The Unusual Bioctahedral Dirhenium(II,III) Complex $[Re_2(\mu\text{-}Cl)(\mu\text{-}C{=}NHBu^t)(\mu\text{-}dppm)_2Cl_2(CNBu^t)_2]PF_6$ [dppm = bis(diphenylphosphino)methane]: A Product of the Non-cleavage Reaction between $Re_2Cl_4(dppm)_2$ and t-Butyl Isocyanide

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A product from the reaction of the triply bonded complex $Re_2Cl_4(dppm)_2$ [dppm = bis(diphenylphosphino)methane] with two equivalents of t-butyl isocyanide is the novel paramagnetic μ-iminyl dirhenium(II,III) complex $[Re_2(\mu\text{-}Cl)(\mu\text{-}C{=}NHBu^t)(\mu\text{-}dppm)_2Cl_2(CNBu^t)_2]PF_6$, a species which is different structurally from the complex $[Re_2Cl_3(dppm)_2(CNBu^t)_3]PF_6$ which is formed when three equivalents of isocyanide ligand are used.

We have established that the reactions of the triply bonded dirhenium(II) complex $Re_2Cl_4(\mu\text{-}dppm)_2$ (**1**) [dppm = bis(diphenylphosphino)methane] with CO and Bu^tNC give complexes of stoicheiometry $Re_2Cl_4(dppm)_2L_n$ (n = 1 or 2) in which the dimetal unit is retained.[1,2] These results not only constitute the first instances where complexes that contain the electron-rich metal–metal triple bond ($\sigma^2\pi^4\delta^2\delta^{*2}$ electronic configuration)[3—5] or the quadruple bond ($\sigma^2\pi^4\delta^2$ configuration)[4,5] are not cleaved by such π-acceptor ligands, but they also provide evidence as to the nature of the intermediates that are formed in the cleavage reactions. Further studies of the reactions between (**1**) and Bu^tNC have demonstrated the existence of a novel paramagnetic complex which contains a bridging $>C{=}NHBu^t$ ligand.

Whereas (**1**) reacts with one equivalent of Bu^tNC to give the A-frame complex $Cl(Bu^tNC)Re(\mu\text{-}Cl)(\mu\text{-}dppm)_2ReCl_2$, the reaction with two equivalents of this ligand in the presence of PF_6^- produces green and yellow isomers of stoicheiometry $[Re_2Cl_3(dppm)_2(CNBu^t)_2]PF_6$.[1] As a by-product of the preparation of the green isomer (reaction in CH_2Cl_2 and metathesis of the resulting insoluble product with KPF_6 in acetone, followed by work-up of the filtrate), we obtained a blue complex (**2**) with a stoicheiometry close to that expected for $[Re_2Cl_3(dppm)_2(CNBu^t)_3]PF_6$ (yield 13%). This complex behaves as a 1:1 electrolyte in acetone (Λ_m = 125 ohm^{-1} cm^2 mol^{-1}, 0.97 × 10^{-3} M) and shows terminal ν(CN) modes in its Nujol mull i.r. spectrum (2145s, 2112s, and *ca.* 2025sh,w cm^{-1}). To our initial surprise we found that this complex is paramagnetic; it displays a complex but well-defined *X*-band e.s.r. spectrum† and does not exhibit discernible ^1H or ^{31}P n.m.r. spectra. It therefore differs from the green diamagnetic complex of stoicheiometry $[Re_2Cl_3(dppm)_2(CNBu^t)_3]Cl$ (**3**) which is formed upon treating (**1**) with three equivalents of Bu^tNC in acetone (yield 92%). While (**3**), like (**2**), behaves as a 1:1 electrolyte (Λ_m = 100 ohm^{-1} cm^2 mol^{-1}, 1.1 × 10^{-3} M in acetone), its i.r. and n.m.r. spectroscopic properties are quite different from those of (**2**).‡ While we have not yet obtained crystals of (**3**) that are suitable for an *X*-ray crystal structure analysis, the related structure of (**2**) (as its water–dichloromethane solvate) has been solved. Crystallographic data support its formulation as the μ-iminyl derivative $[Re_2(\mu\text{-}Cl)(\mu\text{-}C{=}NHBu^t)(\mu\text{-}dppm)_2Cl_2(CNBu^t)_2]PF_6 \cdot H_2O \cdot 0.5CH_2Cl_2$, a conclusion which is in accord with the microanalytical data for (**2**), and its spectroscopic properties and paramagnetic nature (*vide supra*). Accordingly, its prepara-

$Re_2Cl_4(\mu\text{-}dppm)_2$
(**1**)

$[Re_2(\mu\text{-}Cl)(\mu\text{-}C{=}NHBu^t)(\mu\text{-}dppm)_2Cl_2(CNBu^t)_2]PF_6$
(**2**)

$[Re_2Cl_3(dppm)_2(CNBu^t)_3]Cl$
(**3**)

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† This spectrum was recorded in a CH_2Cl_2–toluene glass (40 : 100) at −160 °C. A complex, anisotropic pattern which displays Re and P hyperfine structure is located between 1.6 and 4.4 kG (1 G = 10^{-4} T).

‡ Spectroscopic properties of (**3**): i.r.(Nujol) ν(CN) 2168m, 2139s, and 2101s; i.r.(CH_2Cl_2) ν(CN) 2168m, 2142s, and 2106s cm^{-1}. ^1H N.m.r. (Me_4Si reference, CD_2Cl_2) δ_A +5.77, δ_B +5.64, J_{AB} 13.2 Hz, $J_{P\text{-}H}$ 4.9, 4.5 Hz ($-CH_2-$,4H); δ +1.98, +1.65, +0.89 ($-CMe_3$, 3 × 9H). $^{31}P\{^1H\}$ N.m.r. (external H_3PO_4, 3:1 CH_2Cl_2–[$^2H_6$]acetone) δ_A −6.83, δ_B −12.73 (AA′BB′ pattern).

tion must involve a complex redox–protonation reaction, the mechanism of which has not yet been determined.

Crystals of (**2**) which were suitable for an *X*-ray structure analysis were grown from dichloromethane–diethyl ether. The structure of the $[Re_2(\mu\text{-Cl})(\mu\text{-C=NHBu}^t)(\mu\text{-dppm})_2Cl_2(CNBu^t)_2]^+$ cation is shown in Figure 1.§ Two essentially identical dirhenium cationic units are present in the unit cell along with two PF_6^- anions, two water molecules, and one CH_2Cl_2 molecule of solvation. Surprisingly though, the structure was found to possess a symmetrically bridging isocyanide derived ligand whose presence had not been detected in the i.r. spectrum [*i.e.* no ν(C=N) mode was observed]. The overall geometry of this complex is that of an edged-shared M_2L_{10} type, having two *trans*-bridging dppm ligands with the dirhenium unit further bridged by a chlorine and an isocyanide ligand. In addition, each rhenium atom is also complexed by one terminal isocyanide and one terminal chlorine ligand. The symmetry of the complex is such that all the chlorine atoms are located on one side of the plane that contains the Re_2P_4 unit, with the isocyanide ligands located on the opposite side.

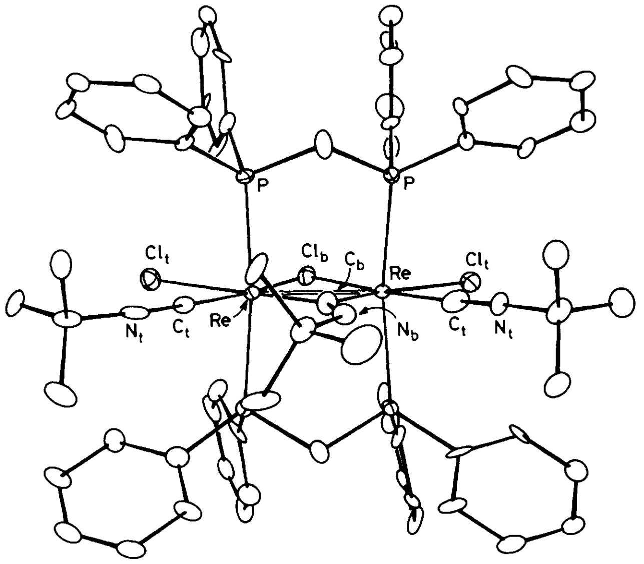

Figure 1. The molecular structure of the cation $[Re_2(\mu\text{-Cl})(\mu\text{-C=NHBu}^t)(\mu\text{-dppm})_2Cl_2(CNBu^t)_2]^+$. Some important distances (Å) and angles (°) are: Re–Re 2.7039(6), Re–Cl_t 2.443(2), Re–Cl_b 2.436(2), Re–P 2.444(2), Re–C_t 2.03(1), Re–C_b 2.03(1), C_t–N_t 1.14(2), N_t–CMe_3 1.47(2), C_b–N_b 1.35(2), N_b–CMe_3 1.49(2), Re–Cl_b–Re 67.4(2), Re–C_b–Re 83.8(5), Re–C_t–N_t 173(1), C_t–N_t–C 174(1), C_b–N_b–C 134(1).

The Re–Re bond distance in (**2**) is 2.704 Å, which is a little longer than that found for $Re_2(\mu\text{-Cl})_2(\mu\text{-dppm})_2Cl_4$ (2.616 Å) and $Re_2(\mu\text{-Cl})_2(\mu\text{-dppm})_2(OC_2H_5)Cl_3$ (2.667 Å) which are derivatives of the doubly bonded Re_2^{6+} core and also possess this same type of M_2L_{10} geometry.[6] Since only three chlorine atoms and one PF_6^- anion per dirhenium unit were located, (**2**) could be considered as formally a derivative of the Re_2^{4+} core and should thus be diamagnetic. In order to explain the paramagnetic nature of this complex, it became apparent that the bridging 'isocyanide' ligand must have become protonated and is in reality a μ-C=$NHCMe_3$ ligand. Protonation of a bridging isocyanide to generate a bridging carbyne or iminyl moiety is known,[7] and in one reported case[8] where protonation occurred at a bridging Me_3CNC ligand, no ν(C=N) mode associated with the bridging iminyl type group was identified in the i.r. spectrum.[9] However, a band at 3295 cm^{-1} was found and assigned to the ν(N–H) mode.[9] In accord with these findings, we were unable to locate a ν(C=N) mode but we did observe a weak band at 3350 cm^{-1} that was not present in the spectra of any of the other isocyanide complexes and which we attribute to the N–H stretching mode. The observed C=N distances for the bridging ligand in the dirhenium unit (1.35 Å) along with the associated C=N–C angle (134°) are also consistent with the idea that 'protonation' has occurred at the nitrogen atom of the bridging isocyanide.[8—10]

Finally, (**2**) can be represented as a carbene complex, or as one in which the μ-C=$NHBu^t$ ligand is bound as an iminyl moiety with a net 1− charge. In these two situations the dirhenium core is formally Re_2^{3+} and Re_2^{5+}, respectively. Based upon the MO treatment for a metal–metal bonded edge-shared bioctahedral structure,[11] this could correspond to Re–Re bond orders of 0.5 and 1.5, respectively. While the observed Re–Re bond distance favours the higher bond order, the uncertainties which arise in the bonding scheme when the complicated μ-C=$NHBu^t$ ligand is present militate against any firm conclusions at this stage.

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§ *Crystal data* for $[Re_2Cl_3(dppm)_2(CNHCMe_3)(CNCMe_3)_2]PF_6\cdot H_2O\cdot 0.5CH_2Cl_2$ at −140 °C: $C_{65.5}H_{75}Cl_4F_6N_3OP_5Re_2$, $M = 1703.41$, monoclinic, space group $P2_1/a$, $a = 22.746(8)$, $b = 25.478(9)$, $c = 23.895(11)$ Å, $\beta = 93.83(3)°$, $U = 13817(17)$ Å^3, $Z = 8$, $D_c = 1.638$ g cm^{-3}, $F(000) = 6600$, $\mu(\text{Mo-}K_\alpha) = 38.7$ cm^{-1}. The structure was solved by conventional heavy-atom methods and refined to $R(F) = 0.060$ and $R_w(F) = 0.066$ for 13880 observed reflections having $F_o^2 > 2\sigma(F_o^2)$. A total of 24303 unique reflections were collected on two crystals ($5° \leqslant 2\theta \leqslant 50°$) on an Enraf-Nonius CAD-4 diffractometer using graphite-monochromated Mo-K_α radiation. Block-diagonal least-squares refinement used anisotropic thermal parameters on the Re, Cl, P, C, N, F, and O atoms (hydrogen atoms not included). The presence of water and dichloromethane of solvation was ascertained from difference maps. A spherical absorption correction (but no extinction coefficient) was applied. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.