DALTON COMMUNICATION

The first direct observation of N–O bond cleavage in the oxidative addition of an oxime to a metal centre. Synthesis and crystal structure of the methyleneamide complex *trans*-[Re(OH)(N=CMe$_2$)(Ph$_2$PCH$_2$CH$_2$PPh$_2$)$_2$][HSO$_4$]

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The first direct observation of oxidative addition of an oxime upon N–O bond cleavage has been reported in the reaction of Me$_2$C=NOH with *trans*-[ReCl(N$_2$)(Ph$_2$PCH$_2$CH$_2$PPh$_2$)$_2$] in the presence of Tl[BF$_4$]–Tl[HSO$_4$], to form, in a single-pot experiment, the methyleneamide complexes *trans*-[Re(OH)(N=CMe$_2$)(dppe)$_2$][A] (A = BF$_4$ **1a** or HSO$_4$ **1b**) which undergo ready replacement of hydroxide by fluoride upon reaction with HBF$_4$; X-ray crystallography (**1b**) showed that the linearly bound methyleneamide behaves as an effective π acceptor and exerts a significant *trans* influence on the hydroxide ligand.

The co-ordination chemistry of oximes, RR′C=NOH, is rich, extensively investigated and has been recently reviewed by two of us.[1] However, at electron-rich metal centres, in particular those which can bind dinitrogen and other substrates of nitrogenase that have been the object of our interest,[2] the co-ordination chemistry is still unknown. Moreover, oxidative addition of oximes to metal centres is an essentially unexplored area. To the best of our knowledge, only one paper has been published, by Deeming *et al.*,[3] on the O–H bond splitting in the oxidative addition of Me$_2$C=NOH to the osmium cluster [Os$_3$(CO)$_{10}$(MeCN)$_2$] giving [Os$_3$(μ-H)(μ-Me$_2$C=NO)(CO)$_{10}$] whose thermal isomerization leads to the hydroxo isomer [Os$_3$(μ-OH)(μ-Me$_2$C=N)(CO)$_{10}$] along with some other unidentified products. The mechanism of the conversion has not been studied, but if it includes the intermediate formation of [Os$_3$(μ-Me$_2$C=NOH)(CO)$_{10}$], as was suggested by the authors,[3] the reaction can be considered as oxidative addition of the oxime due to N–O bond splitting.

We herein report the first direct observation of such a reaction by treatment of a THF solution of *trans*-[ReCl(N$_2$)(dppe)$_2$] (dppe = Ph$_2$PCH$_2$CH$_2$PPh$_2$) with 2-propanone oxime, Me$_2$C=NOH, in the presence of a chloride abstractor, Tl[BF$_4$]–Tl[HSO$_4$], and in sunlight (to promote N$_2$ loss), to give the hydroxo–methyleneamide complexes *trans*-[Re(OH)(N=CMe$_2$)(dppe)$_2$][A] (A = BF$_4$ **1a** or HSO$_4$ **1b**)‡ [equation (1)]. This

trans-[ReCl(N$_2$)(dppe)$_2$] + Me$_2$C=NOH + Tl[A] ⟶
trans-[Re(OH)(N=CMe$_2$)(dppe)$_2$][A] + N$_2$ + TlCl (1)

reaction also provides a novel single-pot synthesis of a methyleneamide (azavinylidene, alkylideneamide or ketimide) complex from a convenient and commercially available precursor, an oxime (see also below).

The X-ray crystal structure analysis§ of compound **1b** shows (Fig. 1) that the methyleneamide ligand is linearly co-ordinated thus behaving as a formal three-electron donor, Re≡N=C(27)Me$_2$, and allowing the complex to attain the 18-electron configuration. The significant double-bond character of the methyleneamide co-ordination bond is indicated by the Re–N distance, 1.901(5) Å, which is shorter than the average value, 2.107 Å, quoted[4] for nitrile complexes of Re, in particular those[5] with an identical co-ordination metal centre. Moreover, the methyleneamide ligand behaves as an effective π-electron acceptor, competing with the diphosphines for the available metal d$_\pi$ electrons, as indicated by the average Re–P distance, 2.461(2) Å, which is identical to that[6] of the related amino-carbyne complex *trans*-[ReCl(CNHMe)(dppe)$_2$][BF$_4$] (in which the CNHMe ligand is a strong π-electron acceptor) and longer

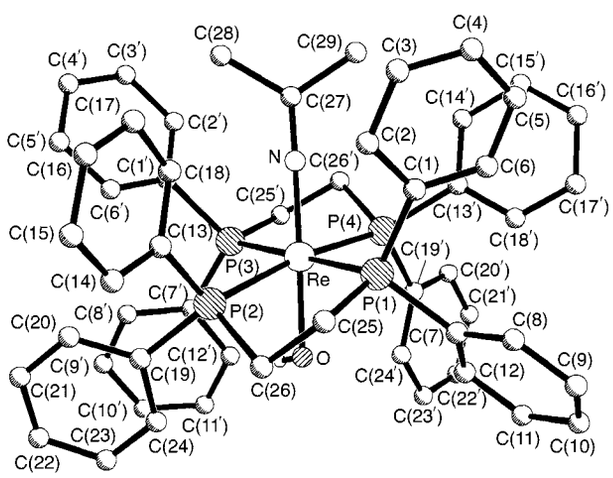

Fig. 1 Molecular structure of the complex cation of *trans*-[Re(OH)(N=CMe$_2$)(dppe)$_2$][HSO$_4$] **1b**. Selected bond distance (Å) and angles (°): Re–N 1.901(5), Re–O 2.015(4), Re–P$_{ave}$ 2.461(2), N–C(27) 1.251(9); Re–N–C(27) 178.9(5)

‡ The oxime (15.3 mg, 0.209 mmol) and the Tl$^+$ salts {61 mg, *ca.* 0.21 mmol, mainly Tl[BF$_4$] with a much smaller amount of Tl[HSO$_4$] which co-precipitated with the former salt in its synthesis by reaction of Tl$_2$SO$_4$ with Ba(OH)$_2$ followed by treatment with [NH$_4$][BF$_4$]} were added to a THF solution (150 cm^3) of *trans*-[ReCl(N$_2$)(dppe)$_2$] (0.10 g, 0.095 mmol), and the products **1** were isolated, after *ca.* 4 h, as brick red solids which were recrystallized from CH$_2$Cl$_2$–Et$_2$O (*ca.* 60% yield). Compound **1a** is the dominant isolated product, but it can contain some co-precipitated **1b** (Found: C, 58.0; H, 4.8; N, 1.1. C$_{55}$H$_{55}$BF$_4$NOP$_4$Re **1a** requires C, 57.7, H, 4.8; N, 1.2%). Selected spectroscopic data: IR (KBr, cm^{-1}): ν(OH) *ca.* 3420s (br); ν(C=N), δ(OH) *ca.* 1640w (br); BF$_4^-$ *ca.* 1090vs and *ca.* 1050vs (**1a**). ^{13}C NMR (CD$_2$Cl$_2$): δ 147.11 (s, N=*C*Me$_2$), 4.90 [q, J_{CH} = 129.4 Hz, N=C(*C*H$_3$)$_2$]. ^{1}H NMR (300 MHz, CD$_2$Cl$_2$): δ 2.70 [s, 6 H, N=C(CH$_3$)$_2$]. ^{31}P-{^{1}H} NMR (CD$_2$Cl$_2$): δ −128.24 [relative to P(OMe)$_3$]. ^{19}F NMR (CD$_2$Cl$_2$): δ −151.46 (s) (relative to CFCl$_3$) (**1a**).

§ Crystal data for **1b**: C$_{55}$H$_{55}$NO$_5$P$_4$ReS, M = 1152.14, triclinic, space group $P\bar{1}$, a = 11.998(2), b = 16.724(2), c = 13.970(2) Å, α = 86.59(1), β = 67.84(1), γ = 75.46(1)°, U = 2511.0(6) Å^3, Z = 2, T = 293(2) K, μ(Mo-Kα) = 2.638 mm^{-1}, 6776 reflections collected, 6427 independent reflections (R_{int} = 0.017), final R indices (all data) $R1$ = 0.0339, $wR2$ = 0.087. CCDC reference number 186/832.

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than the average value, 2.428 Å, reported[4] for Re–dppe bonds, in particular those of comparable nitrile[5] or isocyanide[7] complexes.

Interestingly, the Re–O distance in **1b**, 2.015(4) Å, is significantly longer than the average value, 1.795 Å, quoted[4] for the Re–OH bond length, thus suggesting an appreciable structural *trans* influence of the methyleneamide on the hydroxide ligand, in contrast to the common behaviour observed[8] for linear methyleneamide ligands which do not exhibit an obvious lengthening effect on the *trans* metal–ligand bond. Possibly related to that observation is the ready replacement of the hydroxide ligand by fluoride upon treatment of a CH_2Cl_2 solution of compound **1a** with HBF_4 to give *trans*-$[ReF(N{=}CMe_2)(dppe)_2][BF_4]$ **2**¶ [equation (2)], although the

$$trans\text{-}[Re(OH)(N{=}CMe_2)(dppe)_2][BF_4] + HBF_4 \longrightarrow trans\text{-}[ReF(N{=}CMe_2)(dppe)_2][BF_4] + H_2O{\cdot}BF_3 \quad (2)$$

displacement promoting effect owing to the conceivable protonation of the former ligand to give a labile aqua complex should also play a relevant role.

The formation of compounds **1a** and **1b** can be related to the interesting synthesis of complexes of the type $[(\eta^6\text{-}C_6R_6)M(N{=}CR'R'')(L)][PF_6]$ [M = Os or Ru; R = H or Me; CR′R″ = CPh_2, CMe(Ph), CMe_2 or $C(CH_2)_4CH_2$; L = organophosphine] which were obtained by Werner and co-workers[9] by reaction of the corresponding oximes HON=CR′R″ with $[(\eta^6\text{-}C_6R_6)MHX(L)]$ (X = Cl or I) in the presence of $Ag[PF_6]$. It proceeds *via* the hydride–oxime intermediates $[(\eta^6\text{-}C_6R_6)MH(HON{=}CR'R'')(L)][PF_6]$ which, upon subsequent dehydration when chromatographed over Al_2O_3, yield the final products, without changing the initial metal oxidation state.

In our Re^{I} system, the lability of two ligands (rather than a single one as in the Os or Ru complexes described above), the greater electron richness of the metal centre relative to osmium- and ruthenium-(II) sites, and the ability of the rhenium(I) centre (with a high π-electron releasing character) to form multiple bonds to unsaturated ligands promotes oxidative addition of the oxime to this centre and the preferential cleavage of the N–O bond (to give the π acceptor N=CMe_2 ligand) rather than the split of the O–H bond (which would generate the oximate group without such a π-accepting ability). In addition, the steric hindrance at our centre, with the bulky diphosphines, conceivably also plays a role, favouring the stabilization of a product with end-on co-ordination of a linear group (such as the methyleneamide but not the oxime nor oximate species).

We have previously established[10] a different route for methyleneamide complexes based on the activation to β-protonation of a nitrile ligand by a rhenium centre, *i.e.* at $[ReCl(NCR)(dppe)_2]$ to give $[ReCl(N{=}CHR)(dppe)_2]^+$. In the present work the inability of the oxime (which does not have the π-accepting character possessed by nitriles) to stabilize such an electron-rich site by simple co-ordination prevents the isolation of any oxime intermediate and the reaction proceeds further to give a π-acceptor derivative, the methyleneamide ligand. This work thus extends the rare application of electron-rich metal sites to the synthesis of methyleneamide complexes, which contrasts with their common and quite different preparative procedures[8] involving medium or high oxidation state metal sites.

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¶ Complex **2** precipitated on addition of Et_2O to a CH_2Cl_2 solution (5 cm^3) of **1a** (61 mg, 0.054 mmol) with $[Et_2OH][BF_4]$ (0.18 mmol, 0.84 cm^3 of a 1 : 25 Et_2O diluted solution of commercial 85% HBF_4 in Et_2O), as a brick red solid (*ca.* 65% yield) (Found: C, 56.6; H, 4.6; N, 1.0. $C_{55}H_{55}BF_5NOP_4Re$ requires C, 52.6; H, 4.7; N, 1.2%). Selected spectroscopic data: IR (KBr, cm^{-1}): ν(N=C) 1640w. $^{31}P\text{-}\{^1H\}$ NMR ($CDCl_3$): δ −127.51 [relative to $P(OMe)_3$] (d, $^2J_{PF} \approx 39$ Hz). ^{19}F NMR ($CDCl_3$): δ −196.73 (relative to $CFCl_3$) (qt, $^2J_{PF} \approx 39$ Hz).

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