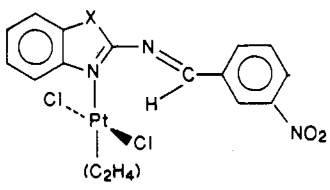
Synthesis and X-ray Structure of Reactive α-Amino Ethers Stabilized via Metal Complexation

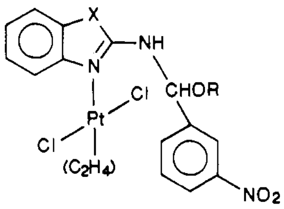
Sir:

Although acetals[1] and cyclic aminals[2] are known compounds, mixed α-amino ethers are relatively rare.[3] Specifically, they are believed to arise as intermediates in the synthesis (or hydrolysis) of Schiff bases, and in one case, a flow NMR study of the reaction of hydroxylamine and acetaldehyde, the "tetrahedral intermediate" $CH_3CH(NHOH)OH$ was identified.[3b] Recent electrochemical studies have suggested[4] that the α-amino ether $PhN(CH_3)CH_2OCH_3$, which is not readily accessible by conventional syntheses, is a useful synthetic precursor. Normally, α-amino ethers are readily hydrolyzed.

In the course of our studies involving cyclometalation chemistry,[5,6] we reacted the platinum–benzimidazole and platinum–benzoxazole derivatives **1** and **2**, with the alcohols ROH (R = Me, Et, *i*-Pr, $CH_3OCH_2CH_2$) to afford the α-amino ethers **3** and **4**, respectively, as yellow solids in good yields.[7] ^1H and ^{13}C NMR spectra[8] are consistent with our formulation with the benzylic proton appearing at δ ~5.87 for **3** and ~6.25 for **4** and the corresponding carbon at δ = 81.76–85.47 for both **3** and **4**. The N–H proton couples to the methine C–H ($^3J_{H-H} \simeq 5$ Hz) indicating a relatively slow exchange rate for this amine and the IR spectra reveal the expected N–H stretching vibrations between 3320 and 3390 cm^{-1}. All of these complexes survive several hours in solutions of wet solvents without decomposition, demonstrating a stabilizing role for the metal. The role of the platinum in this stabilization is uncertain since, on the basis of the ^1H and ^{13}C NMR data for the coordinated ethylene, there are no drastic changes at platinum relative to other well-studied *trans*-[$PtCl_2$-(C_2H_4)(nitrogen ligand)] complexes.[9] The uncoordinated benzamidazole and oxazole do *not* react with alcohols under our reaction conditions. Interestingly for **4a**, removal of the metal, via reaction with PPh_3, to give *trans*-$PtCl_2(PPh_3)_2$, leaves the uncoordinated compound **5** (which hydrolyzes slowly in wet chloroform) so that although they are water sensitive, it would appear that molecules such as **5** are not inherently unstable but rather succumb to the reaction conditions under which they are produced.



1 (X=NH)
2 (X=O, as 5-Cl compd)



3a (R=CH3; X=NH)
b (R=Et; X=NH)
c (R=*i*-Pr; X=NH)

4a (R=CH3; X=O)
b (R=Et; X=O)
c (R=CH2CH2OCH3; X=O, as 5-Cl compd)

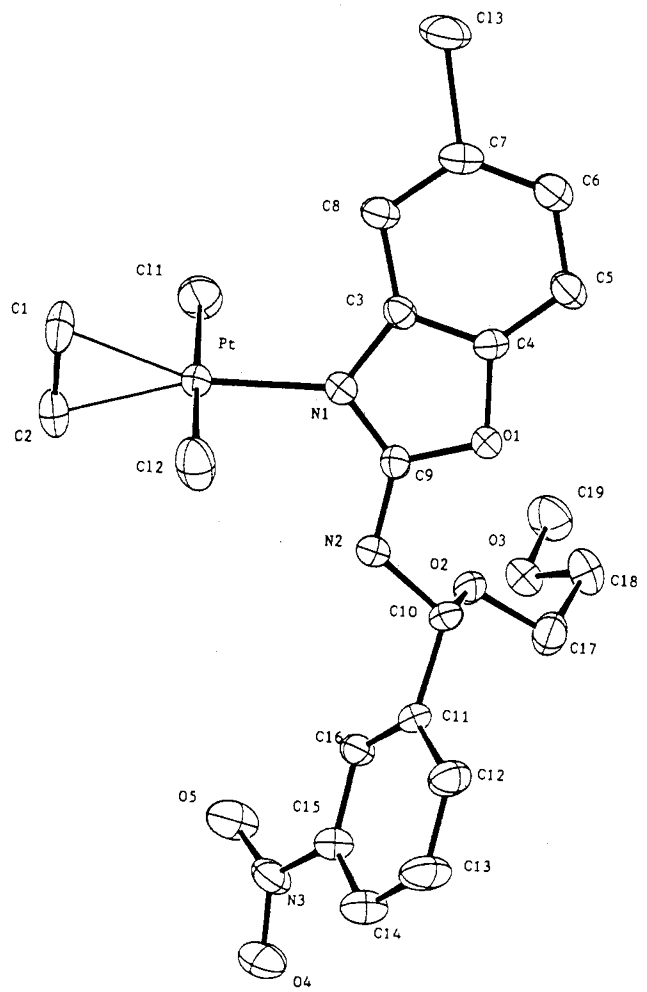
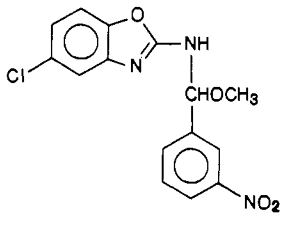


Figure 1. ORTEP view of complex **4c**. Selected bond lengths (Å) and bond angles (deg); Pt–Cl(1) = 2.294 (2), Pt–Cl(2) = 2.286 (2), Pt–C(1) = 2.142 (8), Pt–C(2) = 2.151 (8), Pt–N(1) = 2.068 (5), C(1)–C(2) = 1.426 (13), C(9)–N(2) = 1.337 (8), C(10)–N(2) = 1.454 (8), C(10)–O(2) = 1.414 (8), C(17)–O(2) = 1.464 (9); Cl(1)–Pt–Cl(2) = 178.31 (8), Cl(1)–Pt–N(1) = 90.1 (2), Cl(2)–Pt–N(1) = 88.9 (2), C(1)–Pt–Cl(1) = 91.0 (3), C(2)–Pt–Cl(1) = 90.2 (3).



5

Although speculative, we believe that the ease with which the amine is attacked relates to the electronic environment created by coordination of the ring nitrogen. Coordination polarizes the N=C—N=CH(m-$NO_2C_6H_4$) fragment by withdrawing electron density, thereby making the benzylidene carbon more electrophilic.

---

(1) Meskine, F. A. J. *Synthesis* **1981**, *13*, 501.

(2) Seebach, D.; Imwinkelried, R.; Weber, T. *Modern Synthetic Methods*; Scheffold, R., Ed.; Springer: West Berlin, 1986; Vol. 4, pp 148, 191.

(3) (a) Taylor, L. F.; Urbach, F. L.; Busch, D. H. *J. Am. Chem. Soc.* **1969**, *91*, 1072. (b) Cocivera, M.; Fyfe, C. A.; Effio, A.; Vaish, S. P.; Chen, H. E. *J. Am. Chem. Soc.* **1976**, *98*, 1573.

(4) Shono, T.; Matsumura, Y.; Inoue, K.; Ohimizu, H.; Kashimura, S. *J. Am. Chem. Soc.* **1982**, *104*, 5753.

(5) Albinati, A.; Anklin, C. G.; Ganazzoli, F.; Rüegg, H.; Pregosin, P. S. *Inorg. Chem.* **1987**, *26*, 503 and references therein.

(6) Albinati, A.; Arz, C.; Pregosin, P. S. *Inorg. Chem.* **1987**, *26*, 508. Arz, C.; Anklin, C. G.; Pregosin, P. S. *Magn. Reson. Chem.* **1987**, *25*, 158.

(7) A solution of $K[PtCl_3(C_2H_4)]$ (150 mg, 0.41 mmol) in 15 mL of warm MeOH was treated with the oxazole (123 mg, 0.41 mmol) dissolved in 15 mL of CH_2Cl_2. Stirring at room temperature for 2 h was followed by removal of the solvents in vacuo. Extraction with CH_2Cl_2 followed by precipitation with hexane affords 200 mg of product (78%).

(8) Selected data. **3a**: ^1H NMR (250 MHz) in $CDCl_3$ $\delta(OCH_3) = 3.62$; $\delta(HCO) = 5.79$, $(CH_2{=}CH_2) = 4.95$, $^1J_{Pt-H} = 59$ Hz; ^{13}C NMR (63 MHz) in $CDCl_3$ $\delta(OCH_3) = 55.48$, $\delta(HCO) = 85.37$, $\delta(CH_2{=}CH_2) = 77.45$, $^1J_{Pt-C} = 161$ Hz. **4a**: ^1H NMR (250 MHz) in $CDCl_3$ $\delta(OCH_3) = 3.65$, $\delta(HCO) = 6.15$, $\delta(CH_2{=}CH_2) = 4.92$, $^1J_{Pt-H} = 63$ Hz; ^{13}C NMR (63 MHz) in $CDCl_3$ $\delta(OCH_3) = 56.97$, $\delta(HCO) = 85.47$, $\delta(CH_2{=}CH_2) = 77.44$, $^1J_{Pt-C} = 161$ Hz.

(9) Pregosin, P. S.; Sze, S. N.; Salvadori, P.; Lazzaroni, R. *Helv. Chim. Acta* **1977**, *60*, 2514.

0020-1669/88/1327-2015$01.50/0 © 1988 American Chemical Society

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.

Acknowledgment. C.A. thanks the Swiss National Science Foundation and Ciba-Geigy AG, Basel, Switzerland, for support, and we thank the Johnson Matthey Research Center, Reading, England, for the loan of platinum metal salts.

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$_2$H$_4$)], 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.

---

(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, $Z = 2$, $d_{\text{calcd}} = 1.713$, and μ(Mo) = 63.693. Data were collected at room temperature on a CAD4 diffractometer using graphite-monochromated Mo Kα radiation (λ = 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 ($I_{\text{net}} \geq 2.5\sigma(I)$) 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 ($B_{\text{iso}} = 5.5$ 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.

Istituto di Chimica Farmaceutica
Università di Milano
I-20131 Milano, Italy
Alberto Albinati

Laboratorium für Anorganische Chemie
ETH-Zentrum
CH-8092 Zürich, Switzerland
Christof Arz
Paul S. Pregosin*

Received January 20, 1988

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$_2$Cl$_4$(P-*n*-Pr$_3$)$_4$[2] reacts with an excess of dppbe in refluxing benzene to afford green α-Re$_2$Cl$_4$(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*-Bu$_4$N)$_2$Re$_2$X$_8$ (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·*n*H$_2$O and *trans*-[ReBr$_2$(dppee)$_2$]Br·H$_2$O are formed from the reactions between (*n*-Bu$_4$N)$_2$Re$_2$X$_8$ and *cis*-Ph$_2$PCH=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*-Bu$_4$N)$_2$Re$_2$Cl$_8$ 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*-Bu$_4$N)$_2$Re$_2$Br$_8$ 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*-Bu$_4$N)$_2$Re$_2$Br$_8$ (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$_2$Cl$_2$ (ca. 5

---

(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$_4$P$_4$Re$_2$ (i.e. Re$_2$Cl$_4$(dppbe)$_2$·0.75C$_6$H$_6$): 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*-Bu$_4$NPF$_6$–CH$_2$Cl$_2$ 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$_2$O and *trans*-[ReBr$_2$(dppbe)$_2$]Br in isolated yields ranging from 24 to 48%. Anal. Calcd for C$_{60}$H$_{56}$Cl$_3$O$_4$P$_4$Re: 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$_3$P$_4$Re: C, 54.62; H, 3.67. Found: C, 54.13; H, 3.76. The electronic absorption spectral properties (measured in CH$_2$Cl$_2$) and the CV's of solutions of these complexes recorded in 0.1 M *n*-Bu$_4$NPF$_6$–CH$_2$Cl$_2$ confirm the identity of these products. These properties are very similar to those reported for *trans*-[ReX$_2$(dppee)$_2$]X·*n*H$_2$O (dppee = *cis*-Ph$_2$PCH=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 © 1988 American Chemical Society