2818 *Inorg. Chem.* **1999,** *38,* 2818−2823

Iridium(III, 0, and −I) Complexes Stabilized by 1,1′-Bis(diphenylphosphino)ferrocene (dppf): Synthesis and Characterization. Crystal Structures of [Na(THF)$_5$][Ir(dppf)$_2$]·THF and [Ir(dppf)$_2$]

Bruno Longato,*,†,‡ Lorenzo Riello,† Giuliano Bandoli,§ and Giuseppe Pilloni†

Dipartimento di Chimica Inorganica, Metallorganica ed Analitica, Università di Padova, Via Marzolo 1,
35131 Padova, Italy, Dipartimento di Scienze Farmaceutiche, Università di Padova, Via Marzolo 5,
35131 Padova, Italy, and Centro di Studio sulla Stabilità e Reattività dei Composti di Coordinazione,
CNR, Via Marzolo 1, 35131 Padova, Italy

Received October 2, 1998

The iridium(I) complex stabilized by the organometallic ligand 1,1′-bis(diphenylphosphino)ferrocene (dppf), [Ir(dppf)$_2$]$^+$, **1**, undergoes a cyclometalation reaction in solution to give the iridium(III) hydride [IrH(dppf-(−H))(dppf)]$^+$, **2**, which has been isolated and characterized by spectroscopic methods. The compound is the final product of the intramolecular oxidative addition of the ortho C−H bond of a phenyl substituent of the diphosphine and is formed through an intermediate hydride, which has also been spectroscopically characterized. **1** can be electrochemically reduced to the Ir(0) and Ir(−I) species, [Ir(dppf)$_2$], **3**, and [Ir(dppf)$_2$]$^-$, **4**, respectively, in two reversible single-electron processes. These low-valent metal complexes have been obtained by chemical reduction of **1** with sodium naphthalenide in tetrahydrofuran solution and their crystal and molecular structures determined by single-crystal X-ray analyses. **3** crystallizes in the triclinic system, space group $P\bar{1}$, with $a = 13.019(4)$ Å, $b = 13.765(6)$ Å, $c = 15.549(5)$ Å, $\alpha = 93.74(3)°$, $\beta = 90.35(3)°$, $\gamma = 92.07(3)°$, $V = 2779(2)$ Å^3, and $Z = 2$. Anionic complex **4** crystallizes as sodium-solvated salt [Na(THF)$_5$][Ir(dppf)$_2$]·THF, **4b**, in which the sodium cation is surrounded by five molecules of THF in a slightly distorted trigonal-bipyramidal environment. **4b** crystallizes in the monoclinic system, space group $P2_1/n$, with $a = 13.325(3)$ Å, $b = 23.976(5)$ Å, $c = 26.774(7)$ Å, $\beta = 98.77(2)°$, $V = 8454(4)$ Å^3, and $Z = 4$. The coordination geometry around the metal in neutral d^9 complex **3** is intermediate between the highly distorted square-planar geometry, found earlier in cationic d^8 species **1**, and the almost regular tetrahedral arrangement of the two diphosphines in the anionic d^{10} complex **4**. Reduction of Ir(I) to Ir(0) and Ir(−I) causes a stepwise decrease of the Ir−P bond length of 0.04 Å (average) and 0.05 Å, respectively, with a concomitant increase of the bite angle of the diphosphine which ranges from 94.3° (average) in [Ir(dppf)$_2$]$^+$ to 102.3° in [Ir(dppf)$_2$]$^-$.

Introduction

Iridium is probably the only transition metal able to form homoleptic complexes in which the oxidation number spans six units, ranging from the trivalent cation such as [Ir(CO)$_6$]$^{3+}$ to the related highly reduced species [Ir(CO)$_3$]$^{3-}$ containing the metal in the formal (−III) oxidation state.[1,2] Homoleptic phosphine complexes of this metal in low oxidation states have also been described. Almost all of these species are formed in the electrochemical reduction of alkyl-chained diphosphine Ir(I) complexes which were commonly found to undergo a concerted two-electron reaction, i.e., an EE mechanism with $E_2°$ anodic of $E_1°$, to the iridium(−I) intermediate quenched by proton abstraction from the medium to give the final metal hydride derivative.[3−5] In contrast, two single-electron reduction processes have been observed in the cationic complex with mixed carbonyl and triphenylphosphine ligands, thus providing a means for the electrogeneration of the relatively long-lived zerovalent derivative Ir(CO)(PPh)$_3$.[6]

Some years ago, we reported the characterization of the cationic species [Ir(dppf)$_2$]$^+$, **1**, a highly distorted square-planar complex containing the organometallic ligand 1,1′-bis(diphenylphosphino)ferrocene (dppf).[7] In order to provide information on the interplay of electronic and steric effects of diphosphines on complex reduction and on the factors that determine the relative stability of the rare and intriguing d^9 intermediates,[8] we extended our previous electrochemical investigations to promising complex **1**. The stronger donating ability of dppf compared with other alkyl-chained diphosphine analogues, as well as the destabilizing effects on the complex caused by the larger dppf chelate ring, has already been observed.[9]

---

* Author to whom correspondence should be addressed. E-mail: longato@chim02.chin.unipd.it. Fax: (39)0498275161.

† Dipartimento di Chimica Inorganica, Università di Padova.

‡ Centro di Studio sulla Stabilità e Reattività dei Composti di Coordinazione, CNR.

§ Dipartimento di Scienze Farmaceutiche, Università di Padova.

(1) Bach, C.; Willner, H.; Wang, C.; Rettig, S. J.; Trotter, J.; Aubke, F. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1974.
(2) Ellis, J. E. *Adv. Organomet. Chem.* **1990**, *31*, 1.
(3) Pilloni, G.; Vecchi, E.; Martelli, M. *J. Electroanal. Chem.* **1973**, *45*, 483.
(4) Pilloni, G.; Zotti, G.; Martelli, M. *Inorg. Chem.* **1982**, *21*, 1283.
(5) Morandini, F.; Pilloni, G.; Consiglio, G.; Mezzetti, A. *Organometallics* **1995**, *14*, 3418.
(6) Zotti, G.; S. Zecchin, S.; Pilloni, G. *J. Organomet. Chem.* **1983**, *246*, 61.
(7) Casellato, U.; Corain, B.; Graziani, R.; Longato, B.; Pilloni, G. *Inorg. Chem.* **1990**, *29*, 1193.
(8) Miedaner, A.; Haltiwanger, R. C.; DuBois, D. L. *Inorg. Chem.* **1991**, *30*, 417.

10.1021/ic981166s CCC: $18.00

In this paper the spectroscopic characterization of the cyclometalated complex $[IrH(dppf(-H))(dppf)]^+$, **2**, resulting from the intramolecular oxidative addition of the ortho C−H bond of the phenyl substituents in **1**, is described. The focus of the article is, however, on the synthesis and characterization, including the solid-state X-ray structure, of the unprecedented zerovalent compound $[Ir(dppf)_2]^0$, **3**, and iridium(−I) sodium-solvated salt $[Na(THF)_5][Ir(dppf)_2]\cdot THF$, **4b**, obtained by stepwise reduction of iridium(I) precursor **1**. This series represents a rare example[10] of compounds in which the same set of ligands appears to be able to sustain the metal in four different oxidation states and provides the opportunity to study the structural changes of the $\{IrP_4\}^n$ moiety on changing the charge of the complex ($n = +1, 0, -1$).

Experimental Section

General Procedures and Materials. All reactions and manipulations of solutions were performed under a dinitrogen atmosphere of a Braun MB150 drybox. Anhydrous tetrahydrofuran (THF), toluene, and hexane, purchased from Aldrich, were further purified by distillation over Na/benzophenone. 1,1′-Bis(diphenylphosphino)ferrocene, dppf, was purchased from Aldrich and used as received. Electrochemical grade tetrabutylammonium perchlorate, TBAP, was obtained from Fluka and used without further purification after drying in vacuo at 60 °C. High-purity argon, further purified from oxygen by passage over reduced copper at 450 °C, was used in the electrochemical experiments. $[Ir(dppf)_2]X$ ($X = ClO_4$, **1a**, and BPh_4, **1b**) were prepared as previously reported.[7]

^1H and ^{31}P NMR spectra were obtained at 298 K in 5 mm sample tubes on a Bruker 400 AMX and/or on a JEOL 90 MHz spectrometer. The external references were H_3PO_4 (85% w/w in D_2O) for ^{31}P spectra. ^1H chemical shifts are referred to the residual peak(s) of the deuterated solvents used (Aldrich). IR and electronic spectra were obtained using a Nicolet 5SXC-FTIR and a Cary 5E spectrometer, respectively. X-band continuous wave ESR experiments were carried out using a Bruker ESP 380 spectrometer.

All electrochemical experiments were performed in anhydrous deoxygenated THF solutions with 0.2 mol dm^{-3} TBAP as the supporting electrolyte, using a conventional three-electrode liquid-jacketed cell. Cyclic voltammetry (CV) measurements were performed with an Amel 551 potentiostat modulated by an Amel 566 function generator. The recording device was an Amel model 863 X-Y recorder. The working electrode was a planar gold microelectrode freshly coated with mercury (ca. 0.4 mm^2) surrounded by a platinum spiral counter electrode. Controlled potential electrolyses were performed with an Amel 552 potentiostat linked to an Amel 731 digital integrator. The working electrode was a mercury pool (ca. 12 cm^2), and the counter electrode was external, the connection being made through an appropriate salt bridge. In all cases silver/0.1 mol dm^{-3} silver perchlorate in acetonitrile, separated from the test solution by 0.2 mol dm^{-3} TBAP in THF solution sandwiched between two fritted disks, was used as the reference electrode. Compensation for the *iR* drop was achieved by positive feedback. Ferrocene was added at the end of each experiment as the internal reference. All potentials are referred to the ferrocenium/ferrocene redox couple ($E_{1/2} = +0.080$ V relative to the actual Ag/$AgClO_4$ reference electrode and +0.535 V vs aqueous SCE under the present experimental conditions).

Preparation of the Complexes. $[Ir(dppf)_2]BF_4$ (1c). A solution of $AgBF_4$ (217 mg, 1.12 mmol) in acetone (25 mL) was added to a suspension of $[IrCl(C_8H_{14})_2]_2$[11] (500 mg, 0.56 mmol) in acetone (30 mL) at room temperature under nitrogen. The precipitate of AgCl, formed in a few minutes, was filtered and the resulting orange solution added to a solution of dppf (1.24 g, 2.23 mmol) in CH_2Cl_2 (25 mL). The color of the solution turned immediately to maroon. After 15 min the solution was evaporated under vacuum and the orange residue dissolved in CH_2Cl_2 (20 mL). Addition of methanol (45 mL) afforded a yellow precipitate, which was collected by filtration and washed with methanol and then several times with toluene. The yield of **1c** was 1.07 g (68%). Anal. Calcd for $C_{68}H_{56}BF_4Fe_2Ir$: C, 58.85; H, 4.06. Found: C, 58.52; H, 4.22. $^{31}P\{^1H\}$ NMR (in $CDCl_3$): δ 7.64 (s).

$[IrH(dppf(-H))(dppf)]BF_4$ (2c). A solution of **1** (200 mg) in CH_2Cl_2 (20 mL) was heated at reflux temperature for 2 days. The yellow precipitate formed by addition of hexane was filtered off and recrystallized from CH_2Cl_2/CH_3OH. The yield was essentially quantitative. Anal. Calcd for $C_{68}H_{56}BF_4Fe_2Ir$: C, 58.85; H, 4.06. Found: C, 58.82; H, 4.30. IR (KBr, ν/cm^{-1}): 2196 w (Ir−H). ^1H NMR (400 MHz, in CD_2Cl_2): δ 8.306 (s, 2H), 7.832 (s, 4H), 7.552 and 7.489 (s, 6H), 7.313−6.978 (complex multiplet, 16 H), 6.890 (s, 4H), 6.830 (t, J = 7.4 Hz, 1H), 6.694 (t, J = 7.0 Hz, 4H), 6.310 (t, J = 7.4 Hz), 1H), 5.995 (unresolved multiplet, 1 H) phenyl protons; 5.252 (s, 1H), 5.209 (s, 1 H), 4.661 (s, 1 H), 4.469 (s, 1 H), 4.271 (s, 1 H), 4.228 (s, 1 H), 4.207 (s, 1 H), 3.953 (s, 1 H), 3.950 (s, 2 H), 3.803 (s, 1H), 3.548 (s, 1 H), 3.429 (s, 1 H), 3.039 (s, 1 H), 2.462 (s, 1 H), 1.525 (s, 1 H) cyclopentadienyl protons; −16.00 (ddt, 1 H, $^2J_{PH}$ = 130.5, 16.4, 14.6 Hz) IrH. $^{31}P\{^1H\}$ NMR (36.23 MHz, in CD_2Cl_2): δ 6.18 (ddd, J_{PP} = 348, 18, 15 Hz, 1 P), −3.10 (dt, $^2J_{PP}$ = 348, 16 Hz, 1 P), −3.20 (ddd, $^2J_{PP}$ = 18, 16, 12 Hz, 1 P), −95.88 (q, $^2J_{PP}$ = 12 Hz, 1 P). Mass spectrum (MALDI-TOF): m/z = 1302, ([**1** + H] − BF_4).

$[Ir(dppf)_2]$ (3). A mixture of $[Ir(dppf)_2]BF_4$ (42 mg, 31 μmol) and $[Na(THF)_2][Ir(dppf)_2]$ (45 mg, 31 μmol) was dissolved in 8 mL of a mixture of THF/toluene (1:1 v/v) and stirred a few minutes. The resulting solution was concentrated under vaccum to a small volume (ca. 4 mL) in order to induce the precipitation of $NaBF_4$, which was filtered off. Addition of hexane caused the precipitation of a powdered green solid, which was collected by filtration, washed with hexane, and dried under vacuum. The yield of pure **3** was 57 mg (72%). Anal. Calcd for $C_{68}H_{56}P_4Fe_2Ir$: C, 62.78; H, 4.34. Found: C, 61.24; H, 4.03. Visible−near-IR spectrum in THF: λ_{max} 600 nm (sh, $\epsilon \cong 2100$ M^{-1} cm^{-1}) and 1050 nm (ϵ = 130 M^{-1} cm^{-1}).

$[Na(THF)_2][Ir(dppf)_2]$ (4a). To a THF (4 mL) suspension of **1** (200 mg, 0.14 mmol) was added 15 mL (2 equiv) of a 1.87×10^{-2} mol dm^{-3} THF solution of sodium naphthalenide. In a few minutes, a red-orange solution was obtained, which was concentrated under vacuum to ca. $^1/_2$ of the initial volume, and the precipitate of $NaBF_4$ which formed was filtered off. Addition of hexane gave an orange-red solid, which was collected by filtration, washed with hexane, and carefully dried under vacuum to give 177 mg of a black solid with composition $[Na(THF)_2][Ir(dppf)_2]$, yield 88%. Anal. Calcd for $C_{76}H_{72}O_2P_4Fe_2NaIr$: C, 62.18; H, 4.94. Found: C, 61.94; H, 5.18. ^1H NMR (in toluene-d_8): δ = 7.88 (broad singlet, 16 H, Ph); 6.83 (broad singlet, 24 H, Ph); 4.31 (singlet, 8 H, Cp); 4.06 (s, 8 H, Cp); 3.40 (complex multiplet, 8 H, THF); 1.40 (complex multiplet, 8 H, THF). $^{31}P\{^1H\}$ NMR (in toluene-d_8): δ 7.43 (s). Visible spectrum in THF: λ_{max} 418 nm (ϵ = 13 500 M^{-1} cm^{-1}).

X-ray Diffraction. Suitable dark-red crystals of the d^{10} species, analyzing as $[Na(THF)_5][Ir(dppf)_2]\cdot THF$ (**4b**), were obtained in ca. 24 h from a saturated solution of the complex in toluene upon addition of THF (0.3−0.5 mL/mL of solution), at room temperature. Single crystals (black prisms) of **3** were obtained by slow diffusion of hexane into a toluene solution of $[Ir(dppf)_2]$. The crystals were sealed in a Lindeman capillary and mounted on a Nicolet Siemens R3m/V four-circle automated diffractometer with Mo Kα (λ = 0.710 73 Å) equipped with a graphite monochromator in the incident beam. The intensities of the diffracted beam were measured at room temperature. Unit cell dimensions were obtained from a least-squares fit of 50 reflections on the setting angle $2\theta > 21°$. Data were collected by the $\theta-2\theta$ scan technique, and the intensities of two reflections were monitored periodically. The data were corrected for Lorentz and polarization effects and for absorption. Data collection and structure solution were

---

(9) Gan, K.-S.; Hor, T. S. A. In *Ferrocenes: Homogeneous Catalysis, Organic Synthesis, Materials Science*; Togni, A., Hayashi, T., Eds.; VCH: Weinheim, Germany, 1995.

(10) (a) Schönberg, H.; Boulmaâz, S.; Wörle, M.; Liesum, L.; Schweiger, A.; Grützmacher, H. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 1423. (b) Deblon, S.; Boulmaâz, S.; Mlakar, M.; Schönberg, H.; Grützmacher, H. Presented at the XXXIII International Conference on Coordination Chemistry, Florence, Italy, 1998; Abstract 245.

(11) Herde, J. L.; Lambert J. C.; Senoff, C. V. *Inorg. Synth.* **1974**, *15*, 18.

Table 1. Crystallographic Data for Complexes [Ir(dppf)$_2$], **3**, and [Na(THF)$_5$][Ir(dppf)$_2$]·THF, **4b**

	[Ir(dppf)$_2$]	[Na(THF)$_5$][Ir(dppf)$_2$]·THF
formula	$C_{68}H_{56}P_4Fe_2Ir$	$C_{92}H_{104}O_6P_4Fe_2NaIr$
space group	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)
fw	1300.9	1756.5
a, Å	13.019(4)	13.325(3)
b, Å	13.765(6)	23.976(5)
c, Å	15.549(5)	26.774(7)
α, deg	93.74(3)	90
β, deg	90.35(3)	98.77(2)
γ, deg	92.07(3)	90
V, Å^3	2779(2)	8454(4)
Z	2	4
λ, Å	0.710 73	0.710 73
ρ (calcd), g cm^{-3}	1.555	1.380
μ (Mo Kα), cm^{-1}	30.6	20.4
T, °C	21	21
R^a	0.062	0.043
wR2^b	0.146	0.117

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

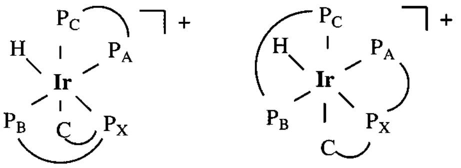


Figure 1. Sketch of the possible structures of the [IrH(dppf(−H))(dppf)]$^+$ ion of isolated **2c**.

carried out using the programs SHELXTL/PC(1994)[12] and SHELXL/93(1993).[13] The structures were solved by the Patterson method for heavy atoms with refinement on F^2 by standard full-matrix least squares. In the last cycles of refinement the Fe, P, O, and C atoms were allowed to vibrate anisotropically, and H atoms were included in ideal positions. The phenyl and cyclopentadienyl rings were refined as rigid bodies, with C−C and C−H distances fixed at 1.395 and 1.08 Å. Anisotropy was introduced only for the non-carbon atoms and for the tetrafluoroborate anion. Crystallographic data and reliability factors are reported in Table 1.

Results and Discussion

Cyclometalation of the Ir(I) Complex [Ir(dppf)$_2$]$^+$. The cationic iridium(I) complex [Ir(dppf)$_2$]$^+$ is indefinitely stable in the solid state, and the X-ray structure of the salt [Ir(dppf)$_2$]BPh$_4$, **1b**, has already been reported.[7] In solution, it slowly converts into the iridium(III) hydrido derivative, [IrH(dppf(−H))(dppf)]$^+$, **2**, resulting from orthometalation of a phenyl group of the phosphine ligands.[14] The reaction occurs in several days at room temperature to give an octahedral complex as the final product, whose spectroscopic data are consistent with the structures sketched in Figure 1.

The hydride ligand is recognized in the IR spectrum by a weak absorption at 2196 cm^{-1}. In the proton NMR spectrum, the hydride resonance appears as a 12-line multiplet at δ −16.00 which can be described as a doublet of a doublet of triplets ($^2J_{PH}$ = 130.5, 16.4, and 14.6 Hz). This pattern is in agreement with a structure in which the hydride is trans to a phosphorus atom, as indicated by the large value of one of the coupling constants ($^2J_{PH(trans)}$ = 130.5 Hz), and in cis position to three ^{31}P nuclei, two of which have the same value of the coupling constant ($^2J_{PH}$ (cis) 14.6 Hz).

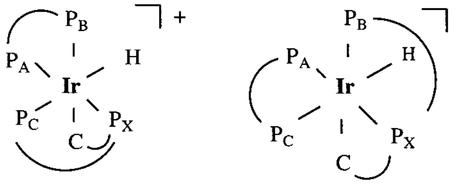


Figure 2. Sketch of the possible structures of the [IrH(dppf(−H))(dppf)]$^+$ ion of intermediate **2c**.

The corresponding ^{31}P{^{1}H} NMR spectrum is characterized by an ABCX multiplet arising from the strongly coupled P$_A$ (δ 6.18) and P$_B$ (δ −3.10) nuclei in mutual trans positions ($^2J_{PP(trans)}$ = 348 Hz), which are further coupled with the atoms P$_C$ and P$_X$ at δ −3.20 and −95.88, respectively, in mutual cis positions ($^2J_{PP(cis)}$ = 15 and 18 Hz). The resonance at highest field, an apparent quartet at −95.88 ppm, is clearly attributable to the phosphorus involved in the four-membered cycle[15] which is trans to the hydride ligand as indicated by the ^{31}P spectrum obtained without proton-decoupling ($^2J_{PH(trans)}$ = 130.5 Hz). Thus, the stereoisomers depicted in Figure 1 result from the two possible connections of P$_X$ and P$_C$ atoms with P$_A$ or P$_B$, respectively.

An octahedral complex of this type lacks any symmetry and consequently all the cyclopentadienyl (Cp) hydrogens are expected to be chemically unequivalent. Accordingly, its ^{1}H NMR spectrum at 400 MHz exhibits 15 singlets in the range δ 5.25−1.52 ppm, attributable to these protons, having all but one the same relative intensity, equal to that of the hydride resonance. Only one signal, at δ 3.950, shows double intensity, indicating that two of the 16 ferrocenyl protons are isochronous. This result rules out the involvement of the Cp rings in the intramolecular C−H oxidative addition to iridium, a reaction observed in thermolysis of the polynuclear ruthenium complex containing a bridging dppf ligand, Ru$_3$(μ-dppf)(CO)$_{10}$.[16]

The formation of **2** occurs through an intermediate which has also been characterized. By monitoring the Ir(I) → Ir(III) conversion by NMR it was possible to detect the initial formation of a hydrido species characterized by a doublet of a doublet of triplets centered at δ −11.65 ($^2J_{PH}$ = 125.7, 20.7, and 14.6 Hz) in the proton spectrum. The ^{31}P{^{1}H} NMR spectrum exhibits an ABCX multiplet in which P$_A$ (δ −8.43) and P$_X$ (−93.25 ppm) are in mutual trans positions ($^2J_{PP}$ = 345 Hz) and weakly coupled with P$_B$ (δ −18.7) and P$_C$ (δ −22.3), with $^2J_{PP(cis)}$ = 12 and 16 Hz. Since the spectrum obtained without proton decoupling indicates that the hydride is trans to P$_C$, the structure of the first product of the cyclometalation reaction of **1** has to be one of those sketched in Figure 2, in which the phosphorus bearing the orthometalated ring (P$_X$) is connected, through the ferrocenyl moiety, to the P$_C$Ph$_2$ unit (left) or the P$_B$Ph$_2$ one (right).

This species slowly isomerizes, probably through a pentacoordinate intermediate, to the final complex **2** in which the hydride ligand is trans to the most shielded phosphorus atom.

---

[12] Sheldrick, G. M. *SHELXTL/PC*, version 5.03; Siemens Analytical X-ray Instruments Inc.: Madison, WI, 1994. *Program for Crystal Structure Determination*; University of Cambridge: Cambridge, 1980.

[13] Sheldrick, G. M. *SHELXTL 93, Program for the Refinement of Crystal Structures*; University of Göttingen: Göttingen, Germany, 1993.

[14] For reviews dealing with related orthometalation processes involving aromatic C−H bonds, see: (a) Constable, E. C. *Polyhedron* **1984**, *3*, 1037. (b) Bruce, M. I. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 73.

[15] (a) Dahleburg, L. *J. Organomet. Chem.* **1983**, *251*, 347. (b) Garrou, P. E. *Chem. Rev.* **1981**, *81*, 229. (c) Cowie, M.; McKeer, I. R.; Loeb, S. J.; Gauthier, M. C. *Organometallics* **1986**, *5*, 860.

[16] (a) Butler, I. R.; Cullen, W. R.; Kim,T.-J.; Rettig, S. J.; Trotter, J. *Organometallics* **1985**, *4*, 972. (b) Bruce, M. I.; Humphrey, P. A.; Shawkataly, O.; Snow, M. R.; Tiekink, E. R. T.; Cullen, W. R. *Organometallics* **1990**, *9*, 2910.

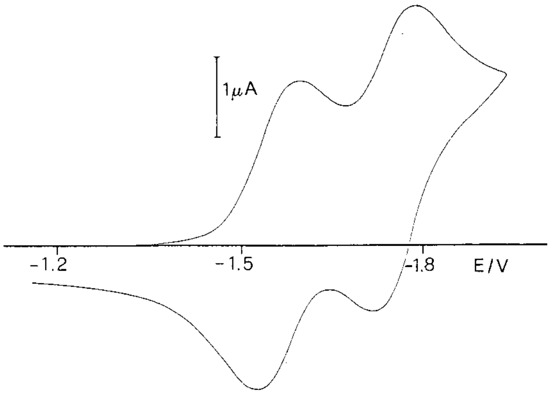


Figure 3. Cyclic voltammogram of 3.2 mM $[Ir(dppf)_2]BPh_4$, **1b**, in THF, 0.2 M TBAP, at 25 °C, scan rate 100 mV/s.

Although the intramolecular oxidative addition of C−H bonds of phenyl-substituted phosphines is quite common for Ir(I) complexes[17] and does occur for $[Ir(PMe_2Ph)_4]^+$ in refluxing CH_3CN,[17d] such a reaction is not reported for the analogues of complex **1** containing alkyl-chained diphosphines. In fact, compounds of the type $[Ir(diphosphine)_2]^+$, where the diphosphines are 1,2-bis(diphenylphosphino)ethane,[18] (*R*)-1-phenyl-1,2-bis(diphenylphosphino)ethane, 1,2-bis(diphenylphosphino)-cyclopentane, (*R*)-1,2-bis(diphenylphosphino)propane, and (2*S*,3*S*)-2,3-bis(diphenylphosphino)butane, are stable.[5]

Reduction of the Ir(I) Species $[Ir(dppf)_2]^+$. A representative cyclic voltammogram of the iridium(I) complex $[Ir(dppf)_2]BPh_4$, **1b**, recorded at 25 °C in THF, 0.2 mol dm^{-3} TBAP, is depicted in Figure 3.

Under these conditions the complex appears to undergo two discrete, chemically reversible, one-electron reductions ($E^1_{1/2} = -1.560$ V, $E^2_{1/2} = -1.755$ V, as mean values of the potentials for cathodic and anodic peak currents), as indicated by the usual parameters ($\Delta E_p \cong 70$ mV; $i_a/i_c = 1$; constancy of E_p and $i_pV^{-1/2}$ with scan rate, V). The course of controlled-potential coulometric experiments and the redox properties of the products are those expected from the voltammetric profile of the depolarizer, i.e., 1 electron/molecule is required for each reduction step, and the reduced species show cyclic voltammetric peaks, anodic and/or cathodic according to the oxidation state, at the appropriate potentials. With electrolysis at a potential midway between the two subsequent half-wave potentials the solution changes from pink to dark brown. The ESR spectrum of the frozen catholyte exhibits a broad unresolved pattern likely due to the absence of coupling between the metal unpaired electron and the phosphorus nuclei. The electronic spectrum of the initial orange $[Ir(dppf)_2]^+$ solution in THF shows bands at 485 and 389 nm ($\epsilon = 1350$ and 2800 M^{-1} cm^{-1}, respectively), while the final dark-brown solution exhibits a broad ligand field band in the near-infrared region ($\lambda_{max} = 1050$ nm; $\epsilon = 130$ M^{-1} cm^{-1}), which is a rather common feature of d^9 compounds with essentially tetrahedral geometry. Further reduction of the dark-brown solution or exhaustive electrolysis of $[Ir(dppf)_2]^+$ at potentials past the second reduction peak produces a red-orange solution which is ESR silent and displays only a strong band at $\lambda_{max} = 418$ nm ($\epsilon = 13\,500$ M^{-1} cm^{-1}) ascribable to a charge-transfer transition. Remarkably, the one-electron reduction solution as well as the spent catholyte, although exceedingly air sensitive, are quite stable in time for several days under carefully deoxygenated N_2.

The electrochemical observations unambiguously point toward the viability of the homoleptic Ir(0) and Ir(−I) dppf complexes along the redox series in eq 1. In particular, the

$$[Ir(dppf)_2]^+ \overset{e}{\rightleftarrows} [Ir(dppf)_2]^0 \overset{e}{\rightleftarrows} [Ir(dppf)_2]^- \quad (1)$$

sequence of the redox potentials allows one to predict that the intermediate d^9 Ir(0) species can be generated by either the one-electron reduction of the precursor $[Ir(dppf)_2]^+$ or the reaction of $[Ir(dppf)_2]^-$ with an equimolar amount of $[Ir(dppf)_2]^+$ in THF. As a matter of fact, $[Ir(dppf)_2]^0$ is in equilibrium with the disproportionated $[Ir(dppf)_2]^+/[Ir(dppf)_2]^-$ ion pair, but the equilibrium lies to the right in eq 2 ($K \cong 2 \times 10^3$), favoring the

$$[Ir(dppf)_2]^+ + [Ir(dppf)_2]^- \rightleftarrows 2[Ir(dppf)_2]^0 \quad (2)$$

radical species in THF at room temperature. Control experiments confirm that the addition of 1 equiv of $[Ir(dppf)_2]^+$ to a red-orange THF solution of electrogenerated $[Ir(dppf)_2]^-$ causes the rapid equilibration of the mixture to the dark-brown $[Ir(dppf)_2]^0$ species.

In an attempt to isolate the single-electron reduction product and/or the fully reduced species for a detailed characterization in the solid state by X-ray analysis, a purely chemical approach to the reduction of **1** employing sodium naphthalenide was undertaken. The results are described below.

Characterization of $[Ir(dppf)_2]$ (3) and $[Ir(dppf)_2]^-$ (4). Addition of 2 equiv of sodium naphthalenide to a THF suspension of $[Ir(dppf)_2]BF_4$, **1c**, forms an orange-red solution from which a black solid analyzing as $[Na(THF)_2][Ir(dppf)_2]$, **4a**, can be isolated in good yield. The ^1H NMR spectrum of the black solid in toluene-d_8 shows two multiplets at δ 3.41 and 1.40 attributable to THF in addition to the resonances due to the phenyl groups (δ 7.87 and 6.80) and to the cyclopentadienyl protons (δ 4.33 and 4.05). The corresponding $^{31}P\{^1H\}$ NMR spectrum is characterized by a single resonance at δ 7.43. Addition of THF causes a shift to lower field of the singlet which is found at δ 12.9 in a 4:1 (v/v) mixture of THF/toluene-d_8.

The black solid, which is soluble in toluene or THF but much less soluble in the mixture of the two solvents, crystallizes from toluene−THF, giving deep-red crystals which have the composition $[Na(THF)_5][Ir(dppf)_2]\cdot THF$, **4b**, as deduced by X-ray analysis. The structure of this sodium-solvated salt is depicted in Figure 4, and the main bond distances and angles are listed in Table 2.

The anion $[Ir(dppf)_2]^-$ contains the Ir atom bound to two chelated dppf molecules in a slightly distorted tetrahedral environment, the geometry expected for an 18-electron tetra-coordinated complex. The coordination planes of the ligands, containing the P(1), Ir, and P(2) atoms and the P(3), Ir, and P(4) atoms, form a dihedral angle of 85°, but only two of the P−Ir−P angles are essentially tetrahedral (Table 2). The bite angles of the diphosphines (P(1)−Ir−P(2) = 104.8° and P(3)−Ir−P(4) = 99.8°) deviate significantly from ideal values, and one of them is very similar to that found in $[Ir(C_8H_{12})(dppf)]^+$

---

[17] (a) Bennett, M. A.; Milner, D. L. *J. Am. Chem. Soc.* **1969**, *91*, 6983. (b) Valentine, J. S. *J. Chem. Soc., Chem. Commun.* **1973**, 857. (c) Longato, B.; Morandini, F.; Bresadola, S. *J. Organomet. Chem.* **1975**, *88*, C7. (d) Crabtree, R. H.; Quirk, J. M.; Felkin, H.; Fillebeen-Khan, T.; Pascard, C. *J. Organomet. Chem.* **1980**, *187*, C32. (e) Crabtree, R. H.; Mellea, M. F.; Mihelcic, J. M.; Quirk, J. M. *J. Am. Chem. Soc.* **1982**, *104*, 107.

[18] (a) Vaska, L.; Chen, L. S.; Miller, W. V. *J. Am. Chem. Soc.* **1971**, *93*, 6671. (b) Johnson, C. E.; Eisemberg, R. *J. Am. Chem. Soc.* **1985**, *107*, 3148.

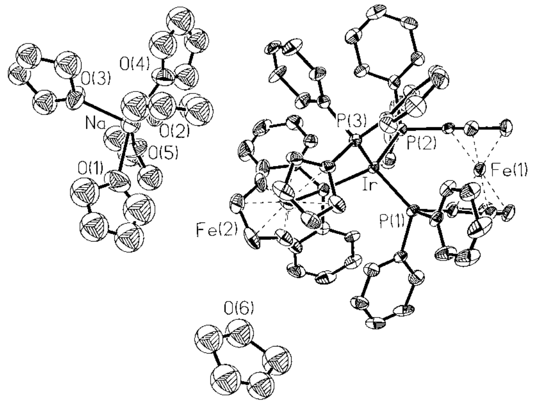


Figure 4. Crystal structure of $[Na(THF)_5][Ir(dppf)_2]\cdot THF$, **4b**. Thermal ellipsoids are drawn at the 40% probability level.

Table 2. Comparision of Selected Bond Distances (Å) and Angles (deg) for $[Ir(dppf)_2]BPh_4$, **1b**, $[Ir(dppf)_2]$, **3**, and $[Na(THF)_5][Ir(dppf)_2]\cdot THF$, **4b**

	1b	**3**	**4b**
	Bond Lengths		
Ir−P(1)	2.317(6)	2.296(3)	2.242(3)
Ir−P(2)	2.389(5)	2.326(3)	2.255(3)
Ir−P(3)	2.337(5)	2.301(4)	2.254(3)
Ir−P(4)	2.343(6)	2.315(3)	2.270(3)
Ir−P(av)[a]	2.346[15]	2.309[8]	2.255[6]
Ir···Fe(av)	4.438	4.366	4.306
	Bond Angles		
P(1)−Ir−P(2)	95.0(2)	102.1(1)	104.8(1)
P(3)−Ir−P(4)	93.6(2)	97.6(1)	99.8(1)
P(2)−Ir−P(3)	98.3(2)	104.5(1)	108.9(1)
P(1)−Ir−P(4)	95.7(2)	105.2(1)	110.4(1)
P(1)−Ir−P(3)	140.6(2)	121.4(1)	113.2(1)
P(2)−Ir−P(4)	145.9(2)	128.1(1)	119.9(1)
	Dihedral Angles		
P(1), Ir, P(2)/P(3), Ir, P(4)	51.0	74.7	85.0

[a] The estimated deviation in square brackets is calculated as $[\ ] = [\sum_n \Delta_i^2/n(n-1)]^{1/2}$ in which Δ_i is the deviation of the ith of n values from the arithmetic mean of the set.

(99.2°).[19] The Ir−P bond distances are in the range 2.242(3)−2.270(3) Å with an average value of 2.255 Å. The cyclopentadienyl rings are staggered (synclinal or gauche), forming angles of 37.9° (Cp1 and Cp2)[20] and 23.0° (Cp3 and Cp4), and slightly tilted away from the Fe center with dihedral angles of 3.6° (Cp1 and Cp2) and 3.4° (Cp3 and Cp4).

The sodium ion is coordinated to the oxygen atoms of five molecules of THF in a distorted trigonal-bipyramidal geometry. The oxygen atoms in the equatorial plane have an average distance (2.32 Å) which is slightly shorter than those in the apical position (2.38 Å), in good agreement with those found for other pentacoordinated sodium complexes.[21] The sixth THF molecule does not interact significantly with the sodium cation.

Ir(0) complex **3** can be conveniently prepared according to eq 2 by reacting equimolar amounts of **1c** and **4a** in THF solution. The reaction occurs instantaneously as shown by the appearance of a black color and the separation of $NaBF_4$. The ESR spectrum of the isolated **3** in toluene (Figure 5) is virtually identical to that already observed during the one-electron reduction of **1b** in THF. The phosphorus and/or iridium hyperfine interactions are unresolved, and the shape of the spectrum is consistent with an axially symmetrical distribution of the ligands with $g_{||}$ (2.19) > $g_{\perp}$ (2.06), a spectral feature observed previously in the related species $Ir(CO)(PPh_3)_3$ and attributed to a tetrahedrally distorted coordination around the metal.[6,22] This hypothesis is confirmed by the single-crystal X-ray analysis of complex **3**, whose structure is shown in Figure 6.

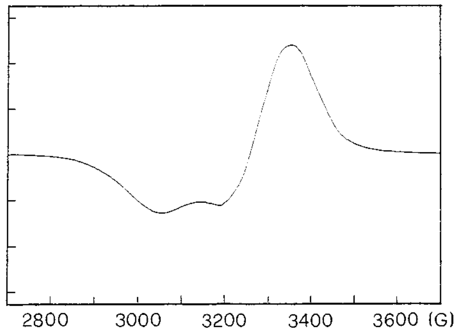


Figure 5. ESR spectrum of $[Ir(dppf)_2]$, **3**, in toluene at $T = 120$ K.

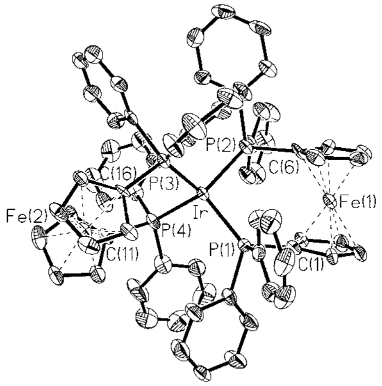


Figure 6. Crystal structure of $[Ir(dppf)_2]$, **3**. Thermal ellipsoids are drawn at the 40% probability level.

The geometrical environment of the Ir atom in $[Ir(dppf)_2]$ is between the highly distorted square-planar $[Ir(dppf)_2]^+$ [7] and the slightly irregular tetrahedral geometry found for $[Ir(dppf)_2]^-$. The average Ir−P bond distance is 2.309 Å, ranging from 2.296(1) to 2.326(3) Å found for Ir−P(1) and Ir−P(4), respectively, and the bite angles of the diphosphines are 102.1(1)° (P(1)−Ir−P(2)) and 97.6(1)° (P(3)−Ir−P(4)). The coordination planes, defined by the atoms P(1), Ir, and P(2) and P(3), Ir, and P(4), form a dihedral angle of 74.7°. The Cp rings of one dppf molecule are staggered (the torsion angle (τ) defined by P(1)−C(1)−C(6)−P(2) is 34.0(1)°), but deviate from this conformation in the second ligand ($\tau = 24.5(1)$°) while maintaining in both cases an almost perfect parallelism (3.3(4)° in Cp1/Cp2 and 2.1(4)° in Cp3/Cp4).

In Table 2 the main structural parameters of this complex are compared with those of the reduced and oxidized analogues **4** and **1**, respectively.

The atom-labeling scheme used in Figures 4 and 6 stems from the observation that the two diphosphines in **1**, as well in **3** and **4**, exhibit significant differences in some structural details. In $[Ir(dppf)_2]^+$, the torsion angle of the cyclopentadienyl rings is 34.8° for a phosphine and only 25.1° for the other one; the diphosphine with larger τ value shows a larger chelation angle

---

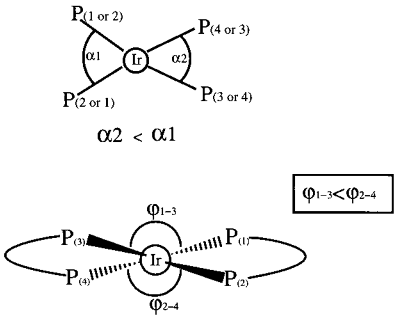
(19) Bedford, R. B.; Chaloner, P. A.; Hitchcock, P. B. *Acta Crystallogr. C* **1993**, 1614.

(20) The notation Cp1, Cp2, etc. refers to the cyclopentadienyl group bound to phosphorus atom P(1), P(2), etc.

(21) Fenton, D. E. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon Press: Oxford, England, 1987; Vol. 3, p 5.

(22) A detailed ESR study in 2-methyltetrahydrofuran at 20 K of $[Ir(dppf)_2]$ and the strictly related $[Rh(dppf)_2]$ will be reported elsewhere.

Scheme 1. Atom-Labeling Scheme Used for the Diphosphines in the Series of Complexes **1**, **3**, and **4**



(95.0(2)° vs 93.6(2)°). We chose to label with P(1), P(2) the diphosphine with larger chelation angle (and larger τ value) and with P(2), P(4) the couple of atoms of different diphosphines forming the larger P−Ir−P angle (<180°) as summarized in Scheme 1.

It can be seen that as the charge of the complex decreases from +1 to −1, the Ir−P distances decrease at first by 0.04 Å and then by 0.05 Å. The average of the two changes is 0.045 Å, a value very similar to that observed in the series of dinuclear complexes $[Re_2Cl_4(PMe_2Ph)_4]^n$ ($n = 0, +1, +2$),[23] but significantly lower than that found in other redox-related pairs of complexes.[24] The decrease of the metal−phosphorus distance on metal-based reduction has been interpreted as the increasing contribution of the M → P π bonding as the formal charge of the metal is decreased.

The shortening of the Ir−P bonds as a result of the addition of electrons to the metal is accompanied by a twist of the four donor atoms toward the tetrahedral geometry required for the d^{10} configuration, without significant changes in the phosphorus−carbon distances. Accordingly, the chelation angles of the two diphosphines increase by 5.6° (average) when Ir(I) is reduced to Ir(0), and a further increase of 2.4° is observed in the subsequent reduction to Ir(−I). The dihedral angle formed by the planes containing P(1), Ir, and P(2) and P(3), Ir, and P(4) increases by 23.7° and 10.3° in the first and second reduction steps, respectively. Taking into account the high flexibility of dppf, documented by the wide range of values (93.6(2)° [7] to 155.9(1)° [25]) observed for the chelation angle, the deviation from the ideal value of the chelation angles in **4** may be attributed to steric crowding of the two bulky ferrocenyl ligands.

Concluding Remarks

The cation $[Ir(dppf)_2]^+$ represents a rare example of Ir(I) complex which undergoes cyclometalation in very mild conditions. The reaction, slow enough to allow the isolation of **1** as a pure compound,[7] is favored by the steric requirements of the dppf ligands as clearly evidenced by the large deviation from the planarity of this d^8 complex. The product of this intramolecular oxidative addition slowly isomerizes to form the six-coordinate d^6 species $[IrH(dppf(-H))(dppf)]^+$ as a single stereoisomer.

The appropriate balance of steric and electronic properties of the organometallic ligand dppf plays an important role in the stabilization of the iridium atom in the d^9 and d^{10} configurations. In fact, compounds **3** and **4** are the first examples of homoleptic Ir(0) and Ir(−I) phosphine complexes characterized by X-ray diffraction. Finally, the comparative analysis of structural parameters of the two redox-related pairs of complexes shows that the most important structural changes of the metal environment occur in the Ir(I) → Ir(0) conversion, indicating a marked propensity of the d^9 species toward the tetrahedral geometry.

Acknowledgment. The authors are indebted to Dr. G. Valle for help in solving the structure of $Ir(dppf)_2$ and Dr. P. Traldi for providing the mass spectral data. Partial support of this work by Ministero dell' Università e della Ricerca Scientifica e Tecnologica (Pharmacological and diagnostic properties of metal complexes) is gratefully acknowledged.

Supporting Information Available: X-ray crystallographic files in CIF format for the structure determinations of $[Ir(dppf)_2]$ and $[Na(THF)_5][Ir(dppf)_2]\cdot THF$. This material is available free of charge via the Internet at http://pubs.acs.org.

IC981166S

---

(23) Cotton, F. A.; Dunbar, K. R.; Falvello, L. R.; Tomas, M.; Walton, R. A. *J. Am. Chem. Soc.* **1983**, *105*, 4950.

(24) See, for example: (a) Connelly, N. G.; Freeman, M. J.; Orpen, A. G.; Sheehan, A. R.; Sheridan, J. B.; Sweigart, D. A. *J. Chem. Soc., Dalton Trans.* **1985**, 1019. (b) Orpen, A. G.; Connelly, N. G. *Organometallics* **1990**, *9*, 1206. (c) Pilloni, G.; Bandoli, G.; Tisato, F.; Corain, B. *J. Chem. Soc., Chem. Commun.* **1996**, 433.

(25) Sato, M.; Shigeta, H.; Sekino, M.; Akabori, S. *J. Organomet. Chem.* **1993**, *458*, 199.