analysis but decomposed upon initial irradiation. For the X-ray analysis of the similar pybox–rhodium complex could be referred to ref 1b. For 3, see also ref 1b.

***cis*-Dichloro(dichloromethyl)[2,6-bis(4,4-dimethyloxazolin-2-yl)pyridine]rhodium(III) (4).** A mixture of 1 (131 mg, 0.36 mmol) and dm-pybox (100 mg, 0.36 mmol) in chloroform (3.6 mL) was stirred at room temperature under nitrogen in the dark for 1 day. The mixture was concentrated under reduced pressure, and the residue was purified by column chromatography with CH_2Cl_2–MeOH as eluent to give 81 mg (0.15 mmol) of the dichloromethyl complex 4 (42%) and 52 mg (0.11 mmol) of 3 (30%). The corresponding equatorial isomer was not detected. 4: orange solids, mp 210 °C dec. ^{1}H NMR ($CDCl_3$): δ 1.75 (s, 6 H, CH_3), 1.80 (s, 6 H, CH_3), 4.59 (d, J = 8.6 Hz, 2 H), 4.67 (d, J = 8.6 Hz, 2 H), 7.46 (d, J_{Rh-H} = 3.4 Hz, 1 H, Rh-$CHCl_2$), 7.94 (d, J = 8.1 Hz, 2 H, pyridine), 8.22 (t, J = 8.1 Hz, 1 H, pyridine). ^{13}C NMR ($CDCl_3$): δ 26.45, 28.74, 69.88, 70.22 (d, J_{Rh-C} = 34.2 Hz, Rh-CH_2Cl), 84.07, 125.75, 139.05, 147.32, 164.84. IR (KBr): 1605 (O—C═N) cm^{-1}. R_f = 0.45 (EtOAc:MeOH = 5:1). Anal. Calcd for $C_{16}H_{21}N_3O_2Cl_3Rh\cdot0.5H_2O$): C, 35.58; H, 3.92; N, 7.78. Found: C, 35.53; H, 3.81; N, 8.20.

***cis*-Dichloro(methyl)[2,6-bis(4,4-dimethyloxazolin-2-yl)pyridine]rhodium(III) (10).** In a sealed tube, a solution of 2 (200 mg, 4.0 mmol) in methanol (10 mL) was heated at 100 °C for 2 days. After concentration the residue was purified by column chromatography with CH_2Cl_2–MeOH to give 155 mg (0.34 mmol) of the methyl complex 10 (83%) and 32 mg (0.06 mmol) of 3 (15%). 10: orange solids, mp 250 °C dec. ^{1}H NMR ($CDCl_3$): δ 1.25 (d, J_{Rh-H} = 2.4 Hz, 3 H, CH_3-Rh), 1.65 (s, 6 H, CH_3), 1.86 (s, 6 H, CH_3), 4.61 (d, J = 13.5 Hz, 2 H), 4.65 (d, J = 13.5 Hz, 2 H), 7.84 (d, J = 7.8 Hz, 1 H, pyridine), 8.12 (t, J = 7.8 Hz, 2 H, pyridine). ^{13}C NMR ($CDCl_3$): δ 3.44 (d, J_{Rh-C} = 19.5 Hz, CH_3-Rh), 27.42, 27.47, 69.17, 84.05, 125.23, 137.29, 146.94, 163.66. IR (KBr): 1610 (O—C═N) cm^{-1}. R_f = 0.3 (CH_2Cl_2:MeOH = 5:1). Anal. Calcd for $C_{16}H_{22}N_3O_2Cl_2Rh$: C, 41.58; H, 4.80; N, 9.09. Found: C, 41.54; H, 5.13; N, 8.41.

Methylation of 3 with Trimethylaluminum. To a suspension of 3 (100 mg, 0.21 mmol) in dichloromethane (4.0 mL) was added a hexane solution of trimethylaluminum (0.36 mmol, 1.2 N, 0.30 mL) at 0 °C. The mixture was stirred to be homogeneous for 10 min and was then quenched with water (2 mL). The organic layer was collected, concentrated, and purified by column chromatography with CH_2Cl_2–MeOH to give 82 mg (0.18 mmol, 86%) of the methyl complex 10.

Supplementary Material Available: Textual presentation of spectroscopic characterization data for 5–9 (2 pages). Ordering information is given on any current masthead page.

Binding of π-Acid Ligands in Diiridium and Rhodium–Iridium Iodo Complexes, Including Rare Examples of Ethylene Coordination in "A-Frame" Compounds. Structure of $[Ir_2I_2(CO)(\mu\text{-}CO)(Ph_2PCH_2PPh_2)_2]\cdot CH_2Cl_2$

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The diiodo species $[MIrI_2(CO)(\mu\text{-}CO)(dppm)_2]$ (M = Ir (1), Rh (3), dppm = $Ph_2PCH_2PPh_2$) are prepared by the reaction of the corresponding chloro complexes, $[MIrCl_2(CO)_2(dppm)_2]$, with KI. Abstraction of one iodide ion in 1 and 3, with use of $AgBF_4$, yields the corresponding A-frame complexes $[MIr(CO)_2(\mu\text{-}I)(dppm)_2][BF_4]$ (M = Ir (2), Rh (4)). All four species react with CO to give tricarbonyl complexes, but further CO addition is not observed. Reaction of 1 with dimethyl acetylenedicarboxylate (DMAD) yields four isomers of $[Ir_2I_2(CO)_2(\mu\text{-}DMAD)(dppm)_2]$, although upon heating of this mixture three of these species transform into the fourth, in which each metal has one iodo and one carbonyl ligand attached, having a structure much like that previously determined for the dichloro analogue. Reaction of the cationic species 2 and 4 with DMAD yields $[MIr(CO)_2(\mu\text{-}I)(\mu\text{-}DMAD)(dppm)_2][BF_4]$, and reaction of the mixed-metal product with CO yields $[RhIrI(CO)_2(\mu\text{-}CO)(\mu\text{-}DMAD)(dppm)_2][BF_4]$, which displays unusually high $^{13}C-^{13}C$ coupling of 47.8 Hz between the bridging carbonyl and the terminally bound carbonyl on Ir. Compounds 1 and 2 react with ethylene to yield the unusual ethylene adducts $[Ir_2(CO)(C_2H_4)(\mu\text{-}I)(\mu\text{-}CO)(dppm)_2][X]$ (X^- = I^-, BF_4^-), in which ethylene is terminally bound to one iridium center. The structure of 1 has been determined by X-ray techniques. This compound crystallizes, as the CH_2Cl_2 solvate, in the space group $P2_1/c$ with a = 20.241 (4) Å, b = 14.153 (2) Å, c = 20.446 (2) Å, β = 112.76 (1)°, V = 5400.7 Å^3, and Z = 4 and has refined to R = 0.041 and R_w = 0.049 on the basis of 5949 observations and 346 parameters varied. This complex has the unusual structure in which one carbonyl is terminally bound and one is bridging. One iodo ligand is opposite the Ir–Ir bond on one metal, while the other iodo group is cis to the Ir–Ir bond on the adjacent metal. Both carbonyl groups are mutually cis.

Introduction

Much of our understanding about oxidative-addition reactions in mononuclear complexes is derived from studies of Vaska's compound, *trans*-$[IrCl(CO)(PPh_3)_2]$, and related species.[1-12] It is well-known, for example, that substitution of the chloride by the better π-donor iodide ligand results in an increase in the rate of oxidative addition of H_2[6,9] and

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also in the rate of O_2 addition[6] and in stronger binding of dioxygen to the metal.[13,14] These effects are consistent with the increase in metal basicity that results from the aforementioned substitution.

The dppm-bridged complexes $[Ir_2Cl_2(CO)_2(dppm)_2]$,[15] $[Ir_2(CO)_2(\mu\text{-}Cl)(dppm)_2]^+$,[15] $[RhIrCl_2(CO)_2(dppm)_2]$,[16,17] and $[RhIr(CO)_2(\mu\text{-}Cl)(dppm)_2]^+$ [17] (dppm = $Ph_2PCH_2PPh_2$) can be considered as homo- and heterobinuclear analogues of Vaska's compound, and from these species it is anticipated that an improved understanding of oxidative additions and small-molecule activation in the presence of adjacent metals will emerge.[17-21] Our interest in small-molecule activation in binuclear systems prompted us to investigate the chemistry of the iodo analogues of the above species. In addition to the electronic effects, alluded to earlier, it was of interest to determine if the larger iodo ligand would give rise to significant steric effects in these binuclear systems. The results of part of this study are reported herein. Related studies on the oxidative-addition reactions of H_2[17] and O_2[22] to the diiridium complexes have already appeared.

Experimental Section

All solvents were appropriately dried and distilled prior to use and were stored under dinitrogen. Reactions were carried out under standard Schlenk conditions. Dinitrogen was passed through columns containing Ridox and 4A molecular sieves to remove traces of oxygen and water, respectively. Silver tetrafluoroborate ($AgBF_4$) and dimethyl acetylenedicarboxylate (DMAD) were purchased from Aldrich Chemical Co., sodium borohydride ($NaBH_4$) was purchased from Anachemia, potassium iodide was purchased from BDH Chemicals, hydrated iridium trichloride was purchased from Johnson-Matthey, and bis(diphenylphosphino)methane (dppm) was purchased from Strem Chemicals. Ethylene (c.p. grade) was purchased from Linde, carbon monoxide (c.p. grade) from Matheson, and ^{13}CO (99%) from Isotec Inc. These and all other reagents were used as received. The compounds *trans*-$[IrCl(CO)(dppm)]_2$[15] and $[RhIrCl_2(CO)_2(dppm)_2]$[16] were prepared by the previously reported procedures. The NMR spectra were recorded on a Bruker AM 400 spectrometer at 400.1 MHz for $^1H\{^{31}P\}$, at 161.9 MHz for $^{31}P\{^1H\}$, and at 100.6 MHz for $^{13}C\{^1H\}$ spectra unless otherwise indicated. Infrared spectra were obtained on a Nicolet 7199 Fourier transform IR spectrometer either as solids in 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 the department. Conductivity measurements were made on 10^{-3} M solutions by using a Yellow Springs Instrument Co. Model 31 conductivity bridge.

Preparation of Compounds. (a) $[Ir_2I_2(CO)(\mu\text{-}CO)(dppm)_2]\cdot CH_2Cl_2$ (1). The compound *trans*-$[IrCl(CO)(dppm)]_2$ (200 mg, 0.156 mmol) was suspended in 20 mL of CH_2Cl_2, to which was added an excess of KI (260 mg, 1.57 mmol) in a minimum volume of methanol. The suspension immediately changed color from deep purple to orange, and after it was stirred for 30 min the solvent was removed in vacuo and the product redissolved in approximately 10 mL of CH_2Cl_2. The solution was filtered and washed with several portions of degassed distilled water to remove the potassium salts. The product was then precipitated by the addition of 25 mL of diethyl ether. The resulting microcrystalline orange solid was collected and dried in vacuo, giving typical yields of 80–85%. Spectroscopic data for 1 and all subsequent compounds are given in Table I. Anal. Calcd for $Ir_2I_2Cl_2P_4O_2C_{53}H_{46}$: C, 41.12; H, 3.00; I, 16.40. Found: C, 40.96; H, 3.00; I, 16.58. In this case the amount of solvent was confirmed in the crystallographic study (vide infra). In other compounds that crystallized with solvent molecules the amount of solvent was confirmed by ^1H NMR spectroscopy.

(b) $[Ir_2(CO)_2(\mu\text{-}I)(dppm)_2][BF_4]\cdot THF$ (2). To a suspension of $[Ir_2I_2(CO)(\mu\text{-}CO)(dppm)_2]$ (1) in 10 mL of THF (80.0 mg, 0.055 mmol) was added $AgBF_4$ in 5 mL of THF (10.0 mg, 0.055 mmol), causing an immediate color change to dark red. The solution was filtered after stirring for an additional 30 min and then concentrated to approximately 5 mL with a rapid dinitrogen flow. Addition of 10 mL of Et_2O resulted in the precipitation of a brick red microcrystalline solid, which was collected and washed with two 5-mL portions of Et_2O and dried in vacuo (75–80% yield). Compound 2 was determined to be weakly conducting in THF solutions (Λ = 16.4 Ω^{-1} cm^2 mol^{-1}) but a normal 1:1 electrolyte in acetone (Λ = 147 Ω^{-1} cm^2 mol^{-1}). Anal. Calcd for $Ir_2IP_4F_4O_3C_{56}BH_{52}$: C, 44.99; H, 3.51; I, 8.49. Found: C, 44.54; H, 3.34; I, 7.24.

(c) $[RhIrI_2(CO)(\mu\text{-}CO)(dppm)_2]$ (3). A mixture of $[RhIrCl_2(CO)_2(dppm)_2]$ (250 mg, 0.021 mmol) and 10 equiv of KI (350 mg, 2.10 mmol) was reacted in $MeOH/CH_2Cl_2$ (10:90, 20 mL) for 2 h, during which time the orange slurry changed to a brown solution. The solvents were removed under vacuum, and the product was redissolved in CH_2Cl_2 (25 mL). The brown solution was filtered under dinitrogen and the volume reduced to ca. 12 mL followed by addition of Et_2O (30 mL). Upon cooling of the solution to 0 °C a brown powder was obtained in 69% yield. Anal. Calcd for $IrRhI_2P_4O_2C_{52}H_{44}$: C, 45.46; H, 3.23; I, 18.48. Found: C, 44.99; H, 3.25; I, 18.57.

(d) $[RhIr(CO)_2(\mu\text{-}I)(dppm)_2][BF_4]$ (4). A THF solution of $AgBF_4$ (14.2 mg, 0.073 mmol, in 5 mL) was added to 3 (100 mg, 0.073 mmol, in 10 mL of THF) and the slurry stirred for 1 h. The red-brown solution was filtered and the volume reduced to ca. 7 mL under vacuum. Diethyl ether (20 mL) was added and the mixture cooled to 0 °C to precipitate the product. The solvents were removed, and the red-brown solid was recrystallized from THF/Et_2O and then collected in 60% yield. Compound 4 was determined to be a 1:1 electrolyte in acetonitrile (Λ = 152 Ω^{-1} cm^2 mol^{-1}). Anal. Calcd for $IrRhIP_4F_4O_2C_{52}BH_{44}$: C, 46.80; H, 3.32; I, 9.51. Found: C, 46.93; H, 3.38; I, 8.94.

(e) $[Ir_2(CO)_2(\mu\text{-}I)(\mu\text{-}CO)(dppm)_2][I]$ (5a). A stream of CO was passed through a CH_2Cl_2 solution of 1, causing an immediate color change to light yellow. Diethyl ether was layered over the CH_2Cl_2 solution and allowed to diffuse slowly for 17 h to precipitate a yellow microcrystalline solid. The solvent was removed, and the solid was dried by rapid dinitrogen flow, giving compound **5a** in 90% yield. Compound **5a** was determined to be 1:1 electrolyte in CH_2Cl_2 solution (Λ = 56.3 Ω^{-1} cm^2 mol^{-1}). Anal. Calcd for $Ir_2I_2P_4O_3C_{53}H_{44}$: C, 42.69; H, 2.97; I, 17.01. Found: C, 42.43; H, 3.06; I, 16.72.

(f) $[Ir_2(CO)_2(\mu\text{-}I)(\mu\text{-}CO)(dppm)_2][BF_4]$ (5b). The procedure was the same as for **5a** except that compound 2 was used instead of compound 1. Carbonyl loss from **5b** occurred very readily upon dinitrogen purge over the solid sample.

(g) $[RhIr(CO)_2(\mu\text{-}I)(\mu\text{-}CO)(dppm)_2][I]$ (6a). A stream of CO was passed through a slurry of 3 (50 mg, 0.036 mmol, in 4 mL of THF) for 1 min. Stirring was continued for an additional 5 min, during which time the solution turned yellow and a yellow solid precipitated. The solvent was removed by evaporation under a stream of CO, and the yellow solid was recrystallized from CO-enriched CH_2Cl_2/Et_2O and collected in 80% yield. Compound **6a** slowly lost CO when placed under a dinitrogen atmosphere. It was found to be approximately a 1:1 electrolyte in acetonitrile (Λ = 105 Ω^{-1} cm^2 mol^{-1}).

(h) $[RhIr(CO)_2(\mu\text{-}I)(\mu\text{-}CO)(dppm)_2][BF_4]$ (6b). A solution of 4 was prepared in THF (15 mL) as described above by using complex 3 (50.0 mg, 0.036 mmol). A stream of CO was passed through the solution for 1 min, and stirring was continued for 5 min. The solvent was removed by evaporation under a stream of CO, and the yellow solid was recrystallized from CO-enriched CH_2Cl_2/Et_2O and collected in 65% yield.

(i) $[Ir_2I_2(CO)_2(\mu\text{-}DMAD)(dppm)_2]\cdot CH_2Cl_2$ (7d). To a CH_2Cl_2 solution of 1 (50.0 mg, 0.034 mmol, in 10 mL) was added 1 equiv of DMAD (4.2 μL). Four products were observed over time. Compound **7d** was obtained as the only product in 95% yield by refluxing the mixture of the four isomers in CH_2Cl_2 for 2 h. After the reaction was complete (as monitored by $^{31}P\{^1H\}$ NMR spectroscopy) the solution was concentrated to half its original volume with rapid dinitrogen flow, and compound **7d** was precipitated by the addition of 10 mL of Et_2O. The solid was then collected,

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Table I. Spectroscopic Data[a]

	IR, cm^{-1}		NMR	
	solid[b]	soln[c]	$\delta(^{31}P\{^1H\})$[d]	$\delta(^1H)$[e]
$[Ir_2I_2(CO)(\mu\text{-}CO)(dppm)_2]$ (**1**)	1948 (vs), 1741 (vs)[f]	1960 (vs), 1742 (st)[f]	7.32 (m), −10.13 (m)[g]	4.71 (m, 2 H), 4.56 (m, 2 H)
$[Ir_2(CO)_2(\mu\text{-}I)(dppm)_2][BF_4]$ (**2**)	1966 (vs), 1937 (st)	1971 (st), 1957 (vs)	13.93 (s)	4.21 (m, 2 H), 3.80 (m, 2 H)
$[RhIrI_2(CO)(\mu\text{-}CO)(dppm)_2]$ (**3**)	1970 (st), 1954 (vs, br), 1763 (st)	1959 (st), 1777 (m)	19.7 (dm, $^1J_{Rh-P}$ = 119.7 Hz),[h] −9.95 (m)[i]	4.59 (m, 4 H)
$[RhIr(CO)_2(\mu\text{-}I)(dppm)_2][BF_4]$ (**4**)	1970 (med, br), 1948 (med, br)	1978 (st), 1960 (st)	19.7 (dm, $^1J_{Rh-P}$ = 125.9 Hz),[h] 15.8 (m)[i]	2.53 (m, 4 H)
$[Ir_2(CO)_2(\mu\text{-}I)(\mu\text{-}CO)(dppm)_2][I]$ (**5a**)	1991 (st), 1949 (vs, br), 1815 (st)	1977 (vs, br), 1872 (med)	−4.46 (s)	4.63 (m, 2 H), 4.13 (m, 2 H)
$[Ir_2(CO)_2(\mu\text{-}I)(\mu\text{-}CO)(dppm)_2]\text{-}[BF_4]$ (**5b**)	1954 (vs, br), 1804 (med)	1970 (vs), 1950 (st), 1825 (w)	−4.81 (s)	4.50 (m, 2 H), 4.21 (m, 2 H)
$[RhIr(CO)_2(\mu\text{-}I)(\mu\text{-}CO)(dppm)_2]\text{-}[I]$ (**6a**)	1963 (vs, br), 1827 (st)	1984 (vs, br), 1848 (med)	26.1 (dm, $^1J_{Rh-P}$ = 95.7 Hz),[h] −6.0 (m)[i]	4.74 (m, 2 H), 4.33 (m, 2 H)
$[RhIr(CO)_2(\mu\text{-}I)(\mu\text{-}CO)(dppm)_2]\text{-}[BF_4]$ (**6b**)	1961 (st, br), 1827 (med)	1985 (vs), 1850 (med)	25.6 (dm, $^1J_{Rh-P}$ = 96.0 Hz),[h] −6.2 (m)[i]	4.4 (m, 4 H)
$[IrI_2(CO)_2(\mu\text{-}DMAD)(dppm)_2]$ (**7a**)	2025 (vs)	2040 (vs), 2008 (st); 1689 (sh), 1705 (med);[k,n] 1548 (w), 1635 (med)[m,n]	−4.08 (s)	4.78 (m, 4 H), 3.51 (s, 6 H)
$[Ir_2I_2(CO)_2(\mu\text{-}DMAD)(dppm)_2]$ (**7b**)	1996 (st), 1977 (med)	1961 (vs, br), 1728 (vs, br)	−23.53 (s)	2.45 (m, 4 H), 1.71 (s, 6 H)
$[Ir_2I_2(CO)_2(\mu\text{-}DMAD)(dppm)_2]$ (**7c**)	2071 (vs); 1685 (med);[k] 1632 (med)[m]	2063 (st)	−29.22 (s)	4.94 (m, 2 H), 4.08 (m, 2 H), 2.89 (s, 6 H)
$[Ir_2I_2(CO)_2(\mu\text{-}DMAD)(dppm)_2]$ (**7d**)	2042 (vs), 1983 (vs); 1695 (med); 1669 (med);[k] 1554 (med)[m]	2033 (vs), 2006 (st), 1982 (st), 1703 (st); 1683 (med), 1662 (med);[k] 1555 (med), 1539 (w)[m]	−35.87 (m)	5.08 (m, 2 H), 4.43 (m, 2 H), 3.53 (s, 3 H), 2.54 (s, 3 H)
$[Ir_2(CO)_2(\mu\text{-}I)(\mu\text{-}DMAD)\text{-}(dppm)_2][BF_4]$ (**8**)	1987 (vs, br); 1705 (med);[k] 1613 (w)[m]	1998 (vs); 1704 (med), 1690 (med);[k] 1613 (w)[m]	−16.86 (s)	4.29 (m, 2 H), 3.97 (m, 2 H), 2.95 (s, 6 H)
$[RhIr(CO)_2(\mu\text{-}I)(\mu\text{-}DMAD)\text{-}(dppm)_2][BF_4]$ (**9**)	2020 (med, sh), 1997 (vs); 1703 (med);[k] 1588 (w)[m]	2031 (med, sh), 2008 (vs); 1705 (med, br);[k] 1587 (w)[m]	16.1 (dm, $^1J_{Rh-P}$ = 89.1 Hz),[h] −13.6 (m)[i]	4.1 (m, 2 H), 4.0 (m, 2 H), 3.1 (s, 3 H), 3.0 (s, 3 H)
$[RhIr(CO)_2(\mu\text{-}CO)(\mu\text{-}DMAD)\text{-}(dppm)_2][BF_4]$ (**10**)	2089 (st), 2055 (vs), 1738 (st); 1712 (st), 1697 (st);[k] 1577 (w)[m]	2091 (m), 2059 (st), 1748 (m); 1707 (m);[k] 1573 (w)[m]	18.6 (dm, $^1J_{Rh-P}$ = 131.0 Hz),[h] −30.4 (m)[i]	4.5 (m, 2 H), 2.8 (m, 2 H), 3.37 (s, 3 H), 1.75 (s, 3 H)
$[Ir_2I(CO)(C_2H_4)(\mu\text{-}CO)(dppm)_2]\text{-}[I]$ (**11a**)	1964 (vs, br), 1804 (med)	1979 (vs, br), 1815 (med)	−5.67 (m), −6.94 (m)	4.22 (m, 2 H), 4.04 (m, 2 H), 2.68 (m, 2 H), 1.58 (m, 2 H)
$[Ir_2I(CO)(C_2H_4)(\mu\text{-}CO)(dppm)_2]\text{-}[BF_4]$ (**11b**)	1959 (vs, br), 1803 (med)	1979 (vs, br), 1817 (med)	−5.69 (m), −6.92 (m)	4.21 (m, 2 H), 3.96 (m, 2 H), 2.69 (m, 2 H), 1.59 (m, 2 H)

[a] Abbreviations used are as follows: w = weak, med = medium, st = strong, vs = very strong, sh = shoulder, br = broad, s = singlet, m = multiplet, dm = doublet of multiplets. [b] Nujol mull. [c] CH_2Cl_2 solution except compounds **2**, **4**, and **5b** (THF). [d] Vs 85% H_3PO_4, 25 °C, in CD_2Cl_2 solvent except compound **2** (THF-d_8). [e] Vs TMS, 25 °C, in CD_2Cl_2 solvent except compound **2** (THF-d_8). [f] ν(CO) unless otherwise noted. [g] −40 °C. [h] $\delta(P_{Rh})$. [i] $\delta(P_{Ir})$. [k] ν(CO) of CO_2Me. [m] ν(C=C). [n] The acetylenic stretches are due to a mix of **7a** and **7b**.

washed with Et_2O, and dried in vacuo. Anal. Calcd for $Ir_2I_2Cl_2P_4O_6C_{59}H_{52}$: C, 42.82; H, 3.17; I, 15.23. Found: C, 42.82; H, 2.93; I, 16.12.

(j) $[Ir_2(CO)_2(\mu\text{-}I)(\mu\text{-}DMAD)(dppm)_2][BF_4]$ (8). The procedure was the same as for **7**, except that compound **2** was used instead of **1** and only one product was formed, which was isolated in 95% yield. Compound **8** was determined to be a 1:1 electrolyte in CH_2Cl_2 solution (Λ = 57.4 Ω^{-1} cm^2 mol^{-1}). Anal. Calcd for $Ir_2IP_4F_4O_6C_{58}H_{50}$: C, 45.54; H, 3.29; I, 8.30. Found: C, 44.57; H, 3.10; I, 8.16.

(k) $[RhIr(CO)_2(\mu\text{-}I)(\mu\text{-}DMAD)(dppm)_2][BF_4]$ (9). A solution of **4** was prepared in THF (10 mL) as described above by using complex **3** (50 mg, 0.036 mmol). After 1 h of stirring, 1.1 equiv of DMAD (4.9 μL) was added and stirring continued for 2 h. The solvents were then removed under vacuum, the residue was redissolved in CH_2Cl_2 (10 mL), and the solution was filtered. Upon being stirred for 24–28 h, the dark solution turned to clear orange and the solvent was reduced to ca. 4 mL under vacuum. Addition of Et_2O (20 mL) resulted in the precipitation of brown-yellow solid, which was dried and collected in 65% yield. Anal. Calcd for $IrRhIP_4F_4O_6C_{58}BH_{50}$: C, 47.20; H, 3.41; I, 8.60. Found: C, 46.88; H, 3.34; I, 8.73.

(l) $[RhIrI(CO)_2(\mu\text{-}CO)(\mu\text{-}DMAD)(dppm)_2][BF_4]$ (10). Compound **9** was prepared as described above from complex **4** (50.0 mg, 0.036 mmol) and redissolved in CH_2Cl_2. A stream of CO was passed through the solution for 30 s, resulting in a very slight change in color of the solution to lighter orange. The solvents were removed by evaporation under a stream of CO. Compound **10** was characterized spectroscopically in CO-enriched CH_2Cl_2 or CD_2Cl_2 solutions.

(m) $[Ir_2(CO)(C_2H_4)(\mu\text{-}I)(\mu\text{-}CO)(dppm)_2][I]$ (11a). Ethylene gas (1 atm) was placed over a 5-mL CH_2Cl_2 solution of $[Ir_2I_2(CO)(\mu\text{-}CO)(dppm)_2]$ (**1**) (30 mg, 0.021 mmol), causing a slight color change from orange to light orange within 1–2 min; the reaction was reversible upon flushing with dinitrogen. To obtain NMR spectra, the reactions were carried out in CD_2Cl_2 solution under an ethylene atmosphere. Compound **11a** was determined to be a 1:1 electrolyte in ethylene-saturated CH_2Cl_2 solution (Λ = 47.3 Ω^{-1} cm^2 mol^{-1}).

(n) $[Ir_2(CO)(C_2H_4)(\mu\text{-}I)(\mu\text{-}CO)(dppm)_2][BF_4]\cdot CH_2Cl_2$ (11b). Ethylene gas (1 atm) was placed over a 5-mL THF solution of $[Ir_2(CO)_2(\mu\text{-}I)(dppm)_2][BF_4]$ (**2**) (28.0 mg, 0.020 mmol), resulting in an immediate color change from red to orange with accompanying precipitation of the product. After the mixture was stirred for 0.5 h, the solvent was removed under vacuum. Compound **11b** is soluble in CH_2Cl_2 and was recrystallized from this solvent. Anal. Calcd for $Ir_2ICl_2P_4F_4O_2C_{55}BH_{50}$: C, 43.00; H, 3.29; I, 8.26. Found: C, 42.85; H, 3.16; I, 8.41.

X-ray Data Collection. Crystals of $[Ir_2I_2(CO)(\mu\text{-}CO)(dppm)_2]\cdot CH_2Cl_2$ (**1**), suitable for an X-ray diffraction study, were obtained by slow diffusion of Et_2O into a saturated CH_2Cl_2 solution of complex **1**. Due to the sensitivity of the crystals to air, one was wedged into a dinitrogen-filled glass capillary, which was flame sealed. Unit cell parameters were obtained from a least-squares refinement of the setting angles of 25 reflections, in the range 22.0° ≤ 2θ ≤ 25.2°, which were accurately centered on an Enraf-Nonius

Table II. Summary of Crystal Data and Details of Intensity Collection

compd	$[Ir_2I_2(CO)(\mu\text{-}CO)(dppm)_2]\cdot CH_2Cl_2$
formula	$Ir_2I_2Cl_2P_4O_2C_{53}H_{46}$
fw	1547.97
cryst shape	monoclinic prism
cryst size, mm	0.34 × 0.24 × 0.048
space group	$P2_1/c$ (No. 14)
cell params	
a, Å	20.241 (4)
b, Å	14.153 (2)
c, Å	20.446 (2)
β, deg	112.76 (1)
V, Å^3	5400.7
Z	4
ρ(calcd), g/cm^3	1.904
temp, °C	22
radiation (λ, Å)	graphite-monochromated Mo Kα (0.710 69)
receiving aperture, mm	3.00 + (tan θ) wide × 4.00 high, 173 from cryst
take-off angle, deg	3.00
scan speed, deg/min	variable between 6.67 and 0.91
scan width, deg	0.75 + (0.347 tan θ) in θ
2θ limits, deg	$0.6 \leq 2\theta \leq 50.0$
no. of unique data collcd	9599 ($h,k,\pm l$)
no. of unique data used ($F_o^2 \geq 3\sigma(F_o^2)$)	5949
linear absorption coeff μ, cm^{-1}	62.91
range of transm factors	0.818–1.574
final no. of params refined	346
error in observn of unit wt	1.454
R	0.041
R_w	0.049

Table III. Positional Parameters and Isotropic Thermal Parameters for Compound 1[a]

atom	x	y	z	B,[b] Å^2
Ir(1)	0.23486 (2)	0.46273 (3)	0.41553 (2)	2.002 (8)
Ir(2)	0.22573 (2)	0.63648 (3)	0.47848 (2)	2.100 (8)
I(1)	0.24372 (4)	0.29948 (5)	0.35289 (4)	3.62 (2)
I(2)	0.37284 (4)	0.66399 (6)	0.51473 (4)	3.83 (2)
Cl(1)[c]	0.4963 (4)	0.5845 (5)	0.1089 (4)	14.2 (3)
Cl(2)[c]	0.5827 (5)	0.6723 (5)	0.2387 (5)	20.7 (3)
P(1)	0.2307 (1)	0.5358 (2)	0.3130 (1)	2.37 (6)
P(2)	0.2028 (2)	0.7191 (2)	0.3731 (1)	2.36 (6)
P(3)	0.2685 (1)	0.3840 (2)	0.5221 (1)	2.23 (6)
P(4)	0.2592 (1)	0.5705 (2)	0.5917 (1)	2.37 (6)
O(1)	0.0957 (4)	0.5136 (5)	0.4111 (4)	3.3 (2)
O(2)	0.1421 (5)	0.7824 (7)	0.5182 (4)	5.9 (2)
C(1)	0.1587 (5)	0.5317 (7)	0.4283 (4)	1.9 (2)
C(2)	0.1754 (6)	0.7295 (8)	0.5044 (6)	3.7 (3)
C(3)	0.2472 (5)	0.6632 (7)	0.3213 (5)	2.6 (2)
C(4)	0.3087 (5)	0.4619 (8)	0.5991 (5)	2.7 (2)
C(5)[c]	0.533 (1)	0.687 (1)	0.151 (1)	13.0 (9)

[a] Phenyl carbon parameters are given in the supplementary material. [b] All atoms in this table were refined isotropically. B values for anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $^4/_3[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$. [c] Atoms Cl(1), Cl(2), and C(5) are those of the CH_2Cl_2 solvent molecule.

CAD4 diffractometer using graphite-monochromated Mo Kα radiation. The systematic absences ($h0l$, l = odd; $0k0$, k = odd) were consistent with the space group $P2_1/c$.

Intensity data were collected on the CAD4 diffractometer in the bisecting mode employing the $\theta/2\theta$ scan technique up to $2\theta = 50.0°$. The scan range was determined as a function of θ to compensate for α_1–α_2 wavelength dispersion, and backgrounds were scanned for 25% of the peak width on either end of the peak scan. The intensities of three standard reflections were measured every 1 h of exposure time in order to monitor crystal and electronic stability. The mean decrease in the intensity of the standards was 6.3%, and a correction was applied by assuming linear decay. The data were processed in the usual manner with a value of 0.04 used for p to downweigh intense reflections.[23] Corrections for Lorenz and polarization effects and for absorption, by using the method of Walker and Stuart,[24] were applied to the data. See Table II for pertinent crystal data and details of intensity collection.

Structure Solution and Refinement. The structure was solved in the space group $P2_1/c$ by using a combination of direct methods and Patterson techniques to locate the metals and the iodine atoms. All other atoms were located after subsequent least-squares and difference Fourier calculations. Electron densities in the regions of the CH_2Cl_2 solvent atoms were somewhat smeared out, giving rise to high thermal parameters for these atoms. All hydrogen atoms were located but were assigned idealized positions on the basis of the geometry of their attached carbon atom and with C–H distances of 0.95 Å; thermal parameters were fixed at 1.2 times that of their attached carbon atom. The hydrogen atoms were included as fixed contributions in the least-squares calculations.

Refinement was carried out by using full-matrix least-squares techniques,[25] minimizing the function $\sum w(|F_o| - |F_c|)^2$, with $w = 4F_o^2/\sigma^2(F_o^2)$. The neutral-atom scattering factors[26,27] and anomalous dispersion terms[28] used in the structure determination programs were obtained from the usual sources. The final model with 346 parameters varied refined to $R = 0.041$ and $R_w = 0.049$. In the final difference Fourier map, the 10 highest residual peaks were in the range 1.09–0.80 e/Å^3 and were located in the vicinities of the iridium and iodine atoms and the dppm ligands. The positional and isotropic thermal parameters for the non-hydrogen atoms, excluding phenyl groups, are given in Table III.

Results and Discussion

The diiodo species $[Ir_2I_2(CO)(\mu\text{-}CO)(dppm)_2]$ (1) is readily prepared from the dichloro precursor, *trans*-$[IrCl(CO)(dppm)]_2$, by reaction with KI. Although these two halide species have analogous stoichiometries, it is clear from the spectroscopic data that the two have very different structures. The dichloride precursor has one carbonyl stretch in the IR spectrum at 1953 cm^{-1} and displays a singlet in the $^{31}P\{^1H\}$ NMR spectrum, indicating that it is symmetric with one chloro and one carbonyl ligand bound to each metal.[15] The diiodo species 1, on the other hand, has two inequivalent metal centers and displays two $^{31}P\{^1H\}$ resonances typical of an AA′BB′ spin system in the NMR spectrum and one terminal (1948 cm^{-1}) and one bridging (1741 cm^{-1}) carbonyl stretch in the IR spectrum. An X-ray structure determination of 1 confirms the unusual unsymmetrical structure.

Compound 1 crystallizes in the space group $P2_1/c$ with one complex molecule and one CH_2Cl_2 solvent molecule in the asymmetric unit. The solvent molecule displays the expected geometry and has no unusual contacts with the complex molecule. A perspective view of the complex, including the numbering scheme, is shown in Figure 1. Selected distances and angles are given in Tables IV and V, respectively.

The complex has the bridging dppm ligands in a normal trans arrangement, but having the dppm methylene groups tilted toward the side of the molecule containing the large iodine atoms. Such an arrangement is atypical of A-frame-like complexes, in which the dppm methylenes

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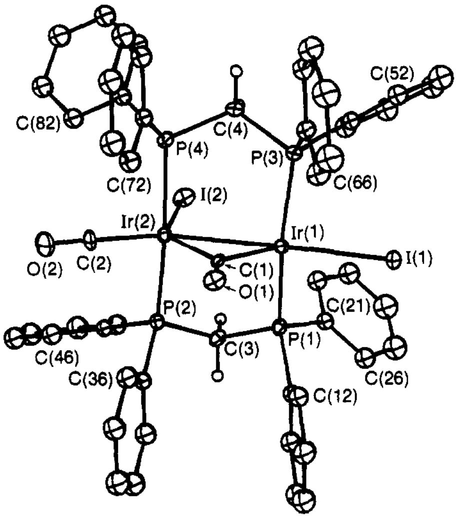

Figure 1. Perspective drawing of $[Ir_2I_2(CO)(\mu\text{-}CO)(dppm)_2]$, showing the numbering scheme. Thermal ellipsoids are shown at the 20% level except for methylene hydrogens, which are shown arbitrarily small. Phenyl hydrogens are omitted.

Table IV. Selected Distances (Å) in $[Ir_2I_2(CO)(\mu\text{-}CO)(dppm)_2]$

Ir(1)–Ir(2)	2.8159 (5)	P(1)–C(21)	1.84 (1)
Ir(1)–I(1)	2.6811 (7)	P(2)–C(3)	1.814 (9)
Ir(1)–P(1)	2.310 (2)	P(2)–C(31)	1.811 (9)
Ir(1)–P(3)	2.303 (2)	P(2)–C(41)	1.838 (9)
Ir(1)–C(1)	1.926 (8)	P(3)–C(4)	1.835 (9)
Ir(2)–I(2)	2.8032 (8)	P(3)–C(51)	1.84 (1)
Ir(2)–P(2)	2.334 (2)	P(3)–C(61)	1.82 (1)
Ir(2)–P(4)	2.340 (2)	P(4)–C(4)	1.808 (9)
Ir(2)–C(1)	2.005 (9)	P(4)–C(71)	1.831 (9)
Ir(2)–C(2)	1.86 (1)	P(4)–C(81)	1.83 (1)
P(1)–C(3)	1.830 (9)	O(1)–C(1)	1.22 (1)
P(1)–C(11)	1.830 (9)	O(2)–C(2)	1.11 (1)

Table V. Selected Angles (deg) in $[Ir_2I_2(CO)(\mu\text{-}CO)(dppm)_2]$

Ir(2)–Ir(1)–I(1)	178.60 (2)	Ir(1)–P(1)–C(3)	114.6 (3)
Ir(2)–Ir(1)–P(1)	92.18 (6)	Ir(1)–P(1)–C(11)	118.6 (3)
Ir(2)–Ir(1)–P(3)	92.17 (6)	Ir(1)–P(1)–C(21)	110.3 (3)
Ir(2)–Ir(1)–C(1)	45.4 (3)	C(3)–P(1)–C(11)	103.3 (4)
I(1)–Ir(1)–P(1)	86.43 (6)	C(3)–P(1)–C(21)	100.7 (4)
I(1)–Ir(1)–P(3)	89.16 (6)	C(11)–P(1)–C(21)	107.7 (4)
I(1)–Ir(1)–C(1)	134.9 (3)	Ir(2)–P(2)–C(3)	110.8 (3)
P(1)–Ir(1)–P(3)	165.70 (9)	Ir(2)–P(2)–C(31)	117.4 (3)
P(1)–Ir(1)–C(1)	98.4 (2)	Ir(2)–P(2)–C(41)	114.9 (3)
P(3)–Ir(1)–C(1)	94.3 (2)	C(3)–P(2)–C(31)	105.4 (4)
Ir(1)–Ir(2)–I(2)	89.48 (2)	C(3)–P(2)–C(41)	105.2 (4)
Ir(1)–Ir(2)–P(2)	92.28 (6)	C(31)–P(2)–C(41)	102.0 (4)
Ir(1)–Ir(2)–P(4)	93.31 (6)	Ir(1)–P(3)–C(4)	113.1 (3)
Ir(1)–Ir(2)–C(1)	43.1 (2)	Ir(1)–P(3)–C(51)	111.4 (3)
Ir(1)–Ir(2)–C(2)	152.5 (4)	Ir(1)–P(3)–C(61)	120.0 (3)
I(2)–Ir(2)–P(2)	89.21 (6)	C(4)–P(3)–C(51)	100.0 (4)
I(2)–Ir(2)–P(4)	85.53 (6)	C(4)–P(3)–C(61)	104.2 (4)
I(2)–Ir(2)–C(1)	132.6 (2)	C(51)–P(3)–C(61)	106.2 (4)
I(2)–Ir(2)–C(2)	118.0 (4)	Ir(2)–P(4)–C(4)	111.3 (3)
P(2)–Ir(2)–P(4)	172.28 (8)	Ir(2)–P(4)–C(71)	117.1 (3)
P(2)–Ir(2)–C(1)	92.6 (2)	Ir(2)–P(4)–C(81)	115.7 (3)
P(2)–Ir(2)–C(2)	88.6 (3)	C(4)–P(4)–C(71)	105.4 (4)
P(4)–Ir(2)–C(1)	95.2 (2)	C(4)–P(4)–C(81)	102.7 (4)
P(4)–Ir(2)–C(2)	88.9 (3)	C(71)–P(4)–C(81)	103.1 (4)
C(1)–Ir(2)–C(2)	109.4 (4)	Ir(1)–C(1)–Ir(2)	91.5 (4)
Ir(1)–C(1)–O(1)	131.4 (7)	P(1)–C(3)–P(2)	111.7 (5)
Ir(2)–C(1)–O(1)	137.1 (7)	P(3)–C(4)–P(4)	113.0 (5)
Ir(2)–C(2)–O(2)	176 (1)		

usually bend toward the group that bridges the metals. However, in this complex the present geometry appears to minimize the potentially more severe steric interactions between the phenyl hydrogens and the iodo ligands. Within the diphosphine ligands the parameters are as expected. Even the slightly longer Ir–P distances involving Ir(2) (2.334 (2), 2.340 (2) Å vs 2.310 (2), 2.303 (2) Å for Ir(1)) are not unexpected, reflecting the greater crowding at this metal center.

In the equatorial plane the ligand arrangement is unusual in two significant ways. First, both of the carbonyl and both of the iodo ligands are mutually cis on adjacent metals, even though the two chloro and two carbonyl ligands in the precursor, $[IrCl(CO)(dppm)]_2$, were mutually trans.[15] This observed arrangement for the diiodo complex is perhaps unexpected on the basis of steric arguments, which would appear to favor a trans arrangement, having the bulky iodo ligands widely separated. The second unusual feature is the unsymmetrical structure adopted by the complex, in which both metals have a terminal iodo and a bridging carbonyl group attached, with one metal having an additional terminal carbonyl ligand. On the basis of the stoichiometry, a symmetric structure in which each metal is bound to one CO and one iodo ligand, as observed in the dichloro analogue,[15] would appear more likely. In addition, the movement of one carbonyl group to the bridging position is accompanied by metal–metal bond formation, a feature that should destabilize the structure by bringing the bulky iodo ligands closer together. It should be noted, however, that the ligand arrangement, having one iodo group opposite the Ir–Ir bond, does not appear to give rise to unfavorable interactions between the iodo groups.

Although the observed geometry of 1 may be the result of steric interactions, another rationale for the adopted structure, particularly the presence of the bridging carbonyl group, is that it serves to relieve the metal centers of some excess electron density, resulting from the good electron-donor iodo ligands. Bridging carbonyl groups are recognized as better π-acids than terminal carbonyls,[29] and conversion of terminal CO ligands into bridging ones has been observed in metal–carbonyl clusters[30,31] and in related binuclear complexes[32] upon substitution of carbonyl groups for electron-donating groups. Such a role for the bridging CO ligand in compound 1 is supported by the low infrared stretching frequency of the group, although this value is not outside of the range displayed by similar diiridium chloro carbonyls.[15] The unsymmetrical geometry has previously been observed in a related dirhodium complex, $[Rh_2Cl_2(CO)(\mu\text{-}CO)((MeO)_2PNEtP(OMe)_2)_2]$.[33] Here too, the carbonyl groups are adjacent to one another, as are the two chloro ligands. In this case it would seem unlikely that the geometry is dictated by steric effects, since the methoxy substituents are smaller than the phenyl groups in the present compound. Furthermore, one should compare this methoxydiphosphane-bridged complex with its phenoxy-substituted analogue, $[RhCl(CO)((PhO)_2PNEtP(OPh)_2)]_2$,[33] which *does* have the symmetric trans structure. The structures of these two species would appear to be consistent with previous arguments regarding compound 1, based on the greater electron-donating ability of the methoxy group compared to the phenoxy group.[34] An analogous geometry has been proposed for $[Rh_2I_2$-

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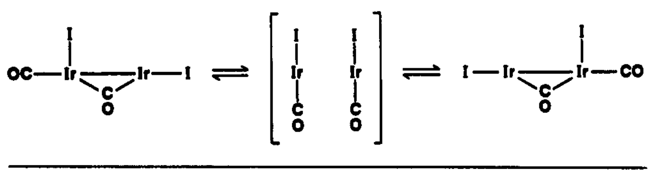
(CO)(μ-CO)(dppm)$_2$][35] and is also suggested for one isomer[36] of the heterobinuclear complex [RhIrCl$_2$(CO)$_2$(dppm)$_2$].

The geometries at each of the iridium centers in compound 1 are reminiscent of two known dppm-bridged complexes. At Ir(1) the geometry resembles that observed in [Rh$_2$X$_2$(μ-CO)(dppm)$_2$] (X = Cl,[37] Br[38]), except that in 1 the iodo ligand is almost colinear with the Ir–Ir bond (178.60 (2)°), whereas the analogous Rh–Rh–Br and Rh–Rh–Cl angles averaged 166.26 and 161.5°, respectively. This difference is probably a consequence of steric repulsions involving I(1) and the proximate phenyl groups in 1. The geometry about Ir(2) closely resembles that observed in [Ir$_2$Cl$_2$(CO)$_2$(μ-CO)(dppm)$_2$],[15] and here again the slight differences in the angles at Ir appear to be steric in origin. The entire structure of compound 1 is closely related to that of the above dichloro tricarbonyl species, merely lacking one carbonyl group on Ir(1).

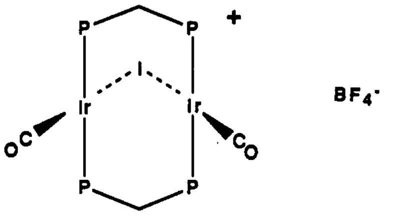
The Ir(1)–Ir(2) separation of 2.8159 (5) Å corresponds to a normal single bond,[15,18,19,39] and the relatively acute Ir(1)–C(1)–Ir(2) angle (91.5 (4)°) is typical for a carbonyl group that is bridging a metal–metal bond. The bonding of this carbonyl is unsymmetrical, being significantly closer to Ir(1) than Ir(2) (1.926 (8) Å vs 2.005 (9) Å). This difference may be due either to electronic or steric factors. The π back-donation to C(1)O(1) should be somewhat lower from Ir(2) due to competition from C(2)O(2) and may partially account for the longer Ir(2)–C(1) distance. It also appears that the proximate phenyl group (ring 7) forces the bridging carbonyl away from Ir(2), as seen in Figure 1. Consistent with this suggestion the H(72)–O(1) nonbonded contact is rather short, at 2.43 Å.

As was observed for the Rh–Cl distances in [Rh$_2$Cl$_2$(CO)(μ-CO){(MeO)$_2$PNEtP(OMe)$_2$}$_2$],[33] the Ir(2)–I(2) bond adjacent to the metal–metal bond is longer (2.8032 (8) Å) than the one opposite the metal–metal bond (Ir(1)–I(1) = 2.6811 (7) Å). Since metal–metal bonds have been shown to cause a "trans lengthening" in such complexes,[18,40–42] the observed reversal in this case must again reflect the greater crowding about Ir(2).

In solution compound 1 appears to be fluxional. As the sample is warmed, the resonances in the ^{31}P{^{1}H} NMR spectrum broaden and coalesce at approximately +35 °C, indicating a fluxional process that exchanges the phosphorus environments. It appears that this fluxionality does not result from iodide dissociation to yield a cationic A-frame species, since a THF solution containing a mixture of 1 and the cationic A-frame species 2 (vide infra) shows broadening of the ^{31}P{^{1}H} resonances of 1 as the temperature is increased, while the resonance of 2 remains sharp. It appears that the fluxionality of 1 occurs by exchange of the carbonyl groups between bridging and terminal sites, as shown.

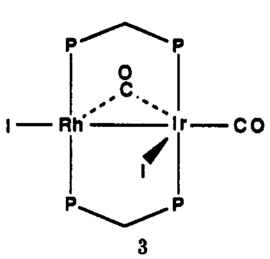


Iodide abstraction from 1 using AgBF$_4$ immediately yields a dark red solution of [Ir$_2$(CO)$_2$(μ-I)(dppm)$_2$][BF$_4$] (2). The isolated solid displays two terminal carbonyl bands (1966, 1937 cm^{-1}) in the infrared spectrum, and elemental analyses indicate the presence of only one iodine atom per dimer. This information, along with the ^{31}P{^{1}H} NMR spectrum (δ 13.93 (s)), which indicates that all four phosphorus atoms are chemically equivalent, leads to the A-frame formulation for the cation of 2, analogous to the chloro- and sulfido-bridged complexes of both rhodium[43,44] and iridium.[15,39] In the infrared spectrum, the carbonyl stretches for compound 2 are at lower frequency than those of the chloro analogue (1989, 1964 cm^{-1}),[15] reflecting the higher π-donor ability of iodine over chlorine. However, the values are still higher than for the neutral sulfido-bridged species (1918, 1902 cm^{-1}),[39] presumably owing in part to the cationic nature of 2. In THF the low conductivity of compound 2 (16.4 Ω^{-1} cm^2 mol^{-1}) suggests rather tight ion pairing; in acetone, however, 2 behaves as a normal 1:1 electrolyte (147 Ω^{-1} cm^2 mol^{-1}).[45] Although the low conductivity in THF suggests the possibility of weak interactions between the fluorine atoms of BF$_4^-$ and one or both metal centers, no indication of such is observed in either the infrared or the ^{19}F NMR spectrum. Compound 2 is also found to readily scavenge Cl$^-$ from CH$_2$Cl$_2$, yielding at least two unidentified unsymmetrical complexes that are presumed to be mixed-halide species; the use of this solvent was subsequently avoided when 2 was involved.



2

The mixed-metal analogue of 1, [RhIrI$_2$(CO)(μ-CO)(dppm)$_2$] (3), is prepared from [RhIrCl$_2$(CO)$_2$(dppm)$_2$] by reaction with KI, much as was noted earlier for the diiridium species. In solution only one species is observed as seen by the ^{31}P{^{1}H} NMR spectrum. This species appears to be exactly analogous to 1, having carbonyl stretches in solution at 1959 and 1777 cm^{-1}. The structure shown for 3, in which the terminal carbonyl ligand is bound to Ir, is consistent with the greater basicity of this metal and with the similarities of the terminal carbonyl stretching frequencies in compounds 1 and 3. Although the geometry shown has the carbonyl ligands in a mutually cis arrangement, as established for 1, we cannot rule out a pseudo-trans arrangement of these groups. There is no evidence of a fluxional process in solution as was observed for 1 and for the dichloro mixed-metal species, [RhIrCl$_2$-



3

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[35] Cowie, M.; Dwight, S. K. *Inorg. Chem.* **1980**, *19*, 2500.

[36] (a) In solution (CH$_2$Cl$_2$) the three carbonyl bands observed (1980, 1970, 1756 cm^{-1}) suggest that in addition to the species having two terminal carbonyls there is another isomer having a carbonyl-bridged structure like that of compound 1. (b) Vaartstra, B. A. Ph.D. Thesis, University of Alberta, 1989; pp 73, 74.

[37] Gelmini, L.; Stephan, D. W.; Loeb, S. J. *Inorg. Chim. Acta* **1985**, *98*, L3.

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

[39] Kubiak, C. P.; Woodcock, C.; Eisenberg, R. *Inorg. Chem.* **1980**, *19*, 2733.

[40] Cowie, M.; Dwight, S. K. *Inorg. Chem.* **1980**, *19*, 209.

[41] Cowie, M.; Gibson, J. A. E. *Organometallics* **1984**, *3*, 984.

[42] Farr, J. P.; Olmstead, M. M.; Balch, A. L. *Inorg. Chem.* **1983**, *22*, 1229.

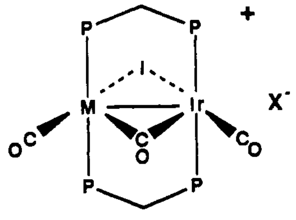
[43] Cowie, M.; Dwight, S. K. *Inorg. Chem.* **1979**, *18*, 2700.

[44] Kubiak, C. P.; Eisenberg, R. *Inorg. Chem.* **1980**, *19*, 2726.

[45] Geary, W. J. *Coord. Chem. Rev.* **1971**, *7*, 81.

$(CO)_2(dppm)_2]$.[36] Conductivity measurements in acetonitrile establish that **3** is a nonelectrolyte, so there is no evidence of I^- dissociation in solution. However, in the solid state, the appearance of three carbonyl bands (1970, 1954, 1763 cm^{-1}) in the IR spectrum suggests the presence of a second species. On the basis of the breadth of the central band it appears that it contains two overlapping peaks; this would suggest that the bands at 1954 and 1763 cm^{-1} correspond to **3** whereas the second species has bands at 1970 and 1954 cm^{-1}. It is proposed that this second species is $[RhIr(CO)_2(\mu\text{-}I)(dppm)_2][I]$ (**4a**), the result of I^- dissociation from **3**, on the basis of the close similarity in the IR bands with those of the BF_4^- salt, $[RhIr(CO)_2(\mu\text{-}I)(dppm)_2][BF_4]$, which are at 1970 and 1948 cm^{-1}. The BF_4^- salt is readily prepared from **3** by reaction with 1 equiv of $AgBF_4$.

Addition of 1 equiv of CO to a solution of $[Ir_2I_2(CO)(\mu\text{-}CO)(dppm)_2]$ (**1**) causes an immediate color change from orange to yellow. The $^{31}P\{^1H\}$ NMR spectrum reveals a single symmetric species, and the infrared spectrum in solution displays terminal (1977 cm^{-1}) and bridging (1872 cm^{-1}) carbonyl stretches. The broadness of the terminal CO stretch suggests that another band is beneath it. No further change is observed upon addition of excess CO to the solution. This information, together with the conductivity measurements (which indicate a 1:1 electrolyte) leads to the formulation $[Ir_2(CO)_2(\mu\text{-}I)(\mu\text{-}CO)(dppm)_2][I]$ (**5a**), having the doubly bridged A-frame geometry previously observed for the chloro-bridged dirhodium analogue[46] and the sulfido-bridged diiridium complex.[39] In contrast, the analogous neutral chloro compound, *trans*-$[IrCl(CO)(dppm)]_2$, did not lose chloride ion upon reaction with 1 equiv of CO but gave a neutral dichloro tricarbonyl species, $[Ir_2Cl_2(CO)_2(\mu\text{-}CO)(dppm)_2]$,[15] which subsequently reacted further with CO to yield a cationic tetracarbonyl species through substitution of Cl^- by CO. Although the structure proposed for **5a** is not totally unexpected, attack at the open coordination site on Ir(1) of **1** would yield a product analogous to the above neutral dichloride species, if I^- loss did not occur. Apparently the steric demands in such a complex are too great, promoting iodide dissociation. Subsequent CO attack, to give a cationic tetracarbonyl complex, as observed for the chloride, also does not appear to occur, again probably for steric reasons. Notably, iodide loss and coordination of an additional carbonyl ligand raises the infrared stretching frequency of the bridging carbonyl in **5a** considerably compared to **1**.

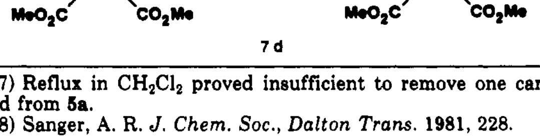


M = Ir, X^- = I^- (**5a**), BF_4^- (**5b**)
M = Rh, X^- = I^- (**6a**), BF_4^- (**6b**)

The cationic iodo-bridged A-frame, **2**, also reacts with 1 equiv of CO yielding a product that is very similar in most respects to compound **5a** and is accordingly formulated as $[Ir_2(CO)_2(\mu\text{-}I)(\mu\text{-}CO)(dppm)_2][BF_4]$ (**5b**). A significant difference, however, is that CO loss from **5b** is very facile, occurring simply upon N_2 purge over a solid sample of **5b**. Loss of CO from **5a** requires 10 min of reflux in THF with an N_2 purge, after which **1** is recovered quantitatively.[47] The reasons for the different labilities of **5a** and **5b** are not obvious, since one might expect the incoming iodide ligand to facilitate CO loss from **5a**. Furthermore, these results are inconsistent with slightly higher infrared stretching frequencies for the carbonyls in **5a** (see Table I), which would suggest weaker Ir–CO bonds compared to those of **5b**. The lability of the third carbonyl group in **5b** is especially surprising when compared with the iodo-bridged dirhodium analogue, which does not readily lose CO;[35,48] we had expected that the iridium species would bind CO even more effectively than the rhodium analogues as was observed for the chloride complexes.[15]

Compound **3** also reacts with CO, resulting in substitution of one I^- ligand by CO to give the doubly bridged A-frame species $[RhIr(CO)_2(\mu\text{-}I)(\mu\text{-}CO)(dppm)_2][I]$ (**6a**). Again the IR spectrum displays only one terminal carbonyl band (1963 cm^{-1}), the width of which suggests a coincidental overlap of the Rh- and Ir-carbonyl stretches, and a bridging carbonyl stretch at 1827 cm^{-1}. The $^{13}C\{^1H\}$ NMR spectrum of **6a** confirms the assignment, displaying three carbonyl resonances at δ 197.3, 191.1, and 177.4. The low-field resonance is due to the bridging carbonyl group, displaying a coupling of 34.7 Hz to Rh, the intermediate resonance corresponds to the Rh-bound carbonyl, displaying a larger coupling to Rh (78.7 Hz), and the high-field resonance is assigned to the Ir-bound carbonyl. This latter resonance displays coupling to two phosphorus nuclei ($^2J_{P-C}$ = 13 Hz) and an additional 13-Hz coupling to another nucleus (either the bridging carbonyl ligand or Rh); the source of the additional coupling was not obvious, since the resonance of the bridging carbonyl was unresolved owing to coupling to the two sets of phosphorus nuclei. The BF_4^- salt **6b** is obtained by CO addition to **4**. The third carbonyl in compounds **6a** and **6b** is lost at a rate comparable to that in **5a** and requires heating in THF for efficient regeneration of the dicarbonyl precursors.

Each of compounds **1** and **2** reacts with dimethyl acetylenedicarboxylate (DMAD), yielding complexes that are assumed to have the organic substrate bound parallel to the Ir–Ir axis as a cis-dimetalated olefin. The alternate binding mode, in which the alkyne is perpendicular to the metal–metal axis, is unknown for dppm-bridged complexes of rhodium or iridium, in which the metals are in the +1 oxidation state or higher. Compound **1** reacts over a 2-h period with 1 equiv of DMAD to yield two isomers **7a** and **7b** in nearly equal concentrations. Both **7a** and **7b** are symmetric species, as judged by the $^{31}P\{^1H\}$ NMR spectrum (singlets at δ −4.08 and −23.53, respectively). Over an additional 18-h period another symmetric species, **7c** (δ −29.22), and an unsymmetrical one, **7d** (multiplet, δ −35.87), appear. No change in the $^{31}P\{^1H\}$ NMR resonances of the four products is observed over the temperature range from 20 to −80 °C. Compound **7d** is the thermodynamically favored species and is obtained quantitatively by refluxing the mixture of four isomers in CH_2Cl_2 for 2 h. The yellow solid finally obtained displays two terminal CO bands in the infrared spectrum (2042, 1983 cm^{-1}) and a band at 1554 cm^{-1}, which is assigned to the C–C stretch



7d

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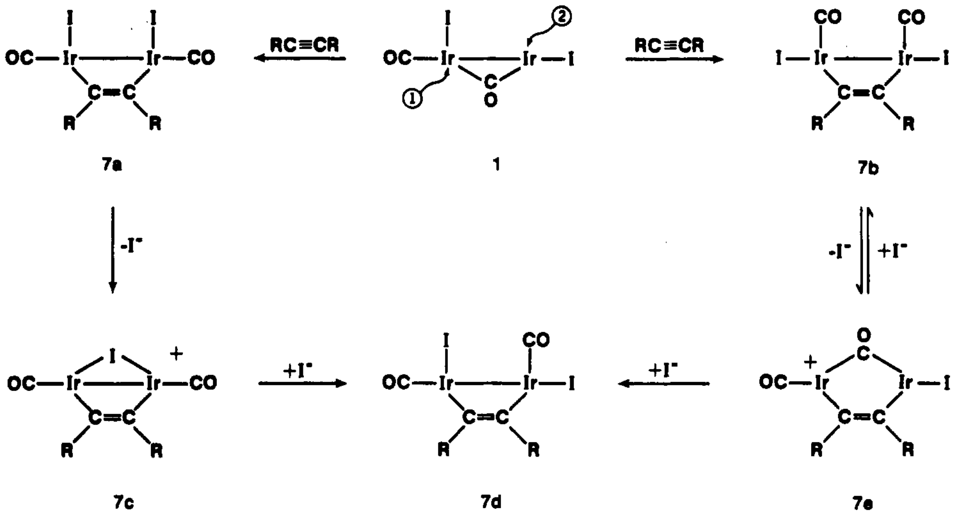
(46) (a) Cowie, M.; Mague, J. T.; Sanger, A. R. *J. Am. Chem. Soc.* **1978**, *100*, 3628. (b) Cowie, M. *Inorg. Chem.* **1979**, *18*, 286.

(47) Reflux in CH_2Cl_2 proved insufficient to remove one carbonyl ligand from **5a**.

(48) Sanger, A. R. *J. Chem. Soc., Dalton Trans.* **1981**, 228.

Scheme I



of the coordinated acetylene. The similarity of the spectral parameters of compound **7d** and the structurally characterized dichloro species $[Ir_2Cl_2(CO)_2(\mu\text{-DMAD})(dppm)_2]$[18] suggests an analogous formulation for this species. However, in solution compound **7d** is significantly different, as evidenced by additional terminal CO bands in the infrared spectrum (2033, 2006, 1982 cm^{-1}) as well as low-frequency stretch at 1703 cm^{-1} that is distinguishable from the carboxylate bands by its intensity. Two acetylenic stretches are also observed (1555, 1539 cm^{-1}). The solution characteristics may indicate a facile fluxionality in which one carbonyl group moves from a terminal to a bridging position. Furthermore, the carbonyl-bridged form of **7d** should not be unexpected, being rather analogous to the geometry adopted by compound **1**. Although carbonyl-bridge formation might be electronically favorable, as previously discussed for **1**, it also appears to be sterically favorable, since this transformation retains hexacoordination at one metal center, while the coordination number at the other metal is reduced from 6 to 5. Further alleviation of steric crowding could presumably occur by loss of I^-; however, there is no evidence for this, with conductivities in CH_2Cl_2 being very low (2.3 Ω^{-1} cm^2 mol^{-1}). Furthermore, introduction of more polar solvents in an attempt to induce iodide loss only causes precipitation of the complex. Clearly, the iodide loss noted earlier upon CO addition to **1** cannot be solely sterically induced, since such loss is not observed upon addition of the bulkier alkyne ligands. Loss of CO is also apparently unfavorable, and in contrast to the chloro analogue of **7d**, refluxing under N_2 purge in higher boiling solvents does not produce a monocarbonyl species but eventually leads to decomposition.

The symmetric intermediates leading to **7d** could not be unequivocally identified. However, on the basis of previous studies[18,19] and spectroscopic data (Table I) obtained by monitoring the progress of the reaction, their natures can be assigned with reasonable confidence, as shown in Scheme I. Although the solid-state structure of **1** suggests that attack at the 16-electron iridium center should occur (site 2) giving rise to **7b**, the fluxionality of **1** in solution must be recalled, and thus the exact nature of the reactive intermediates resulting in **7a** and **7b** is not clear. The methylene proton resonances in the ^1H NMR spectrum (see Table I) were assignable to each of **7a**–**d** by selective ^{31}P decoupling. The carboxylate methyl resonances were then easily assigned by comparing their integrations with those of the methylene protons. Due to the similarity in the concentrations of **7a** and **7b**, the infrared bands corresponding to each of these species cannot be unambiguously assigned. However, in the solid they are tentatively assigned according to the previously discussed chloro analogue of **7d**,[18] in which the carbonyl ligand opposite the Ir–Ir bond displayed a higher CO stretch (2023 cm^{-1}) than the one opposite the Ir–DMAD linkage (1999 cm^{-1}). In solution the assignment of carbonyl bands due to **7a** and **7b** is not so clear, although the higher frequency bands are again assigned to **7a**. In particular, it seems clear that the bridging carbonyl band (1728 cm^{-1}) must result from **7b**, since only in this species are the carbonyl ligands in a position to move to the bridging site, presumably as previously proposed for **7d**. The bands due to the alkyne ligands in **7a** and **7b** could not be confidently assigned. Bands due to isomer **7c** can be identified, since they grow in later in the reaction sequence. This species is proposed to be cationic, since the $^{31}P\{^1H\}$ NMR spectrum indicates that it too is symmetrical, and it appears that the transformation of **7a** to **7d** must occur via iodide dissociation. Compound **7e**, proposed as an intermediate between **7b** and **7d**, was not observed. In support of this scheme, addition of 1 equiv of $AgBF_4$ to a THF solution containing all four isomers yields only two products, as revealed by $^{31}P\{^1H\}$ NMR spectroscopy: a symmetrical species (δ −16.86), which corresponds exactly to compound **8** (the BF_4^- salt of **7c**; vide infra), and an unsymmetrical species (δ −0.04, −29.07), which must be the BF_4^- salt of **7e**. The ratio of these two products indicates that all of the **7d** originally present was converted to the BF_4^- salt of **7e** upon reaction with $AgBF_4$, which is consistent with labilization of the iodide ligand on the more sterically congested iridium center in the carbonyl-bridged form of **7d**. Subsequent addition of excess KI to these products gave only **7d**.

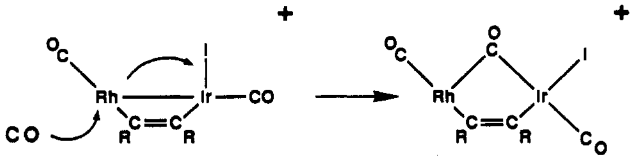
The cationic A-frame complex $[Ir_2(CO)_2(\mu\text{-I})(dppm)_2][BF_4]$ (**2**) also reacts slowly with DMAD, producing a yellow solution over 2 h. The $^{31}P\{^1H\}$ NMR spectrum reveals a single product, **8**, having four chemically equivalent phosphorus atoms. The solid isolated from the reaction displays a single terminal carbonyl stretch in the infrared spectrum at 1987 cm^{-1} and a C–C stretch of the coordinated acetylenic moiety at 1613 cm^{-1}. From this information the compound is formulated as $[Ir_2(CO)_2(\mu\text{-I})(\mu\text{-DMAD})(dppm)_2][BF_4]$ (**8**), the analogue of **7c**. Although there are some differences in the spectroscopic parameters of these two species, their similarity is particularly evident in the ^1H NMR spectra (see Table I).

It is important to note that compound **8** appears to result from alkyne attack in the "pocket" of **2**. In contrast, the analogous chloro- and acetate-bridged A-frames, $[Ir_2(CO)_2(\mu\text{-}Cl)(dppm)_2]^+$ and $[Rh_2(CO)_2(\mu\text{-}O_2CCH_3)(dppm)_2]^+$, yielded products which indicated that alkyne attack occurred on the "outsides" of the complexes, adjacent to the bridging anionic groups.[18,49] Such proposals are also supported by an X-ray structure determination of $[Ir_2(CO)(CF_3C_2CF_3)(\mu\text{-}S)(\mu\text{-}CO)(dppm)_2]$,[50] which shows the hexafluorobutyne group bound to one metal, adjacent to sulfur on the outside of the complex. Apparently, the presence of the large iodo group in **2** inhibits attack at an adjacent site and instead directs attack to the A-frame pocket on the opposite face of the dimer. It appears that in both **1** and **2** the bulky iodo ligands exert a significant steric influence, as shown by the contrasts noted between the chemistry of these species and the chloro analogues and by the relatively slow rate of reaction with DMAD in both cases.

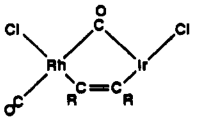
The mixed-metal species **3** also reacts with DMAD in a manner much like that of **1**, resulting in the appearance of at least four species. This chemistry was not pursued further, since it appeared that the reaction paralleled that of **1**.

The addition of 1 equiv of DMAD to a THF solution of the mixed-metal A-frame, **4**, results in an initial change in color of the brown slurry to green, followed by a return of the brown color within minutes. No further changes were observed upon stirring overnight. A $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture reveals the presence of two major species ((i) δ 11.6 ($^1J_{Rh-P}$ = 112 Hz), −21.5; (ii) δ 16.1 ($^1J_{Rh-P}$ = 89 Hz), −13.6), both having patterns consistent with AA′BB′X spin systems. Although no further changes were observed in THF, removal of the solvent and redissolution in CH_2Cl_2 resulted in the transformation of species i into ii over a 1–2-day period. Subsequent characterization of this final product reveals that it is $[RhIr(CO)_2(\mu\text{-}I)(\mu\text{-}DMAD)(dppm)_2][BF_4]$ (**9**), the mixed-metal analogue of **8**. The IR spectrum of **9** contains two terminal carbonyl bands (2020, 1997 cm^{-1}), which are higher in frequency than those of **4**, in accord with the increased oxidation state. Replacement of one Ir in **8** by Rh results in an increase in the carbonyl stretching frequencies for the latter, as is expected owing to the lower basicity of Rh. Apparently the effect of the less basic Rh center is transmitted to the adjacent Ir since *both* carbonyl stretches for **9** are higher than for **8**. The $^{13}C\{^1H\}$ NMR spectrum of **9** shows two carbonyl resonances (δ 186.9, 173.8). Broad-band phosphorus decoupling transforms the first multiplet into a doublet of doublets, having coupling to Rh of 64 Hz and to the other carbonyl of ca. 5 Hz, and transforms the high-field resonance to a doublet with coupling to the Rh-bound carbonyl. The observation of three-bond $^{13}CO-^{13}CO$ coupling suggests an approximately colinear arrangement for the carbonyls and the Rh–Ir bond, as has previously been proposed for $[RhIrCl(CO)_3(\mu\text{-}DMAD)(dppm)_2][ClO_4]$.[21]

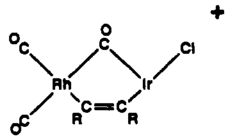
Complex **9** reacts reversibly with CO to yield the tricarbonyl species $[RhIrI(CO)_2(\mu\text{-}CO)(\mu\text{-}DMAD)(dppm)_2][BF_4]$ (**10**). We suggest that reaction proceeds with movement of the iodide ligand out of the bridging position to form a sixteen-electron rhodium, eighteen-electron iridium species, followed by CO attack at Rh and movement of a carbonyl to the bridging position. A mechanism very similar to this has been suggested by Mague for CO addition to $[RhIrCl(CO)_2(\mu\text{-}DMAD)(dppm)_2][ClO_4]$.[21] The IR spectrum of **10** shows terminal carbonyl bands at 2089 and 2055 cm^{-1} and a bridging band at 1738 cm^{-1}, together with bands from the DMAD group. Valuable information regarding the positions of the three carbonyl ligands is obtained from the $^{13}C\{^1H\}$ NMR spectra, with and without selective ^{31}P decoupling. The resonance at δ 190.2 is a doublet of triplets with coupling to Rh of 53.4 Hz and to the two adjacent phosphorus atoms of 10.4 Hz. Selective ^{31}P decoupling experiments confirm this assignment. The high-field resonance (δ 157.1) also appears as a doublet of triplets (J = 47.8, 5.8 Hz), suggesting that it too is bound to Rh. However irradiation of the Rh-bound phosphorus nuclei has no effect on this resonance, whereas irradiating the Ir-bound phosphorus nuclei results in simplification of this ^{13}C resonance to a doublet. Although the 47.8-Hz coupling constant is in the range normally observed for Rh coupling, two points about such an assignment are worrisome. First, the chemical shift of this resonance is farther upfield than is normally observed for Rh-bound carbonyls, appearing more characteristic of an Ir-bound species, but more importantly this carbonyl is coupled to the Ir-bound and *not* the Rh-bound phosphorus nuclei. Examination of the complex resonance at δ 201.4 offers important information about the nature of this coupling. Selectively decoupling each set of phosphorus nuclei (Rh- or Ir-bound) simplifies this resonance to a different set of doublet of doublets of triplets in each case. In addition to the coupling to the phosphorus nuclei, coupling of 19.5 Hz is observed to Rh and an additional coupling identical with that observed in the high-field carbonyl resonance. Clearly, this coupling is two-bond coupling between these two carbonyl ligands. The magnitude of this interaction is uncharacteristically large and must mean that these carbonyls are mutually trans, as shown earlier. Unfortunately, there is little published data with which to compare this value. Mague and co-workers[49] have reported values of ca. 14 Hz involving trans carbonyls, and we have previously observed values of ca. 21 Hz.[51] Although not reported as such, close examination of Mague's work on the $[RhIrCl_2(CO)_2(dppm)_2]$ system[21] does however suggest that couplings comparable to that reported for **10** have been observed. For the most part the report in question deals with complexes that all have sixteen-electron rhodium, eighteen-electron iridium configurations, as is frequently observed. The two exceptions are $[RhIrCl_2(CO)(\mu\text{-}CO)(\mu\text{-}DMAD)(dppm)_2]$ and $[RhIrCl(CO)_2(\mu\text{-}CO)(\mu\text{-}DMAD)(dppm)_2][ClO_4]$, which were assigned structures A and B, respectively.[21] Our attention



10

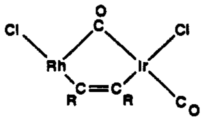


A

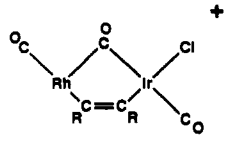


R = CO$_2$Me

B



C



D

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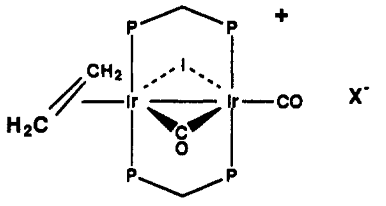
(49) (a) Mague, J. T.; DeVries, S. H. *Inorg. Chem.* **1982**, *21*, 1632. (b) Mague, J. T. *Inorg. Chem.* **1983**, *22*, 1158.

(50) Vaartstra, B. A.; Cowie, M. *Organometallics* **1989**, *8*, 2388.

(51) Antonelli, D. M.; Cowie, M. *Inorg. Chem.* **1990**, *29*, 4039.

was drawn to the $^{13}C\{^1H\}$ NMR data, in which resonances at δ 164.9 (A) and δ 158.9 (B) were assigned as Rh-bound carbonyls having coupling to Rh of 42.0 and 48.0 Hz, respectively. It is significant that this ^{13}CO chemical shift for B is within 1 ppm of that in the iodo analogue **10**. On the basis of new information obtained for compound **10**, the two compounds of Mague are reassigned structures C and D, on the assumption that the large couplings identified due to Rh are in fact ^{13}C–^{13}C couplings. Again, for these two species the resonances for the bridging carbonyls are presumably too complex to allow observation of the ^{13}C–^{13}C coupling in question. These new formulations are now in line with the other observations on these RhIr systems in which Ir, and not Rh, is coordinatively saturated.

Without doubt the most unusual products in the reactions of compounds **1** and **2** in this study are those obtained in their reactions with ethylene. These compounds, $[Ir_2I(CO)(C_2H_4)(\mu\text{-}CO)(dppm)_2][X]$ ($X^- = I^-$ (**11a**), BF_4^- (**11b**)) appear, on the basis of their spectral data, to be identical apart from the anions involved and appear to be the first characterized olefin adducts of A-frame species. In solution both **11a** and **11b** have carbonyl stretches at ca. 1979 and 1816 cm^{-1}, suggesting that one carbonyl ligand is terminal while the other is bridging. Both compounds show ^1H resonances for the dppm methylene protons at ca. δ 4.2 and 4.0 and for the ethylene group at ca. δ 2.7 and 1.6. Although the two phosphorus resonances are separated by only about 1.2 ppm in each of these compounds, selective phosphorus decoupling experiments were achieved through a careful choice of decoupling power. Decoupling the lower field ^{31}P resonance in **11b** results in a collapse of both ethylene proton resonances to apparent triplets (as is observed on broad-band ^{31}P decoupling) whereas decoupling the high-field ^{31}P resonance results in no change in these proton resonances. These experiments confirm that the ethylene molecule is bound to only one iridium center, as shown. This structure is also consistent with the $^{31}C\{^1H\}$ NMR spectra, in which the two resonances at δ 38.5 and 31.2 are assigned to the coordinated ethylene, on the basis of the similarity of their chemical shifts to other terminally bound ethylene ligands.[52]



$X^- = I^-$ (**11a**), BF_4^- (**11b**)

Although the structure shown for the cation of compounds **11a** and **11b** is not unambiguously determined from the data available, the doubly bridged A-frame structure is favored owing to the very close resemblance of the IR and $^{31}P\{^1H\}$NMR spectral parameters with those of the closely related tricarbonyl species **5a** and **5b**. Unfortunately, we have not yet succeeded in obtaining suitable crystals of **11a** or **11b** to confirm the ethylene binding mode, which as noted is unprecedented in these A-frame compounds. It appears that the substituents on the olefins are generally involved in unfavorable repulsions with the ortho-hydrogens of the dppm phenyl groups. Consistent with this idea, tetrafluoroethylene, having larger fluorine substituents, does not react with **1**, although it does react slowly with **2**, and this reaction is being investigated. It seems that for the very electron-rich metal centers in **1** and **2** the small ethylene ligand is an effective enough π-acid to give strong binding of this group, while being small enough to minimize repulsions.

Although the reaction between **1** and ethylene is reversible upon flushing the system with N_2, the ethylene molecule is not lost from **11b**. It appears that ethylene loss is promoted by iodide coordination; therefore, the addition of (PPN)I (PPN = $(Ph_3P)_2N$) to solutions of **11b** results in loss of ethylene.

Neither the neutral mixed-metal species **3** nor its related cationic A-frame **4** reacts directly with ethylene. It appears that the presence of Rh has the effect of deactivating the Ir center. This effect has been previously observed; whereas the diiridium complex **1** forms a stable O_2 adduct,[22] the mixed-metal analogue **3** fails to react with O_2.[53]

Conclusions

Substitution of the chloro ligands in *trans*-$[IrCl(CO)(dppm)]_2$ by iodo ligands, to give $[Ir_2I_2(CO)(\mu\text{-}CO)(dppm)_2]$ (**1**), results in the expected increase in basicity of the metal centers, brought about by the better electron-donating ability of I^- compared to Cl^-. One obvious manifestation of this substitution shows up in the lower carbonyl stretching vibrations of derivatives of **1** compared with the chloro analogues. More dramatically, however, this substitution results in substantial rearrangement from the symmetric structure of the dichloride, in which both carbonyls are terminally bound, to the unsymmetrical structure in which one is bridging. It appears that this unsymmetrical structure is favored by the greater π-accepting ability of carbonyl ligands when bridging.

Surprisingly perhaps, no iodo complex having more than three carbonyl ligands was observed. This is in contrast to the analogous chemistry of the chloro analogues involving both Ir_2[15] and RhIr[54] systems, for which tetracarbonyls were characterized. In addition, carbonyl loss from the iodo-bridged tricarbonyls was more facile than from the iodo-bridged dirhodium species.[35,48] The reasons for this are not clear.

Although the diiridium and rhodium–iridium iodo complexes react with dimethyl acetylenedicarboxylate to give alkyne-bridged species, the greater basicity of the iodo complexes is most dramatically seen in the formation of the unusual ethylene adducts, $[Ir_2I(CO)(C_2H_4)(\mu\text{-}CO)(dppm)_2][X]$ ($X^- = I^-, BF_4^-$), which are formed directly in the reactions of **1** or **2** with ethylene. No such complex was ever observed with the chloride analogues. The binding of ethylene in this cationic iodo species is a clear manifestation of the greater basicity of the metals.

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Supplementary Material Available: Tables of positional and thermal parameters for the phenyl carbons, thermal parameters for the anisotropic atoms, idealized hydrogen parameters, and bond distances and angles within the phenyl rings (7 pages); a listing of observed and calculated structure amplitudes (30 pages). Ordering information is given on any current masthead page.

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