

A d⁴-Thiolato–Dinitrogen Complex. The Synthesis and Crystal Structure of [Re(N₂)(SC₆H₂-2,4,6-Prⁱ₃)₃(PPh₃)]

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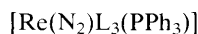
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[ReH₇(PPh₃)₂] or [ReH₅(PPh₃)₃] reacted with L [L = 2,4,6-triisopropylthiophenol (Htipt) or HSC₆H₂-2,6-Prⁱ₂,4-Br (Hdipbt)] in toluene, under dinitrogen, to give [Re(N₂)(tipt)₃(PPh₃)] and [Re(N₂)(dipbt)₃(PPh₃)], respectively in good yield, and under similar conditions 2,6-dimethylthiophenol (Hdmt) or 2,6-dimethoxythiophenol (Hdmot) gave [Re(dmt)₃(PPh₃)] and [Re(dmot)₃(PPh₃)] respectively; the complex [Re(dmt)₃(PPh₃)(PPh₂H)] was also isolated from the same reaction with Hdmt.

There is now compelling spectroscopic and other evidence that the dinitrogen binding site in nitrogenase is ligated predominantly by sulfur.¹ Despite intensive efforts, dinitrogen complexes with any type of sulfur co-ligands have proved elusive,² and to date only five well characterised examples have been reported. These are [Mo(N₂)₂(PMePh₂)₂(PPh₂CH₂CH₂SMe)],³ [Re(S–S)(N₂)(PMe₂Ph)₃] (S–S = dithiocarbamate or dithiophosphinate),⁴ *mer*-[OsCl(SC₆F₅)(N₂)(PMe₂Ph)₃],⁵ *trans*-[Mo(N₂)₂(Me₈16[ane]-S₄)]⁶ and [(Et₂NCS₂)₃Nb(N₂)Nb(S₂CNEt₂)₃].⁷ Most of these have the metals in relatively low oxidation states, and with the exception of the last two, have comparatively low proportions of sulfur in the metal coordination sphere. We here report the high-yield synthesis from a hydride precursor of a d⁴, fourteen-electron, five-coordinate rhenium thiolato–dinitrogen complex and the subtle dependence of the product on the nature of the substituents present on the thiol aromatic ring.

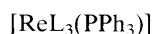
The title complex, [Re(N₂)(tipt)₃(PPh₃)] **1** was prepared by reaction of a suspension of [ReH₇(PPh₃)₂]⁸ in toluene with 3 equiv. of Htipt under dinitrogen. The product was isolated as extremely air- and moisture-sensitive green crystals by adding dry methanol to the concentrated reaction solution and standing for 2 d (75.5% yield). Satisfactory elemental analyses for this complex and the others reported below were obtained. Alternatively, [ReH₅(PPh₃)₃]⁸ could be employed as starting material for the preparation of complex **1**, but in lower yield and with hydride by-product. The complex [Re(N₂–

(dipbt)₃(PPh₃)] **2** was prepared analogously, using the thiol Hdipbt. By contrast, [ReH₇(PPh₃)₂] reacted with Hdmt under similar conditions to give a mixture of two products. The first was isolated as purple crystals by hexane extraction of the residue remaining after the removal of the toluene solvent, and shown to be [Re(dmt)₃(PPh₃)(PPh₂H)] **5**. The green residue left from the hexane extraction was recrystallised from toluene–hexane to give [Re(dmt)₃(PPh₃)] **3** in good yields. Under similar conditions the thiol Hdmot gave [Re(dmot)₃(PPh₃)] **4**.



1 L = tipt

2 L = dipbt

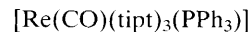


3 L = dmt

4 L = dmot



5



6

Htipt = 2,4,6-Prⁱ₃C₆H₂SH, Hdipbt = 4-Br-2,6-Prⁱ₂C₆H₂SH, Hdmt = 2,6-Me₂C₆H₄SH, Hdmot = 2,6-(MeO)₂C₆H₄SH

The formation of the dinitrogen complex is in interesting contrast to the formation of the complexes [MoH(tipt)₃(PR₃)_n] (PR₃ = PMe₂Ph, n = 2; PR₃ = PPh₂Me, n = 1) by a variety of routes, including the reaction of [MoH₄(PR₃)₄] with Htipt.⁹ In the rhenium system there is no evidence for the formation of the dihydride [ReH₂(tipt)₃(PPh₃)] even under

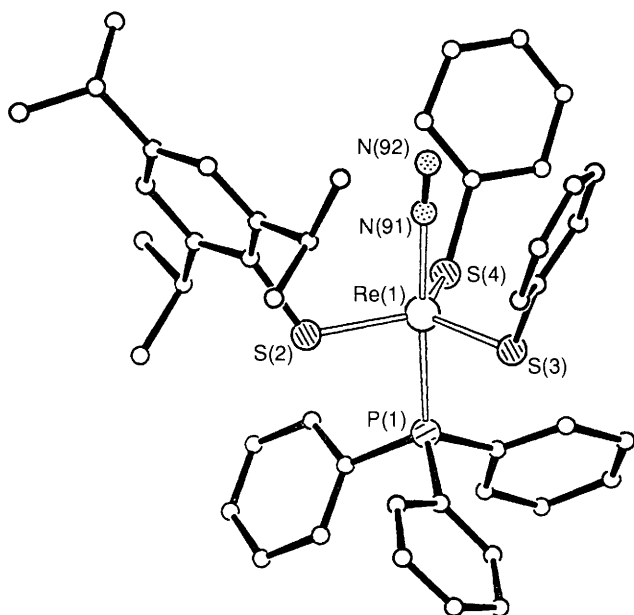


Fig. 1 A view of one of the two very similar complex molecules **1**, in crystals of $[\text{Re}(\text{N}_2)(\text{tipt})_3(\text{PPh}_3)] \cdot 0.5$ toluene, indicating the atomic numbering scheme. Selected bond distances (\AA) and bond angles ($^\circ$) (dimensions for the second molecule follow those for the molecule shown): $\text{Re}(1)\text{-N}(91)$ 2.004(12), 1.994(10); $\text{N}(91)\text{-N}(92)$ 1.01(2), 1.11(2); $\text{Re}(1)\text{-P}(1)$ 2.366(3), 2.406(3); mean $\text{Re}(1)\text{-S}$ 2.251(4), 2.253(2); mean $\text{P}(1)\text{-Re}(1)\text{-S}$ 87.0(4), 85.8(3); $\text{P}(1)\text{-Re}(1)\text{-N}(91)$ 177.4(3), 179.0(2); mean $\text{N}(91)\text{-Re}(1)\text{-S}$ 93.0(9), 94.2(5); mean $\text{S-Re}(1)\text{-S'}$ 119.7(12), 119.5(8). Some isopropyl substituents have been omitted for clarity.

H_2 , and it appears that, if formed, the dihydride is very unstable with respect to the elimination of dihydrogen.

The ^1H NMR spectrum of complex **1** in CDCl_3 (80 MHz) indicated that the three tipt ligands were equivalent. Two doublets at δ 0.97 and 1.15 were assigned to the methyl groups of the 2-, 6- and 4-isopropyl groups respectively, and indicated high symmetry with 2- and 6-isopropyl groups equivalent. Resonances due to the methine protons of the 2-isopropyl groups were located at δ 3.53 and for the 4-isopropyl at δ 2.85 as well defined heptets. The thiolato-aromatic protons appeared as a singlet at δ 6.88. The relative integral intensities for aliphatic methyl protons *vs.* aromatic protons were consistent with the proposed stoichiometry. The $^{31}\text{P}\{^1\text{H}\}$ NMR showed a singlet resonance at δ 26.00 with respect to an H_3PO_4 reference.

In the IR spectrum of complex **1**, a strong band at 2130 cm^{-1} was assigned to $\nu(\text{N} \equiv \text{N})$. This is the highest N_2 stretching frequency yet reported for dinitrogen complexes of rhenium.^{4,10} When the compound was exposed to air as a solid for a few minutes the band at 2130 cm^{-1} disappeared. The high value for $\nu(\text{N} \equiv \text{N})$ is as expected for a complex with a relatively high formal oxidation state.

The cyclic voltammogram of **1** measured in toluene saturated with $[\text{Bu}^n_4\text{N}][\text{BF}_4]^{11}$ (scan rate 1 V s^{-1} ; 25°C) at a platinum electrode showed a one-electron irreversible oxidation at $E_{\text{pa}} + 0.753\text{ V}$ *vs.* standard calomel electrode (SCE). No reduction waves were observed in the range 0 to -1.7 V . The analogous carbonyl complex $[\text{Re}(\text{CO})(\text{tipt})_3(\text{PPh}_3)]$ **6** showed a partially reversible oxidative one-electron couple at $E_{\text{pa}} + 1.468\text{ V}$ and $E_{\text{pc}} + 1.400\text{ V}$ *vs.* SCE (in 0.2 mol dm^{-3} $[\text{Bu}^n_4\text{N}][\text{BF}_4]$ in CH_2Cl_2 at room temperature).

Complex **3** showed no IR bands between 1000 and 900 cm^{-1} , confirming the absence of oxo groups. The $^{31}\text{P}\{^1\text{H}\}$ spectrum of **3** exhibited a singlet at δ 20.12 consistent with the presence of the one PPh_3 group. Compound **5** had an IR band at 2320 cm^{-1} assigned to $\nu(\text{P-H})$. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **5** showed doublets at δ 11.59 due to PPh_3 and δ -11.75 due to PPh_2 , with coupling constant $J(\text{P-P}) = 254.9\text{ Hz}$. This

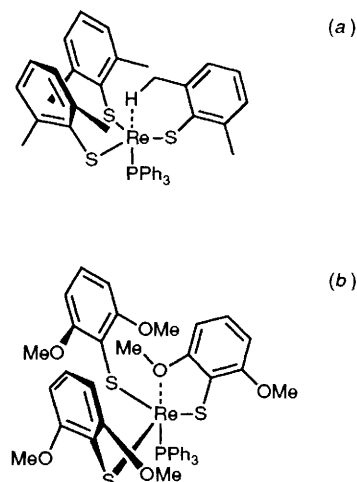


Fig. 2 (a) The schematic structure of $[\text{Re}(\text{dmt})_3(\text{PPh}_3)]$ **3** and (b) a proposed structure for $[\text{Re}(\text{dmot})_3(\text{PPh}_3)]$ **5**

value is typical for *trans*-phosphine ligands. In the case of complex **4**, the MeO group protons appear as singlets at δ 3.70, 3.85, 2.29 and 2.40 (ratio 2:2:1:1), consistent with ligation of one of the methoxy oxygens to the metal, and the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum consisted of a singlet at δ 19.349. The FAB mass spectra showed a molecular ion at m/z 956.14 which corresponds to $[\text{Re}(\text{dmot})_3(\text{PPh}_3)]$.

A single-crystal X-ray structure determination was carried out for complex **1**,[†] and a perspective view of one of the two very similar, independent molecules in the crystal is presented in Fig. 1, together with selected bond lengths and angles. The overall geometry about the rhenium is trigonal bipyramidal, with the dinitrogen and phosphine ligands occupying the axial sites, and the thiolate sulfurs in the equatorial plane. The Re atoms are displaced by 0.12 and 0.17 \AA from the equatorial planes towards the dinitrogen ligands. In contrast to the structures of other trigonal bipyramidal tipt complexes¹² all the aromatic groups are disposed to the same side of the equatorial plane, presumably owing to the steric effect exerted by the triphenylphosphine ligands. The thiol phenyl groups thus comprise an umbrella-like structure providing a cavity for the dinitrogen ligand, and this may contribute to the relative stability of the fourteen-electron complex. The rhenium-sulfur distances are typical for Re^{III} thiolato-complexes, and the N-N distance is similar to those encountered in other terminal dinitrogen complexes. The Re-N distances of 1.994(10) and 2.004(12) \AA are indicative of some multiple bonding between the nitrogen and the metal. A disordered toluene solvate molecule was located with one major, resolved orientation and one less resolved, overlapping arrangement.

The X-ray crystal structures of complexes **3** and **5** have also been determined. Both have trigonal bipyramidal geometries, with equatorial thiolato-ligands, and full details will be reported elsewhere. The schematic structure of complex **3** and a proposed structure for complex **4** are shown in Fig. 2. In complex **5** the axial sites are occupied by PPh_3 and PPh_2 ligands, the latter possibly having arisen *via* intermediate formation of an $(\eta^6\text{-C}_6\text{H}_5)\text{PPh}_2$ species and subsequent

[†] *Crystal data:* $\text{C}_{63}\text{H}_{84}\text{N}_2\text{PReS}_3 \cdot 0.5\text{C}_7\text{H}_8$, $M = 1228.8$. Triclinic, $P\bar{1}$ (no. 2), $a = 17.642(3)$, $b = 21.545(3)$, $c = 18.402(2)\text{ \AA}$; $\alpha = 76.783(10)$, $\beta = 94.073(10)$, $\gamma = 108.979(12)^\circ$; $V = 6439.2\text{ \AA}^3$, $Z = 4$, $D_c = 1.267\text{ g cm}^{-3}$, $F(000) = 2556$; $\mu(\text{Mo-K}\alpha) = 20.7\text{ cm}^{-1}$, $\lambda(\text{Mo-K}\alpha) = 0.71069\text{ \AA}$. 11 980 unique reflections ($\theta_{\text{max}} = 25^\circ$) measured by diffractometer, 10 861 (with $I > \sigma_I$) used in structure determination by heavy-atom method, and refinement by large-block-matrix least-squares methods. Final $R = 0.055$, $R_w = 0.058$,¹⁷ data weighted $w = (\sigma_F^2 + 0.00141F^2)^{-1}$. Atomic coordinates, bond lengths and angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

elimination of benzene.¹³ In complex **3** one axial site is occupied by an agostic interaction¹⁴ with one of the thiolato-methyl substituents, and the other by triphenylphosphine. Analogous interactions have been identified in ruthenium thiolato complexes such as [Ru(tipt)₄] in which a methine hydrogen of one of the isopropyl groups is involved in bonding to the metal.¹⁵

The coordinated dinitrogen in complex **1** is readily displaced by two-electron donor ligands such as CO, MeCN and Bu^tNC to give [Re(CO)(tipt)₃(PPh₃)], [Re(CO)₂(tipt)₃], [Re(MeCN)(tipt)₃(PPh₃)] and [Re(Bu^tNC)₂(dmt)₃]. The X-ray crystal structures of the last two complexes have been determined and confirm the expected trigonal bipyramidal geometries. The combination of size and donor strength for Bu^tNC results in the replacement of the phosphine and dinitrogen ligands. Analogous sterically hindered thiolato-complexes have been reported for technetium.¹⁶ An investigation of the reactions of the N₂ complex with acid and hydric reducing agents is in progress and will be reported elsewhere.

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