Reactions of the Binuclear Complexes $[MIr(CO)_3(Ph_2PCH_2PPh_2)_2]$ (M = Rh, Ir) with Alkyl Halides: Dramatic Reactivity Differences as a Function of Metal Combination and Alkyl Halide

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Reactions of $[Ir_2(CO)_3(dppm)_2]$ (**1**; dppm = $Ph_2PCH_2PPh_2$) with CH_3I and CH_3OCH_2I give the oxidative-addition products $[Ir_2(R)(I)(CO)(\mu\text{-}CO)(dppm)_2]$ (R = CH_3 (**3**), CH_2OCH_3 (**4**)). The X-ray structure determination of **4**·CH_2Cl_2 shows that the alkyl group is the sole terminal ligand on one metal while the iodo and a carbonyl are terminally bound to the adjacent metal. The mixed-metal analogue $[RhIr(CO)_3(dppm)_2]$ (**2**) does not react with CH_3I but reacts with CH_3OCH_2I to give $[RhIr(CH_2OCH_3)(I)(CO)(\mu\text{-}CO)(dppm)_2]$ (**5**). Reaction of **3** or **5** with methyl triflate results in iodide abstraction to yield the known compound $[Ir_2(CH_3)(CO)(\mu\text{-}CO)(dppm)_2][CF_3SO_3]$ and $[RhIr(CH_2OCH_3)(CO)(\mu\text{-}CO)(dppm)_2][CF_3SO_3]$ (**8**), respectively. In the mixed-metal compound iodide removal results in migration of the methoxymethyl group from Rh to Ir. Iodide abstraction from **4** results in a double C−H bond activation to yield the methoxycarbyne-bridged $[Ir_2(H)_2(CO)_2(\mu\text{-}COCH_3)(dppm)_2][CF_3SO_3]$ (**6**). In the reactions of **4** and **5** with methyl triflate some methoxide abstraction also occurs, yielding the methylene-bridged products $[MIr(CO)_2(\mu\text{-}CH_2)(\mu\text{-}I)(dppm)_2][CF_3SO_3]$ (M = Ir (**7**), Rh (**9**)) as minor products in between 15 and 30% yield. The reactions of $[MIr(CO)_3(dppm)_2]$ (M = Ir (**1**), Rh (**2**)) with CH_2I_2 and ICH_2CN yield $[MIr(CO)_2(\mu\text{-}I)(\mu\text{-}CO)(Ph_2PCHPPh_2)(dppm)]$ (M = Ir (**10**), Rh (**11**)) together with CH_3I and CH_3CN, respectively, by hydrogen abstraction from one of the dppm ligands and iodine atom coordination at the metals. Reactions of **1** with allyl bromide and benzyl bromide yield the bromo analogue $[Ir_2(CO)_2(\mu\text{-}Br)(\mu\text{-}CO)(Ph_2PCHPPh_2)(dppm)_2]$ (**12**). The X-ray structure of **10**·THF has been determined and shows a planar Ir−P−C(H)−P−Ir moiety, short P−C bonds (1.72(2) Å), and a 122(1)° angle at carbon of the $Ph_2PC(H)PPh_2$ ligand, as expected for sp^2 hybridization and partial multiple-bond character in the P−C bonds.

Introduction

As part of an ongoing interest in the synthesis and reactivity of binuclear complexes containing hydrocarbyl fragments,[1] we have initiated a study into the synthesis of binuclear alkyl complexes by the oxidative addition of alkyl halides to binuclear diiridium and rhodium−iridium complexes. Oxidative-addition reactions of alkyl halides are of fundamental interest and have been much studied, particularly in the case of low-valent, late transition metals.[2] Furthermore, the addition of methyl iodide to late-metal complexes is of enormous practical significance since it represents one of the key steps in the industrial conversion of methanol into acetic acid.[3−5] Although the majority of acetic acid production is based on a rhodium-based catalyst,[3−5] which has been identified as possibly the most successful example of an industrial process catalyzed by a metal complex,[5] BP Chemicals has recently introduced a related iridium-

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based catalyst system.[6] Both systems continue to generate considerable interest.[5,7,8]

Although the initial interest in alkyl halide oxidative additions concentrated on mononuclear complexes,[2] there has been considerable subsequent interest in multimetal systems, particularly binuclear ones.[9−17] Even in a relatively simple binuclear complex the second metal introduces additional reactivity possibilities, particularly if two different metals are involved. In homobinuclear systems, based for example on an M^{n+}/M^{n+} core, the following reactivity patterns have been identified: (1) oxidative addition of one alkyl halide (RX) unit to one metal to give an $M^{n+}/M^{(n+2)+}$ product;[12,13,14b] (2) addition of one RX unit across the dimetal framework to give an $M^{(n+1)+}/M^{(n+1)+}$ core;[9,10,14a,16a,b] (3) addition of two RX units (one to each metal) to give an $M^{(n+2)+}/M^{(n+2)+}$ product;[11,13,14b] and (4) in the case in which the organic substrate contains two C−X bonds, cleavage of both C−X bonds to give an $M^{(n+2)+}/M^{(n+2)+}$ framework, bridged by the resulting hydrocarbyl fragment.[11,16c]

In addition to the intrinsic interest in oxidative addition to bimetallic frameworks, particularly those having metals (Rh, Ir) used commercially in the acetic acid synthesis, we also considered that addition of substituted methyl halides (XCH_2Y; X = halide, Y = substituent) could constitute a useful route to complexes containing substituted methyl ligands, by oxidative addition of the carbon−halide bond. We had shown that the methyl complex $[Ir_2(CH_3)(CO)_2(dppm)_2][CF_3SO_3]$ underwent facile, and sometimes reversible, methyl C−H bond cleavage upon addition of substrate molecules,[1j,m,p] and we were interested in generating analogous compounds in which one or more of the methyl hydrogens were replaced by different substituents, to determine the tendencies of these substituted methyl groups to undergo C−H bond activation. Certainly a recent study has suggested that C−H bond activation should be enhanced by substituting a hydrogen by an electron-withdrawing substituent.[18]

In this study we report the reactions of $[Ir_2(CO)_3(dppm)_2]$ (**1**)[19] and $[RhIr(CO)_3(dppm)_2]$ (**2**)[20] with various alkyl halides.

Experimental Section

General Comments. The compounds $[Ir_2(CO)_3(dppm)_2]$[19] and $[RhIr(CO)_3(dppm)_2]$[20] were prepared as previously reported. The elemental analyses attempted on purified samples of a number of the diiridium compounds were unsatisfactory due to some contamination by traces of the previously characterized diiodo dicarbonyl species $[Ir_2(I)_2(CO)(\mu\text{-}CO)(dppm)_2]$,[21] the tricarbonyl iodide $[Ir_2(I)(CO)_2(\mu\text{-}CO)(dppm)_2][I]$,[21] or other uncharacterized species that could not be removed. Characterization for these compounds is based primarily on spectroscopic methods. The $^{31}P\{^1H\}$, $^{13}C\{^1H\}$, and ^1H NMR and IR spectroscopic data for all new compounds are given in Table 1.

Preparation of Compounds. (a) $[Ir_2(I)(CH_3)(CO)(\mu\text{-}CO)(dppm)_2]$ (3). A 30 mg (0.025 mmol) sample of $[Ir_2(CO)_3(dppm)_2]$ (**1**) was dissolved in 20 mL of benzene, and 18.2 μL (0.30 mmol) of CH_3I was added. The mixture was stirred overnight, resulting in a color change from orange to yellow. The volume of benzene was reduced to about 2 mL, and the yellow product precipitated by the slow addition of pentane. Washing of the product by 10 mL of pentane and drying under a slow stream of dinitrogen gave 24.3 mg of a mixture consisting of 85% of **3** and 15% of the previously characterized $[Ir_2(CO)_2(\mu\text{-}I)(\mu\text{-}CO)(dppm)_2][I]$.[21] Recrystallization attempts failed to separate these compounds, which were present in every attempt to prepare **3**, with the amount of impurity ranging from 15 to 30% of the total product.

(b) Reaction of 3 with Methyl Triflate. A 30 mg (0.023 mmol) sample of $[Ir_2I(CH_3)(CO)_2(dppm)_2]$ (**3**) was dissolved in 10 mL of CH_2Cl_2, and 2.56 μL (0.023 mmol) of methyl triflate was added via syringe, resulting in a color change from yellow to red. The solution was stirred at ambient temperature for 1 h, after which the solvent volume was reduced to 1 mL and the product precipitated by the slow addition of diethyl ether. A red precipitate of the previously characterized $[Ir_2(CH_3)(CO)(\mu\text{-}CO)(dppm)_2][CF_3SO_3]$[1m] was identified by $^{31}P\{^1H\}$ and ^1H NMR spectra. Carrying out the reaction with the use of $[Ir_2I(^{13}CH_3)(CO)_2(dppm)_2]$ (**^{13}C-3**) and unlabeled methyl triflate yielded $[Ir_2(^{13}CH_3)(CO)(\mu\text{-}CO)(dppm)_2][CF_3SO_3]$ and CH_3I with no ^{13}C label incorporated into the iodomethane, whereas reaction of unlabeled **3** with $^{13}CH_3OSO_2CF_3$ resulted in no $^{13}CH_3$ incorporation into the methyl complex, but formation of $^{13}CH_3I$, as identified by $^{13}C\{^1H\}$ NMR spectroscopy.

(c) $[Ir_2(CH_2OCH_3)(I)(CO)(\mu\text{-}CO)(dppm)_2]$ (4). Compound **1** (50 mg, 0.040 mmol) was dissolved in 10 mL of benzene, and CH_3OCH_2I (3.6 μL, 0.040 mmol) was added by syringe. (*Caution: α-halo ether compounds are extremely toxic.*) The solution was stirred for 1 h, during which time the color

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Table 1. Spectroscopic Data for Compounds

compound	IR cm^{-1} [a,b]	NMR [c,d]		
		δ (^{31}P{^{1}H}) [e]	δ (^{1}H) [f,g]	δ (^{13}C) [g]
$[Ir_2(CH_3)(I)(CO)(\mu\text{-}CO)(dppm)_2]$ (**3**)	1977(s), 1815(m)	20.9(m), −7.4(m)	4.60(m, 2H), 4.40(m, 2H), −0.40(t, 3H, $^3J_{PH}$ = 8.0 Hz)	197.6(tt, *C*O, $^2J_{PC}$ = 9.1, 4.3 Hz), 175.2(t, *C*O, $^2J_{PC}$ = 13.0 Hz), 17.5 (t, *C*H$_3$, $^2J_{PC}$ = 6.3 Hz)
$[Ir_2(CH_2OCH_3)(I)(CO)(\mu\text{-}CO)(dppm)_2]$ (**4**)	1936(vs), 1732(s)	18.6(m), −6.4(m)	4.48(b, 4H), 3.30(t, $^3J_{PH}$ = 4.4 Hz, 2H), 1.95(s, 3H) [h]	199.8(b, *C*O), 175.8(b, *C*O)
$[RhIr(CH_2OCH_3)(I)(CO)(\mu\text{-}CO)(dppm)_2]$ (**5**)	1932(s), 1745(s)	30.8 (dm, $^1J_{RhP}$ = 163.7 Hz), −3.8(m)	4.42(m, 2H), 4.20(m, 2H), 2.93(td, 2H, $^3J_{PH}$ = 6.9 Hz, $^2J_{RhH}$ = 2.8 Hz), 2.02 (s, 3H)	212.7(dm, $^1J_{RhC}$ = 40.1 Hz, $^2J_{CC}$ = 6.0 Hz, *C*O), 179.5(m, *C*O)
$[Ir_2(H)_2(CO)_2(\mu\text{-}COCH_3)(dppm)_2][CF_3SO_3]$ (**6**)	1975(vs)	−2.1(m), −4.6(m), −14.3(m), −18.1(m) [i]	5.05(s, 3H), 4.81(m, 1H), 4.08(m, 1H), 3.22(m, 1H), −11.12(m, 1H), −11.20(m, 1H) [i]	316.6(tt, $^2J_{PC}$ = 55, 4 Hz, *C*OCH$_3$), 173.5(b, 2*C*O), 77.5(t, $^4J_{PC}$ = 10 Hz, CO*C*H$_3$) [i]
$[RhIr(CH_2OCH_3)(CO)(\mu\text{-}CO)(dppm)_2][CF_3SO_3]$ (**8**)		22.2−20.6 (second-order multiplet)	4.43(m, 2H), 3.98(m, 2H), 2.58(b, 2H), 2.27(s, 3H)	182.5(bs, *C*O), 177.7(dt, $^1J_{RhC}$ = 71.3 Hz, *C*O)
$[Ir_2(CO)_2(\mu\text{-}I)(\mu\text{-}CO)(Ph_2PCHPPh_2)(dppm)]$ (**10**)	1948(vs) 1801(s)	−1.4(m), −10.1(m)	4.60(m, 1H), 4.23(m, 1H), 2.07(tt, J_{PH} = 10.0, 3.5 Hz, 1H)	194.4(tt, $^2J_{PC}$ = 12.2, 4.9 Hz, *C*O), 183.2(m, 2*C*O)
$[RhIr(CO)_2(\mu\text{-}I)(\mu\text{-}CO)(Ph_2PCHPPh_2)(dppm)]$ (**11**)	1953(bs), 1823(m)	25.3(dm, $^1J_{RhP}$ = 124.0 Hz), 15.7(dm, $^1J_{RhP}$ = 114.0 Hz), −6.1(m), −12.7(m)	4.60(m, 1H), 4.41(m, 1H), 2.03(tt, J_{PH} = 7.0, 3.3 Hz, 1H)	204.3(dm, $^1J_{RhC}$ = 38.0 Hz, *C*O), 195.2(d, $^1J_{RhC}$ = 71.1 Hz, *C*O), 182.0(bs, *C*O)

[a] IR abbreviations: vs = very strong, s = strong, m = medium, w = weak, sh = shoulder, b = broad. [b] Nujol mull or CH_2Cl_2 cast unless otherwise stated. [c] NMR abbreviations: s = singlet, t = triplet, m = multiplet, q = quintet, b = broad. [d] NMR data at 25 °C in CD_2Cl_2 unless otherwise stated. [e] ^{31}P chemical shifts referenced to external 85% H_3PO_4. [f] Chemical shifts for the phenyl hydrogens are not given. [g] ^{1}H and ^{13}C chemical shifts referenced to TMS. [h] −40 °C. [i] -80 °C.

changed from orange to yellow. The volume was reduced to ca. 3 mL, and a bright yellow powder was precipitated with addition of pentane. The isolated solid was washed (2 × 10 mL pentane) and dried under argon and then in vacuo. Yield: 86%. Anal. Calcd for $Ir_2IP_4O_3C_{54}H_{49}$: C, 46.95; H, 3.58; I, 9.19. Found: C, 46.65; H, 3.34; I, 10.16.

(d) $[RhIr(CH_2OCH_3)(I)(CO)(\mu\text{-}CO)(dppm)_2]$ (5). To a slurry of 45 mg (0.039 mmol) of $[RhIr(CO)_3(dppm)_2]$ (**2**) in 3 mL of toluene was added CH_3OCH_2I (3.3 μL, 0.039 mmol), and the resulting mixture was then stirred. The suspension dissolved within 0.5 h, and after 1.5 h of stirring, the color of the solution turned yellow from orange. A 10 mL portion of pentane was added, causing the precipitation of a yellow solid (36 mg, 71%). Anal. Calcd for $IrRhIP_4O_3C_{54}H_{49}$: C, 50.10; H, 3.78; I, 9.82. Found: C, 49.97; H, 4.07; I, 10.65.

(e) $[Ir_2(H)_2(CO)_2(\mu\text{-}COCH_3)(dppm)_2][CF_3SO_3]$ (6). Compound **4** (31 mg, 0.022 mmol) was dissolved in 10 mL of benzene, and $CH_3SO_3CF_3$ (2.5 μL 0.022 mmol) was added, causing an immediate color change from yellow to light red. The solution was stirred for 1 h, during which time the color changed to dark yellow. The solvent volume was reduced to ca. 3 mL, and a yellow solid was obtained by addition of pentane. The isolated solid was washed (2 × 10 mL pentane) and dried under argon and then in vacuo. Yield: 78%. The compound $[Ir_2(CO)_2(\mu\text{-}I)(\mu\text{-}CH_2)(dppm)_2][CF_3SO_3]$ (**7**)[22] was also produced in the reaction in ca. 15% yield, as determined by ^{31}P{^{1}H} NMR of a reaction carried out in an NMR tube. These products could not be separated, so were characterized by NMR techniques. The minor product (**7**) was identified based on a comparison of the spectral data with that of the previously characterized compound.[22]

(f) $[RhIr(CH_2OCH_3)(CO)_2(dppm)_2][CF_3SO_3]$ (8). A 20 mg (0.015 mmol) sample of $[RhIr(CH_2OCH_3)(I)(CO)_2(dppm)_2]$ (**5**) was dissolved in 0.5 mL of CD_2Cl_2 in an NMR tube at −78 °C. Methyl triflate (1.8 μL, 0.015 mmol) was added; the mixture was allowed to stand at this temperature for 0.5 h and then gradually allowed to warm to ambient temperature, causing a change in the color of the solution from yellow to purple. NMR analysis carried out immediately indicated the presence of **8** together with 20−30% of $[RhIr(CO)_2(\mu\text{-}I)(\mu\text{-}CH_2)(dppm)_2][CF_3SO_3]$ (**9**)[23] in solution. Our failure to separate these products precluded elemental analysis. The use of trimethylsilylmethyl triflate in the reaction with **5** gave a product distribution similar to that described above.

(g) $[Ir_2(CO)_2(\mu\text{-}I)(\mu\text{-}CO)(Ph_2PCHPPh_2)(dppm)]$ (10). Compound **1** (30 mg, 0.024 mmol) was dissolved in 6 mL of THF, and CH_2I_2 (2.0 μL, 0.025 mmol) was added. The solution changed color over 0.5 h from orange to yellow and was stirred an additional 0.5 h. The solvent was then removed, and the residue was dissolved in 2 mL of CH_2Cl_2 and cooled to 0 °C. A flocculent yellow precipitate was obtained upon addition of 20 mL of a 50:50 mixture of Et_2O/hexane. The precipitate was washed with the Et_2O/hexane mixture (2 × 10 mL) and dried under argon and then in vacuo. Yield: 75%.

(h) Reaction of $[Ir_2(CO)_3(dppm)_2]$ with ICH_2CN. Compound **1** (43.6 mg, 0.035 mmol) was dissolved in 7 mL of benzene, and ICH_2CN (2.6 μL, 0.036 mmol) was added. The solution was stirred for 10 min, during which time the color changed from orange to yellow. The solvent was then reduced to ca. 2 mL, and a bright yellow powder was obtained upon addition of 10 mL of pentane. The precipitate was washed with pentane (2 × 10 mL) and dried under argon and then in vacuo. NMR spectra run on the isolated sample showed the production of compound **10**. CH_3CN was detected in a ^{1}H NMR spectrum run on the crude reaction mixture.

(i) $[RhIr(CO)_2(\mu\text{-}I)(\mu\text{-}CO)(Ph_2PCHPPh_2)(dppm)]$ (11). A 39 mg (0.034 mmol) sample of compound **2** was dissolved in 5 mL of benzene, CH_2I_2 (2.7 μL, 0.034 mmol) was added, and the mixture was stirred for 1 h, during which time the color of the solution changed from orange to dull yellow. The solvent was removed in vacuo, and recrystallization from benzene/pentane afforded a yellow microcrystalline solid (28 mg, 64%).

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(22) (a) Torkelson, J. R. Ph.D. Thesis, University of Alberta, 1998, Chapter 5. (b) Torkelson, J. R.; Muritu, J.; McDonald, R.; Cowie, M. Manuscript in preparation. (c) Spectral parameters for compound **7**: IR, ν(CO) 1962 cm^{-1}; NMR, ^{31}P{^{1}H} δ −7.9(s); ^{1}H δ 10.01 (q, $^3J_{PH}$ = 8.3 Hz, 2H), 5.02 (m, 2H), 4.19 (m, 2H).

(23) (a) Oke, O. Ph.D. Thesis, University of Alberta, 1999, Chapter 6. (b) Spectral parameters for compound **9**: IR, ν(CO) 1958 cm^{-1}; NMR, ^{31}P{^{1}H} δ 21.5 (dm, $^1J_{RhP}$ = 110.4 Hz), −5.8 (m); ^{1}H δ 10.79 (qd, 2H), 4.80 (m, 2H), 4.37 (m, 2H); ^{13}C{^{1}H} 191.9 (dt, $^1J_{RhC}$ = 66.3 Hz, CO), 183.5 (t, CO).

Table 2. Crystallographic Data for Compounds 4 and 10

	$[Ir_2(CH_2OCH_3)(I)(CO)(\mu\text{-}CO)(dppm)_2]$ (**4**)$\cdot CH_2Cl_2$[a]	$[Ir_2(CO)_2(\mu\text{-}I)(\mu\text{-}CO)(Ph_2PCHPPh_2)(dppm)]$(**10**)$\cdot$THF
formula	$C_{54.7}H_{50.25}Cl_2I_{1.15}Ir_2O_{2.85}P_4$[a]	$C_{57}H_{51}IIr_2O_4P_4$
fw	1478.31	1435.16
cryst dimens, mm	0.34 × 0.12 × 0.06	0.42 × 0.24 × 0.03
cryst syst	monoclinic	triclinic
space group	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)
a, Å	20.0497 (9)	12.905 (2)
b, Å	13.9589 (6)	18.492 (3)
c, Å	20.9456 (8)	11.963 (2)
α, deg	90.0	97.020 (14)
β, deg	112.732 (3)	113.434 (12)
γ, deg	90.0	78.438 (12)
V, Å^3	5406.7 (4)	2563.5 (7)
Z	4	2
d_{calcd}, g cm^{-3}	1.816	1.859
μ, mm^{-1}	16.89	5.960
diffractometer	Siemens P4/RA[b]	Enraf-Nonius CAD4[c]
radiation (λ, Å)	graphite-monochromated Cu Kα (1.54178)	graphite-monochromated Mo Kα (0.71073)
T, °C	−60	−50
scan type	$\theta-2\theta$	$\theta-2\theta$
2θ (max), deg	113.5	50.0
no. of unique reflns	7213	8964
no. of observns (NO)	5827 ($F_o^2 \geq 2\sigma(F_o^2)$)	4784 ($F_o^2 \geq 2\sigma(F_o^2)$)
range of abs corr factors	0.4129−0.1633	1.255−0.844
residual density, e/Å^3	2.282 and −1.976	1.782 and −1.820
$R_1(F_o^2 > 2\sigma(F_o^2))$[d]	0.0552	0.0622
wR_2 (all data)	0.0725	0.1784
GOF(*S*)[e]	1.060 [$F_o^2 \geq -3\sigma(F_o^2)$]	1.015 [$F_o^2 \geq -3\sigma(F_o^2)$]

[a] The sample crystallized as a mixture of 85% of compound **4** and 15% of $[Ir_2I_2(CO)(\mu\text{-}CO)(dppm)_2]\cdot CH_2Cl_2$. [b] Programs for diffractometer operation and data collection were those of the XSCANS system supplied by Siemens. [c] Programs for diffractometer operation and data collection were those supplied by Enraf-Nonius. [d] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^4)]^{1/2}$. [e] $S = [\sum w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$ (n = number of data; p = number of parameters varied; $w = [\sigma^2(F_o^2) + (a_0P)^2 + a_1P]^{-1}$ where $P = [\max(F_o^2, 0) + 2F_c^2]/3$). For **4** $a_0 = 0.0832$, $a_1 = 25.9490$; for **10** $a_0 = 0.0608$, $a_1 = 0.9018$.

Microanalysis results for **11** were always low in percent carbon and high in percent iodine due to the coproduction of between 15 and 25% of $[RhIr(CO)_2(\mu\text{-}I)(\mu\text{-}CO)(dppm)_2][I]$. A typical result is given. Anal. Calcd for $IrRhP_8O_3C_{53}H_{43}$: C, 49.86; H, 3.37; I, 9.95. Found: C, 49.17; H, 3.34; I, 10.96.

(j) Reactions of $[Ir_2(CO)_3(dppm)_2]$ with Benzyl Bromide and Allyl Bromide. A 30 mg (0.025 mmol) of $[Ir_2(CO)_3(dppm)_2]$ was dissolved in 0.6 mL of benzene-d_6 in an NMR tube, and 2.9 μL (0.025 mmol) of benzyl bromide (or 8.2 μL (0.10 mmol) of allyl bromide) was added via syringe. In each case the solution color changed from orange to yellow within 15 min. NMR spectroscopy showed three phosphine-containing products in an approximate ratio 1:1:0.5. One species was identified as $[Ir_2(CO)_2(\mu\text{-}Br)(\mu\text{-}CO)(Ph_2PCHPPh_2)(dppm)]$ (**12**) on the basis of its very similar NMR spectral parameters compared to the iodo analogue **11**. All attempts to separate the three products failed, so compound **12** was never isolated pure. NMR: ^1H δ 4.72 (m, 1H), 4.32 (m, 1H), 2.10 (tt, $^2J_{PH}$ = 8.0 Hz, $^4J_{PH}$ = 4.3 Hz, 1H); $^{31}P\{^1H\}$ δ 5.5 (m), −5.0 (m).

X-ray Data Collection. Crystals of each compound, suitable for X-ray diffraction, were grown via slow diffusion of diethyl ether into a concentrated CH_2Cl_2 (**4**) or THF (**10**) solution of the compound and were mounted and flame-sealed in glass capillaries under solvent vapor to minimize decomposition or deterioration due to solvent loss. For each compound, three reflections were chosen as intensity standards and were remeasured every 120 min of X-ray exposure time; in no case was decay evident. Crystal parameters and details of data collection are summarized in Table 2.

For compound **4**$\cdot CH_2Cl_2$ the cell parameters and the systematic absences defined the space group as $P2_1/c$, whereas for **10**$\cdot$THF the cell parameters, the lack of absences, and the diffraction symmetry suggested the space groups $P1$ or $P\bar{1}$, the latter of which was established by successful refinement of the structure. Absorption corrections to **10**$\cdot$THF were applied by the method of Walker and Stuart,[24] whereas for **4**$\cdot CH_2Cl_2$ the crystal faces were indexed and measured, and an absorption correction was carried out by Gaussian integration.

Structure Solution and Refinement. For each structure, the positions of the iridium and phosphorus atoms were found using the direct-methods program SHELXS-86;[25] the remaining atoms were found using a succession of least-squares and difference Fourier maps. Refinement of each structure proceeded using the program SHELXL-93.[26] Hydrogen atom positions were calculated by assuming idealized sp^2 or sp^3 geometries about their attached carbon atoms (as appropriate) and were given thermal parameters 120% of the equivalent isotropic displacement parameters of their attached carbons. Further details of structure refinement (other than described below) and final residual indices may be found in Table 2.

Although all of the non-hydrogen atoms of $[Ir_2(CH_2OCH_3)(I)(CO)(\mu\text{-}CO)(dppm)_2]$ (**4**)$\cdot CH_2Cl_2$ were located, the carbon and oxygen atoms of the terminal methoxymethyl group (C(3), O(3)) did not behave well in least-squares refinements. A difference Fourier map at this stage located another peak near C(3) and O(3), at approximately 2.7 Å from Ir(2). Successful refinement of the structure was achieved by placing an iodide in 15% occupancy at the peak site. The iodide ligand has

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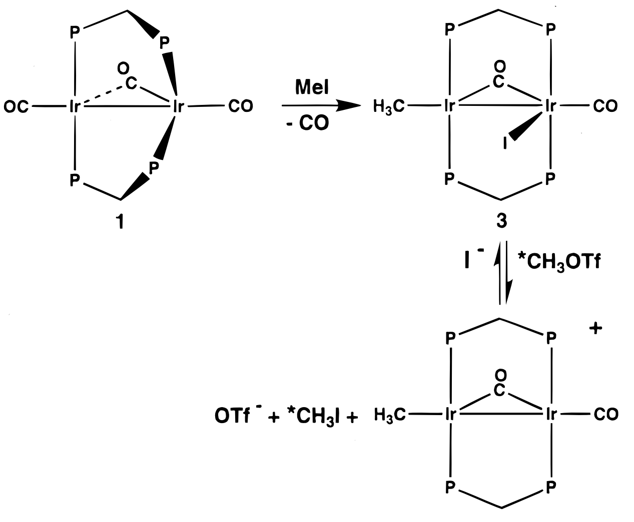
(24) Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158−166.

(25) Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467.

(26) Sheldrick, G. M. *SHELXL-93*, Program for crystal structure determination; University of Göttingen, Germany, 1993. Refinement on F_o^2 for all reflections (all of these having $F_o^2 \geq -3\sigma(F_o^2)$). Weighted *R*-factors wR_2 and all goodnesses of fit *S* are based on F_o^2; conventional *R*-factors R_1 are based on F_o, with F_o set to zero for negative F_o^2. The observed criterion of $F_o^2 > 2\sigma(F_o^2)$ is used only for calculating R_1 and is not relevant to the choice of reflections for refinement. *R*-factors based on F_o^2 are statistically about twice as large as those based on F_o, and *R*-factors based on ALL data will be even larger.

Scheme 1



resulted from cocrystallization of the diiodo species $[Ir_2(I)_2(CO)(\mu\text{-}CO)(dppm)_2]$,[21] which frequently can be formed as a minor impurity in the preparation of **4**; its presence was confirmed by NMR spectra of the dissolved crystals. Compound **4** and $[Ir_2(I)_2(CO)(\mu\text{-}CO)(dppm)_2]$ are isomorphous. The disorder was resolved and all atoms were refined anisotropically, giving the methoxy substituents (C(3), O(3), C(4)) an occupancy of 85% and the iodide ligand (I(2)) an occupancy of 15%. All atoms refined well, indicating that the two disordered molecules superimpose almost exactly.

Location of all the atoms in compound **10** proceeded smoothly.

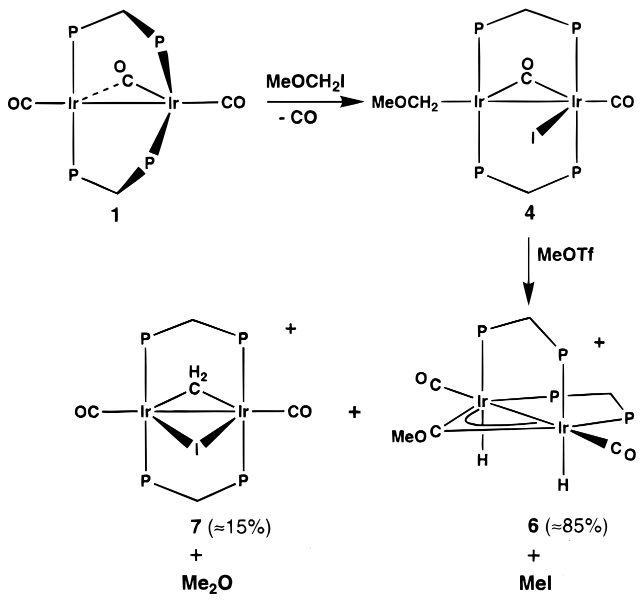
Results and Characterization of Compounds

The compound $[Ir_2(CO)_3(dppm)_2]$ (**1**) reacts with methyl iodide, accompanied by carbonyl loss, to yield the targeted oxidative-addition product $[Ir_2(CH_3)(I)(CO)(\mu\text{-}CO)(dppm)_2]$ (**3**), as shown in Scheme 1. Both the $^{13}C\{^1H\}$ and ^1H NMR spectra show the methyl group resonance as a triplet, indicating that it is terminally bound to one iridium with coupling to the two adjacent ^{31}P nuclei on this metal. Furthermore, the $^{13}C\{^1H\}$ NMR data indicate that one carbonyl is terminally bound while one is bridging. Although the available data do not indicate the positioning of the iodo ligand, the structure shown is proposed on the basis of the close similarity in the $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra with those of compound **4**, the structure of which has been determined (vide infra). Reaction of **3** with methyl triflate leads to iodide abstraction (as methyl iodide) to give the known compound $[Ir_2(CH_3)(CO)(\mu\text{-}CO)(dppm)_2][CF_3SO_3]$.[1m] The use of $^{13}CH_3$-labeled methyl triflate results in exclusive formation of $^{13}CH_3I$ and unlabeled metal-containing product, indicating that the function of the methyl triflate is merely to abstract the iodide ion and that the original methyl group in **3** remains coordinated to Ir. The use of silver salts to effect iodide removal is not recommended with this series of compounds, giving irreproducible mixtures of products. The use of methyl triflate, on the other hand, works well, as has been previously reported.[1c,14b]

Surprisingly perhaps, the mixed-metal analogue of **1**, namely, $[RhIr(CO)_3(dppm)_2]$ (**2**), fails to react with CH_3I under the same conditions as noted for **1**.

Compound **1** also reacts with the iodomethyl methyl ether (CH_3OCH_2I) losing carbon monoxide in the process and producing the methoxymethyl iodide compound $[Ir_2(CH_2OCH_3)(I)(CO)(\mu\text{-}CO)(dppm)_2]$ (**4**), as outlined in Scheme 2. The ^1H NMR spectrum of **4** at ambient temperature shows the methylene protons of the methoxymethyl ligand as a broad signal at δ 3.30, with the methyl protons appearing as a singlet at δ 1.95. Cooling the sample to −40 °C causes the broad methylene signal to sharpen into a triplet, indicating terminal coordination on Ir, which is supported by selective ^{31}P decoupling experiments that show the methylene coupling to only the phosphorus nuclei that give rise to the downfield signal in the $^{31}P\{^1H\}$ NMR spectrum. The ^1H chemical shifts observed correspond well to those observed for other methoxymethyl compounds.[27] At ambient temperature the $^{31}P\{^1H\}$ NMR spectrum shows sharp AA′BB′ signals at δ 18.6 and −6.4. The carbonyl bands in the infrared spectrum appear at 1936 and 1732 cm^{-1}, suggesting a terminal and bridging orientation, which is supported by the carbonyl resonances in the $^{13}C\{^1H\}$ NMR spectrum that appear as broad signals at δ 175.8 and 199.8, respectively. Confirmation of the proposed structure for **4** in the solid state comes from the X-ray structure determination, as shown in Figure 1. Selected distances and angles are given in Table 3. This structure is essentially identical to the previously characterized diiodo compound $[Ir_2(I)_2(CO)(\mu\text{-}CO)(dppm)_2]$,[21] with one of the iodo ligands being replaced by the methoxymethyl ligand, and crystals of compound **4** are in fact contaminated with ca. 15% of this diiodo compound that is isomorphous with the methoxymethyl species (see Experimental Section). As a result, the structure is disordered, containing 85% of **4** with 15% of the superimposed diiodide. However, this disorder affected only the superimposed methoxymethyl and iodo groups, which refined well despite this disorder. The phosphines are in a trans arrangement at each metal, with angles of

Scheme 2



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[27] (a) Jolly, P. W.; Pettit, R. *J. Am. Chem. Soc.* **1966**, *88*, 5044. (b) Brookhart, M.; Nelson, G. O. *J. Am. Chem. Soc.* **1977**, *99*, 6099. (c) Brookhart, M.; Tucker, J. R.; Flood, T. C.; Jensen, J. *J. Am. Chem. Soc.* **1980**, *102*, 1203. (d) Thorn, D. L.; Tulip, T. H. *J. Am. Chem. Soc.* **1981**, *103*, 5984. (e) Thorn, D. L. *Organometallics* **1982**, *1*, 879. (f) Calabrese, J. C.; Roe, D. C.; Thorn, D. L.; Tulip, T. H. *Organometallics* **1984**, *3*, 1223.

Table 3. Selected Interatomic Distances and Angles for Compound 4

(a) Distances (Å)

atom 1	atom 2	distance	atom 1	atom 2	distance
Ir(1)	Ir(2)	2.8527(7)	Ir(2)	P(4)	2.281(3)
Ir(1)	I(1)	2.8025(10)	Ir(2)	C(2)	1.924(12)
Ir(1)	P(1)	2.324(3)	Ir(2)	C(3)	2.08(2)
Ir(1)	P(3)	2.328(3)	O(1)	C(1)	1.13(2)
Ir(1)	C(1)	1.858(15)	O(2)	C(2)	1.185(14)
Ir(1)	C(2)	2.061(13)	O(3)	C(3)	1.39(2)
Ir(2)	I(2)[a]	2.708(8)	O(3)	C(4)	1.37(2)
Ir(2)	P(2)	2.299(3)			

(b) Angles (deg)

atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle
Ir(2)	Ir(1)	I(1)	85.10(3)	I(2)	Ir(2)	C(2)[a]	131.5(4)
Ir(2)	Ir(1)	C(1)	154.6(4)	P(2)	Ir(2)	P(4)	167.54(11)
Ir(2)	Ir(1)	C(2)	42.4(3)	C(2)	Ir(2)	C(3)	139.2(7)
I(1)	Ir(1)	C(1)	120.3(4)	C(3)	O(3)	C(4)	112.8(15)
I(1)	Ir(1)	C(2)	127.5(3)	Ir(1)	C(1)	O(1)	173.5(13)
P(1)	Ir(1)	P(3)	173.86(10)	Ir(1)	C(2)	Ir(2)	91.4(5)
Ir(1)	Ir(2)	I(2)[a]	175.3(2)	Ir(1)	C(2)	O(2)	134.0(10)
Ir(1)	Ir(2)	C(2)	46.2(4)	Ir(2)	C(2)	O(2)	134.6(10)
Ir(1)	Ir(2)	C(3)	174.4(6)	Ir(2)	C(3)	O(3)	115.6(12)

[a] I(2) corresponds to the 15% superimposed [Ir$_2$I$_2$(CO)(μ-CO)(dppm)$_2$] molecule that is disordered with compound **4**.

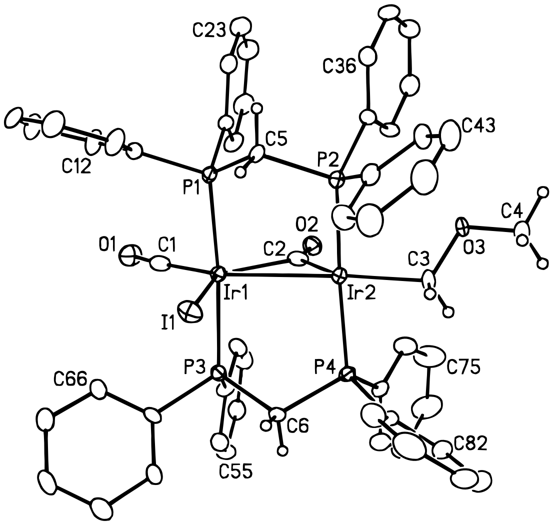
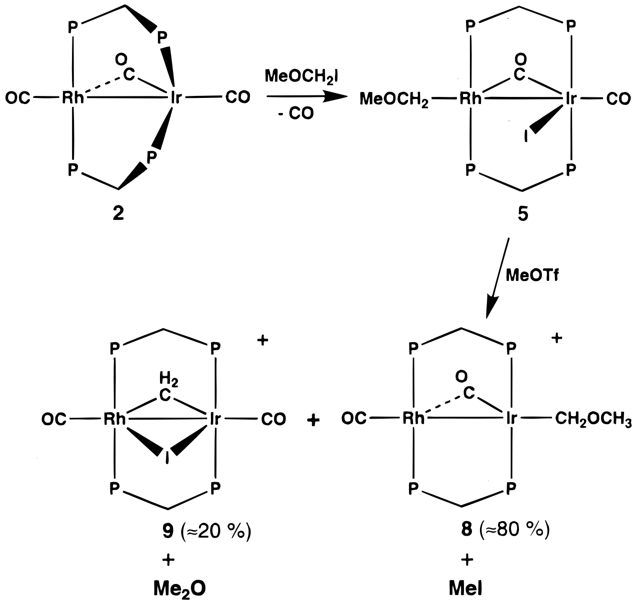


Figure 1. Perspective view of [Ir$_2$(CH$_2$OCH$_3$)(I)(CO)(μ-CO)(dppm)$_2$] (**4**). Thermal ellipsoids are shown at the 20% probability level except for hydrogens, which are shown artificially small. Phenyl hydrogens are omitted.

173.9(1)° for P(1)−Ir(1)−P(3) and 167.5(1)° for P(2)−Ir(2)−P(4). The metal−metal separation of 2.8527(7) Å corresponds to a normal Ir−Ir single bond.[28] The carbonyls are mutually cis, with one in a terminal position almost opposite the Ir−Ir bond and the other bridging the two metals in an unsymmetrical fashion, being slightly closer to Ir(2) than Ir(1) (1.92(1) vs 2.06(1) Å). The iodo ligand of compound **4** is terminally bound to the same metal as the terminal carbonyl and is on the face opposite the bridging carbonyl. The methoxymethyl group is the only terminal ligand on the adjacent metal, falling opposite the metal−metal bond and having an Ir(1)−Ir(2)−C(3) angle of 174.4(6)°, analogous to one of the iodo groups in the diiodo species mentioned above.

Scheme 3



It is interesting that the carbonyls do not assume a symmetrical arrangement with one on each metal as found for *trans*-[IrCl(CO)(dppm)]$_2$,[28c] but instead adopt the unsymmetrical arrangement as observed for [Ir$_2$(I)$_2$(CO)(μ-CO)(dppm)$_2$].[21] Since this geometry does not appear to be sterically driven, we assume that the bridging carbonyl is necessary to make use of its better π-accepting properties in this position.[29]

The mixed-metal analogue [RhIr(CO)$_3$(dppm)$_2$] (**2**) also reacts with CH$_3$OCH$_2$I to give the oxidative-addition product [RhIr(CH$_2$OCH$_3$)(I)(CO)(μ-CO)(dppm)$_2$] (**5**), which like the diiridium compound has also undergone loss of a carbonyl, as shown in Scheme 3. The methoxymethyl group is bound to Rh, as shown in the ^{1}H NMR spectrum, in which the methylene protons appear as a triplet of doublets, with coupling to the two

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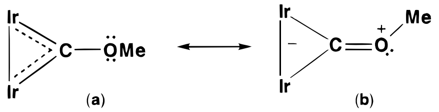
(28) (a) Kubiak, C. P.; Woodcock, C.; Eisenberg, R. *Inorg. Chem.* **1980**, *19*, 2733. (b) Sutherland, B. R.; Cowie, M. *Organometallics* **1984**, *3*, 1869. (c) Sutherland, B. R.; Cowie, M. *Inorg. Chem.* **1984**, *23*, 2324. (d) Sutherland, B. R.; Cowie, M. *Organometallics* **1985**, *4*, 1801. (e) Xiao, J.; Cowie, M. *Organometallics* **1993**, *12*, 463.

(29) 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; p 112.

adjacent ^{31}P nuclei (6.9 Hz) and to Rh (2.8 Hz). The carbonyl region of the $^{13}C\{^1H\}$ NMR spectrum is similar to that of **4**, except for the 40 Hz coupling to Rh observed for the bridging carbonyl in compound **5**. A structure for **5**, much like that of **4**, is therefore proposed.

Removal of the iodo ligands from **4** and **5**, by addition of methyl triflate, to yield the methoxymethyl analogues of the methyl complexes $[MIr(CH_3)(CO)_2(dppm)_2][CF_3SO_3]$ (M = Rh,^{1n} Ir^{1m}) has led to very different results. Reaction of **4** with methyl triflate does result primarily in iodide loss (as methyl iodide); however the anticipated product was not obtained. Instead, iodide loss is accompanied by a double C−H activation of the methoxymethyl ligand to give the methoxycarbyne-bridged product $[Ir_2(H)_2(CO)_2(\mu\text{-}COCH_3)(dppm)_2][CF_3SO_3]$ (**6**), as shown in Scheme 2. Methyl triflate addition also resulted in about 10−15% production of compound **7** (as determined by $^{31}P\{^1H\}$ NMR) and dimethyl ether (by ^{1}H NMR), through electrophilic attack at the methoxy group (compound **7** has been previously characterized and will be reported elsewhere).[22] The $^{13}C\{^1H\}$ NMR spectrum of compound **6** shows the characteristic carbyne signal at low field (δ 316.6) as a pseudo triplet of triplets ($^2J_{C-P}$ = 55, 4 Hz). Although this signal is at slightly higher field than has been observed for methoxycarbynes (δ 345−390),[30−33] it falls into the range typically observed for other carbyne signals (δ 200−350).[34] The larger P−C coupling constant indicates that the carbyne is trans to one set of phosphines, while the smaller value corresponds to cis coupling to the other pair of phosphorus nuclei. At room temperature the $^{31}P\{^1H\}$ NMR spectrum for this compound shows broad signals at δ −3.2 and −16.7, which sharpen upon cooling to −80 °C, to a pattern consistent with an ABCD spin system, having multiplets centered at δ −2.1, −4.6, −14.3, and −18.1. Compound **6** is believed to have a cis-phosphine orientation based on the large difference in carbon−phosphorus coupling observed for the carbyne carbon, the four multiplets observed for the phosphines at low temperatures, and the inequivalence of the dppm protons that appear in the ^{1}H NMR spectrum as multiplets at δ 4.81, 4.08, 3.22, with the fourth signal believed to be obscured by the phenyl protons. The methyl group of the methoxy substituent appears at δ 5.05 as a singlet. At room temperature the ^{1}H NMR spectrum shows the hydrides as one broad and unresolved second-order multiplet, which sharpens into a complex pattern at δ −11.16 upon cooling the sample to −80 °C. Broad-band ^{31}P decoupling resolves this pattern into two broad singlets at δ −11.12 and −11.20. ^{1}H NMR experiments with selective ^{31}P decoupling were attempted in order to elucidate the stereochemistry; however these experiments were equivocal because of the close proximity of the chemical shifts of the phosphorus AB and CD signals that did not allow full decoupling of one signal without affecting another. Decoupling the high-field phosphorus resonances had a larger effect on the hydride multiplet than decoupling the low-field resonances, indicating a larger coupling of the hydrides to the former. The two different couplings are consistent with each hydride being trans to a similar phosphorus nucleus, and therefore more strongly coupled to them, and cis to the others, to which they display a smaller coupling. Similar hydride signals have previously been observed for the cis-phosphine, silylene-bridged dihydride complexes $[Ir_2(H)_2(CO)_2(\mu\text{-}SiR_2)(dppm)_2]$.[35] These silylene-bridged species contain hydrides that have a trans−cis arrangement to the dppm phosphines, and on the basis of spectral similarities the structure shown in Scheme 2 is proposed for compound **6**.

The broadening of the $^{31}P\{^1H\}$ and ^{1}H signals upon warming suggests a fluxional process that averages the four inequivalent phosphorus nuclei into two sets. The fact that the three observed dppm methylene signals do not change upon warming indicates that this fluxional process does not average the four inequivalent methylene protons into two, further supporting the proposed structure shown in Scheme 2, in which the hydrides are eclipsed on adjacent metals. Such a process can be rationalized by rotation of the methoxy group around the C−OCH$_3$ bond. The resonance representations of the bridging methoxycarbyne, shown below, suggest partial π-character in the carbon−oxygen bond that is presumed to be responsible for the hindered rotation of the methoxy substituent that gives rise to the limiting $^{31}P\{^1H\}$ and ^{1}H NMR spectra at low temperature. Note that in representation **b**, the orientation of the methyl group differentiates one Ir center from the other, which together with the different ^{31}P environments on each metal gives rise to four inequivalent ^{31}P environments. Rapid rotation about the C−O bond at higher temperatures would give rise to only two ^{31}P environments and an AA′BB′ spin system. An identical orientation of the bridging methoxycarbyne group was observed in the solid-state structures of a related diruthenium complex[32] and an Ru$_3$ cluster,[31a] and the cluster complex also displayed fluxionality resulting from restricted rotation about the carbyne−oxygen bond. The partial C−O π-character proposed is also supported by crystal structures of these methoxycarbyne-bridged compounds,[31a,32] in which the C−OMe bond lengths of 1.245(7) and 1.299(8) Å were found to be intermediate between a normal single and double bond. Unfortunately we have not yet been able to confirm the unusual structure proposed for **6** by X-ray techniques owing to the failure to obtain X-ray quality crystals.



Compound **6** is found to be rather unreactive. Attempts to convert the carbyne moiety into a carbene by addition of nucleophiles gave no reaction; presumably, the contribution from resonance structure **b** results in

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(30) (a) Hodali, H. A.; Shriver, D. F. *Inorg. Chem.* **1979**, *18*, 1236. (b) Holt, E. M.; Whitmire, K. H.; Shriver, D. F. *J. Organomet. Chem.* **1981**, *213*, 125. (c) Kolis, J. W.; Basolo, F.; Shriver, D. F. *J. Am. Chem. Soc.* **1982**, *104*, 5626. (d) Fong, R. H.; Hersh, W. H. *Organometallics* **1985**, *4*, 1468.

(31) (a) Johnson, B. F. G.; Lewis, J.; Orpen, A. G.; Raithby, P. R.; Suss, G. *J. Organomet. Chem.* **1979**, *173*, 187. (b) Gavens, P. D.; Mays, M. J. *J. Organomet. Chem.* **1978**, *162*, 389.

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the carbyne carbon being less electrophilic. Similarly, attempts to deprotonate one of the M−H moieties by addition of base failed. Reaction of compound **6** with trimethylsilyl triflate resulted in complete decomposition of the complex presumably by removal of the methoxy group of the carbyne, leaving a highly reactive "carbide" species, which reacted further. Attempts at inducing reductive elimination of H_2 from the complex by refluxing in THF also left **6** unchanged.

The mixed-metal analogue $[RhIr(CH_2OCH_3)(I)(CO)(\mu\text{-}CO)(dppm)_2]$ (**5**) reacts with methyl triflate in the expected manner, resulting in loss of methyl iodide and generation of the targeted methoxymethyl complex $[RhIr(CH_2OCH_3)(CO)(\mu\text{-}CO)(dppm)_2][CF_3SO_3]$ (**8**). As in the reaction of the diiridium analogue, the analogous methylene-bridged $[RhIr(CO)_2(\mu\text{-}I)(\mu\text{-}CH_2)(dppm)_2][CF_3SO_3]$ (**9**)[23] was also obtained as a minor product (20−30%) by abstraction of the methoxy group as dimethyl ether. Both the $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ spectra of compound **8** closely resemble those of the methyl analogue $[RhIr(CH_3)(CO)(\mu\text{-}CO)(dppm)_2][CF_3SO_3]$;[1n] in particular the carbonyl resonances (δ 182.5(s), 177.7 (dt, $^1J_{RhC}$ = 71 Hz)) differ from those of the methyl analogue by only a couple of ppm. The lower field chemical shift of the Ir-bound carbonyl, compared to that on Rh, suggests a weak semibridging interaction of this group, although the expected coupling to Rh is too small to be resolved. In the methyl analogue, the semibridging carbonyl at δ 184.9 in the $^{13}C\{^1H\}$ NMR spectrum displayed a 7 Hz coupling to Rh. Removal of the iodide ion is accompanied by migration of the methoxymethyl group from Rh to Ir.

Attempts to generate species containing either a terminal iodomethyl group or a bridging methylene group, through oxidative addition of a single C−I bond or both C−I bonds of CH_2I_2, respectively, did not proceed as anticipated in reactions of CH_2I_2 with either compound **1** or **2**. Instead, the compounds $[MIr(CO)_2(\mu\text{-}I)(\mu\text{-}CO)(Ph_2PCHPPh_2)(dppm)]$ (M = Ir (**10**), Rh (**11**)), resulting from hydrogen atom abstraction from one dppm methylene group and iodine atom addition to the metals, were obtained. In both cases the only organic product observed was methyl iodide. Similarly, the reactions of **1** and **2** with ICH_2CN gave the same metal complexes **10** and **11**, together with acetonitrile, as shown in Scheme 4. The NMR spectral data are very similar for compounds **10** and **11**, apart from the appropriate Rh coupling observed for **11**. For compound **10**, three proton resonances, consistent with the loss of one hydrogen, appear in the ^1H NMR spectrum as two multiplets at δ 4.60, 4.23 and a triplet of triplets at δ 2.07. The last signal is consistent with the methyne hydrogen of the $Ph_2PCHPPh_2$ group, showing coupling values of 10 and 3.5 Hz to phosphorus. The $^{31}P\{^1H\}$ NMR spectrum of this compound differs from our usual AA′BB′ spin systems due to the large coupling constants (ca. 300 Hz) between the A and B phosphorus nuclei owing to their trans alignment at the metals; in our previous examples of AA′BB′ spin systems the P_A and P_B nuclei are bound to different metals and are coupled through the methylene unit with coupling constants of ca. 80 Hz. The P−C−P coupling constants, obtained from a simulation of the $^{31}P\{^1H\}$ NMR spectrum of **10**, are consistent with the formulation shown, in which the larger coupling (129 vs 80 Hz) results from coupling through the sp^2 carbon of the methyne (PCHP) compared to sp^3 hybridization of the methylene carbon in the PCH_2P group. The derived coupling constants for compounds **10** and **11** are summarized in Chart 1.

Scheme 4

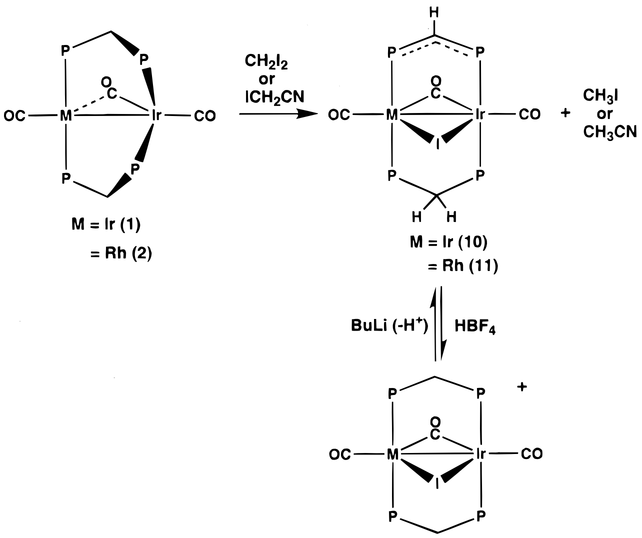
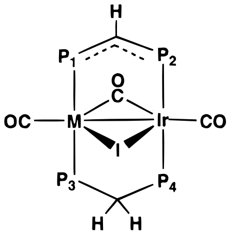


Chart 1



M = Ir (10)	M = Rh (11)
$J_{P1\text{-}P2}$ = 129 Hz	$J_{P1\text{-}P2}$ = 132 Hz
$J_{P3\text{-}P4}$ = 80 Hz	$J_{P3\text{-}P4}$ = 83 Hz
$J_{P1\text{-}P3} = J_{P2\text{-}P4}$ = 295 Hz	$J_{P1\text{-}P3}$ = 291 Hz
$J_{P1\text{-}P4} = J_{P2\text{-}P3}$ = 28 Hz	$J_{P2\text{-}P4}$ = 288 Hz
	$J_{P1\text{-}P4} = J_{P2\text{-}P3}$ = 29 Hz
	$J_{Rh\text{-}P1}$ = 124 Hz
	$J_{Rh\text{-}P3}$ = 114 Hz

Confirmation of the proposed structure for **10** in the solid state comes from the X-ray structure determination, a representation of which is shown in Figure 2, with selected distances and angles given in Table 4. The structure, having the iodo group on the face opposite the bridging carbonyl, looks remarkably like the carbonyl-bridged A-frames $[Rh_2(CO)_2(\mu\text{-}Cl)(\mu\text{-}CO)(dppm)_2][BPh_4]$,[36] $[Rh_2(CO)_2(\mu\text{-}H)(\mu\text{-}CO)(dppm)_2][CH_3C_6H_4SO_3]$,[37] $[Ir_2(CO)_2(\mu\text{-}S)(\mu\text{-}CO)(dppm)_2]$,[28a] and $[Ir_2(CO)_2(\mu\text{-}H)(\mu\text{-}CO)(dppm)_2][BF_4]$,[38] apart from the subtle differences resulting from hydrogen loss from one methylene unit in the present compound. Loss of the hydrogen from C(4) is clearly evident in a comparison of the geometry at this atom compared with that at C(5). The P(1)−C(4)−P(2) angle of 122.2(12)° for the $Ph_2PCHPPh_2$ group, compared to the normal dppm angle of 112.7(10)° at C(5), reflects the rehybridization of C(4) from sp^3 to sp^2. Also consistent with the difference in rehybridization, and the π-delocalization over the P(1)−C(4)−P(2) fragment, are the shorter P−C bond lengths (P(1)−C(4) = 1.72(2) Å, P(2)−C(4) = 1.72(2) Å vs P(3)−C(5) = 1.82(2) Å, P(4)−C(5) = 1.81(2) Å). Bond lengths and angles of the PCHP group compare well with those observed in $[Rh_2(CO)_2(\mu\text{-}NHCH_3)(Ph_2PCHPPh_2)(dppm)]$ that resulted from deprotonation of one dppm group (P−C

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Table 4. Selected Interatomic Distances and Angles for Compound 10

(a) Distances (Å)

atom 1	atom 2	distance	atom 1	atom 2	distance
Ir(1)	Ir(2)	2.7828(11)	Ir(2)	C(2)	2.05(2)
Ir(1)	I	2.831(2)	Ir(2)	C(3)	1.84(2)
Ir(1)	P(1)	2.352(5)	P(1)	C(4)	1.72(2)
Ir(1)	P(3)	2.341(5)	P(2)	C(4)	1.72(2)
Ir(1)	C(1)	1.85(2)	P(3)	C(5)	1.82(2)
Ir(1)	C(2)	2.04(2)	P(4)	C(5)	1.81(2)
Ir(2)	I	2.835(2)	O(1)	C(1)	1.15(2)
Ir(2)	P(2)	2.351(5)	O(2)	C(2)	1.18(2)
Ir(2)	P(4)	2.323(5)	O(3)	C(3)	1.14(2)

(b) Angles (deg)

atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle
Ir(2)	Ir(1)	I	60.66(4)	C(2)	Ir(2)	C(3)	118.2(8)
Ir(2)	Ir(1)	C(1)	165.2(7)	Ir(1)	I	Ir(2)	58.83(3)
Ir(2)	Ir(1)	C(2)	47.2(5)	Ir(1)	P(1)	C(4)	115.4(7)
I	Ir(1)	C(1)	134.1(7)	Ir(2)	P(2)	C(4)	115.2(7)
I	Ir(1)	C(2)	107.8(5)	Ir(1)	P(3)	C(5)	112.9(6)
P(1)	Ir(1)	P(3)	173.1(2)	Ir(2)	P(4)	C(5)	112.2(6)
C(1)	Ir(1)	C(2)	118.1(8)	Ir(1)	C(1)	O(1)	173.0(22)
Ir(1)	Ir(2)	I	60.51(4)	Ir(1)	C(2)	Ir(2)	85.9(7)
Ir(1)	Ir(2)	C(2)	47.0(5)	Ir(1)	C(2)	O(2)	137.7(15)
Ir(1)	Ir(2)	C(3)	165.1(6)	Ir(2)	C(2)	O(2)	136.3(15)
I	Ir(2)	C(2)	107.4(5)	Ir(2)	C(3)	O(3)	176.2(17)
I	Ir(2)	C(3)	134.4(6)	P(1)	C(4)	P(2)	122.2(12)
P(2)	Ir(2)	P(4)	174.5(2)	P(3)	C(5)	P(4)	112.7(10)

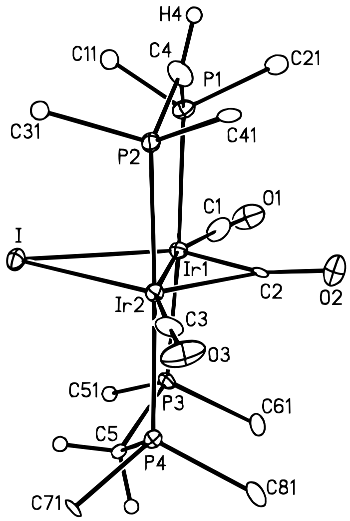

Figure 2. Perspective view of $[Ir_2(CO)_2(\mu\text{-}I)(\mu\text{-}CO)(Ph_2PCHPPh_2)(dppm)]$ (**10**) in which only the ipso carbons of the phenyl rings are shown. Thermal ellipsoids as for Figure 1.

lengths of 1.738(8) and 1.736(8) Å; P−C−P angle of 119.3(4)°).[39] Figure 2 clearly displays a nearly planar arrangement of the Ir(1)−Ir(2)−P(2)−C(4)−P(1) ring and can be compared to the Ir(1)−Ir(2)−P(4)−C(5)−P(3) ring, in which the sp^3-hybridized C(5) is distinctly out of the plane of the other four atoms, as is normally observed in dppm-bridged compounds.[1] The planarity in the case of the former presumably allows for more favorable π-overlap with the p orbital of the PC(H)P carbon.

Reaction of compounds **10** and **11** with $HBF_4{\cdot}OEt_2$ results in protonation at the CH group of the $Ph_2PCHPPh_2$ moiety, generating the previously characterized $[MIr(CO)_2(\mu\text{-}I)(\mu\text{-}CO)(dppm)_2][BF_4]$ (M = Ir, Rh),[21] and reaction of these cationic complexes with butyllithium results in deprotonation of one dppm group to regenerate **10** and **11**.

In a preliminary attempt to probe the generality of the assumed radical process that generates compounds **10** and **11**, compound **1** was reacted under identical conditions with allyl bromide and benzyl bromide. In each case the same three products were obtained in the approximate proportions 1:1:0.5. The $^{31}P\{^1H\}$ NMR spectrum of the major product has resonances at δ 5.5 and −5.0 and appears very similar to that of **10**, leading us to propose that this product is $[Ir_2(CO)_2(\mu\text{-}Br)(\mu\text{-}CO)(Ph_2PCHPPh_2)(dppm)]$ (**12**), the bromo analogue of **10**. Toluene has also been identified by ^1H NMR in the reaction of benzyl bromide, but propene could not be detected in the allyl bromide reaction owing to the excess of this reagent used. The other two metal-containing products have not yet been identified.

Discussion

Oxidative Additions. Attempts to access binuclear alkyl complexes involving the "$Ir_2(dppm)_2$" and the "$RhIr(dppm)_2$" frameworks, through oxidative addition of alkyl halides to the respective low-valent metal precursors, have succeeded with methyl iodide and iodomethyl methyl ether, but have resulted in a number of notable and unexpected failures, which will subsequently be discussed. The diiridium complex $[Ir_2(CO)_3(dppm)_2]$ (**1**) reacts readily with both CH_3I and CH_3OCH_2I to give the targeted oxidative-addition products $[Ir_2(R)(I)(CO)(\mu\text{-}CO)(dppm)_2]$ (R = CH_3 (**3**), CH_2OCH_3 (**4**)) (see Schemes 1 and 2), whereas the mixed-metal RhIr analogue (**2**) reacts only with CH_3OCH_2I, yielding $[RhIr(CH_2OCH_3)(I)(CO)(\mu\text{-}CO)(dppm)_2]$ (**5**) (see Scheme 3). In all cases the structures of these oxidative-addition products are essentially identical, having the alkyl group on one metal and the iodo ligand on the other, giving rise to M(+1)/Ir(+1) centers resulting from formal oxidation of both metals. These compounds bear a remarkable resemblance to the diiodo complexes $[MIr(I)_2(CO)(\mu\text{-}CO)(dppm)_2]$ (M = Rh, Ir),[21] which is not too surprising since the methyl and iodo groups are thought to behave as electronically similar ligands[40] and are also sterically comparable.[41] The failure of $[RhIr(CO)_3(dppm)_2]$ (**2**) to react with CH_3I is presumably due to the lower nucleophilicity of Rh compared to Ir.[42] Certainly the stability of the targeted $[RhIr(CH_3)(I)(CO)(\mu\text{-}CO)(dppm)_2]$ is not a problem, since this compound has previously been synthesized by I^- attack on $[RhIr(CH_3)(CO)(\mu\text{-}CO)(dppm)_2][CF_3SO_3]$.[1n] Iodide attack on an intermediate, cationic methyl complex is generally acknowledged as constituting the last step in the S_N2 oxidative addition of CH_3I to low-valent, late transition metal complexes,[2] suggesting that the unfavorable step, resulting in the failure of **2** to react with methyl iodide, is the initial nucleophilic attack. Substituting a hydrogen on methyl iodide by the electron-withdrawing methoxy group[43] to give ICH_2OCH_3 apparently increases the electrophilicity of this alkyl halide group enough to favor reaction with the RhIr precursor.

In mixed-metal alkyl complexes the tendency of the alkyl fragment to bind to one metal or the other is a significant variable, since the binding site has important implications regarding the subsequent reactivity of this alkyl fragment. In these RhIr compounds we observe an interesting migration of the alkyl group from one metal to the other, depending upon the presence or absence of the iodide ligand. Although the alkyl group in $[RhIr(CH_2OCH_3)(I)(CO)(\mu\text{-}CO)(dppm)_2]$ (**5**) is bound to Rh, removal of the iodo ligand is accompanied by migration of the methoxymethyl fragment to Ir. This behavior mirrors that observed previously in which I^- addition to $[RhIr(CH_3)(CO)(\mu\text{-}CO)(dppm)_2]^+$ caused the methyl group to migrate from Ir to Rh.[1n] Whether the alkyl group binds to one metal or the other is not a straightforward question and appears dependent upon a number of factors including metal−alkyl and metal−ancillary ligand bond strengths. We have also previously noted[1p] that for monocationic "Rh(+1)Ir(+1)X" complexes the anionic (X) ligand is invariably bound to Ir, leaving the positive charge on the less electronegative Rh.[44]

The iodomethyl complex **3** can also be generated from I^- addition to the previously characterized $[Ir_2(CH_3)(CO)(\mu\text{-}CO)(dppm)_2]^+$. In this context it is interesting that the addition of a number of neutral substrates (CO, SO_2, PR_3, CNR) to this methyl-containing species resulted in cleavage of one methyl C−H bond, yielding the corresponding methylene-bridged, hydrido products.[1m] We find it curious that addition of the anionic group (I^-) does not also lead to C−H bond cleavage, but instead leaves the methyl group intact.

C−H Bond Cleavage of the Methoxymethyl Group. Our interest in the chemistry of the methoxymethyl ligand arose from two ideas: first, removal of the methoxy group by electrophiles has been reported[27] and seemed a promising route to methylene-bridged complexes; and second, we were interested in the effect of substituents on the α-carbon of an alkyl group on the tendency of this alkyl group to undergo C−H bond cleavage. In the first case, the generation of the methylene-bridged complexes **7** and **9** as minor products in the reactions of $[MIr(CH_2OCH_3)(I)(CO)(\mu\text{-}CO)(dppm)_2]$ (M = Ir (**4**), Rh (**5**)) with methyl triflate clearly demonstrates the potential for this strategy. However, these reactions are not discussed further here since they form part of another study on methylene-bridged binuclear complexes.[22,23] The second objective, to investigate the effect of substituents on an alkyl ligand on its tendency to undergo C−H bond cleavage, was initiated by reports in which the reactivity of C−H bonds appeared to be promoted by the introduction of electron-withdrawing substituents on the α-carbon.[18,45] However, even with this latter goal in mind we were unprepared for the dramatic difference observed between the methyl complex **3** and its methoxymethyl analogue **4**. Whereas iodide removal from **3** generates the expected methyl complex $[Ir_2(CH_3)(CO)(\mu\text{-}CO)(dppm)_2]^+$, the equivalent reaction with **4** is accompanied by C−H bond cleavage involving *both* hydrogens on the α-carbon, to give the methoxycarbyne-bridged dihydride **6** (see Scheme 2). As previously noted, replacement of one Ir by Rh causes a dramatic drop in reactivity such that iodide removal from the RhIr analogue **5** yields the cationic methoxymethyl complex **8**. We remain puzzled by the extreme ease of the double C−H bond activation in the diiridium system, and the scope of this promotion of reactivity by adjacent substituents will be further probed by the incorporation of different substituents. Presumably, one factor favoring the methoxycarbyne-bridged product is the resonance stability gained through π-delocalization involving the methoxy group, as noted earlier.

Hydrogen Atom Abstraction. In view of the above-noted promotion of C−H bond cleavage by incorporation of electronegative substituents on the α-carbon, we looked at the incorporation of CH_2CN and CH_2I groups into the Ir_2 and RhIr complexes through the oxidative addition of ICH_2CN and CH_2I_2, respectively, with compounds **1** and **2**. Although CH_2I_2 is known to undergo a double-oxidative addition to binuclear complexes, generating methylene-bridged products,[11,16c] it is also known to add across only one C−I bond, generating CH_2I species[14a,15,16c] of the type targeted. It was our anticipation that the Ir_2 complex might give rise to the double-oxidative addition, whereas the less reactive RhIr analogue might give the targeted CH_2I product. Surprisingly, both substrates ICH_2CN and CH_2I_2 react with both compounds **1** and **2** to give the respective products $[MIr(CO)_2(\mu\text{-}I)(\mu\text{-}CO)(Ph_2PCHPPh_2)(dppm)]$ (M = Ir (**10**), Rh (**11**)) together with CH_3CN and CH_3I. Although these reactions appear to be free-radical processes, we observe no inhibition by the addition of the radical inhibitors duroquinone, hydroquinone, or 9,10-dihydroanthracene or by addition of the radical

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scavenger di-*tert*-butylnitroxide. Similarly, these reactions appeared unaffected when carried out in the dark.

The participation of radical processes in the oxidative additions of alkyl halides to Rh(I) and Ir(I) is well documented,[7c,46,47] and the failure of duroquinone to affect such processes has been noted and has been rationalized in terms of caged radical species.[7c] In the present study the alkyl halides for which a radical process appears to be involved (CH_2I_2, ICH_2CN, $CH_2=CHCH_2Br$, and $C_6H_5CH_2Br$) are those known to give rise to more stable radicals by virtue either of resonance stabilization or of stabilization by electron-withdrawing groups.[48,49] Certainly, polyhalomethanes CH_nX_{4-n} are known to display a greater tendency to undergo radical processes than the monohalo counterparts,[47b,49] in agreement with our observation of a radical-induced process involving CH_2I_2.

Conclusions

Oxidative addition of CH_3I and CH_3OCH_2I is shown to be a useful route for the preparations of the binuclear alkyl complexes $[Ir_2(R)(I)(CO)(\mu\text{-}CO)(dppm)_2]$ (R = CH_3 (**3**), CH_2OCH_3 (**4**)) and $[RhIr(CH_2OCH_3)(I)(CO)(\mu\text{-}CO)(dppm)_2]$ (**5**). The failure of this method to generate the analogous mixed-metal methyl compound by oxidative addition of CH_3I to $[RhIr(CO)_3(dppm)_2]$ demonstrates the deactivating effect of substituting one Ir by the less nucleophilic Rh. Our goal of activating C−H bonds in alkyl ligands by substituting an α-hydrogen by a methoxy substituent has been an overwhelming (if unexpected) success. Therefore, removal of the iodo ligand from **4** is accompanied by activation of both C−H bonds on the α-carbon, yielding the methoxycarbyne-bridged dihydride $[Ir_2(H)_2(CO)_2(\mu\text{-}COMe)(dppm)_2][CF_3SO_3]$ (**6**). Subsequent attempts to investigate the tendencies of the CH_2I and CH_2CN ligands to undergo similar C−H bond cleavage have not succeeded, owing to our failure to obtain the targeted $[MIr(CH_2Y)(I)(CO)_2(dppm)_2]$ (M = Rh, Ir; Y = I, CN) products by oxidative addition of CH_2I_2 and ICH_2CN to the $[MIr(CO)_3(dppm)_2]$ (M = Rh, Ir) precursors. These alkyl iodides react with the precursor complexes by a free-radical process, resulting in the unexpected hydrogen abstraction from one dppm ligand and iodine atom addition to the metals yielding $[MIr(CO)_2)(\mu\text{-}I)(\mu\text{-}CO)(Ph_2PCHPPh_2)(dppm)]$. Further studies are underway to probe the fascinating promotion of C−H bond activation by electron-withdrawing substituents, and other routes to the target products $[MIr(CH_2Y)(I)(CO)_2(dppm)_2]$ are under investigation.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada (NSERC) and the University of Alberta for financial support of the research and for scholarships (to J.R.T.), and NSERC for funding of the P4/RA diffractometer.

Supporting Information Available: Tables of X-ray experimental details, atomic coordinates, interatomic distances and angles, anisotropic thermal parameters, and hydrogen parameters for compounds **4** and **10**. This material is available free of charge via the Internet at http://pubs.acs.org.

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