

Heterobinuclear Alkyl Complexes of Rhodium and Iridium. Migratory Insertion or Ir-to-Rh Migration of a Methyl Group in Reactions with Small Molecules

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The reaction of $[\text{RhIr}(\text{CO})_3(\text{dppm})_2]$ ($\text{dppm} = \text{Ph}_2\text{PCH}_2\text{PPh}_2$) with methyl triflate yields $[\text{RhIr}(\text{CH}_3)(\text{CO})_3(\text{dppm})_2][\text{CF}_3\text{SO}_3]$ (**2**), having the methyl group and two terminal carbonyls on Ir and one carbonyl on Rh. An Ir \rightarrow Rh dative bond is proposed, giving Rh^+ a 16e square planar configuration. Reaction of **2** with hydrogen at ambient temperature yields $[\text{RhIrH}(\text{CO})_2(\mu\text{-H})_2(\text{dppm})_2]^+$ and methane. At 0 °C the intermediate $[\text{RhIrH}(\text{CH}_3)(\text{CO})_2(\mu\text{-H})(\text{dppm})_2][\text{CF}_3\text{SO}_3]$ is observed which under H_2 yields the trihydride species and CH_4 upon warming. Protonation of **2** with HCl and $\text{CF}_3\text{SO}_3\text{H}$ yields $[\text{RhIr}(\text{CH}_3)(\text{CO})_2(\mu\text{-H})(\mu\text{-Cl})(\text{dppm})_2]^+$ and $[\text{RhIr}(\text{CH}_3)(\text{CO})_2(\mu\text{-H})(\mu\text{-CO})(\text{dppm})_2]^{+2}$, respectively. The reaction of **2** with CO resulted in decomposition to several unidentified products. Reaction of **2** with CN^tBu yields the iminoacyl product $[\text{RhIr}(\text{CO})_2(\mu\text{-}^t\text{BuN}=\text{CMe})(\text{dppm})_2]^+$ via migratory insertion. Two intermediates in the formation of the iminoacyl species were identified at low temperature yielding some information about the subsequent migratory insertion. Although the reaction of **2** with SO_2 does not yield the SO_2 -insertion product, it does yield $[\text{RhIr}(\text{C}(\text{O})\text{-CH}_3)(\text{CO})_2(\mu\text{-SO}_2)(\text{dppm})_2]^+$, the product of methyl migration to Rh and migratory insertion of the methyl to a carbonyl group. A mechanism is proposed on the basis of the characterization of low-temperature intermediates. With ethylene, the substitution of one carbonyl in **2** and migration of the methyl group to Rh occurs. The structures of $[\text{RhIr}(\text{CH}_3)(\text{CO})_3(\text{dppm})_2][\text{CF}_3\text{SO}_3]\cdot\text{CH}_2\text{Cl}_2$ (**2**) and $[\text{RhIr}(\text{CO})_2(\mu\text{-}^t\text{BuN}=\text{CMe})(\text{dppm})_2][\text{CF}_3\text{SO}_3]$ (**8**) have been determined by X-ray crystallography. Compound **2** has a trigonal bipyramidal ligand arrangement at Ir with the methyl group opposite Rh. In addition the 18e Ir forms a dative bond to Rh giving the latter a square planar geometry. Compound **8** has an "A-frame" geometry in which the bridging iminoacyl group binds to Rh via nitrogen and to Ir via carbon.

Introduction

Alkyl complexes of the Co-triad metals are known to be involved as key intermediates in a variety of important catalytic processes such as the carbonylation of methanol,¹ the hydrogenation of carbon monoxide,² and olefin hydrogenation, hydroformylation, and hydrosilylation.³ Although work on mononuclear alkyl complexes of these metals has resulted in an improved understanding of the involvement of the metal-alkyl species in catalysis,⁴ very little has been reported on binuclear derivatives, in spite of continuing interest in utilizing complexes containing adjacent metals as catalysts.⁵

Interest, within this research group, in utilizing binuclear, dppm-bridged complexes of Rh and Ir as models for transformations occurring at two or more adjacent metal centers⁶ led to the investigation of alkyl derivatives of such complexes. As part of this study, the syntheses and reactivities of the complexes $[\text{MRe}(\text{CH}_3)(\text{CO})_4(\text{dppm})_2][\text{CF}_3\text{SO}_3]$ ($\text{M} = \text{Rh}, \text{Ir}$) have been reported,^{6c} and more recently a series of related alkyl compounds involving the Rh/Os,⁷ Rh/Mn,⁸ Rh/Mo,⁹ and

Rh/W⁹ combinations of metals have also been characterized and studied. Interestingly, in all the complexes characterized, the alkyl group was found to be coordinated to the *unsaturated* group 9 metal.

In this paper, methylation of the heterobinuclear species $[\text{RhIr}(\text{CO})_3(\text{dppm})_2]$ (**1**),^{6m} in which both metals are from group 9, is reported. It was of interest to establish whether the methyl group would bind to Rh, as in previous, related complexes^{6c,7–9} or whether binding to the heavier congener would be favored. It was also of interest to determine the reactivity of an alkyl group in a binuclear complex having a more labile Rh center adjacent to a less labile third-row metal such as

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Table 1. Spectroscopic Data for the Compounds^a

compd	IR, <i>b,c</i> cm ⁻¹	NMR		
		$\delta(^{31}\text{P}\{^1\text{H}\})^d$	$\delta(^1\text{H})^{e,f}$	$\delta(^{13}\text{C}\{^1\text{H}\})^e$
[RhIr(CH ₃)(CO) ₃ (dppm) ₂]-[CF ₃ SO ₃] ₂ (2)	1986 (s), 1971 (vs), 1912 (vs)	29.8 (dm, ¹ J _{Rh-P} = 120.0 Hz), -5.5 (m)	4.33 (m, 4H), -0.08 (t, 3H)	183.7 (dt, 1C, ¹ J _{Rh-C} = 75.0 Hz), 187.9 (t, 2C)
[RhIr(CH ₃)(H)(<i>μ</i> -H)(CO) ₂ -(dppm) ₂][CF ₃ SO ₃] ₂ (3)		25.7 (dm, ¹ J _{Rh-P} = 110.3 Hz), -1.1 (m)	4.42 (m, 2H), 4.07 (m, 2H), -0.16 (t, 3H), -10.02 (m, 1H, ¹ J _{Rh-H} = 15 Hz), -12.47 (m, 1H, ¹ J _{Rh-H} = 24 Hz, ² J _{P(Rh)-H} = 11.2 Hz)	187.5 (dt, 1C, ¹ J _{Rh-C} = 75.1 Hz), 174.4 (t, 1C)
[RhIr(CO) ₃ (<i>μ</i> -H)(dppm) ₂]-[CF ₃ SO ₃] ₂ (5)		22.7 (dm, ¹ J _{Rh-P} = 113.3 Hz), -4.8 (m)	4.43 (m, 4H), -10.2 (bm, 1H)	186.2 (dt, 1C, ¹ J _{Rh-C} = 79 Hz), 179.4 (b, 2C)
[RhIr(CH ₃)(CO) ₂ (<i>μ</i> -H)(<i>μ</i> -Cl)-(dppm) ₂][CF ₃ SO ₃] ₂ (6) ^g	1982 (s), 1932 (s)	22.1 (dm, ¹ J _{Rh-P} = 111.0 Hz), -4.4 (m)	4.40 (m, 2H), 3.83 (m, 2H), -0.25 (t, 3H), -9.50 (m, 1H, ¹ J _{Rh-H} = 22.0 Hz)	189.3 (dt, 1C, ¹ J _{Rh-C} = 84.5 Hz), 164.4 (t, 1C)
[RhIr(CH ₃)(CO) ₂ (<i>μ</i> -CO)-(<i>μ</i> -H)(dppm) ₂][CF ₃ SO ₃] ₂ (7) ^g	2000 (s), 1977 (vs), 1864 (med)	28.0 (dm, ¹ J _{Rh-P} = 98.3 Hz), -11.3 (m)	4.93 (m, 2H), 4.20 (m, 2H), 0.67 (t, 3H), -10.08 (bm, 1H)	199.9 (dtt, 1C, ¹ J _{Rh-C} = 26.2 Hz), 186.0 (dt, 1C, ¹ J _{Rh-C} = 76.5 Hz), 165.6 (m, 1C)
[RhIr(CO) ₂ (<i>μ</i> -C(CH ₃)=N ^t Bu)(dppm) ₂][CF ₃ SO ₃] ₂ (8)	1964 (vs), 1945 (s)	15.4 (dm, ¹ J _{Rh-P} = 132.6 Hz), 4.7 (m)	4.10 (m, 2H), 2.95 (m, 2H), 0.82 (s, 3H), 0.80 (s, 9H)	195.0 (dt, 1C, ¹ J _{Rh-C} = 65.4 Hz), 191.3 (t, 1C)
[RhIr(CH ₃)(CO) ₃ (^t BuNC)-(dppm) ₂][CF ₃ SO ₃] ₂ (9)		10.5 (dm, ¹ J _{Rh-P} = 138.5 Hz), -16.7 (m)	5.48 (m, 2H), 5.13 (m, 2H), 0.92 (s, 9H), -1.18 (t, 3H)	181.3 (dt, ¹ J _{Rh-C} = 74 Hz), 181.9 (dt, ¹ J _{Rh-C} = 77 Hz), 176.3 (t)
[RhIr(CH ₃)(CO) ₂ (^t BuNC)-(dppm) ₂][CF ₃ SO ₃] ₂ (10)		11.9 (dm, ¹ J _{Rh-P} = 140.9 Hz), -20.6 (m)	5.15 (m, 2H), 4.86 (m, 2H), 0.93 (s, 9H), 0.22 (t, 3H)	180.2 (dt, 1C, ¹ J _{Rh-C} = 68.5 Hz), 233.3 (b, 1C)
[RhIr(CH ₃)(CO) ₂ (C ₂ H ₄)-(dppm) ₂][CF ₃ SO ₃] ₂ (11)	1985 (s) ⁱ	32.6 (dm, ¹ J _{Rh-P} = 141.1 Hz), 5.4 (m)	3.32 (m, 4H), 0.75 (t, 4H), 0.35 (td, 3H, ² J _{Rh-H} = 3.0 Hz)	204.7 (dm, 2C, ¹ J _{Rh-C} = 20.0 Hz)
[RhIr(CH ₃)(CO) ₃ (SO ₂)-(dppm) ₂][CF ₃ SO ₃] ₂ (12)		20.9 (m), ^k -1.8 (m)	4.85 (m, 2H), 3.45 (m, 2H), 0.33 (t, 3H)	194.9 (dt, 1C, ¹ J _{Rh-C} = 56.3 Hz), 178.4 (t, 1C), 175.2 (dt, 1C, ¹ J _{Rh-C} = 63.4 Hz)
[RhIr(CH ₃)(CO) ₂ (<i>μ</i> -SO ₂)-(dppm) ₂][CF ₃ SO ₃] ₂ (13)		37.7 (dm, ¹ J _{Rh-P} = 138.2 Hz), -0.8 (m)	4.12 (m, 2H), 3.50 (m, 2H), 1.08 (td, ² J _{Rh-H} = 3.7 Hz, 3H)	180.6 (dt, 1C), 170.3 (dt, 1C, ² J _{C-C} = 13.6 Hz)
[RhIr(CO) ₂ (COCH ₃)(<i>μ</i> -SO ₂)-(dppm) ₂][CF ₃ SO ₃] ₂ (14) ^g	2030 (s), 1986 (vs), 1640 (m), 1055 (m) ^j	27.4 (dm, ¹ J _{Rh-P} = 156.6 Hz), -1.2 (m)	4.18 (m, 2H), 3.40 (m, 2H), 1.15 (s, 3H)	255.5 (d, 1C, ¹ J _{Rh-C} = 34.2 Hz), 172.7 (dt, 1C), 168.7 (dt, 1C, ² J _{C-C} = 12.6 Hz)

^a Abbreviations used: med = medium, st = strong, vs = very strong, s = singlet, d = doublet, t = triplet, m = multiplet, dt = doublet of triplets, dm = doublet of multiplets, bs = broad singlet, b = broad. ^b Nujol mull on KBr disk unless otherwise stated. ^c Values are for $\nu(\text{CO})$. ^d Vs 85% H₃PO₄, -40 °C in CD₂Cl₂ unless otherwise stated. ^e Vs TMS, -40 °C in CD₂Cl₂ solvent unless otherwise stated. ^f Resonances for phenyl protons appear as multiplets in the range δ 6.9–8.1 for all compounds. ^g NMR data at 25 °C. ^h NMR data at -80 °C. ⁱ IR in CH₂Cl₂. ^j $\nu(\text{SO})$ second SO stretch obscured by triflate anion stretches. ^k Magnitude of Rh–P coupling could not be determined because of the nature of the multiplet.

Ir, which should in turn be more prone to oxidative addition. Methylation of the above RhIr complex was also undertaken to provide comparisons with the related studies on the dirhodium¹⁰ and diiridium analogues.^{11,12} A preliminary report of some of this work has appeared.¹¹

Experimental Section

General Comments. All solvents were dried (using the appropriate drying agents) and distilled before use and were stored under argon. Deuterated solvents used for NMR experiments were degassed and stored under argon over molecular sieves. Reactions were carried out at room temperature (unless otherwise stated) by using standard Schlenk procedures, and compounds, that were isolated as solids were purified by recrystallization. A flow rate of ca. 0.2 mL s⁻¹ was

employed for all reactions which involved purging a solution with a gas. Purified argon, ethylene, and hydrogen were purchased from Linde. Carbon monoxide, sulfur dioxide, and hydrogen chloride gas were all purchased from Matheson. ¹³CO (99%) was supplied by Isotec Inc. All gases were used as received. Hydrated rhodium(III) chloride was purchased from Engelhard Scientific, whereas triflic acid, methyl triflate, *tert*-butyl isocyanide, trimethylphosphine, and triphenyl phosphite were obtained from Aldrich. The compound [RhIr(CO)₃(dppm)₂]₂ (**1**)^{6m} was prepared as previously reported.

The NMR spectra were recorded on a Bruker AM-400 spectrometer at 400.1 MHz for ¹H, at 161.9 MHz for ³¹P{¹H} and at 100.6 MHz for ¹³C{¹H} spectra. The ¹³C{¹H}{³¹P} NMR spectra were obtained on a Bruker WH-200 spectrometer operating at 50.32 MHz. All ¹³C{¹H} NMR spectra were obtained using ¹³CO-enriched samples unless otherwise stated. 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. Carbonyl stretches reported are for nonisotopically enriched samples. Spectroscopic parameters for the compounds prepared are found in Table 1. Elemental analyses were performed by the microanalytical service within the department.

Preparation of Compounds. (a) [RhIr(CH₃)(CO)₃(dppm)₂][CF₃SO₃]₂ (**2**). The compound [RhIr(CO)₃(dppm)₂]₂ (**1**) (200 mg, 0.174 mmol) was dissolved in 20 mL of benzene, to which was added 1 equiv (19.7 μ L, 0.174 mmol) of methyl triflate. The solution was stirred for 3 h during which time the orange solution became cloudy and a brown solid precipitated. The volume of the solvent was reduced to about 5 mL, and precipitation was completed by adding 30 mL of diethyl ether. The brown solid was collected and washed with three 10 mL portions of Et₂O and dried under an argon stream and then in vacuo (70–77% yield). Anal. Calcd for IrRhSP₄F₃O₆C₅₅H₄₇: C, 50.35; H, 3.61. Found: C, 50.17; H, 3.83.

(b) [RhIr(CO)₃(*μ*-H)(dppm)₂][CF₃SO₃]₂ (**5**). A 55 mg amount of [RhIrCH₃(CO)₃(dppm)₂][CF₃SO₃]₂ (**2**) was dissolved

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in 0.6 mL of CD_2Cl_2 in an NMR tube at 0 °C under N_2 . An atmosphere of H_2 was flushed through the solution briefly (*ca.* 2 min), and the reaction system was allowed to stand at 0 °C for 1 h, after which the solution was cooled to -78 °C and the H_2 atmosphere was removed. An atmosphere of dinitrogen was introduced, and the temperature was then warmed slowly to ambient conditions. The ^1H and ^{13}C NMR spectra were taken immediately.

(c) $[\text{RhIr}(\text{CH}_3)(\text{CO})_2(\mu\text{-H})(\mu\text{-Cl})(\text{dppm})_2][\text{CF}_3\text{SO}_3]$ (6). Compound **2** (100 mg, 0.076 mmol) was dissolved in 20 mL of CH_2Cl_2 . Slightly more than 1 equiv of HCl (in the form of 10 mg of *N,N*-dimethylacetamide·HCl, 0.081 mmol) in 10 mL of CH_2Cl_2 was added, causing an immediate color change from orange to light yellow. The solution was stirred for 2 h during which time the color slowly darkened to a deeper yellow. The solvent was removed under vacuum, and the orange solid was recrystallized from $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ giving a 60% yield. Anal. Calcd for $\text{IrRhClSP}_4\text{F}_3\text{O}_5\text{C}_{54}\text{H}_{48}$: C, 49.12; H, 3.66; Cl, 2.68. Found: C, 48.38; H, 3.43; Cl, 3.93. Analytical results are variable owing to loss of the CH_2Cl_2 of crystallization. The above results, obtained over a short time span, to ensure consistent results among the different elements, agree well with the calculated values if 0.25 equiv of CH_2Cl_2 is assumed (calcd: C, 48.56; H, 3.64; Cl, 3.96).

(d) $[\text{RhIr}(\text{CH}_3)(\text{CO})_3(\mu\text{-H})(\text{dppm})_2][\text{CF}_3\text{SO}_3]_2$ (7). To a solution of **2** (100 mg, 0.076 mmol) in 10 mL of CH_2Cl_2 was added 1 equiv (6.7 μL , 0.076 mmol) of $\text{CF}_3\text{SO}_3\text{H}$, causing the dark orange solution to change to a yellow color instantly. After the solution was stirred for 1 h, the solvent volume was reduced to *ca.* 5 mL and the yellow solid was precipitated by the addition of 15 mL of Et_2O . The solid was then collected, washed with Et_2O , and dried under an argon stream. It was then recrystallized from $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$, dried again under an argon stream, and then under vacuo (67% yield). Anal. Calcd for $\text{IrRhS}_2\text{P}_4\text{F}_6\text{O}_9\text{C}_{56}\text{H}_{48}$: C, 46.11; H, 3.30. Found: C, 45.49; H, 2.96.

(e) $[\text{RhIr}(\text{CO})_2(\mu\text{-C}(\text{CH}_3)=\text{N}^t\text{Bu})(\text{dppm})_2][\text{CF}_3\text{SO}_3]$ (8). To a solution of **2** (80 mg, 0.016 mmol) in 10 mL of CH_2Cl_2 was added 1 equiv (6.9 μL , 0.061 mmol) of $^t\text{BuNC}$. The color of the solution changed from orange to brown then to purple. After the solution was stirred for 3 h, the solvent was removed under vacuum giving a purple solid. Diethyl ether was layered over a CH_2Cl_2 solution of the purple solid and allowed to diffuse slowly giving purple crystals of the product in about 2 days (67% yield). Anal. Calcd for $\text{IrRhSP}_4\text{F}_3\text{O}_5\text{NC}_{59}\text{H}_{56}$: C, 51.83; H, 4.13; N, 1.02. Found: C, 51.09; H, 4.03; N, 1.13.

(f) $[\text{RhIr}(\text{CH}_3)(\text{CO})_2(\text{C}_2\text{H}_4)(\text{dppm})_2][\text{CF}_3\text{SO}_3]$ (11). Ethylene was passed through a 5 mL CH_2Cl_2 solution of **2** (80 mg, 0.061 mmol) for *ca.* 1 min. The solution was then stirred under a static atmosphere of the gas for 18 h. To obtain NMR spectra, the reaction was carried out in CD_2Cl_2 solution under an ethylene atmosphere. The solid product was not isolated in this reaction.

(g) $[\text{RhIr}(\text{CO})_2(\text{COCH}_3)(\mu\text{-SO}_2)(\text{dppm})_2][\text{CF}_3\text{SO}_3]$ (14). Compound **2** (80 mg, 0.061 mmol) was dissolved in 5 mL of CH_2Cl_2 . Sulfur dioxide gas was then passed through the solution for about 1 min. The color of the solution changed instantly from orange to dark brown and then to red. The mixture was then stirred under a static atmosphere of the gas for 1.5 h, after which time the product was precipitated, washed with ether, and dried under an argon stream. The solid was then recrystallized from $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ and dried again under a stream of argon (84% yield). Anal. Calcd for $\text{IrRhS}_2\text{P}_4\text{F}_3\text{O}_8\text{C}_{55}\text{H}_{47}$: C, 48.01; H, 3.44; S, 4.66. Found: C, 48.30; H, 3.86; S, 4.58.

Characterization of Low-Temperature Intermediates.

(a) Reaction of Compound 2 with H_2 . In an NMR tube 30 mg (0.023 mmol) of **2** was dissolved in 0.6 mL of CD_2Cl_2 under an N_2 atmosphere, and the solution was cooled in an ice/salt bath. Dihydrogen was passed through the solution for *ca.* 3 min, and the mixture was allowed to stand for 2 h at this temperature, after which the NMR spectra were obtained at 0 °C. Observation of the solution at earlier times or at lower

temperatures showed only incomplete reaction. $[\text{RhIr}(\text{CH}_3)(\text{H})(\mu\text{-H})(\text{CO})_2(\text{dppm})_2][\text{CF}_3\text{SO}_3]$ (**3**) was the only species other than **2** and **4** observed.

(b) Reaction of Compound 2 with $^t\text{BuNC}$. The procedure in (a) was duplicated except that 1 equiv of neat $^t\text{BuNC}$ (2.6 μL , 0.023 mmol) was syringed into the solution at -78 °C in a dry ice-acetone bath. The orange solution darkened immediately and so was taken immediately for NMR characterization. At temperatures below -40 °C several intermediates were observed which could not be identified owing to their low concentrations and overlapping signals. At -40 °C the major species was shown to be $[\text{RhIr}(\text{CH}_3)(\text{CO})_3(^t\text{BuNC})(\text{dppm})_2][\text{CF}_3\text{SO}_3]$ (**9**). Upon warming of the sample in the NMR probe to 0 °C, a second species $[\text{RhIr}(\text{CH}_3)(\text{CO})_2(^t\text{BuNC})(\text{dppm})_2][\text{CF}_3\text{SO}_3]$ (**10**) was identified. This species transformed to **8** upon further warming.

(c) Reaction of Compound 2 with Sulfur Dioxide. Compound **2** (30 mg, 0.023 mmol) was dissolved in 0.6 mL of CD_2Cl_2 in an NMR tube, capped with a rubber septum, and cooled to *ca.* -60 °C by immersing it in a dry ice/chloroform mixture. Sulfur dioxide gas was passed through the solution for 1 min, and NMR spectra of this solution were obtained immediately afterward at -40 °C. The spectra showed the presence of $[\text{RhIr}(\text{CH}_3)(\text{CO})_3(\text{SO}_2)(\text{dppm})_2][\text{CF}_3\text{SO}_3]$ (**12**). The sample was allowed to warm to room temperature and was maintained at this temperature for another 10 min. The NMR spectra of the solution, obtained afterward at -40 °C, showed the presence of $[\text{RhIr}(\text{CH}_3)(\text{CO})_2(\mu\text{-SO}_2)(\text{dppm})_2][\text{CF}_3\text{SO}_3]$ (**13**). Alternatively, compound **13** was obtained by passing SO_2 gas through a solution of **2** (30 mg, 0.023 mmol) in 0.6 mL of CD_2Cl_2 , until the solution color changed from orange to red (*ca.* 1 min). The solution was then transferred quickly to a rubber septum-capped NMR tube under nitrogen, and the reaction was quenched by immersing the tube in a dry ice/chloroform bath until the NMR spectra were obtained shortly afterward.

X-ray Data Collection. **(a) $[\text{RhIr}(\text{CH}_3)(\text{CO})_3(\text{dppm})_2][\text{CF}_3\text{SO}_3]\cdot\text{CH}_2\text{Cl}_2$ (2).** Orange crystals of **2** were obtained by slow diffusion of ether into a concentrated CH_2Cl_2 solution of the compound. Several suitable crystals were mounted and flame sealed in glass capillaries under solvent vapor to minimize decomposition or deterioration due to solvent loss. Data were collected on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated $\text{Mo K}\alpha$ radiation. Unit cell parameters were obtained from a least-squares refinement of the setting angles of 25 reflections in the range $20.0^\circ \leq 2\theta \leq 24.0^\circ$. The monoclinic diffraction symmetry and the systematic absences ($0k0$, $k = \text{odd}$) were consistent with the space groups $P2_1$ or $P2_1/m$; the noncentrosymmetric space group was established by successful refinement of the structure.

Intensity data were collected at 22 °C using the $\theta/2\theta$ scan technique to a maximum $2\theta = 50.0^\circ$, collecting reflections with indices of the form $+h, \pm k, \pm l$. Backgrounds were scanned for 25% of the peak width on either side of the peak scan. Three reflections were chosen as intensity standards, being remeasured at 120-min intervals of X-ray exposure time. There was no significant systematic decrease in the intensities of these standards; thus, no decomposition correction was applied. A total of 6760 unique reflections were measured and processed in the usual way, using a value of 0.04 for p^{13} to downweight intense reflections; 6248 of these were considered to be observed ($F_o^2 \geq 3\sigma(F_o^2)$) and were used in subsequent calculations. Absorption corrections were applied to the data using the method of Walker and Stuart.^{14,15}

(b) $[\text{RhIr}(\text{CO})_2(\mu\text{-C}(\text{CH}_3)=\text{N}^t\text{Bu})(\text{dppm})_2][\text{CF}_3\text{SO}_3]$ (8). Diffusion of ether into a concentrated CH_2Cl_2 solution of **8** yielded purple crystals of the complex, several of which were mounted and flame sealed in glass capillaries under solvent

(13) Doedens, R. J.; Ibers, J. A. *Inorg. Chem.* **1967**, *6*, 204.

(14) Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A: Found Crystallogr.* **1983**, *A39*, 158.

(15) Programs used were those of the Enraf-Nonius Structure Determination Package by B. A. Frenz, in addition to local programs by R. G. Ball.

Table 2. Crystallographic Data for [RhIr(CH₃)(CO)₃(dppm)₂][CF₃SO₃]·CH₂Cl₂ (2**) and [RhIr(CO)₂(μ-C(CH₃)=N^tBu)(dppm)₂][CF₃SO₃] (**8**)**

	compd	
	2	8
formula	C ₅₆ H ₄₉ Cl ₂ F ₃ IrO ₆ P ₄ RhS	C ₅₉ H ₅₆ Cl ₂ F ₃ IrNO ₅ P ₄ RhS
fw	1396.99	1367.18
cryst shape	monoclinic prism	monoclinic prism
cryst dimens, mm	0.48 × 0.38 × 0.32	0.44 × 0.32 × 0.30
space group	<i>P2</i> ₁ (No. 4)	<i>P2</i> ₁ / <i>n</i> (nonstandard setting of <i>P2</i> ₁ / <i>c</i> , No. 14)
temp, °C	22	-65
radiation (λ, Å)	graphite-monochromated Mo Kα (0.710 69)	
unit cell params		
<i>a</i> , Å	10.482(7)	12.708(2)
<i>b</i> , Å	25.435(5)	24.237(3)
<i>c</i> , Å	11.391(3)	20.328(2)
β, deg	114.07(3)	98.87(2)
<i>V</i> , Å ³	2773(4)	6186(2)
<i>Z</i>	2	4
ρ(calcd), g cm ⁻³	1.673	1.468
linear abs coeff (μ), cm ⁻¹	29.329	25.823
range of transm factors	0.901–1.094	0.913–1.037
max 2θ, deg	50.0	50.0
scan type	θ/2θ	θ/2θ
scan rate, deg/min		
tot. unique reflcns	6760 (<i>h, ±k, ±l</i>)	11 042 (<i>+h, +k, l</i>)
tot. observns (NO)	6248 (<i>F</i> _o ² ≥ 3 <i>s</i> (<i>F</i> _o ²))	3029 (<i>F</i> _o ² ≥ 3 <i>s</i> (<i>F</i> _o ²))
final no. params	660	362
varied (NV)		
error in obs of unit weight (GOF) ^a	2.119	1.570
<i>R</i> ^b	0.040	0.072
<i>R</i> _w ^c	0.055	0.072

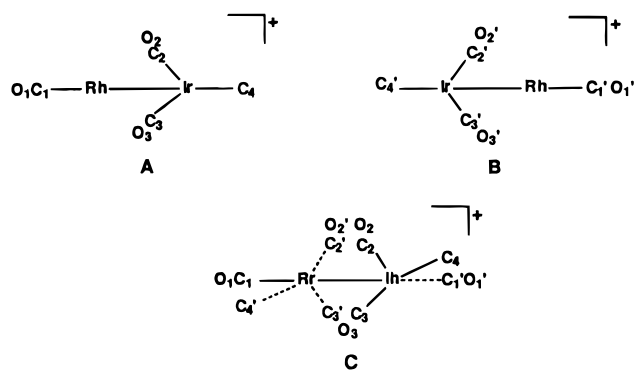
^a GOF = [Σ*w*(|*F*_o| - |*F*_c|)²/(NO - NV)]^{1/2} where *w* = 4*F*_o²/σ²(*F*_o²).
^b *R* = Σ||*F*_o| - |*F*_c||/Σ|*F*_o|. ^c *R*_w = [Σ*w*(|*F*_o| - |*F*_c||)²/Σ*w F*_o²]^{1/2}.

vapor to minimize decomposition or deterioration due to solvent loss. Data collection and the derivation of unit-cell parameters proceeded in a manner similar to that above, except that data collection was carried out at a different temperature. The monoclinic diffraction symmetry and the systematic absences (*h*0*l*, *h* + *l* = odd; 0*k*0, *k* = odd), were consistent with the space group *P2*₁/*n*.

Intensity data were collected at -65 °C using the θ/2θ scan technique to a maximum 2θ = 50.0°, collecting reflections with indices of the form +*h*, +*k*, ±*l*. Of 11 042 unique reflections measured, 3029 were considered to be observed and were used in subsequent calculations, with absorption corrections applied as above. See Table 2 for crystal data and more information on X-ray data collection for both compounds.

Structure Solution and Refinement. (a) [RhIr(CH₃)(CO)₃(dppm)₂][CF₃SO₃]·CH₂Cl₂ (**2**). The structure of **2** was solved in the space group *P2*₁ using standard Patterson and Fourier techniques. Although location of all atoms was straightforward, initial refinements resulted in unusually high thermal parameters for the atoms of the carbonyl groups and the methyl carbon atom. In addition the isotropic thermal parameter for Ir was unusually high and that of Rh was unusually low. A difference Fourier calculation at this stage showed the presence of superimposed methyl and carbonyl groups. This together with the anomalous thermal parameters for the metals led to the model shown (Chart 1) in which two of the molecules, represented as **A** and **B** in the diagram (the dppm ligands are omitted for clarity), are disordered in approximately a 60:40 ratio (determined from the relative peak intensities of the ordered and disordered atoms and by refinement of the occupancy factors of the disordered carbonyl oxygen atoms). The two molecules, **A** and **B**, are superimposed such that they have the metal atom positions overlapping. This is represented as **C**, in which Rr and Ir indicate the disordered Rh and Ir positions with Rr being 60% Rh and Ir being 60% Ir. The solid lines connect atoms of the major rotomer whereas the dashed lines show the minor one. The disordered atoms are either unprimed or primed, with the former having the higher occupancy. Two positions are resolved for the half-occupancy oxygen atoms O(2) and O(2)' of the second carbonyl,

Chart 1



whereas the two half-occupancy oxygens of the third disordered carbonyl are superimposed so that only one full occupancy O(3) is resolved. There was no apparent disorder involving the phosphine groups, which appeared to be well behaved. A similar kind of disorder was observed in the X-ray structure determination of [RhMn(CO)₃(μ-CO₃)(dppm)₂].^{6g}

All non-hydrogen atoms of the complex cation and anion were located. In addition, one molecule of CH₂Cl₂ per formula unit of complex was also located. Full matrix least-squares refinements proceeded so as to minimize the function Σ*w*(|*F*_o| - |*F*_c|)², where *w* = 4*F*_o²/σ²(*F*_o²). Atomic scattering factors^{16,17} and anomalous dispersion terms¹⁸ were taken from the usual tabulations. Hydrogen atoms, with the exception of the methylene chloride hydrogens, were included as fixed contributions but not refined. Their idealized positions were calculated from the geometries about the attached carbon atoms, using a C-H bond length of 0.95 Å, and they were assigned thermal parameters 20% greater than the equivalent isotropic *B*s of their attached C atoms.

The final model, with 660 parameters refined, converged to values of *R* = 0.041 and *R*_w = 0.056. Since the space group *P2*₁ is chiral, refinement of the structure in the opposite hand was also carried out, but this yielded significantly poorer residuals (*R* = 0.047 and *R*_w = 0.067), suggesting that the original solution was the right one. In the final difference Fourier map the 10 highest residuals (1.8–1.1 e/Å³) were found to be in the vicinity of the metal and carbonyl groups. A typical carbon atom in an earlier synthesis had an electron density of ca. 5.9 e/Å³. The positional and isotropic thermal parameters of the non-hydrogen atoms of **2** are given in Table 3.

(b) [RhIr(CO)₂(μ-C(CH₃)=N^tBu)(dppm)₂][CF₃SO₃] (**8**). The structure was solved in the space group *P2*₁/*n* using standard Patterson and Fourier techniques. Refinement proceeded as described for compound **2**. All non-hydrogen atoms were ultimately located. Hydrogen atoms, as well as the carbon atom of the triflate anion, were included as fixed contributions as described earlier.

The triflate anion was found to be badly behaved. Although the SO₃ moiety was located and refined well, the CF₃ moiety did not refine well. These atoms were located in the Fourier maps, but the carbon atom invariably refined toward the fluorine atom positions. This carbon atom was fixed at its observed position and was not refined. The thermal parameters for the fluorines were very high, consistent with the smeared out electron density observed in their positions on Fourier maps. The final model, with 362 parameters refined, converged to values of *R* = 0.072 and *R*_w = 0.072. In the final difference Fourier map, the 10 highest residuals (1.6–1.0 e/Å³) were found to be in the vicinity of the phenyl rings, the carbonyl groups, the triflate anion, and the dppm methylene groups. A typical carbon atom in an earlier synthesis had an

(16) Cromer, D. T.; Waber, J. T. *International Tables for Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2A.

(17) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

(18) Cromer, D. T.; Liberman, D. *J. Chem. Phys.* **1970**, *53*, 1891.

Table 3. Positional and Thermal Parameters for the Core Atoms of [RhIr(CH₃)(CO)₃(dppm)₂]-[CF₃SO₃]-CH₂Cl₂ (2)^a

atom	x	y	z	B, ^b Å ²
Ir	0.20140(4)	0.00000	-0.09826(4)	2.39(1)*
Rh	0.35373(5)	0.02892(2)	0.15216(4)	2.36(1)*
P(1)	0.1539(2)	-0.0847(1)	-0.0479(2)	2.40(6)*
P(2)	0.3001(2)	-0.0479(1)	0.2311(2)	2.49(6)*
P(3)	0.2529(2)	0.0775(1)	-0.1782(2)	2.54(6)*
P(4)	0.4012(2)	0.1131(1)	0.1011(2)	2.53(6)*
O(1)	0.570(2)	0.0549(9)	0.414(2)	10.1(6)
O(1)'	-0.016(3)	-0.025(1)	-0.363(2)	8.0(7)
O(2)	0.501(1)	-0.0365(5)	0.018(1)	4.6(3)
O(2)'	0.531(2)	-0.0346(8)	0.047(2)	4.3(4)
O(3)	0.0326(8)	0.0662(4)	0.022(1)	7.8(3)*
C(1)	0.494(2)	0.0462(8)	0.320(2)	5.0(4)
C(1)'	0.075(1)	-0.0163(6)	-0.277(1)	0.1(2)
C(2)	0.388(2)	-0.0217(8)	-0.048(2)	4.1(4)
C(2)'	0.470(2)	-0.010(1)	0.084(2)	3.7(5)
C(3)	0.090(2)	0.0405(6)	-0.030(1)	3.2(3)
C(3)'	0.141(3)	0.051(1)	0.071(2)	4.1(6)
C(4)	0.098(3)	-0.031(1)	-0.291(3)	8.4(7)
C(4)'	0.451(3)	0.054(1)	0.337(2)	4.1(6)
C(5)	0.2655(8)	-0.1024(4)	0.1172(8)	2.5(2)*
C(6)	0.2913(8)	0.1318(4)	-0.0648(8)	3.0(2)*

^a Phenyl carbons and atoms of the triflate anion and the solvent molecule are given in the Supporting Information. Numbers in parentheses are estimated standard deviations in the least significant digits in this and all subsequent tables. The atoms labeled Rh and Ir are actually a 60:40 mix of Rh/Ir and Ir/Rh, respectively, owing to disorder (see Experimental Section). Primed atoms have 40% occupancy and are related to the unprimed (60% occupancy) atoms by the rotational disorder. ^b Starred *B* values are for atoms refined anisotropically. *B* values for the anisotropically refined atoms are given in the form of the equivalent isotropic Gaussian displacement parameter defined as $\frac{1}{3}[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos \gamma)\beta_{12} + ac(\cos \beta)\beta_{13} + bc(\cos \alpha)\beta_{23}]$.

Table 4. Positional and Thermal Parameters for the Core Atoms of [RhIr(CO)₂(μ-C(CH₃)=N^tBu)-(dppm)₂][CF₃SO₃] (8)^a

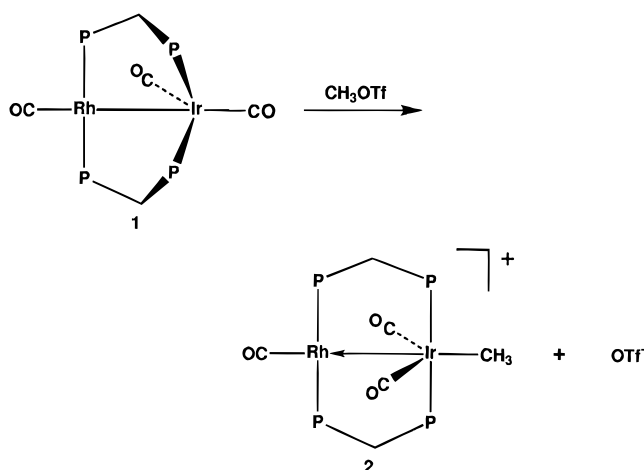
atom	x	y	z	B, ^b Å ²
Ir	0.1047(1)	0.92373(4)	0.26515(6)	2.29(2)*
Rh	0.3106(2)	0.93613(8)	0.3533(1)	2.38(6)*
P(1)	0.0581(6)	0.8438(3)	0.3154(4)	2.8(2)*
P(2)	0.2640(6)	0.8599(3)	0.4115(4)	2.9(2)*
P(3)	0.1430(6)	0.9921(3)	0.1942(3)	2.5(2)*
P(4)	0.3439(6)	1.0134(3)	0.2933(4)	2.7(2)*
O(1)	-0.007(1)	0.9988(7)	0.3452(9)	4.0(6)*
O(2)	0.355(2)	1.0006(7)	0.4787(9)	5.0(7)*
N	0.314(2)	0.8860(7)	0.2675(9)	2.2(6)*
C(1)	0.032(2)	0.967(1)	0.308(1)	3.5(7)
C(2)	0.336(2)	0.977(1)	0.429(1)	3.2(6)
C(3)	0.207(2)	0.843(1)	0.172(1)	3.7(7)
C(4)	0.215(2)	0.878(1)	0.229(1)	3.0(6)
C(5)	0.422(2)	0.858(1)	0.254(1)	3.4(7)
C(6)	0.452(3)	0.874(1)	0.193(2)	5.8(9)
C(7)	0.415(2)	0.798(1)	0.263(1)	4.8(8)
C(8)	0.507(2)	0.876(1)	0.308(1)	4.1(7)
C(9)	0.177(2)	0.8119(9)	0.362(1)	1.7(5)
C(10)	0.278(2)	1.009(1)	0.207(1)	2.7(6)

^a Phenyl carbons and atoms of the triflate anion are given in the Supporting Information. ^b Starred *B* values are for atoms refined anisotropically. *B* values for the anisotropically refined atoms are given in the form of the equivalent isotropic Gaussian displacement parameter defined as $\frac{1}{3}[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos \gamma)\beta_{12} + ac(\cos \beta)\beta_{13} + bc(\cos \alpha)\beta_{23}]$.

electron density of ca. 3.5 e/Å³. The positional and isotropic thermal parameters of the non-hydrogen atoms are given in Table 4.

Results and Discussion

(a) Preparation and Characterization of [RhIr(CH₃)(CO)₃(dppm)₂][CF₃SO₃] (2). Earlier work in this research group and by Eisenberg and co-workers had shown that protonation of the complexes [Ir₂(CO)₃(dppm)₂], [Rh₂(CO)₃(dppm)₂], and their heterobinuclear analogue, [RhIr(CO)₃(dppm)₂] (1), yielded the hydrido-bridged complexes, [Ir₂(CO)₂(μ-CO)(μ-H)(dppm)₂][BF₄],¹⁹ [Rh₂(CO)₂(μ-CO)(μ-H)(dppm)₂][BF₄],²⁰ and [RhIr(CO)₃(μ-

Scheme 1

H)(dppm)₂][BF₄],^{6m} respectively, by apparent electrophilic attack at the metal–metal bond. On the basis of these results, the reaction of compound 1 with the electrophile CH₃⁺ (in the form of methyl triflate (MeOTf)) was attempted, in efforts to obtain a CH₃-bridged analogue of these hydrido-bridged species. However, unlike the protonations, reaction of 1 with methyl triflate does not yield the targeted methyl-bridged species but instead gives [RhIr(CH₃)(CO)₃(dppm)₂][CF₃SO₃] (2), having the methyl group terminally bound to Ir (see Scheme 1). Although initial attack may occur at the Rh–Ir bond, this cannot be confirmed, since even at low temperature only 2 was observed. It should be noted, however, that protonation and alkylation of an analogous RhOs complex appear to occur at a site on the saturated Os center remote from Rh⁷ and not at the Rh–Os bond, suggesting that electrophilic attack occurs directly at the saturated Ir center in compound 1 also.

The ¹H NMR spectrum of 2 shows the methyl resonance as a triplet at δ -0.08, and selective ³¹P-decoupling experiments confirm that the methyl protons are coupled to only the phosphorus nuclei on Ir. The absence of Rh coupling to the methyl protons also supports the model in which the methyl group is bound to Ir but is equivocal since such coupling is only 2–4 Hz, at most, in related Rh-bound methyl species (*vide infra*).^{6f,7–9} The ¹³C{¹H} NMR spectrum of a ¹³CO-enriched sample, which shows a doublet of triplets at δ 183.7 (¹J_{Rh–C} = 75.0 Hz) and a triplet at δ 187.9, with relative intensities 1:2, respectively, indicates that compound 2 has one terminal carbonyl group on Rh and two on Ir. Taken together the NMR spectroscopic data clearly establish the structure of 2, having one terminal carbonyl group bound to Rh and the methyl group as well as two terminal carbonyl groups bound to Ir.

This proposed structure is confirmed by the X-ray structure determination. The asymmetric unit of compound 2 contains the complex cation, a triflate anion, and one molecule of CH₂Cl₂ solvent. The geometries of the triflate anion and the solvent molecule are as expected, and there are no unusual contacts involving the solvent and the ions. A perspective drawing of the cation of this compound is shown in Figure 1. Although as noted earlier, the non-phosphine components of the

(19) Sutherland, B. R.; Cowie, M. *Organometallics* **1985**, *4*, 1637.
(20) (a) Kubiak, C. P.; Woodcock, C.; Eisenberg, R. *Inorg. Chem.* **1982**, *21*, 2119. (b) Kubiak, C. P.; Eisenberg, R. *J. Am. Chem. Soc.* **1980**, *102*, 3637.

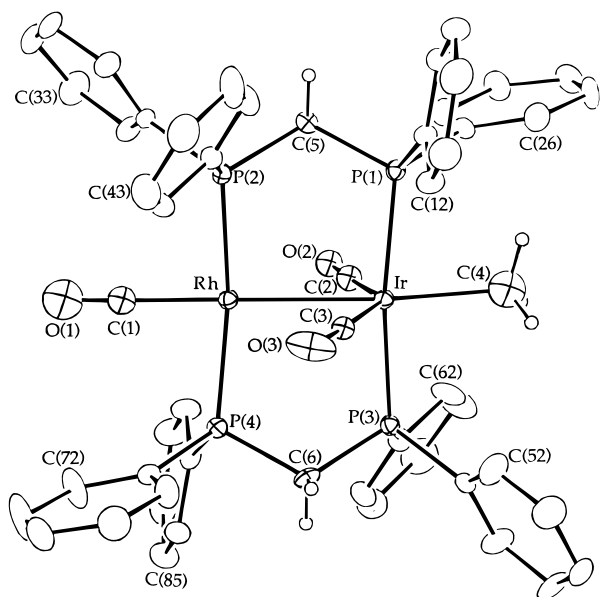


Figure 1. Perspective view of the $[\text{RhIr}(\text{CH}_3)(\text{CO})_3(\text{dppm})_2]^+$ cation, showing the numbering scheme. Thermal ellipsoids are shown at the 20% level except for the methyl and methylene hydrogens, which are shown artificially small, and the phenyl hydrogens, which are omitted. The carbonyl and methyl groups are disordered in a 60:40 mix; only the major contributor is shown.

Table 5. Selected Distances (Å) in $[\text{RhIr}(\text{CH}_3)(\text{CO})_3(\text{dppm})_2][\text{CF}_3\text{SO}_3]\cdot\text{CH}_2\text{Cl}_2$ (2)^a

(a) Bonded Distances			
Ir–Rh	2.743(1)	P(2)–C(5)	1.831(8)
Ir–P(1)	2.336(2)	P(2)–C(31)	1.827(7)
Ir–P(3)	2.327(2)	P(2)–C(41)	1.820(8)
Ir–C(1)′	1.97(1)	P(3)–C(6)	1.821(9)
Ir–C(2)	1.88(2)	P(3)–C(51)	1.819(8)
Ir–C(3)	1.94(1)	P(3)–C(61)	1.803(8)
Ir–C(4)	2.16(3)	P(4)–C(6)	1.830(8)
Rh–P(2)	2.316(2)	P(4)–C(71)	1.813(8)
Rh–P(4)	2.326(2)	P(4)–C(81)	1.816(8)
Rh–C(1)	1.93(2)	O(1)–C(1)	1.06(2) ^b
Rh–C(2)′	1.96(2)	O(1)′–C(1)′	1.07(3)
Rh–C(3)′	2.11(2)	O(2)–C(2)	1.15(2)
Rh–C(4)′	2.04(3)	O(2)′–C(2)′	1.09(2) ^b
P(1)–C(5)	1.820(8)	O(3)–C(3)	1.20(1)
P(1)–C(11)	1.782(8)	O(3)–C(3)′	1.11(2)
P(1)–C(21)	1.834(8)		
(b) Nonbonded Distances			
Rh–C(2)	2.77(1)	P(1)–P(2)	3.060(3)
Rh–C(3)	2.71(1)	P(3)–P(4)	3.055(3)

^a The atoms labeled Rh and Ir are actually a 60:40 mix of Rh/Ir and Ir/Rh, respectively, owing to disorder (see Experimental Section). Primed atoms have 40% occupancy and are related to the unprimed (60% occupancy) atoms by the rotational disorder. ^b O(2) is disordered over two positions (O(2), O(2)′) whereas there is only one position resolved for O(3), although it is probably two closely spaced, unresolved, half-occupancy oxygen atoms.

cation are disordered in a 60:40 ratio, only the molecule having the larger occupancy is shown. In Tables 5 and 6 the parameters involving both disordered molecules are shown, with the atoms of the minor species being primed; however, only the parameters of the major species are discussed, since they are more reliable.

Owing to the disorder, there will be some uncertainty in the metal–ligand parameters; nevertheless, the crystal structure does confirm the gross overall structure of compound **2**. As is observed in most other binuclear dppm-bridged systems,²¹ the diphosphine groups are oriented trans to each other about the metal centers and are cis to the ligands in the equatorial plane.

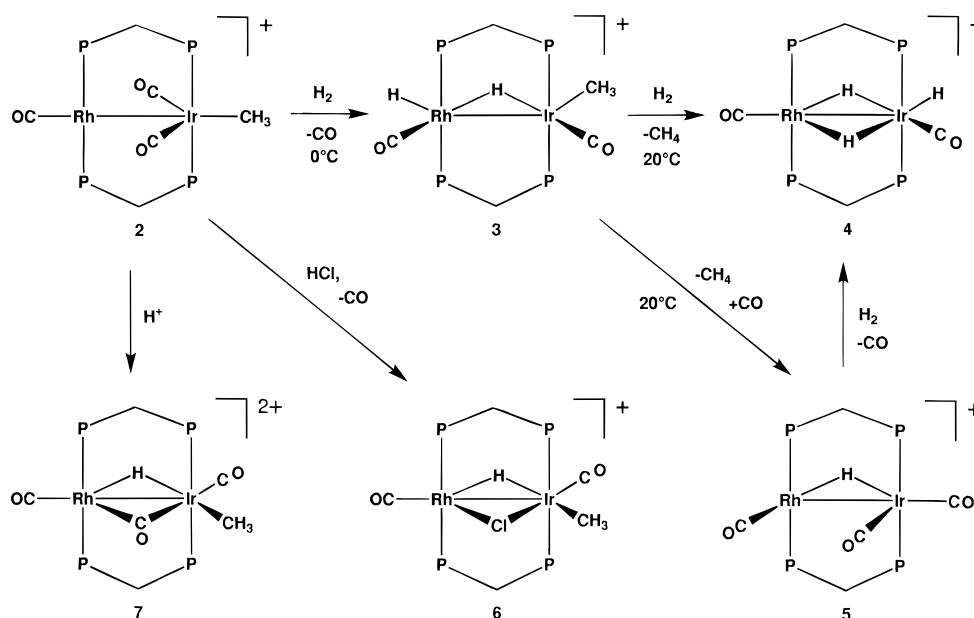
Table 6. Selected Angles (deg) in $[\text{RhIr}(\text{CH}_3)(\text{CO})_3(\text{dppm})_2][\text{CF}_3\text{SO}_3]\cdot\text{CH}_2\text{Cl}_2$ (2)^a

Rh–Ir–P(1)	94.95(5)	C(2)′–Rh–C(4)′	116(1)
Rh–Ir–P(3)	92.74(5)	C(3)′–Rh–C(4)′	111(1)
Rh–Ir–C(1)′	173.7(4)	Ir–P(1)–C(5)	111.6(2)
Rh–Ir–C(2)	70.7(5)	Ir–P(1)–C(11)	118.7(3)
Rh–Ir–C(3)	68.2(4)	Ir–P(1)–C(21)	112.6(2)
Rh–Ir–C(4)	173.2(7)	C(5)–P(1)–C(11)	103.8(3)
P(1)–Ir–P(3)	170.17(7)	C(5)–P(1)–C(21)	105.3(4)
P(1)–Ir–C(1)′	86.4(4)	C(11)–P(1)–C(21)	103.5(4)
P(1)–Ir–C(2)	87.6(5)	Rh–P(2)–C(5)	112.0(2)
P(1)–Ir–C(3)	99.6(4)	Rh–P(2)–C(31)	117.8(3)
P(1)–Ir–C(4)	81.0(7)	Rh–P(2)–C(41)	113.1(3)
P(3)–Ir–C(1)′	86.6(4)	C(5)–P(2)–C(31)	101.6(3)
P(3)–Ir–C(2)	89.2(5)	C(5)–P(2)–C(41)	107.6(3)
P(3)–Ir–C(3)	88.9(4)	C(31)–P(2)–C(41)	103.6(4)
P(3)–Ir–C(4)	90.7(7)	Ir–P(3)–C(6)	112.7(2)
C(2)–Ir–C(3)	138.8(6)	Ir–P(3)–C(51)	118.3(2)
C(2)–Ir–C(4)	103.5(8)	Ir–P(3)–C(61)	113.5(3)
C(3)–Ir–C(4)	117.8(8)	C(6)–P(3)–C(51)	100.5(3)
Ir–Rh–P(2)	92.56(5)	C(6)–P(3)–C(61)	106.3(4)
Ir–Rh–P(4)	94.73(5)	C(51)–P(3)–C(61)	104.1(4)
Ir–Rh–C(1)	167.9(6)	Rh–P(4)–C(6)	112.8(3)
Ir–Rh–C(2)′	69.1(6)	Rh–P(4)–C(71)	113.9(2)
Ir–Rh–C(3)′	63.5(6)	Rh–P(4)–C(81)	117.1(3)
Ir–Rh–C(4)′	174.8(8)	C(6)–P(4)–C(71)	104.2(4)
P(2)–Rh–P(4)	170.22(7)	C(6)–P(4)–C(81)	103.3(3)
P(2)–Rh–C(1)	91.0(5)	C(71)–P(4)–C(81)	104.3(4)
P(2)–Rh–C(2)′	90.8(6)	Rh–C(1)–O(1)	178(2)
P(2)–Rh–C(3)′	90.5(6)	Ir–C(1)′–O(1)′	163(2)
P(2)–Rh–C(4)′	88.0(7)	Ir–C(2)–O(2)	178(1)
P(4)–Rh–C(1)	83.1(5)	Rh–C(2)′–O(2)′	176(2)
P(4)–Rh–C(2)′	97.9(6)	Ir–C(3)–O(3)	174(1)
P(4)–Rh–C(3)′	86.9(6)	P(1)–C(5)–P(2)	113.9(4)
P(4)–Rh–C(4)′	84.1(7)	P(3)–C(6)–P(4)	113.6(4)
C(2)′–Rh–C(3)′	132.6(9)		

^a Labeling as in footnotes of Table 5.

Rh has a distorted square-planar geometry as expected for Rh(1+) species, while Ir has a distorted trigonal-bipyramidal geometry (ignoring the metal–metal bond). The discussion of the nature of the metal–metal interaction requires a concomitant consideration of metal oxidation states. If the positive charge is considered to be localized on Ir, then the oxidation-state assignment is Ir(2+)/Rh(0), and this d^7/d^9 system would require a conventional metal–metal bond to give a diamagnetic compound. The other possibility places the positive charge on Rh, yielding d^8/d^8 , Ir(1+)/Rh(1+) centers. In this situation, the Ir has an 18-electron configuration and the trigonal-bipyramidal geometry observed is as expected. However, the Rh center has only 14 valence electrons and requires an Ir → Rh dative bond to give a square-planar 16-electron configuration at this atom. We favor this latter view. The Ir → Rh dative bond would utilize filled nonbonding d_{xy} or $d_{x^2-y^2}$ orbitals on Ir and would require no rehybridization of the trigonal-bipyramidal Ir center, whereas the Ir(2+)/Rh(0) system, having a normal covalent bond, would result in rehybridization of Ir to give an octahedral geometry at this metal. In addition, the carbonyl stretches, which are all lower than 1990 cm^{-1} , are more consistent with Ir(1+). The Rh–Ir distance (2.743(1) Å), which is significantly shorter than the intraligand P(1)–P(2) and P(3)–P(4) distances (3.060(3) and 3.055(3) Å, respectively), indicates substantial attraction of the adjacent metal centers and is therefore consistent with some form of metal–metal bond. This distance is similar to that observed in the precursor, $[\text{RhIr}(\text{CO})_3(\text{dppm})_2]$ (2.7722(7) Å),^{6m} which was also proposed to have a dative bond, in this case between an 18e Ir(1–) center and the 14e

Scheme 2



Rh(1+) center. The distortion of the geometry around each metal in **2** is caused by the two metals being drawn together as a result of the strong dative interaction.

The assignment of the methyl group as being bound to Ir is supported by the successful refinement of the structure with a 60% and 40% occupancy for O(1) and O(1') respectively, with O(1) on the end of the molecule having 60% occupancy for Rh. This indicates that this carbonyl group (C(1)O(1)), which is trans to the metal-metal bond, is bound to Rh, placing the methyl group on Ir. The essentially linear Ir-C-O linkages, as well as the magnitude of the contacts between Rh and C(2) and C(3) (2.77(1) and 2.71(1) Å, respectively), preclude any significant semibridging interaction between Rh and the carbonyls C(2)-O(2) and C(3)-O(3). This is supported by the lack of Rh coupling for these carbonyl resonances in the ¹³C NMR spectrum.

One of the interesting features of compound **2** is that it has the methyl group bound to the *saturated* Ir metal. Although this is not surprising, on the basis of the presumed stronger Ir-CH₃ bond compared to Rh-CH₃,²² it differs from all analogous alkyl complexes of Rh/Re,^{6f} Rh/Os,⁷ Rh/Mn⁸, Rh/Mo⁹ and Rh/W⁹ which have the alkyl groups bound to the *unsaturated* Rh metal. However the stronger Ir-CH₃ bond cannot be the sole reason for favoring the structure of **2** since the isoelectronic species [RhOs(CH₃)(CO)₃(dppm)₂]⁷ has a Rh-bound methyl group, in spite of our assumption of a greater Os-CH₃ bond strength.²³ In addition, facile migration of the methyl group from Ir to Rh is later described upon substitution of a carbonyl in **2** by other π -acid ligands (*vide infra*).

(b) Reactivity Studies. (i) Hydrido Methyl Complexes. Having successfully prepared the "RhIr" methyl species **2**, we undertook an investigation of its reactivity. Among the topics of interest was the reaction

of **2** with hydrogen sources, in order to establish the role of the different metals in the reductive elimination of methane. Surprisingly, little has been established about the natures of hydrido-alkyl intermediates in the elimination of alkanes from adjacent metals. In a related dipalladium system, methane evolution from [Pd₂H(CH₃)(μ -Cl)(dppm)₂]⁺ and methane and ethane evolution from [Pd₂(CH₃)₂(μ -H)(dppm)₂]⁺ occurred under mild conditions,²⁴ whereas the related platinum complexes [Pt₂(CH₃)₂(μ -H)(dppm)₂]⁺ and [Pt₂H(CH₃)(μ -H)(dppm)₂] were found to be thermally stable to methane loss.²⁵ Although methane elimination was observed in two dirhodium A-frames,¹⁰ [Rh₂(CH₃)(CO)(μ -CO)(dppm)₂]⁺ and [Rh₂(CO)₂(μ -CH₃CO)(dppm)₂]⁺, upon reaction with H₂, the hydrido-methyl intermediates were not observed. Similarly, the reductive elimination of methane from the mixed-metal species [MRe(CH₃)(CO)₄(dppm)₂]⁺ (M = Rh, Ir) was found in a previous study to occur readily upon reaction with H₂, but no hydrido-methyl intermediates were observed down to -80 °C. A hydride-bridged methyl complex was observed at -60 °C upon reaction of the above IrRe compound with a hydride source, and this species eliminated methane at ambient temperature.^{6f}

Reaction of **2** with H₂ at ambient temperature yields the known trihydride species [RhIr(H)(CO)₂(μ -H)₂(dppm)₂][CF₃SO₃]⁺ (**4**),^{6m} through methane and CO evolution, as shown in Scheme 2. If this reaction is carried out at 0 °C, the dihydrido-methyl intermediate [RhIr(H)(CH₃)(CO)₂(μ -H)(dppm)₂][CF₃SO₃]⁺ (**3**) is observed. This species displays two hydride resonances (δ -10.02, -12.47) and a methyl signal (δ -0.16) in the ¹H NMR spectrum.

Phosphorus decoupling experiments allow us to establish that the hydride ligand at higher field is terminally bound to Rh, with a Rh-H coupling constant of ca. 24 Hz, while the other is bridging, having ¹J_{RhH}

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(23) Although we have not seen comparisons of Rh-CH₃ and Os-CH₃ bond strengths in analogous complexes, our assumptions are based on extrapolations of the studies done. See for example ref 22 and: Armentrout, P. B. *Bonding Energetics in Organometallic Compounds*; Marks, T. J., Ed.; American Chemical Society: Washington, DC, 1990; Chapter 2.

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(25) (a) Brown, M. P.; Cooper, S. J.; Frew, A.; Manijlović-Muir, L.; Muir, K. W.; Puddephatt, R. J.; Thomson, M. A. *J. Chem. Soc., Dalton Trans.* **1982**, 299. (b) Azam, K. A.; Puddephatt, R. J. *Organometallics* **1983**, *2*, 1396.

= 15 Hz; the methyl group is seen to be bound to Ir. Only two carbonyl resonances are observed in the $^{13}\text{C}\{-^1\text{H}\}$ NMR spectrum, with one CO bound to each metal. This product has a geometry consistent with H_2 attack at the coordinatively unsaturated Rh center. However, attempts to observe the initial product of H_2 addition, which is presumed to precede CO loss, failed, with no reaction being noted at temperatures much lower than 0 °C; only **3** and **4** were observed on slowly warming the sample under H_2 from lower temperatures. It was of interest to establish whether reductive elimination of methane would occur from Ir or whether migration of the methyl group to Rh would occur with elimination occurring from this center. In the only alkyl intermediate observed, the methyl group remains bound to Ir, with one hydrido ligand in a bridging position. This geometry can readily give rise to methane loss via transfer of the bridging hydride to iridium, followed by reductive elimination from this metal. Although elimination should occur more readily from the second-row metal, it appears in this case to be occurring from Ir. This parallels a previous study on related RhOs compounds,⁷ in which reductive elimination of methane also occurred from the third-row metal (Os) in preference to Rh.

In the absence of excess H_2 , methane loss from **3** generates the previously reported,^{6m} hydride-bridged A-frame $[\text{RhIr}(\text{CO})_3(\mu\text{-H})(\text{dppm})_2][\text{CF}_3\text{SO}_3]$ (**5**), having scavenged the CO originally lost from **2**. The ^1H NMR spectrum of this species shows the bridging hydride resonance as a complex multiplet at $\delta -10.2$, while the $^{13}\text{C}\{-^1\text{H}\}$ NMR displays two carbonyl resonances in a 1:2 intensity ratio, with only one displaying coupling (79 Hz) to Rh. This monohydride species generates **4** upon reaction with H_2 , with accompanying CO loss.

Related hydrido–methyl species can also be obtained by protonation. For example, the reaction of **2** with 1 equiv of HCl gives $[\text{RhIr}(\text{CH}_3)(\text{CO})_2(\mu\text{-H})(\mu\text{-Cl})(\text{dppm})_2][\text{CF}_3\text{SO}_3]$ (**6**). This product represents a rare example involving Rh, in which a hydrido–methyl complex is stable to methane elimination at room temperature to the extent that it can be isolated as a solid.²⁶ Although the relative positions of the equatorial ligands are not known, the failure of **6** to eliminate methane leads us to assume that the hydride and methyl groups are not adjacent. The hydride ligand is clearly bridging, as shown by the multiplet at $\delta -9.50$ in the ^1H NMR spectrum, which collapses to a doublet of triplets on selectively decoupling each of the Rh-bound and Ir-bound phosphorus resonances in turn and to a doublet ($^1J_{\text{Rh-H}} = 22.0$ Hz) upon broadband ^{31}P -decoupling. As in **3**, the methyl group again remains coordinated to Ir as demonstrated by the $^1\text{H}\{^{31}\text{P}\}$ NMR experiments. The formation of **6** is accompanied by CO loss, as indicated by its $^{13}\text{C}\{-^1\text{H}\}$ NMR spectrum, which shows a doublet of triplets at $\delta 189.3$ ($^1J_{\text{Rh-C}} = 84.5$ Hz) and an equal intensity triplet at $\delta 164.4$, indicating the presence of only one CO ligand each on Rh and Ir. A similar product, $[\text{RhIr}(\text{CH}_3)(\text{CO})_2(\mu\text{-H})(\mu\text{-CO})(\text{dppm})_2][\text{CF}_3\text{SO}_3]_2$ (**7**), is obtained on reacting **2** with $\text{CF}_3\text{SO}_3\text{H}$, except that carbonyl loss does not occur and the bridging chloride ligand in **6** is replaced by a bridging carbonyl. The $^{13}\text{C}\{-^1\text{H}\}$ NMR spectrum of compound **7** shows a doublet of triplets of triplets at $\delta 199.9$ ($^1J_{\text{Rh-C}} = 26.2$ Hz), a

doublet of triplets at $\delta 186.0$ ($^1J_{\text{Rh-C}} = 76.5$ Hz), and a multiplet at $\delta 165.6$ in the appropriate ratios, indicating the presence of a bridging carbonyl group (the coupling to Rh of 26.2 Hz is in the range expected for a bridging carbonyl²⁷) and a terminal carbonyl group each on Rh and Ir.

Although the hydrido–methyl species **6** and **7** are possible models for intermediates in methane elimination from adjacent metal centers, their subsequent reductive elimination reactions were not pursued since our interests lay in establishing the nature of the intermediates preceding CH_4 loss in order to gain information about the functions of the different metals. Under forcing conditions we would not be able to observe and characterize such intermediates. However, in a related study, the protonation of the analogous species, $[\text{RhOs}(\text{CH}_3)(\text{CO})_3(\text{dppm})_2]$, as well as methylation of the hydrido analogue, has yielded valuable insights into reductive elimination from these metals.⁷

(ii) Reaction of 2 with π -Acid Ligands. In an attempt to induce migratory insertion of the methyl group and concomitant C–C or C–X (X = heteroatom) bond formation, the reactions of compound **2** with π -acceptor ligands such as carbon monoxide, *tert*-butyl isocyanide, ethylene, and sulfur dioxide were attempted. Reactions with alkynes were also investigated, but this forms the basis of another paper.²⁸

In the reaction of compound **2** with CO a large number of products resulted, and these were not characterized. In this reaction mixture no species was identified which could be formulated as an acetyl species resulting from the expected migratory insertion of the methyl and a carbonyl group.

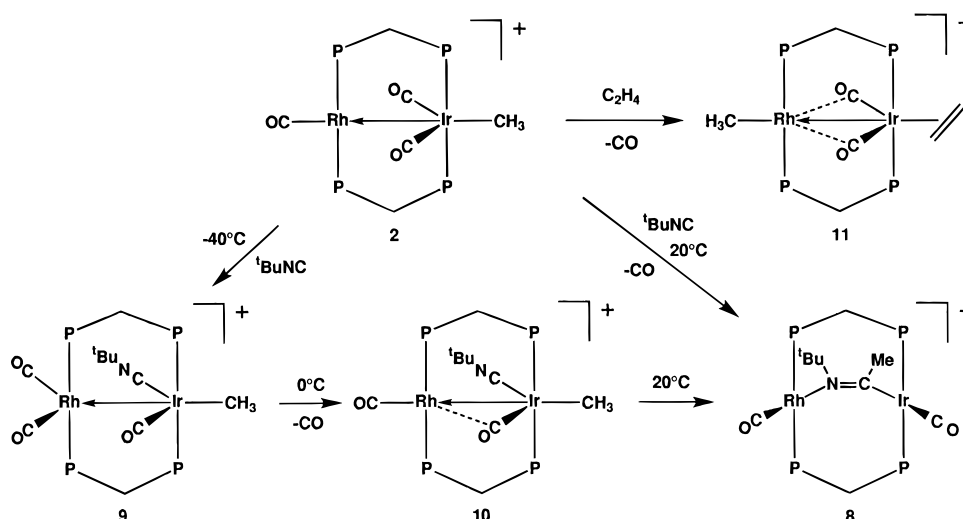
The reaction of **2** with $^t\text{BuNC}$ occurs readily, yielding $[\text{RhIr}(\text{CO})_2(\mu\text{-}^t\text{BuN}=\text{CMe})(\text{dppm})_2][\text{CF}_3\text{SO}_3]$ (**8**), the product of isocyanide insertion into the Ir–methyl bond and CO loss. This transformation is accompanied by movement of the resulting iminoacyl group to the bridging position, yielding the mixed-metal, iminoacyl analogue of the dirhodium, acetyl-bridged species $[\text{Rh}_2(\text{CO})_2(\mu\text{-CH}_3\text{CO})(\text{dppm})_2]^+$.¹⁰ The ^1H NMR spectrum of **8** shows the methyl and *tert*-butyl resonances as singlets at $\delta 0.82$ and 0.80 , respectively. Formal insertion of the $^t\text{BuNC}$ ligand into the Ir– CH_3 bond has resulted in the expected downfield shift for this methyl resonance, and its appearance as a singlet results from its position one atom further removed from Ir, such that coupling to the phosphorus nuclei is no longer observed. The structure shown in Scheme 3, having the iminoacyl nitrogen bound to Rh rather than to Ir, could not be established from the available spectroscopic data but has been established crystallographically (vide infra). The $^{13}\text{C}\{-^1\text{H}\}$ NMR spectrum of **8** shows two carbonyl resonances as a doublet of triplets at $\delta 195.0$ ($^1J_{\text{Rh-C}} = 65.4$ Hz) and a triplet at $\delta 191.3$, while the IR spectrum shows CO stretches at 1964 and 1945 cm^{-1} , indicating that there is one terminally bound carbonyl on each metal. The absence of an absorption in the 2000–2190 cm^{-1} range (as expected for a $\text{C}\equiv\text{N}$ stretch^{29a}) is consistent with the insertion of the isocyanide ligand into the Ir– CH_3 bond, reducing the C–N bond order. The resulting

(27) Jenkins, J. A.; Cowie, M. *Organometallics* **1992**, *11*, 2767.

(28) (a) Antwi-Nsiah, F. H.; Oke, O.; Cowie, M. *Organometallics* **1996**, *15*, 506. (b) Antwi-Nsiah, F. H. Ph.D. Thesis, The University of Alberta, Edmonton, 1994; Chapter 4.

(26) See also: Wang, C.; Ziller, J. W.; Flood, T. C. *J. Am. Chem. Soc.* **1995**, *117*, 1647.

Scheme 3



C=N stretch is probably obscured by the absorptions due to the dppm phenyl groups and is not observed.

In an attempt to identify intermediates in the transformation of **2** to **8**, in order to elucidate the steps involved, the reaction with ^tBuNC was carried out at -80 °C and slowly warmed while observing NMR spectral changes (¹H, ¹³C, and ³¹P). Between -80 and -40 °C the major product observed is a tricarbonyl species **9**, shown in Scheme 3. Its ¹³C{¹H} NMR spectrum indicates that two carbonyls (overlapping at δ 181.3 and 181.9) are bound to Rh ($^1J_{\text{Rh-C}} = 74$ and 77 Hz, respectively) with only one (δ 176.3) on Ir. The methyl group is shown, by ¹H NMR with selective ³¹P-decoupling, to be bound to Ir, and the protons of the *tert*-butyl group are observed as a singlet at δ 0.92. In the absence of ¹³C-labeled ^tBuNC we were unable to observe the resonance for the isocyanide carbon, so the site of coordination of this group is unknown. It is assumed to be bound to Ir, as shown, on the basis of similarities to related mixed-metal species previously characterized by us.^{6f,h} The site of ^tBuNC attack on compound **2** should be at the unsaturated Rh center; however, such an adduct was not identified. At -80 °C several unidentified intermediates were observed, but their low concentration and the overlap of signals prevented their identification. As the reaction mixture is warmed to 0 °C, compound **9** disappears to be replaced by [RhIr(CH₃)(CO)₂(^tBuNC)(dppm)₂][CF₃SO₃] (**10**), which is shown by ¹³C{¹H} NMR to be a dicarbonyl species, having one CO (δ 180.2, $^1J_{\text{Rh-C}} = 68.5$ Hz) terminally bound to Rh, and by ¹H NMR to have the methyl group still on Ir. The low-field ¹³C resonance for the second carbonyl (δ 233.3) suggests a bridging mode, in which interaction with Rh must be weak, since no resolvable Rh coupling is observed in this slightly broadened resonance (20 Hz at half-height). Again the ^tBuNC group is assumed to be bound to Ir, yielding a species analogous to **2**, apart from the proposed semibringing carbonyl interaction in **10**. Upon further warming, **10** transforms to the iminoacyl-bridged product **8**. Although migratory insertions are known to occur more readily at Rh than Ir, we see no evidence for a rearrangement bringing the isocyanide and methyl groups

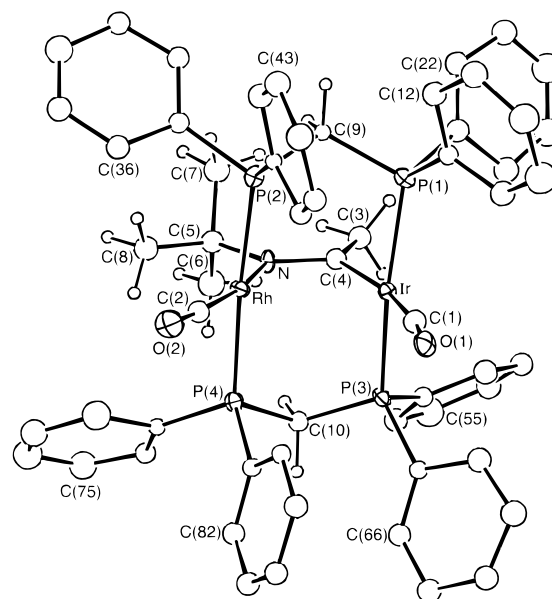


Figure 2. Perspective view of the [RhIr(CO)₂(μ -C(CH₃)=N^t-Bu)(dppm)₂]⁺ cation, showing the numbering. Thermal parameters are as in Figure 1.

to Rh; instead it appears that the coupling of the methyl and isocyanide ligands occurs on Ir. The ease of this migratory insertion, transforming **10** to **8**, is in contrast to the failure of the isoelectronic, tricarbonyl precursor **2** to undergo a similar migration involving one of the carbonyls but is consistent with the greater tendency for isocyanides to insert.^{29b}

The coordination mode of the iminoacyl ligand was established by an X-ray determination of compound **8**, which shows that this group bridges the metals such that it is N-bound to Rh and C-bound to Ir. Figure 2 shows a perspective view of the complex cation. Relevant bond lengths and angles are given in Tables 7 and 8. Within the cation, the diphosphine groups are oriented approximately *trans* to each other about the metal centers (P(1)–Ir–P(3) = 167.4(2)° and P(2)–Rh–P(4) = 175.8(3)°) and are both *cis* to the other atoms coordinated to the metal nuclei, resulting in a distorted square-planar geometry about both metals. Formation of the iminoacyl complex is accompanied by elongation of the Rh–Ir separation from 2.743(1) Å in the precursor complex **2** (*vide supra*) to 2.950(2) Å. Although this Rh–Ir separation is intermediate between those in com-

(29) (a) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987, pp 148 and 372. (b) *Ibid.*, pp 377–378.

Table 7. Selected Distances (Å) in [RhIr(CO)₂(μ-C(CH₃)=N^tBu)(dppm)₂][CF₃SO₃] (8)

(a) Bonded Distances			
Ir-P(1)	2.310(7)	P(3)-C(10)	1.75(2)
Ir-P(3)	2.297(6)	P(3)-C(51)	1.81(2)
Ir-C(1)	1.72(3)	P(3)-C(61)	1.83(2)
Ir-C(4)	2.02(2)	P(4)-C(10)	1.82(2)
Rh-P(2)	2.319(7)	P(4)-C(71)	1.76(2)
Rh-P(4)	2.310(7)	P(4)-C(81)	1.85(2)
Rh-N	2.13(2)	O(1)-C(1)	1.23(3)
Rh-C(2)	1.82(2)	O(2)-C(2)	1.15(2)
P(1)-C(9)	1.83(2)	N-C(4)	1.39(2)
P(1)-C(11)	1.80(2)	N-C(5)	1.59(3)
P(1)-C(21)	1.83(2)	C(3)-C(4)	1.43(3)
P(2)-C(9)	1.80(2)	C(5)-C(6)	1.42(3)
P(2)-C(31)	1.80(2)	C(5)-C(7)	1.47(3)
P(2)-C(41)	1.84(2)	C(5)-C(8)	1.47(3)
(b) Nonbonded Distances			
Ir-Rh	2.950(2)	P(3)-P(4)	3.04(1)
P(1)-P(2)	3.04(1)		

Table 8. Selected Angles (deg) in [RhIr(CO)₂(μ-C(CH₃)=N^tBu)(dppm)₂][CF₃SO₃] (8)

(a) Bond Angles			
P(1)-Ir-P(3)	167.4(2)	Rh-N-C(4)	114(1)
P(1)-Ir-C(1)	95.1(8)	Rh-N-C(5)	120(1)
P(1)-Ir-C(4)	86.6(6)	C(4)-N-C(5)	125(2)
P(3)-Ir-C(1)	93.7(8)	Ir-C(1)-O(1)	170(2)
P(3)-Ir-C(4)	86.6(6)	Rh-C(2)-O(2)	177(2)
C(1)-Ir-C(4)	168(1)	Ir-C(4)-N	110(1)
P(2)-Rh-P(4)	175.8(3)	Ir-C(4)-C(3)	131(2)
P(2)-Rh-N	90.1(5)	N-C(4)-C(3)	119(2)
P(2)-Rh-C(2)	91.5(7)	N-C(5)-C(6)	113(2)
P(4)-Rh-N	90.1(5)	N-C(5)-C(7)	109(2)
P(4)-Rh-C(2)	89.1(7)	N-C(5)-C(8)	108(2)
N-Rh-C(2)	168.6(9)	C(6)-C(5)-C(7)	114(2)
Ir-P(1)-C(9)	109.6(7)	C(6)-C(5)-C(8)	108(2)
Rh-P(2)-C(9)	114.5(7)	C(7)-C(5)-C(8)	104(2)
Ir-P(3)-C(10)	111.9(7)	P(1)-C(9)-P(2)	114(1)
Rh-P(4)-C(10)	111.5(7)	P(3)-C(10)-P(4)	117(1)
(b) Torsion Angles			
P(1)-Ir-Rh-N	87.2(6)	C(4)-Ir-Rh-P(4)	93.1(8)
P(3)-Ir-Rh-N	-82.9(6)	C(4)-Ir-Rh-P(2)	-88.9(8)

compound **2**, which has a Rh-Ir bond, and that in [RhIr(H)₂(CO)₂(μ-CI)(dppm)₂][BF₄] (3.0651(5)Å),^{9p} which has no Rh-Ir bond, it is suggested that there is no Rh-Ir bond in **8**, since this situation is more consistent with electron counting, in which both metals are d⁸ square-planar centers. This is also the view taken in the report of the acetyl-bridged dirhodium analogue, which has an almost identical metal-metal separation.¹⁰ The iminoacyl bridge lies in the equatorial plane, perpendicular to the metal-phosphorus plane, and the Ir-C(4) and Rh-N distances of 2.02(2) and 2.13(2) Å, respectively, are within the expected range for Ir-C and Rh-N single bonds. Also the C-C bonds within the iminoacyl ligand are consistent with single bonds. The N-C(4) separation of 1.39(2) Å is longer than those of the bridging iminoacyl ligands in [Os₃(CO)₁₀(μ-H)(μ-η²-C₆H₅C=NCH₃)] (1.278(10) Å)³⁰ and [Fe₂(η²-C(Mes)N^tBu)₂(μ-C(Mes)=N^t-Bu)₂] (Mes = 2,4,6-Me₃C₆H₂; 1.295(10) Å)³¹ and is also longer than a normal N=C bond (ca. 1.30 Å³²). The geometries around C(4) and N are trigonal planar, with the Ir-C(4)-C(3) angle (131(2)°) slightly increased at the expense of the Ir-C(4)-N angle (110(1)°), while the *tert*-butyl group adopts a normal tetrahedral geometry. The carbonyl geometries and distances are normal for such terminally bound groups.

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The insertion of an isocyanide ligand into a M-C σ bond is well documented.^{31,33} Whether the resulting iminoacyl group is bonded in a mono- or bidentate manner depends ultimately on the electronic configuration and the required coordination geometry of the metals in the complex.^{33a} In **8**, coordination of the nitrogen lone pair to Rh gives this metal the square-planar geometry characteristic of Rh (1+). Compound **8** is very similar to [Pd₂(μ-CH₃N=CCH₃)(CNCH₃)₂(dppm)₂]³⁺,^{33c} which was obtained by the insertion of an isocyanide into a Pd-CH₃ bond. Other examples of bridging iminoalkyl ligands,³⁴ and closely related bridging formimidoyl³⁵ ligands are known.

The reaction of compound **2** with ethylene does not result in insertion of the unsaturated ligand into the Ir-methyl bond as was observed with *tert*-BuNC; nevertheless, it gives an interesting species, resulting from substitution of a carbonyl and the accompanying migration of the methyl group from Ir to Rh to give [RhIr(CH₃)(CO)₂(C₂H₄)(dppm)₂][CF₃SO₃] (**11**). This species is analogous to [RhOs(CH₃)(CO)₃(dppm)₂],⁷ in having the methyl group coordinated to the *unsaturated* Rh rather than to the *saturated* metal center, as shown earlier in Scheme 3. The four ethylene protons are equivalent, giving rise to a triplet at δ 0.75, while the methyl group resonance appears as a doublet of triplets at δ 0.35 (²J_{Rh-H} = 3.0 Hz) in the ¹H NMR spectrum. Selective ³¹P-decoupling experiments confirm that the ethylene protons are coupled to the Ir-bound phosphorus nuclei whereas the methyl protons are coupled to the phosphorus nuclei bound to Rh. Both carbonyls interact with Rh as shown by their coupling of 20.0 Hz to this metal and are assumed to be semibridging on the basis that this coupling is less than in symmetrically-bridged carbonyls. Ethylene adducts of dppm-bridged binuclear complexes of Rh or Ir are extremely rare (to our knowledge the complexes, [Ir₂(CO)(C₂H₄)(μ-I)(μ-CO)(dppm)₂][X] (X = I, BF₄),^{6e} [Ir₂(CH₃)(CO)₂(C₂H₄)(dppm)₂][BF₄],¹¹ and [Ir₂(C₂H₄)(CO)₂(μ-H)(dppm)₂][BF₄]³⁶ are the only other examples); thus, compound **11** and that previously described for the diridium analogue,¹¹ both of which have an accompanying alkyl group, are unusual. Furthermore, methyl migration from one transition metal to another, as was observed in the above reaction with ethylene, is also rare, having been observed in only a few cases.^{10,11,37} It should be recalled, however, that alkyl transfer from a main-group to a transition metal is common in alkyl-transfer reactions of Grignard reagents, as well as other alkyl-transfer reagents of aluminum, zinc, mercury, and tin,³⁸ and compounds in which a methyl group bridges aluminum and a transition metal have been characterized.³⁹ Such methyl-bridged species can be viewed as models for methyl-group transfer from one metal to another.

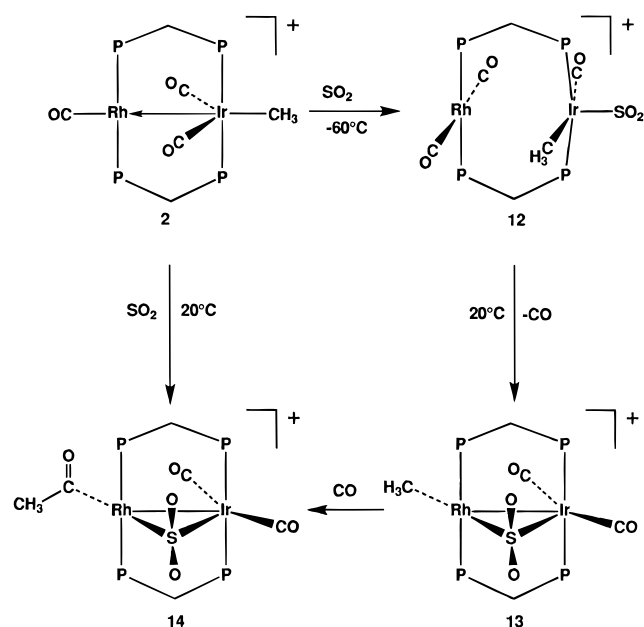
Sulfur dioxide is also known to insert into metal-alkyl bonds. However, the mechanism is not of migra-

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Scheme 4



tory insertion, as observed with CO, but involves electrophilic attack directly at the alkyl group.⁴⁰ It was therefore of interest to determine whether compound **2** would undergo SO₂ insertion. Compound **2** does react with SO₂ at ambient temperature but not to give an S-bound sulfinate, via SO₂ insertion. Instead, the reaction leads to the formation of the acetyl complex [RhIr(CO)₂(COCH₃)(μ-SO₂)(dppm)₂][CF₃SO₃] (**14**) (see Scheme 4). The ¹H NMR spectrum of **14** shows the resonance of the acetyl protons as a singlet at δ 1.15 and the ¹³C{¹H} spectrum shows three carbonyl resonances of equal intensity. Two doublets of triplets are observed for the Ir-bound carbonyls at δ 172.7 and 168.7 with coupling to the two adjacent phosphorus nuclei and to each other (12.6 Hz). This C–C coupling is less than the values of 25 Hz observed between a carbon nucleus of the bridging acetylene and a CO in [Ir₂(I)(CO)₂(μ-HC₂H)(dppm)₂][I] (acetylenic and carbonyl carbons ¹³C-enriched), in which a trans orientation of the alkyne and this CO ligand was proposed,^{6a} and between two mutually trans carbonyls in [RhOs(NCMe)(CO)₃(μ-H)(dppm)₂][BF₄]₂⁷ but is close to the 13 Hz observed between a CO ligand and the vinylidene α carbon in [Ir₂(CH₃)(CO)₃(μ-C=CH₂)(dppm)₂][CF₃SO₃].²⁸ It is therefore proposed that these Ir-bound carbonyls in **14** deviate from an exactly trans orientation. The third ¹³C resonance at δ 255.5 appears as a doublet (¹J_{Rh–C} = 34.2 Hz) and is assigned to the acetyl carbonyl, which is bound to Rh. The chemical shift and magnitude of the Rh–C coupling of this carbonyl group is similar to that of [RhRe-

(COCH₃)(CO)₄(dppm)₂][CF₃SO₃].^{6f} In the IR spectrum the acetyl C–O stretch appears at 1640 cm⁻¹, and one of the SO stretches of the SO₂ group appears at 1055 cm⁻¹; the second SO₂ stretch is presumably obscured by the triflate anion stretches. The spectroscopic data do not unambiguously establish the binding mode of the SO₂ ligand; however, the high tendency for this ligand to bridge late metals, the low SO stretch,⁴¹ and the characterization of a closely related SO₂-bridged diiridium complex¹² suggest a bridged mode for the SO₂ group in this species also.

When the reaction of **2** with SO₂ is started at ca. –60 °C, the intermediate, [RhIr(CH₃)(CO)₂(SO₂)(dppm)₂][CF₃SO₃] (**12**), is observed in solution. On standing at room temperature for about 10 min, compound **12** is transformed to a second intermediate, [RhIr(CH₃)(CO)₂(μ-SO₂)(dppm)₂][CF₃SO₃] (**13**), which in turn is transformed to the acetyl product, **14**, after 1 h at room temperature. In the ¹H NMR spectrum of compound **12**, the dppm-methylene resonances appear as multiplets at δ 4.85 and 3.45, while the methyl resonance appears as a broad signal at δ 0.33. Selective ³¹P-decoupling experiments show that the methyl group is still bound to Ir, as decoupling the resonance due to the Ir-bound phosphorus nuclei leads to the collapse of the broad methyl resonance into a sharp singlet, while decoupling the other ³¹P resonance has no effect. The ¹³C{¹H} NMR spectrum shows doublets of triplets at δ 194.9 (¹J_{Rh–C} = 56.3 Hz) and 175.2 (¹J_{Rh–C} = 63.4 Hz), as well as a triplet at δ 178.4, indicating the presence of two terminal CO ligands on Rh and one on Ir. A terminal coordination mode is proposed for the SO₂ group in compound **12**, on the basis that transfer of a CO from Ir to Rh has occurred, which would leave Ir electron deficient. A bridging SO₂ is ruled out since it would inhibit methyl transfer from Ir to Rh, accompanied by CO transfer in the reverse direction, as is observed in subsequent transformations (*vide infra*). Although we have no spectroscopic data that would allow us to establish whether the Ir–SO₂ moiety is planar or pyramidal,⁴² a pyramidal sulfur is assumed on the basis of analogies with the known structures for the closely related [MCl(CO)(SO₂)(PPh₃)₂] (M = Rh, Ir) complexes.⁴³ The structure shown for **12** in Scheme 4 also depicts a tetragonal pyramidal Ir center, in which SO₂ occupies the apical site, as was observed in the above mononuclear analogues.

The ¹H NMR spectrum of compound **13** shows the dppm methylene resonances as multiplets at δ 4.12 and 3.50, as well as the methyl resonance as a triplet of doublets at δ 1.08 (²J_{Rh–H} = 3.7 Hz). The presence of Rh coupling to the methyl protons indicates that the methyl group has now migrated to Rh, as was observed

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in the reaction of **2** with ethylene, and is in contrast to the reaction of **2** with ^tBuNC, previously noted, in which the methyl group remained on Ir. This is confirmed in the present case by selective ³¹P-decoupling experiments. The ¹³C{¹H} NMR spectrum shows two doublets of triplets at δ 180.6 and 170.3 (²J_{C-C} = 13.6 Hz), indicating the presence of only two CO ligands on Ir and indicating that the transformation from **12** to **13** involves CO loss. The 13.6 Hz coupling between the carbonyl carbons again suggests an orientation that is probably intermediate between exactly cis and trans, as was proposed for **14**. The change of the methyl resonance from a triplet of doublets in **13** to a sharp singlet in **14** is consistent with the assignment of the latter as an acetyl complex in which four-bond coupling between the methyl protons and the phosphorus nuclei is not observed.

On the basis of the intermediates and the acetyl product observed in the reaction of **2** with SO₂, the reaction pathway shown in Scheme 4 is proposed. Apparently, there is migration of one CO ligand from Ir to Rh accompanied by the coordination of SO₂ to the former metal to yield compound **12**. This compound then loses one CO ligand and undergoes CO migration from Rh to Ir, concomitant with methyl migration from Ir to Rh, and movement of the SO₂ ligand into the more favored bridging position⁴¹ to yield compound **13**. The latter species recoordinates CO, resulting in migratory insertion to give the acetyl product, **14**. No insertion of the SO₂ ligand into the Ir–methyl bond is observed at any stage in this reaction. Apparently the methyl group of **2** is not nucleophilic enough to result in direct attack by the SO₂ electrophile; instead attack at the metal occurs ultimately yielding the acetyl product.

Conclusions

Electrophilic attack of [RhIr(CO)₃(dppm)₂] by CH₃⁺ does not yield the targeted methyl-bridged species analogous to the protonation product, [RhIr(CO)₃(μ-H)(dppm)₂]⁺. Instead, the product obtained, [RhIr(CH₃)(CO)₃(dppm)₂][CF₃SO₃] (**2**), has the methyl group terminally bound to the saturated Ir center. This is hardly surprising in view of the stronger Ir–CH₃ bond compared to Rh–CH₃ but is in contrast to all other analogous compounds of Rh/Mo,⁹ Rh/W,⁹ Rh/Mn,⁸ Rh/Re,^{6c} and Rh/Os,⁷ which have the alkyl group terminally bound to the unsaturated Rh. In this regard the most enlightening contrast is between compound **2** and the isoelectronic Rh/Os compound [RhOs(CH₃)(CO)₃(dppm)₂],⁷ which has a Rh-bound methyl group in spite of an expected stronger Os–CH₃ bond.²³ It is significant, however, that **2** is a monocationic complex whereas the Rh/Os species is neutral. As a result, both metals in **2** can have their favored +1 oxidation state (assuming that with CH₃ on Ir the positive charge is localized on Rh or vice versa), whereas for the Rh/Os compound the observed structure has a favored Rh⁺/Os⁰ formulation, while a structure having CH₃ on Os would yield a lessfavorable Rh⁰/Os⁺ formulation. It may be that the structure of the Rh/Os compound reflects the favored oxidation states whereas for Rh/Ir the bond strengths determine the structure.

Compound **2** is also the middle member of the series of compounds having the formula [MM'(CH₃)(CO)₃(dppm)₂]⁺ (M, M' = Rh, Ir). The three compounds are dramatically different, with only the mixed-metal ana-

logue **2** being a simple methyl complex. The dirhodium species is in fact an acetyl-bridged compound, in which migratory insertion of the methyl and one carbonyl has occurred,¹⁰ while the diiridium species is a methylene-bridged hydride, which has resulted from C–H activation of the methyl group.^{11,12} These differences reflect the greater tendency for migratory insertions to occur at Rh and for oxidative addition to occur on Ir.

In spite of the stronger Ir–CH₃ bond in **2**, migration of the methyl group to Rh occurs readily upon substitution of a carbonyl by either ethylene or sulfur dioxide. This metal-to-metal migration of the methyl group presumably passes *via* a methyl-bridged species, although such an intermediate was not observed in this study. Alkyl-bridged complexes have previously been proposed in similar metal-to-metal migrations^{10,11,37} as well as in C–H activation of an alkyl group by an adjacent metal.^{10,37,44–49} In addition, a number of alkyl-bridged complexes involving the d- and f-block metals have now been characterized,^{44–46,48,50,51} in which several binding modes have been identified. It is not clear what factors (electronic and steric) are responsible for migration of the methyl group from Ir to Rh, nor is it clear under what conditions a methyl-bridged species might be stable. We are currently continuing our investigation of the factors involved in stabilizing alkyl-bridged species, with interests in inducing C–H activation of this bridged alkyl, to give an alkylidene-bridged hydride product, as we have observed in the related diiridium system.^{11,12}

Attempts to effect migratory insertion and concomitant C–C bond formation did succeed in the reaction of **2** with ^tBuNC. Although mechanistic information is not available, the final product and the observed intermediates suggest that migratory insertion has occurred at Ir. This presents an interesting contrast to the analogous diiridium system for which migratory insertion of

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^tBuNC did not occur,¹² suggesting a subtle involvement of the adjacent Rh center which somehow helps labilize the Ir. Another possibility, of course, is that the reaction of **2** with ^tBuNC proceeds via methyl migration to Rh, followed by migratory insertion and migration of the resulting iminoacyl group back to Ir. However, we see no evidence to support this latter suggestion.

In the reactions of **2** with C₂H₄ and ^tBuNC the coordinatively unsaturated Rh center is presumed to be the initial site of attack, although no species corresponding to attack at this site was observed. In preliminary studies involving the reaction of **2** with PMe₃, an intermediate, having the phosphine bound to Rh, has been observed at low temperature,⁵² supporting the proposal of initial attack at Rh. This study is currently ongoing.

The reaction of **2** with SO₂ may differ from the reactions with C₂H₄, *tert*-BuNC, and PMe₃, since sulfur

dioxide is capable of reacting as an electrophile.⁵³ It may be, therefore, that initial attack by this group occurs at the *saturated Ir center*. If so, this would parallel earlier suggestions of electrophilic attack of either H⁺ or CH₃⁺ at the saturated metals in compound **1** (*vide infra*) and in a series of isoelectronic rhodium–osmium compounds.⁷

It is anticipated that further work on alkyl complexes of these and related mixed-metal species will continue to shed light on the involvement of the different metals in the fundamental processes relevant to catalysis.

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Supporting Information Available: Tables of positional and thermal parameters for the phenyl groups, anion atoms, and solvent atoms, anisotropic thermal parameters, bond lengths and angles within the phenyl groups, anion, and solvent molecules, and hydrogen positional and thermal parameters (15 pages). Ordering information is given on any current masthead page.

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