Synthesis and Structure of the Rhenium Phenylamido Complex $Re(\eta^5\text{-}C_5H_5)(NO)(PPh_3)(\dot{N}HPh)$; An Unprecedented Pyramidal Amido Ligand

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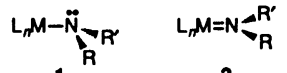
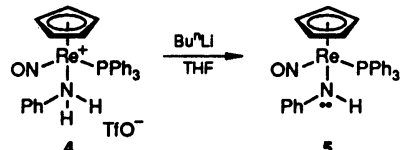
In contrast to metal amido complexes that have been structurally characterized to date, the title compound exhibits a pyramidal phenylamido ligand.

Amido ligands ($-\dot{N}R_2$) form stable adducts with nearly all the elements.[1] When attached to a saturated carbon atom, the amido moiety exhibits a pyramidal geometry **1**, with inversion barriers commonly in the 6–8 kcal mol^{-1} range (1 cal = 4.184 J).[2] However, to our knowledge all structurally characterized main group and transition metal amido complexes exhibit a planar geometry at nitrogen.[1,3–5] In many cases, this can be attributed to the presence of low-lying acceptor orbitals on the metal, which allow multiple bonding as in **2**. Thus, we sought to probe structure and bonding in chiral d^6, coordinatively



1 **2**



4 **5**

Scheme 1

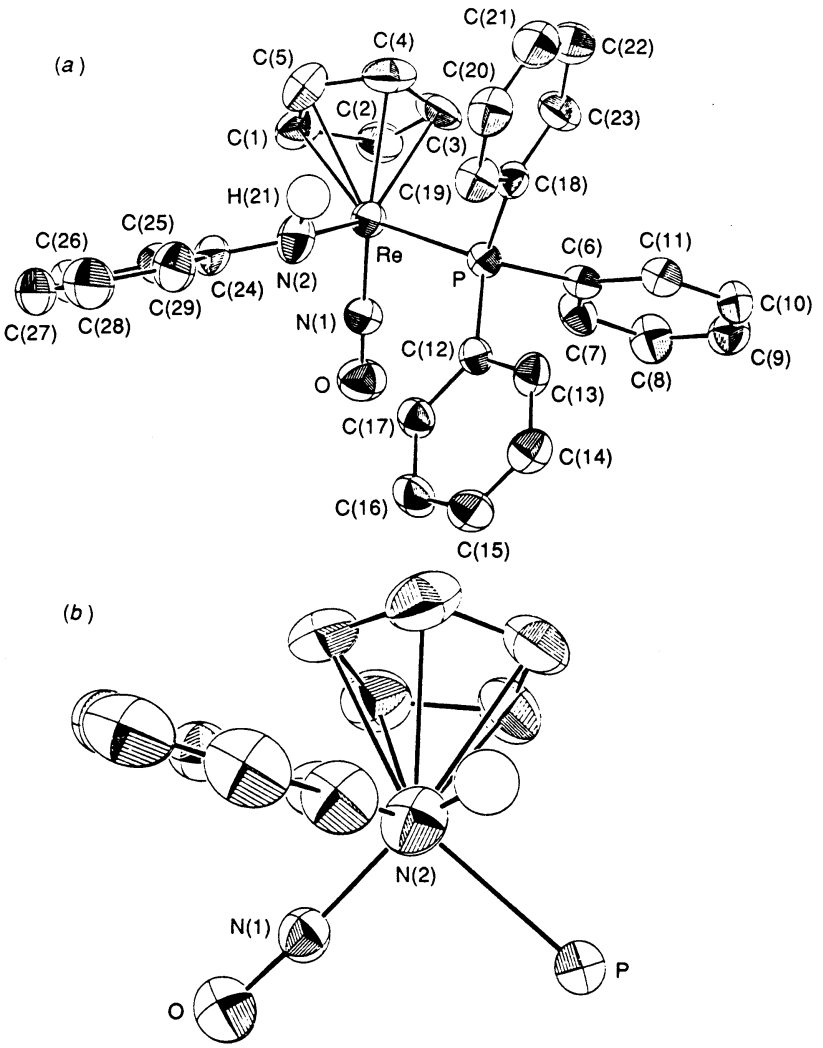


Fig. 1 Structure of phenylamido complex **5**: (*a*) Numbering diagram; (*b*) Newman-type projection down the N(2)–Re bond with the PPh_3 phenyl groups omitted. Selected bond lengths (Å) and angles (°): Re–N(2) 2.076(6), N(2)–C(24) 1.371(9), N(2)–H(21) 0.929(6), Re–N(1) 1.733(6), Re–P 2.355(2), N(1)–O 1.227(7); Re–N(2)–C(24) 129.1(5), Re–N(2)—H(21) 109.3(5), C(24)–N(2)–H(21) 107.1(6), P–Re–N(1) 93.3(2), N(1)–Re–N(2) 103.5(3), P–Re–N(2) 86.2(2), Re–N(1)–O 173.1(5).

saturated, 18 valence-electron amido complexes of the formula $Re(\eta^5\text{-}C_5H_5)(NO)(PPh_3)(\dot{N}RR')$.[6] In this communication, we report the first crystal structure of a metal complex with a pyramidal amido ligand.

The trifluoromethanesulphonate complex $Re(\eta^5\text{-}C_5H_5)(NO)(PPh_3)(OTf)$ **3** and aniline (5 equiv.) were combined in toluene.[6] This gave the aniline complex $[Re(\eta^5\text{-}C_5H_5)(NO)(PPh_3)(NH_2Ph)]^+ TfO^-$ **4** (yield 93%), which was then treated with Bu^nLi (1.0 equiv.) in tetrahydrofuran (THF) at −80 °C (Scheme 1). Workup gave orange plates of the phenylamido complex $Re(\eta^5\text{-}C_5H_6)(NO)(PPh_3)(\dot{N}HPh)$ **5** (yield 63%). The new complexes **4** and **5** were characterized by microanalysis, and IR and NMR (^1H, ^{13}C, ^{31}P) spectroscopy.† The ^1H NMR spectrum of **3** exhibited only a single set of resonances, even at −115 °C {[$^2H_8$]THF}.

X-Ray diffraction data were measured for **5** and the structure determined is shown in Fig. 1.‡ The amido hydrogen [H(21)] was easily located from the final Fourier difference map, and a lone pair (LP) position was calculated. As illustrated in Fig. 1, the amido nitrogen atom [N(2)] is distinctly pyramidalized. The sum of the three bond angles about N(2) [129.1(5)°, 109.3(5)°, 107.1(6)°] is 345.5°: much less than the 360° that would be found for a trigonal–planar atom. For comparison, the sum of the bond angles about nitrogen in aniline is *ca.* 345°.[7]

† *Selected NMR data* for **4** ($CDCl_3$): ^1H (δ) 5.43 (s, C_5H_5), 5.39 (s, br, NH), 5.35 (s, br, NH'); $^{13}C\{^1H\}$ (δ) C_6H_5 at 149.03 (d, J_{CP} 2.7 Hz), 129.36 (s), 125.93 (s), 119.79 (s); PPh_3 at 133.42 (d, J_{CP} 10.9 Hz), 131.63 (d, J_{CP} 2.4 Hz), 131.41 (d, J_{CP} 55.1 Hz), 129.49 (d, J_{CP} 10.7 Hz); 120.49 (q, J_{CF} 319.4 Hz, CF_3), 91.75 (s, C_5H_5); $^{31}P\{^1H\}$ (δ) 20.0 (s). **3** [$^2H_8$]THF: ^1H (δ) 5.27 (s, C_5H_5), 3.69 (d, J_{HP} 7.3 Hz, NH); $^{13}C\{^1H\}$ (δ) C_6H_5 at 163.20 (d, J_{CP} 4.1 Hz), 128.38 (s), 118.17 (s), 113.27 (s); PPh_3 at 134.79 (d, J_{CP} 10.8 Hz), 134.55 (d, J_{CP} 51.4 Hz), 131.17 (s), 129.26 (d, J_{CP} 9.9 Hz); 92.25 (s, C_5H_5); $^{31}P\{^1H\}$ (δ) 25.3 (s). Satisfactory elemental analyses were obtained for all new compounds.

‡ *Crystal data* for **5**: $C_{29}H_{26}N_2OPRe$, M = 635.7, orthorhombic, space group *Pbca* (No. 61), a = 16.303(1), b = 18.272(1), c = 16.547(1) Å, Z = 8, U = 4929.16 Å^3, D_c = 1.71 g cm^{-3}, μ = 50.85 cm^{-1}. Final R = 0.0354 (R_w = 0.0459) for 2855 independent reflections with $I > 3\sigma(I)$, measured in the 2θ range 2–50° at 16 °C with Mo–Kα radiation on a Syntex $P\bar{1}$ diffractometer. The structure was solved using the Patterson heavy-atom method. All non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were calculated except H(21) which was found on the difference map. Hydrogen atoms were added to the structure factor calculations but their positions were not refined. This results in some understatement of the estimated standard deviations (esds) associated with the X–N(2)–H(21) bond angles. 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.

Other structural features of **5** merit note. First, the pyramidal amido nitrogen is a stereocentre. Thus, two diastereoisomers are possible. Based upon dynamic NMR properties of dimethylamido complex $Re(\eta^5\text{-}C_5H_5)(NO)(PPh_3)(\dot{N}Me_2)$ reported previously,[6] these should readily interconvert in solution ($\Delta^{\ddagger}G < 8$ kcal mol^{-1}). However, only one is found in crystalline **5** (*SS,RR*). Second the Re–N(2) conformation in **5** directs the amido phenyl ring into the large interstice between the cyclopentadienyl and nitrosyl ligands [torsion angles: P–Re–N(2)–C(24) 157°; P–Re–N(2)–LP 56°]. The plane of the phenyl ring is coincident with the Re–N(2) bond (angular deviation < 1°) and allows delocalization of the nitrogen lone pair. The isoelectronic benzyl complex (−)-(*R*)-$Re(\eta^5\text{-}C_5H_5)(NO)(PPh_3)(CH_2Ph)$ exhibits an analogous Re–C conformation, but orthogonal phenyl ring orientation.[8] Finally, the lone pair position in **5** is comparable to those in the corresponding neutral phosphido and cationic sulphide complexes (P–Re–X–LP torsion angles 59–60°).[9]

To our knowledge, only a few coordinatively saturated amido complexes have been structurally characterized. These include two planar chelated bis(silyl) amido iridium complexes,[4b,c] and the rhenium phenylamido complex $Re(Me_3P)_4(N_2)(NHPh)$.[4a] An amido hydrogen position was calculated for the latter, and gave some indication of a slightly pyramidalized nitrogen (sum of amido bond angles = 353°). Also, structures of three d^8 platinum(II) amido complexes of the formula $(L)_2Pt(X)(NRR')$ have been reported: $(Et_3P)_2Pt(H)(NHPh)$ **6**, (dppe)Pt(Me)(NMePh) [dppe = bis(diphenylphosphino)ethane], and $(Et_3P)_2Pt(Cl)(NPh_2)$.[5] Although these compounds are formally coordinatively unsaturated, they lack low-lying metal acceptor orbitals for π-bonding. Nonetheless, each exhibits a planar amido ligand. Further, Trogler has conducted Xα calculations on **6** (sum of amido bond angles = 356°), and finds a Pt–N π bond order of zero.[5a]

In summary, our data suggest that pyramidal amido ligands may be more widespread than thought previously; particularly in coordinatively saturated metal complexes where the nitrogen bears simple alkyl or aryl substituents. Regardless of the nature of the metal, the amido ligand lone pair is clearly an important determinant of structural, dynamic and chemical properties. Further studies of **5** and related amido complexes are in progress.

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