A novel two-electron mixed-valence Ir(II)–Ir(0) complex

Alan F. Heyduk and Daniel G. Nocera*

Department of Chemistry, Massachusetts Institute of Technology, 6-335, 77 Massachusetts Avenue, Cambridge, MA 02139-4307, USA. E-mail: nocera@mit.edu

An Ir^{II}–Ir^0 mixed-valence complex, Ir$_2$\{MeN-[P(OEt^{F3})$_2$]$_2$\}$_3$Cl$_2$ (OEt^{F3} = OCH$_2$CF$_3$), has been prepared by treatment of Ir$_2$Cl$_2$(cod)$_2$ with 3 equiv. of MeN-[P(OEt^{F3})$_2$]$_2$; donor ligands (CNBu^t and PEt$_3$) add to the binuclear core, which provides a novel platform for the multielectron activation of small molecule substrates.

Few ligand systems are able to support the intramolecular disproportionation of a symmetric binuclear metal core. The bis(difluorophosphino)methylamine (dfpma) ligand,[1] CH$_3$N(PF$_2$)$_2$, therefore, is distinguished by its ability to drive the conversion of binuclear Rh^I(μ-X$_2$)Rh^I (X = Cl, Br or I) dimers to two-electron mixed-valence X$_2$Rh^{II}–Rh^0 complexes.[2] When a long-lived excited state can be incorporated into the electronic structure of the two-electron mixed-valence center, controlled multielectron photoreactivity may be achieved.[3] For instance, we have recently accomplished a four-electron photoreaction among discrete molecular species, for the first time, by using a dσ* excited state to interconvert among Rh(0,0)$_2$(dfpma)$_3$(L)$_2$, Rh(II,0)$_2$(dfpma)$_3$X$_2$(L) and Rh(II,II)$_2$(dfpma)$_3$X$_4$ (L = PF$_3$, η^1-dfpma or PPh$_3$).[4] By spanning reduced LRh^0–Rh^{0}L and oxidized X$_2$Rh^{II}–Rh^{II}X$_2$ brethren, the X$_2$Rh^{II}–Rh^{0}L complex sustains the multielectron reactivity of the Rh$_2$ dfpma system. This multielectron design strategy is general as long as a two-electron mixed-valence complex can be stabilized with respect to its symmetric congener.

With the understanding that M^{n+2}–M^n complexes are a keystone to multielectron photoreactivity, we sought to expand the concept of two-electron mixed valency to other transition metals. Our initial attempts focused on iridium, for which Ir^0–Ir^{II} cores are unknown.[5] Efforts to use the dfpma ligand to develop a parallel chemistry to that of Rh, however, were met with frustration as mixtures of Ir^I monomers and various oligomerization products were obtained. Introduction of more sterically demanding OR substituents on P could avoid these problematic reactions while providing us with the additional flexibility of tuning the electronic properties[6] of the two-electron mixed-valence core by R substitution. As we now report, an excursion into Ir chemistry with the bidentate diphosphazane, MeN[P(OEt^{F3})$_2$]$_2$ (OEt^{F3} = OCH$_2$CF$_3$), successfully afforded two-electron mixed-valence compounds and not the oligomers that plague Ir dfpma chemistry.

Addition of HOEt^{F3} to a cold Et$_2$O solution of MeN(PCl$_2$)$_2$[1,7] and NEt$_3$ results in the formation of MeN[P(OEt^{F3})$_2$]$_2$ in good yields.[8] Ir$_2$Cl$_2$(cod)$_2$ was treated with 3 equiv. of the ligand in CH$_2$Cl$_2$ at room temperature. The solution immediately turned yellow and then slowly darkened to orange–brown. Over several days, a fine green powder precipitated from the reaction solution. Single crystals of the compound, which analyzes as Ir$_2$\{MeN[P(OEt^{F3})$_2$]$_2$\}$_3$Cl$_2$ (1),† were obtained from saturated CH$_2$Cl$_2$ solutions of 1 at 22 °C.

X-Ray diffraction analysis of 1 reveals the unsymmetrical coordination sphere of the Ir^0–Ir^{II} binuclear core displayed in Fig. 1.‡ In a structural departure from Rh–dfpma chemistry, two of the three bidentate ligands adopt a bridging coordination mode with the third ligand binding as a chelate. The Ir^0 center possesses a trigonal bipyramidal coordination geometry that is typical for d^9 metals composing a binuclear core.[2,9] Two

equatorial sites of the Ir^0 center are coordinated by phosphites from the bridging MeN[P(OEt^{F3})$_2$]$_2$ ligands with the third equatorial site occupied by one end of a chelating MeN-[P(OEt^{F3})$_2$]$_2$ ligand. The other end of the chelating ligand resides at an axial coordination site of the Ir^0 center. The apical position of the square pyramid that defines the coordination geometry about the neighboring Ir^{II} center is reciprocally capped by the Ir^0 center. Two *cis*-equatorial sites are occupied by phosphites from the bridging ligands, while the other two equatorial sites are occupied by chloride ligands. An Ir–Ir bond distance of 2.7871(8) Å is typical of singly bonded binuclear iridium complexes.[10]

Although 1 shows little solubility in non-coordinating solvents, the 16-e$^-$ Ir^{II} center readily receives donor ligands at its open coordination site, rendering more soluble derivatives. Addition of CNBu^t or PEt$_3$ to suspensions of 1 in CH$_2$Cl$_2$ results in the rapid dissolution of the solid to form bright yellow solutions.† Pale yellow crystals of the CNBu^t (2) and PEt$_3$ (3) derivatives were obtained upon the addition of pentane to reaction solutions that had been concentrated by solvent evaporation. Ligand occupation of the vacant axial site of the Ir^{II} center of 1 is confirmed by an X-ray crystal structure of 2.‡ Excepting changes along the P$_{ax}$–Ir^0–Ir^{II}–L axis, the X-ray crystal structure of 2, is very similar to that of 1.

As determined from ^{1}H and ^{31}P NMR spectroscopy, the solid state coordination geometries of 1–3 are preserved in solution. Whereas the methylene protons of the ligand's OCH$_2$CF$_3$ group are not well resolved, two distinct resonances in a 2 : 1 ratio are observed for the methyl groups of both the bridging and chelating MeN[P(OEt^{F3})$_2$]$_2$ ligands. The integration ratios for the protons of CNBu^t and PEt$_3$ in 2 and 3, respectively, compared to those of the proton resonances of MeN-[P(OEt^{F3})$_2$]$_2$ establish the incorporation of only one ligand into the diiridium coordination sphere. The ^{31}P NMR spectra presented in Fig. 2 reveal congruent solution structures for 1–3. Two signals at δ *ca.* 46 and 95 are maintained in each of the spectra, consistent with the preserved equatorial arrangement of phosphites in 1–3. The resonance at δ 46 is assigned to the P(5) phosphite of the Ir^0 equatorial plane and the resonance at δ 95
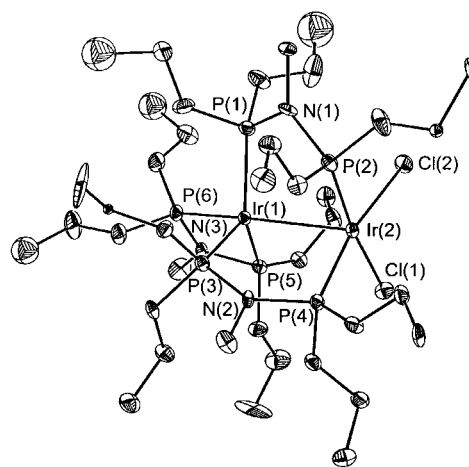

Fig. 1 ORTEP representation of 1, with fluorine atoms omitted for clarity. Thermal ellipsoids are drawn at the 25% probability level.
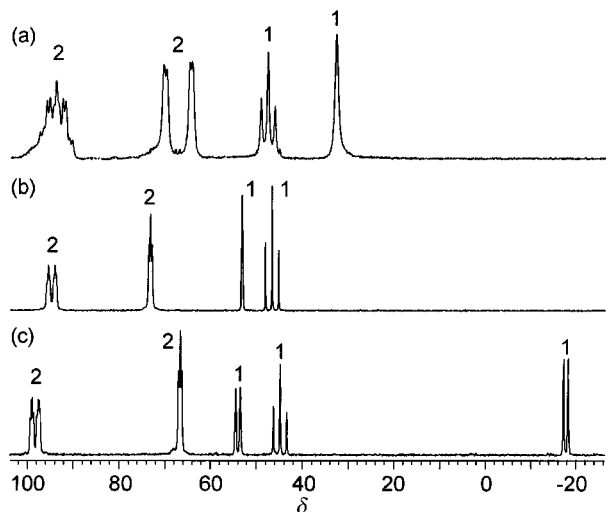
Fig. 2 ^{31}P NMR (121.488 MHz) of the two-electron mixed-valence compounds (a) **1**, (b) **2** and (c) **3** in CD$_3$CN, referenced to an external 85% H$_3$PO$_4$ standard. The relative integration values are indicated for each phosphorus resonance.

is consistent with the P(2)/P(4) equatorial phosphites coordinated to the Ir^{II} center. Conversely, differences are observed for the resonance associated with the axial phosphite [P(6)]. The high frequency shift of the P(6) resonance from δ 32.7 in **1** to δ 52.5 and 53.3 in **2** and **3**, respectively, is in accordance with the structural perturbations induced by the presence of the donor ligand in the axial coordination site of Ir^{II}. The observed increase in the Ir^0–P$_{ax}$ bond distance [d(Ir(1)–P(6)) = 2.238(6) Å in **2** vs d(Ir(1)–P(6)) = 2.206(4) Å in **1**] upon coordination of the donor ligand is expected to result in decreased Ir$^0 \rightarrow$ P$_{ax}$ π-backbonding and consequently a shift of the axial phosphite resonance to higher frequency. The ^3J(P$_{ax}$,PEt$_3$) coupling for **3**, and its absence in **1** and **2**, follows logically from the coordination of a phosphorus donor ligand along the metal–metal bond. The only other significant difference in the three spectra of Fig. 2 is the collapse of the resonances at δ 64.7 and 70.5 of **1**, assigned to the remaining Ir^0 phosphites [P(1) and P(3)], to give triplet signals at δ 72.5 and 66.0 for **2** and **3**, respectively.

Initial investigations of the reactivity of the Ir^{II}–Ir^0 compounds suggest a facile oxidative-addition chemistry. Suspensions of **1** in CH$_2$Cl$_2$ yield homogeneous, yellow solutions upon the introduction of H$_2$, I$_2$, HCl and PhICl$_2$. As exemplified by the reaction between **1** and PhICl$_2$, the addition products are consistent with the presence of an Ir$^I \rightarrow$Ir^{III} dative bond, with both metals assuming an octahedral coordination geometry. The NMR spectrum of the isolated product, Ir$_2$\{MeN-[P(OEt^{F3})$_2$]$_2$\}$_3$Cl$_4$, shows that the coordination of the bridging and chelating phosphites remains unchanged. In contrast to **1**, reactions of **2** and **3** with strong oxidants proceed sluggishly and not at all with H$_2$. This arrested reactivity of the latter complexes suggests that ligand dissociation should precede the oxidative-addition of substrates when the diiridium core is coordinatively saturated.

Previous reactivity studies of bimetallic complexes indicate that the presence of two-electron mixed valence cores inhibit oxidation–reduction chemistry.[11] Thus, our observation that the mixed-valence Ir^{II}–Ir^0 core undergoes facile redox conversions is noteworthy. Current investigations are continuing to explore the structure, spectroscopy and reactivity of the Ir^{II}–Ir^0 compounds and their addition products.

Notes and references

† *Experimental Procedures:* **1**: in a nitrogen atmosphere, 734 mg (1.51 mmol) of MeN[P(OEt^{F3})$_2$]$_2$ was added to a solution of 331 mg (0.493

mmol) of Ir$_2$Cl$_2$(cod)$_2$ (Strem) dissolved in 15 mL of CH$_2$Cl$_2$. The mixture was stirred at room temp. for 24 h during which a dark precipitate formed. A green powder precipitated from solution over several days. The solid was collected by filtration, washed with 5 mL of C$_6$H$_6$ and three 5 mL aliquots of pentane and then dried *in vacuo* to yield 590 mg (62%) of the analytically pure product. C$_{27}$H$_{33}$Cl$_2$F$_{36}$Ir$_2$N$_3$O$_{12}$P$_6$; found: C, 17.06; H, 1.65; N, 2.29; P, 9.63; requires: C, 16.92; H, 1.74; N, 2.19; P, 9.70%. ^{1}H NMR (CD$_3$CN, 300 MHz, TMS) δ 2.576 (t, 10.5 Hz, 3 H), 2.763 (s, 6 H), 4.0–5.5 (m, 24 H). ^{31}P NMR (CD$_3$CN, 121 MHz, 85% H$_3$PO$_4$) δ 32.710 (s), 47.665 (dd, 299, 292 Hz), 64.702 (m), 70.509 (m), 94.002 (m). UV–VIS (CH$_2$Cl$_2$) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}): 271 (11 400), 348 (1090), 402 (1480), 509 (140).

2: in an N$_2$ atmosphere, a few drops of CNBu^t were added to a suspension of **1** (201 mg, 0.105 mmol) in 8 mL of CH$_2$Cl$_2$ at room temperature. The solution immediately turned yellow and all the solid dissolved. After a few hours the solvent volume was reduced to 2 mL and 10 mL of pentane was added. Cooling the solution to −35 °C over 24 h resulted in the formation pale yellow crystals exhibiting a plate morphology. Yield 155 mg (74%). C$_{32}$H$_{42}$Cl$_2$F$_{36}$Ir$_2$N$_4$O$_{12}$P$_6$; found: C, 19.30; H, 2.18; N, 2.86; requires: C, 19.22; H, 2.12; N, 2.80%. ^{1}H NMR (CD$_3$CN, 300 MHz, TMS) δ 1.510 (s, 9 H), 2.494 (dd, 12.3, 9.0 Hz, 3 H), 2.730 (dt, 9.0, 3.6 Hz, 6 H), 4.15–4.95 (m, 24 H). ^{31}P NMR (CD$_3$CN, 121 MHz, 85% H$_3$PO$_4$) δ 46.056 (t, 290 Hz), 52.509 (s), 72.530 (t, 75.4 Hz), 93.960 (dm, 290 Hz). UV–VIS (CH$_2$Cl$_2$) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}): 302 (13 400).

3: in an N$_2$ atmosphere, PEt$_3$ (19 mg, 0.160 mmol) was added to **1** (102 mg, 0.053 mmol) in 10 mL of CH$_2$Cl$_2$ at room temperature. The solution immediately turned yellow and all the solid dissolved. The solution was concentrated and 10 mL of pentane was added. Cooling to −35 °C overnight caused a yellow microcrystalline solid to precipitate from solution. Yield 87 mg (81%). C$_{33}$H$_{48}$Cl$_2$F$_{36}$Ir$_2$N$_3$O$_{12}$P$_7$; found: C, 19.58; H, 2.55; N, 2.12; requires: C, 19.22; H, 2.12; N, 2.80%. ^{1}H NMR (CD$_3$CN, 300 MHz, TMS) δ 1.230 (dt, 13.2, 7.6 Hz, 9 H), 2.114 (dq, 7.4, 7.5 Hz, 6 H), 2.559 (dd, 11.7, 8.7 Hz, 3 H), 2.648 (m, 6 H), 4.040 (m, 2 H), 4.29–4.87 (m, 18 H), 5.010 (m, 4 H). ^{31}P NMR (CD$_3$CN, 121 MHz, 85% H$_3$PO$_4$) δ: −18.189 (dd, 205 Hz, 18.8 Hz), 44.238 (t, 288 Hz), 53.340 (d, 208 Hz), 65.967 (t, 71.4 Hz), 97.496 (dm, 291 Hz).

‡ *Crystal data*: **1**: C$_{27}$H$_{29}$Cl$_2$F$_{36}$Ir$_2$N$_3$O$_{12}$P$_6$, M = 1912.65, monoclinic, space group $C2/c$, a = 22.6597(5), b = 12.8038(2), c = 40.1310(6) Å, β = 92.4210(10)°, U = 11632.8(4) Å^3, Z = 8, D_c = 2.184 g cm^{-3}, T = 183(2) K, μ = 4.996 mm^{-1}, $wR2$ = 0.1441 (8322 independent reflections), $R1$ = 0.0669 [$I > 2\sigma(I)$]. C(8), C(14) and the CF$_3$ group of C9 were disordered between two positions. The fluorine atoms on C(5) and C(7) were placed in an idealized, tetrahedral geometry.

2: C$_{32.5}$H$_{43}$Cl$_3$F$_{36}$Ir$_2$N$_4$O$_{12}$P$_6$, M = 2042.28, monoclinic, space group $P2_1/n$, a = 13.0879(2), b = 54.4519(9), c = 18.4318(3) Å, β = 101.1890(10)°, U = 12885.9(4) Å^3, Z = 8, D_c = 2.105 g cm^{-3}, T = 183(2) K, μ = 4.558 mm^{-1}, $wR2$ = 0.1787 (18440 independent reflections), $R1$ = 0.0892 [$I > 2\sigma(I)$]. The asymmetric unit contains two chemically identical, but crystallographically different molecules; the CF$_3$ groups were generated in an idealized, tetrahedral geometry then refined anisotropically. CCDC 182/1301.

1 J. F. Nixon, *J. Chem. Soc. A*, 1968, 2689.
2 J. I. Dulebohn, D. L. Ward and D. G. Nocera, *J. Am. Chem. Soc.*, 1988, **110**, 4054; 1990, **112**, 2969; J. Kadis, Y.-g. K. Shin, J. I Dulebohn, D. L. Ward and D. G. Nocera, *Inorg. Chem.*, 1996, **35**, 811.
3 C. M. Partigianoni and D. G. Nocera, *Inorg. Chem.*, 1990, **29**, 2033; C. M. Partigianoni, C. Turró, T. L. C. Hsu, I. J. Chang and D. G. Nocera, *Adv. Chem. Ser.*, 1993, **238**, 147; D. G. Nocera, *Acc. Chem. Res.*, 1995, **28**, 209; T. L. C. Hsu, S. A. Helvoigt, C. M. Partigianoni, C. Turró and D. G. Nocera, *Inorg. Chem.*, 1995, **34**, 6186; D. S. Engebretson, E. Graj, G. E. Leroi and D. G. Nocera, *J. Am. Chem. Soc.*, 1999, **121**, 868.
4 A. F. Heyduk, A. M. Macintosh and D. G. Nocera, *J. Am. Chem. Soc.*, 1999, **121**, 5023.
5 The Cambridge Structure Database (CSD) was searched, as were the Science Citation Index and Chemical Abstracts using the key words 'iridium' and 'mixed-valence.'
6 C. A. Tolman, *Chem. Rev.*, 1977, **77**, 313.
7 R. B. King and J. Gimeno, *Inorg. Chem.*, 1978, **17**, 2390.
8 A. L. Odom, A. F. Heyduk and D. G. Nocera, manuscript in preparation.
9 M. A. Bennett and D. J. Patimore, *Inorg. Chem.*, 1971, **10**, 2387; R. B. King, M. Chang and M. G. Newton, *J. Organomet. Chem.*, 1985, **296**, 15.
10 B. R. Sutherland and M. Cowie, *Inorg. Chem.*, 1984, **23**, 2324; C. P. Kubiak, C. Woodcock and R. Eisenberg, *Inorg. Chem.*, 1980, **19**, 2733.
11 B. Bosnich, *Inorg. Chem.*, 1999, **38**, 2554; D. G. McCollum and B. Bosnich, *Inorg. Chim. Acta*, 1998, **270**, 13.