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Water addition to a two-electron mixed-valence bimetallic center†‡

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Water adds to the two-electron mixed-valence $Ir^{0,II}_2$ core of $Ir_2(tfepma)_3Cl_2$ (tfepma = $MeN[P(OCH_2CF_3)_2]_2$) to cleanly generate an $Ir^{I,III}_2$ hydride. Dehydrohalogenation across the Ir–Ir bond returns the complex to an $Ir^{0,II}_2$ species.

Two-electron mixed valence (M^n–M^{n+2}) complexes exhibit a rich ground- and excited-state multielectron chemistry. Particularly intriguing is the facile elimination of hydrogen from two-electron mixed valence metal-hydride cores with HX as the primary substrate.[1,2] For the case of dirhodium complexes, HX addition to a $Rh^{0,0}_2$ center produces a Rh^0–$Rh^{II}X_2$ complex and dihydrogen. The Rh^{II}–X bond may be photoactivated,[3,4] thus permitting the construction of a photocatalytic cycle for the production of hydrogen from homogeneous HX solutions.[5] Owing to an interest in photochemical hydrogen generation, especially from water,[6] we began exploring reactions to produce reactive metal hydrides of M^n–M^{n+2} complexes directly from H_2O. We now report the reaction of H_2O with the two-electron mixed-valence species, $(tfepma)_3Ir_2Cl_2$ (**1**),[7] [tfepma = bis(bis-(trifluoroethoxy)phosphino)methylamine, $MeN[P(OCH_2CF_3)_2]_2$]. Oxidative addition of water at ambient temperatures to the bimetallic $Ir^{0,II}_2$ core leads to the production of an unusual diiridium hydride.

Addition of H_2O to **1** proceeds smoothly in either THF or CH_2Cl_2, though solutions of the latter are heterogeneous and require longer reaction times. In either medium, the reaction endpoint is signaled by the appearance of a homogeneous orange solution. Clear colorless crystals of the product (**2**) deposit from CH_2Cl_2 solutions layered with pentane.§ X-ray diffraction analysis¶ reveals the unsymmetrical coordination sphere of the $Ir^{I,III}_2$ binuclear core displayed in Fig. 1. The Ir–Ir bond distance of 2.7315(7) Å is consistent with singly bonded binuclear iridium complexes.[8,9] The complex is distinguished by the apparent open coordination site on the Ir(2) center and an unusual two-atom phosphite bridging ligand, which forms upon tfepma P–N bond cleavage. Though the iridium hydride could not be located crystallographically, an appropriate open coordination site with a P(2)–Ir(2)–P(6) angle of 149.90 (10)° indicates its existence. The strain induced by the four-atom ring constricts the bimetallic center, thus explaining the relatively short Ir–Ir bond. The four-atom ring causes the primary coordination sphere of the Ir(2) center to deviate from an authentic octahedral coordination geometry as indicated by the considerable divergence of the P(5)–Ir(2)–P(6) and P(6)–Ir(2)–Ir(1) angles (104.27(10)° and 69.48(7)°, respectively) from 90°. The bridging P(6)–O(13) bond is short (1.521 (7) Å) considering that the average distance of all other phosphite bonds is 1.608 (10) Å.

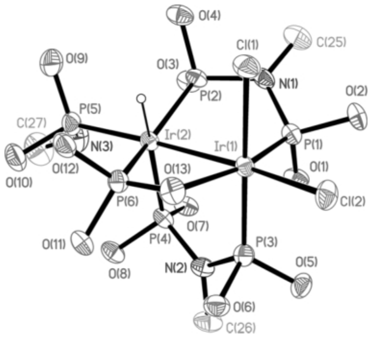

Fig. 1 Solid state structure of **2** with CF_3CH_2 atoms omitted for clarity, Ir(1)–H inserted into structure; ellipsoids drawn at the 50% probability level. Selected bond lengths [Å]: Ir(1)–Ir(2) 2.7315(7), Ir(1)–O(13) 2.183(6), P(6)–O(13) 1.521(7), Ir(2)–P(6) 2.287(2), $(P–O)_{avg}$ 1.608(10), Ir(1)–Cl(1) 2.427(2), Ir(1)–Cl(2) 2.495(2), Ir(2)–P(5) 2.257(2).

^1H and ^{31}P NMR spectroscopy confirm that the solid-state coordination geometry of **2** is preserved in solution. Two distinct resonances of equal integration indicate the incorporation of one water molecule (Figure S1a).‡ Those same signals are absent (Figure S1b) when D_2O is the substrate, allowing for the assignment of the two doublet of quartets at 3.78 and at −11.28 ppm to N–H and Ir–H, respectively. Though the methylene protons of tfepma are unresolved, three N–Me resonances (2.94, 2.80, and 2.72 ppm) are observed and they indicate a low symmetry complex. Typically it is not possible to make absolute assignments for N–Me signals in this system. However, the addition of D_2O reduces the coupling pattern (dq to d) of the 2.72 ppm resonance thus pinning it to the methyl of the terminal phosphino amine.

The $^{31}P\{^1H\}$ NMR spectrum shows six distinct resonances for unique environments of each of the six phosphorus atoms of the ligands. As is typical of M^n–M^{n+2} complexes bound by phosphorus ligands, large coupling constants are observed between phosphorus atoms in trans ligating positions. The phosphorus resonance of the four-atom ring appears as a doublet of triplets at 39.75 ppm (J_{PP} = 689 Hz), split by its trans partner at 80.13 ppm (J_{PP} = 688 Hz). The significant upfield shift of the wayward P(6) resonance is in accordance with its unique coordination environment. A broader resonance at 52.44 ppm follows logically from the coordination of P(5) along the metal–metal bond. The remaining resonances at 80.30, 61.64 and 58.77 ppm exhibit small J_{PP} couplings consistent with their cis dispositions to phosphorus neighbors. The 80.30 ppm signal for P(4) appears in the chemical shift range of its Ir^I–P counterparts, whereas the P(1) and P(3) resonances are shifted upfield due to coordination at an Ir^{III} center.

The reaction of **1** with water to yield **2** proceeds by the reaction sequence shown in Scheme 1. Two electron donor ligands have been shown by variable temperature NMR[1] and DFT[2] studies to reversibly add to the equatorial coordination site of the Ir^{II} center; the CH_3CN[1] and NH_3[10] adducts have been structurally characterized. Residing in the equatorial coordination site, small molecules are readily activated across the diiridium bond, in this case to produce a hydrido-hydroxo species. We depict **2** as a mixed valence Ir^I–Ir^{III} species possessing a dative metal–metal bond; alternatively **2** may be formulated as an Ir^{II}–Ir^{II} species with a discrete metal–metal bond. Water activation may proceed either by oxidative addition across the Ir–Ir bond to yield **2** or by direct attack of the oxygen on the P–N bond of the chelating ligand followed by protonation of the Ir^0 metal center. Isolation of late transition metal hydroxide complexes is typically complicated by their subsequent reactivity and relatively few are structurally characterized.[11] This situation prevails here. If a coordinated hydroxide forms, it is

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† We dedicate this paper to the memory of our colleague and friend, Ian P. Rothwell.

‡ Electronic supplementary information (ESI) available: ^1H NMR spectra of **2** and **2(D)** and ^{31}P NMR spectrum of **2** and tables for X-ray structure determination of **2** and **3**. See http://www.rsc.org/suppdata/cc/b4/b402426e/

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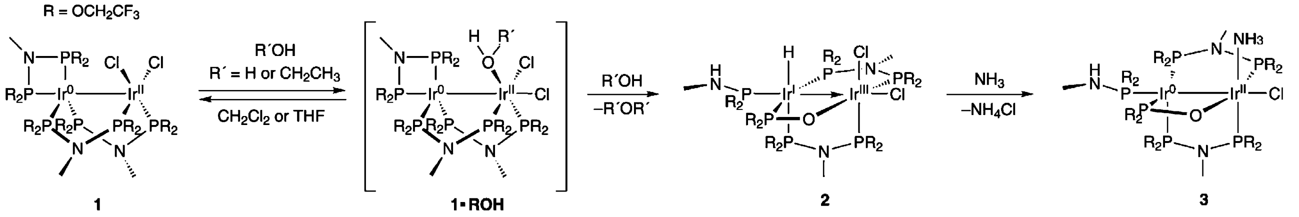

Scheme 1

ideally oriented to attack the adjacent phosphorus atom and initiate P–N bond cleavage. Regardless of pathway, hydride formation and ligand cleavage appear to be metal based inasmuch free ligand does not react with water.

Subsequent treatment of **2** with bases, such as NH_3, yields dehydrohalogenated product **3**‖; HCl is trapped as NH_4Cl. Hydride removal is signified by the absence of a hydride resonance in the −10 to −14 ppm region of the ^1H NMR spectrum. The appearance of a broad singlet at 3.093 ppm (3 H) is ascribed to bound NH_3. Large ($0.5 \times 0.1 \times 0.1$ cm^3) bright yellow crystals deposit from a concentrated solution of **3** in CH_2Cl_2 layered with pentane. The solution of the X-ray single crystal structure** is shown in Fig. 2. The structure of **3** is largely similar to that of **2** but obvious differences include the Ir^{II} bound amine with an Ir(1)–N(1) bond distance of 2.180 (4) Å and relaxation of the coordination sphere about the Ir^0 center to a trigonal bipyramidal geometry (∠ P(4)–Ir(2)–P(6) = 120.48 (5)°) as a result of hydride removal. As in **2**, the ring constrains the Ir–Ir bond in **3** and distorts the coordination spheres of both iridiums (∠ O(13)–Ir(1)–Ir(2) = 79.93 (10)° and ∠ P(6)–Ir(2)–Ir(1) = 67.52 (4)°).

Consistent with the reaction sequence outlined in Scheme 1, **2** is also obtained quantitatively from the reaction of **1** and ethanol. Typically, β-hydride elimination from ethoxide is facile to yield aldehyde and metal-hydride.[12] However, this reaction is circumvented by the coordinative saturation of the **1·ROH** adduct. In the absence of β-H elimination, intermolecular attack of the co-ordinated ethoxide may result in the production of diethyl ether. A ^1H NMR spectrum of the reacted solution does indeed establish diethyl ether as the organic byproduct.

In summary, water adds to the growing roster of small molecule substrates that react at a two-electron mixed valence core. The generation of a two-electron mixed valence metal-hydride from water is intriguing in view of the propensity of such platforms to expel hydrogen. However, the results reported here reveal the susceptibility of the P–N bond to nucleophilic attack. Studies are underway to develop ligand frameworks that can support two-electron mixed valency and at the same time resist attack by the conjugate base of nucleophilic proton donors.

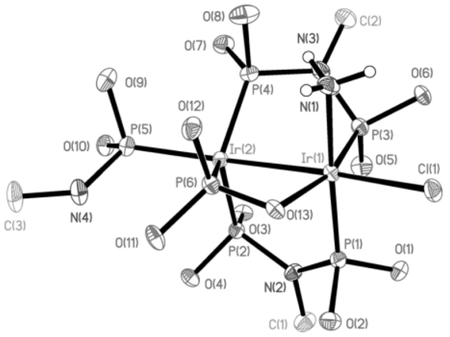

Fig. 2 Solid state structure of **3** with CF_3CH_2 atoms omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å]: Ir(1)–Ir(2) 2.7356(3), Ir(1)–O(13) 2.159(4), P(6)–O(13) 1.537(4), Ir(2)–P(6) 2.2504(14), $(P–O)_{avg}$ 1.624(10), Ir(1)–Cl(1) 2.4267(1), Ir(1)–N(1) 2.180(4), Ir(2)–P(5) 2.2250(13).

Notes and references

§ *Experimental Procedures* **2**: The starting complex, **1**, was prepared according to literature methods.[7] In a nitrogen atmosphere, a vial fitted with a septum screw cap was charged with 410 mg (0.214 mmol) of **1** and CH_2Cl_2 (8 mL). To the stirring heterogeneous mixture was added 20 μL of water. After 2 h all material dissolved to give an orange homogeneous solution. Volatiles were removed and the resulting orange solid was triturated and washed with pentane and then dried *in vacuo* overnight. Clear colorless **2** was crystallized in 51% (212 mg) yield from cold CH_2Cl_2 layered with pentane. The same product is obtained from the reaction of **1** in CH_2Cl_2 with excess anhydrous ethanol (dried over Na 50 mg per 25 mL) in 85% yield. ^1H NMR (THF-d$_8$, 500 MHz, TMS) δ/ppm: 2.719 (dd, 11.5 Hz, 3 H), 2.798 (t, 7.5 Hz, 3 H), 2.937 (t, 7.5 Hz, 3 H), 3.780 (dq, 29 Hz, 5 Hz, 1 H), 4.2–5.9 (m, 24 H), −11.280 (dq, 186 Hz, 15 Hz, 1 H). ^{31}P NMR (CD_2Cl_2, 202 MHz, 85% H_3PO_4) δ/ppm: 39.75 (dt, 689 Hz, 21.9 Hz), 52.4 (s), 58.77 (ddd, 120 Hz, 38.5 Hz, 11 Hz), 61.64 (ddd, 167 Hz, 40.5 Hz, 14.5 Hz), 80.13 (ddt, 688 Hz, 120 Hz, 29.4 Hz), 80.35 (ds, 167 Hz, 27.5 Hz).

¶ *Crystal Data*: **2**: $C_{29}H_{39}Cl_6F_{36}Ir_2N_3O_{13}P_6$, M = 2103.54, triclinic, space group $P\bar{1}$, a = 12.986(3), b = 13.113(3), c = 20.921(4) Å, α = 90.11(3)°, β = 94.36(3)°, γ = 114.35(3)°, U = 3233.9(11) Å^3, Z = 2, D_c = 2.160 g cm^{-3}, T = 193(2) K, μ = 4.664 mm^{-1}, $wR2$ = 0.1238 (13554 independent reflections), $R1$ = 0.0684 [$I > 2\sigma(I)$]. CCDC 231788. See http://www.rsc.org/suppdata/cc/b4/b402426e/ for crystallographic data in .cif or other electronic format.

‖ *Experimental Procedures* **3**: In a sealed glass reactor, a degassed solution of **2** (140 mg, 0.072 mmol) in CH_2Cl_2 (10 mL) was charged with 2.5 equivalents of anhydrous NH_3 gas. The vessel was sealed and heated for 9 h at 75 °C in an oil bath. During the course of reaction a white precipitate of NH_4Cl formed and it was removed by filtration. The filtrate was layered with pentane and crystallized product was obtained in 87% (120 mg) yield. ^1H NMR (CD_2Cl_2, 500 MHz, TMS) δ/ppm: 2.645 (dd, 10 Hz, 6 Hz, 3 H), 2.713 (d, 8.5 Hz, 5 Hz, 3 H), 2.775 (dd, 9 Hz, 6.5 Hz, 3 H), 3.093 (bs, 3 H), 3.6–5.3 (m, 24 H), 3.975 (dq, 27.5 Hz, 5.5 Hz, 1 H). ^{31}P NMR (CD_2Cl_2, 202 MHz, 85% H_3PO_4) δ/ppm: 61.4 (qt, 121 Hz, 49.5 Hz, 11 Hz, 1 P), 66.5–69.8 (m, 3 P), 86.2 (m, 1 P), 96.4 (m, 1 P).

** *Crystal Data*: **3**: $C_{27}H_{37}ClF_{36}Ir_2N_4O_{13}P_6$, M = 1915.28, triclinic, space group $P\bar{1}$, a = 12.3142(6), b = 13.3025(6), c = 38.7180(18) Å, α = 89.2460(10)°, β = 84.5030(10)°, γ = 65.7210(10)°, U = 5752.4(5) Å^3, Z = 4, D_c = 2.212 g cm^{-3}, T = 100(2) K, μ = 5.008 mm^{-1}, $wR2$ = 0.0941 (23538 independent reflections), $R1$ = 0.0394 [$I > 2\sigma(I)$]. CCDC 240137. See http://www.rsc.org/suppdata/cc/b4/b402426e/ for crystallographic data in .cif or other electronic format.

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