Mono(sulfido)-bridged mixed-valence nitrosyl complex: protonation and oxidative addition of iodine across the Ir(ii)–Ir(0) bond†

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Treatment of [Cp*IrH(SH)(PMe$_3$)] (Cp* = η^5-C$_5$Me$_5$) with [IrCl$_2$(NO)(PPh$_3$)$_2$] in the presence of triethylamine yielded the sulfido-bridged Ir^{II}Ir^0 complex [Cp*Ir(PMe$_3$)(μ-S)Ir-(NO)(PPh$_3$)], which further reacted with I$_2$ and triflic acid to give the diiodo complex [Cp*Ir(PMe$_3$)(μ-I)(μ-S)IrI-(NO)(PPh$_3$)] and the hydrido complex [Cp*Ir(PMe$_3$)(μ-H)(μ-S)Ir(NO)(PPh$_3$)][OSO$_2$CF$_3$], respectively.

Unsymmetrical homodinuclear complexes in which the metal centres have different oxidation states and ancillary ligand sets have the potential to provide unique reaction sites owing to the polarity of the metal centres.[1] The nitrosyl ligand would be a suitable component of such mixed-valence species because it is capable of supporting a wide range of oxidation states of the metal centre by changing its coordination mode.[2] Our recent studies revealed that the reactions of the iridium nitrosyl complex [IrCl$_2$(NO)(PPh$_3$)$_2$] **1** with thiols and thiolato anions afford thiolato complexes with a variety of oxidation states, coordination geometries and nuclearities, exemplified by dinuclear complexes ranging from Ir$^0_2$ to Ir$^{III}_2$; even an Ir^{I}Ir^{III} mixed-valence complex [Ir(NO)(PPh$_3$)(μ-SPr^i)$_3$IrCl$_2$(PPh$_3$)] has further been derived.[3] In the quest for polarised diiridium centres with different ancillary ligands, we have replaced the thiolato sources in these reactions by hydrosulfido complexes, which can be regarded as metallathiols.[4] We report here the reaction of **1** with the hydrosulfido complex [Cp*IrH(SH)(PMe$_3$)] **2**,[5] leading to the formation of the unsymmetrical complex [Cp*Ir(PMe$_3$)(μ-S)Ir(NO)(PPh$_3$)] **3** with an unusual Ir^{II}Ir^0 oxidation state. Oxidative addition reactions towards **3** to give Ir^{III}Ir^I and Ir$^{III}_2$ complexes are also described.

Treatment of **1** with **2** in the presence of triethylamine resulted in the formation of the mono(sulfido)-bridged diiridium complex **3** (Scheme 1).‡ The strong band at 1684 cm^{-1} in the IR spectrum of **3** is ascribed to a linear nitrosyl ligand bound to an electron-rich iridium centre; the frequency is much lower than that of the related Ir^I complex [Ir(NO)(SC$_6$H$_3$Me$_2$-2,6)$_2$(PPh$_3$)] (1817 cm^{-1}) and comparable to those of the Ir$^0_2$ complex [Ir(NO)(μ-SBu^t)(PPh$_3$)]$_2$ (1646 and 1676 cm^{-1}).[3a] The diamagnetic nature of **3** is suggested by the sharp resonances for Cp* and PMe$_3$ ligands in the ^{1}H NMR spectrum, which also indicates the absence of hydrido and hydrosulfido ligands in **3**. An X-ray analysis has disclosed the detailed structure of **3** (Fig. 1).§ Considering the short Ir–Ir distance [2.643(1) Å] as well as the low NO stretching frequency and diamagnetism, the Ir–Ir interaction is best described as an Ir^{II}–Ir^0 single bond. Indeed, the structure of **3** may be related to the symmetrical Ir$^{II}_2$ and Ir$^0_2$ complexes [(Cp*Ir)$_2$(μ-S)(μ-

CH$_2$=CHCH=CH$_2$)][6] and [{Ir(NO)(PPh$_3$)}$_2$(μ-O)] **4**.[7] If this Ir–Ir bond is disregarded, the Cp*Ir half-sandwich fragment is ligated only by a phosphine and a bridging sulfido ligand, whilst the geometry around the Ir(2) atom is T-shaped. The Ir(1)–S(1) distance [2.323(3) Å] is longer than the Ir(2)–S(1) distance [2.241(4) Å]. The anisotropy of the diiridium centre bridged only by a sulfido ligand is induced by the strongly π-accepting linear nitrosyl ligand and electron-donating Cp* and phosphine ligands. The Ir^{II}Ir^0 mixed-valence complexes are rare; the only precedent is [Ir$_2$Cl$_2$(tfepma)$_3$] **5** [tfepma = MeN-{P(OCH$_2$CF$_3$)$_2$}$_2$], which has recently been synthesised by diphosphazane-triggered disproportionation of two Ir^I centres into Ir^{II} and Ir^0.[8]

The cyclic voltammogram of the Ir^{II}Ir^0 complex **3** shows an irreversible oxidation wave at 0.28 V (*vs.* saturated calomel electrode, in CH$_2$Cl$_2$). We thus examined chemical oxidation of
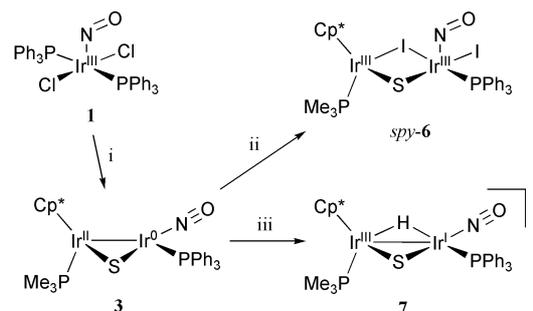
Scheme 1 *Reagents and conditions*: i, [Cp*IrH(SH)(PMe$_3$)] **2** (0.84 equiv.), Et$_3$N (3 equiv.), r.t.; ii, I$_2$ (1 equiv.), 195 K to r.t.; iii, CF$_3$SO$_3$H (1 equiv.), r.t.
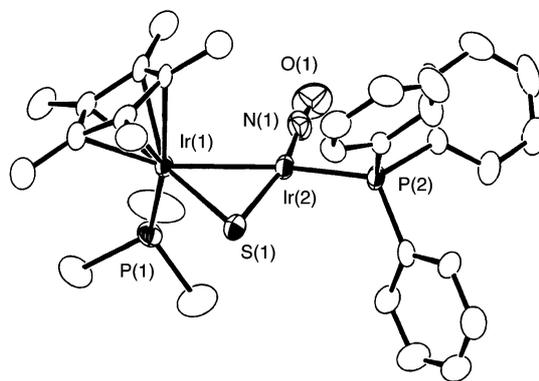
Fig. 1 Molecular structure of **3**. Hydrogen atoms are omitted for clarity. Selected interatomic distances (Å) and angles (°): Ir(1)–Ir(2) 2.643(1), Ir(1)–S(1) 2.323(3), Ir(2)–S(1) 2.241(4), Ir(2)–N(1) 1.75(2), N(1)–O(1) 1.20(2), Ir(1)–S(1)–Ir(2) 70.7(1), Ir(2)–N(1)–O(1) 173(1).

3. When **3** was treated with an equimolar amount of I_2, the diiodo complex $[Cp*Ir(PMe_3)(\mu\text{-I})(\mu\text{-S})IrI(NO)(PPh_3)]$ **6** was obtained. Interestingly, the $^{31}P\{^1H\}$ NMR spectrum of **6** at 233 K exhibits three pairs of signals ascribed to the PMe_3 and PPh_3 ligands, and these signals are averaged into two broad signals at 293 K. Furthermore, two NO stretching bands at 1518s and 1800m cm^{-1} are observed in the IR spectrum recorded in CH_2Cl_2 solution at room temperature. These observations indicate that three isomers, including both linear and bent nitrosyl complexes, are in equilibrium in solution.[9] We succeeded in isolating one of the three isomers by careful recrystallization.[¶] The solid-state IR spectrum of the isolated species, *spy*-**6**, exhibits only one NO stretching band at 1518 cm^{-1}. To confirm the structure of the isomer, an X-ray analysis has been carried out (Fig. 2).[§] As suggested by the IR spectrum, the nitrosyl ligand at the apical position of the square pyramidal Ir(2) atom is bent with the Ir–N–O angle of 128(1)°, and thus the metal centres have formally been oxidised to Ir$^{III}_2$. The Ir–Ir distance [3.636(1) Å] is long enough to preclude any direct metal–metal interaction. One of the iodine [I(1)] bridges the two Ir atoms, whilst the other [I(2)] is coordinated only to the Ir(2) atom as a terminal ligand. These results sharply contrast with the reactions of the oxo-bridged symmetrical complex **4** with $HgCl_2$ or X_2 (X = Br, I), which afford the linear-nitrosyl Ir$^I_2$ complexes $[\{Ir(NO)X(PPh_3)\}_2(\mu\text{-O})]$ without bridging halides.[7] Formation of a nitrosyl-bridged diiodo complex $[\{(cod)IrI\}_2(\mu\text{-NO})(\mu\text{-pz})_2][BF_4]$ (cod = 1,5-cyclooctadiene, pzH = pyrazole) from an unsymmetrical dinuclear nitrosyl complex $[(cod)Ir(NO)(\mu\text{-pz})_2Ir(cod)][BF_4]$ and iodine has also been reported.[10]

On the other hand, protonation of **3** by triflic acid resulted in the formation of the Ir^{III}Ir^I hydrido complex $[Cp*Ir(PMe_3)(\mu\text{-H})(\mu\text{-S})Ir(NO)(PPh_3)][OSO_2CF_3]$ **7** with a linear nitrosyl ligand.[‖] The ^1H NMR spectrum of **7** is featured by a doublet of doublets at δ −9.83, which indicates that the protonation occurred across the Ir–Ir bond. The $^{31}P\{^1H\}$ NMR and IR spectra are also congruent with the structure of **7** shown in Scheme 1. Unlike the Ir^{II}Ir^0 complex **5**[8] and some other related sulfur-bridged Ir$^{II}_2$ complexes $[Ir_2(\mu\text{-S})_2(PPh_3)_4]$[11] and $[Cp*Ir(\mu\text{-SPr}^i)IrCp*][OSO_2CF_3]$,[12] **3** failed to react with H_2 gas (1 atm) at room temperature.

In summary, the mono(sulfido)-bridged unsymmetrical mixed-valence complex **3** has been synthesised in a rational manner using the metallathiol **2**. The nitrosyl ligand in **3** seems to stabilise the unusual Ir^{II}Ir^0 core structure having only one bridging atom and an open coordination site between the metal centres. Furthermore, facile oxidative addition reactions towards **3** substantiate that the mono(sulfido)-bridged diiridium centre can enjoy a wide range of formal oxidation states, namely, Ir^{II}Ir^0, Ir^{III}Ir^I and Ir$^{III}_2$, by virtue of the linear–bent isomerization of the nitrosyl ligand. Another important consequence of the present study is the potential usefulness of the

hydrido–hydrosulfido complexes as synthons for mono(sulfido)-bridged flexible polynuclear frameworks.[13]

Notes and references

‡ Yield 75% (based on **2**). $\delta_H(C_6D_6)$ 7.02–7.89 (15 H, m, PPh$_3$), 2.07 (15 H, s, C$_5$Me$_5$), 1.37 (9 H, d, J_{PH} 9.8 Hz, PMe$_3$); $\delta_P(C_6D_6)$ 0.0, −43.9 (1 P each, d, J_{PP} 15.3 Hz); $\tilde{v}$(NO)/cm^{-1} 1684s (KBr). In the absence of triethylamine, the reaction afforded a complex mixture containing a small amount of **3**.

§ *Crystal data* for **3**: $C_{31}H_{39}Ir_2NOP_2S$, M = 920.10, monoclinic, a = 12.841(4), b = 16.136(6), c = 15.616(6) Å, β = 98.33(3)°, U = 3201(1) Å^3, T = 296 K, space group $P2_1/n$ (no. 14), Z = 4, μ(Mo-Kα) = 85.18 cm^{-1}, 7956 reflections measured, 7358 unique (R_{int} = 0.023). The final $R(R_w)$ were 0.050(0.050) [I > 3.0$\sigma(I)$, based on F]. For *spy*-**6**: $C_{31}H_{39}I_2Ir_2NOP_2S$, M = 1173.91, triclinic, a = 10.715(4), b = 12.613(3), c = 13.637(4) Å, α = 75.57(2), β = 81.65(2), γ = 85.08(3)°, U = 1763.5(9) Å^3, T = 296 K, space group $P\bar{1}$ (no. 2), Z = 2, μ(Mo-Kα) = 94.85 cm^{-1}, 8468 reflections measured, 8100 unique (R_{int} = 0.093). The final $R(R_w)$ were 0.048(0.050) [I > 3.0$\sigma(I)$, based on F]. CCDC 197634 and 197635. See http://www.rsc.org/suppdata/cc/b2/b211021k/ for crystallographic data in CIF or other electronic format.

¶ Yield 93% (as *spy*-**6**). δ_H(CD$_2$Cl$_2$, at r.t.) 7.34–7.65 (15 H, m, PPh$_3$), 1.80 (9 H, br d, J_{PH} 10.2 Hz, PMe$_3$), 1.73 (15 H, br s, C$_5$Me$_5$); δ_P(CD$_2$Cl$_2$) −0.5, −34.2 (1 P each, br s; at r.t.); 15.0, 3.6, −0.2, −24.4, −31.1, −32.6 (*ca.* 2 P : 1 P : 8 P : 1 P : 2 P : 8 P, s; at 233 K); $\tilde{v}$(NO)/cm^{-1} 1518s (KBr); 1518s, 1800m (CH$_2$Cl$_2$). We currently believe that *spy*-**6** is the major isomer in equilibrium because the frequency of its NO stretching band in the solid state is exactly the same as that of the major isomer in solution. In addition, one of the minor isomers in equilibrium is deduced to be the cationic, square-planar complex $[Cp*Ir(PMe_3)(\mu\text{-I})(\mu\text{-S})Ir(NO)I]I$ with a linear nitrosyl ligand; the formulation is based on the comparison of the spectral data ($^{31}P\{^1H\}$ NMR and IR) of the minor isomer and the species obtained from treatment of **6** with silver triflate. See also the ESI.†

‖ Yield 97%. δ_H(CDCl$_3$) 7.49–7.61 (15 H, m, PPh$_3$), 2.11 (15 H, s, C$_5$Me$_5$), 1.66 (9 H, d, J_{PH} 11.0 Hz, PMe$_3$), −9.83 (1 H, dd, J_{PH} 47.0, 18.9 Hz, Ir$_2$H); δ_P(CDCl$_3$) −1.1, −33.9 (1 P each, d, J_{PP} 5.5 Hz); $\tilde{v}$(NO)/cm^{-1} 1773s, $\tilde{v}$(SO)/cm^{-1} 1268s (KBr).

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Fig. 2 Molecular structure of *spy*-**6**. Hydrogen atoms are omitted for clarity. Selected interatomic distances (Å): Ir(1)–Ir(2) 3.636(1), Ir(1)–I(1) 2.695(1), Ir(1)–S(1) 2.369(3), Ir(2)–I(1) 2.829(1), Ir(2)–I(2) 2.710(1), Ir(2)–S(1) 2.299(3), Ir(2)–N(1) 1.87(1), N(1)–O(1) 1.17(1).