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Cationic Polyhydrido Cluster Complexes. Crystal and Molecular Structures of $\{Ir_3[Ph_2P(CH_2)_3PPh_2]_3(H)_7(CO)\}^{2+}$ and $\{Ir_3[Ph_2P(CH_2)_2(2\text{-}py)]_3(H)_7\}^{2+}$

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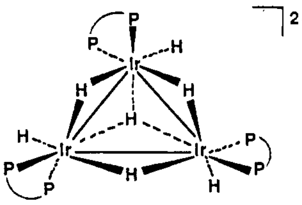
Two new cationic polyhydrido cluster complexes of iridium have been synthesized and characterized by single-crystal X-ray diffraction and by IR and ^1H and ^{31}P NMR spectroscopy. $[Ir_3(dppp)_3(H)_7(CO)]^{2+}$ (**2**) and $[Ir_3(PN)_3(H)_7]^{2+}$ (**5**), where dppp = 1,3-bis(diphenylphosphino)propane and PN = 1-(2-pyridyl)-2-(diphenylphosphino)ethane, were synthesized by the reaction of CO with $[Ir_3(dppp)_3(H)_7]^{2+}$ (**1**) in CH_2Cl_2 solution and H_2 with $[Ir(PN)(COD)]^+$ (**4**) in CH_3OH solution, respectively. Both complexes belong to the monoclinic $P2_1/c$ space group ($\mathbf{2}(BF_4)_2 \cdot 2C_2H_4Cl_2$, $a = 13.465$ (3) Å, $b = 24.903$ (7) Å, $c = 26.32$ (1) Å, $\beta = 91.67$ (3)°, $R = 0.049$; $\mathbf{5}(PF_6)_2 \cdot C_3H_6O$, $a = 11.510$ (8) Å, $b = 22.925$ (4) Å, $c = 25.024$ (7) Å, $\beta = 98.83$ (5)°, $R = 0.075$). The hydride positions were not located in the crystal structure analyses but were deduced from structural and ^1H NMR data. The molecular structure of **2** consists of a bilateral triangle of three iridium atoms with a carbonyl at the vertex and a chelating dppp ligand on each iridium atom. ^1H NMR data with use of acetone-d_6 as solvent showed that **2** possesses four doubly bridging hydrides and three terminal hydrides, yielding C_1 symmetry. The molecular structure of **5** consists of an approximately equilateral triangle of three iridium atoms (average Ir–Ir distance 2.746 (1) Å) with one PN ligand chelated to each iridium atom. ^1H NMR analysis, with use of CD_2Cl_2 as solvent, showed that **5** has one triply bridging hydride and six terminal hydrides, giving C_3 symmetry. $[Ir_3(dppp)_3(H)_7(CH_3C_6H_4NC)]^{2+}$ (**3**), a complex structurally analogous to **2**, was synthesized from **1** and *p*-tolyl isocyanide in CH_2Cl_2 solution and characterized by IR and ^1H and ^{31}P NMR spectroscopy. $[Ir(PN)(COD)]^+$ (**4**), the starting material in the synthesis of **5**, was synthesized from $[Ir(COD)(acetone)_2]^+$ and 1 equiv of PN in acetone solution. **4** was characterized by IR and ^1H and ^{31}P NMR spectroscopy and shown to consist of an approximately square-planar geometry with both the P and N atoms of the PN ligand coordinated.

Introduction

Two polyhydrido iridium cluster complexes that contain chelating diphosphine ligands were previously synthesized by the reaction of $[Ir(dppp)(COD)]BF_4$ [COD = 1,5-cyclooctadiene, dppp = 1,3-bis(diphenylphosphino)propane] with hydrogen in a methanol solution.[1] These cationic cluster compounds were formulated as $[Ir_3(dppp)_3(H)_7]^{2+}$ (**1**) and $[Ir_2(dppp)_2(H)_5]^+$ and were structurally determined by single-crystal X-ray diffraction.[1] Complexes of this general type have been isolated from catalytic hydrogenation reactions with $[IrL_2(COD)]^+$ (L = tertiary phosphine or pyridine).[2,3] Therefore, because of its catalytic potential, the hydrogenation products of the complex $[Ir(PP)(COD)]^+$ ($PP = Ph_2P(CH_2)_nPPh_2$; n = 2–4) were characterized.[1] Further interest in this class of unusual hydrido-bridged compounds has developed because of their use as precursors for the synthesis of mixed-metal clusters.[4]



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As an extension of this work, and because of interest in polyhydrido cluster complexes,[4-10] we have examined the reaction chemistry of **1** with several two-electron-donor compounds. Among the substrates tried, carbon monoxide and *p*-tolyl isocyanide formed stable adducts with **1**, analogous to the solvated C_1 isomer of **1** that was observed in both acetone and acetonitrile solution.[1] The structure of **1** in CD_3CN solution was deduced by ^1H NMR data and proposed to contain four doubly bridging hydrides and three terminal hydrides with a coordinated CD_3CN molecule (C_1 symmetry). However, this adduct was not structurally characterized in the solid state. Therefore, we report here the synthesis of $[Ir_3(dppp)_3(H)_7(CO)]^{2+}$ (**2**), $[Ir_3(dppp)_3(H)_7(CH_3C_6H_4NC)]^{2+}$ (**3**), and their deuterium analogues, which were isolated in good yield and characterized by IR and ^1H and ^{31}P NMR spectroscopy. Complex **2** as a BF_4^- salt was also structurally characterized by single-crystal X-ray diffraction.

The use of rhodium and iridium PN complexes [PN = 1-(2-pyridyl)-2-(diphenylphosphino)ethane] as catalysts for the homogeneous decarbonylation of aldehydes has also been studied in our laboratory. Since M–L (M = Rh, Ir; L = tertiary phosphine) bond rupture was postulated to be an important step in the mechanism of this decarbonylation reaction with diphosphine complexes[5,11-13] and because M–N bonds should be weaker than M–P bonds, it was expected that the use of a bidentate ligand containing one P and one N donor would lead to higher catalytic activities. In complexes of this type that contain various PN donor ligands, it has been shown that the N donor group could be readily displaced by CO and phosphines.[14-17] Therefore, as a part of the decarbonylation study, and for a better understanding of the differences between PN and PP complexes, the synthesis, characterization, and reactivity of various Rh and Ir PN complexes have been explored. One of the systems studied has involved the hydrogenation of the complex $[Ir(PN)(COD)]^+$ (**4**). In methanol solution this reaction resulted in the synthesis of $[Ir_3(PN)_3(H)_7]^{2+}$

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(**5**), which is structurally similar to **1**. Therefore, in addition to complexes **2** and **3**, we report here the synthesis and structural characterization of **4** and **5**. **5** was isolated as a PF_6^- salt in good yield and was characterized by single-crystal X-ray diffraction in addition to IR and ^1H and ^{31}P NMR spectroscopy.

Experimental Section

Physical Measurements and Reagents. ^2D, ^1H, and ^{31}P NMR spectra were recorded at 46.1, 300, and 121.5 MHz, respectively, with the use of a Nicolet NT-300 spectrometer. Some ^1H and ^{31}P spectra were also recorded at 270 and 40.5 MHz, respectively, with the use of a Bruker HX-270 spectrometer. ^{31}P NMR spectra were run with proton decoupling and are reported in ppm relative to the external standard H_3PO_4 (85%). ^2D chemical shifts are reported in ppm relative to the external standard $CDCl_3$. Infrared spectra were recorded on a Beckman Model 4250 grating spectrophotometer. Iridium trichloride hydrate was obtained from Johnson Matthey, Inc., and 1,5-cyclooctadiene (COD) from Aldrich Chemical Co. D_2 was obtained from Matheson Co. as was CO, and both were of CP grade with 99.5% purity. 1,3-Bis(diphenylphosphino)propane (dppp) was purchased from Strem Chemicals and used without further purification. Methyl alcohol-d_1 (99.5%) was purchased from Aldrich Chemical Co. All solvents were reagent grade, and dichloromethane was run through a neutral alumina column prior to use. $[Ir(dppp)(COD)]BF_4$,[1] $[Ir_3(dppp)_3(H)_7](BF_4)_2$,[1] $[Ir(PPh_3)_2(COD)]BF_4$,[18] and *p*-tolyl isocyanide ($CH_3C_6H_4NC$)[19] were made according to the literature. All manipulations were carried out under a purified N_2 atmosphere by using standard Schlenk techniques unless stated otherwise.

Synthesis of Compounds. $\mathbf{[Ir_3(dppp)_3(H)_7(CO)](BF_4)_2}$ $\mathbf{(2(BF_4)_2)}$ was prepared as follows. A 35-mg sample of recrystallized $[Ir_3(dppp)_3(H)_7](BF_4)_2$ (**1**) was added to 3.0 mL of frozen and degassed CH_2Cl_2 in a Kontes Griffin–Worden pressure tube. The mixture was freeze–thaw–degassed three times and was kept frozen in vacuo until it was connected to a CO tank. The stainless steel tubing between the pressure tube and CO tank was flushed three times with CO. The solution of **1** was then charged with 40 psig of CO and stirred at 25 °C for $^1/_2$ h (prolonged treatment with CO led to several other products). The solution gradually turned from a deep yellow to a bright yellow after about 15 min. The CO pressure was released, and the solution was transferred to a Schlenk tube under nitrogen. Heptane was added to the solution, immediately giving a bright yellow precipitate. Slow recrystallization from 1,2-dichloroethane/heptane yielded pale yellow rectangular platelike crystals, which slowly lost solvent upon removal from the mother liquor. IR (KBr): $\nu(CO) = 1998$ (s), 1960 cm^{-1} (sh); $\nu(IrH) = 2040$ (m), 2110 (w), 2244 cm^{-1} (vw). ^1H NMR (acetone-d_6, 25 °C, 270 MHz): δ −8.60 (d, $J = 70$ Hz, int = 1), −12.35 (t, $J = 59$ Hz, int = 1), −12.84 (s, int = 1), −16.75 (d, $J = 68$ Hz, int = 1), −17.38 (d of d, $J = 54$ and 26 Hz, int = 1), −18.33 (s, int = 1), −20.87 (m, int = 1). ^{31}P NMR (CH_2Cl_2, 35 °C, 40.5 MHz): δ −7.9 (d of d, int ≈ 1), −12.1 (t, int ≈ 1), −16.7 (m, int ≈ 1), −20.1 (m, int ≈ 1), −29.5 (m, int ≈ 2). Anal. Calcd for $Ir_3P_6C_{82}H_{85}OB_2F_8{\cdot}0.7CH_2Cl_2$: C, 47.71; H, 4.18. Found: C, 47.69; H, 4.33. The partial incorporation of solvent was determined by the best fit of the analytical data. $[Ir_3(dppp)_3(H)_7(CO)](BF_4)_2$ was also synthesized by slowly bubbling CO through a deoxygenated CH_2Cl_2 solution of **1** at 25 °C for several hours; however, this method did not give as fast or as complete a conversion.

$\mathbf{[Ir_3(dppp)_3(D)_7(CO)](BF_4)_2}$ was prepared by the same procedure for the synthesis of **2** using $[Ir_3(dppp)_3(D)_7](BF_4)_2$.[20] IR (KBr): $\nu(CO) = 2005$ (s), 1989 cm^{-1} (sh); $\nu(IrD) = 1610$ cm^{-1} (m) [$\nu(IrH)/\nu(IrD) = 1.39$]. Other iridium–deuteride stretches were obscured by the absorption of the phosphine ligands.

$\mathbf{[Ir_3(dppp)_3(H)_7(CH_3C_6H_4NC)](BF_4)_2}$ $\mathbf{(3(BF_4)_2)}$ was prepared by the reaction of $[Ir_3(dppp)_3(H)_7](BF_4)_2$ (**1**) and *p*-tolyl isocyanide. Deoxygenated CH_2Cl_2 was added to a mixture of **1** (46.1 mg, 0.023 mmol) and $CH_3C_6H_4NC$ (3 mg, 0.026 mmol). The reaction mixture was stirred in a warm water bath at about 40 °C for $^1/_2$ h. Et_2O was added to the solution, giving a yellow precipitate. The product was washed with Et_2O and recrystallized from CH_2Cl_2/Et_2O. IR (KBr): $\nu(IrH) = 2146$ cm^{-1} (m). The isocyanide absorption was obscured by the iridium–hydride absorptions and was therefore identified in the deuterium-labeled analogue (vide infra). ^1H NMR (acetone-d_6, 25 °C, 270 MHz): δ −9.01 (d, $J = 76$ Hz, int = 1), −12.30 (t, $J = 61$ Hz, int = 1), −14.48 (s, int = 1), −16.67 (d, $J = 68$ Hz, int = 1), −17.63 (t, $J = 45$ Hz, int = 1), −18.44 (s, int = 1), −21.86 (pseudoquartet, $J \approx 20$ Hz, int = 1). ^{31}P NMR (acetone, 35 °C, 40.5 MHz): δ −10.8 (m), −12.5 (m), −15.9 (m), −24.1 (m), −30.4 (m).

$\mathbf{[Ir_3(dppp)_3(D)_7(CH_3C_6H_4NC)](BF_4)_2}$ was prepared in a manner analogous to that for **3** by using $[Ir_3(dppp)_3(D)_7](BF_4)_2$.[20] IR(KBr): $\nu(RN{=}C) = 2130$ cm^{-1} (s).

1-(2-Pyridyl)-2-(diphenylphosphino)ethane (PN) was prepared according to the method of Uhlig and Maaser.[21] The crude product was purified by using a silica gel chromatography column and eluted with diethyl ether. Evaporation of the ether left white crystals of the ligand, mp 58 °C. ^{31}P NMR: δ −15.7 (s, CH_2Cl_2); δ −14.3 (s, acetone). The mass spectrum of the PN ligand had a parent peak at *m/z* 291.

$\mathbf{[Ir(PN)(COD)]PF_6}$ $\mathbf{(4(PF_6))}$. A solution of $AgPF_6$ (365 mg, 1.44 mmol) in 5 mL of acetone was added to a stirred suspension of $[Ir(COD)Cl]_2$[22] (441 mg, 1.31 mmol of Ir) in 10 mL of acetone, giving an immediate white precipitate of AgCl. The slurry was stirred for 15 min and filtered over diatomaceous earth. To the stirred, yellow-orange filtrate was added a solution of PN (420 mg, 1.44 mmol) in 15 mL of isopropyl alcohol. The resulting red-orange solution was stirred for 15 min and concentrated in vacuo to a total volume of about 15 mL, during which time an orange powder precipitated from the solution. Recrystallization of this powder from acetone/diethyl ether gave red-orange crystals, yield 832 mg (86%). Anal. Calcd for $IrPNC_{27}H_{30}PF_6$: C, 44.02; H, 4.10; N, 1.90. Found: C, 44.09; H, 4.21; N, 1.95. ^{31}P NMR (acetone, 25 °C): δ 20.4 (s). ^1H NMR (acetone-d_6, 25 °C): δ 4.8 (broad, unresolved, diene protons). IR (KBr pellet): ν(py CN) = 1610 cm^{-1}.

$\mathbf{[Ir_3(PN)_3(H)_7](X)_2}$ $\mathbf{(5(X)_2, X = PF_6^-, BF_4^-)}$. In a typical synthesis, a suspension of crushed $[Ir(PN)(COD)]PF_6$ (335 mg, 0.46 mmol) in 5 mL of methanol was stirred under 1 atm of H_2 for 2 h. The initially orange-red solution turned yellow after 5 min, and after 10 min a yellow powder started precipitating from the solution. After 2 h all of the $[Ir(PN)(COD)]PF_6$ had been consumed, leaving a yellow powder and yellow mother liquor. The yellow powder was filtered and washed with Et_2O; yield 220 mg (80%). Crystals suitable for a single-crystal X-ray analysis were obtained by recrystallization from acetone/ethanol. Anal. Calcd for $Ir_3C_{57}H_{61}N_3P_5F_{12}$: C, 39.17; H, 3.52; N, 2.40. Found: C, 39.00; H, 3.68; N, 2.30. ^{31}P NMR (CH_2Cl_2, 25 °C): δ 16.9 (s). ^1H NMR (CD_2Cl_2, 25 °C, hydride region): δ −1.96 (quartet, $J = 47$ Hz, int = 1), −18.69 (d, $J = 12$ Hz, int = 3), −22.45 (d, $J = 26$ Hz, int = 3). IR (KBr): $\nu(IrH) = 2200$ (br), 1730 cm^{-1} (br); ν(py CN) = 1608 cm^{-1}. IR (CH_2Cl_2): $\nu(IrH) = 2190$ (br), 1758 cm^{-1} (br); ν(py CN) = 1609 cm^{-1}. IR (acetone): $\nu(IrH) = 2240$ (sh), 2160 cm^{-1} (br) (the use of acetone prevented the observation of the other $\nu(IrH)$ and ν(py CN) vibrations).

$\mathbf{[Ir_3(PN)_3(D)_7](PF_6)_2}$ was synthesized by the method used for the synthesis of **5**, except D_2 was used and MeOD was used as the solvent. IR (KBr): $\nu(IrD) = 1580$, 1250 cm^{-1} [$\nu(IrH)/\nu(IrD) = 1.39$, 1.38, respectively]. ^2D NMR (CH_2Cl_2): δ −18.6 (broad s, int = 4), −22.2 (broad s, int = 3).

X-ray Structure Determinations. Collection and Reduction of X-ray Data. A summary of crystal data is presented in Table I. A crystal of $[Ir_3(PN)_3(H)_7](PF_6)_2{\cdot}C_3H_6O$ ($\mathbf{5}(PF_6)_2{\cdot}C_3H_6O$) was sealed inside a 0.3-mm capillary tube filled with acetone/ethanol solution, since the crystals were found to slowly lose solvent of crystallization in the absence of the solvent mixture. In a similar manner, a crystal of $[Ir_3(dppp)_3(H)_7(CO)](BF_4)_2{\cdot}2C_2H_4Cl_2$ ($\mathbf{2}(BF_4)_2{\cdot}2C_2H_4Cl_2$) was sealed inside a capillary tube filled with 1,2-dichloroethane/heptane solution. The crystal classes and space groups were unambiguously determined by the Enraf-Nonius CAD4-SDP peak search, centering, and indexing programs and by a Delaunay reduction calculation.[23] The monoclinic space group $P2_1/c$ was chosen from the systematic absences observed during data collection for both compounds ($h0l$, $l = 2n + 1$; $0k0$, $k = 2n + 1$) and was verified by successful solution and refinement of the structures (vide infra). The intensities of three standard reflections were measured every 1.5 h of

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(20) $[Ir_3(dppp)_3(D)_7](BF_4)_2$ was synthesized in a manner analogous to that for **1**.[1] D_2 was bubbled through a MeOD solution of $[Ir(dppp)(COD)]BF_4$. $[Ir_2(dppp)_2(D)_5]BF_4$ was also produced in this reaction and separated from the trimer as previously reported for the hydrido analogues.[1] The analysis of $[Ir_3(dppp)_3(D)_7](BF_4)_2$ is as follows: Ir (KBr): $\nu(IrD)$ 1558 cm^{-1}. ^2D NMR (15.36 MHz, CH_2Cl_2, 25 °C): δ − 7.99 (d, $J_{trans\text{-}P\text{–}D} = 10$ Hz), −8.7 (quartet underlying peak at δ −7.99, $J_{trans\text{-}P\text{–}D} = 5$ Hz), −15.23 (broad s). Chemical shifts were referenced to the internal standard CD_2Cl_2 (δ 5.30).

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Table I. Summary of Crystal Data and Intensity Collection for $\mathbf{2}(BF_4)_2$ and $\mathbf{5}(PF_6)_2$

	$[Ir_3(dppp)_3(H)_7(CO)](BF_4)_2\cdot 2C_2H_4Cl_2$ ($\mathbf{2}(BF_4)_2\cdot 2C_2H_4Cl_2$)	$[Ir_3(PN)_3(H)_7](PF_6)_2\cdot C_3H_6O$ ($\mathbf{5}(PF_6)_2\cdot C_3H_6O$)
Crystal Parameters and Measurement of Intensity Data		
cryst syst	monoclinic	monoclinic
space group	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)
cell params		
T, °C	23	23
a, Å	13.460 (3)	11.510 (8)
b, Å	24.966 (7)	22.925 (4)
c, Å	26.31 (1)	25.024 (7)
β, deg	91.81 (3)	98.83 (5)
V, Å^3	8836 (8)	6525 (8)
Z	4	4
calcd density, g/cm^3	1.669	1.838
abs coeff, cm^{-1}	50.6	66.6
max, min, av trans factors	1.00, 0.82, 0.92	1.00, 0.59, 0.78
formula	$Ir_3C_{86}H_{93}B_2Cl_4F_8OP_6$	$Ir_3C_{60}H_{67}F_{12}ON_3P_5$
fw	2220.6	1805.7
diffractometer	CAD4	
radiation	Mo Kα (λ = 0.71069 Å), graphite monochromatized	
scan type; range (2θ), deg	ω–2θ; 0–46	ω–2θ; 0–50
no. of unique reflcns measd (region)	12245 ($+h,+k,\pm l$)	12066 ($+h,+k,\pm l$)
no. of obsd reflns[a]	7520 [$F_o^2 \geq 3\sigma(F_o^2)$]	8367 [$F_o^2 \geq 3\sigma(F_o^2)$]
Refinement by Full-Matrix Least Squares		
no. of params	496	438
R[b]	0.049	0.075
R_w[b]	0.064	0.087
GOF[b]	1.49	3.34
P[a]	0.06	0.03

[a] The intensity data were processed as described in: *CAD4 and* SDP-*PLUS User's Manual*; B. A. Frenz: College Station, TX, 1982. The net intensity $I = [K/\mathrm{NPI}](C - 2B)$, where K = 20.1166(attenuator factor), NPI = ratio of fastest possible scan rate to scan rate for the measurement, C = total count, and B = total background count. The standard deviation in the net intensity is given by $[\sigma(I)]^2 = (K/\mathrm{NPI})^2[C + 4B + (PI)^2]$, where P is a factor used to downweight intense reflections. The observed structure factor amplitude F_o is given by $F_o = (I/Lp)^{1/2}$, where Lp = Lorentz and polarization factors. The $\sigma(I)$'s were converted to the estimated errors in the relative structure factors $\sigma(F_o)$ by $\sigma(F_o) = {}^1/_2[\sigma(I)/I]F_o$. [b] The function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w = 1/[\sigma(F_o)]^2$. The unweighted and weighted residuals are defined as $R = \sum(||F_o| - |F_c||)/\sum|F_o|$ and $R_w = [(\sum w(|F_o| - |F_c|)^2)/(\sum w|F_o|^2)]^{1/2}$. The error is an observation of unit weight (GOF) is $[\sum w(|F_o| - |F_c|)^2/(\mathrm{NO} - \mathrm{NV})]^{1/2}$, where NO and NV are the numbers of observations and variables, respectively.

Table II. Positional Parameters and Their Estimated Standard Deviations for Core Atoms in $[Ir_3(dppp)_3(H)_7(CO)](BF_4)_2\cdot 2C_2H_4Cl_2$ ($\mathbf{2}(BF_4)_2\cdot 2C_2H_4Cl_2$)[a]

atom	x	y	z	B, Å^2
Ir1	0.28723 (4)	0.08382 (2)	0.29632 (2)	2.63 (1)
Ir2	0.20485 (4)	0.12034 (2)	0.18873 (2)	2.78 (1)
Ir3	0.29078 (4)	0.00859 (2)	0.22454 (2)	2.58 (1)
P11	0.3890 (3)	0.1456 (2)	0.3363 (2)	3.32 (9)
P12	0.1596 (3)	0.1086 (2)	0.3467 (2)	3.51 (9)
P21	0.1577 (3)	0.2102 (2)	0.1857 (2)	3.48 (9)
P22	0.0729 (3)	0.1035 (2)	0.1312 (2)	3.62 (9)
P31	0.3764 (3)	−0.0254 (2)	0.1579 (2)	3.06 (8)
P32	0.3272 (4)	−0.0642 (2)	0.2735 (2)	3.8 (1)
C	0.325 (1)	0.1287 (6)	0.1495 (6)	4.0 (4)
O	0.3956 (9)	0.1302 (5)	0.1302 (5)	5.4 (3)
C1	0.332 (1)	0.2095 (6)	0.3533 (6)	3.8 (3)*
C2	0.236 (1)	0.2030 (7)	0.3871 (7)	4.9 (4)*
C3	0.146 (1)	0.1812 (7)	0.3597 (6)	4.2 (3)*
C4	0.027 (1)	0.2193 (7)	0.1996 (7)	4.7 (4)*
C5	−0.049 (1)	0.1938 (7)	0.1610 (7)	5.3 (4)*
C6	−0.044 (1)	0.1339 (7)	0.1535 (7)	5.3 (4)*
C7	0.368 (1)	−0.0985 (6)	0.1504 (6)	3.6 (3)*
C8	0.402 (1)	−0.1305 (6)	0.1967 (6)	4.1 (3)*
C9	0.326 (1)	−0.1289 (7)	0.2396 (7)	4.6 (4)*

[a] Starred values are for atoms refined isotropically. Counterions, solvent molecules, and phenyl group positional parameters are provided in the supplementary material. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as ${}^4/_3[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$.

Table III. Positional Parameters and Their Estimated Standard Deviations for Core Atoms in $[Ir_3(PN)_3(H)_7](PF_6)_2\cdot C_3H_6O$ ($\mathbf{5}(PF_6)_2\cdot C_3H_6O$)[a]

atom	x	y	z	B, Å^2
Ir1	−0.11120 (6)	0.15045 (3)	0.18481 (3)	2.59 (1)
Ir2	0.04093 (6)	0.09454 (3)	0.12693 (2)	2.72 (1)
Ir3	0.01963 (6)	0.05840 (3)	0.22982 (2)	2.79 (1)
P1	−0.1335 (4)	0.2383 (2)	0.2191 (2)	3.2 (1)
P2	0.1790 (4)	0.1340 (2)	0.0855 (2)	3.6 (1)
P3	0.1608 (5)	0.0400 (2)	0.2983 (2)	3.5 (1)
N1	−0.237 (1)	0.1653 (6)	0.1164 (5)	3.0 (3)*
N2	0.070 (1)	0.0093 (6)	0.0992 (5)	2.9 (3)*
N3	−0.118 (1)	0.0326 (6)	0.2734 (6)	3.5 (3)*
C11	−0.228 (2)	0.2838 (9)	0.1711 (8)	4.6 (4)*
C12	−0.208 (2)	0.2715 (9)	0.1133 (8)	4.5 (4)*
C13	−0.267 (2)	0.2163 (9)	0.0896 (7)	4.3 (4)*
C14	−0.349 (2)	0.2190 (9)	0.0430 (8)	5.1 (5)*
C15	−0.405 (2)	0.171 (1)	0.0221 (9)	6.2 (6)*
C16	−0.383 (2)	0.117 (1)	0.0484 (9)	5.9 (5)*
C17	−0.299 (2)	0.1178 (9)	0.0949 (7)	4.0 (4)*
C21	0.252 (2)	0.0785 (9)	0.0502 (8)	5.0 (5)*
C22	0.274 (2)	0.024 (1)	0.0827 (9)	5.6 (5)*
C23	0.168 (2)	−0.0133 (9)	0.0846 (8)	4.4 (4)*
C24	0.170 (2)	−0.071 (1)	0.0688 (9)	6.0 (5)*
C25	0.079 (2)	−0.107 (1)	0.071 (1)	6.6 (6)*
C26	−0.024 (2)	−0.087 (1)	0.0861 (9)	5.3 (5)*
C27	−0.027 (2)	−0.0290 (9)	0.0988 (8)	4.3 (4)*
C31	0.099 (2)	0.0168 (8)	0.3581 (8)	4.3 (4)*
C32	−0.007 (2)	0.057 (1)	0.3634 (8)	5.1 (5)*
C33	−0.116 (2)	0.0402 (8)	0.3294 (7)	3.8 (4)*
C34	−0.219 (2)	0.0306 (9)	0.3496 (8)	4.9 (5)*
C35	−0.320 (2)	0.016 (1)	0.3170 (9)	6.2 (6)*
C36	−0.322 (2)	0.008 (1)	0.2624 (9)	5.6 (5)*
C37	−0.217 (2)	0.0183 (9)	0.2435 (8)	4.4 (4)*

[a] See footnote *a* of Table II.

X-ray exposure time, and the intensities were found to decrease slightly for $\mathbf{5}(PF_6)_2$, but no decay was noted for $\mathbf{2}(BF_4)_2$. This decay was corrected by use of the program CHORTA with maximum and minimum correction factors of 1.33 and 0.98.[24] The data were corrected for Lorentz, polarization, and background effects. Empirical absorption corrections were applied for both compounds by use of ψ-scan data and the program EAC.[23]

Solution and Refinement of the Structures. The structures were solved by conventional heavy-atom techniques. The Ir atoms were located by Patterson syntheses. Full-matrix least-squares refinement and difference Fourier calculations were used to locate all remaining non-hydrogen atoms. The atomic scattering factors were taken from the usual tabulation,[24] and the effects of anomalous dispersion were included in F_c by using Cromer and Ibers' values of $\Delta f'$ and $\Delta f''$.[25] For $\mathbf{5}(PF_6)_2$, the Ir, P, and F atoms were refined with anisotropic thermal parameters. The positions of the hydrogen atoms from the PN ligands were calculated with use of the program HYDRO[23] (C–H distance set at 0.95 Å) and included in the structure factor calculations but were not refined. The final difference Fourier map did not reveal significant residual electron density. The Ir hydrides and acetone (solvate) hydrogen atoms were not located in the final difference Fourier maps and were not included. For $\mathbf{2}(BF_4)_2$, the Ir, P, and carbonyl atoms were refined with anisotropic thermal parameters. Hydrogen atoms were not located in the final difference Fourier map and therefore were not included. The final positional and thermal parameters of the refined atoms within the coordination cores are given in Tables II and III. ORTEP drawings of the cations including the labeling schemes and selected distances and angles are shown in Figures 1 and 3. A complete listing of thermal parameters, positional parameters, calculated positions for the hydrogen atoms, distances, angles, least-squares planes, and structure factor amplitudes are included as supplementary material.[26]

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(24) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, Table 2.2.4.

(25) Cromer, D. T. *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, Table 2.3.1.

(26) See paragraph at the end of the paper regarding supplementary material.

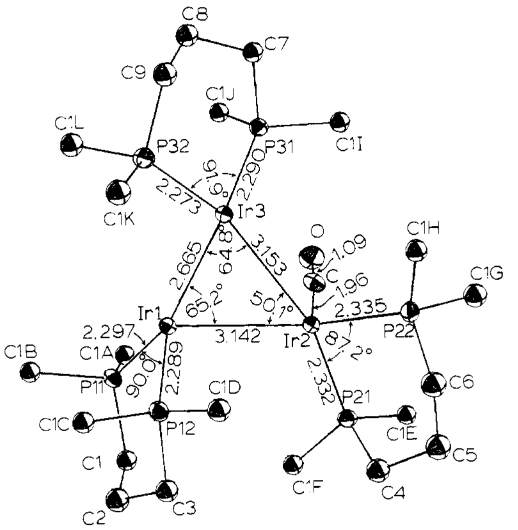


Figure 1. ORTEP drawing of the coordination core of $2(BF_4)_2$ with selected bond distances. Ellipsoids are drawn with 50% probability boundaries. Phenyl rings have been omitted for clarity. Selected angles (deg) are as follows: Ir2–Ir1–Ir3, 65.16 (2); Ir1–Ir2–Ir3, 50.09 (1); Ir1–Ir3–Ir2, 64.75 (2); Ir2–Ir1–P11, 113.98 (9); Ir2–Ir1–P12, 101.15 (9); Ir3–Ir1–P11, 140.75 (9); Ir3–Ir1–P12, 129.20 (9); P11–Ir1–P12, 90.0 (1); Ir1–Ir2–P21, 113.43 (9); Ir1–Ir2–P22, 140.46 (9); Ir1–Ir2–C, 103.4 (4); Ir3–Ir2–P21, 163.39 (9); Ir3–Ir2–P22, 107.39 (9); Ir3–Ir2–C, 87.1 (4): P21–Ir2–P22, 87.2 (1); P21–Ir2–C, 96.2 (4); P22–Ir2–C, 107.6 (4); Ir2–C–O, 174 (1); Ir1–Ir3–P31, 145.47 (9); Ir1–Ir3–P32, 99.82 (9); Ir2–Ir3–P31, 106.73 (8); Ir2–Ir3–P32, 161.40 (9); P31–Ir3–P32, 91.9 (1). Esd's in the last significant figure for Ir–Ir, Ir–P, Ir–C, and C–O distances are 1, 3, 2, and 2, respectively.

Results and Discussion

$[Ir_3(dppp)_3(H)_7(CO)](BF_4)_2$ ($2(BF_4)_2$) was prepared in good yield upon the addition of CO to $[Ir_3(dppp)_3(H)_7](BF_4)_2$ ($1(BF_4)_2$) in CH_2Cl_2 solution under 40 psig of CO followed by recrystallization from $C_2H_4Cl_2$/heptane. A single-crystal X-ray diffraction analysis of **2** was carried out in order to determine the solid-state structure of this analogue of the previously observed solvated C_1 isomer of **1**.[1] The structure of the coordination core of the dication **2** is shown in Figure 1, along with distances and angles. The structure consisted of well-separated dications, BF_4^- anions, and two $C_2H_4Cl_2$ solvate molecules, with no unusually short intermolecular contacts. The charge of the dication was confirmed by the location and refinement of the two tetrafluoroborate anions.

The molecular structure of the dication consists of a bilateral triangle of three iridium atoms and a carbonyl at the vertex with a dihedral angle of 74.6° between the planes formed by [Ir1–Ir2–C] and the three Ir atoms. The Ir–Ir separations are 3.142 (1), 3.153 (1), and 2.665 (1) Å, and the triangle vertex angles are 50.09 (1), 65.16 (2), and 64.75 (2)°. Each iridium atom has a chelated dppp ligand, similar to the case for **1**.[1] The overall geometry and stereochemistry of **2** can best be appreciated by a consideration of the dihedral angles between planes. The planes formed by the IrPP chelate rings [Ir1–P11–P12], [Ir2–P21–P22], and [Ir3–P31–P32] have dihedral angles of 83.2, 35.9, and 35.9°, respectively, with the plane of the Ir_3 triangle.

The hydride ligands were not located by difference Fourier analysis, but their positions were inferred from structural and NMR data (vide infra). The M–M–P angles, α, have been previously used to establish whether a trans P–M–H hydride ligand is bridging or terminal, as was discussed in detail in the structural analysis of **1**.[1] In **2** the two Ir–P vectors (Ir1–P11 and Ir3–P31) intersect at a position that is located approximately equidistant from Ir1 and Ir3, is on the opposite side of the Ir_3 triangular plane from the carbonyl, and is about 1.0 Å above the plane. The placement of the doubly bridging hydrido ligand H2 at this position is supported by ^1H NMR data (vide infra). The average value of the α angles (Ir3–Ir1–P11 and Ir1–Ir3–P31) is 143.1° and is nearly the same as the average α value (143.5°) of the starting trimer **1**, which has an analogous structure with bridging hydrides.[1]

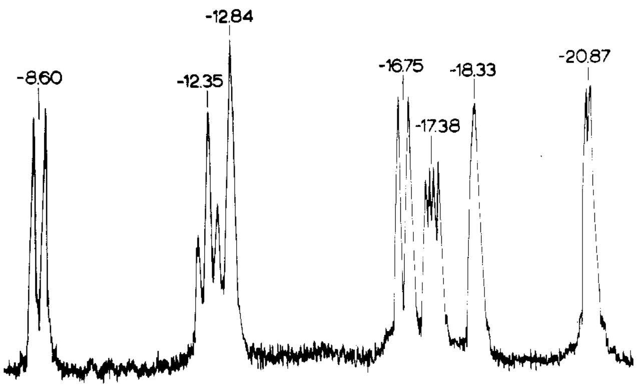
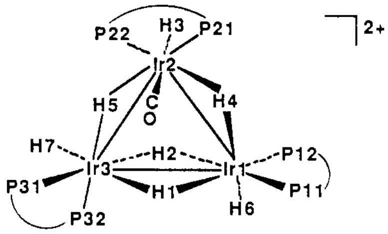


Figure 2. ^1H NMR spectrum of $[Ir_3(dppp)_3(H)_7(CO)](BF_4)_2$ in the hydride region recorded with acetone-d_6 as solvent at 25 °C.

Note that the Ir1–P11 and Ir3–P31 vectors are nearly coplanar, with a dihedral angle between the [Ir1–Ir3–P11] and [Ir1–Ir3–P31] planes of 15.2°. This same method can be applied to locate the other doubly bridging hydrido ligand, H5, and similar structural arguments can be applied to locate the remaining hydride ligands with NMR results that are entirely consistent with the assignments shown in the drawing of **2** (vide infra). There is also a terminal hydride on Ir2 that is trans to the carbonyl ligand. The Ir2–C distance of 1.96 (2) Å is indicative of this since it is slightly long but is within the observed range (1.85–1.98 Å) for iridium–carbonyl bonds that are trans to hydrides.[27-29]

The assignment of the bridging hydrides is also consistent with the Ir–Ir separations. In **2**, the average of the Ir–Ir bonds bridged by only one hydride is 3.148 (1) Å. In **1**, each Ir–Ir bond is bridged by one hydride ligand and a triply bridging hydride is equally shared by all three Ir atoms. Therefore, the average Ir–Ir separation in **1** is smaller and equals 2.772 (1) Å.[1] In the dimeric species, $[Ir_2(dppp)_2(H)_5]^+$, the Ir–Ir bond is bridged by three hydrides and separated by a distance of 2.514 (1) Å.[1] The Ir1–Ir3 bond (2.665 (1) Å) in **2** is bridged by two hydrides and is consistent with this observed trend in bond lengths.

The above qualitative analysis suggests that **2** possesses four doubly bridging hydrides trans to Ir–P bonds. By close examination of the X-ray and the ^1H NMR results (vide infra), the structure is proposed. The structure has no symmetry and is designated as C_1. The Ir(III) coordination cores in **2** are six-coordinate, IrP_2H_4 or $IrP_2(CO)H_3$, and probably are distorted octahedral with no unusually short contacts between Ir and phenyl C atoms (the shortest distance is 3.40 Å for Ir3–C1K).



2

The P21–Ir2–P22 chelate bite angle (87.2 (1)°) is small compared to the other two P–Ir–P bite angles (average 91.0 (1)°) and the range (87.9–93.4°) observed in other dppp complexes.[1,30-33] The P21- and P22–Ir distances (average 2.334 (3) Å) are longer than the other P–Ir distances (average 2.287 (3) Å) in **2**. This is presumably due to a combination of steric and electronic effects

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resulting from the carbonyl group on Ir2 and is consistent with the observation that large M–L distances usually result in small chelate bite angles. Within the dppp ligands, distances and angles are similar to those found in **1** and are within the range observed for other dppp complexes.[1,30–32] The tetrafluoroborate anions and $C_2H_4Cl_2$ solvate molecules showed some signs of disorder; however, reasonable distances and angles were obtained.

The ^1H NMR spectra of **2**$(BF_4)_2$ were recorded at 25 and −70 °C with use of acetone-d_6 as solvent. The spectrum recorded at 25 °C is reproduced in Figure 2 and, except for minor peak positional shifts, is identical with the −70 °C spectrum. This is in contrast to the case for complex **1**, which showed dynamic behavior in solution. The spectrum of **2** was assigned by analogy to the chemical shifts and coupling constants of the similar polyhydrido iridium diphosphine clusters. Bridging hydrides usually resonate at lower field (δ −6 to −9) than terminal hydrides (δ −20 to −24) for these hydrido iridium diphosphine complexes, which is opposite the observed trend in hydrido carbonyl cluster complexes.[34] Since **2** contains a carbonyl group, a compromised effect was expected and seen; i.e., the hydrides close to the carbonyl behaved similarly to those in carbonyl clusters, whereas the hydrides far from the CO behaved similarly to those in diphosphine clusters. The doublet at δ −8.60 (J = 70 Hz) is assigned to the bridging hydride H1, which is trans to a single phosphorus atom, P12. The triplet at δ −12.35 (J = 59 Hz) results from the bridging hydride H2, which is trans to two equivalent phosphorus atoms P11 and P31. The broad singlet at δ −18.33 and multiplet at δ −20.87 are assigned to the two terminal hydrides on Ir1 and Ir3. The assignments thus far are analgous to those of complex **1** in CD_3CN (C_1 isomer).[1] The remaining broad singlet at δ −12.84 results from H3, which is trans to the carbonyl group. This chemical shift is consistent with a metal hydride trans to a high trans-influencing ligand such as CO, and the assignment was verified by comparison of the NMR data of **2** with those of the acetonitrile solvate of **1**.[1] The doublet at δ −16.75 (J = 68 Hz) results from H4, which is trans to a single phosphorus atom, P22. The doublet of doublets resonance at δ −17.38 (J = 54 and 26 Hz) results from H5, which is roughly trans to two inequivalent phosphines, P21 and P32. The assignment of the signals due to H3, H4, and H5 is consistent with the general trend observed for hydrido carbonyl clusters.

The existence of a hydride trans to a carbonyl was further supported by IR spectroscopy. The CO stretching frequencies in **2** shifted a few wavenumbers higher for the deuterium analogue of **2**, from 1998 (s) and 1960 cm^{-1} (sh) to 2005 (s) and 1989 cm^{-1} (sh). The ^{31}P NMR spectrum of **2**$(BF_4)_2$ recorded at 35 °C with use of CH_2Cl_2 as solvent was complex, so an individual assignment of peaks was not attempted. However, the spectrum consisted of five separate peaks with intensities of ca. 1:1:1:1:2 and is consistent with a complex of C_1 symmetry, which would give rise to six nonequivalent P atoms.

$[Ir_3(dppp)_3(H)_7(CH_3C_6H_4NC)](BF_4)_2$ (3$(BF_4)_2$) was prepared by the reaction of **1** with *p*-tolyl isocyanide in CH_2Cl_2 solution and characterized by IR and ^{31}P and ^1H NMR spectroscopy. The ^1H NMR spectrum of **3** was recorded at 25 °C with use of acetone-d_6 as solvent and was very similar to that of **2** with analogous assignments. The only noticeable difference was a shift of ca. 1.6 ppm in the resonance due to the hydride trans to the coordinated *p*-tolyl isocyanide or CO. All of the other resonances shifted by less than 0.5 ppm. Also, the resonance due to H5, which was a doublet of doublets (J = 54 and 26 Hz) in the CO adduct, became a triplet (J = 45 Hz) in **3**. The ^{31}P NMR spectrum of **3** was also very similar to that of **2** and was indicative of a complex with six nonequivalent phosphorus atoms. In the IR spectrum (KBr), the terminal IrH stretches obscured the NC stretch of the coordinated *p*-tolyl isocyanide in **3**, so the deuterium analogue was prepared, in which ν(RN=C) was found to be at 2130 cm^{-1}.

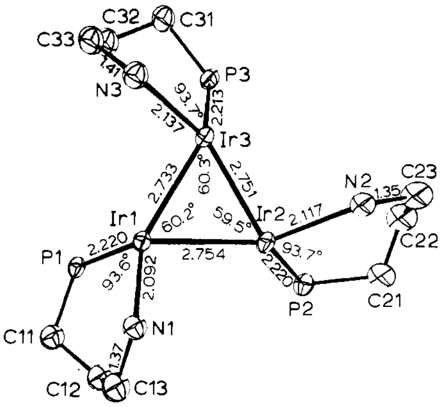

Figure 3. ORTEP drawing of the coordination core of **5**$(PF_6)_2$ with selected distances. Ellipsoids are drawn with 50% probability boundaries. Phenyl rings have been omitted for clarity. Selected angles (deg) are as follows: Ir2–Ir1–Ir3, 60.19 (1); Ir1–Ir2–Ir3, 59.52 (1); Ir1–Ir3–Ir2, 60.29 (1); Ir2–Ir1–P1, 138.27 (7); Ir3–Ir1–P1, 129.09 (7); Ir1–Ir2–P2, 127.94 (7); Ir3–Ir2–P2, 137.16 (8); Ir1–Ir3–P3, 139.36 (8); Ir2–Ir3–P3, 128.43 (7); Ir2–Ir1–N1, 93.5 (2); Ir3–Ir1–N1, 136.9 (2); Ir1–Ir2–N2, 138.2 (2); Ir3–Ir2–N2, 94.0 (2); Ir1–Ir3–N3, 91.1 (2); Ir2–Ir3–N3, 137.7 (2); P1–Ir1–N1, 93.6 (2); P2–Ir2–N2, 93.7 (2); P3–Ir3–N3, 93.7 (2). Esd's in the last significant figure for Ir–Ir, Ir–P, Ir–N, and N–C distances are 1, 3, 8, and 1, respectively.

$[Ir(PN)(COD)]PF_6$ (4(PF_6)) was synthesized in a manner analogous to the preparation of the related $[Ir(PP)(COD)]^+$ complexes.[1] Thus, acetone solutions of $[Ir(COD)((CH_3)_2CO)_2]^+$ reacted immediately with 1 equiv of PN to form complex **4** in good yield, which was characterized by IR and ^1H and ^{31}P NMR spectroscopy. The ^{31}P NMR spectrum of **4**, recorded with acetone as solvent, consisted of a singlet at δ 20.4. This resonance shifted 24.7 ppm relative to the free PN ligand (δ −14.3, acetone). In the ^1H NMR spectrum of **4** with use of acetone-d_6 as solvent the alkene hydrogens of coordinated COD were detected as a broad unresolved resonance at δ 4.8. Similar broad resonances have been observed in the ^1H NMR spectra of other $[Ir(PP)(COD)]^+$ complexes synthesized in this lab.[35,36]

Because PN and related PN donor ligands have been shown to function as both bidentate and phosphorus-bound monodentate ligands, it is important to carefully examine whether the N atom is coordinated. The highest frequency deformation mode of the pyridyl ring, ν(py CN), has proven to be a useful indicator for the coordination of the N atom in complexes that contain a pyridyl ring.[37–39] Relative to the signal for the free ligand, ν(py CN) shifts ca. 15–25 cm^{-1} to higher frequency upon coordination of the N atom of the pyridyl ring. The observation of ν(py CN) at 1610 cm^{-1} in the KBr infrared spectrum of **4** corresponds to a shift of 21 cm^{-1} relative to the signal for the free PN ligand and confirms that the PN ligand is bidentate (ν(py CN) = 1589 cm^{-1} for free PN). These data are consistent with an approximately square planar 16e Ir(I) cationic complex in which both the P and N atoms of the PN ligand are coordinated.

Complexes of the type $[Ir(PP)(COD)]^+$ have been shown to be very active homogeneous hydrogenation catalysts.[2] Although the activity of **4** as a hydrogenation catalyst was not investigated, **4** was found to react very rapidly with 1 atm of H_2 at 25 °C in methanol solution. This reaction led to the formation of the polyhydrido cluster $[Ir_3(PN)_3(H)_7]^{2+}$ (**5**) in good yield.

$[Ir_3(PN)_3(H)_7](PF_6)_2\cdot C_3H_6O$ (5$(PF_6)_2\cdot C_3H_6O$) was characterized by single-crystal X-ray analysis. An ORTEP drawing of the coordination core with selected distances and angles is shown in Figure 3. The structure consisted of well-separated dications, PF_6^- anions, and an acetone solvate molecule, with no unusually short intermolecular contacts. The charge of the dication was confirmed by the location and successful refinement of two hexafluorophosphate anions.

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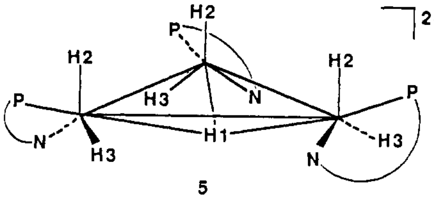
The structure of the dication resembles those of the two previously reported Ir trimers $[Ir_3(dppp)_3(H)_7]^{2+}$ (**1**)[1] and $[Ir_3(PCy_3)(C_5H_5N)_3(H)_7]^{2+}$ (**6**, PCy_3 = tricyclohexylphosphine)[2,40] and consists of an equilateral triangle of three Ir atoms with one PN ligand chelated to each Ir atom. The Ir–Ir distances of 2.754 (1), 2.733 (1), and 2.751 (1) Å are consistent with the formation of single bonds[41] and are similar to the distances found in complexes **1** and **6**. The triangle vertex angles are 60.19 (1), 59.52 (1), and 60.29 (1)°. The dication has approximately C_3 symmetry, and the N and P atoms lie on opposite sides of the Ir triangle. A least-squares plane calculation for the Ir, P, and N atoms shows that the three planes defined by [P1–P2–P3], [Ir1–Ir2–Ir3], and [N1–N2–N3] are nearly parallel. The largest dihedral angle between these planes is 4.7°. The three planes defined by [P*n*–Ir*n*–N*n*] (*n* = 1–3) are tilted 50.0, 54.9, and 51.6° relative to the plane of Ir atoms. A similar stereochemistry was observed for complexes **1** and **6**.[1,40]

The hydride ligands were not located by difference Fourier analysis, but their positions were inferred. ^1H NMR data indicated that one hydride, H1, is trans to three equivalent phosphorus atoms (δ −1.96, quartet, J = 47 Hz, int = 1). Inspection of Figure 3 shows that the three Ir–P vectors intersect at a point approximately above the center of the Ir triangular plane on the side opposite the P atoms. The placement of a triply bridging hydride ligand at this position is stereochemically reasonable and consistent with the ^1H NMR data. Similar arguments have been used for the placement of the triply bridging hydride in **1** and **6**.[1,2,40] It has been suggested that the bonding of the triply bridging hydride in these complexes is best considered a four-center, two-electron interaction.[1,2,40] Two nonequivalent terminal hydrides are believed to be bound to each Ir atom on the basis of IR and ^1H NMR evidence (vide infra). A similar assignment was proposed for **6**;[2,40] however, **1** is believed to contain three doubly bridging hydrides and three terminal hydrides.[1] In **1** a significant structural trans influence was observed for the phosphorus atoms trans to the doubly bridging hydrides compared to the influence for those trans to the triply bridging hydride. The Ir–N distances observed in **5** are not unusually long (vide infra) and are therefore consistent with a structure that does not have doubly bridging hydrides trans to the N atoms.

The Ir–P distances range from 2.213 (3) to 2.220 (3) Å and average 2.218 (3) Å. These distances are short compared to the analogous distances in **1** and **6** (average 2.243 and 2.286 Å, respectively). This is probably due to the reduced steric crowding in **5** relative to that in **1** and **6** and the different electronic requirement of PN as compared to that of dppp and PCy_3. The weak structural trans influence of a triply bridging hydride accounts for the short Ir–P distances in these three complexes.[1] The Ir–N distances range from 2.092 (8) to 2.137 (8) Å and average 2.115 (8) Å and are similar to those reported for **6** (average 2.139 Å).[40] The PN "bite angles" are identical within experimental error (93.7 (2)°) and are slightly larger than those observed for other Rh and Ir PN complexes (83.4–91.1°) synthesized in our lab.[42] A comparison of these PN "bite angles" with typical bite angles of diphosphine ligands reveals that PN is a very flexible ligand and most closely resembles the ligand dppp (range 87.9–93.4°).[1,30–33] The latter observation is not surprising since both ligands have a three-carbon backbone. It is interesting to note that the formation of the trimeric cluster **1** and the dimeric species $[Ir_2(dppp)_2(H)_5]^+$ has been correlated with the P–Ir–P bite angle: ligands with large bite angles (dppb, dppp) and monodentate phosphines have been shown to favor the dimer, while ligands with smaller bite angles (dppp, dppe) favor formation of the trimer.[1,35] The mixed P/N donor systems have not been studied as extensively; however, only clusters similar to the trimer **1** were detected when monodentate P and N donor ligands were used.[2,40,43] This may be due to steric as well as electronic factors since the presence of smaller pyridine ligands may favor the formation of larger clusters.

Within the PN ligands the distances and angles are not unusual and are similar to those in other Ir and Rh PN complexes.[42] The phenyl and pyridyl rings are all planar within experimental error. Some of the distances and angles within the phenyl and pyridyl rings (range 1.24 (2)–1.54 (2) Å) deviate from accepted values; however, such deviations are not unusual in the X-ray structures of large clusters that contain several heavy atoms. The two hexafluorophosphate anions and the acetone solvate molecule showed some signs of disorder; however, reasonable distances and angles were obtained.

The IR and ^{31}P and ^1H NMR spectra of **5** in CH_2Cl_2 solution were all consistent with the solid-state structure of **5** (vide supra) and resembled the spectroscopic data of **6** very closely.[40] The stereochemical arrangement of hydrides proposed for **5** is



5

In support of the proposed structure, the ^1H NMR spectrum of **5** in CH_2Cl_2 solution showed three hydride resonances of relative intensities of 1:3:3. The triply bridging hydride, H1, assigned to the quartet at δ −1.96 is coupled to the three equivalent trans phosphorus atoms. The P–H coupling observed for H1, 47 Hz, is within the range expected for a triply bridging hydride trans to three phosphorus atoms.[1,40] Similar quartet resonances were observed for **1** and **6**.[1,40] Two doublets at δ −18.69 and −22.45 (J = 12 and 26 Hz, respectively) resulted from the equivalent sets of terminal hydrides, H2 and H3, which are cis to the phosphorus atom of the PN ligand. These signals displayed normal cis P–H coupling (10–30 Hz).[34,44] Individual assignments for H2 and H3, however, were not made. The ^{31}P NMR spectrum of **5** with CH_2Cl_2 as solvent consisted of a singlet at δ 16.9, which is consistent with the C_3 symmetry of **5**.

IR spectroscopic data further supported a terminal hydride formulation of H2 and H3, although the exact implications of these data are not well-understood. Two IrH stretches characteristic of a terminal hydride were observed in the infrared spectrum of **5** at 2200 and 1730 cm^{-1} (KBr). This assignment was verified by the observation of ν(IrD) at 1580 and 1250 cm^{-1} (ν(IrH)/ν(IrD) = 1.39 and 1.38, respectively) in the deuteriated analogue of **5** (vide infra). For complex **6**, similar IrH stretches were observed at 2240 and 1770 cm^{-1}. The absorption at 1730 cm^{-1} is unusually low for most terminal iridium hydrides (2250–1900 cm^{-1}) but falls within the range observed for a hydride trans to another hydride (1650–1750 cm^{-1}).[34,44] These data suggest that one set of the Ir–H bonds is weaker than the other set; however, the reason for this effect is not clearly understood. It is possible that the hydrides H2 and H3 are mutually trans, and one of the hydrides experiences a much larger trans effect than the other. An alternative explanation is that H2 or H3 interacts weakly with an adjacent Ir atom and this shifts ν(IrH) to a lower energy. Such an interaction must be weak since X-ray and ^1H NMR data were not consistent with a bridging hydride formulation (vide supra). This interaction is plausible, however, since **1** contains a set of three doubly bridging hydrides.[1] It is also possible that a second isomer of **5** gives rise to the band at 1730 cm^{-1}. This is a less likely alternative since the IR spectra of **5** in CH_2Cl_2 and KBr were essentially the same, and no such isomer, or fluxional behavior, was observed in variable-temperature (−50 to +25 °C) ^1H NMR

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studies of **5** in CD_2Cl_2 solution. The ^1H NMR spectra of **5** with acetone-d_6 as solvent were invariant over the temperature range of −85 to +25 °C and were similar to that obtained in CD_2Cl_2, with only minor shifts in peak positions.

The ^1H NMR spectrum of **5** with CD_3CN as solvent at 25 °C was complex and provided evidence for a C_1 isomer of **5** with no detectable resonances due to the C_3isomer. The presence of a triplet at δ −5.85 (J_{P-H} = 72 Hz) and absence of the quartet at δ −1.96 due to H1 are consistent with the presence of a doubly bridging hydride that is trans to two phosphorus atoms and support the presence of an acetonitrile adduct of **5**. There were also large resonances between −20 and −26 ppm that may be due to the six nonequivalent terminal hydrides expected in a C_1 isomer; however, the spectrum was very complex possibly due to the presence of other hydride species. Therefore, the resonances were not assigned.

Since complex **5** is believed to contain two sets of terminal hydrides, the Ir atoms are coordinatively unsaturated relative to the Ir atoms in complex **1**. In light of the reactivity of **1** with coordinating solvents and two-electron donors, it is not surprising that **5** reacts with acetontrile. It was similarly expected that **5** would form an adduct with acetone; however, no conclusive evidence for such an adduct was obtained.

The deuterium analogue of **5** was synthesized in a manner analogous to that for **5**, with D_2 and CH_3OD as solvent. Attempts to synthesize this with D_2 and CH_3OH as solvent were unsuccessful and resulted only in the formation of **5**. Furthermore, refluxing **5** in CH_3OD did not result in H/D exchange as determined by IR spectroscopy. Similar results were observed for **1** and its deuterium analogue.[20,35] These results imply that one of the precursors to **5** undergoes H/D exchange with CH_3OD. For complex **1**, it was proposed that the intermediate *cis*-$[Ir(dppp)(H)_2(solvent)_2]^+$ underwent H/D exchange with protic solvents such as CH_3OD. This intermediate was detected in ^1H NMR studies of the hydrogenation of $[Ir(dppp)(COD)]^+$ in acetone solution.[45] It is likely that a similar hydride species, *cis*-$[Ir(PN)(H)_2(solvent)_2]^+$, also undergoes H/D exchange with CH_3OD; however, no attempts to identify such an intermediate have been carried out for this system.

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Registry No. **1**, 73178-86-6; **2**$(BF_4)_2$, 112021-56-4; **2**$(BF_4)_2 \cdot 2C_2H_4Cl_2$, 112067-95-5; **3**$(BF_4)_2$, 112021-52-0; **4**$(PF_6)$, 112021-45-1; **5**$(PF_6)_2$, 112021-47-3; **5**$(PF_6)_2 \cdot C_6H_6O$, 112068-61-8; **5**$(BF_4)_2$, 112021-48-4; $[Ir_3(dppp)_3(D)_7(CO)](BF_4)_2$, 112021-58-6; $[Ir_3(dppp)_3(D)_7(CH_3C_6H_4NC)](BF_4)_2$, 112021-54-2; $[Ir(COD)Cl]_2$, 12112-67-3; $[Ir_3(PN)_3(D)_7](PF_6)_2$, 112021-50-8.

Supplementary Material Available: ORTEP drawings of **2** and **5** and listings of distances and angles, general temperature factor expressions, final positional and thermal parameters for all atoms including counterions and solvate molecules, calculated hydrogen atom positions, and least-squares planes (28 pages); listings of observed and calculated structure factor amplitudes (70 pages). Ordering information is given on any current masthead page.

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[45] H_2 was bubbled through an acetone solution of $[Ir(dppp)(COD)]^+$ in an NMR tube at −78 °C, resulting in a color change from burgundy to yellow indicative of the intermediate *cis*-$[Ir(H)_2(dppp)(COD)]^+$. ^1H NMR (acetone-d_6, −70 °C, 270 MHz): δ −9.80 (d of d, J = 85 and 10 Hz), −12.5 (t, J = 14 Hz). ^{31}P NMR: (CH_2Cl_2, −74 °C, 40.5 MHz): δ −14.07 (d, J = 31 Hz), −29.05 (d of d, J = 31 and 20 Hz). This solution was then warmed to 25 °C for ca. 3 min and shown to contain, as one of the major products, *cis*-$[Ir(H)_2(dppp)(solvent)_2]^+$. ^1H NMR (acetone-d_6, 25 °C, 270 MHz): δ −25.14 (t, J = 21 Hz). Other resonances observed in this reaction mixture were not identified but probably resulted from species in which COD was partially hydrogenated.

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Synthesis and Spectroscopic and Redox Properties of Binuclear Copper(II) Ketimine Schiff-Base Complexes. Further Studies of a Novel Class of π-Molecular Complexes Derived from Binuclear Copper(II) Complexes

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The preparation, spectral properties, and redox characteristics of a series of copper(II) Schiff-base complexes are reported. The series consists of dinuclear copper(II) complexes of the 2,2-dimethyl-7-((4-X-phenyl)imino)-3,5-octanedionato ligand where X = OCH_3, CH_3, H, Cl, Br, or NO_2 and the ligand 2,2-dimethyl-7-(X-imino)-3,5-octanedionato where X = methyl, ethyl, *n*-propyl, or *n*-butyl. A Hammett plot, for the former, of $E_{1/2}$ vs $2\sigma_p$ is linear and has a slope of 0.08. The complexes are rigorously diamagnetic at room temperature, which allows ^1H NMR data to be obtained. Unusual chemical shifts are observed due to anisotropy generated by the aromatic ketimine substituent and the presence of the copper(II) center. The structures of bis[2,2-dimethyl-7-(ethylimino)-3,5-octanedionato]dicopper(II)–$^1/_2$-benzene, $Cu_2(PAAet)_2 \cdot {}^1/_2C_6H_6$, and bis[2,2-dimethyl-7-(*n*-propylimino)-3,5-octanedionato]dicopper(II), $Cu_2(PAApr)_2$, have been determined by X-ray diffraction. The former is composed of stacks of benzene molecules sandwiched between the copper complexes in an ADAADA... pattern. Crystal data are as follows: $P\bar{1}$; $a = 9.438$ (4), $b = 13.323$ (2), $c = 11.384$ (1) Å; $\alpha = 75.68$ (1), $\beta = 89.68$ (2), $\gamma = 82.34$ (2)°; $Z = 2$; $R = 0.039$ and $R_w = 0.054$ for 3824 observed reflections. $Cu_2(PAApr)_2$ consists of the nonsolvated molecule centered on an inversion center in the space group $P2_1/c$. Crystal data are as follows: $a = 11.277$ (6), $b = 6.249$ (1), $c = 19.237$ (3) Å; $\beta = 94.47$ (3)°; $Z = 2$; $R = 0.030$ and $R_w = 0.038$ for 1771 observed reflections. The structural parameters for these compounds are compared with those of the more highly solvated molecules $Cu_2(PAAan)_2 \cdot C_6H_6$ and $Cu_2(PAApnan)_2 \cdot 2C_6H_6$ and are discussed in light of a π-molecular interaction between solvent and complex.

Introduction

An important development in the field of coordination chemistry has been the design and synthesis of ligands capable of binding two or more transition-metal ions. Examples of such ligand systems include monocyclic[1] and bicyclic[2] hexaamines, cyclic[3] and acyclic[4] Schiff bases, polycyclic "cryptands",[5] "earmuffs",[6] and "wishbones",[7] "face-to-face",[8] "capped",[9] and "crowned"[10] por-

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