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Registry No. 1, 74977-82-5; 2, 92418-47-8; 3, 92419-22-2; 4a, 92314-38-0; 4b, 92418-51-4; 5a, 92418-48-9; 5a·CH_3CN, 92419-23-3; 5b, 92469-42-6; 6a, 92418-49-0; 6b, 92469-43-7; 7, 92314-40-4; 8, 92314-41-5; 9, 92314-42-6; 10, 92314-44-8; 11, 92314-46-0; 12, 92270-14-9; 13, 92314-48-2; 14, 92314-51-7; 15, 92345-43-2; 16, 92345-44-3; 17, 92314-53-9; 18, 92314-55-1; $[Ir_2Cl_2(B)_4]$ (B = cyclooctene), 12246-51-4; Ir, 7439-88-5.

Supplementary Material Available: A listing of observed and calculated structure factors and tables of anisotropic temperature factors and calculated hydrogen positional parameters (87 pages). Ordering information is given on any current masthead page.

Neutral and Cationic Alkyne-Bridged Complexes of Iridium and the Structure of $[Ir_2Cl_2(CO)_2(\mu\text{-}CH_3O_2CC_2CO_2CH_3)(Ph_2PCH_2PPh_2)_2]\cdot 2CH_2Cl_2$

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The reactions of *trans*-$[IrCl(CO)(DPM)]_2$ with dimethyl acetylenedicarboxylate (DMA), hexafluro-2-butyne (HFB), and acetylene yield the species $[Ir_2Cl_2(CO)_2(\mu\text{-}RC_2R)(DPM)_2]$ (R = CO_2CH_3, CF_3, H) in which the alkyne ligand bridges the two iridium centers as a cis-dimetalated olefin. In contrast, no reaction is observed with 2-butyne. Refluxing the DMA and HFB adducts in toluene results in CO loss to produce $[Ir_2Cl_2(CO)(\mu\text{-}RC_2R)(DPM)_2]$ (R = CO_2CH_3, CF_3). The reaction of $[Ir_2Cl_2(CO)_2(\mu\text{-}RC_2R)(DPM)_2]$ (R = CO_2CH_3, CF_3) with $AgBF_4$ produces the cationic compounds $[Ir_2Cl(CO)_2(\mu\text{-}RC_2R)(DPM)_2][BF_4]$ that are observed to be fluxional on the NMR time scale. Isomers of these latter two compounds can be prepared by the reaction of DMA and HFB with $[Ir_2(CO)_2(\mu\text{-}Cl)(DPM)_2][BF_4]$. Both sets of isomers react with CO to give $[Ir_2Cl(CO)_3(\mu\text{-}RC_2R)(DPM)_2][BF_4]$. Refluxing these tricarbonyl species regenerates the isomers obtained by the $AgBF_4$ route. $[Ir_2Cl_2(CO)_2(\mu\text{-}DMA)(DPM)_2]\cdot 2CH_2Cl_2$ crystallizes in the space group $P\bar{1}$ with a = 11.880 (2) Å, b = 23.514 (3) Å, c = 11.689 (1) Å, α = 95.429 (9)°, β = 110.389 (9)°, γ = 77.999 (10)°, and Z = 2. The structure was refined to R = 0.037 and R_w = 0.067 based on 7796 unique observed reflections and 367 variables.

Introduction

The chemistry of DPM-bridged, binuclear complexes of rhodium (DPM = $Ph_2PCH_2PPh_2$) with activated acetylenes such as dimethyl acetylenedicarboxylate (DMA) and hexafluoro-2-butyne (HFB) is now rather well established.[1-6] In all cases reported, the acetylene molecules are found to bridge the two metal centers parallel to the metal–metal axis, in what is often referred to as a cis-dimetalated olefin geometry. This is in constrast to an analogous DAM-bridged cobalt species (DAM = $Ph_2AsCH_2AsPh_2$)[7] in which the acetylene molecule binds perpendicular to the Co–Co bond in a pseudotetrahedral geometry and to some binuclear rhodium complexes, not bridged by DPM or similar groups, which also display the pseudotetrahedral acetylenic binding mode.[8,9]

We have shown, for example, that the binuclear complexes $[Rh_2X_2(\mu\text{-}CO)(DPM)_2]$ and *trans*-$[RhCl(CO)(DPM)]_2$ (X = Cl, Br, I) react with DMA and HFB to yield the unusual species $[Rh_2X_2(\mu\text{-}CO)(\mu\text{-}RC_2R)(DPM)_2]$ (R = CO_2Me, CF_3),[1] in which the bridging acetylene group is accompanied by a bridging carbonyl ligand and no metal–metal bond. The resulting carbonyl geometry (with angles about carbon of near 120°) is found to be more reminiscent of an organic carbonyl than of a classical inorganic carbonyl group. Somewhat analogous complexes, also containing "ketonic" carbonyl groups, have recently been prepared by the reaction of $[Rh_2(CO)_2(\mu\text{-}O_2CCH_3)(DPM)_2]^+$ with the above activated acetylenes.[3,4] The acetylene-bridged complexes $[Rh_2X_2(\mu\text{-}RC_2R)(DPM)_2]$ have also been prepared,[2] and their metal–metal bond reactivities have recently been studied.[5,6]

However, at the time this study was undertaken, no analogous chemistry of binuclear, DPM-bridged complexes of iridium had been reported. We therefore sought to extend the acetylene chemistry of the rhodium complexes to those of iridium, anticipating that a broader range in reactivities might be observed. Herein, we report the results of this study, a preliminary report of which has previously been presented.[10]

Experimental Section

All solvents were appropriately dried and distilled prior to use and were stored under dinitrogen. Reactions were performed

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(1) (a) Cowie, M.; Southern, T. G. *J. Organomet. Chem.* **1980**, *193*, C46. (b) Cowie, M.; Southern, T. G. *Inorg. Chem.* **1982**, *21*, 246.

(2) Cowie, M.; Dickson, R. S. *Inorg. Chem.* **1981**, *20*, 2682.

(3) Mague, J. T.; DeVries, S. H. *Inorg. Chem.* **1982**, *21*, 1632.

(4) Mague, J. T. *Inorg. Chem.* **1983**, *22*, 1158.

(5) Cowie, M.; McKeer, J. R. *Inorg. Chim. Acta* **1982**, *65*, L107.

(6) Cowie, M.; Dickson, R. S.; Hames, B. W. *Organometallics*, following paper in this issue.

(7) Bird, P. H.; Fraser, A. R.; Hall, D. N. *Inorg. Chem.* **1981**, *20*, 2682.

(8) Dickson, R. S.; Pain, G. N.; Mackay, M. F. *Acta Crystallogr., Sect. B* **1979**, *B35*, 2321.

(9) Bennett, M. A.; Johnson, R. N.; Robertson, G. B.; Turney, T. W.; Whimp, P. O. *Inorg. Chem.* **1976**, *15*, 97.

(10) Cowie, M.; Sutherland, B. R. Abstract IN8-8, 66th Canadian Chemical Conference; Calgary, June 1983.

0276-7333/84/2303-1869$01.50/0

Table I. Infrared Stretching Frequencies

compound	ν(CO), cm^{-1}		other, cm^{-1}
	solid[a]	soln[b]	
3, $[Ir_2Cl_2(CO)_2(\mu\text{-DMA})(DPM)_2]$	2023 (s), 1999 (s)	2044 (s), 2005 (m)	1549 (w);[c] 1653 (m), 1674 (m)[d]
4, $[Ir_2Cl_2(CO)_2(\mu\text{-HFB})(DPM)_2]$	2024 (s)	2021 (s)	1549 (w)[c]
5, $[Ir_2Cl_2(CO)_2(\mu\text{-}HC_2H)(DPM)_2]$	1977 (s), 1968 (s)	1982 (br, s)	1533 (w)[c]
6, $[Ir_2Cl_2(CO)(\mu\text{-DMA})(DPM)_2]$	2004 (s)	2009 (s)	1554 (w);[c] 1696 (m), 1674 (m)[d]
7, $[Ir_2Cl_2(CO)(\mu\text{-HFB})(DPM)_2]$	2009 (s), 1988 (m)	*e*	
8, $[Ir_2Cl(CO)_2(\mu\text{-DMA})(DPM)_2][BF_4]$	2025 (s), 1982 (s)	2039 (s, br)	1538 (w);[c] 1708 (m), 1691 (m)[d]
9, $[Ir_2Cl(CO)_2(\mu\text{-HFB})(DPM)_2][BF_4]$	2045 (s), 2033 (s)	2048 (m), 2036 (s), 2004 (m)	1565 (w)[c]
10, $[Ir_2Cl(CO)_3(\mu\text{-DMA})(DPM)_2][BF_4]$	2085 (s), 2040 (sh), 2038 (s)	2070 (s), 2057 (s), 2029 (s)	1572 (w);[c] 1699 (m), 1712[d]
11, $[Ir_2Cl(CO)_3(\mu\text{-HFB})(DPM)_2][BF_4]$	2075 (m), 2049 (s), 2038 (s)	2091 (m), 2053 (br, s)	1562 (w)[c]
12, $[Ir_2Cl(CO)_2(\mu\text{-DMA})(DPM)_2][BF_4]$	2095 (s), 2055 (s)	*f*	1559 (w);[c] 1702 (m), 1679 (m)[d]
13, $[Ir_2Cl(CO)_2(\mu\text{-HFB})(DPM)_2][BF_4]$	2901 (s), 2054 (s)	*f*	1573 (w)[c]

[a] Nujol mull. [b] CH_2Cl_2 solution. [c] ν(C=C) of coordinated alkyne. [d] ν(C=O) of CO_2CH_3. [e] Insoluble in CH_2Cl_2. [f] Reacted with NaCl cells.

Table II. NMR Spectral Results

compound	$^{31}P\{^1H\}$,[a] δ	^1H,[b] δ (CH_3)	^{19}F,[c] δ
3, $[Ir_2Cl_2(CO)_2(\mu\text{-DMA})(DPM)_2]$	−27.4 (m), −29.5 (m)[h]	2.80 (s), 3.24 (s)	
4, $[Ir_2Cl_2(CO)_2(\mu\text{-HFB})(DPM)_2]$	−26.9 (m), −34.7 (m)		−48.23 (q), −54.42 (q)
5, $[Ir_2Cl_2(CO)_2(\mu\text{-}HC_2H)(DPM)_2]$	−22.4 (m), −25.4 (m)	6.13 (s), 6.52 (s)	
6, $[Ir_2Cl_2(CO)(\mu\text{-DMA})(DPM)_2]$	+6.1 (m), −29.8 (m)	2.18 (s), 2.75 (s)	
7, $[Ir_2Cl_2(CO)(\mu\text{-HFB})(DPM)_2]$	*g*		
8, $[Ir_2Cl(CO)_2(\mu\text{-DMA})(DPM)_2][BF_4]$	+9.6 (m), −22.7 (m)	2.19 (s), 2.65 (s)[e]	
9, $[Ir_2Cl(CO)_2(\mu\text{-HFB})(DPM)_2][BF_4]$	+5.4 (m), −28.1 (m), −14.9 (s)		−48.16 (q), −52.47 (q),[f] −51.24 (s)
10, $[Ir_2Cl(CO)_3(\mu\text{-DMA})(DPM)_2][BF_4]$	−29.9 (m)[d]	2.67 (s), 3.52 (s)[d] 2.27 (s), 3.47 (s)[c]	
11, $[Ir_2Cl(CO)_3(\mu\text{-HFB})(DPM)_2][BF_4]$	−34.5 (m), −37.5 (m)		−51.50 (q), −54.55 (q)
12, $[Ir_2(CO)_2Cl(\mu\text{-DMA})(DPM)_2][BF_4]$	+1.9 (m), −29.9 (m)	2.96 (s), 2.28 (s)[e]	
13, $[Ir_2(CO)_2Cl(\mu\text{-HFB})(DPM)_2][BF_4]$	+5.4 (m), −28.1 (m)		−46.60 (q), −47.61 (q)

[a] Vs. 85% H_3PO_4; −40 °C. [b] Phenyl H's typically occurred from δ 6.5 to 7.5 and DPM methylene H's typically occurred from δ 3.5 to 5.0. [c] Vs. external $CFCl_3$; room temperature. [d] Room temperature. [e] −60 °C. [f] −40 °C. [g] Insoluble. [h] Abbreviations: m = multiplet; s = singlet; q = quartet.

under modified Schlenk conditions using dinitrogen which had been passed through columns of Ridox and 4A molecular sieves in order to remove traces of oxygen and water, respectively. Hydrated iridium(III) chloride was obtained from Johnson-Matthey and bis(diphenylphosphino)methane (DPM) was purchased from Strem Chemicals. Carbon monoxide was purchased from Matheson and used as received. *trans*-$[IrCl(CO)(DPM)]_2$ (**1**) and $[Ir_2(CO)_2(\mu\text{-}Cl)(DPM)_2][BF_4]$ (**2**) were prepared by the previously reported procedures.[11] Variable-temperature $^{31}P\{^1H\}$ NMR spectra were recorded at 36.43 MHz on a Bruker HFX-90 spectrometer with Fourier transform capability. An external acetone-d_6 lock was used and the chemical shifts were referenced to external 85% H_3PO_4. The temperature was measured by a thermocouple inserted directly into the probe. ^1H NMR spectra were run on a Bruker WH-400 spectometer at room temperature unless otherwise stated. Infrared spectra were recorded on a Nicolet 7199 Fourier transform interferometer either as solids in Nujol mulls on KBr plates or as solutions in NaCl cells with 0.5-mm path length windows. Elemental analyses were performed within the department.

Preparation of Compounds. (a) $[Ir_2Cl_2(CO)_2(\mu\text{-DMA})(DPM)_2]\cdot 2CH_2Cl_2$ (3). The addition of 15.2 μL (0.16 mmol) of dimethyl acetylenedicarboxylate (DMA) to 200 mg (0.16 mmol) of $[IrCl(CO)(DPM)]_2$ (**1**), dissolved in 20 mL of CH_2Cl_2, produced an immediate color change from purple to light yellow. The solution was stirred for an additional $^1/_2$ h during which time no further changes were observed. The volume was reduced to 10 mL under N_2, and 10 mL of diethyl ether was slowly added. The solution was placed in the freezer overnight, resulting in the precipitation of **3** as a crop of pale yellow prisms. The solid was collected and washed with two 10-mL portions of ether and then dried in vacuo for 2 h. Typical isolated yields were 90%. Compound **3** was determined to be a nonelectrolyte in CH_2Cl_2 solutions ($\Lambda_m(10^{-3}\ M) \leq 0.5\ \Omega^{-1}\ cm^2\ mol^{-1}$).[12] Spectroscopic parameters for this and all subsequent compounds are given in Tables I and II. Anal. Calcd for $Ir_2Cl_6P_4O_6C_{60}H_{54}$: C, 45.27; H, 3.42; Cl, 13.36. Found: C, 45.17; H, 2.89; Cl, 13.16. In this and all subsequent compounds that crystallized with solvent molecules, the presence and amount of solvent was confirmed by ^1H NMR where possible.

(b) $[Ir_2Cl_2(CO)_2(\mu\text{-HFB})(DPM)_2]\cdot 2CH_2Cl_2$ (4). A 200-mg (0.16-mmol) sample of $[IrCl(CO)(DPM)]_2$ was placed in a 100-mL three-neck flask that was evacuated and then charged with 1 atm of hexafluoro-2-butyne (HFB). A 15-mL sample of CH_2Cl_2 was added to the flask, and the resulting solution was stirred under the HFB atmosphere for $^1/_2$ h during which time the color changed from purple to yellow. The volume was concentrated to ca. 5 mL under N_2, and the flask was placed in the freezer for 48 h during which time a light yellow crystalline solid separated from the solution. The precipitate was collected and washed with two 10-mL portions of ether and dried in vacuo for 2 h. Typical isolated yields were 75–80%. Essentially quantitative yields were obtained when the solution was taken completely to dryness under N_2; however, this gave **4** as a glassy yellow solid. Conductivity measurements on a CH_2Cl_2 solution of the crystalline material showed it to be nonconducting ($\Lambda_m(10^{-3}\ M) \leq 0.5\ \Omega^{-1}\ cm^2\ mol^{-1}$). Anal. Calcd for $Ir_2Cl_6P_4F_6O_2C_{58}H_{48}$: C, 43.21; H, 3.00. Found: C, 43.21; H, 3.02.

(c) $[Ir_2Cl_2(CO)_2(\mu\text{-}HC_2H)(DPM)_2]\cdot 0.5CH_2Cl_2$ (5). The preparation of compound **5** was carried out as described above for **4** except that acetylene (C_2H_2) was used instead of HFB. The initial crude product obtained in this manner was purified (as determined by $^{31}P\{^1H\}$ NMR) by several recrystallizations from CH_2Cl_2/ether. Typical isolated yields were 70–75% of a pale

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[11] Cowie, M.; Sutherland, B. R. *Inorg. Chem.* **1984**, *23*, 2324.

[12] Typically a 1:1 electrolyte, such as $[Rh_2(\mu\text{-}Cl)(\mu\text{-}CO)(CO)_2(DPM)_2][BF_4]$, gives a value of ca. 45 Ω^{-1} cm^2 mol^{-1}.

yellow microcrystalline solid. A CH_2Cl_2 solution of the solid proved to be a nonconducting ($\Lambda_m(10^{-3}\ M) \leq 0.5\ \Omega^{-1}\ cm^2\ mol^{-1}$). Anal. Calcd for $Ir_2Cl_3P_4O_2C_{54.5}H_{47}$: C, 48.54; H, 3.51; Cl, 7.89. Found: C, 48.08; H, 3.64; Cl: 7.75.

(d) $[Ir_2Cl_2(CO)(\mu\text{-DMA})(\mu\text{-DPM})_2]\cdot 2CH_2Cl_2$ (6). A 200-mg (0.13-mmol) sample of compound **3** was suspended in 10 mL of toluene and refluxed under a slow N_2 stream for 12 h during which time a light purple powder precipitated from solution. The resulting suspension was cooled in an ice bath, and the colorless mother liquor was removed. The residue was dried first under an N_2 stream and then under vacuum. Recrystallization from CH_2Cl_2 and ether yielded a crop of dark purple needles. Typical isolated yields were 90–95%. When dissolved in CH_2Cl_2, compound **6** proved to be nonconducting ($\Lambda_m(10^{-3}\ M) \leq 0.5\ \Omega^{-1}\ cm^2\ mol^{-1}$). Anal. Calcd for $Ir_2Cl_6P_4O_5C_{59}H_{54}$: C, 45.31; H, 3.48. Found: C, 45.53; H, 3.50.

(e) $[Ir_2Cl_2(CO)(\mu\text{-HFB})_2(DPM)_2]\cdot{}^1/_2C_7H_8$ (7). The reaction was carried out the same as described for **6** except that **4** was used instead of **3**. The purple solid obtained from the refluxed toluene solution proved to be highly insoluble in all common solvents making purification and subsequent characterization difficult. Typical isolated yields were about 80%. Anal. Calcd for $Ir_2Cl_2P_4F_6OC_{58.5}H_{48}$: C, 48.10; H, 3.35. Found: C, 48.44; H, 3.27.

(f) $[Ir_2Cl(CO)_2(\mu\text{-DMA})(DPM)_2][BF_4]$ (Isomer 1) (8). To a slurry of 250 mg (0.16 mmol) of **3** in 10 mL of THF was added dropwise 1 equiv of $AgBF_4$ (34.2 mg, 0.16 mmol) dissolved in 2 mL of THF. The solution immediately changed from light yellow to dark orange, and an orange precipitate appeared. Complete precipitation was induced by the addition of 30 mL of diethyl ether. The solid was collected and dried under an N_2 stream. The resulting residue was redissolved in 10 mL of CH_2Cl_2 and filtered under dinitrogen. The addition of ether yielded a red-orange microcrystalline product in approximately 90% yield. Compound **10** was determined to be 1:1 electrolyte in CH_2Cl_2 solutions ($\Lambda_m(10^{-3}\ M) = 56.6\ \Omega^{-1}\ cm^2\ mol^{-1}$). Anal. Calcd for $Ir_2ClP_4F_4O_6C_{58}BH_{50}$: C, 47.27; H, 3.42; Cl, 2.41. Found: C, 46.78; H, 3.44; Cl, 2.39.

(g) $[Ir_2Cl(CO)_2(\mu\text{-HFB})(DPM)_2][BF_4]$ (Isomer 1) (9). The reaction was carried out as described above for **8**, except that 180 mg (0.11 mmol) of **4** was used along with 24.7 mg (0.11 mmol) of $AgBF_4$. The resulting light orange microcrystalline product was obtained in approximately 90–95% yield. Conductivity measurements of this solid in CH_2Cl_2 indicated that it was a 1:1 electrolyte ($\Lambda_m(10^{-3}\ M) = 44.2\ \Omega^{-1}\ cm^2\ mol^{-1}$). Anal. Calcd for $Ir_2Cl_1P_4F_{10}O_2C_{56}B_1H_{52}$: C, 45.04; H, 2.97. Found: C, 44.98; H, 3.11.

(h) $[Ir_2Cl(CO)_3(\mu\text{-DMA})(DPM)_2][BF_4]\cdot CH_2Cl_2$ (10). Method A. An atmosphere of carbon monoxide was placed over a solution of 200 mg (0.14 mmol) of **8** in 10 mL of CH_2Cl_2 resulting in an immediate color change from dark orange to pale yellow. The addition of 20 mL of diethyl resulted in the precipitation of a white microcrystalline solid that was collected and dried under a stream of CO. Typical isolated yields were 90–95%. Conductivity measurements on a CH_2Cl_2 solution of this solid showed it to be a 1:1 electrolyte ($\Lambda_m(10^{-3}\ M) = 55.7\ \Omega^{-1}\ cm^2\ mol^{-1}$). Anal. Calcd for $Ir_2Cl_3P_4F_4O_7C_{60}BH_{52}$: C, 45.42; H, 3.30; Cl, 6.70. Found: C, 45.32; H, 3.31; Cl, 6.69.

(i) $[Ir_2Cl(CO)_3(\mu\text{-HFB})(DPM)_2][BF_4]$ (11). Method A. Compound **11** was prepared by the same procedure described for **10** except that **9** was used instead of **8**. The reaction produced a white microcrystalline solid in 90–95% yield. Compound **11** was determined to be a 1:1 electrolyte in CH_2Cl_2 solutions ($\Lambda_m(10^{-3}\ M) = 47.7\ \Omega^{-1}\ cm^2\ mol^{-1}$). Anal. Calcd for $Ir_2ClP_4F_{10}O_3C_{57}BH_{44}$: C, 44.99; H, 2.91. Found: C, 44.71; H, 2.95.

(j) $[Ir_2Cl(CO)_2(\mu\text{-DMA})(DPM)_2][BF_4]$ (Isomer 2) (12). To a solution of 100 mg of $[Ir_2(CO)_2(\mu\text{-Cl})(DPM)_2][BF_4]$ (0.075 mmol) in 10 mL of CH_2Cl_2 at −78 °C was added 1 equiv of DMA (7.4 μL, 0.075 mmol) producing a rapid color change from dark red-orange to purple. The solution was stirred for 5 min, and then 30 mL of diethyl was added resulting in the precipitation of a dark purple solid. The solid was collected and washed with two 10-mL portions of ether at room temperature and then dried in vacuo for 2 h. Typical isolated yields were 90–95%. Compound **14** was shown to be a 1:1 electrolyte in CH_2Cl_2 solutions ($\Lambda_m(10^{-3}\ M) = 49.8\ \Omega^{-1}\ cm^2\ mol^{-1}$). Anal. Calcd for $Ir_2ClP_4F_4O_6C_{58}BH_{50}$: C, 47.28; H, 3.42; Cl, 2.41. Found: C, 47.52; H, 3.44; Cl, 2.50.

(k) $[Ir_2Cl(CO)_2(\mu\text{-HFB})(DPM)_2][BF_4]$ (Isomer 2) (13). A 100-mg sample of $[Ir_2(CO)_2(\mu\text{-Cl})(DPM)_2][BF_4]$ (0.075 mmol) was placed in a three-neck flask that was evacuated and then filled with 1 atm of HFB. A 10-mL sample of CH_2Cl_2 was then added and the resulting solution stirred under the HFB atmosphere for 15 min during which time the solution color changed from dark red-orange to purple. The HFB atmosphere was replaced with N_2 and the volume reduced to 5 mL. A 20-mL sample of diethyl ether was added resulting in the precipitation of a dark purple solid in 90–95% yield. The solid was collected and washed with diethyl ether and dried in vacuo for 2h. Conductivity measurements on a CH_2Cl_2 solution of **15** showed it to be a 1:1 electrolyte ($\Lambda_m(10^{-3}\ M) = 52.3\ \Omega^{-1}\ cm^2\ mol^{-1}$). Anal. Calcd for $Ir_2ClP_4O_2F_{10}C_{56}BH_{44}$: C, 45.04; H, 2.97. Found: C, 45.01; H, 3.15.

(l) $[Ir_2Cl(CO)_3(\mu\text{-DMA})(DPM)_2][BF_4]\cdot CH_2Cl_2$ (10). Method B. An atmosphere of carbon monoxide was placed over a solution of 200 mg (0.14 mmol) of **12** in 10 mL of CH_2Cl resulting in an immediate color change from dark purple to pale yellow. The addition of 20 mL of diethyl ether resulted in the precipitation of a white microcrystalline solid. The solid was collected and dried under a stream of CO. The product obtained from this reaction was indistinguishable in all of its physical properties to that obtained from method A. Typical yields were 90–95%.

(m) $[Ir_2Cl(CO)_3(\mu\text{-HFB})(DPM)_2][BF_4]$ (11). Method B. The procedure used was identical with that described above for **13** except that **13** was used instead of **12**. The reaction produced a white microcrystalline solid in 90–95% yield that was indistinguishable in all of its physical properties to that obtained from method A.

Attempted Reactions. (n) Attempted Reaction of $[IrCl(CO)(DPM)]_2$ (1) and $[Ir_2(CO)_2(\mu\text{-Cl})(DPM)_2][BF_4]$ (2) with $CH_3C{\equiv}CCH_3$. To a solution of $[IrCl(CO)(DPM)]_2$ (**1**) (200 mg, 0.16 mmol) in 15 mL of CH_2Cl_2 was added an excess of 2-butyne (50 μL, 0.64 mmol). The resulting solution was stirred for 3 h with no apparent color change. Examination of the infrared and NMR spectra indicated that no reaction had taken place. The solution was then refluxed for 2 h after which time the infrared and $^{31}P\{^1H\}$ NMR spectra showed only starting material. Similar results were obtained by using $[Ir_2(CO)_2(\mu\text{-Cl})(DPM)_2][BF_4]$ (**2**) instead of (**1**).

(o) Attempted Reaction of $[Ir_2(CO)_2(\mu\text{-Cl})(DPM)_2][BF_4]$ (2) with HC_2H. A 200-mg (0.15-mmol) sample was placed in a 100-mL three-neck flask that was evacuated and then charged with 1 atm of acetylene. A 15-mL sample of CH_2Cl_2 was added to the flask and immediately produced a dark brown-black solution. This solution was stirred under the acetylene atmosphere for $^1/_2$ h during which time no further changes were observed. The solvent was removed under vacuum, leaving a dark brown glassy solid. A $^{31}P\{^1H\}$ NMR spectrum of this solid showed it to contain at least three major species and a number of minor ones. No attempts were made to separate and identify these products.

X-ray Data Collection. Crystals of $[Ir_2Cl_2(CO)_2(\mu\text{-DMA})(DPM)_2]\cdot 2CH_2Cl_2$ (**3**) of suitable quality for an X-ray study were obtained by the slow diffusion of diethyl ether into a saturated CH_2Cl_2 solution of the title complex. A light yellow prism was mounted on a glass fiber in the air and coated with shellac.

Preliminary film data showed $\bar{1}$ Laue symmetry and no systematic absences, consistent with the space groups $P1$ and $P\bar{1}$. The centrosymmetric space group was chosen and later verified by the successful refinement of the structure with acceptable positional parameters, thermal parameters, and agreement indices. Accurate cell parameters were obtained by a least-squares refinement of the setting angles of 12 carefully centered reflections chosen from diverse regions of reciprocal space ($50° \leq 2\theta \leq 60°$, Cu Kα radiation) and obtained by using a narrow X-ray source (see Table III for pertinent crystal data). A cell reduction[13] failed to show the presence of higher symmetry. The reduced cell is reported.

Data were collected on a Picker four-circle automated diffractometer equipped with a scintillation counter and pulse-height analyzer, tuned to accept 90% of the Cu Kα peak. Background

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[13] The cell reduction was performed by using a modification of TRACER II by S. L. Lawson. See: Lawson, S. L.; Jacobsen, R. A. "The Reduced Cell and Its Crystallographic Applications", Ames Laboratory Report IS-1141; USAEC: Iowa State University, Ames, IA, Apr 1965.

Table III. Summary of Crystal Data and Intensity Collection Details

compd	$[Ir_2Cl_2(CO)_2(\mu\text{-DMA})(DPM)_2]\cdot 2CH_2Cl_2$
formula	$Ir_2Cl_6P_4O_6C_{60}H_{54}$
fw	1580.07
cell parameters	
a, Å	11.880 (2)
b, Å	23.514 (3)
c, Å	11.689 (1)
α, deg	95.429 (9)
β, deg	110.389 (9)
γ, deg	77.999 (10)
Z	2
V, Å^3	2992.93
space group	C_i^1–$P\bar{1}$
cryst shape	triclinic prism with faces of the form {100}, {010}, {113}, {011}
cryst dimens, mm	0.356 × 0.096 × 0.396
cryst vol, mm^3	6.55×10^{-3}
temp, °C	23
radiation	Cu Kα (λ = 1.540 562 Å) filtered with 0.5 mil nickel foil
μ, cm^{-1}	122.914
range in abs corr factors (as applied to F_o^2)	0.116–0.383
receiving aperature	4 mm × 4 mm, 30 cm from crystal
takeoff angle, deg	3.4
scan speed, deg/min	2 in 2θ
scan range	0.6° below Kα_1 to 0.6° above Kα_2
bkgd counting time, s	10 (3° < 2θ ≤ 99.4°), 20 (99.4° < 2θ ≤ 121)
2θ limits	3.0° < 2θ ≤ 121.0°
final no. of variables	367
data collected	$\pm h,\pm k,l$; 9868
unique data used ($F_o^2 \geq 3\sigma(F_o^2)$)	7796
error in observn of unit wt	1.588
R	0.037
R_w	0.067

counts were measured at both ends of the scan range with stationary crystal and counter. The intensities of three standard reflections were measured every 100 reflections, and four additional standards were measured three times a day. No significant variation in the intensities of the standards was noted during data collection so no corrections were applied.

The intensities of 9868 reflections (3° < 2θ ≤ 121°) were measured by using Ni-filtered Cu Kα radiation. Data were processed in the usual manner with a value of 0.04 for p.[14] Of these, 7796 were unique and had $F_o^2 \geq 3\sigma(F_o^2)$; these were used in subsequent calculations. Absorption corrections were applied to the data by using Gaussian integration.[15]

Structure Solution and Refinement. The positions of the two independent Ir atoms were obtained from a sharpened Patterson synthesis. Subsequent refinements and difference Fourier calculations led to the location of all other atoms. Atomic scattering factors were taken from Cromer and Waber's tabulation[16] for all atoms except hydrogen, for which the values of Stewart et al.[17] were used. Anomalous dispersion[18] terms for Ir, Cl, and P were included in F_c. The carbon atoms of all phenyl rings were refined as rigid groups having D_{6h} symmetry, C–C distances of 1.392 Å, and independent isotropic thermal parameters. All hydrogen atoms of the DPM ligands were located and included as fixed contributions in the least-squares refinements but were not themselves refined. Their idealized positions were calculated from the geometries about their attached carbon atoms by using C–H distances of 0.95 Å. Hydrogen atoms were assigned isotropic thermal parameters of 1 Å^2 greater than the isotropic thermal parameter (or equivalent isotropic thermal parameter of anisotropic atoms) of their attached carbons. The positions of the methyl carboxylate hydrogen atoms were not clearly defined; only a smear of electron density was observed in their approximate locations. No attempt was made to resolve these atom positions.

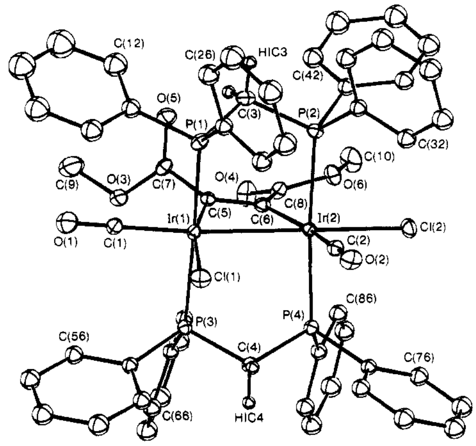

Figure 1. Perspective view of $[Ir_2Cl_2(CO)_2(\mu\text{-DMA})(DPM)_2]$, showing the numbering scheme. The numbering on the phenyl carbon atoms starts at the carbon bonded to phosphorus and increases sequentially around the ring. 20% thermal ellipsoids are shown.

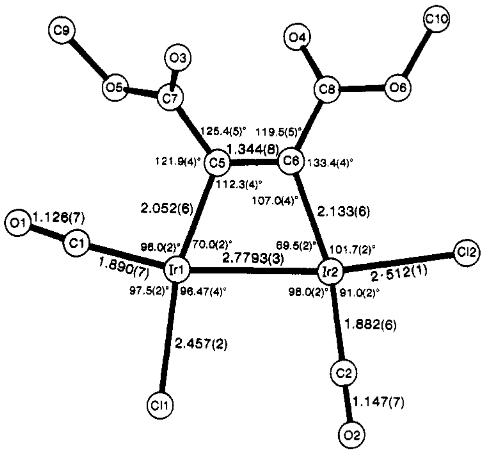

Figure 2. Representation of the inner coordination sphere of the complex in the approximate plane of the metal atoms and the alkyne molecule. Some relevant bond lengths and angles are shown.

The final model in space group $P\bar{1}$ with 367 parameters refined converged to R = 0.037 and R_w = 0.067.[19] In the final difference Fourier map, the 20 highest residuals (0.72–0.36 e/Å^3) were in the vicinity of the iridium atoms and the acetylene methyl carbons. A typical carbon on an earlier synthesis had an electron density of about 7–8 e/Å^3. The final positional parameters of the group and non-hydrogen atoms are given in Tables IV and V. The derived hydrogen position and thermal parameters and a listing of the observed and calculated structure amplitudes are available.[20]

Description of Structure of $[Ir_2Cl_2(CO)_2(\mu\text{-DMA})(DPM)_2]\bullet 2CH_2Cl_2$ (3)

The title complex crystallizes in the space group $P\bar{1}$ with two complex molecules and four solvent CH_2Cl_2 molecules

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[14] Doedens, R. I.; Ibers, J. A. *Inorg. Chem.* **1967**, *6*, 204.

[15] For the programs used in the solution and refinement, see: Cowie, M.; Dwight, S. K. *Inorg. Chem.* **1980**, *19*, 2508.

[16] Cromer, D. T.; Waber, J. T. "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2 A.

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

[18] Cromer, D. T.; Liberman, D. *J. Chem. Phys.* **1970**, *53*, 1891.

[19] $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$.

[20] Supplementary material.

Table IV. Positional and Equivalent Isotropic Thermal Parameters for the Nongroup Atoms of $[Ir_2Cl_2(CO)_2(\mu\text{-DMA})(DPM)_2]\cdot 2CH_2Cl_2$

atom	x^a	y	z	B, Å^2	atom	x	y	z	B, Å^2
Ir(1)	0.17707 (2)	0.228630 (10)	0.34596 (2)	2.32	O(4)	0.1208 (4)	0.3386 (2)	−0.0050 (5)	4.55
Ir(2)	−0.06276 (2)	0.261175 (10)	0.19192 (2)	2.16	O(5)	0.3754 (4)	0.2738 (2)	0.2243 (4)	4.12
Cl(1)	0.12724 (16)	0.20209 (7)	0.51861 (14)	3.78	O(6)	−0.0649 (4)	0.31519 (19)	−0.0801 (4)	3.65
Cl(2)	−0.26575 (13)	0.30123 (7)	0.03732 (15)	3.60	C(1)	0.3490 (6)	0.2133 (3)	0.4196 (6)	3.04
Cl(3)^b	0.4026 (3)	0.45110 (13)	0.8755 (3)	9.49	C(2)	−0.1401 (5)	0.2301 (3)	0.2807 (6)	2.90
Cl(4)	0.5735 (4)	0.43022 (15)	0.7488 (4)	10.70	C(3)	0.1061 (6)	0.1367 (3)	0.1010 (6)	3.25
Cl(5)	0.4678 (4)	0.1277 (2)	0.7418 (3)	12.71	C(4)	0.0235 (5)	0.3467 (3)	0.4554 (5)	2.75
Cl(6)	0.3057 (4)	0.08954 (15)	0.8380 (4)	11.06	C(5)	0.1745 (5)	0.2591 (2)	0.1861 (5)	2.41
P(1)	0.18086 (15)	0.13363 (7)	0.26449 (15)	3.05	C(6)	0.0613 (5)	0.2834 (2)	0.1160 (5)	2.61
P(2)	−0.04915 (14)	0.17884 (6)	0.06282 (14)	2.76	C(7)	0.2849 (5)	0.2489 (3)	0.1502 (6)	2.91
P(3)	0.17675 (13)	0.32093 (6)	0.44948 (14)	2.55	C(8)	0.0448 (6)	0.3143 (3)	0.0064 (6)	2.99
P(4)	−0.09078 (13)	0.34796 (6)	0.30325 (13)	2.42	C(9)	0.4917 (7)	0.2582 (4)	0.2018 (10)	6.67
O(1)	0.4518 (4)	0.2058 (2)	0.4581 (5)	4.84	C(10)	−0.0871 (8)	0.3446 (4)	−0.1905 (7)	5.64
O(2)	−0.1870 (5)	0.2115 (2)	0.3356 (5)	4.37	C(D1)	0.5540 (9)	0.4306 (4)	0.8891 (10)	7.23
O(3)	0.2957 (4)	0.2170 (2)	0.0646 (4)	4.21	C(D2)	0.3456 (12)	0.1475 (5)	0.8011 (11)	8.86

[a] Estimated standard deviations in the least significant figure(s) are given in parentheses in this and all subsequent tables. [b] The dichloromethanes of solvation consist of C(D1), Cl(3), Cl(4) and C(D2), Cl(5), Cl(6).

Table V. Derived Parameters for the Rigid-Group Atoms of $[Ir_2Cl_2(CO)_2(\mu\text{-DMA})(DPM)_2]\cdot 2CH_2Cl_2$

atom	x^a	y	z	B, Å^2	atom	x	y	z	B, Å^2
C(11)	0.3364 (4)	0.0960 (5)	0.292 (3)	3.92 (13)	C(51)	0.274 (3)	0.3139 (3)	0.610 (3)	2.75 (10)
C(12)	0.390 (2)	0.0845 (5)	0.2014 (16)	6.1 (2)	C(52)	0.2271 (9)	0.3113 (3)	0.7025 (5)	3.58 (12)
C(13)	0.513 (2)	0.0582 (5)	0.2312 (14)	9.0 (3)	C(53)	0.306 (3)	0.3018 (5)	0.822 (3)	4.78 (16)
C(14)	0.5816 (4)	0.0433 (5)	0.351 (3)	8.2 (3)	C(54)	0.432 (3)	0.2949 (3)	0.849 (3)	4.81 (15)
C(15)	0.528 (2)	0.0548 (5)	0.4417 (16)	7.0 (2)	C(55)	0.4785 (9)	0.2974 (3)	0.7558 (5)	4.26 (14)
C(16)	0.405 (2)	0.0811 (5)	0.4119 (14)	5.19 (17)	C(56)	0.400 (3)	0.3069 (5)	0.636 (3)	3.51 (12)
C(21)	0.1169 (5)	0.07750 (19)	0.3066 (5)	3.44 (12)	C(61)	0.2162 (4)	0.38545 (16)	0.4086 (4)	2.74 (10)
C(22)	0.0194 (5)	0.09122 (16)	0.3506 (5)	4.24 (14)	C(62)	0.2073 (4)	0.39423 (16)	0.2894 (4)	3.31 (11)
C(23)	−0.0369 (4)	0.0474 (2)	0.3653 (3)	5.74 (19)	C(63)	0.2243 (4)	0.44685 (18)	0.2588 (3)	4.40 (14)
C(24)	0.0042 (5)	−0.01006 (19)	0.3361 (5)	6.4 (2)	C(64)	0.2501 (4)	0.49070 (16)	0.3474 (4)	4.58 (15)
C(25)	0.1017 (5)	−0.02377 (16)	0.2921 (5)	6.4 (2)	C(65)	0.2590 (4)	0.48193 (16)	0.4666 (4)	4.72 (15)
C(26)	0.1580 (4)	0.0200 (2)	0.2774 (3)	4.88 (16)	C(66)	0.2420 (4)	0.42931 (18)	0.4972 (3)	3.56 (12)
C(31)	−0.1491 (4)	0.12787 (19)	0.0590 (4)	3.23 (11)	C(71)	−0.2322 (4)	0.3631 (2)	0.3418 (6)	2.66 (10)
C(32)	−0.2641 (4)	0.15062 (15)	0.0671 (5)	3.96 (13)	C(72)	−0.2347 (5)	0.3409 (3)	0.4470 (5)	3.72 (13)
C(33)	−0.3466 (3)	0.1141 (2)	0.0529 (3)	5.02 (16)	C(73)	−0.3416 (8)	0.3533 (3)	0.4760 (6)	4.66 (15)
C(34)	−0.3142 (4)	0.05478 (19)	0.0307 (4)	5.58 (18)	C(74)	−0.4459 (4)	0.3878 (2)	0.3998 (6)	4.98 (16)
C(35)	−0.1992 (4)	0.03204 (15)	0.0226 (5)	5.57 (18)	C(75)	−0.4434 (5)	0.4100 (3)	0.2947 (5)	4.83 (15)
C(36)	−0.1167 (3)	0.0686 (2)	0.0367 (3)	4.51 (15)	C(76)	−0.3365 (8)	0.3976 (3)	0.2657 (6)	3.75 (12)
C(41)	−0.091 (4)	0.1878 (4)	−0.1026 (13)	3.42 (12)	C(81)	−0.0960 (4)	0.41649 (14)	0.2375 (4)	2.89 (11)
C(42)	−0.0028 (15)	0.1859 (4)	−0.156 (4)	4.42 (15)	C(82)	−0.0796 (4)	0.46653 (18)	0.3103 (3)	3.63 (12)
C(43)	−0.037 (3)	0.1892 (5)	−0.283 (4)	6.02 (19)	C(83)	−0.0848 (4)	0.51835 (15)	0.2585 (4)	4.55 (15)
C(44)	−0.160 (4)	0.1944 (4)	−0.3549 (13)	5.86 (19)	C(84)	−0.1064 (4)	0.52012 (14)	0.1338 (4)	4.61 (15)
C(45)	−0.2480 (15)	0.1964 (4)	−0.301 (4)	5.35 (17)	C(85)	−0.1228 (4)	0.47007 (18)	0.0610 (3)	4.25 (14)
C(46)	−0.214 (3)	0.1931 (5)	−0.175 (4)	4.00 (13)	C(86)	−0.1176 (4)	0.41826 (15)	0.1128 (4)	3.52 (12)

Rigid-Group Parameters

	$x_c{}^a$	y_c	z_c	δ^b	ϵ	η
ring 1	0.4590 (2)	0.06964 (17)	0.3216 (4)	1.834 (4)	1.566 (15)	4.636 (15)
ring 2	0.0606 (3)	0.03372 (15)	0.3213 (3)	0.006 (3)	0.693 (3)	0.963 (3)
ring 3	−0.2317 (3)	0.09133 (14)	0.0448 (3)	0.087 (3)	0.373 (3)	0.835 (3)
ring 4	−0.1254 (3)	0.19113 (13)	−0.2287 (3)	4.599 (3)	1.88 (3)	3.10 (3)
ring 5	0.3528 (3)	0.30437 (12)	0.7292 (3)	4.598 (3)	2.61 (2)	5.91 (2)
ring 6	0.2331 (3)	0.43808 (12)	0.3780 (3)	0.185 (3)	1.666 (3)	4.326 (2)
ring 7	−0.3391 (3)	0.37545 (12)	0.3708 (3)	2.055 (3)	0.663 (6)	0.102 (6)
ring 8	−0.1012 (3)	0.46830 (12)	0.1857 (3)	3.194 (3)	1.741 (3)	2.097 (2)

[a] x_c, y_c, and z_c are the fractional coordinates of the centroid of the rigid group. [b] The rigid-group orientation angles δ, ϵ, and Å (radians) are the angles by which the rigid body is rotated with respect to a set of axes x, y, and z. The origin is the center of the ring, x is parallel to a^*, z is parallel to c, and v is parallel to the line defined by the interaction of the plane containing a^* and b^* with the plane containing b and c.

in the unit cell; all are well separated with no unusually short contacts between them. Both independent solvent molecules are crystallographically well behaved and display the expected geometry. A perspective view of the complex, including the numbering scheme, is shown in Figure 1 (phenyl hydrogens have the same number as their attached carbon atom). A view of the approximate plane of the metals and the bridging acetylene group is shown in Figure 2 along with some relevent bond lengths and angles.

The overall geometry of the complex is essentially as expected for a binuclear species bridged by two mutually trans DPM ligands. Within the DPM framework, the bond lengths and angles are all normal (Tables VI and VII, respectively) and similar to those found in other DPM-bridged complexes of iridium.[10,20,21] Each metal has a slightly distorted octahedral geometry in which the coordination sites are occupied by the two trans phosphorus atoms, a mutually cis terminal carbonyl and chloride ligand, one end of the bridging acetylene group, bound as a

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(21) Eisenberg, R.; Kubiak, C. P.; Woodcock, C. *Inorg. Chem.* **1980**, *19*, 2733.

Table VI. Selected Distances (Å) in $[Ir_2Cl_2(CO)_2(\mu\text{-DMA})(DPM)_2]\cdot 2CH_2Cl_2$

Ir(1)-Ir(2)	2.7793 (3)	C(8)-O(6)	1.340 (7)
Ir(1)-Cl(1)	2.457 (2)	C(9)-O(5)	1.462 (8)
Ir(2)-Cl(2)	2.512 (1)	C(10)-O(6)	1.438 (8)
Ir(1)-P(1)	2.342 (2)	P(1)-C(3)	1.807 (7)
Ir(1)-P(3)	2.383 (2)	P(2)-C(3)	1.825 (7)
Ir(2)-P(2)	2.354 (2)	P(3)-C(4)	1.819 (6)
Ir(2)-P(4)	2.342 (2)	P(4)-C(4)	1.821 (6)
Ir(1)-C(1)	1.890 (7)	P(1)-C(11)	1.807 (4)
Ir(2)-C(2)	1.882 (6)	P(1)-C(21)	1.834 (4)
Ir(1)-C(5)	2.052 (6)	P(2)-P(31)	1.842 (4)
Ir(2)-C(6)	2.133 (6)	P(2)-C(41)	1.842 (4)
C(1)-O(1)	1.126 (7)	P(3)-C(51)	1.828 (3)
C(2)-O(2)	1.147 (7)	P(3)-C(61)	1.827 (3)
C(5)-C(6)	1.344 (8)	P(4)-C(71)	1.845 (3)
C(5)-C(7)	1.479 (8)	P(4)-C(81)	1.830 (3)
C(6)-C(8)	1.467 (8)	C(D1)-Cl(3)[a]	1.72 (1)
C(7)-O(3)	1.219 (7)	C(D1)-Cl(4)	1.73 (1)
C(8)-O(4)	1.215 (7)	C(D2)-Cl(5)[a]	1.78 (1)
C(7)-O(5)	1.330 (7)	C(D2)-Cl(6)	1.67 (1)

[a] The dichloromethane molecules of solvation consist of C(D1),Cl(3),Cl(4) and C(D2),Cl(5),Cl(6).

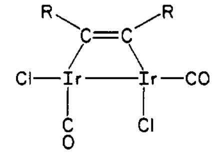
cis-dimetalated olefin, and the Ir–Ir bond. The major distortions from octahedral geometry about each metal result from the strain imposed by the bridging acetylene ligand (vide infra) accompanying the Ir–Ir bond, and as a consequence the Ir–Ir–acetylene angles (average 69.8°) are rather acute. The respective carbonyl and chloride ligands on each metal are chemically inequivalent; on Ir(1), the Cl atom is pseudotrans to the acetylene group and the carbonyl is opposite the Ir–Ir bond; on Ir(2) the positions are reversed.

The iridium–iridium distance of 2.7793 (3) Å is typical of that observed for an Ir–Ir single bond and is comparable to the values found in analogous Ir–DPM systems.[10,22] This distance is significantly shorter than the intraligand P–P distances (2.989 (2) and 3.001 (2) Å), indicating a compression along the Ir–Ir axis as expected for a metal–metal bonded system. Both Ir–Cl distance are somewhat long. The Ir(1)–Cl(1) distance (2.457 (2) Å) can be explained based on the high trans influence of the σ-bonded alkenyl carbon of the cis-dimetalated olefin, however, the Ir(2)–Cl(2) length is even longer (2.512(1) Å) and must be attributed to an even higher trans influence of the Ir–Ir interaction. Although trans lengthening by a metal-metal bond does not seem to be widely examined phenomenon, several reports alluding to such an effect have appeared recently.[23-25] The parameters involving the carbonyl groups are quite normal with no significant differences between the two ligands, in spite of their different environments.

As noted earlier, the acetylene molecule is bound parallel to the metal–metal axis in a cis-dimetalated olefin geometry. Consistent with this, the geometries of the metalated carbons are reminiscent of sp^2 hybridization and the C(5)–C(6) distance (1.344 (8) Å) is close to that of a normal carbon–carbon double bond. The methoxycarbonyl substituents are twisted by an angle of ca. 116° with respect to each other such that one group (attached to C(6)) lies close to the metal–metal–acetylene plane, while the other (attached to C(5)) is almost perpendicular to this plane. The twisting most likely occurs in order to minimize unfavorable nonbonded contacts with the phenyl groups. Although most of the parameters concerning this bridging acetylene group are comparable to those of related structures,[1,26] the DMA ligand in the present case is rather unsymmetrically bonded; not only is the Ir(1)–C(5) bond length (2.052 (6) Å) significantly shorter than that of Ir(2)–C(6) (2.133 (6) Å) but also the angles about C(5) and C(6) differ appreciably (see Figure 2). We suggest that this latter asymmetry results from an attempt to minimize the above nonbonded contacts. Since, as noted earlier, these groups are oriented essentially at right angles, their interactions with the phenyl groups should differ appreciably leading to the observed asymmetry in the orientation of the ligand with respect to the metals. This results in a slight twist of the acetylene group from the Ir–Ir axis (ca. 5.7 (2)°) as can be seen in Figure 1. C(5) lies above the plane defined by the iridium atoms and the center of the C(5)–C(6) bond, most likely because of the interactions involving C(5) and its attached substituents with phenyl ring 6. A similar skewing of the acetylene group was observed in $[Rh_2Cl_2(\mu\text{-CO})(\mu\text{-DMA})(DPM)_2]$; however, in this case the acetylene was symmetrically bonded to each metal.[1] The difference in the metal–carbon bond lengths may result from the above steric interactions but may also be a result of the differing trans influence of the chloride and carbonyl groups opposite this acetylene ligand. A similar asymmetry was observed for another acetylene-bridged complex, $[Rh_2Cl(CNMe)_2(\mu\text{-HFB})(DPM)_2]^+$ where the ligands on each metal differ significantly.[6]

Discussion of Results

(i) Neutral Complexes. The addition of dimethyl acetylenedicarboxylate (DMA) to a solution of *trans*-$[IrCl(CO)(DPM)]_2$ (1) produces an immediate reaction as evidenced by a color change from purple to light yellow. The solid isolated, formulated as $[Ir_2Cl_2(CO)_2(\mu\text{-DMA})(DPM)_2]$ (3) displays carbonyl stretches in the IR spectrum at 2023 and 1999 cm^{-1}, as well as stretches at 1674 and 1653 cm^{-1} due to the carboxylate groups and one at 1549 cm^{-1} due to the coordinated acetylenic moiety. The low acetylenic stretch is consistent with either of two binding modes for this group; when the acetylene is bound perpendicular to the metal–metal axis (μ-η^2-binding mode), this stretch has been observed in the range from 1491 to 1595 cm^{-1},[27,28] whereas when it binds parallel to the metal–metal axis (as a cis-dimetalated olefin), a range in stretches from 1639 to 1643 cm^{-1} has been reported.[29,30] Although the observed stretch is more consistent with the perpendicular binding mode, the X-ray structure determination, described earlier, establishes that the acetylene is bound as a cis-dimetalated olefin, as shown below in structure I (see also Figures 1 and 2). As such, this is one



R=CO_2Me (3), CF_3 (4), H (5)

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[22] Cowie, M.; Sutherland, B. R., unpublished results.

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

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

[25] Farr, J. P.; Olmstead, M. M.; Balch, A. L. *Inorg. Chem.* **1983**, *22*, 1229 and references therein.

[26] Mague, J. T. *Inorg. Chem.* **1983**, *22*, 45.

[27] Boag, N. M.; Green, M.; Howard, J. A. K.; Spencer, J. L.; Stansfield, R. F. D.; Thomas, M. D. O.; Stone, F. G. A.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1980**, 2182.

[28] Restivo, R. J.; Ferguson, G. F.; Ng, T. W.; Carty, A. J. *Inorg. Chem.* **1977**, *16*, 172.

[29] Dickson, R. S.; Pain, G. N. *J. Chem. Soc., Chem. Commun.* **1979**, 297.

[30] Jarvis, A. C.; Kemmitt, R. D. W.; Russell, D. R.; Tucker, P. A. *J. Organomet. Chem.* **1978**, *159*, 341.

Table VII. Selected Angles (deg) in $[Ir_2Cl_2(CO)_2(\mu\text{-DMA})(DPM)_2]\cdot 2CH_2Cl_2$

P(1)-Ir(1)-Ir(2)	90.18 (4)	Ir(1)-C(5)-C(6)	112.3 (4)	C(11)-P(1)-C(3)	107.0 (3)
P(3)-Ir(1)-Ir(2)	92.17 (4)	Ir(2)-C(6)-C(5)	107.0 (4)	C(21)-P(1)-C(3)	102.6 (3)
P(2)-Ir(2)-Ir(1)	92.90 (4)	Ir(1)-C(5)-C(7)	121.9 (4)	C(31)-P(2)-C(41)	98.9 (2)
P(4)-Ir(2)-Ir(1)	92.12 (3)	Ir(2)-C(6)-C(8)	133.4 (4)	C(31)-P(2)-C(3)	106.9 (2)
P(1)-Ir(1)-P(3)	173.81 (5)	C(6)-C(5)-C(7)	125.4 (5)	C(41)-P(2)-C(3)	101.7 (3)
P(2)-Ir(2)-P(4)	174.27 (5)	C(5)-C(6)-C(8)	119.5 (5)	C(51)-P(3)-C(61)	101.2 (2)
Cl(1)-Ir(1)-Ir(2)	96.47 (4)	C(5)-C(7)-O(3)	123.0 (6)	C(51)-P(3)-C(4)	104.1 (2)
Cl(2)-Ir(2)-Ir(1)	170.65 (4)	C(6)-C(8)-O(4)	124.0 (6)	C(61)-P(3)-C(4)	103.5 (2)
P(1)-Ir(1)-Cl(1)	91.43 (6)	C(5)-C(7)-O(5)	114.5 (5)	C(71)-P(4)-C(81)	102.3 (2)
P(3)-Ir(1)-Cl(1)	82.81 (5)	C(6)-C(8)-O(6)	113.7 (5)	C(71)-P(4)-C(4)	100.4 (2)
P(2)-Ir(2)-Cl(2)	88.51 (5)	O(5)-C(7)-O(6)	122.3 (5)	C(81)-P(4)-C(4)	105.9 (2)
P(4)-Ir(2)-Cl(2)	86.09 (5)	O(4)-C(8)-O(6)	122.3 (6)	P(1)-C(11)-C(12)	123.6 (3)
P(1)-Ir(1)-C(1)	90.8 (2)	C(7)-O(5)-C(9)	116.1 (6)	P(1)-C(11)-C(16)	116.4 (3)
P(3)-Ir(1)-C(1)	87.7 (2)	C(8)-O(6)-C(10)	116.7 (5)	P(1)-C(21)-C(22)	122.1 (3)
P(2)-Ir(2)-C(2)	95.3 (2)	P(1)-C(3)-P(2)	100.7 (3)	P(1)-C(21)-C(26)	117.3 (3)
P(4)-Ir(2)-C(2)	86.7 (2)	P(3)-C(4)-P(4)	111.0 (3)	P(2)-C(31)-C(32)	118.3 (3)
P(1)-Ir(1)-C(5)	91.3 (2)	Ir(1)-P(1)-C(3)	108.9 (2)	P(2)-C(31)-C(36)	121.4 (3)
P(3)-Ir(1)-C(5)	94.8 (2)	Ir(1)-P(1)-C(11)	110.6 (2)	P(2)-C(41)-C(42)	121.4 (3)
P(2)-Ir(2)-C(6)	81.7 (2)	Ir(1)-P(1)-C(21)	125.8 (2)	P(2)-C(41)-C(46)	118.5 (3)
P(4)-Ir(2)-C(6)	97.5 (2)	Ir(2)-P(2)-C(3)	112.6 (2)	P(3)-C(51)-C(52)	122.2 (2)
Cl(1)-Ir(1)-C(1)	97.5 (2)	Ir(2)-P(2)-C(31)	115.0 (2)	P(3)-C(51)-C(56)	117.6 (2)
Cl(2)-Ir(2)-C(2)	91.0 (2)	Ir(2)-P(2)-C(41)	119.9 (2)	P(3)-C(61)-C(62)	121.7 (2)
Cl(1)-Ir(1)-C(5)	166.2 (2)	Ir(1)-P(3)-C(4)	107.0 (2)	P(3)-C(61)-C(66)	117.9 (2)
Cl(2)-Ir(2)-C(6)	101.7 (2)	Ir(1)-P(3)-C(51)	111.2 (1)	P(4)-C(71)-C(72)	120.5 (2)
C(1)-Ir(1)-C(5)	96.0 (2)	Ir(1)-P(3)-C(61)	127.5 (1)	P(4)-C(71)-C(76)	119.5 (2)
C(2)-Ir(2)-C(6)	166.8 (2)	Ir(2)-P(4)-C(4)	112.5 (2)	P(4)-C(81)-C(82)	120.8 (2)
C(5)-Ir(1)-Ir(2)	70.0 (2)	Ir(2)-P(4)-C(71)	114.9 (1)	P(4)-C(81)-C(86)	119.2 (2)
C(6)-Ir(2)-Ir(1)	69.5 (2)	Ir(2)-P(4)-C(81)	118.7 (1)	Cl(3)-C(D1)-Cl(4)	111.2 (6)
Ir(1)-C(1)-O(1)	176.0 (6)	C(11)-P(1)-C(21)	100.4 (2)	Cl(5)-C(D2)-Cl(6)	112.1 (7)
Ir(2)-C(2)-O(2)	179.4 (5)				

of the lowest acetylenic stretches observed for this geometry and is certainly lower than related rhodium complexes that have been studied in this group.[1,2,5,6] This is probably a reflection of the more basic metal center in the case of iridium and the concomitant greater π back-donation to the acetylene group. The strong Ir-acetylene bond is also evidenced by the fact that refluxing **1** in toluene leads to carbonyl loss but no loss of the acetylene ligand (vide infra). The solution characteristics suggest that the same structure is maintained in solution; a $^{31}P\{^1H\}$ NMR spectrum shows an AA′BB′ pattern (see Table II), indicating that both iridium centers are chemically inequivalent and the solution IR spectrum is quite similar to that in the solid (see Table I). Furthermore, compound **3** is a nonelectrolyte, suggesting that no significant chloride dissociation occurs.

With hexafluoro-2-butyne (HFB), reaction with compound **1** yields a single species that we formulate as $[Ir_2Cl_2(CO)_2(\mu\text{-HFB})(DPM)_2]$ (**4**), having a similar structure to that of **3**. Unlike compound **3**, however, this HFB adduct displays only one carbonyl stretch at 2024 cm^{-1}. Nevertheless we formulate this as a dicarbonyl species on the basis of its subsequent reactions (vide infra); in particular removal of Cl^- by the addition of Ag^+ quantitatively yields a cationic dicarbonyl complex. It would seem that in compound **4** both carbonyl bands are accidentally coincident. Changing the bridging group from DMA to HFB might be expected to have relatively little effect on the carbonyl ligand that is cis to these bridging groups but a greater effect on the trans carbonyl. This suggests that the higher carbonyl stretch in compound **3** (2023 cm^{-1}), which is close to that observed in **4** (2024 cm^{-1}), corresponds to the carbonyl ligand that is opposite the Ir–Ir bond, and the lower stretch of 1999 cm^{-1} in **3** is due to the carbonyl that is trans to the Ir–acetylene linkage. On the basis of greater group electronegativity of CF_3 compared to CO_2Me,[31] HFB should be a better π-acceptor ligand than DMA, which should result in a higher CO stretching frequency for the carbonyl trans to HFB. Presumably, in **4** this increase in CO frequency is sufficient to bring it into coincidence with the one opposite the Ir–Ir bond, giving rise to only one observed carbonyl stretch. These arguments are consistent with our findings in related complexes of rhodium where CO and SO_2 groups were found to be more labile for HFB-bridged complexes than for the DMA analogues.[6]

Compound **1** also reacts with acetylene (C_2H_2) to give a species having carbonyl stretches at 1977 and 1968 cm^{-1} and a stretch for the coordinated acetylene group at 1533 cm^{-1}. This species has a $^{31}P\{^1H\}$ NMR spectrum that is very similar to those of **3** and **4** and shows two ^1H resonances (6.13 and 6.52 ppm) in the region typical for olefin hydrogens. On the basis of these data, on the conductivity measurements, which indicate that it is a nonelectrolyte, and on its elemental analysis, we formulate this acetylene adduct as $[Ir_2Cl_2(CO)_2(\mu\text{-}C_2H_2)(DPM)_2]$ (**5**), having a structure similar to those of **3** and **4**. The carbonyl stretches for this species are both much lower than those of **3** and **4**, consistent with the substitution of the very electron-withdrawing CO_2Me and CF_3 groups by hydrogen atoms. Formation of the acetylene adduct **5** confirms that strongly electron-withdrawing groups are not required for complex formation. However, it is to be noted that substituting H for the slightly electron-donating methyl group in 2-butyne results in no adduct formation (see Experimental Section).

Loss of one of the carbonyl groups in compound **3** can be affected by refluxing the species in toluene. The new species $[Ir_2Cl_2(CO)(\mu\text{-DMA})(DPM)_2]$ (**6**) displays a complex pattern in the $^{31}P\{^1H\}$ NMR spectrum and displays only one carbonyl band (2004 cm^{-1}) in the IR spectrum. If the carbonyl group trans to the acetylenic moiety in **3** is lost, either species II or III could result, whereas loss of the CO trans to the Ir–Ir bond would yield IV. It is expected that the carbonyl group in **3** having the higher stretching frequency should be less tightly bound and on the basis of our assignment of these carbonyl bands suggests that it is the CO trans to the Ir–Ir bond that is labile, yielding structure IV. A similar product, $[Ir_2Cl_2(CO)(\mu$-

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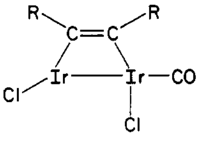
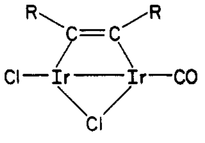
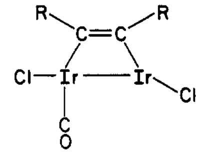
[31] Kosower, E. M. "An Introduction to Physical Organic Chemistry"; Wiley; New York, 1968: p 49.

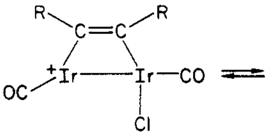

II

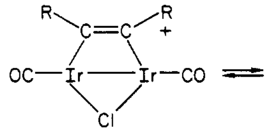

III

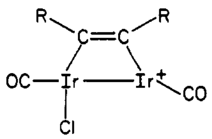

IV

HFB)(DPM)$_2$], is obtained upon refluxing compound 4 in toluene; however, its lack of solubility in all solvents tried precludes its characterization in solution. An IR spectrum of 7 displays two carbonyl bands at 2009 and 1988 cm^{-1}, suggesting that two different products are formed. Such an interpretation is not inconsistent with the IR spectrum of the precursor 4, which showed that both carbonyl stretches are coincident, suggesting similar binding abilities of these groups. The two isomers observed would then result from CO loss from opposite the Ir–acetylene linkage to give either structure II or III or from opposite the Ir–Ir bond to give IV.

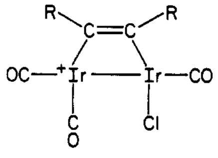
(ii) Cationic Complexes. We find that the most direct route to cationic acetylene adducts utilizes either chloride abstraction from the neutral acetylene adducts or direct reaction of the acetylenes with the cationic A-frame complex $[Ir_2(CO)_2(\mu\text{-}Cl)(DPM)_2]^+$ (2).[11] Another route, used by Mague and co-workers, involves alkyne addition to and subsequent CO loss from $[Ir_2Cl(CO)_4(DPM)_2][BPh_4]$.[32] Looking first at chloride removal from the neutral species, we find that the reactions of compounds 3 and 4 with $AgBF_4$ yield $[Ir_2Cl(CO)_2(\mu\text{-}RC{\equiv}CR)(DPM)_2][BF_4]$ (R = CO_2CH_3 (8), CF_3 (9)). Although the precursor to compound 9 (compound 4) displays only one carbonyl stretch, both species 8 and 9 show the two expected CO stretches (see Table I). At −40 °C both compounds display sharp, well-resolved patterns in the $^{31}P\{^1H\}$ NMR spectra that appear as a pair of pseudotriplets.[33] In addition, a small singlet appears in the spectrum of 9. However, upon warming, the peaks of the "triplets" begin to broaden and at ambient temperature have begun to collapse into the base line; the singlet in the spectrum of 9 collapses into the base line along with the other signals. The ^1H and ^{19}F resonances due to the CH_3 and CF_3 groups in compounds 8 and 9, respectively behave in an analogous manner. This temperature dependence is consistent with a fluxional process process as diagrammed in V–VII. Structures V and VII are chemically equivalent and give rise to the two pseudotriplets in the $^{31}P\{^1H\}$ NMR spectrum, one for each of the two inequivalent ends of the dimer. The singlet observed in the spectrum of 9 is due to the symmetrical chloro-bridged intermediate VI. At higher temperatures the fluxional process, which interchanges the two different phosphorus environments by chloride transfer from one metal to the other, is facilitated, and the high-temperature limiting spectrum (which was not obtained) should appear as a singlet. Although a resonance for VI is observed in the $^{31}P\{^1H\}$ NMR spectra of 9 (in approximately 8% abundance), no evidence for an analogous species is observed in the spectra of compound 8. It is not clear why the unsymmetrical species (V or VII) should predominate over the chloro-bridged isomer VI, since the somewhat analogous tricarbonyl species $[Ir_2(CO)_2(\mu\text{-}Cl)(\mu\text{-}CO)(DPM)_2]^+$ exists only as the symmetric species.[11] However, it is conceivable that the strain involved in bridging the Ir–Ir bond by the alkyne (bound as a cis-dimetalated olefin) and the chloro ligand, both of which favor large metal–metal separations, is enough to destabilize the symmetric structure. It is also not clear why none of the symmetric species is observed for compound 8. The unsymmetrical forms V and VII are obtained from the neutral parent compounds (3 and 4) by removal of the chloride ligand that is trans to the Ir–Ir bond. Removal of this chloride ligand, rather than the one which is cis to the Ir–Ir bond, is consistent with the much longer Ir–Cl distance found for the former in the structure determination of 3, suggesting that this chloro ligand is more weakly bound.


V


VI


VII

Compounds 8 and 9 react rapidly with carbon monoxide to give pale yellow, almost colorless solutions from which white microcrystalline solids are obtained. The IR spectra of these solids display three terminal carbonyl bands and, on the basis of the structures suggested for the precursors 8 and 9, are formulated as shown in VIII. These geometries are consistent with the observed NMR spectra (^1H, ^{19}F, and $^{31}P\{^1H\}$) and have been confirmed by X-ray structural determinations for both R = CO_2Me[32] and R = CF_3.[34] Although no temperature dependence was observed in the $^{31}P\{^1H\}$ NMR spectrum of 11, the DMA analogue 10 displays unusual temperature dependence, as shown in Figure 3. At room temperature the $^{31}P\{^1H\}$ NMR spectrum of 10 appears as a normal AA′BB′ pattern; however, as the temperature is lowered, the pattern compresses and eventually appears as a sharp singlet at −60 °C. At no time during the process is any line broadening observed, strongly arguing against a dynamic process that averages the phosphorus environments. Instead, we suggest that the chemical shift for each chemically inequivalent phosphorus nucleus is temperature dependent; but rather than moving in the same direction at roughly the same rate, as normally occurs, the chemical shifts move together, becoming equivalent at −60 °C. At lower temperatures the AA′BB′ pattern should reemerge; however, we were unable to obtain spectra due to instrumental limitations. In the ^1H NMR spectrum, a similar phenomenon is observed in which the chemical shift of one methyl group changes from 2.67 to 2.27 ppm over the temperature range from 0 to −60 °C, while the other methyl resonance remains essentially fixed at 3.5 ppm (see Table II); again no broadening is observed. An analogous temperature dependence in the $^{31}P\{^1H\}$ NMR spectrum of $[Pd_2ClI(DPM)_2]$, has previously been reported,[35] except that in this case the crossover of


VIII

R = CO_2Me (10), CF_3 (11)

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[32] Mague, J. T.; Klein, C. L.; Mageste, R. J.; Stevens, E. D. *Organometallics*, preceding paper in this issue.

[33] Very similar spectra have previously been analyzed and have been shown to be consistent with the spin system proposed. See: Gibson, J. A. E.; Cowie, M. *Organometallics* **1984**, *3*, 722.

[34] Cowie, M.; Sutherland, B. R., unpublished results.

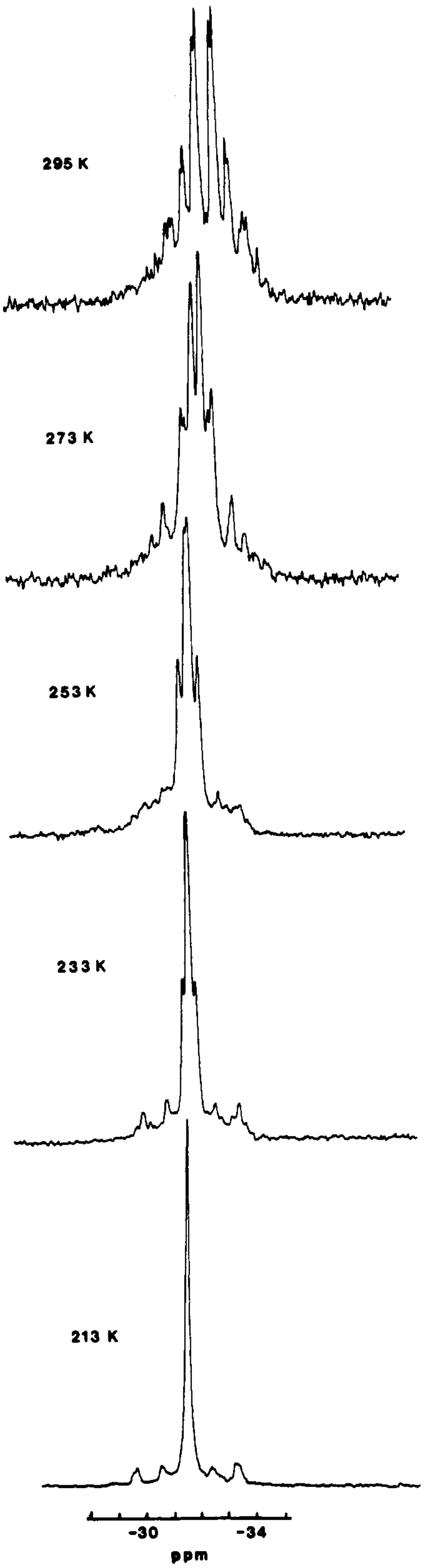
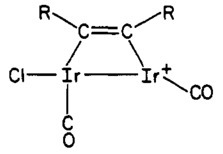


Figure 3. $^{31}P\{^1H\}$ NMR spectra of $[Ir_2Cl(CO)_3(\mu\text{-}DMA)(DPM)_2][BF_4]$ as a function of temperature.

the two sets of resonances occurred at a much higher temperature (35 °C). Refluxing compounds **10** and **11** in toluene for 6 h regenerates the parent dicarbonyl species **8** and **9**.

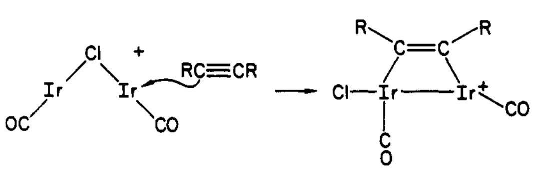
A second route to cationic dicarbonyl acetylene complexes, involving the reactions of acetylenes with the A-frame complex $[Ir_2(CO)_2(\mu\text{-}Cl)(DPM)_2][BF_4]$ (**2**), has also been studied. Addition of DMA or HFB to solutions of **2** produces an immediate color change from red to dark purple-brown, and purple solids can be obtained. These species each show two carbonyl stretches at ca. 2093 and 2055 cm^{-1}, which together with the other spectral information suggests that they be formulated as isomers of **8** and **9**, $[Ir_2Cl(CO)_2(\mu\text{-}RC{\equiv}CR)(DPM)_2][BF_4]$ (R = CO_2CH_3 (**12**), CF_3 (**13**)). Compounds **12** and **13** are clearly different from their respective isomers **8** and **9**, described earlier (see Tables I and II). In particular, compounds **12** and **13** do not show fluxional behavior in the NMR spectra, as was observed for **8** and **9**. We suggest therefore that the structures of compounds **12** and **13** are as shown in IX,



IX

R=CO_2Me (12), CF_3 (13)

with the Cl ligand trans to the Ir–Ir bond instead of cis to it. Clearly, facile fluxionality via a symmetric intermediate, as was described for **8** and **9**, is not possible for these species since significant rearrangement would be required in order to obtain the chloro-bridged intermediate (structure VI). Why structure IX is obtained for compounds **12** and **13**, instead of the isomeric structure V or VII, is readily understood when one considers the site of alkyne attack in compound **3**. If attack were to occur between the metals, in the enclosed bridging site, one would expect species V or VII to result; however, attack at one of the terminal vacant sites, as diagrammed in eq 1, would, after migration of the ligands around the



(1)

framework, yield structure IX. In the analogous rhodium A-frame $[Rh_2(CO)_2(\mu\text{-}Cl)(DPM)_2]^+$, attack by CO has been demonstrated to occur at this terminal site.[36] In addition, the reaction of a related acetate-bridged rhodium A-frame, $[Rh_2(CO)_2(\mu\text{-}O_2CCH_3)(DPM)_2]^+$, with HFB has also been shown to yield a product having a geometry much as that proposed for structure IX, except that for the rhodium species one carbonyl group bridges the two metals with no accompanying metal–metal bond.[3,4]

Although compounds **12** and **13** are not fluxional in solution, they do with time in CH_2Cl_2 solution convert to their isomers **8** and **9**. At present, it is not clear how this rearrangement occurs since no intermediate has been observed. However, two routes seem likely, involving either loss of CO or Cl$^-$ from the iridium which is coordinatively saturated followed by recoordination. Attempts to trap the intermediates in the above dissociation, by flushing the system with N_2 to remove CO or by addition of Ag$^+$ to trap free Cl$^-$, failed and had no significant affect on the rate of isomerization, although the latter gives rise to small amounts of two unidentified species. It is also interesting that the rate of isomerization of **12** is much faster than that of **13**; the former is complete within 1 h whereas the latter

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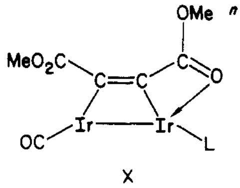
(35) Hunt, C. T.; Balch, A. L. *Inorg. Chem.* **1982**, *21*, 1641.

(36) (a) Cowie, M.; Mague, J. T.; Sanger, A. R. *J. Am. Chem. Soc.* **1978**, *100*, 3628. (b) Mague, J. T.; Sanger, A. R. *Inorg. Chem.* **1979**, *18*, 2060.

requires aproximately 2 weeks at room temperature. This rate difference can be rationalized on the basis of stabilization of the electron-deficient intermediate, which results from either CO or Cl^- dissociation, by coordination of one of the carboxylate oxygen atoms as shown for structure X. That **8** and **9** are favored over **10** and **11** may reflect the preference for a π-acceptor versus a π-donor ligand in the sites trans the Ir–Ir bond (cf. the long Ir–Cl bond in **3**).

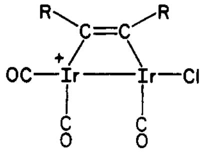


X

L=CO, n=2; L=Cl, n=1

$[Ir_2(CO)_2(\mu\text{-}Cl)(DPM)_2][BF_4]$ also reacts readily with acetylene (HC≡CH); however, a mixture of products is obtained and none has yet been characterized. As was the case for *trans*-$[IrCl(CO)(DPM)]_2$ (**1**), no reaction of compound **2** with 2-butyne was observed.

Compounds **12** and **13** react rapidly with CO to give the previously observed tricarbonyl species **10** and **11**. Our initial expectation was that the isomeric structure XI



XI

would result; however, no species other than **10** and **11** is observed. This is perhaps not surprising, considering that compounds **12** and **13** were shown to isomerize, and this isomerization may be accelerated in the presence of excess CO. Again, the preferred geometry has the chloro ligand opposite the metal–acetylene linkage instead of trans to the Ir–Ir bond.

Conclusions

The syntheses outlined, involving the reactions of *trans*-$[IrCl(CO)(DPM)]_2$ and $[Ir_2(CO)_2(\mu\text{-}Cl)(DPM)_2][BF_4]$ with alkynes, present convenient routes to both neutral and cationic iridium complexes containing bridging alkyne groups. Not surprisingly, these iridium complexes have the alkyne ligands bound as cis-dimetalated olefins as was observed in the analogous rhodium compounds[1–6] and as has been discussed by Hoffman and co-workers.[37,38]

In many respects the iridium chemistry parallels that of rhodium but there are significant differences that are consistent with the differences between second- and third-row metals. For example, in several of the rhodium complexes the bridging alkyne groups are accompanied by bridging carbonyl ligands, and in fact these compounds are some of the few examples of bridging carbonyl complexes with no accompanying metal–metal bonds.[1,3,4,39–41] On the other hand, no bridging carbonyls are observed in the iridium complexes described, as is consistent with the lower tendency of the third-row transition metals to have bridging carbonyl groups. We also observe a much greater tendency for the more basic iridium complexes to bind CO compared with their rhodium counterparts. For example, when *trans*-$[RhCl(CO)(DPM)]_2$ reacts with DMA or HFB, one carbonyl group is very labile and only the monocarbonyl complexes $[Rh_2Cl_2(\mu\text{-}CO)(\mu\text{-}RC_2R)(DPM)_2]$ are isolated.[1] However, with iridium the dicarbonyl alkyne adducts are obtained and removal of a carbonyl group can be effected only with difficulty.[42] Similarly, a series of tricarbonyl alkyne complexes has been prepared and isolated with iridium, whereas with rhodium these analogues are not obtained.[43]

Owing to the lower lability of third-row metal complexes compared to their second-row analogues, we had hoped to observe examples of alkyne attack and coordination at one of the terminal sites in these complexes. However, rearrangement to complexes having bridging alkynes is very facile, even with iridium, so although the initial products probably have the alkynes coordinated at only one metal, such species are never observed.

This study of the iridium alkyne complexes complements the well-studied rhodium chemistry and is useful in defining the similarities and differences between binuclear complexes of these metals. It is anticipated that further comparisons of such systems will aid in the eventual understanding of the involvement of adjacent metal centers in the activation of small molecules and in catalysis.

Acknowledgment. We thank the University of Alberta and the Natural Sciences and Engineering Research Council of Canada for support of this research and NSERC (Canada) for a graduate scholarship to B.R.S.

Registry No. **1**, 66125-35-7; **2**, 90552-98-0; **3**, 92270-15-0; **4**, 92270-16-1; **5**, 92270-17-2; **6**, 92270-18-3; **7**, 92270-19-4; **8**, 92270-21-8; **9**, 92270-23-0; **10**, 92270-25-2; **11**, 92284-13-4; Ir, 7439-88-5.

Supplementary Material Available: A listing of observed and calculated structure factor amplitudes and tables of anisotropic temperature factors and calculated hydrogen parameters (25 pages). Ordering information is given on any current masthead page.

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(37) Hoffman, D. M.; Hoffman, R. *Inorg. Chem.* **1981**, *20*, 3543.

(38) Hoffman, D. M.; Hoffman, R.; Fisel, C. R. *J. Am. Chem. Soc.* **1982**, *104*, 3858.

(39) Colton, R.; McCormick, M. J.; Pannan, C. D. *Aust. J. Chem.* **1978**, *31*, 1425.

(40) Brown, M. P.; Keith, A. N.; Manojlovic-Muir, L.; Muir, K. W.; Puddephatt, R. J.; Seddon, K. R. *Inorg. Chim. Acta* **1979**, *34*, L223.

(41) Pringle, P. G.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1983**, 889.

(42) Carbonyl removal from monocarbonyl species and the compounds derived therefrom will be the subject of future publication (B. R. Sutherland and M. Cowie).

(43) Cowie, M.; Dickson, R. S., unpublished results.