an isomer. We have not investigated these isomers further, except to show that when $^{13}CH_3OTf$ is used, $^{13}CH_3$ incorporation occurs initially at Ir, with eventual scrambling of the label through all methyl sites, even at −78 °C. However, if the reaction is carried out under an atmosphere of CO, the trimethyl dicarbonyl product [RhIr$(CH_3)_3$(μ-CO)$_2$(dppm)$_2$][CF_3SO_3] (**11**) is formed, having spectral parameters that are almost identical to those of **10** (apart from the additional proton resonances due to the butyl group), indicating that it has an analogous structure, as diagrammed in Scheme 4. No evidence of migratory insertion is seen at the low pressure of CO investigated.

Discussion

The substitution of the chloride ligands in *trans*-[RhIrCl_2(CO)$_2$(dppm)$_2$] (**1**) by a pair of alkyl groups, to yield the products [RhIr(R)$_2$(μ-CO)(dppm)$_2$] (R = CH_3 (**2**), CH_2Ph (**3**)), is accompanied by loss of a carbonyl ligand, much as observed in the analogous dirhodium chemistry.[15] We had anticipated that this mixed-metal complex, in which one Rh had been replaced by a less labile Ir,[30] might be less prone to CO loss than the Rh_2 species, but this appears not to be the case. Loss of a carbonyl in *either* system upon replacement of Cl by CH_3 is surprising to us since the methyl group is generally thought to be a better donor than chloride, being comparable to an iodo ligand,[31] suggesting that the carbonyls would be more tightly bound than in the dichloro species. Consistent with this idea, the dicarbonyl product (**4**), once synthesized by CO addition to **2** at −80 °C, does not readily lose CO. The stage at which carbonyl loss occurs, in the transformation of **1** to **2**, is not known, but the irreversible formation of [RhIr$(CH_3)_2$(CO)$_2$(dppm)$_2$] (**4**) makes it clear that it cannot occur from a species such as **4**.

Chart 2



Irreversible addition of CO to **2** yields **4**, having the unexpected structure diagrammed as **C** in Chart 2. One might have expected compound **4** to have a structure **D**, analogous to the dichlorodicarbonyl precursor (**1**), a series of homobinuclear analogues,[32] and to the closely related [RhIrCl_2(CO)$_2$(depm)$_2$], containing the bis(diethylphosphino) methane ligand.[32c] In **C** both methyl groups are bound to Ir, giving a Rh(0)/Ir(+2) oxidation-state formulation, instead of the Rh(+1)/Ir(+1) formulation of **D**. The observed structure (**C**) will be favored by the greater number of stronger bonds associated with the third-row metal,[33] by the additional presence of a Rh−Ir bond, and by the greater tendency of Ir to assume a higher oxidation state.[31,34] Nevertheless, it remains puzzling that the closely related species **1** and **4** have different structures.

At approximately −40 °C under an atmosphere of CO the dicarbonyl compound **4** is transformed reversibly into the tricarbonyl product [RhIr$(CH_3)_2$(CO)$_3$(dppm)$_2$] (**5**). NMR experiments establish that the geometry of **5** is much like that of **4** in which both methyl groups remain bound to Ir with the additional carbonyl bound to Rh. The subsequent observation that warming a mixture of **5** and CO to ambient temperature results in the formation of acetone and [RhIr(CO)$_3$(dppm)$_2$] raises some interesting questions about the roles of the different metals in acetone formation. Presumably, formation of acetone from the dimethyl compound **5** proceeds via an unobserved acetyl- and methyl-containing intermediate from which reductive elimination of acetone occurs. On the basis of the well-established tendencies for migratory insertions involving metals within a given triad,[35] we would have expected acetyl formation to have occurred preferentially at Rh. However, the geometries

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of **4** and **5**, in which both methyl groups are bound to Ir, and the observation, in the $^{13}C\{^{1}H\}$ NMR spectrum of the reaction mixture, of an Ir-bound acyl group and the absence of signals for a Rh-bound acyl suggests that migratory insertion occurs at Ir. Although migratory insertion at Ir in preference to Rh is initially surprising, insertion at the heavier metal will be favored to some degree by the higher oxidation state of this metal.[36] We cannot rule out that methyl migration back to Rh occurs with subsequent migratory insertion at this metal, but no evidence of this is observed. The proposal of migratory insertion occurring at Ir suggests an interesting possibility that this process could somehow be promoted by the presence of the adjacent Rh center. Unfortunately the diiridium analogue has never been investigated, so we are unable to make this comparison. However, enhancement of migratory insertion at Pd and Pt by an adjacent Co center has been noted.[2h] We assume further that reductive elimination of acetone from a methyl, acetyl species also occurs from Ir. As noted earlier, reductive elimination is predominantly intramolecular, and we have observed no 2,3-butanedione, as was reported in the dirhodium system.[15a] Although the formation of this diketone was found to be intermolecular, it presumably results from carbonyl insertion into both Rh−CH_3 bonds under higher CO pressures, to generate a bis-acetyl intermediate. The absence of such a species in our Rh/Ir chemistry is consistent with the lower tendency for migratory insertion on Ir.[35] The appearance of both $(CH_3)_2CO$ and $(CH_3)_2{}^{13}CO$ when ^{13}CO is reacted with unenriched **2** indicates that migratory insertion involving both the original and added CO occurs, indicating that carbonyl scrambling is occurring at some stage in the reaction.

The failure of either the di- or tricarbonyl products (**4** or **5**) to reductively eliminate ethane, even though both methyl groups are mutually *cis* on the same metal, is consistent with previous findings that elimination of two alkyl groups is unfavorable, owing to the unfavorable reorientation energy of the directional alkyl groups.[37]

Compound **2** is susceptible to oxidative addition, reacting readily with H_2, CH_3I, n-C_4H_9I, and CH_3OTf. Addition of the alkyl groups was shown by labeling studies to be on Ir. More facile oxidative addition at the third-row metal in preference to the second-row analogue is not unexpected.[38] The observation that addition of CH_3I results in a product in which the two oxidative-addition fragments are mutually *trans* and not *cis* is also in keeping with previous observations in related mononuclear species.[39] In the case of methyl triflate addition to **2**, addition at low temperature showed that the methyl group initially attacks Ir, but that subsequent scrambling of the labeled CH_3 group over the other methyl sites occurs readily. In the iodo complexes **8** and **9** binding of the iodo ligand in a bridging site presumably inhibits the "merry-go-round" movement of equatorial ligands that is presumably responsible for ligand transfer from metal to metal, whereas for the triflate species loss of labile triflate anion will allow the scrambling to occur. Consistent with this proposal, replacement of the iodo ligand by CO results in migration of the *n*-butyl group from Ir to Rh in the transformation of **9** to **10**.

Oxidative addition of H_2 to compound **2** yields the dihydride $[RhIrH(CH_3)_2(\mu\text{-}H)(\mu\text{-}CO)(dppm)_2]$ (**6**), in which concerted addition in the A-frame "pocket", probably at Ir, has occurred, much as has been previously observed in $[RhIr(CO)_2(\mu\text{-}C_2Ph)(dppm)_2][CF_3SO_3]$,[27] $[RhIr(CO)_2(\mu\text{-}S)(dppm)_2]$,[28] and $[RhIr(CO)_2(\mu\text{-}Cl)(dppm)_2][BF_4]$.[28] Compound **6**, in which there is a pair of mutually *cis* hydride and methyl groups (one at Rh and the other at Ir), is believed to be the first example of its kind, and its stability for brief periods is surprising; we had expected reductive elimination of methane with concomitant decomposition of the complex, which presumably accounts for its lack of long-term stability (although we made no attempt to detect the products of decomposition).

The second step in the tandem addition of H_2 and CO to **2** yields the dihydrido, methyl acetyl product **7** (Scheme 3), in which migratory insertion has occurred at Rh to yield a product that is structurally analogous to the dimethyl precursor (**6**). The observation of migratory insertion at Rh in preference to Ir is consistent with well-established trends.[35] The addition of CO to **7** is in contrast to that noted earlier for **2**, in that migration of the Rh-bound methyl group to Ir does not occur. In the earlier observation (vide supra) we had noted that methyl migration from Rh to Ir resulted in Ir having a favored higher oxidation state. For **7** we can formulate a favorable Rh(+1)/Ir(+3) formulation, so methyl migration is not necessary. As a consequence, carbonyl addition presumably occurs at Rh followed by migratory insertion at that metal.

Crossover experiments establish that reductive elimination of acetaldehyde occurs preferentially by an intramolecular process. As noted, small amounts of the crossover products are obtained. The intramolecular reductive elimination is consistent with the mutually *cis* arrangement of the acetyl and hydride ligands at Rh, from which reductive elimination should be favorable. We also note that methane elimination from compound **7** yields significant amounts of the crossover products $^{13}CH_4$ and CH_3D in addition to those expected ($^{13}CH_3D$ and CH_4) for a concerted reductive-elimination process. We assume that reductive elimination of acetaldehyde from Rh occurs in preference to methane elimination from Ir, for which the metal−ligand bonds are stronger.[33] Elimination of acetaldehyde presumably yields a highly reactive intermediate which must not undergo concerted methane elimination.

Conclusions

Studies of the type described in this paper can be important in helping us understand the roles of adjacent metals in processes of relevance to catalysis by bimetallic species. Although much of what is observed for the

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Rh/Ir compounds under study is consistent with anticipated trends within a triad, some observations are contrary to expectations. As examples of reactivity proceeding as anticipated, oxidative addition is observed to occur at Ir in preference to Rh, while in one compound migratory insertion occurs preferentially at Rh. However, the observation, in a closely related compound, of migratory insertion appearing to occur at Ir in preference to Rh demonstrates how metals in close proximity can give rise to unexpected reactivity. In this case, facile ligand redistribution over the metals has led to a change in oxidation states of metals, which has led to concomitant changes in reactivity that would have been less favored in mononuclear systems.

This latter observation also demonstrates that small clusters have limits concerning their utility as models for reactivity at metal surfaces, and processes such as migratory insertion can be dictated by the natures of the ancillary ligands and the oxidation states of the individual metals, leading to reversals of trends usually associated with different metals. Such effects seem less likely on surfaces.

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Supporting Information Available: Tables of X-ray experimental details, atomic coordinates, interatomic distances and angles, anisotropic thermal parameters, and hydrogen parameters for compounds **8** and **10**. $^{31}P\{^1H\}$ and ^1H NMR spectra for compounds **2** and **6** and $^{31}P\{^1H\}$ NMR spectra at 0, −40, and −80 °C for compound **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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