An alternative explanation involves coordination of the imine function in a five-coordinate transition state. The question of the *stability* of **3** and **4** could conceivably be related to a weak coordination of either the NH or OR moieties. Experiments to distinguish these possibilities by using palladium and other ligand combinations are in progress, and we shall expand on these shortly; however, suitable crystals of **4c** have been grown, and its structure has been determined (see Figure 1).[10] The molecule shows the expected square-planar geometry about platinum with trans chloride ligands. There are no exceptional bond lengths or angles with respect to the coordination sphere; however, we note that the benzoxazole is approximately perpendicular to the coordination plane and there is a rather long C–C separation in the coordinated ethylene ligand, 1.426 (13) Å. The organic fragment reveals that the ethylene glycol monomethyl ether has attacked the imine carbon to afford an amino ether structure.

The position of the amino ether relative to the metal shows that neither N(2) nor O(2) are within 3.5 Å of the metal. Moreover, the separations are too long for Cl···H–N hydrogen bonding, so that, at least in the solid state, we find no compelling structural feature favoring stabilization.

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Registry No. **1**, 114443-32-2; **2**, 114424-73-6; **3a**, 114424-74-7; **3b**, 114424-75-8; **3c**, 114424-76-9; **4a**, 114424-77-0; **4b**, 114424-78-1; **4c**, 114424-79-2; **5**, 114424-81-6; K[$PtCl_3(C_2H_4)$], 12012-50-9; *trans*-$PtCl_2(PPh_3)_2$, 14056-88-3; 2-((*m*-nitrophenyl)methyleneimino)benzimidazole, 76061-09-1; 5-chloro-2-((*m*-nitrophenyl)methyleneimino)-benzoxazole, 114424-80-5.

Supplementary Material Available: Final positional parameters (Table I), anisotropic thermal parameters (Table II), bond distances and angles (Table III), and torsion angles (Table IV) (8 pages); F_o/F_c values (Table V) (36 pages). Ordering information is given on any current masthead page.

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[10] X-ray diffraction data for **4c**: crystals are pale yellow and air stable. A prismatic crystal of 0.13 × 0.25 × 0.20 mm was used for data collection, space group $P\bar{1}$, with $a = 10.024$ (3) Å, $b = 11.242$ (9) Å, $c = 13.158$ (2) Å, $\alpha = 96.07$ (3)°, $\beta = 107.01$ (2)°, $\gamma = 109.52$ (3)°, $V = 1301.9$ Å^3, $Z = 2$, $d_{calcd} = 1.713$, and $\mu(Mo) = 63.693$. Data were collected at room temperature on a CAD4 diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.71069$ Å). Conditions: $\theta/2\theta$ scan mode with a scan width given by $\Delta = (1.20 + 0.35 \tan \theta)°$; variable scan speed to ensure a constant statistical precision; maximum scan speed 20° min^{-1}; maximum counting time 60 s; prescan rejection limit 0.55; prescan acceptance limit 0.025. A total of 4561 independent reflections ($\pm h, \pm k, l$) were collected in the range $2.9° \leq \theta \leq 25.0°$ and corrected for absorption by using scans of three high χ reflections, with transmission factors in the range 0.62–0.99. A total of 3352 observed reflections ($I_{net} \geq 2.5\sigma(I)$) were used for the solution and refinement; the structure was solved by Patterson and Fourier methods, with all non-hydrogen atoms located and refined anisotropically by full-matrix least squares and the contribution of the hydrogen atoms (except for C(1) and C(2)) in calculated positions included ($B_{iso} = 5.5$ Å^2, C–H = 0.98 Å) but not refined. All calculations were carried out with the Nonius SDP package using scattering factors and $\Delta f'$ and $\Delta f''$ from: *International Tables for X-ray Crystallography*; Ibers, J. A., Hamilton, W. C., Eds.; Kynoch: Birmingham, England, 1974; Vol. IV. No extinction correction was applied. $R = 0.044$, $R_w = 0.056$, and $w = 1/\sigma^2(F_o)$, with the largest shift/esd = 0.02.

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Reduction of Nitriles to Imido Species by Quadruply Bonded Dirhenium(III) Complexes

Sir:

Transition-metal complexes that contain organoimido and related ligands constitute an extensive and important class of molecules whose chemistry is of considerable current interest.[1] In the course of examining the reactions of quadruply bonded and triply bonded dirhenium complexes with the bidentate phosphine ligand 1,2-bis(diphenylphosphino)benzene (abbreviated dppbe), we have encountered a novel reaction in which a nitrile is converted to an alkylimido ligand by the rhenium complex without the addition of an extraneous reducing agent. This is an important development in our exploitation of the redox characteristics of multiply bonded dirhenium species.[2]

While the triply bonded complex $Re_2Cl_4(P\text{-}n\text{-}Pr_3)_4$[2] reacts with an excess of dppbe in refluxing benzene to afford green α-$Re_2Cl_4(dppbe)_2$,[3] the quadruply bonded octahalodirhenate(III) anions are cleaved into mononuclear *trans*-[$ReX_2(dppbe)_2$]X complexes in the reaction of $(n\text{-}Bu_4N)_2Re_2X_8$ (X = Cl, Br) with dppbe in alcohol solvents.[5] The latter reaction course is similar to that in which *trans*-[$ReCl_2(dppee)_2$]Cl·nH_2O and *trans*-[$ReBr_2(dppee)_2$]Br·H_2O are formed from the reactions between $(n\text{-}Bu_4N)_2Re_2X_8$ and *cis*-$Ph_2PCH{=}CHPPh_2$ (dppee) in alcohol solvents.[6]

In contrast to the preceding reactions, the neutral mononuclear rhenium(II) complex *trans*-$ReCl_2(dppbe)_2$ is formed as orange-red crystals in yields of ca. 40% from the reaction of $(n\text{-}Bu_4N)_2Re_2Cl_8$ with dppbe (3- or 4-fold excess) in refluxing nitriles RCN (R = Me, Et, Ph). This complex, which is a rare example of a *mononuclear* rhenium(II) species that contains only halide and phosphine ligands, has essentially the same structure as that of the recently characterized compound *trans*-$ReCl_2(dppee)_2$.[7] While the related reaction of $(n\text{-}Bu_4N)_2Re_2Br_8$ with dppbe in refluxing acetonitrile for periods of 18–100 h affords *trans*-$ReBr_2(dppbe)_2$ as a major product, the corresponding reaction in propionitrile proceeds differently. A mixture of $(n\text{-}Bu_4N)_2Re_2Br_8$ (0.10 g, 0.07 mmol), dppbe (0.12 g, 0.27 mmol), and EtCN (10 mL) was refluxed for 17 h, the reaction mixture cooled to room temperature and filtered, and the filtrate evaporated to dryness. The residue was redissolved in CH_2Cl_2 (ca. 5

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[1] For important reviews of this subject see: (a) Nugent, W. A.; Haymore, B. L. *Coord. Chem. Rev.* **1980**, *31*, 123. (b) Chisholm, M. H.; Rothwell, I. P. In *Comprehensive Coordination Chemistry*; Pergamon: Oxford, England, 1987; Vol. 2, Chapter 13.4.

[2] (a) Cotton, F. A.; Walton, R. A. *Multiple Bonds Between Metal Atoms*; Wiley: New York, 1982. (b) Cotton, F. A.; Walton, R. A. *Struct. Bonding* (*Berlin*) **1985**, *62*, 1.

[3] Yield: 33%. Anal. Calcd for $C_{64.5}H_{52.5}Cl_4P_4Re_2$ (i.e. $Re_2Cl_4(dppbe)_2\cdot 0.75C_6H_6$): C, 52.85; H, 3.61; Cl, 9.67. Found: C, 52.97; H, 4.01; Cl, 9.65. This complex contains chelating dppbe ligands and has properties consistent with its formulation as a centrosymmetric α-isomer in which the overall rotational geometry is eclipsed.[2,4] The cyclic voltammogram (CV) of a solution of this complex in 0.1 M $n\text{-}Bu_4NPF_6$–CH_2Cl_2 shows the presence of a reversible one-electron oxidation at $E_{1/2} = +0.28$ V, an irreversible oxidation at $E_{p,a} = +1.16$ V, and an irreversible reduction at $E_{p,c} = -1.50$ V vs Ag/AgCl. The Nujol mull electronic absorption spectrum displays a characteristic absorption at ~860 nm, while the low-frequency IR spectrum (Nujol mull) has ν(Re–Cl) modes at 312 s and 285 m cm^{-1}.

[4] (a) Anderson, L. B.; Bakir, M.; Walton, R. A. *Polyhedron* **1987**, *6*, 1483. (b) Cole, N. F.; Cotton, F. A.; Powell, G. L.; Smith, T. J. *Inorg. Chem.* **1983**, *22*, 2618. (c) Ebner, J. R.; Tyler, D. R.; Walton, R. A. *Inorg. Chem.* **1976**, *15*, 833.

[5] Methanol, ethanol, and 1-propanol were used as solvents, and reaction times ranged from a few hours to 3 days. Workup of the reaction filtrates gave *trans*-[$ReCl_2(dppbe)_2$]Cl·$4H_2O$ and *trans*-[$ReBr_2(dppbe)_2$]Br in isolated yields ranging from 24 to 48%. Anal. Calcd for $C_{60}H_{56}Cl_3O_4P_4Re$: C, 57.31; H, 4.49. Found: C, 57.35; H, 4.02. IR (Nujol mull): ν(OH) at 3310 w cm^{-1}. Anal. Calcd for $C_{60}H_{48}Br_3P_4Re$: C, 54.62; H, 3.67. Found: C, 54.13; H, 3.76. The electronic absorption spectral properties (measured in CH_2Cl_2) and the CV's of solutions of these complexes recorded in 0.1 M $n\text{-}Bu_4NPF_6$–CH_2Cl_2 confirm the identity of these products. These properties are very similar to those reported for *trans*-[$ReX_2(dppee)_2$]X·nH_2O (dppee = *cis*-$Ph_2PCH{=}CHPPh_2$).[6]

[6] Bakir, M.; Fanwick, P. E.; Walton, R. A. *Polyhedron* **1987**, *6*, 907.

[7] The full details of the crystal structure of *trans*-$ReCl_2(dppbe)_2$ will be reported in due course (Fanwick, P. E., unpublished results).

0020-1669/88/1327-2016$01.50/0

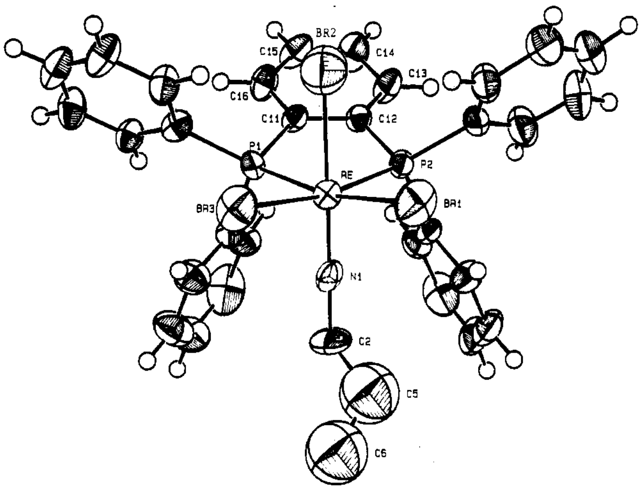

Figure 1. ORTEP view of the structure of Re(N-*n*-Pr)Br_3(dppbe). The thermal ellipsoids are drawn at the 50% probability level. This view represents half of the disorder associated with the CH_2CH_3 fragment of the *n*-propylimido ligand. Atoms C(5) and C(6) have counterparts C(3) and C(4) in the other half of the disorder. Important bond lengths (Å) and angles (deg) are as follows: Re–Br(1) = 2.551 (1), Re–Br(2) = 2.525 (2), Re–Br(3) = 2.563 (1), Re–P(1) = 2.411(3), Re–P(2) = 2.415 (3), Re–N(1) = 1.719 (8), N(1)–C(2) = 1.41 (1), Br(2)–Re–N(1) = 171.2 (2), Br(1)–Re–P(1) = 168.32 (7), Br(3)–Re–P(2) = 169.96 (7), Br(1)–Re–Br(3) = 86.88 (4), Re–N(1)–C(2) = 178.7 (8).

mL) and the solution layered with diethyl ether. The purple crystals that resulted (0.03 g) were washed with hexanes and diethyl ether and dried.[8] A solution of this product in 0.1 M *n*-Bu_4NPF_6–CH_2Cl_2 showed well-defined redox properties (as measured by the cyclic voltammetric technique) with $E_{1/2}(\mathrm{ox})$ = +1.17 V, $E_{\mathrm{p,c}}$ = −1.30 V, and $E_{\mathrm{p,c}}$ = −1.60 V vs Ag/AgCl. For the oxidation at $E_{1/2}$ = +1.17 V, $E_{\mathrm{p,a}} - E_{\mathrm{p,c}}$ = 150 mV and $i_{\mathrm{p,a}}/i_{\mathrm{p,c}}$ = 1.0 for v = 200 mV s^{-1}; under these same conditions there were no coupled oxidation waves associated with the reductions at −1.30 and −1.60 V. A single crystal of this compound was selected and subjected to an X-ray structure analysis. This complex proved to be the (organoimido)rhenium(V) complex Re(N-*n*-Pr)Br_3(dppbe), the structure of which is shown in Figure 1.[9-12]

The Re–N and N–C bond distances (1.719 (8) and 1.41 (1) Å, respectively) and the linearity of the Re–N–C angle (178.7 (8)°) are clearly in accord with an alkylimido moiety and an interaction best represented as[1a,13,14]

$$\mathrm{Re{\equiv}N{-}CH_2CH_2CH_3}$$

This gives an 18-electron count for the metal center, and the absence of a structural trans effect for the Re–Br bond trans to Re(N-*n*-Pr) is therefore to be expected.[1a] To our knowledge, this is the first crystal structure determination on an (alkylimido)rhenium(V) complex where R is other than methyl.

The mechanism by which Re(N-*n*-Pr)Br_3(dppbe) is formed remains to be established. However, in view of the relative facility with which *trans*-$ReX_2(\mathrm{dppbe})_2$ is formed in the reactions between $(n\text{-}Bu_4N)_2Re_2X_8$ and dppbe in nitrile solvents, it is not unreasonable that a rhenium(I) intermediate is involved in the formation of Re(N-*n*-Pr)Br_3(dppbe). A four-electron oxidation of such an entity would then provide the four electrons necessary for the reduction of the nitrile ligand. Interestingly, there is a very recent report by Wilkinson and co-workers[15] in which the complex cation *trans*-$[CrCl(NCMe)(dmpe)_2]^+$ (dmpe = $Me_2PCH_2CH_2PMe_2$) is converted into *trans*-$[Cr(NEt)Cl(dmpe)_2]^+$ by a methanolic solution of $Ba(SO_3CF_3)_2$. The resulting chromium(IV) species, which is "isoelectronic" with Re(N-*n*-Pr)Br_3(dppbe), is apparently formed by a mechanism that is quite different from that by which the rhenium(V) complex is formed in *neat* propionitrile.

In view of the interest in the reduction of nitriles to give amines[16] and its reverse (i.e. the oxidation of coordinated amines to give nitriles),[17] our findings are of importance since imine intermediates are likely in both of these reactions. As a means of synthesizing alkylimido complexes this reaction is quite novel,[1a] and we are now examining the mechanistic and synthetic implications and the scope of this and related reactions. Full structural details will be published in due course.

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Supplementary Material Available: A table of atomic coordinates and an ORTEP view of Re(N-*n*-Pr)Br_3(dppbe) showing the full atomic numbering scheme (3 pages). Ordering information is given on any current masthead page.

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(8) The ^1H NMR spectrum of this complex (in $CDCl_3$) shows resonances at δ +1.42 (m, $NCH_2C\mathit{H}_2CH_3$), +0.70 (t, $NCH_2CH_2C\mathit{H}_3$), and −0.56 (m, $NC\mathit{H}_2CH_2CH_3$) that we attribute to the resonances of the alkylimido group. Like those in other (alkylimido)rhenium(V) complexes, the α-CH_2 group is subject to deprotonation to give $\mathrm{ReN{=}CHCH_2CH_3}$. See: Chatt, J.; Dosser, R. J.; King, F.; Leigh, G. J. *J. Chem. Soc., Dalton Trans.* **1976**, 2435.

(9) Crystals of $Re(NC_3H_7)Br_3$(dppbe) are monoclinic, space group $P2_1/c$, with a = 16.677 (2) Å, b = 10.852 (2) Å, c = 18.382 (4) Å, β = 95.81 (1)°, V = 3310 (2) $Å^3$, Z = 4, d_{calcd} = 1.833 g/cm^3, and μ = 74.26 cm^{-1}. X-ray diffraction data were collected at 22 °C on a 0.39 × 0.35 × 0.06 mm crystal for 4594 independent reflections having $4 < 2\theta < 45°$ on an Enraf-Nonius CAD4 diffractometer using graphite-crystal-monochromated Mo$K\alpha$ radiation (λ = 0.71073 Å). Details of the crystal data collection and reduction methods are the same as those described elsewhere.[10] An empirical absorption correction was applied,[11] but no correction for extinction was made. During the course of the structure analysis, it became apparent that the CH_2CH_3 fragment of the *n*-propylimido ligand was disordered. This ligand is contained within a pocket that is formed by two of the phenyl rings of dppbe. A model was developed in which this fragment was disordered about the plane that contains the Br(2)–Re–N(1)–C(2) unit and bisects the bond C(11)–C(12) of the dppbe ligand (Figure 1). Half of the disorder is shown in Figure 1 with the alkyl chain C(2)–C(3)–C(4) (not shown) representing the other half. Consequently, atoms C(3), C(4), C(5), and C(6) reflect sites of half-occupancy. The rather large thermal parameters associated with C(3), C(4), C(5), and C(6) reveal some inadequacies in this model. Nonetheless, this is a satisfactory solution overall. All atoms except these four carbon atoms were refined anisotropically, and corrections for anomalous scattering were applied to these atoms.[12] Positions for the hydrogen atoms of the dppbe ligand were calculated by assuming idealized geometry and a C–H distance of 0.95 Å. While the hydrogen atoms were used in the calculation of F_o, they were not included in the least-squares refinement. The final residuals were R = 0.055 and R_w = 0.079 for 3135 data with $I > 3\sigma(I)$.

(10) Fanwick, P. E.; Harwood, W. S.; Walton, R. A. *Inorg. Chim. Acta.* **1986**, *122*, 7.

(11) Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A: Found Crystallogr.* **1983**, *A39*, 158.

(12) (a) Cromer, D. T. *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, Table 2.3.1. (b) For the scattering factors used in the structure solution see: Cromer, D. T.; Waber, J. T. *Ibid.*, Table 2.2B.

(13) Bright, D. A.; Ibers, J. A. *Inorg. Chem.* **1969**, *8*, 703.

(14) Shandles, R. S.; Murmann, R. K.; Schlemper, E. O. *Inorg. Chem.* **1974**, *13*, 1373.

(15) Barron, A. R.; Salt, J. E.; Wilkinson, G.; Motevalli, M.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1987**, 2947.

(16) See, for example: Rhodes, L. F.; Venanzi, L. M. *Inorg. Chem.* **1987**, *26*, 2692.

(17) Keene, F. R.; Salmon, D. J.; Meyer, T. J. *J. Am. Chem. Soc.* **1976**, *98*, 1884.

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Metalation and Transmetalation of a Binuclear Complex of Nickel(0). Molecular Alloys of Nickel and Palladium

Sir:

Metal–metal bonds between two or more different metal atoms are of fundamental interest.[1,2] The chemical and physical con-