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Synthesis of Binuclear Cationic Complexes of Iridium Containing a Dimetalated Olefin and the Crystal and Molecular Structures of $[Ir_2(CO)_3Cl(\mu\text{-}H_3CO_2CC{=}CCO_2CH_3)((C_6H_5)_2PCH_2P(C_6H_5)_2)_2]PF_6\cdot CH_3CN$

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A new synthesis of $[Ir_2(CO)_3Cl(\mu\text{-}CO)(DPM)_2]A$ (DPM = bis(diphenylphosphino)methane; A = BPh_4, PF_6, ClO_4) is reported. These complexes react with dimethyl acetylenedicarboxylate and methyl propiolate to yield the dimetalated olefin derivatives $[Ir_2(CO)_3Cl(\mu\text{-}H_3CO_2CC{=}CCO_2CH_3)(DPM)_2]A$ and $[Ir_2(CO)_3Cl(\mu\text{-}HC{=}CCO_2CH_3)(DPM)_2]BPh_4$. The former (A = ClO_4, PF_6) loses one carbonyl group on refluxing in tetrahydrofuran. In solution these dicarbonyl complexes undergo chloride exchange between the two metal atoms and add trimethyl phosphite to give $[Ir_2(CO)_2(P(OMe)_3)(\mu\text{-}H_3CO_2CC{=}CCO_2CH_3)(DPM)_2]ClO_4$. When A = BPh_4, decarbonylation occurs similarly, but the product reacts with the anion to yield the phenyl derivative $[Ir_2(CO)_2(C_6H_5)(\mu\text{-}H_3CO_2CC{=}CCO_2CH_3)(DPM)_2]BPh_4$ plus $[Ir_2(CO)_2Cl_2(\mu\text{-}H_3CO_2CC{=}CCO_2CH_3)(DPM)_2]$. The phenyl complex adds 1 equiv of *tert*-butyl isocyanide to yield $[Ir_2(CO)_2(CNC(CH_3)_3)(C_6H_5)(\mu\text{-}H_3CO_2CC{=}CCO_2CH_3)(DPM)_2]BPh_4$ and reacts with carbon monoxide to form $[Ir_2(CO)_3(C_6H_5)(\mu\text{-}H_3CO_2CC{=}CCO_2CH_3)(DPM)_2]BPh_4$. An excess of *tert*-butyl isocyanide converts $[Ir_2(CO)_3Cl(\mu\text{-}H_3CO_2CC{=}CCO_2CH_3)(DPM)_2]BPh_4$ to $[Ir_2(CNC(CH_3)_3)_4(\mu\text{-}H_3CO_2CC{=}CCO_2CH_3)(DPM)_2]^{2+}$, which was isolated as the tetraphenylborate salt. $[Ir_2(CO)_3Cl(\mu\text{-}H_3CO_2CC{=}CCO_2CH_3)(DPM)_2]PF_6\cdot CH_3CN$ crystallizes in the space group $P2_1/n$ with $a = 10.531$ (9) Å, $b = 27.522$ (3) Å, $c = 20.233$ (4) Å, $\beta = 92.40$ (4)°, $V = 5859.2$ Å^3, and $Z = 4$. The structure was refined by using the 8129 independent reflections with $I \geq 3\sigma(I)$ to final residuals of $R = 0.034$ and $R_w = 0.044$. Each iridium atom in the binuclear cation can be considered to have a distorted square-pyramidal coordination with a carbonyl ligand in the apical position, a phosphorus atom of each DPM ligand in trans-basal positions, and a carbon atom of the dimetalated olefin. Completing the basal plane of Ir_1 is a second carbonyl ligand while for Ir_2 it is the chloride ligand. The Ir_1–Ir_2 distance of 2.8933 (2) Å is indicative of the presence of a metal–metal single bond.

Introduction

We have previously reported the synthesis of a variety of cationic, binuclear complexes of rhodium containing a dimetalated olefin by the reaction of $[Rh_2(CO)_2(\mu\text{-}O_2CCH_3)(DPM)_2]PF_6$ (DPM = bis(diphenylphosphino)methane) or $[Rh_2(CNC(CH_3)_3)_4(DPM)_2](BPh_4)_2$ with electrophilic acetylenes such as dimethyl acetylenedicarboxylate (DMAD) and hexafluorobut-2-yne (HFB).[1] Several of these were found to react readily with dihydrogen to produce the corresponding olefin and regenerate the original dimer. Attempts to explore the mechanism of the hydrogenation have so far proven inconclusive so we turned our attention to the synthesis of iridium analogues in the hope that intermediate hydrido species might be sufficiently stable to be characterized. We report here on the initial phase of this study. When this work was substantially complete, we became aware that a number of the complexes synthesized had also been prepared by a different route.[2]

Experimental Section

Preparation of Complexes. All solvents were appropriately dried and distilled before use and were stored under dinitrogen. Although most complexes appear stable to air and mosture, standard Schlenk techniques (dinitrogen atomsphere unless otherwise specified) were routinely used in all preparative reactions. Bis(diphenylphosphino)methane was purchased from Strem Chemicals while sodium tetraphenylborate and ammonium hexafluorophosphate were obtained from Alfa Inorganics. Chlorobis(cyclooctene)iridium(I) dimer[3] and sodium tetra-*p*-tolylborate[4] were prepared by published methods. All other chemicals were reagent grade and were used without further purification. Infrared spectra were obtained on a Perkin-Elmer Model 683 spectrophotometer in Nujol mulls unless otherwise specified. Proton NMR spectra were obtained at 90.0 MHz on a Varian EM-390 spectrometer with chemical shifts referred to internal tetramethylsilane (δ 0.0). Phosphorus-31 NMR spectra were obtained at 24.15 MHz on a JEOL FX-60 Fourier transform spectrometer (flip angle 45°, pulse repetition rate 5 s) with proton noise decoupling. Phosphorus chemical shifts are referred to

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[1] Mague, J. T.; DeVries, S. H. *Inorg. Chem.* **1982**, *21*, 1632.

[2] Sutherland, B. R.; Cowie, M. *Organometallics*, following paper in this issue.

[3] Herde, J. L.; Lambert, J. C.; Senoff, C. V. *Inorg. Synth.* **1974**, *15*, 19.

[4] Williams, J. L. R.; Doty, J. C.; Grisdale, P. J.; Searle, R.; Regan, T. H.; Happ, G. P.; Maier, D. P. *J. Am. Chem. Soc.* **1967**, *89*, 5153.

external 85% H_3PO_4 (δ 0.0) and are positive downfield. All spectra were obtained at ambient probe temperature (ca. 30 °C) unless otherwise specified. Spectral simulations were performed by using a local version of the LAOCOON-3 program of Bothner-By and Castellano.[5] Analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

[$Ir_2(CO)_3Cl(\mu\text{-}CO)((C_6H_5)_2PCH_2P(C_6H_5)_2)_2$]A (A = $B(C_6H_5)_4$ (1), PF_6 (2), ClO_4 (3)). The following improved procedure was used to prepare 1[6] and its analogues. To a solution of bis(diphenylphosphino)methane (0.342 g, 0.890 mmol) and 0.5 mmol of $NaB(C_6H_5)_4$, NH_4PF_6, or $NaClO_4$ in 10 mL of acetone under carbon monoxide was added slowly via syringe a suspension of [Ir_2Cl_2(cyclooctene)$_4$] (0.400 g, 0.444 mmol) in 20 mL of acetone. The initial red suspension slowly lightened to a pale yellow solution, and after 30 min a pale yellow microcrystalline precipitate began to form. Complete precipitation was effected by addition of diethyl ether while a CO atmosphere was maintained. The solid was filtered under CO pressure, extracted with dichloromethane, and filtered and the product crystallized by addition of diethyl ether (all under CO). The identity of the products was established by a comparison of their ^{31}P NMR spectra[7] with the literature data for 1[6] and their infrared spectra with that reported for [$Ir_2(CO)_3(\mu\text{-}CO)Cl(DPM)_2$]Cl.[9]

[$Ir_2(CO)_3Cl(\mu\text{-}H_3CO_2CC{=}CCO_2CH_3)((C_6H_5)_2PCH_2P(C_6H_5)_2)_2$]A (A = BPh_4 (4), PF_6 (5), ClO_4 (6)). A solution of **1**, **2**, or **3** in 10 mL of dichloromethane was reacted with an excess of dimethyl acetylenedicarboxylate and was stirred for 1 h. Addition of diethyl ether precipitated the product as pale yellow microcrystals that were collected and recrystallized from dichloromethane–diethyl ether. The products proved (vide infra) to be mixtures of two isomers. Anal. Calcd for $C_{83}H_{73}P_4O_7ClBIr_2$ (**4**): C, 57.39; H, 4.24; Cl, 2.04. Found: C, 57.5; H, 4.5; Cl, 2.1. Isomer **4a**: IR $\nu_{C\equiv O}$ 2073 (m), 2054 (s), 2030 (vs) cm^{-1}, $\nu_{C=C}$ 1565 (m) cm^{-1}; ^1H NMR (CD_2Cl_2) δ 3.45 (s, 3 H), 2.75 (s, 3 H, CO_2CH_3); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ −31.7, −33.5 ($^2J_{PP}$ = 378, 323, $^2J_{PP'}$ = 41.2, $^4J_{PP'}$ = 13.9 Hz) (For the explanation of the notation for coupling constants used here and below see ref 7). Isomer **4b**: IR $\nu_{C\equiv O}$ 2078 (m), 2023 (vs), 2001 (m) cm^{-1}, $\nu_{C=C}$ 1565 (m) cm^{-1}; ^1H NMR (CD_2Cl_2) δ 3.30 (s, 3 H), 2.60 (s), (3 H, CO_2CH_3); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ −19.6, −32.0 ($^2J_{PP}$ = 375, 342, $^2J_{PP'}$ = 34.5, $^4J_{PP}'$ = 6.7 Hz). Anal. Calcd for $C_{59}H_{50}P_5O_7F_6ClIr_2$ (**5**): C, 45.43; H, 3.24; Cl, 2.27; F, 7.31. Found: C, 44.7; H, 3.8; Cl, 2.5; F, 7.3. Isomer **5a**: IR $\nu_{C\equiv O}$ 2075 (m), 2046 (s), 2038 (vs) cm^{-1}, $\nu_{C=C}$ 1558 (m) cm^{-1}; ^1H NMR (CD_2Cl_2) δ 3.51 (s, 3 H), 2.72 (s, 3 H, CO_2CH_3); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ −31.6, −33.2 ($^2J_{PP}$ = 378, 323, $^2J_{PP'}$ = 40.9, $^4J_{PP'}$ = 14.4 Hz). Isomer **5b**: IR $\nu_{C\equiv O}$ 2089 (m), 2051 (vs) 1995 (m) cm^{-1}, $\nu_{C=C}$ 1558 (m) cm^{-1}; ^1H NMR (CD_2Cl_2) δ 3.31 (s, 3 H), 2.52 (s, 3 H, CO_2CH_3); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ −18.2, −32.2 ($^2J_{PP}$ = 375, 342, $^2J_{PP'}$ = 32.0, $^4J_{PP'}$ = 7.9 Hz). Anal. Calcd for $C_{59}H_{50}P_4O_{11}Cl_2Ir_2$ (**6**): C, 46.79; H, 3.33; Cl, 4.68. Found: C, 46.5, H, 3.2; Cl, 4.3. Isomer **6a**: IR $\nu_{C\equiv O}$ 2077 (m), 2045 (s), 2039 (vs) cm^{-1}, $\nu_{C=C}$ 1568 (m) cm^{-1}, ^1H NMR (CD_2Cl_2) δ 3.49 (s, 3 H), 2.76 (s, 3 H, CO_2CH_3); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ −31.6, −33.3 ($^2J_{PP}$ 378, 323, $^2J_{PP'}$ = 41.2, $^4J_{PP'}$ = 14.2 Hz). Isomer **6b**: IR $\nu_{C\equiv O}$ 2085 (sh), 1998 (m) cm^{-1}, $\nu_{C=C}$ 1568 cm^{-1}; ^1H NMR (CD_2Cl_2) δ 3.92 (s, 3 H), 2.51 (s, 3 H, CO_2CH_3); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ −18, −32.1 ($^2J_{PP}$ = 375, 342, $^2J_{PP'}$ = 33.0, $^4J_{PP'}$ = 6.4 Hz).

[$Ir_2(CO)_3Cl(\mu\text{-}HC{=}CCO_2CH_3)((C_6H_5)_2PCH_2P(C_6H_5)_2)_2$]$B(C_6H_5)_4\cdot CH_2Cl_2$ (7). This was prepared in the same manner as the previous complex and obtained as pale yellow crystals from dichloromethane–diethyl ether. Unlike **4**–**6** a single isomer appeared to be formed. Anal. Calcd for $C_{81}H_{70}P_4O_5Cl_3BIr_2$ (**7**): C, 55.62; H, 4.04; Cl, 6.08. Found: C, 55.8; H, 3.9; Cl, 7.0. **7**: IR $\nu_{C\equiv O}$ 2082 (s), 2035 (vs), 2000 (m) cm^{-1}, $\nu_{C=C}$ 1533 (m) cm^{-1}; ^1H NMR (CD_2Cl_2) δ 3.28 (s, 3 H, CO_2CH_3); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ −26.9, −27.7 ($^2J_{PP}$ = 358.5, 341.5, $^2J_{PP'}$ = 35.0, $^4J_{PP'}$ = 9.7 Hz).

[$Ir_2(CO)_2Cl(\mu\text{-}H_3CO_2CC{=}CCO_2CH_3)((C_6H_5)_2PCH_2P(C_6H_5)_2)_2$]$A\cdot C_4H_8O$ (A = PF_6 (8), ClO_4 (9)). A suspension of 0.25 g of either **5a,b** or **6a,b** in 10 mL of tetrahydrofuran was refluxed overnight under a nitrogen purge. The yellow solid soon dissolved in the hot solvent, and the solution slowly became dark orange. At the end of the reflux period, **9** had precipitated as orange microcrystals while **8** could be obtained as dark brown orange crystals by dilution of the cooled solution with diethyl ether. Both products were filtered off, washed with diethyl ether, and dried in vacuo. The presence of the solvent molecule was confirmed by ^1H NMR. Anal. Calcd for $C_{62}H_{58}P_5O_7F_6ClIr_2$ (**8**): C, 46.42; H, 3.65; Cl, 2.21; F, 7.11. Found: C, 46.4; H, 3.5; Cl, 2.1; F, 7.1. IR $\nu_{C\equiv O}$ **8**: 2046 (vs), 2024 (vs) cm^{-1}, $\nu_{C=C}$ 1558 (m) cm^{-1}; ^1H NMR (CD_2Cl_2) δ 2.54 (br 6 H CO_2CH_3), 3.65 (m, 4 H), 1.79 (m, 4 H, C_4H_8O); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −30 °C) δ +5.0 (t), −27.1 (t, J_{PP} = 29.9 Hz). Anal. Calcd for $C_{62}H_{58}P_4O_{11}Cl_2Ir_2$ (**9**): C, 47.78; H, 3.76; Cl, 4.55. Found: C, 47.4; H, 3.8; Cl, 4.5. **9**: IR $\nu_{C\equiv O}$ 2402 (vs), 2018 (vs) cm^{-1}, $\nu_{C=C}$ 1545 (m) cm^{-1}; ^1H NMR (CD_2Cl_2) δ 2.54 (br, s, 6 H, CO_2CH_3), 3.65 (m, 4 H), 1.79 (m, 4 H, CH_4H_8O); $^{31}P\{^1H\}$ NMR (CD_2Cl_2 −12 °C) δ +8.8 (t), −23.2 (t, J_{PP} = 29.8 Hz).

[$Ir_2(CO)_2(P(OCH_3)_3)Cl(\mu\text{-}H_3CO_2CC{=}CCO_2CH_3)((C_6H_5)_2PCH_2P(C_6H_5)_2)_2$]$ClO_4$ (10). To a solution of 0.200 g (0.128 mmol) of **9** in 10 mL of acetone was added 0.016 g (0.128 mmol) of trimethyl phosphite whereupon the red-orange solution immediately became pale yellow. Addition of diethyl ether and hexane precipitated the product as pale yellow crystals that were filtered off and recrystallized from dichloromethane–diethyl ether–hexane. Anal. Calcd for $C_{61}H_{59}P_5O_{13}Cl_2Ir_2$ (**10**): C, 45.49; H, 3.70; P, 9.62. Found: C, 45.5; H, 3.40; P, 9.1. **10**: IR $\nu_{C\equiv O}$ 2029 (vs), 2014 (vs) cm^{-1}, $\nu_{C=C}$ 1545 (m) cm^{-1}; ^1H NMR (CD_2Cl_2) δ 3.70 (s, 3 H), 3.32 (s, 3 H, CO_2CH_3), 3.06 (d, J_{P-H} = 11.7 Hz, 9 H, $P(OCH_3)_3$); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ +44.7 (m), −32.7 (m).

[$Ir_2(CO)_2(C_6H_5)(\mu\text{-}H_3CO_2CC{=}CCO_2CH_3)((C_6H_5)_2PCH_2P(C_6H_5)_2)_2$]$B(C_6H_5)_4\cdot C_4H_8O$ (11). A solution of 0.25 g of **4a,b** in 10 mL of tetrahydrofuran was refluxed under a nitrogen purge for 36 h. The yellow solution slowly became orange and ultimately a dark red. By the end of the reaction a yellow precipitate indentified as [$Ir_2(CO)_2Cl_2(\mu\text{-}H_3CO_2CC{=}CCO_2CH_3)((C_6H_5)_2PCH_2P(C_6H_5)_2)_2$] (vide infra) had also formed. The reaction mixture was filtered and the filtrate diluted with diethyl ether and hexane. Upon standing overnight at room temperature the product was obtained as dark red crystals. Although the solvent in the product appears tightly bound, prolonged residence in vacuo led to some loss and a change in color from dark red to brown. Anal. Calcd for $C_{92}H_{86}P_4O_7BIr_2$ (**11**): C, 60.61; H, 4.76. Found: C, 60.8; H, 4.8. **11**: IR $\nu_{C\equiv O}$ 2012 (vs), 1993 (m) cm^{-1}, $\nu_{C=C}$ 1545 (w) cm^{-1}; ^1H NMR (CD_2Cl_2) δ 3.29 (s, 3 H), 2.13 (s, 3 H, CO_2CH_3), 3.65 (m, 4 H), 1.79 (m, 4 H, C_4H_8O); $^{31}P\{^1H\}$ NMR δ +8.7, −23.3 ($^2J_{PP}$ = 372, 342, $^2J_{PP'}$ = 28.1, $^4J_{PP'}$ = 8.3 Hz).

[$Ir_2(CO)_2Cl_2(\mu\text{-}H_3CO_2CC{=}CCO_2CH_3)((C_6H_5)_2PCH_2P(C_6H_5)_2)_2$]$\cdot 2CH_2Cl_2$ (12). This complex was initially obtained as a side product in the formation of **11** as described above. It can also be formed by the reaction of either **8** or **9** with 1 equiv of lithium chloride in acetone solution. Recrystallization from

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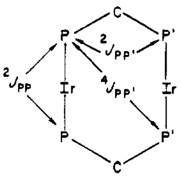
[5] Castellano, S.; Bothner-By, A. R. *J. Chem. Phys.* **1964**, *41*, 3863.

[6] Mague, J. T.; Sanger, A. R. *Inorg. Chem.* **1979**, *18*, 2060.

[7] The original analysis[6] of the AA′BB′ pattern observed for the 40.48 MHz $^{31}P\{^1H\}$ NMR spectrum of 1 appears incorrect. Because fewer degeneracies occur when it is obtained at 24.15 MHz and because some of the weak lines were also found in the latter spectrum, a better estimate of the values of the *trans*-P–Ir–P couplings could be made. With the notation



and values of $^2J_{PP}$ in the range 300–400 Hz,[8] the spectrum could be satisfactory simulated with $^2J_{PP}$ (corresponds to $J_{AA'}$ and $J_{BB'}$) = 385 and 320; $^2J_{PP'}$ (corresponds to J_{AB}) = 65.8, and $^4J_{PP'}$ (corresponds to $J_{AB'}$) = 25.3 Hz. With these parameters, the original 40.48-MHz spectrum could also be satisfactorily simulated. In this and the simulations of the AA′BB′ ^{31}P NMR spectra of the complexes reported here it was generally not possible to refine $^2J_{PP}$, with the LAOCOON-3 program since the weakest lines needed to determine $^2J_{PP}$ were usually not observed. Instead, values comparable to those reported[8] for some mononuclear iridium complexes were chosen and the other spectral parameters refined. Further refinement involved successive cycles of manual adjustment of $^2J_{PP}$ followed by refinement of the remaining parameters. In most instances, therefore, while the reported values for $^2J_{PP}$ are reasonable, they are only approximate and it is not possible to say which is $J_{AA'}$ and which is $J_{BB'}$.

[8] Pregosin, P. S.; King, R. W. "^{31}P and ^{13}C NMR of Transition Metal Phosphine Complexes"; Springer-Verlag: New York, 1979; Tables 18b, 19, 21.

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

dichloromethane–diethyl ether produces bright yellow crystals sometimes having a slight greenish cast. The presence and quantity of solvating dichloromethane was established by ^{1}H NMR speectroscopy in dimethyl sulfoxide-d_6. Anal. Calcd for $C_{60}H_{54}P_4O_6Cl_6Ir_2$ (**12**): C, 45.93; H, 3.48, Cl, 13.56. Found: C, 45.2; H, 3.4; Cl, 13.0. **12**: IR $\nu_{C\equiv O}$ 2026 (vs), 2000 (vs) cm^{-1}, $\nu_{C=C}$ 1541 (m) cm^{-1}; ^{1}H NMR (CD_2Cl_2) δ 2.82 (s, 3 H), 3.22 (s, 3 H, CO_2CH_3); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ −28.5, −32.1 ($^2J_{PP}$ = 416.7, 395.1 $^2J_{PP'}$ = 45.2, $^4J_{PP'}$ = 10.3 Hz).

[$Ir_2(CO)_3(C_6H_5)$(μ-$H_3CO_2CC{=}CCO_2CH_3$)(($C_6H_5PCH_2P(C_6H_5)_2)_2$]$B(C_6H_5)_4$ (13). A dichloromethane solution of **11** was purged with carbon monoxide whereupon the color rapidly changed from dark red to pale yellow. Dilution with diethyl ether afforded the product as pale yellow microcrystals. These tend to lose carbon monoxide in vacuo with a change in color to orange, but the original color can be restored by blowing carbon monoxide over the solid. Anal. Calcd for $C_{89}H_{78}P_4O_7BIr_2$ (**13**): C, 60.09; H, 4.43; P, 6.96. Found: C, 60.3; H, 4.3; P, 7.2. **13**: IR $\nu_{C\equiv O}$ 2064 (sh), 2056 (s), 2022 (vs) cm^{-1}, $\nu_{C=C}$ 1533 (m) cm^{-1}; ^{1}H NMR (CD_2Cl_2) δ 3.50 (s, 3 H), 2.44 (s, 3 H, CO_2CH_3); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ −24.4, −29.4 ($^2J_{PP}$ = 292.1, 267.1, $^2J_{PP'}$ = 32.0, $^4J_{PP'}$ = 5.2 Hz).

[$Ir_2(CO)_2(CNC(CH_3)_3)(C_6H_5)$(μ-$H_3CO_2CC{=}CCO_2CH_3$)(($(C_6H_5)_2PCH_2P(C_6H_5)_2)_2$]$B(C_6H_5)_4\cdot C_4H_8O$ (17). To a solution of **11** (0.216 g, 0.118 mmol) in 20 mL of tetrahydrofuran was added a tetrahydrofuran solution of 0.008 g (0.118 mmol) of *tert*-butyl isocyanide dropwise with stirring. The dark red-brown solution lightened during this time to finally become a pale brownish orange. Following filtration the solution was diluted with diethyl ether and hexane and upon standing overnight the product formed as off-white flakes. These were collected, washed with diethyl ether, and dried briefly in vacuo. Anal. Calcd for $C_{97}H_{95}P_4O_7NBIr_2$ (**17**): C, 61.12; H, 5.03; N, 0.74. Found C, 60.8; H, 4.8; N, 0.74. **17**: IR $\nu_{C\equiv N}$ 2179 (s) cm^{-1}, $\nu_{C\equiv O}$ 2014 (vs), 1981 (s) cm^{-1}, $\nu_{C=C}$ 1530 (w) cm^{-1}; ^{1}H NMR (CD_2Cl_2) δ 3.48 (s, 3 H), 2.48 (s, 3 H, CO_2CH_3), 1.17 (s, 9 H, $C(CH_3)_3$); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ −22.8, −26.7 ($^2J_{PP}$ = 288, 291, $^2J_{PP'}$ = 31.1, $^4J_{PP'}$ = 6.1 Hz).

[$Ir_2(CNC(CH_3)_3)_4$(μ-$H_3CO_2CC{=}CCO_2CH_3$)(($(C_6H_5)_2PCH_2P(C_6H_5)_2)_2$]$(B(C_6H_5)_4)_2\cdot CH_2Cl_2$ (18). To a solution of 0.300 g (0.173 mmol) of **4a** in 10 mL of acetone was added 0.072 g (0.864 mmol) of *tert*-butyl isocyanide. The light yellow solution effervesced and took on a slight greenish cast. After the mixture was stirred for 2 h, an acetone solution of 0.059 g (0.173 mmol) of sodium tetraphenylborate was added and the resulting cloudy solution was filtered through a pad of diatomaceous earth and diluted with diethyl ether to precipitate pale yellow crystals. These were dissolved in dichloromethane; the solution was filtered and diluted with diethyl ether to afford the product as pale yellow needles in essentially quantitative yield. Anal. Calcd for $C_{125}H_{124}P_4N_4O_4Cl_2B_2Ir_2$ (**18**): C, 63.96; H, 5.34; N, 2.39. Found: C, 64.1; H, 5.9; N, 2.2. **18**: IR $\nu_{C\equiv N}$ 2198 (s) 2180 (s) cm^{-1}, $\nu_{C=C}$ 1607 (m) cm^{-1}; ^{1}H NMR (CD_2Cl_2) δ 3.48 (s, 6 H, CO_2CH_3), 1.25 (s, 18 H), 0.53 (s, 18 H, $C(CH_3)_3$); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ −24.1 (s).

Table I. Summary of Crystal Data and Intensity Collection

compd	[$Ir_2(CO)_3Cl$(μ-$H_3CO_2CC{=}CCO_2CH_3$)(DPM)$_2$]$PF_6\cdot CH_3CN$
fw	1600.89
formula	$C_{61}H_{53}P_5O_7F_6ClNIr_2$
cell parameters	
a, Å	10.531 (9)
b, Å	27.522 (3)
c, Å	20.233 (4)
β, deg	92.40 (4)
V, Å^3	5859.2
Z	4
d(calcd), g cm^{-3}	1.82
systematic absences	$h0l$, $h + l = 2n + 1$; $0k0$, $k = 2n + 1$
space group	$P2_1/n$
cryst dimens, mm	0.99 × 0.66 × 0.58
temp, K	100
radiatn	Mo Kα (λ = 0.70930 Å), graphite monochromated
takeoff angle, deg	2.95
scan range	0.9 + 0.35 tan θ
scan speed, deg/min	1.5–10 (in ω)
total bkgd time/ scan time	0.5
2θ range, deg	2.8–50
scan mode	ω–2θ
unique data used ($I \geqslant 3\sigma(I)$)^a	8129
final no. of parameters varied	748
error in observn of unit weight	1.57
R^b	0.0339
$R_w{}^c$	0.0435

^{a} $\sigma(I) = [(C + 4B) + (0.03(C + 4B))^2]^{1/2}$ (C = total scan count; B = total background count). ^{b} $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{c} $R_w = (\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2)^{1/2}$ ($w = 1/\sigma^2(F_o)$).

X-ray Diffraction Study. Yellow columnar crystals of **5a** were grown by slow diffusion of hexane into a solution of the complex in a mixture of tetrahydrofuran and acetonitrile. Among the mass of badly fractured crystals produced were two or three that appeared to be undamaged. One of these, in the shape of a rectangular parallelepiped, was selected and mounted on an Enraf-Nonius CAD-4 diffractometer. Final lattice parameters determined by a least-squares fit of $[(\sin\theta)/\lambda]^2$ values for 25 high-order reflections accurately centered on the diffractometer are presented in Table I together with other data pertinent to the data collection. A total of 10332 independent reflections were measured at 100 K with three standard reflections being monitored at 2-h intervals. No significant change in the intensities of the standards was noted. The data were corrected for Lorentz and polarization effects. An empirical absorption correction was employed to compensate for a 14% variation in absorption as a function of φ.[10] The structure was solved by direct methods using the MULTAN program package[11] that revealed the positions of the two iridium atoms on the initial *E* map. The remaining non-hydrogen atoms were located from subsequent Fourier maps following full-matrix least-squares refinement of the positional and thermal parameters of the atoms located up to that point. All scattering factors[12] were corrected for the effects of anomalous dispersion. Because of the large number of parameters, the least-squares refinement had to be carried out in blocks. In each cycle all positional parameters and one fourth of the anisotropic thermal parameters were refined. This was continued with a different block of the thermal parameters being included in subsequent cycles. In the final stages of the refinement, the hydrogen atoms were included in the structure factor calculations with fixed positions based on sp^2 or sp^3 geometry about the associated carbon atom, a carbon-hydrogen bond length of 0.95 Å, and fixed thermal parameters of 2.0 Å.^{2} These parameters were not refined but were updated periodically. Convergence was assumed when no parameter shift was more than 0.1 times its estimated standard deviation. Final fractional coordinates for all non-hydrogen atoms are given in Table II while important bond lengths and interbond angles are listed in Tables III and IV, respectively.

Results and Discussion

Chemical Studies. A summary of the major reactions performed in this study is given in Figure 1. Addition of an acetone suspension of [Ir_2Cl_2(cyclooctene)$_4$] to an acetone solution of DPM and sodium tetraphenylborate under a carbon monoxide atmosphere yields an essentially quantitative yield of [$Ir_2(CO)_3$(μ-CO)Cl(DPM)$_2$]BPh_4 (**1**) after 30 min. The hexafluorophosphate (**2**) and perchlorate (**3**) salts are prepared similarly. This method is to be preferred to that originally reported[6] for **1** because of the

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[10] In these and all other computations performed, the programs constituting the CAD-4 SDP package (B. Frenz (1982)) were used.

[11] Main, P.; Woolfson, M. M.; Germain, G. *Acta Crystallogr., Sect. A* 1977, *A27*, 368.

[12] "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV.

Table II. Fractional Atomic Coordinates

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
Ir(1)	0.66992 (2)	0.13046 (1)	0.26312 (1)	C(21)	0.9474 (8)	0.0816 (3)	0.5149 (4)
Ir(2)	0.66732 (2)	0.06695 (1)	0.14929 (1)	C(22)	0.9848 (8)	0.0540 (3)	0.4628 (5)
Cl	0.4538 (2)	0.05125 (6)	0.10022 (9)	C(23)	0.9036 (7)	0.0475 (3)	0.4069 (4)
P(1)	0.6733 (2)	0.06213 (6)	0.33405 (8)	C(24)	0.8683 (6)	0.2308 (2)	0.2285 (3)
P(2)	0.7288 (1)	0.19668 (6)	0.19625 (8)	C(25)	0.9914 (7)	0.2178 (3)	0.2110 (4)
P(3)	0.6738 (2)	0.13413 (6)	0.07852 (8)	C(26)	1.0948 (7)	0.2439 (3)	0.2360 (4)
P(4)	0.6422 (2)	−0.00126 (6)	0.21641 (8)	C(27)	1.0777 (6)	0.2824 (3)	0.2784 (4)
P(5)	0.4076 (2)	0.22987 (7)	0.4378 (1)	C(28)	0.9569 (6)	0.2953 (3)	0.2966 (4)
F(1)	0.5145 (4)	0.1927 (2)	0.4650 (2)	C(29)	0.8521 (6)	0.2692 (3)	0.2709 (4)
F(2)	0.5123 (4)	0.2646 (2)	0.4104 (3)	C(30)	0.6092 (6)	0.2444 (2)	0.1851 (3)
F(3)	0.4151 (5)	0.2569 (2)	0.5069 (2)	C(31)	0.6052 (6)	0.2745 (2)	0.1299 (4)
F(4)	0.3994 (5)	0.2019 (2)	0.3692 (2)	C(32)	0.5151 (7)	0.3095 (3)	0.1238 (4)
F(5)	0.3025 (4)	0.1942 (2)	0.4650 (3)	C(33)	0.4307 (7)	0.3178 (3)	0.1728 (4)
F(6)	0.3001 (5)	0.2660 (2)	0.4114 (3)	C(34)	0.4359 (6)	0.2896 (3)	0.2276 (4)
O(1)	0.3809 (4)	0.1411 (2)	0.2472 (2)	C(35)	0.5241 (6)	0.2520 (2)	0.2347 (3)
O(2)	0.7348 (4)	0.1985 (2)	0.3796 (2)	C(36)	0.5308 (6)	0.1683 (2)	0.0532 (3)
O(3)	0.7817 (5)	0.0054 (2)	0.0428 (3)	C(37)	0.5393 (7)	0.1994 (3)	−0.0026 (3)
O(4)	0.9833 (4)	0.0109 (2)	0.1779 (3)	C(38)	0.4378 (7)	0.2276 (3)	−0.0207 (4)
O(5)	1.0155 (4)	0.0795 (2)	0.1204 (3)	C(39)	0.3270 (7)	0.2271 (3)	0.0144 (4)
O(6)	1.0762 (4)	0.0981 (2)	0.2664 (3)	C(40)	0.3195 (6)	0.1968 (3)	0.0680 (4)
O(7)	0.9661 (4)	0.1469 (2)	0.3305 (2)	C(41)	0.4203 (6)	0.1673 (2)	0.0874 (3)
N(1)	0.2423 (7)	0.0963 (2)	0.6088 (4)	C(42)	0.7426 (6)	0.1180 (2)	0.0009 (3)
C(1)	0.7288 (6)	0.0068 (2)	0.2952 (3)	C(43)	0.6700 (6)	0.0915 (3)	−0.0437 (4)
C(2)	0.7782 (6)	0.1792 (2)	0.1150 (3)	C(44)	0.7211 (7)	0.0733 (3)	−0.0996 (4)
C(3)	0.9560 (6)	0.0526 (2)	0.1646 (3)	C(45)	0.8467 (7)	0.0801 (3)	−0.1106 (4)
C(4)	0.8455 (6)	0.0789 (2)	0.1907 (3)	C(46)	0.9209 (7)	0.1050 (3)	−0.0660 (4)
C(5)	0.8524 (6)	0.1073 (2)	0.2439 (3)	C(47)	0.8697 (7)	0.1248 (3)	−0.0103 (4)
C(6)	0.9775 (6)	0.1165 (2)	0.2799 (4)	C(48)	0.7038 (6)	−0.0571 (2)	0.1821 (3)
C(7)	1.0825 (7)	0.1579 (3)	0.3677 (4)	C(49)	0.8013 (6)	−0.0842 (2)	0.2114 (3)
C(8)	1.1222 (9)	0.0570 (4)	0.0897 (5)	C(50)	0.8406 (7)	−0.1267 (3)	0.1825 (4)
C(9)	0.7110 (6)	0.1721 (2)	0.3381 (3)	C(51)	0.7851 (7)	−0.1423 (2)	0.1229 (4)
C(10)	0.4851 (6)	0.1381 (2)	0.2543 (3)	C(52)	0.6887 (6)	−0.1146 (2)	0.0927 (4)
C(11)	0.7350 (6)	0.0276 (2)	0.0814 (3)	C(53)	0.6474 (6)	−0.0725 (2)	0.1227 (3)
C(12)	0.5313 (6)	0.0459 (2)	0.3769 (3)	C(54)	0.4831 (6)	−0.0202 (2)	0.2396 (3)
C(13)	0.4484 (6)	0.0817 (3)	0.3960 (3)	C(55)	0.3850 (6)	0.0127 (2)	0.2436 (3)
C(14)	0.3476 (7)	0.0698 (3)	0.4542 (4)	C(56)	0.2673 (6)	−0.0016 (3)	0.2656 (3)
C(15)	0.3296 (7)	0.0220 (3)	0.4542 (4)	C(57)	0.2492 (6)	−0.0496 (3)	0.2830 (4)
C(16)	0.4109 (7)	−0.0138 (3)	0.4351 (4)	C(58)	0.3451 (7)	−0.0825 (3)	0.2778 (4)
C(17)	0.5122 (6)	−0.0018 (3)	0.3972 (3)	C(59)	0.4639 (6)	−0.0683 (2)	0.2561 (4)
C(18)	0.7859 (6)	0.0696 (2)	0.4045 (3)	C(60)	0.3225 (9)	0.1249 (3)	0.6099 (4)
C(19)	0.7495 (7)	0.0984 (3)	0.4579 (4)	C(61)	0.4254 (9)	0.1597 (3)	0.6119 (5)
C(20)	0.8329 (8)	0.1042 (3)	0.5118 (4)				

Table III. Interatomic Distances (Å)[a]

Ir(1)-P(1)	2.366 (1)	Ir(2)-P(3)	2.342 (1)
Ir(1)-P(2)	2.368 (1)	Ir(2)-P(4)	2.339 (1)
Ir(1)-C(5)	2.077 (5)	Ir(2)-C1	2.461 (1)
Ir(1)-C(9)	1.935 (5)	Ir(2)-C(4)	2.055 (5)
Ir(1)-C(10)	1.962 (5)	Ir(2)-C(11)	1.910 (5)
C(1)-P(1)	1.821 (5)	C(2)-P(2)	1.810 (5)
C(1)-P(4)	1.819 (5)	C(2)-P(3)	1.798 (5)
C(4)-C(5)	1.330 (7)	Ir(1)-Ir(2)	2.8933 (2)

[a] Numbers in parentheses are estimated standard deviations in the least significant digit.

Table IV. Interbond Angles (deg)[a]

P(1)-Ir(1)-P(2)	163.95 (4)	P(3)-Ir(2)-P(4)	174.87 (4)
P(1)-Ir(1)-C(5)	83.0 (1)	P(3)-Ir(2)-C(4)	94.3 (1)
P(1)-Ir(1)-C(9)	89.8 (2)	P(3)-Ir(2)-C(11)	89.2 (2)
P(1)-Ir(1)-C(10)	97.6 (1)	P(3)-Ir(2)-C1	86.56 (5)
P(2)-Ir(1)-C(5)	82.1 (1)	P(4)-Ir(2)-C(4)	90.8 (1)
P(2)-Ir(1)-C(9)	86.4 (2)	P(4)-Ir(2)-C(11)	91.0 (2)
P(2)-Ir(1)-C(10)	98.5 (1)	P(4)-Ir(2)-C1	88.33 (5)
C(5)-Ir(1)-C(9)	98.5 (2)	C(4)-Ir(2)-C(11)	91.3 (2)
C(5)-Ir(1)-C(10)	159.8 (2)	C(4)-Ir(2)-Cl	179.1 (1)
P(9)-Ir(1)-C(10)	101.6 (2)	C(11)-Ir(2)-Cl	88.4 (2)
P(2)-C(2)-P(3)	111.3 (3)	P(4)-C(1)-P(1)	108.9 (3)
Ir(1)-C(5)-C(4)	108.2 (4)	Ir(2)-C(4)-C(5)	116.3 (4)
Ir(1)-C(5)-C(6)	131.2 (5)	Ir(2)-C(4)-C(3)	119.6 (4)
C(4)-C(5)-C(6)	120.6 (4)	C(3)-C(4)-C(5)	124.1 (5)
C(9)-Ir(1)-Ir(2)	167.6 (2)	C(11)-Ir(2)-Ir(1)	157.6 (2)

[a] Numbers in parentheses are estimated standard deviations in the least significant digit.

much shorter reaction time and the more efficient use of iridium. Unlike the original report,[6] preparations of **1** by this route yield a product showing three terminal carbonyl bands as was found for $[Ir_2(CO)_3(\mu\text{-}CO)Cl(DAM)_2]BPh_4$ (DAM = bis(diphenylarsino)methane).[13] The infrared spectra of **2** and **3** also show three terminal carbonyl bands as does $[Ir_2(CO)_3(\mu\text{-}CO)Cl(DPM)_2]Cl$.[9] We are uncertain about the discrepancy between the infrared data reported by Sanger[6] for **1** and those obtained in this study, particularly since the ^{31}P NMR spectra appear to be the same. Possibly the different preparative route leads to an alternative arrangement of the carbonyl ligands. Despite this, the infrared data obtained here are quite consistent with the proposed structures. Although the mull spectra of **2** and **3** show a single absorption for the bridging carbonyl ligand, that of **1** exhibits a distinct splitting. While this may be due to solid-state effects, it could also indicate the presence of a second isomer (**1b**), a possibility which is supported by the observation that the AA′BB′ ^{31}P NMR spectrum of **1** shows a number of weak resonances suggestive of the presence of a second AA′BB′ pattern.

Complexes **1**–**3** react readily with an excess of dimethyl acetylenedicarboxylate (DMAD) to give **4**–**6**, respectively, which on the basis of elemental analyses, infrared and NMR spectral data, and a single-crystal, X-ray structure determination of **5a** (vide infra) are formulated as the

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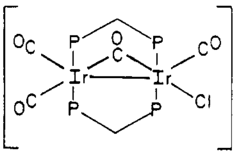
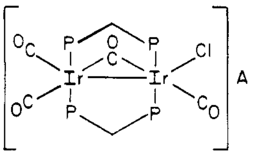
(13) Mague, J. T.; DeVries, S. H. *Inorg. Chem.* **1980**, *19*, 3743.

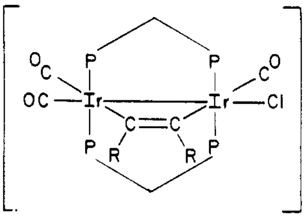


1a, A = BPh$_4$
2, A = PF$_6$
3, A = ClO$_4$



1b, A = BPh$_4$

dimetalated olefin complexes [$Ir_2(CO)_3Cl(\mu-H_3CO_2CC=CCO_2CH_3)(DPM)_2$]A. When prepared in this fashion, **4–6** are frequently obtained as isomeric mixtures. Thus the ^1H NMR spectra show two sets of resonances for the nonequivalent carboxymethyl groups of the olefinic ligand while the ^{31}P NMR spectra (Figure 2) show two overlapping AA′BB′ patterns with small (isomer a) and large (isomer b) chemical shift differences between the two pairs of phosphorus nuclei. Instrumental limitations have prevented a resolution of the overlapping multiplets that occur in the high-field region. Nevertheless it seems reasonably certain that the mirror image of the pattern centered at ca. −19.5 ppm does occur in the high-field region. Comparison of this latter region with the spectrum of **4a** alone (Figure 3) permits the identification of the two strongest lines of the high-field multiplet expected for **4b**. From these the companion of the closely spaced doublet signal appearing at ca. −18.2 ppm is calculated to lie directly under the intense pair of lines for **4a** at ca. −33 ppm. Additionally, comparison of the overlapped region in Figure 2 with the spectrum of **4a** (Figure 3) shows significant additional intensity in this region as well as near −32 ppm that would be consistent with the presence of the remainder of the lines expected for the upfield component of the pattern assigned to **4b**. Since the sample of **5** used for the structure determination contained a negligible amount of isomer **b** (by ^{31}P NMR), we assign the structure shown in Figure 4 to isomer **a** while that of isomer **b** most likely has the chloride ligand along the metal–metal axis.



4b, A = BPh$_4$, R = CO$_2$CH$_3$
5b, A = PF$_6$, R = CO$_2$CH$_3$
6b, A = ClO$_4$, R = CO$_2$CH$_3$

We find that both isomers also result when the reaction is carried out under carbon monoxide, but when DMAD reacts with [$Ir_2(CO)_2(\mu-CO)(\mu-Cl)(DPM)_2$]BPh$_4$,[6] the product is **4a** with only a trace of **4b** being formed. Monitoring the reaction of DMAD with **1** in the presence of carbon monoxide by ^{31}P NMR showed that as increments of the acetylene were added AA′BB′ spectra attributable to both **4a** and **4b** grew in while that for **1** showed a corresponding decrease. During the course of the experiment, the relative amounts of **4a** and **4b** appeared to remain approximately the same, and complete conversion had occurred at the point where slightly more than 1 equiv has been added. No other species were detected. In a separate experiment the mixture of **4a** and **4b** used to obtain the ^{31}P NMR spectrum shown in Figure 2 (CH_2Cl_2/CD_2Cl_2 solution) was allowed to stand, and after 2 days nearly complete isomerization of the **4b** present to **4a** had occurred. These experiments suggest that in the reaction of **1–3** to give **4–6** both isomers **a** and **b** are formed initially in the reaction. It seems unlikely that isomer **b** is the sole initial product for two reasons. First, the relative amounts of **4a** and **4b** observed in the former experiment appear to remain approximately the same throughout its course and there is more of **4a** present. In addition, this experiment required about 3 h to complete while the isomerization of **4b** to **4a** took much longer. It thus appears that while isomer **b** can only be formed in significant amounts from [$Ir_2(CO)_3(\mu-CO)Cl(DPM)_2$]$^+$, isomer **a** results from the reaction of either this species or its decarbonylation product [$Ir_2(CO)_2(\mu-CO)(\mu-Cl)(DPM)_2$]$^+$. The relative proportions of the two isomers obtained from **1–3** in any given preparation must therefore depend upon both the reaction time and the extent to which these become decarbonylated prior to the addition of the acetylene (partial conversion of **1–3** to [$Ir_2(CO)_2(\mu-CO)(\mu-Cl)(DPM)_2$]$^+$ occurs on dissolution in the absence of carbon monoxide[6]).

While it is tempting to attribute the formation of two isomers of **4–6** when DMAD reacts with **1–3** and only one when the reactant is [$Ir_2(CO)_2(\mu-CO)(\mu-Cl)(DPM)_2$]$^+$ to the fact that the iridium atoms are nonequivalent in the former and equivalent in the latter, the available data are insufficient to permit a detailed discussion of the mechanism. It is clear however that isomer **a** is the thermodynamically stable isomer of **4–6** since, as discussed above, isomer **b** converts to isomer **a** on standing in solution, but we have been unable to effect the reverse conversion. The mechanism of the isomerization is unclear since its rate does not appear to be markedly affected by the presence of either carbon monoxide or chloride ion. We tentatively suggest that it could occur by loss of the axial chloride ligand in isomer **b** which would allow the carbonyl ligand on this same metal to move toward the site thus vacated. Reattachment of the chloride ligand on the opposite side of this carbonyl ligand would then form isomer **a**. In support of this we note that the axial Ir–Cl distance in [$Ir_2(CO)_2Cl_2(\mu-H_3CO_2CC=CCO_2CH_3)(DPM)_2$] is quite long,[2] suggesting that the axial chloride ligand in isomer **b** could be rather weakly bound.

In contrast to the related rhodium complexes studied earlier,[1] no evidence was found for bridging carbonyl ligands reflecting the decreased tendency of third-row elements to support this mode of carbon monoxide coordination.

Complex **1** also reacts readily with methyl propiolate to give yellow crystals of **7**, which is formulated as [$Ir_2(CO)_3Cl(\mu-HC=CCO_2CH_3)(DPM)_2$]BPh$_4$. That the acetylene has reacted to form a dimetalated olefin rather than an acetylide is indicated by the absence of an infrared absorption attributable to $\nu_{C\equiv C}$[14] and the presence of a band of medium intensity at 1533 cm^{-1} that is comparable to those assigned to $\nu_{C=C}$ in **4–6**. Furthermore there is no evidence for an Ir–H resonance in the ^1H NMR spectrum that would result were oxidative addition of the acetylenic C–H bond to have occurred. While this is not not necessarily conclusive since elimination of HCl or loss of a proton could have occurred subsequently, the analytical and infrared data support the presence of one chlorine and one tetraphenylborate ion in the product making both of these possibilities unlikely. Finally, the infrared spectrum in the carbonyl region is quite similar to those found for **4–6**. Interestingly the ^{31}P NMR spectrum shows a single AA′BB′ pattern, indicating that only one isomer is formed. Although it is not possible to say with certainty which of the two possible orientations of the methyl propiolate

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[14] Hutton, A. T.; Pringle, P. G.; Shaw, B. L. *Organometallics* **1983**, *2*, 1889.

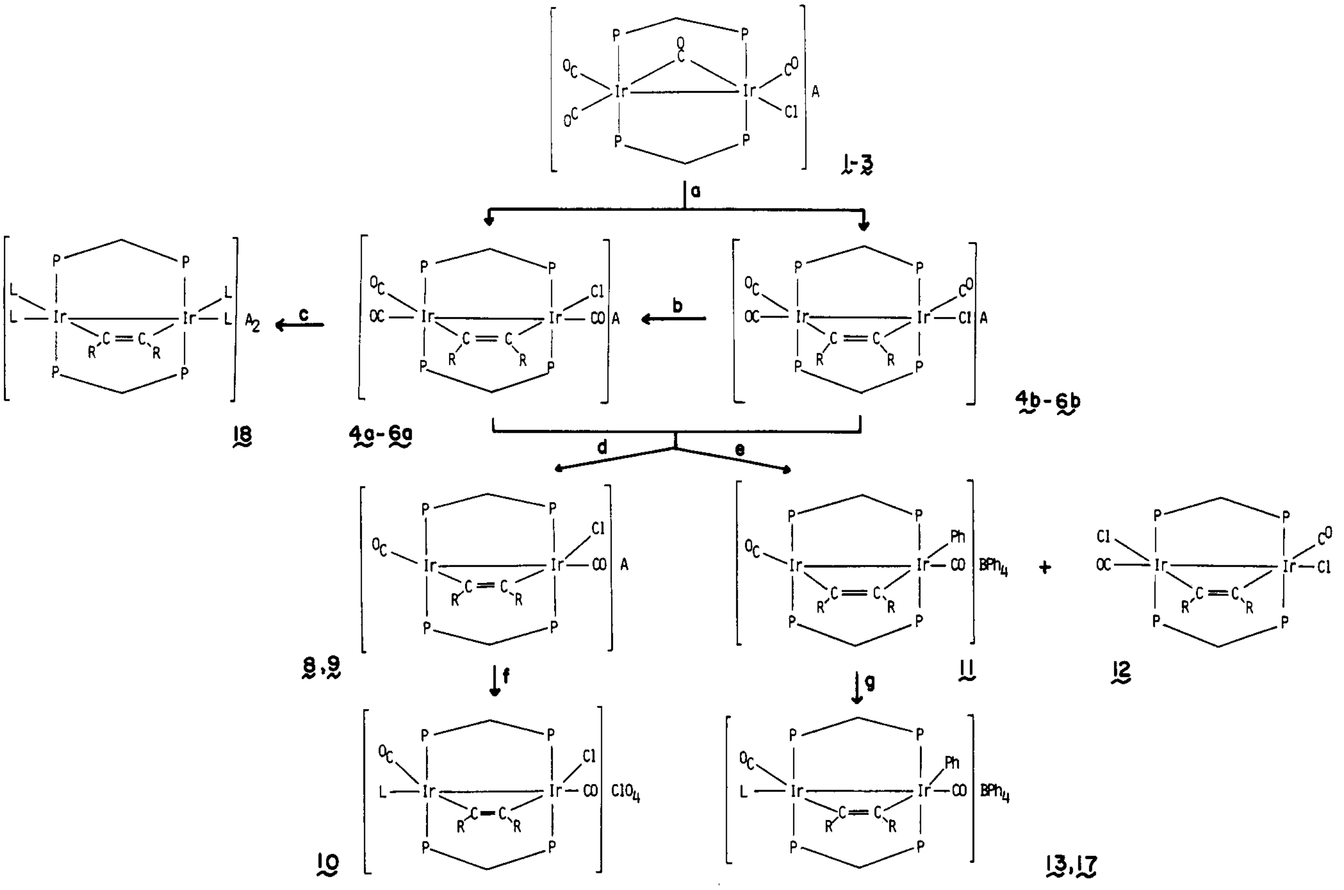
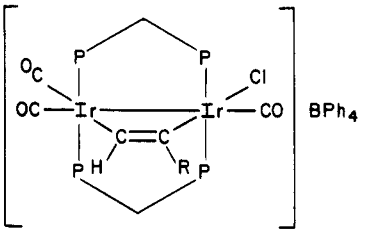
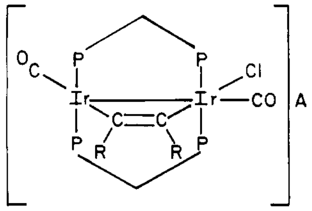


Figure 1. Reaction chemistry of $[Ir_2(CO)_3(\mu\text{-}CO)Cl(DPM)_2]^+$ and derivatives: (a) R_2C_2 (R = CO_2CH_3, A = BPh_4, PF_6, ClO_4); (b) Δ, THF, CO; (c) L = CN-t-Bu, A = BPh_4; (d) Δ, THF/acetone, A = PF_6, ClO_4. (e) Δ, THF/acetone, A = BPh_4. (f) L = CO, $P(OCH_3)_3$, A = ClO_4; (g) L = CO, CN-*t*-Bu, A = BPh_4.

ligand is present, we feel that that shown is more likely since it places the less electronegative carbon on the metal that formally bears the positive charge. The ready formation of 7 contrasts with preliminary observations on the rhodium systems $[Rh_2(CO)_2(\mu\text{-}X)(DPM)_2]PF_6$ (X = Cl, O_2CCH_3) where methyl propiolate reacts with difficulty if at all and then no dimetalated olefin complex forms.[15]



7, R = CO_2CH_3



8, A = PF_6, R = CO_2CH_3
9, A = ClO_4, R = CO_2CH_3

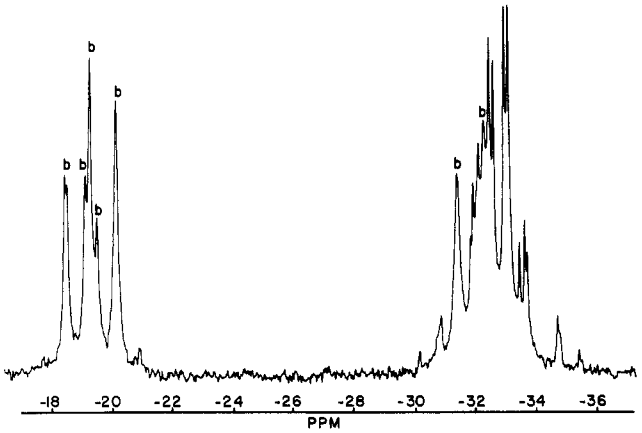


Figure 2. The $^{31}P\{^1H\}$ NMR spectrum of $[Ir_2(CO)_3Cl(\mu\text{-}H_3CO_2CC{=}CCO_2CH_3)(DPM)_2]BPh_4$ (4). Peaks marked b are those assigned to isomer 4b; the remainder are assigned to isomer 4a.

Prolonged refluxing of 5a,b and 6a,b in tetrahydrofuran yields red-brown 8 and orange 9 which are obtained as tetrahydrofuran solvates and which show only two carbonyl bands in their infrared spectra. They are therefore formulated dicarbonyl species. The ^{31}P NMR spectra of both complexes at room temperature consist of two broad, featureless resonances; however, at temperatures below −12 °C they appear as pairs of approximate triplets. Evidently the chemical shift difference between the two pairs of phosphorus nuclei is sufficiently large that the spectra are approximately first order. We attribute the dynamic behavior observed at higher temperatures to exchange of chloride between the two ends of the molecule, viz., eq 1. Although we have not been able to detect the presence of the proposed chlorine-bridged intermediate, in the related species derived from hexafluorobuty-2-yne, this species has been detected in solution at low temperature.[2] Although it could be argued that the fluxional behavior is the result

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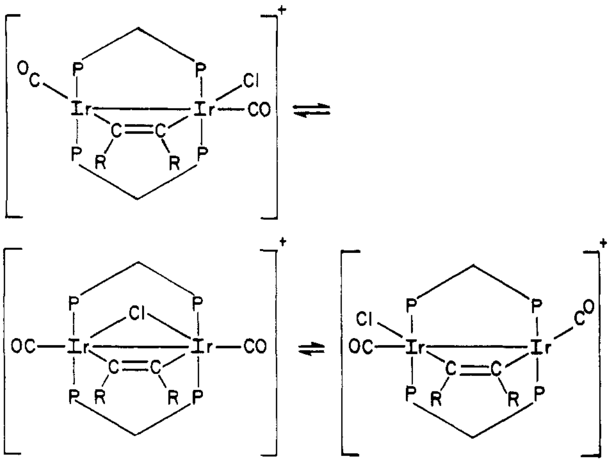
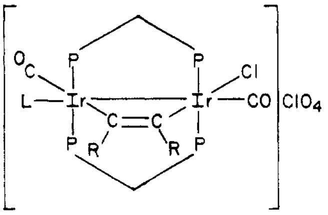
[15] Mague, J. T.; McCurdy, W., unpublished observations.



(1)

of rapid exchange of the solvating tetrahydrofuran at the formally positive iridium atom, this does not seem likely since this should only affect the resonance of the phosphorus nuclei attached to this iridium while in fact both resonances broaden to the same extent as the temperature is raised. Indeed if tetrahydrofuran is added to a dichloromethane solution of **9** at −20 °C, the ^{31}P NMR shows that the high-field resonance is unaffected but the low-field resonance collapses to a broad, featureless absorption. Further addition of a few drops of acetonitrile to this solution causes the color to change from red-orange to yellow, and the ^{31}P NMR spectrum now consists of a nonfluxional AA′BB′ pattern over the temperature range −20 to +30 °C with δ(P) of −16.8 and −37.6. This is attributed to the formation of $[Ir_2(CO)_2Cl(NCCH_3)(\mu\text{-}H_3CO_2CC{=}CCO_2CH_3)(DPM)_2]ClO_4$ in which the solvent molecule is bound sufficiently strongly that no exchange occurs. A similar result is seen when chloride ion is added to a solution of **9** whereupon the color becomes yellow and a static spectrum identical with that observed for **12** (vide infra) is now seen. This spectrum is unaffected by the presence of excess chloride, suggesting that **12** does not readily exchange chloride. The observation of the chloride exchange process in **8** and **9** provides further support for the structure assigned since if the chloride ligand were along the metal–metal axis, this process would be expected to be far less facile.

Complexes **8** and **9** readily react with carbon monoxide to regenerate **5** and **6**, respectively (isomer **a** only) while **9** also adds 1 equiv of trimethyl phosphite to yield **10** which



10, R = CO_2CH_3, L = $P(OMe)_3$

is formulated as $[Ir_2(CO)_2(P(OCH_3)_3)Cl(\mu\text{-}H_3CO_2CC{=}CCO_2CH_3)(DPM)_2]ClO_4$ on the basis of elemental analysis and infrared spectral data. Although two isomers are possible, only one appears to be formed, and while it is not possible with the data available to determine which is produced, that shown is preferred on steric grounds. The ^{31}P NMR spectrum shows multiplets assignable to the phosphite and DPM phosphorus atoms but is not of sufficient resolution to permit a detailed analysis. The chemical shifts of the DPM ligand are very similar and in the range expected but that for the phosphite is considerably upfield from what has been found previously for the related rhodium complex $[Rh_2(P(OCH_3)_3)(O_2CCH_3)(\mu\text{-}CO)(\mu\text{-}H_3CO_2CC{=}CCO_2CH_3)(DPM)_2]PF_6$ (δ(P), 118.2)[1] and for several mononuclear iridium phosphite complexes.[16] At present we have no explanation for this result.

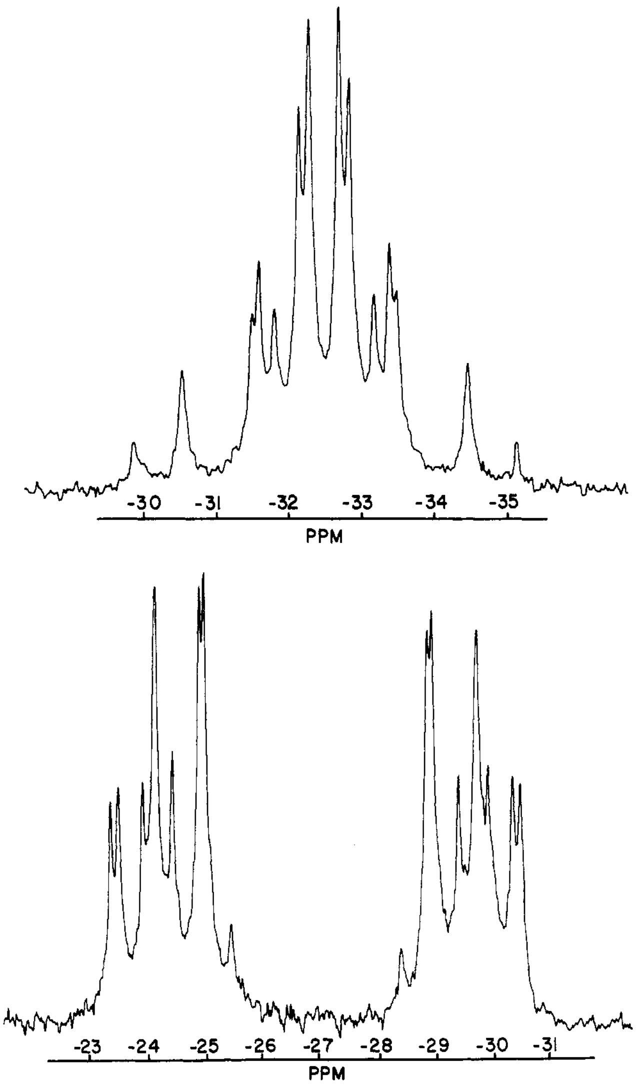


Figure 3. The $^{31}P\{^1H\}$ NMR spectra of $[Ir_2(CO)_3Cl(\mu\text{-}H_3CO_2CC{=}CCO_2CH_3)(DPM)_2]BPh_4$, isomer **4a** (top), and $[Ir_2(CO)_3(C_6H_5)(\mu\text{-}H_3CO_2CC{=}CCO_2CH_3)(DPM)_2]BPh_4$, **13** (bottom).

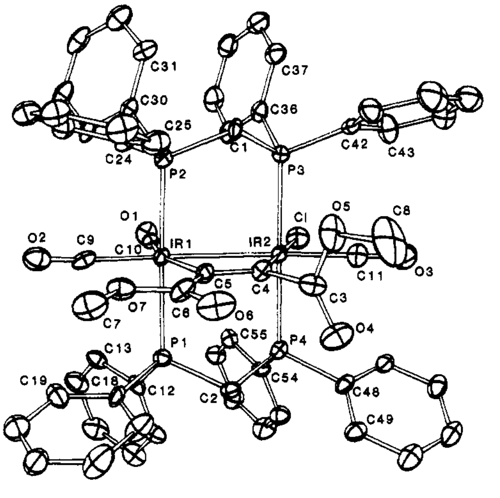
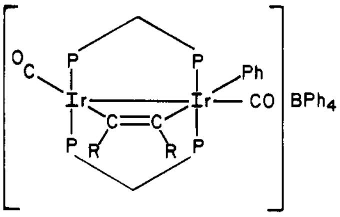
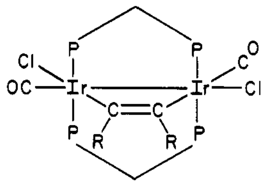


Figure 4. Perspective view of the dimeric cation $[Ir_2(CO)_3Cl(\mu\text{-}H_3CO_2CC{=}CCO_2CH_3)(DPM)_2]^+$ of **5a**. Thermal ellipsoids are drawn at the 50% probability level. The numbering of the carbon atoms in the phenyl rings continues sequentially around each ring from those labeled.

Unlike 5 and 6, 4 does not undergo simple thermal decarbonylation. When refluxed in tetrahydrofuran under a dinitrogen purge, the solution changes from yellow to orange to dark red but a yellow solid also separates after several hours. The red crystals obtained from the solution analyze as $[Ir_2(CO)_2(C_6H_5)(\mu\text{-}H_3CO_2CC{=}CCO_2CH_3)(DPM)_2]BPh_4{\cdot}C_4H_8O$ (11) while the yellow precipitate is characterized as $[Ir_2(CO)_2Cl_2(\mu\text{-}H_3CO_2CC{=}CCO_2CH_3)(DPM)_2]$ (12). While 12 is fully characterized by the analytical and spectroscopic data provided in the Experimental Section (AA'BB' pattern for the ^{31}P NMR spectrum), we note that the same complex has been prepared independently by another route and structurally characterized by X-ray crystallography.[2] The spectroscopic data for both samples are in good agreement.



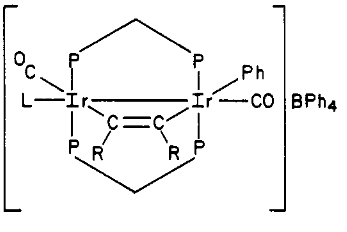
11, R = CO_2CH_3



12, R = CO_2CH_3

For the characterization of 11 we note that it contains no chloride, has infrared and ^{31}P NMR (AA'BB' pattern) spectra very similar to those for 8 and 9, and shows no spectroscopic evidence for the presence of a hydride or an ortho-metalated ligand. Further, the ^1H NMR spectrum shows that both carboxymethyl groups of the olefinic ligand remain intact while the infrared spectrum confirms that the tetraphenylborate counterion is still present. Thus it appears that 11 has a structure very similar to that for 8 and 9 with evidently the same formal oxidation states for the two metal atoms. This in turn indicates the presence of a formally uninegative ligand bound to one metal. The observation that the ^{31}P NMR spectrum shows no evidence for fluxionality at room temperature indicates that unlike 8 and 9, this ligand must not be capable of bridging the two metals. All the data are thus consistent with 11 containing an iridium-bound phenyl group, and it is only with this formulation that the analytical data can be satisfactorily fit. (While it could be argued that the presence of solvating tetrahydrofuran weakens this argument, careful integration of the ^1H NMR spectrum shows that there is exactly one solvent molecule present per dimer). The source of the phenyl ligand must be the tetraphenylborate ion, and while this transformation is rare in transition-metal chemistry, it has been found previously that $[PtH(NO_3)(PEt_3)_2]$ reacts with sodium tetraphenylborate in methanol to yield $[Pt(C_6H_5)(PEt_3)_2(\mu\text{-}H)Pt(H)(PEt_3)_2]BPh_4$.[17,18] Also sodium tetraphenylborate is known to react readily with mercury(II) chloride to produce phenylmercuric chloride.[19] While the details of the conversion of 4 to 11 have not been elucidated, monitoring the reaction by ^{31}P NMR spectroscopy shows that a fluxional species that appears to be analogous to 8 and 9 is formed after short reaction times. Since 4 can be recovered unchanged (except for the isomerization noted earlier) when refluxed under carbon monoxide, it appears that the $[Ir_2(CO)_2Cl(\mu\text{-}H_3CO_2CC{=}CCO_2CH_3)(DPM)_2]^+$ cation is the reactive species toward tetraphenylborate. Further evidence for the formulation of 11 will be discussed below.

Complex 11 reacts readily with carbon monoxide to afford a yellow species showing three terminal carbonyl absorptions very similar to those observed for 4–6 and analyzing as $[Ir_2(CO)_3(C_6H_5)(\mu\text{-}H_3CO_2CC{=}CCO_2CH_3)(DPM)_2]BPh_4$ (13). Significantly, however, the ^{31}P NMR spectrum of 13 is noticeably different from that for 4 (Figure 3), indicating further that unlike 8 and 9 which add carbon monoxide to regenerate 5 and 6, 11 cannot contain the $[Ir_2(CO)_2Cl(\mu\text{-}H_3CO_2CC{=}CCO_2CH_3)(DPM)_2]^+$ cation.



13, R = CO_2CH_3, L = CO

To further confirm the identity of 11 and the source of the phenyl group, $[Ir_2(CO)_3Cl(\mu\text{-}H_3CO_2CC{=}CCO_2CH_3)(DPM)_2]B(p\text{-tol})_4$ was prepared by the route used for 4 but with sodium tetra-*p*-tolylborate and was refluxed in tetrahydrofuran under a dinitrogen purge. As with 4, 12 precipitates from the solution and from the filtrate was obtained a red crystalline solid (14) having virtually identical spectroscopic properties to that found for 11 apart from the obvious differences due to the *p*-tolyl moieties present. Complex 14 also reacts readily with carbon monoxide to yield yellow 15 having spectroscopic properties essentially the same as those for 13. Attempts to convert 15 to its perchlorate salt were unsuccessful, and while it seemed reasonable that 15 is the *p*-tolyl analogue of 13, the presence of the tetra-*p*-tolylborate anion made it impossible to confirm the presence of an iridium-bound *p*-tolyl group. Therefore, 9 was refluxed with 1 equiv of sodium tetra-*p*-tolylborate in tetrahydrofuran. The resulting dark red solution was reacted with carbon monoxide to give a yellow solution from which yellow crystals of 16 were obtained that have identical infrared and ^{31}P NMR spectra to those for 13 and 15 apart from those differences due to the different counterions. The significant feature of the ^1H NMR spectrum of 16 is a new singlet resonance at 2.02 ppm that is slightly upfield of the *p*-methyl resonance for the tetra-*p*-tolylborate ion and integrates correctly for one methyl group. These results confirm that 15 and 16 contain the same cation and that 14 and 15 are the *p*-tolyl analogues of 11 and 13, respectively. This result further suggests that it is $[Ir_2(CO)_2Cl(\mu\text{-}H_3CO_2CC{=}CCO_2CH_3)(DPM)_2]^+$ which is the reactive species toward the tetraphenylborate ion.

Complex 11 reacts readily with 1 equiv of *tert*-butyl isocyanide to yield off-white crystals of 17 that on the basis of analytical and spectroscopic data (AA'BB' pattern for the ^{31}P NMR spectrum) can be formulated as $[Ir_2(CO)_2(CNC(CH_3)_3)(C_6H_5)(\mu\text{-}H_3CO_2CC{=}CCO_2CH_3)(DPM)_2]BPh_4$. Although the precise stereochemistry is uncertain, the relatively large separation of the carbonyl stretching frequencies suggests that the carbonyl groups are in rather different environments and the structure shown is the most probable.

An excess of *tert*-butyl isocyanide reacts with **4a** to replace the chloride and all the carbonyl ligands. Addition of 1 equiv of sodium tetraphenylborate allows the isolation of 18, which is characterized by analytical and spectro-

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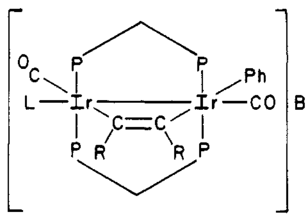
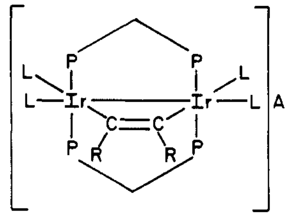


17, R = CO_2CH_3, L = $CNC(CH_3)_3$



18, R = CO_2CH_3, L = $CNC(CH_3)_3$, A = BPh_4

scopic data as $[Ir_2(CNC(CH_3)_3)_4(\mu\text{-}H_3CO_2CC{=}CCO_2CH_3)(DPM)_2](BPh_4)_2$. The complex is thus the iridium analogue of $[Rh_2(CNC(CH_3)_3)_4(\mu\text{-}RC{=}CR)(DPM)_2](BPh_4)_2$ (R = CO_2CH_3, CF_3)[1] and is assigned a comparable structure. Complex **18** is also the major product from the reaction of dimethyl acetylenedicarboxylate with $[Ir_2(CNC(CH_3)_3)_4(\mu\text{-}CO)(DPM)_2](BPh_4)_2$,[13] but the need to carry out the reaction at reflux in tetrahydrofuran seems to lead to the formation of some side products that were difficult to remove. Reaction of **4a** with 1 equiv of *tert*-butyl isocyanide yields a bright yellow solid that analyzes for $[Ir_2(CO)_2(CNC(CH_3)_3)Cl(\mu\text{-}H_3CO_2CC{=}CCO_2CH_3)(DPM)_2]BPh_4$;[20] however, the spectroscopic data indicate that this material is not a single compound. The major component as judged by the ^1H and ^{31}P NMR spectra is most probably the chloro analogue of **17**. At least one other species appears to be present, but attempts to remove the impurities were unsuccessful.

Crystallographic Studies. The structure of **5a** consists of discrete, binuclear cations $[Ir_2(CO)_3Cl(\mu\text{-}H_3CO_2CC{=}CCO_2CH_3)(DPM)_2]^+$ and hexafluorophosphate anions interspersed with molecules of solvent acetonitrile. There are no unusually short intermolecular contacts. A perspective view of the cation is presented in Figure 4. The two iridium atoms are bridged by the two DPM ligands that occupy axial positions and the dimetalated olefin moiety that occupies the equatorial plane. The coordination in the equatorial plane is completed by two carbonyl ligands on Ir(1) and by a carbonyl and a chlorine ligand on Ir(2). The C(4)–C(5) distance of 1.330 (7) Å compares favorably with that found in $[Ir_2(CO)_2Cl_2(\mu\text{-}H_3CO_2CC{=}CCO_2CH_3)(DPM)_2]$[2] (1.345 (8) Å) and in $[Rh_2(P(OMe)_3)(O_2CCH_3)(\mu\text{-}CO)(\mu\text{-}H_3CO_2CC{=}CCO_2CH_3)(DPM)_2]PF_6$[21] (1.342 (17) Å) and with the correspondingly comparable Ir(1)–C(5) and Ir(2)–C(4) distances clearly indicates that the dimethyl acetylenedicarboxylate is bound as a dimetalated olefin. The Ir(1)–Ir(2) distance of 2.8933 (2) Å is only slightly longer than the corresponding distances found in $[Ir_2(CO)_2Cl_2(\mu\text{-}H_3CO_2CC{=}CCO_2CH_3)(DPM)_2]$ (2.7793 (3) Å),[2] $[Ir_2(CO)_2Cl_2(\mu\text{-}CO)(DPM)_2]$ (2.779 (1) Å),[9] and $[Ir_2(CO)_2(\mu\text{-}CO)(\mu\text{-}S)(DPM)_2]$ (2.843 (2) Å),[22] all of which are proposed to contain a metal–metal single bond. On the other hand, it is considerably shorter than the nonbonded Rh–Rh separation (3.386 (1) Å) found in the related complex $[Rh_2(P(OMe)_3)(O_2CCH_3)(\mu\text{-}CO)(\mu\text{-}H_3CO_2CC{=}CCO_2CH_3)(DPM)_2]PF_6$.[21] Formally each iridium atom would have a 17-electron configuration in the absence of metal–metal interaction so that to accomodate the observed diamagnetism, some form of metal–metal interaction is necessary. That this is best considered to be a metal–metal bond is indicated by the intraligand phosphorus–phosphorus separations (P(1)···P(4) = 2.961 (2) Å; P(2)···P(3) = 2.979 (2) Å) that are definitely longer than the metal–metal distance.

The ligands about Ir(2) are disposed in a very nearly square-pyramidal array. The largest deviation is with P(3) that is canted away from C(4) presumably to minimize contacts between the methyl group attached to O(5) and the phenyl group that lies just above it. The coordination about Ir(1) is considerably more distorted from a square-pyramidal geometry. This is reflected both in the C(5)–Ir(1)–C(10) angle of 159.8 (2)° (cf. the C(4)–Ir(2)–Cl angle of 179.1 (1)°) and the significant bending of P(1) and P(2) *toward* O(7). Also, C(9) is 10° closer to being collinear with the Ir(1)–Ir(2) vector than is C(11). This last distortion together with the large Ir(1)–C(5)–C(6) angle of 131.2 (5)° is probably to avoid too close a contact between the carbonyl (C(9)O(2)) and carboxymethyl groups. As it is, the C(9)···O(7) distance of 2.785 (6) Å is only slightly longer than a normal van der Waals contact. The reason for the displacement of the carbonyl group C(10)O(1) toward the chloride is less clear, but it may be that this position allows it to most satisfactorily "interleave" between the ortho hydrogen atoms of the phenyl groups on that side of the molecule. There is also no immediately obvious reason for the bending of P(1) and P(2) toward O(7). Possibly this may be also to minimize contacts between the carbonyl group C(10)O(1) and the adjacent phenyl rings, but it also appears from inspection of models that the bending of P(3) toward the chloride tends to cause at least P(2) to bend toward O(7) in order to avoid straining the P(2)-C(2)-P(3) angle.

As was observed in $[Rh_2(P(OMe)_3)(\mu\text{-}CO)(\mu\text{-}MeO_2CC{=}CCO_2CH_3)(O_2CMe)(DPM)_2]PF_6$[21] the carboxymethyl groups are nearly perpendicular to one another (interplanar angle 85.7°), which serves to minimize the contacts between them and with the adjacent carbonyl ligands. Also as is generally observed in complexes of this type, the phenyl groups are staggered and the methylene carbon atoms of the DPM ligands are both on the same side of the molecule as the dimetalated olefin ligand, which best serves to minimize intramolecular contacts. The phenyl groups are planar within experimental error, and their metrical parameters are unexceptional. Both the hexafluorophosphate ion and the solvent acetonitrile also have normal geometries.

Conclusions

The complexes $[Ir_2(CO)_3Cl(\mu\text{-}CO)(DPM)_2]A$ (A = BPh_4, ClO_4, PF_6) readily react with dimethyl acetylenedicarboxylate and methyl propiolate to form binuclear derivatives in which the acetylenes are bound as dimetalated olefins. These lose one carbonyl group on refluxing under nitrogen and when the counterion is tetraphenylborate react with this ion to form a mixture of $[Ir_2(CO)_2Cl_2(\mu\text{-}H_3CO_2CC{=}CCO_2CH_3)(DPM)_2]$ and $[Ir_2(CO)_2(C_6H_5)(\mu\text{-}H_3CO_2CC{=}CCO_2CH_3)(DPM)_2]BPh_4$. The decarbonylated complexes can coordinate one Lewis base ligand. The structure of $[Ir_2(CO)_3Cl(\mu\text{-}H_3CO_2C{=}CCO_2CH_3)(DPM)_2]PF_6$ has been determined.

Acknowledgment. Support of this work by the Gulf Oil Foundation and the Tulane University Chemistry

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[20] Anal. Calcd for $C_{87}H_{82}P_4O_6ClNBIr_2$: C, 58.30; H, 4.62; Cl, 0.78. Found: C, 58.4; H, 4.6; Cl, 0.98.

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Department (to J. T. Mague) is gratefully acknowledged. E.D.S. thanks the National Science Foundation (Grant No. CHE 8311704) for funds to purchase the diffractometer.

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$_3$CN, 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$_2$Cl$_2$(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 $[\mathrm{Ir_2Cl_2(CO)_2(\mu\text{-}CH_3O_2CC_2CO_2CH_3)(Ph_2PCH_2PPh_2)_2]\cdot 2CH_2Cl_2}$

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Received June 4, 1984

The reactions of *trans*-[IrCl(CO)(DPM)]$_2$ with dimethyl acetylenedicarboxylate (DMA), hexafluro-2-butyne (HFB), and acetylene yield the species [Ir$_2$Cl$_2$(CO)$_2$(μ-RC$_2$R)(DPM)$_2$] (R = CO$_2$CH$_3$, 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$_2$Cl$_2$(CO)(μ-RC$_2$R)(DPM)$_2$] (R = CO$_2$CH$_3$, CF$_3$). The reaction of [Ir$_2$Cl$_2$(CO)$_2$(μ-RC$_2$R)(DPM)$_2$] (R = CO$_2$CH$_3$, CF$_3$) with AgBF$_4$ produces the cationic compounds [Ir$_2$Cl(CO)$_2$(μ-RC$_2$R)(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)$_2$(μ-Cl)(DPM)$_2$][BF$_4$]. Both sets of isomers react with CO to give [Ir$_2$Cl(CO)$_3$(μ-RC$_2$R)(DPM)$_2$][BF$_4$]. Refluxing these tricarbonyl species regenerates the isomers obtained by the AgBF$_4$ route. [Ir$_2$Cl$_2$(CO)$_2$(μ-DMA)(DPM)$_2$]·2CH$_2$Cl$_2$ 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$_2$PCH$_2$PPh$_2$) 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$_2$AsCH$_2$AsPh$_2$)[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$_2$X$_2$(μ-CO)(DPM)$_2$] and *trans*-[RhCl(CO)(DPM)]$_2$ (X = Cl, Br, I) react with DMA and HFB to yield the unusual species [Rh$_2$X$_2$(μ-CO)(μ-RC$_2$R)(DPM)$_2$] (R = CO$_2$Me, 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)$_2$(μ-O$_2$CCH$_3$)(DPM)$_2$]$^+$ with the above activated acetylenes.[3,4] The acetylene-bridged complexes [Rh$_2$X$_2$(μ-RC$_2$R)(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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