Organometallics **1991**, *10*, 513–516

purification by silica gel chromatography, 131 mg (63%) of deuterated indanone **13**.

13: colorless crystals from hexane–benzene; ^{1}H NMR (360 MHz, $CDCl_3$) δ 3.23 and 3.65 (br s, br s, 0.62 H, CHH), 7.17–7.34 (m, 5 H, Ph), 7.42, 7.53, 7.65, 7.81 (t, d, t, d, 4 H, arom); MS *m/z* 211, 210, 209.

Registry No. **1a**, 501-65-5; **1b**, 14309-60-5; **1c**, 3287-02-3; **1d**, 7380-78-1; **1e**, 5172-02-1; **1f**, 13343-79-8; **1g**, 673-32-5; **1h**, 19339-46-9; **2a**, 16619-12-8; **2b**, 117482-13-0; **2c**, 117482-15-2; **2d**, 108840-75-1; **2e**, 23909-34-4; **3**, 7317-52-4; **4**, 103-29-7; **5b**, 117482-14-1; **5c**, 784-75-8; **5d**, 1086-43-7; **5e**, 14087-87-7; **6f**, 117482-16-3; **6g**, 17496-14-9; **7**, 131588-13-1; **8**, 1083-56-3; **9**, 131567-54-9; **10**, 131567-55-0; **11**, 39253-52-6; **12**, 19096-31-2; $Co_2(CO)_8$, 10210-68-1; Ph_3P, 603-35-0; $[Co(CO)_3(PBu_3)]_2$, 14911-28-5; HC≡CH, 74-86-2; PPh_2Me, 1486-28-8; $PPhMe_2$, 672-66-2; PBu_3, 998-40-3; hexadeuteriobenzene, 1076-43-3; pentadeuteriophenyl iodide, 7379-67-1; 2-bromo-2-phenylindan-1-one, 5728-94-9.

Notes

Heterobimetallic Complexes Derived from $[(\eta^5\text{-}C_5H_5)FeCl(CH_3N(PF_2)_2)_2]$. Crystal and Molecular Structure of $[(\eta^5\text{-}C_5H_5)Fe(\mu\text{-}CH_3N(PF_2)_2)_2IrCl_2(P(CH_3)_2C_6H_5)]$

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Summary: The reaction of $[(\eta^5\text{-}C_5H_5)FeCl(CH_3N(PF_2)_2)_2]$ with $[Rh_2Cl_2(CO)_4]$ and $[IrCl(CO)(P(CH_3)_2C_6H_5)_2]$ forms $[(\eta^5\text{-}C_5H_5)Fe(\mu\text{-}CH_3N(PF_2)_2)_2RhCl_2]$ and $[(\eta^5\text{-}C_5H_5)Fe(\mu\text{-}CH_3N(PF_2)_2)_2IrCl_2(P(CH_3)_2C_6H_5)]$, respectively. The iron–iridium complex crystallizes in the orthorhombic space group $P2_12_12_1$ with a = 9.901 (2) Å, b = 16.622 (2) Å, c = 32.160 (4) Å, Z = 8, 3919 reflections with $I \geq 3\sigma(I)$, R = 0.035, and R_w = 0.050. The Ir–Fe distances in the two independent molecules are 2.838 (2) and 2.828 (2) Å, indicating significant metal–metal interaction.

The ligands $RN(PX_2)_2$ (R = alkyl; X = F, alkoxy, phenoxy) have been studied extensively in recent years.[1-14] Particularly with $CH_3N(PF_2)_2$, a number of binuclear[9-12] and trinuclear[4,5] complexes with unusual structures have been synthesized. As part of our continuing interest in heterobimetallic complexes stabilized by "short-bite" phosphorus ligands, we considered that $[(\eta^5\text{-}C_5H_5)FeCl(\eta^1\text{-}CH_3N(PF_2)_2)_2]$[13] should be a suitable starting point for such species.

Experimental Section

All reactions were carried out under an atmosphere of purified nitrogen with use of standard Schlenk techniques. Solvents were purified by standard methods and distilled under nitrogen prior to use. Literature methods were used to prepare $[RhCl(COD)]_2$ (COD = cycloocta-1,5-diene),[2] $[Ir(CO)Cl(PMe_2Ph)_2]$,[15] and $[(\eta^5\text{-}C_5H_5)FeCl(\eta^1\text{-}CH_3N(PF_2)_2)_2]$.[13] ^{1}H and $^{31}P\{^1H\}$ NMR spectra were obtained on an IBM-Bruker AF-200 spectrometer at 200.132 and 81.015 MHz, respectively. Proton and phosphorus chemical shifts are respectively referred to tetramethylsilane (δ 0.0) and 85% H_3PO_4 (δ 0.0) with positive shifts downfield of the reference. Infrared spectra were obtained on a Mattson-Cygnus 100 Fourier transform spectrophotometer in Nujol mulls. Microanalyses were performed by Galbraith Laboratories, Knoxville, TN.

$[(\eta^5\text{-}C_5H_5)Fe(\mu\text{-}CH_3N(PF_2)_2)_2IrCl_2(P(CH_3)_2C_6H_5)]$ (1). To a solution of 0.200 g (0.389 mmol) of $[Ir(CO)Cl(PMe_2Ph)_2]$ in 10 mL of toluene was added 0.191 g (0.389 mmol) of $[cpFeCl(MeN(PF_2)_2)_2]$. After it was heated at ca. 60 °C for 6 h, the solution had become a dark brown-orange. The solution was concentrated to ca. 1 mL under reduced pressure and transferred to a 1 × 20 cm column of alumina (Brockman I). The column was washed with hexane followed by elution with diethyl ether/hexane (1:1 v/v), which removed a red-orange band. Concentration of the eluate under reduced pressure afforded the product as glistening brown-orange needles. The supernatant was removed via syringe, and the crystals were washed with 2 mL of cold hexane and dried in vacuo (yield 75%). Anal. Calcd for $C_{15}H_{22}N_2P_5F_8Cl_2FeIr$: C, 21.04; H, 2.60. Found: C, 21.6; H, 2.6. ^{1}H NMR (C_6D_6): δ 7.50 (m),[16] 7.09 (m, 5 H, C_6H_5), 4.88 (t (J = 1.1 Hz), 5 H, C_5H_5), 2.22 (dd (J = 9.4, 6.2 Hz), 6 H, N–CH_3), 1.90 (d (J = 11.5 Hz), 6 H, P–CH_3). $^{31}P\{^1H\}$ NMR (C_6D_6): δ −19.0 (t ($^2J_{P-P}$ = 75.6 Hz)), 89.9 (tm), 191.2 (tm).

$[(\eta^5\text{-}C_5H_5)Fe(\mu\text{-}CH_3N(PF_2)_2)_2RhCl_2]$ (2). A suspension of 0.151 g (0.306 mmol) of $[RhCl(COD)]_2$ in 20 mL of diethyl ether was purged with carbon monoxide for several minutes and then stirred under atmosphere of carbon monoxide for 20 min. To the resulting orange solution was added 0.300 g (0.612 mmol) of $[cpFeCl(MeN(PF_2)_2)_2]$, whereupon gas evolution occurred and a dark green solid precipitated. This was filtered off, washed with diethyl ether, and redissolved in dichloromethane. Dilution of this solution with toluene and concentration under reduced pressure afforded the product as a dark green powder in essentially quantitative yield. Anal. Calcd for $C_7H_{11}N_2P_4F_8Cl_2FeRh$: C,

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(16) Key to NMR peak multiplicities: s, singlet; d, doublet; t, triplet; m, multiplet; dd, doublet of doublets; tm, triplet of multiplets.

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Table I. Crystallographic Data for $[cpFe(\mu\text{-}MeN(PF_2)_2)_2IrCl_2(PMe_2Ph)]$ (1)

formula	$C_{15}H_{22}P_5F_8N_2Cl_2FeIr$
fw	856.17
cryst syst	orthorhombic
space group	$P2_12_12_1$ (No. 19)
a, Å	9.901 (2)
b, Å	16.622 (2)
c, Å	32.160 (4)
V, Å^3	5293
Z	8
ρ(obsd), ρ(calcd), g cm^{-3}	2.15, 2.15
radiatn	Mo Kα, graphite monochromated, λ = 0.71073 Å
linear abs coeff, cm^{-1}	61.1
range of transmissn factor	0.832–0.996
θ range, deg	0.5–25.0
scan type	ω–2θ
scan width, deg	0.80 + 0.20 tan θ
scan rate, deg min^{-1}	1.3–16.5
attn factor	11.87
programs used	Enraf-Nonius SDP
p factor in weight^d	0.04
no. of unique data	5193
no. of data, $I \geq 3\sigma(I)$	3919
no. of variables	443
largest shift/esd in final cycle	0.05
R^a	0.035
$R_w^{b,d}$	0.050
GOF^c	1.65

[a] $R = \sum|F_o - |F_c||/\sum F_o$. [b] $R_w = [\sum w(F_o - |F_c|)^2/\sum w(F_o)]^{1/2}$. [c] $GOF = [\sum w(F_o - |F_c|)^2/(N_o - N_v)]^{1/2}$, where N_o and N_v are respectively the numbers of observations and variables. [d] The weighting scheme used in the final refinement was $w = 1/(\sigma_F)^2$, where $\sigma_F = \sigma_{F^2}/2F$ and $\sigma_{F^2} = [(\sigma_I)^2 + (pF^2)^2]^{1/2}$.

13.37; H, 1.77; Cl, 11.28. Found: C, 14.0; H, 1.8; Cl, 12.4. ^{1}H NMR ($CDCl_3$): δ 5.15 (s, 5 H, C_5H_5), 3.05 (t (J = 7.4 Hz), 6 H, N–CH_3). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 125.3 (tm), 195.6 (tm).

$[(\eta^5\text{-}C_5H_5)Fe(\mu\text{-}CH_3N(PF_2)_2)_2RhCl_2(P(CH_3)_2C_6H_5)]$ (3). A solution of 0.154 g (0.245 mmol) of **2** in 10 mL of dichloromethane was treated with 0.034 g (0.245 mmol) of dimethylphenylphosphine, whereupon the dark yellow-green solution immediately became a dark brown-orange. The solvent was removed in vacuo and the gummy residue extracted with diethyl ether. The filtered extracts were diluted with hexane and concentrated in vacuo to afford the product as dark brown crystals in ca. 80% yield. Anal. Calcd for $C_{15}H_{22}N_2P_5F_8Cl_2FeRh$: C, 23.49; H, 2.90. Found: C, 24.6; H, 3.1. ^{1}H NMR (C_6D_6): δ 7.53 (m), 7.09 (m, 5 H, C_6H_5), 4.91 (s, 5 H, C_5H_5), 2.26 (m, 6 H, N–CH_3), 1.84 (d (J = 11.9 Hz), 6 H, P–CH_3). ^{31}P{^{1}H} NMR (C_6D_6): δ −21.9 (m), 135.4 (tm), 187.8 (tm).

X-ray Crystallography. The crystals of **1** obtained as described above proved to be of X-ray quality. A parallelepiped measuring 0.16 × 0.23 × 0.50 mm was cut from a larger crystal, mounted on a glass fiber, and coated with a film of epoxy cement. General procedures for data collection on the Enraf-Nonius CAD-4 diffractometer as well as for data reduction, structure solution, and refinement have been published.[2] Specifics for the present work are given in Table I. The choice of the orthorhombic system indicated by the CAD-4 software was confirmed by the observation of *mmm* diffraction symmetry, and the space group was uniquely determined by the systematic absences observed in the data collection. The final unit cell parameters were obtained by the least-squares refinement of the setting angles of 25 reflections (7.94 ≤ θ ≤ 19.87°) that had been accurately centered on the diffractometer. Only statistical fluctuations were observed in the intensity monitors over the course of the data collection. An empirical absorption correction based on ψ scans for four reflections near χ = 90° was applied. Coordinates for two independent iridium atoms were obtained from an origin-removed Patterson map and those of the remaining non-hydrogen atoms from successive difference Fourier maps. In the final stages, all atoms except carbon and nitrogen were refined anisotropically and many hydrogen atoms were visible in a difference map. These were placed in idealized positions (C–H = 0.95 Å) and included as fixed contributions to the structure factors riding on the attached carbon atoms with isotropic thermal parameters 30% larger than those of the corresponding carbon atoms. It was not possible to reliably locate hydrogen atoms associated with the methyl groups containing C(2)–C(4). Following convergence of the original model, the opposite enantiomer was refined, leading to significantly higher values for R and R_w, indicating the correctness of the original choice. The final difference map was essentially featureless. Final positional parameters for the refined atoms appear in Table II; additional crystallographic data are included as supplementary material (Tables S1–S7).

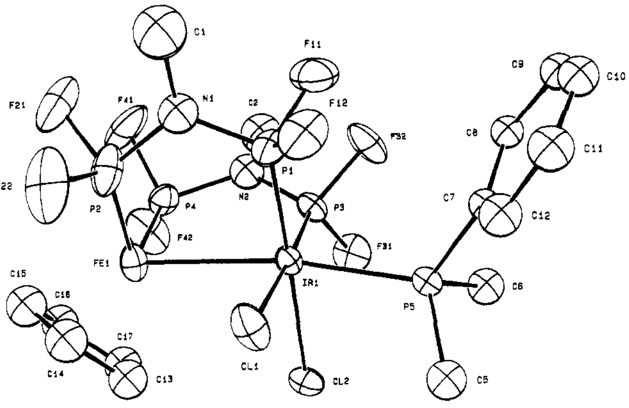

Figure 1. Perspective view of $[cpFe(\mu\text{-}MeN(PF_2)_2)_2IrCl_2(PMe_2Ph)]$ (molecule 1) with hydrogen atoms omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level.

Results and Discussion

Reaction of $[cpFeCl(MeN(PF_2)_2)_2]$ with $[IrCl(CO)(PMe_2Ph)_2]$ and $[RhCl(CO)_2]_2$ affords products that were analyzed respectively as $[cpFeIrCl_2(PMe_2Ph)(MeN(PF_2)_2)_2]$ (**1**) and $[cpFeRhCl_2(MeN(PF_2)_2)_2]$ (**2**). Complex **2** reacts immediately with dimethylphenylphosphine to give a product that was analyzed as $[cpFeRhCl_2(PMe_2Ph)(MeN(PF_2)_2)_2]$ (**3**). The infrared spectra of **1**–**3** show no evidence for the presence of a carbonyl ligand. The NMR spectra of **1** are wholly consistent with the solid-state structure (Figure 1). Thus, there is a single resonance for the *N*-methyl protons of the fluorophosphine ligands, while the ^{31}P{^{1}H} NMR spectrum shows three resonances of relative intensity 2:2:1 in order of increasing field. The two low-field resonances can be roughly described as triplets of multiplets with the large triplet splitting attributable to $^1J_{P-F}$, indicating assignment to the fluorophosphine ligand. The lowest field resonance has approximately the same chemical shift as that for the coordinated phosphorus atoms in $[cpFeCl(MeN(PF_2)_2)_2]$ and is therefore assigned to the phosphorus atoms coordinated to iron. The resonance for the dimethylphenylphosphine ligand appears as a sharp triplet upfield of phosphoric acid. The resonance for the cyclopentadienyl protons shows a small coupling to the iron-bound phosphorus atoms. The ^{1}H and ^{31}P{^{1}H} NMR spectra of **3** are very similar to those for **1**, indicating **3** has the same structure. The resonance due to the phosphorus atom of the dimethylphenylphosphine ligand is an approximate quartet, which suggests that the coupling of this atom to rhodium and to the phosphorus atoms of the bridging ligands have comparable magnitudes (ca. 89 Hz). The NMR spectra of **2** are also very similar to those for **1** and **3**, but without the high-field phosphorus resonance, indicating that **2** has basically the same structure except for the absence of an axial ligand on rhodium.

Although the dimethylphenylphosphine ligand in **1** adopts two different rotational orientations in the solid state (vide infra), both of which place the ligand methyl groups in different environments, these groups are

Table II. Positional Parameters (Esd's in Parentheses) for [cpFeIrCl$_2$(PMe$_2$Ph)(MeN(PF$_2$)$_2$)$_2$]^a

atom	*x*	*y*	*z*	*B*, Å^2	atom	*x*	*y*	*z*	*B*, Å^2
Ir(1)	0.03821 (6)	0.10292 (3)	0.12005 (2)	3.04 (1)	Ir(2)	0.54510 (6)	0.67531 (3)	0.15061 (2)	2.671 (9)
Fe(1)	0.2321 (3)	0.2246 (1)	0.13612 (8)	4.22 (5)	Fe(2)	0.7585 (2)	0.5683 (1)	0.16941 (7)	3.43 (4)
Cl(1)	0.1837 (5)	0.0538 (3)	0.0652 (2)	6.0 (1)	Cl(3)	0.6937 (4)	0.7417 (2)	0.1019 (1)	4.54 (9)
Cl(2)	0.1459 (4)	0.0168 (3)	0.1709 (2)	5.3 (1)	Cl(4)	0.6097 (5)	0.7672 (3)	0.2059 (1)	4.98 (9)
P(1)	−0.0490 (6)	0.1778 (3)	0.0721 (1)	4.58 (9)	P(6)	0.4922 (4)	0.5956 (2)	0.0997 (1)	3.54 (8)
P(2)	0.1679 (7)	0.2849 (3)	0.0842 (2)	6.6 (1)	P(7)	0.7329 (5)	0.5120 (3)	0.1129 (2)	4.8 (1)
P(3)	−0.0838 (4)	0.1532 (3)	0.1689 (1)	3.62 (8)	P(8)	0.6278 (5)	0.4969 (2)	0.2025 (1)	3.82 (9)
P(4)	0.1007 (5)	0.2795 (2)	0.1762 (2)	4.27 (9)	P(9)	0.4239 (4)	0.6117 (2)	0.1959 (1)	3.59 (8)
P(5)	−0.0987 (4)	−0.0144 (2)	0.1094 (1)	3.82 (9)	P(10)	0.3866 (4)	0.7816 (2)	0.1362 (1)	3.48 (8)
F(11)	−0.197 (1)	0.2079 (7)	0.0790 (4)	7.7 (3)	F(61)	0.356 (1)	0.5510 (6)	0.1037 (3)	5.6 (2)
F(12)	−0.078 (1)	0.1399 (6)	0.0302 (3)	7.2 (3)	F(62)	0.462 (1)	0.6351 (5)	0.0574 (2)	4.8 (2)
F(21)	0.151 (2)	0.3772 (6)	0.0857 (4)	9.5 (4)	F(71)	0.746 (1)	0.4171 (6)	0.1106 (3)	8.0 (3)
F(22)	0.269 (2)	0.289 (1)	0.0481 (4)	12.1 (4)	F(72)	0.840 (1)	0.5266 (9)	0.0787 (4)	8.8 (4)
F(31)	−0.099 (1)	0.1033 (6)	0.2101 (3)	5.7 (2)	F(81)	0.668 (1)	0.4706 (8)	0.2467 (3)	8.8 (3)
F(32)	−0.2360 (9)	0.1601 (7)	0.1613 (4)	7.0 (3)	F(82)	0.594 (1)	0.4087 (6)	0.1871 (5)	8.1 (3)
F(41)	0.058 (2)	0.3687 (6)	0.1696 (4)	10.0 (4)	F (91)	0.2743 (9)	0.5946 (7)	0.1829 (4)	7.0 (3)
F(42)	0.150 (1)	0.2941 (8)	0.2226 (4)	8.6 (3)	F(92)	0.388 (1)	0.6558 (6)	0.2371 (3)	6.1 (2)
N(1)	0.024 (2)	0.2612 (9)	0.0599 (5)	6.0 (3)*	N(3)	0.591 (1)	0.5222 (8)	0.0854 (4)	4.7 (3)*
N(2)	−0.055 (2)	0.2435 (8)	0.1863 (5)	5.6 (3)*	N(4)	0.471 (2)	0.5243 (7)	0.2128 (4)	4.5 (3)*
C(1)	−0.031 (3)	0.311 (2)	0.0244 (9)	10.2 (8)*	C(3)	0.563 (2)	0.471 (1)	0.0472 (7)	6.9 (5)*
C(2)	−0.144 (3)	0.285 (1)	0.2175 (8)	8.3 (6)*	C(4)	0.374 (2)	0.473 (1)	0.2376 (7)	7.0 (5)*
C(5)	0.003 (2)	−0.102 (1)	0.0976 (6)	5.5 (4)*	C(18)	0.263 (2)	0.795 (1)	0.1760 (5)	4.4 (3)*
C(6)	−0.195 (2)	−0.044 (1)	0.1569 (6)	5.3 (4)*	C(19)	0.463 (2)	0.879 (1)	0.1338 (6)	5.6 (4)*
C(7)	−0.229 (2)	−0.0121 (8)	0.0699 (5)	3.4 (3)*	C(20)	0.330 (2)	0.815 (1)	0.0525 (6)	4.8 (4)*
C(8)	−0.348 (2)	0.0267 (9)	0.0753 (5)	3.7 (3)*	C(21)	0.254 (2)	0.805 (1)	0.0178 (7)	6.1 (5)*
C(9)	−0.449 (2)	0.0241 (9)	0.0456 (5)	4.4 (3)*	C(22)	0.146 (2)	0.758 (1)	0.0149 (6)	6.2 (5)*
C(10)	−0.421 (2)	−0.008 (1)	0.0075 (6)	5.0 (4)*	C(23)	0.108 (2)	0.714 (1)	0.0508 (6)	5.5 (4)*
C(11)	−0.303 (2)	−0.042 (1)	0.007 (6)	6.2 (5)*	C(24)	0.181 (2)	0.7242 (9)	0.0868 (5)	4.0 (3)*
C(12)	−0.201 (2)	−0.044 (1)	0.0302 (6)	5.7 (4)*	C(25)	0.291 (2)	0.7731 (8)	0.0869 (5)	3.3 (3)*
C(13)	0.381 (2)	0.136 (1)	0.1395 (6)	6.2 (5)*	C(26)	0.927 (2)	0.547 (1)	0.2053 (6)	6.3 (5)*
C(14)	0.416 (2)	0.195 (1)	0.1103 (7)	7.4 (5)*	C(27)	0.966 (2)	0.548 (1)	0.1672 (6)	6.5 (4)*
C(15)	0.427 (2)	0.268 (1)	0.1337 (7)	7.1 (5)*	C(28)	0.936 (2)	0.627 (1)	0.1509 (6)	6.0 (4)*
C(16)	0.402 (2)	0.253 (1)	0.1735 (7)	6.1 (4)*	C(29)	0.876 (2)	0.670 (1)	0.1844 (6)	5.6 (4)*
C(17)	0.367 (2)	0.171 (1)	0.1781 (6)	6.1 (4)*	C(30)	0.865 (2)	0.622 (1)	0.2181 (6)	6.0 (4)*

^{a} Starred values denote atoms refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $^4/_3[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos\gamma)B_{12} + ac(\cos\beta)B_{13} + bc(\cos\alpha)B_{23}]$.

equivalent in the ^{1}H NMR spectrum, suggesting that at least at room temperature there is free rotation about the Ir–P bond. The room-temperature ^{31}P NMR spectrum of 2 in CO-saturated CDCl$_3$ shows a slight upfield shift and noticeable broadening for the resonance assigned to the rhodium-bound phosphorus atoms, suggesting formation of a labile CO adduct with the carbonyl ligand presumably bound to rhodium in the axial position. The apparent lability of this adduct (we were unable to isolate it) as compared with the stable dimethylphenylphosphine adduct 3 can be explained by the significant electron-withdrawing ability of the fluorophosphine ligands. Thus, good σ-donors can bond in the empty axial position in 2 but ligands such as CO, which depend on significant π-backbonding to form stable adducts, cannot do so effectively because of the lack of sufficient electron density on rhodium.

The relatively long Ir–Fe distance in 1 (vide infra) suggested a weak metal–metal interaction that might be susceptible to cleavage. To this end, a toluene solution of 1 containing excess methyl iodide was heated at ca. 60 °C overnight, but no reaction appeared to occur (NMR evidence). Under similar conditions 1 did appear to react with molecular iodine but the brick red solid obtained was too insoluble to obtain satisfactory NMR spectra and the elemental analysis could not be fit to a reasonable formula. It thus appears that the metal–metal bond in 1 is not a site of great reactivity. This is probably due primarily to steric shielding (see Figure 1).

The crystal structure of 1 consists of well-separated molecules with no unusual intermolecular contacts. There are two independent molecules in the asymmetric unit, one of which is shown in Figure 1 (molecule 1). As can be seen from Table III, there is little difference in the bond distances or interbond angles between the two molecules; however, they do differ in the rotational orientation of the dimethylphenyphosphine ligand and in the twist about the metal–metal axis (see Figures S1 and S2). Thus, with use of the plane defined by the two metals and the centroid of the cyclopentadienyl ring as a reference, the axial phosphine ligand in molecule 2 is rotated clockwise by ca. 40° from its position of molecule 1 while the IrCl$_2$P$_2$ moiety in molecule 2 is twisted counterclockwise by ca. 20° relative to its position in molecule 1. This undoubtedly reflects packing effects in the solid state, since as noted above, there is no NMR evidence for different conformers in solution.

The average Ir–Fe distance of 2.833 (2) Å is considerably longer than those found in [cp*IrFe$_2$(μ-CO)$_2$(CO)$_7$] (2.616 (7), 2.698 (7) Å),[17] [cpFe(CO)(μ-CO)(μ–CF$_2$)Ir(CO)Cl(PMe$_2$Ph)$_2$] (2.7178 (4) Å),[18] and [Fe(CO)$_3$(μ-PPh$_2$)$_2$Ir(COD)Cl] (2.703 (1) Å)[19] but is shorter than that in [Fe(CO)$_3$(PPh$_3$)(μ-PPh$_2$)Ir(CO)$_2$(PPh$_3$)] (2.960 (1) Å).[20] As has been discussed for the last complex, there are two limiting descriptors for the metal–metal interaction and therefore also for the formal oxidation states of the two metals. These are a covalent bond between 17-electron Fe(II) and Ir(II) centers or a donor–acceptor interaction from an 18-electron Fe(I) to a 16-electron Ir(III) center. We are inclined toward the latter description because of

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Table III. Selected Bond Distances (Å) and Interbond Angles (deg) for $[cpFeIrCl_2(PMe_2Ph)(MeN(PF_2)_2)_2]$

molecule 1		molecule 2	
	Bond Distances		
Ir(1)–Fe(1)	2.838 (2)	Ir(2)–Fe(2)	2.828 (2)
Ir(1)–P(1)	2.162 (4)	Ir(2)–P(9)	2.165 (3)
Ir(1)–P(3)	2.151 (4)	Ir(2)–P(6)	2.170 (3)
Ir(1)–P(5)	2.401 (3)	Ir(2)–P(10)	2.409 (3)
Ir(1)–Cl(1)	2.420 (4)	Ir(2)–Cl(4)	2.432 (3)
Ir(1)–Cl(2)	2.422 (4)	Ir(2)–Cl(3)	2.417 (3)
Fe(1)–P(2)	2.050 (6)	Fe(2)–P(8)	2.054 (4)
Fe(1)–P(4)	2.047 (4)	Fe(2)–P(7)	2.061 (4)
Fe(1)–C(13)	2.09 (2)	Fe(2)–C(29)	2.11 (2)
Fe(1)–C(14)	2.06 (2)	Fe(2)–C(30)	2.09 (2)
Fe(1)–C(15)	2.07 (2)	Fe(2)–C(26)	2.06 (2)
Fe(1)–C(16)	2.12 (2)	Fe(2)–C(27)	2.09 (2)
	Interbond Angles		
Fe(1)–Ir(1)–P(1)	89.4 (1)	Fe(2)–Ir(2)–P(9)	87.9 (1)
Fe(1)–Ir(1)–P(3)	88.3 (1)	Fe(2)–Ir(2)–P(6)	86.6 (1)
Fe(1)–Ir(1)–P(5)	171.11 (9)	Fe(2)–Ir(2)–P(10)	171.78 (9)
Fe(1)–Ir(1)–Cl(1)	88.3 (1)	Fe(2)–Ir(2)–Cl(4)	92.4 (1)
Fe(1)–Ir(1)–Cl(2)	90.0 (1)	Fe(2)–Ir(2)–Cl(3)	88.4 (1)
P(1)–Ir(1)–P(3)	94.2 (1)	P(9)–Ir(2)–P(6)	94.3 (1)
P(1)–Ir(1)–P(5)	98.1 (1)	P(9)–Ir(2)–P(10)	97.3 (1)
P(1)–Ir(1)–Cl(1)	85.0 (2)	P(9)–Ir(2)–Cl(4)	87.7 (1)
P(1)–Ir(1)–Cl(2)	176.7 (2)	P(9)–Ir(2)–Cl(3)	176.1 (1)
P(3)–Ir(1)–P(5)	95.9 (1)	P(6)–Ir(2)–P(10)	98.4 (1)
P(3)–Ir(1)–Cl(1)	176.5 (1)	P(6)–Ir(2)–Cl(4)	177.9 (1)
P(3)–Ir(1)–Cl(2)	89.1 (1)	P(6)–Ir(2)–Cl(3)	86.4 (1)
P(5)–Ir(1)–Cl(1)	87.6 (1)	P(10)–Ir(2)–Cl(4)	81.4 (1)
P(5)–Ir(1)–Cl(2)	82.2 (1)	P(10)–Ir(2)–Cl(3)	86.4 (1)
Cl(1)–Ir(1)–Cl(2)	91.8 (2)	Cl(4)-Ir(2)-Cl(3)	91.6 (1)
Ir(1)–Fe(1)–P(2)	89.4 (2)	Ir(2)–Fe(2)–P(8)	90.2 (1)
Ir(1)–Fe(1)–P(4)	90.1 (1)	Ir(2)–Fe(2)–P(7)	90.3 (1)
Ir(1)–Fe(1)–C′[a]	132.5	Ir(2)–Fe(2)–C″[a]	121.5
P(2)–Fe(1)–P(4)	95.6 (2)	P(8)–Fe(2)–P(7)	96.7 (2)
P(2)–Fe(1)–C′	123.8	P(8)–Fe(2)–C″	127.1
P(4)–Fe(1)–C′	124.5	P(7)–Fe(2)–C″	121.4

[a] C′ or C″ is the centroid of the cyclopentadienyl ring.

the rather long metal–metal distance, although there are no structural criteria that can be applied to unequivocally distinguish between them. We do note that the metal–metal distance is slightly *longer* than the intraligand P- - -P separation (2.787 (5)–2.816 (6) Å), suggesting that the metal–metal interaction is not strong. Considering the iridium to be formally Ir(III) is also consistent with the most unusual feature of 1, namely the net transfer of a chlorine ligand from iron to iridium that has occurred during the synthesis. While extensive mechanistic speculation is unwarranted, it is tempting to suggest that this occurs via formal oxidative addition of the Fe–Cl bond to the original Ir(I) center, most likely following initial attachment of the fluorophosphine ligand(s).

The Ir–Cl distances compare well with those trans to phosphorus in *mer*- and *fac*-$[IrCl_3(PMe_2Ph)_3]$[21] (2.434 (1)–2.468 (2) Å), while the Ir–PMe_2Ph distances are somewhat longer than those trans to phosphorus in *mer*-$[IrCl_3(PMe_2Ph)_3]$ (2.363 (1)–2.384 (1) Å)[21] and *mer*-$[IrCl_2(H_2O)(PMe_2Ph)_3]ClO_4$ (2.366 (3), 2.392 (3) Å).[22] They are, however, quite comparable to two of the Ir–P distances in *trans*-$[IrCl_2(PMe_2Ph)_4]ClO_4$ (2.416 (1), 2.424 (2) Å).[23] Clearly these long distances reflect a significant trans influence of the Fe–Ir interaction but do not permit a distinction between the two possible descriptions noted above.

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Registry No. 1, 131067-38-4; 2, 131067-39-5; 3, 131067-40-8; $[Ir(CO)Cl(PMe_2Ph)_2]$, 22685-99-0; $[RhCl(CO)_2]_2$, 14523-22-9; $[CpFeCl(MeN(PF_2)_2)_2]$, 64387-50-4.

Supplementary Material Available: Figures showing the conformations of the two independent molecules of 1, together with tables of nonessential interatomic distances, interbond angles, calculated hydrogen atom positions, anisotropic thermal parameters, rms amplitudes of anisotropic displacement, and torsion angles (19 pages); a table of observed and calculated structure factors (40 pages). Ordering information is given on any current masthead page.

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Photochemical Reaction of a Diplatinum μ-Phenylethenylidene Complex with Diphenylacetylene: Unusual Formation of a μ-η¹:η³-Butadienediyl Complex

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Summary: Photochemical reaction of a diplatinum μ-alkenylidene complex with $PhC\equiv CPh$ occurs with C–C coupling of the alkenylidene and alkyne moieties to give an expanded, unsaturated μ-η^1:η^3-butadienediyl ligand. Structural and isotopic-labeling studies indicate that this reaction proceeds by an unusually complex mechanism.

We reported recently that the cationic diplatinum μ-phenylethenylidene complex $[Pt_2(\mu\text{-}C{=}CHPh)(C{\equiv}CPh)(PEt_3)_4][BF_4]$ (1) exhibits pronounced photochemical reactivity reminiscent of that of the well-studied anionic diplatinum complex $[Pt_2(P_2O_5H_2)_4]^{4-}$, even though these two compounds are structurally dissimilar.[2] For example, complex 1 reacts under photolysis with methyl iodide to give analogous neutral diplatinum iodide or diiodide compounds or with 2-propanol to give catalytic production of

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