Synthesis, Structure, and Reactivity of Chiral Rhenium Amido Complexes of the Formula (η^5-C_5H_5)Re(NO)(PPh_3)(NRR′)

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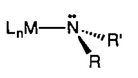
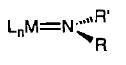
Reactions of primary and secondary amine complexes [(η^5-C_5H_5)Re(NO)(PPh_3)(NHRR′)]$^+$ TfO$^-$ [**2**; R/R′ = H/H (**a**), H/CH_3 (**b**), H/C_6H_5 (**d**), CH_3/CH_3 (**f**), $CH_2CH_2CH_2CH_2$ (**h**)] with *n*BuLi give amido complexes (η^5-C_5H_5)Re(NO)(PPh_3)(NRR′) (**1**) in quantitative NMR yields. Although **1d** can be isolated in pure form, **1f** is converted upon workup into a dimeric bridging bis(amido) complex, *cis*-[(η^5-C_5H_5)Re(NO){μ-N(CH_3)$_2$}]$_2$. The crystal structure of **1d** exhibits a pyramidal amido nitrogen atom. The diastereotopic methyl groups in **1f** readily exchange, as assayed by variable-temperature NMR. Complexes **1a,f** react with TfOH to regenerate **2a,f**, and with TfOR″ to give the corresponding alkylated amine complexes. The basicities and nucleophilicities of the amido nitrogen atoms are shown to be greater than those of organic amines.

The amido fragment $-NR_2$ is one of the most common functional groups in organic and inorganic compounds, and is an important determinant of physical and chemical properties. Accordingly, transition-metal amido complexes have attracted the interest of numerous investigators[1–2]. Among other attributes, amido complexes exhibit a potentially rich catalytic chemistry[3], and are intermediates in unusual bond-activation processes[4]. However, several unsolved chemical and structural issues remain extant.

For example, when a $-NR_2$ moiety binds to a saturated carbon atom, the lone pair remains localized on the nitrogen atom and the pyramidal geometry shown in **A** is obtained. Inversion barriers of 6–8 kcal/mol are typical[5]. However, to our knowledge all structurally characterized main-group and transition-metal complexes of *organic* amido fragments exhibit a trigonal planar geometry at the nitrogen atom[1,2,6–9]. In many compounds, this can be attributed to the presence of low-lying acceptor orbitals on the metal atom, which allow multiple bonding as in **B**. However, in some cases it has been shown that suitable metal acceptor orbitals are absent[8,9b].



A



B

We have had an ongoing interest in adducts of the chiral d^6 16-valence-electron rhenium Lewis acid [(η^5-C_5H_5)Re(NO)(PPh_3)]$^+$ (**I**) and heteroanionic Lewis bases such as phosphides ($-PR_2$)[10], alkoxides ($-OR$)[11], and halides ($-X$)[12]. The electronic properties of both **I** and selected complexes have been studied in detail[10a,13]. No low-lying, rhenium-centered π-acceptor orbitals have been identified. Thus, we sought to investigate the structure and reactivity of *coordinatively saturated* amido complexes (η^5-C_5H_5)Re(NO)(PPh_3)(NRR′) (**1**). In this paper, we report (1) high-yield syntheses of **1**, (2) a crystal structure that shows a pyramidal amido nitrogen atom, (3) amido ligand inversion/rotation barriers, (4) reactions that establish enhanced amido nitrogen basicity and nucleophilicity, and (5) a facile conversion of one compound to a dimeric bridging bis(amido) complex. Portions of this work have been communicated[14].

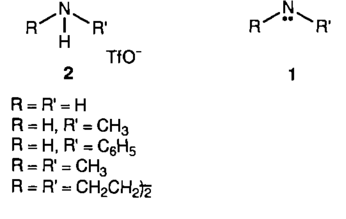
$$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^+ \ \mathbf{I}$$

Results

1. Synthesis and Characterization of Amido Complexes

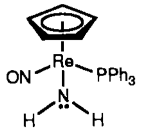
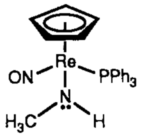
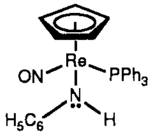
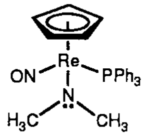
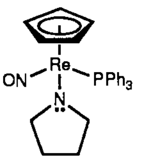
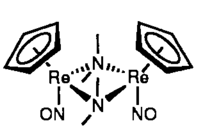
It has been previously shown that primary and secondary phosphane complexes of the formula [(η^5-C_5H_5)Re(NO)(PPh_3)(PHRR′)]$^+$ X$^-$ are deprotonated by K$^+$ *t*BuO$^-$ to the corresponding phosphido complexes (η^5-C_5H_5)Re(NO)(PPh_3)(PRR′)[10]. Hence, the analogous amine complexes [(η^5-C_5H_5)Re(NO)(PPh_3)(NHRR′)]$^+$ TfO$^-$ [**2**; R/R′ = H/H (**a**), H/CH_3 (**b**), H/C_6H_5 (**d**), CH_3/CH_3 (**f**), $CH_2CH_2CH_2CH_2$ (**h**)][15] were treated with 1.0 equiv. of *n*BuLi in THF at −80 °C (Scheme 1). The amido complexes (η^5-C_5H_5)Re(NO)(PPh_3)(NRR′) (**1a,b,d,f,h**) were formed in quantitative yields, as assayed by ^{31}P-NMR spectroscopy. Identical de-

Scheme 1. Synthesis of amido complexes (η^5-C_5H_5)Re(NO)(PPh_3)-(NRR′) (**1**)



Chem. Ber. **1992**, *125*, 815–824 © VCH Verlagsgesellschaft mbH, D-6940 Weinheim, 1992 0009–2940/92/0404–0815 $ 3.50+.25/0

Table 1. Spectroscopic characterization of new rhenium amido complexes

Complex	IR (cm^{-1}, KBr)	^{1}H NMR (δ)^a	^{13}C{^{1}H} NMR (ppm)^b	^{31}P{^{1}H} NMR (ppm)^c
 **1a**	υ_{NO} 1637 vs	7.42-7.27 (m, 15H of $3C_6H_5$), 5.23 (s, C_5H_5), 2.02 (s, br, NH_2).^{d}	PPh_3 at: 134.91 (d, J= 52.2, *i*), 134.71 (d, J=10.7, *o*), 131.23 (s, *p*), 129.43 (d, J=9.9, *m*); 92.58 (d, J=2.3, C_5H_5).^{d}	25.8 (s)^d
 **1b**	υ_{NO} 1631 vs	7.52-7.29 (m, 15H of $3C_6H_5$), 5.24 (s, C_5H_5), 3.15 (s, CH_3), 0.85 (m, br, NH).^{d}	PPh_3 at: 135.29 (d, J=52.5, *i*), 134.651 (d, J=10.2, *o*), 131.01 (s, *p*), 129.13 (d, J=10.2, *m*); 92.67 (s, C_5H_5), 52.46 (s, CH_3).^{d}	28.2 (s)^d
 **1d**	υ_{NO} 1618 vs	7.54-7.36 (m, 15H of $4C_6H_5$), 6.81-6.73 (m, 2H of $4C_6H_5$), 6.40-6.33 (m, 2H of $4C_6H_5$), 6.19-6.12 (m, 1H of $4C_6H_5$), 5.27 (s, C_5H_5), 3.69 (d, J_{HP}=7.3 NH).	C_6H_5 at: 163.20 (d, J=4.1, *i*), 128.38 (s, *m*), 118.17 (s, *o*), 113.27 (s, *p*); PPh_3 at: 134.79 (d, J=10.8, *o*), 134.55 (d, J=51.4, *i*), 131.17 (s, *p*), 129.26 (d, J=9.9, *m*); 92.25 (s, C_5H_5).	25.3 (s)
 **1f**	υ_{NO} 1634 vs	7.52-7.36 (m, 6H of $3C_6H_5$), 7.35-7.10 (m, 9H of $3C_6H_5$), 5.04 (s, C_5H_5), 2.75 (s, br, $2CH_3$).^{d}	PPh_3 at: 137.33 (d, J=50.8, *i*), 134.78 (d, J=10.5, *o*), 130.58 (s, *p*), 128.84 (d, J=10.1, *m*); 91.41 (s, C_5H_5), 62.38 (d, J=2.3, $2CH_3$).^{d}	19.7 (s)^d
 **1h**	υ_{NO} 1634 vs	7.59-7.49 (m, 6H of $3C_6H_5$), 7.42-7.34 (m, 9H of $3C_6H_5$), 5.12 (s, C_5H_5), 2.83 (m, $2CH_2N$), 1.28 (m, 2 CH_2).^{d}	PPh_3 at: 137.28 (d, J=50.3, *i*), 134.55 (d, J=10.5, *o*), 130.47 (s, *p*), 128.71 (d, J=10.1, *m*); 91.12 (s, C_5H_5), 67.91 (s, $2CH_2N$), 28.37 (s, $2CH_2$).^{d}	19.7 (s)^d
 **cis-4f**	υ_{NO} 1626 vs	5.27 (s, $2C_5H_5$), 4.11 (s, $2CH_3$), 2.66 (s, $2CH_3$).	92.58 (s, C_5H_5), 75.02 (s, $2CH_3$), 66.67 (s, $2CH_3$).	

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[a] At 300 MHz and ambient probe temperature unless noted in [D_8]THF and referenced to residual THF (δ = 1.73); all couplings are to ^{1}H unless noted and are in Hz. — [b] At 75 MHz and ambient probe temperature unless noted in [D_8]THF and referenced to residual THF (δ = 67.4); all couplings are to ^{31}P unless noted and are in Hz; assignments of resonances to phenyl carbon atoms are made as described in: W. E. Buhro, S. Georgiou, J. M. Fernández, A. T. Patton, C. E. Strouse, J. A. Gladysz, *Organometallics* **1986**, *5*, 956. — [c] At 32 MHz and ambient probe temperature unless noted in [D_8]THF and referenced to external H_3PO_4. — [d] Spectrum taken at −20°C.

protonations could also be effected with freshly sublimed K^+ $tBuO^-$.

Low-temperature solvent removal gave amido complexes **1** as spectroscopically pure powders that contained the by-product Li^+ TfO^-. Attempts at further purification were generally unsuccessful[16]. However, in the case of phenylamido complex **1d**, careful crystallization gave analytically pure orange plates in 63% yield (Experimental). Crystalline **1d** did not exhibit detectable air or moisture sensitivity over a period of weeks. In contrast, when solutions of **1** were exposed to air for ca. 1 h, protonation to amine complexes **2** occurred.

Amido complexes **1** were characterized by IR and NMR (^{1}H, ^{13}C, ^{31}P) spectroscopy, as summarized in Table 1. The IR-ν_{NO} values were typical of neutral (η^5-C_5H_5)Re(NO)(PPh_3)(X) complexes[10–12]. The ^{31}P-NMR chemical shifts of the primary amido complexes (**1a,b,d**; δ = 28.2–25.3) were downfield of those of the secondary amido complexes (**1f,h**; δ = 19.7). Amine complexes **2**, which give ^{31}P-NMR resonances 5–8 ppm upfield from those of **1**, show an analogous trend[15]. The possibility of lithium-ion binding to **1** was considered. However, the ^{1}H- and ^{13}P-NMR spectra of analytically pure **1d** and the powder containing Li^+ TfO^- were identical.

The nitrogen substituents in the symmetrically substituted amine complexes **2a,f,h** are diastereotopic, and exhibit distinct ^{1}H- and/or ^{13}C-NMR resonances[15]. However, as shown in Table 1, the nitrogen substituents in the corresponding amido complexes **1a,f,h** gave only a single set of ^{1}H- and/or ^{13}C-NMR resonances at ambient probe temperature. The basis for this degeneracy is established below.

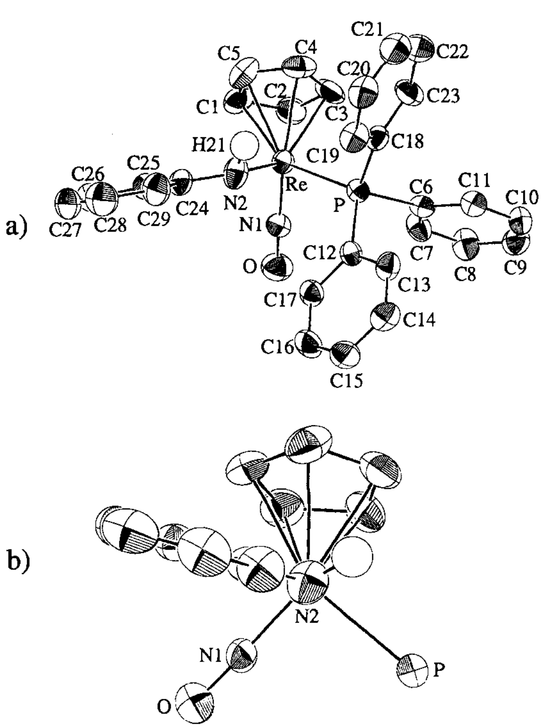


Figure 1. Structure of phenylamido complex **1d**: (a) Numbering diagram; (b) Newman-type projection down the N–Re bond with the PPh_3 phenyl groups omitted. – Selected bond lenghts [Å], bond angles [°], and torsion angles [°] in **1d**[a]

Re–N2	2.076(6)	Re–C4	2.315(7)
Re–P	2.355(2)	Re–C5	2.343(8)
Re–N1	1.733(6)	N2–C24	1.371(9)
N1–O	1.227(7)	N2–H21	0.929(6)
Re–C1	2.321(7)	P–C6	1.826(7)
Re–C2	2.266(7)	P–C12	1.825(7)
Re–C3	2.244(7)	P–C18	1.816(7)
N2–Re–P	86.2(2)	Re–N2–H21	109.3(5)
N2–Re–N1	103.5(3)	C24–N2–H21	107.1(6)
P–Re–N1	93.3(2)	N2–C24–C25	123.5(7)
Re–N1–O	173.1(5)	N2–C24–C29	119.8(7)
Re–N2–C24	129.1(5)		
P–Re–N2–C24	156.9(6)	N1–Re–N2–C24	64.4(6)
P–Re–N2–H21	–69.9(5)	N1–Re–N2–H21	–162.3(5)
P–Re–N2–LP	56.2(4)	Re–N2–C24–C29	179.4(5)
		Re–N2–C24–C25	0(1)

[a] Bond lengths and angles involving the phenyl rings have been omitted; LP = lone pair.

2. Crystal Structure of 1d

X-ray data were collected on **1d** under the conditions summarized in Table 2. Refinement (Experimental) yielded the atomic coordinates given in Table 3 and the structures, bond lengths, bond angles, and torsion angles shown in Figure 1. The amido hydrogen atom (H21) was unambiguously located from the final Fourier difference map but not refined. Thus, the error limits associated with all angles involving H21 in Figure 2 are understated. A lone-pair (LP) position was calculated.

As illustrated in Figure 1, the amido nitrogen atom (N2) in **1d** is distinctly pyramidal, and thus constitutes a second stereocenter. Since only one diastereomer is observed, "chiral recognition" between the rhenium fragment **I** and the $-NHC_6H_5$ moiety is essentially complete in the solid state. The sum of the three bond angles about N2 [129.1(5), 109.3(5), 107.1(6)°] is 345.5° – intermediate between the values for trigonal planar and idealized tetrahedral atoms (360°, 328.5°). Also, the N2–Re–NO and N2–Re–P bond angles [103.5(3), 86.2(2)°] differ significantly from the 90° expected in an idealized octahedral metal complex.

A least-squares plane was calculated for the amido phenyl group. The Re and N2 atoms were only 0.035 and 0.021 Å removed from the plane. Also, the Re–N2–C24–C25 and Re–N2–C24–C29 torsion angles were 0(1) and 179.4(5)°. Thus, the Re–N2 bond is essentially coplanar with the phenyl group (angle < 1°). Importantly, this conformation allows some delocalization of the nitrogen lone pair into the aromatic ring. Hence, amido complexes **1a,b,f,h**, which lack an unsaturated substituent, are likely to be even more pyramidalized.

3. Dynamic Behavior of 1d,f

With the pyramidal geometry of the amido ligands in **1** established, a more detailed interpretation of their NMR spectra was sought. In particular, the observation of a single set of resonances for the diastereotopic nitrogen substituents in **1a,f,h** suggested the operation of facile exchange processes. Thus, ^{1}H-NMR spectra of dimethylamido complex **1f** were recorded in [D$_8$]THF from -114 to -44°C (Figure 2). Two methyl resonances were observed in the low-temperature limit (δ = 2.46 and 2.84; -114°C; $\Delta\nu$ = 69.1 Hz). These coalesced at -102°C, and a standard analysis[17] gave $\Delta G^{\ddagger}(T_c)$ = 7.8 kcal/mol for methyl group exchange.

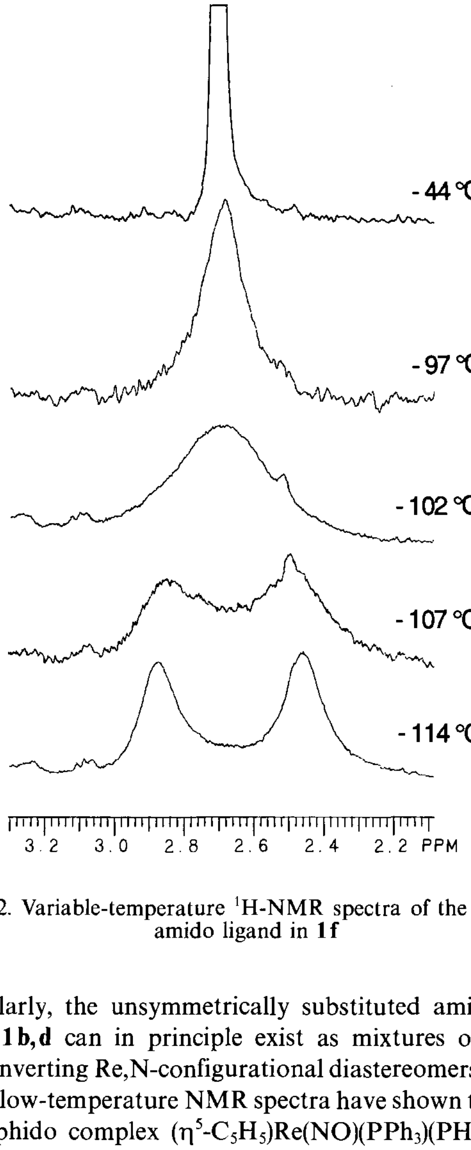


Figure 2. Variable-temperature ^{1}H-NMR spectra of the dimethylamido ligand in **1f**

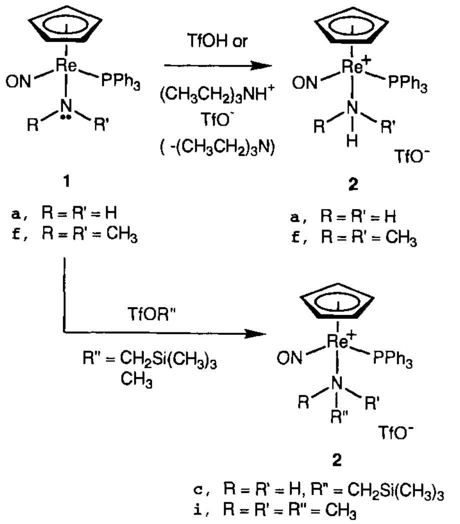
Similarly, the unsymmetrically substituted amido complexes **1b,d** can in principle exist as mixtures of rapidly interconverting Re,N-configurational diastereomers. For example, low-temperature NMR spectra have shown the phenylphosphido complex (η^5-C_5H_5)Re(NO)(PPh$_3$)(PHC$_6$H$_5$) to be a (50 ± 2):(50 ± 2) mixture of diastereomers [$\Delta G^{\ddagger}$(243 K) = 11.5 kcal/mol][10b]. Thus, a ^{1}H-NMR spectrum of phenylamido complex **1d** was recorded in [D$_8$]THF at -115°C. Only one set of amido proton and cyclopentadienyl resonances was observed. No evidence was noted for any decoalescence phenomena. However, the nitrogen inversion barrier in aniline is only 1.5 kcal/mol[5c].

The amido carbon (NC) ^{13}C-NMR resonances of **1d,f** show three-bond C,P couplings ($^3J_{CP}$) at 25°C and -20°C, respectively (Table 1). These data can be used to calculate lower limits of 12 kcal/mol and 10 kcal/mol, respectively, for $\Delta G^{\ddagger}$ for amido or PPh$_3$ ligand dissociation from **1d** and **1f**. Also, experiments described elsewhere establish much higher barriers for both PPh$_3$ dissociation and inversion of configuration at the rhenium atom ($\Delta H^{\ddagger}$ = 26−28 kcal/mol for a primary amido complex)[18]. Thus, the mechanisms for methyl group exchange in **1f**, and diastereomer interconversion in **1d**, involve neither ligand dissociation nor inversion of configuration at the rhenium atom.

4. Reactions of 1 and Electrophiles

The phosphido complexes (η^5-C_5H_5)Re(NO)(PPh$_3$)(PRR′) were found to be very reactive towards electrophiles[10]. Thus, **1a,f** and triflic acid (HOTf, 1.0 equiv.) were allowed to react in THF at room temperature (Scheme 2). The corresponding amine complexes **2a,f** were formed quantitatively, as assayed by ^{31}P-NMR spectroscopy. Next, **1a,f** and the ammonium salt (CH$_3$CH$_2$)$_3$NH$^+$ TfO$^-$ (1.0 equiv.) were combined at -80°C. Within 5 min, **2a,f** had been formed quantitatively, as determined by ^{31}P NMR (**2**/**1** = >98:<2). Hence, the amido ligand nitrogen atoms in **1** are at least two pK units more basic than those of organic tertiary amines.

Scheme 2. Reactions of amido complexes **1a,f** with electrophiles



Reactions of **1** and alkylating agents were investigated. First, **1f** and methyl triflate (CH$_3$OTf, 1.0 equiv.) were allowed to react in dichloromethane at -80°C. Workup gave the previously reported trimethylamine complex [(η^5-C_5H_5)Re(NO)(PPh$_3$){N(CH$_3$)$_3$}]$^+$ TfO$^-$ (**2i**)[15] in 56% yield. NMR experiments showed that no methyl transfer occurred when **1f** and tetramethylammonium triflate [(CH$_3$)$_4$N$^+$ TfO$^-$, 1−10 equiv.] were combined in THF, even after 1 h at 20°C. Also, **1a** and (CH$_3$)$_3$SiCH$_2$OTf (1.2 equiv.) were allowed to react in dichloromethane at -80°C. The sample was transferred to a -60°C-NMR probe, and a ^{31}P-NMR spectrum showed the formation of the previously characterized amine complex [(η^5-C_5H_5)Re(NO)(PPh$_3$){NH$_2$CH$_2$Si(CH$_3$)$_3$}]$^+$ TfO$^-$ (**2c**)[15] to be complete (<5 min). Workup of a preparative reaction gave **2c** in 62% yield.

Finally, a -80°C-[D$_8$]THF solution containing a (27 ± 2):(73 ± 2) mixture of **1f** and trimethylamine was prepared. Then CH$_3$OTf was added to give a ca. 27:73:12 reactant ratio. A ^{1}H-NMR spectrum of an aliquot was recorded at -50°C. The CH_3OTf had been consumed, but only **1f** had undergone methylation. The **1f**/**2f** ratio was $(57 \pm 2):(43 \pm 2)$, as assayed by integration of the cyclopentadienyl resonances. No $(CH_3)_4N^+ \; TfO^-$ – which is furthermore inert to **1f** as established above – was detected. Thus, the amido ligand nitrogen atoms in **1** are much more nucleophilic than those in organic tertiary amines.

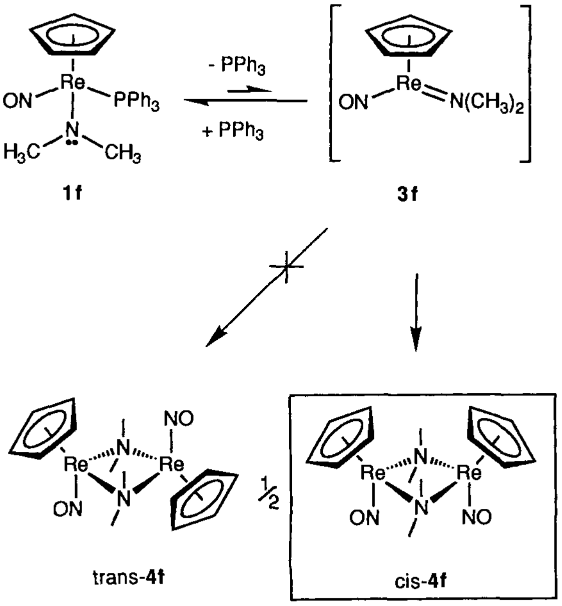
5. Decomposition of 1f

A crystallization procedure analogous to that used for **1d** was attempted with **1f**. Purple needles were obtained. Surprisingly, ^{1}H- and ^{13}C-NMR spectra showed the absence of aryl protons and carbon atoms. Further, no ^{31}P-NMR resonances were observed. Thus, the material isolated did not contain a PPh_3 ligand, nor any fragment thereof. However, cyclopentadienyl and two methyl ^{1}H- and ^{13}C-NMR resonances were evident.

It has been shown that amido complexes **1** can undergo reversible PPh_3 ligand dissociation[18]. Good evidence has been acquired for anchimeric assistance of the amido ligand lone pair. In the case of **1f**, this would give the reactive intermediate $(\eta^5\text{-}C_5H_5)Re(NO)[=N(CH_3)_2]$ (**3f**), as shown in Scheme 3. Subsequent dimerization, or reaction of **1f** and **3f**, could lead to the bridging bis(amido) complex $[(\eta^5\text{-}C_5H_5)Re(NO)\{\mu\text{-}N(CH_3)_2\}]_2$ (**4f**). Thus, a mass spectrum of the product was obtained. The molecular ion (m/z = 652; ^{187}Re), as well as the microanalysis (Experimental), agreed with that expected for **4f**. The yield calculated from this molecular weight was 35%, and IR and NMR data are summarized in Table 1.

In principle, *cis* and *trans* isomers of **4f** are possible (Scheme 3). However, the observation of two methyl ^{1}H- and ^{13}C-NMR resonances eliminated the more symmetrical *trans*-**4f**, in which all of the methyl groups can be exchanged by an inversion center or mirror plane[19]. Thus, the crystalline product was assigned as *cis*-**4f**, in which the pairs of methyl groups *syn* and *anti* to the cyclopentadienyl ligand are diastereotopic and should give distinct resonances.

Scheme 3. Decomposition of dimethylamido complex **1f**



We sought to assay whether the exclusive isolation of *cis*-**4f** was due to a stereoselective process, or an artifact of workup. Thus, a sample of **1f** was generated in $[D_8]$THF in an NMR tube and warmed to room temperature. A ^{31}P-NMR spectrum showed only **1f** (δ = 19.7) and free PPh_3 ($\delta = -4.6$). A ^{1}H-NMR spectrum revealed only cyclopentadienyl and methyl resonances corresponding to **1f** and *cis*-**4f** (2:1). The sample was kept for 10 minutes at 80°C. The cyclopentadienyl ^{1}H-NMR region showed signals due to *cis*-**4f** (ca. 67%), **1f**, and three minor peaks. Thus, the formation of *cis*-**4f** is highly stereoselective.

Discussion

1. Synthesis of Amido Complexes

Scheme 1 establishes that amido complexes **1** are easily accessible in quantitative spectroscopic yields by deprotonation of the corresponding amine complexes **2**. The generation of analogous optically active amido complexes has been described elsewhere[14a,18]. Hence, **1** can be viewed as a new generation of chiral bases that are readily available in optically pure form. Accordingly, synthetic applications are currently under investigation.

Roundhill has recently prepared several "isoelectronic" ruthenium amido complexes of the formula $(\eta^5\text{-}C_5H_5)Ru(PR_3)_2(NHR)$ by similar deprotonation procedures[20]. Also, nucleophilic additions to cationic imine complexes of the type $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^1\text{-}RN{=}CR'R'')]^+ \; X^-$ provide another route to **1**[21]. This type of reaction is often highly diastereoselective[21,22], and thus has potential for asymmetric organic synthesis. Hence, increasing interest in this class of compounds can be anticipated.

2. Structure of 1d

Apparently, **1d** is the first metal complex of a pyramidal organic amido ligand to be structurally characterized. The sum of the bond angles about the nitrogen atom (345.5°) is essentially identical to that found in aniline [345.4°; H–N–H 113.6(2)°, H–N–C 115.9(2)°][23]. The nitrogen–phenyl bond [1.371(9) Å] is only slightly shorter than that in aniline [1.402(2) Å]. Thus, the rhenium fragment **I** does not markedly perturb the structure of the $-NHC_6H_5$ moiety.

However, the converse is not true. As noted above, the N2–Re–NO and N2–Re–P bond angles in **1d** deviate substantially from 90° [103.5(3), 86.2(2)°]. Analogous but even more pronounced distortions are observed in the alkoxide complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)\{OCH(CH_3)C_6H_5\}$, which exhibits O–Re–NO and O–Re–P bond angles of 105.5(2) and 80.0(1)°[24]. However, structures of numerous other (η^5-C_5H_5)Re(NO)(PPh_3)(X) compounds show X−Re−NO and X−Re−P bond angles much closer to 90° (X = R, COR, Ar, PR_2, I, GeR_2X, etc.)[10,25,26]. Thus, this phenomenon appears to be limited to ligands that are regarded as strong π donors[9a,27]. Recently, similar distortions have been noted in the related cationic ruthenium chloride complex [(η^5-C_5H_5)Ru(NO)(PPh_3)(Cl)]$^+$ PF_6^- [Cl−Ru−NO 102.0(2)°, Cl−Ru−P 86.4(1)°][28].

Anionic Lewis bases should have a greater electrostatic affinity for the cationic Lewis acid **1** than neutral Lewis bases. Accordingly, the rhenium−nitrogen bond in **1d** [2.076(6) Å] is shorter than those in the cationic isoquinoline complex [(η^5-C_5H_5)Re(NO)(PPh_3)(NC_9H_7)]$^+$ TfO^- [2.147(3) Å][29] and dimethylamine complex [(η^5-C_5H_5)Re(NO)(PPh_3){$NH(CH_3)_2$}]$^+$ TfO^- [2.193(4) Å][15]. However, opposite trends have been found for corresponding $-PR_2$/PR_3 and −I/IR adducts of **I**[10a,25c]. These have been attributed to repulsive interactions between ligand lone pairs and occupied rhenium d orbitals. Thus, there appears to be either a diminution of such repulsive interactions in **1**, or compensating attractive interactions − possibly linked to the structural distortions noted above. A theoretical study of these possibilities is in progress.

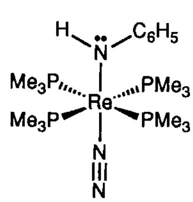
3. Structures of Other Amido Complexes

Several previously reported crystal structures are particularly relevant to that of **1d**. First, Hursthouse and Wilkinson have determined the structure of the rhenium phenylamido complex *trans*-Re(PMe_3)$_4$(N_2)(NHC_6H_5) (**5**; Figure 3)[6]. Both **1d** and **5** are formally octahedral, contain rhenium in the +1 oxidation state, and achieve coordinative saturation without π donation from the nitrogen atom. Unfortunately, the amido hydrogen atom in **5** could not be located. A calculated position gave some indication of a slightly pyramidalized nitrogen (sum of amido bond angles: 353°). The rhenium−nitrogen bond in **5** [2.20(1) Å] is longer than that in **1d**, and HN−Re−P bond angles range from 83.4(5) to 86.8(5)°[30].

Fryzuk has solved the structures of the chelating iridium *disilyl* amido complexes **6**, **7** shown in Figure 3[7]. In each case, the metal is coordinatively saturated in the absence of π donation. Nonetheless, planar amido ligands are observed (sum of amido bond angles: 359−360°). However, all silyl-substituted amines apparently exhibit planar geometries[1,31]. Also, the chelate rings in **6**, **7** may further constrain pyramidalization. Thus, acyclic, alkyl-substituted analogs of **6**, **7** may resemble **1d**.

The structures of several d^8 platinum(II) amido complexes of the formula *cis*-(L)$_2$Pt(X)(NRR′) have been reported (**8**−**10**; Figure 3)[8]. Although these compounds are coordinatively *un*saturated without π donation from the nitrogen atom, they lack low-lying metal acceptor orbitals of appropriate symmetry. Nonetheless, each exhibits a planar amido ligand (sums of amido bond angles: **9**: 357°; **10**: 356°). Further, Xα calculations on **10** indicate a platinum−nitrogen π-bond order of zero[8a].

Recently, Feldman and Calabrese have determined the structures of the d^1 titanium(III) amido complexes (η^5-C_5Me_5)$_2$Ti{$N(CH_3)C_6H_5$} (**11a**) and (η^5-C_5Me_5)$_2$Ti{$N(CH_3)C_6H_5$}(CN-*n*-C_4H_9) (**11b**)[9b]. In the absence of π bonding, the valence electron counts on titanium are 15 and 17, respectively. In **11a**, steric effects prevent overlap of the amido ligand lone pair and low-lying metal acceptor orbitals. In **11b**, no acceptor orbitals of correct symmetry are available. Nonetheless, as with **8**−**10**, the amido nitrogen is planar in both compounds (sums of amido bond angles: 359°).



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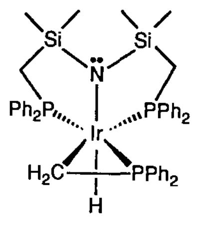

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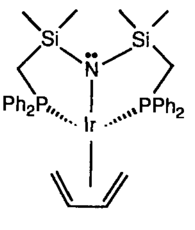

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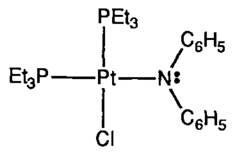

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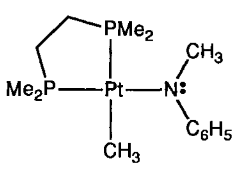

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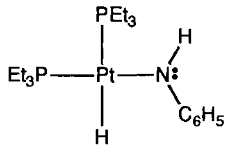

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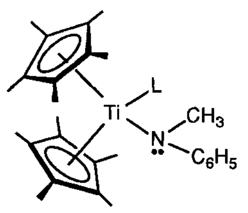

11

L= a, vacant
b, CN-*n*-C_4H_9

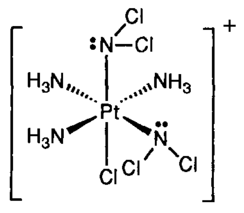

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Figure 3. Some relevant structurally characterized transition-metal amido complexes

Finally, the structure of the platinum bis(dichloroamido) complex *mer,cis*-[Pt(NH_3)$_3$(NCl_2)$_2$Cl]$^+$ Cl^- (**12**) has also been reported[32]. This compound initially escaped our attention, as the Cambridge Structural Database is restricted to carbon−containing molecules. The platinum is coordinatively saturated without π bonding, and both dichloroamido ligands are strongly pyramidalized (sums of amido bond angles: ca. 324°). Haloamines commonly exhibit much higher nitrogen inversion barriers than alkylamines[5a,b], thus indicating a stronger energetic preference for pyramidal geometries.

4. Conformational and Configurational Properties of Amido Ligands

The Re–NHC_6H_5 bond conformation in **1d** (Figure 1) is similar to the Re–PR_2 and Re–SR_2 bond conformations found in analogous phosphido and cationic sulfide complexes[10a,33]. In each case, the lone pair (LP) occupies the compressed interstice between the nitrosyl and bulky PPh_3 ligand. The Ph_3P–Re–X–LP torsion angles fall in the narrow range of 56.2 to 59.7°, as summarized in Figure 4. The stereoelectronic basis for this conformational preference has been analyzed at length elsewhere[10a,33].

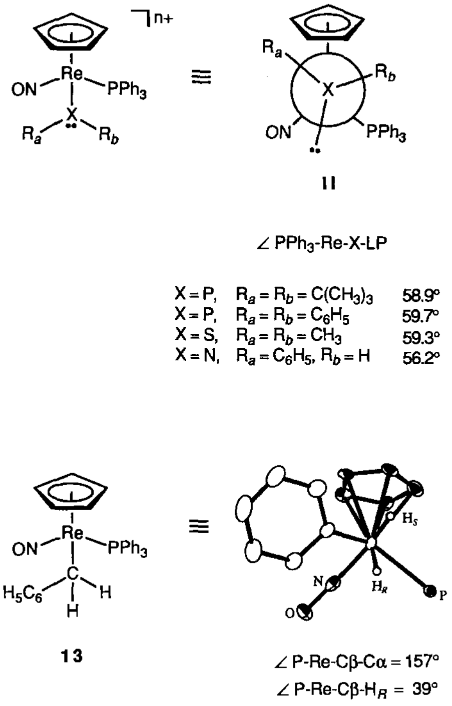
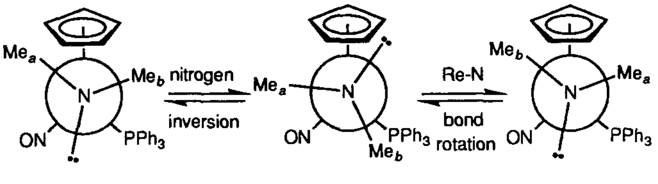


Figure 4. Conformations of phosphido, sulfide, and alkyl complexes of the rhenium fragment $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^+$ (**I**)

The phenylamino complex **1d** is isoelectronic with the benzyl complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2C_6H_5)$ (**13**), the crystal structure of which has also been determined (Figure 4)[25a]. In both compounds, the phenyl group occupies the interstice between the small nitrosyl and medium-sized cyclopentadienyl ligands. The Ph_3P–Re–X–C_6H_5 torsion angles are identical (157°). In contrast, the benzene ring conformations are orthogonal. Hence, electronic effects must largely determine the orientations of the aryl groups. The phenyl plane in **13** maximizes overlap with the Re–CH_2 bond, whereas that in **1d** allows a high degree of overlap with the nitrogen lone pair.

The data given above establish that the amido methyl substituents in **1f** exchange by a nondissociative pathway that does not involve inversion of configuration at the rhenium atom. This can be accomplished by a combination of nitrogen inversion and rhenium–nitrogen bond rotation, as illustrated in Scheme 4. In theory, either step could be rate-determining.

Scheme 4. Mechanism for exchange of the diastereotopic methyl groups in dimethylamido complex **1f**



Trimethylamine exhibits a nitrogen inversion barrier of 7.5 kcal/mol[5a] – close to the $\Delta G^{\neq}$ value of 7.8 kcal/mol for methyl group exchange in **1f**. However, phosphorus and sulfur inversion barriers have been shown to be dramatically lowered when an alkyl substituent is replaced by the rhenium fragment **I**[11,33]. This suggests that the barrier to nitrogen inversion in **1f** is much less than 7.5 kcal/mol, and thus rhenium–nitrogen bond rotation is most likely rate-limiting for methyl group exchange.

5. Reactivity of Amido Complexes

Scheme 2 and supporting experiments establish that relative to an alkyl substituent, the rhenium fragment **I** significantly enhances amido nitrogen basicity and nucleophilicity. Similar trends are evident in analogous phosphido complexes[10]. We have proposed that these properties arise from destabilizing interactions between filled metal d orbitals and the ligand lone pairs. Recently, Roundhill has also documented high basicities and nucleophilicities in the ruthenium amido complexes $(\eta^5\text{-}C_5H_5)Ru(PR_3)_2(NHR)$[20].

As noted above, amido complexes **1** also undergo reversible PPh_3 ligand dissociation, with anchimeric assistance of the amido ligand lone pair[18]. This can eventually lead to decomposition, as in the conversion of **1f** to the bridging bis(amido) complex *cis*-**4f**. Thus, the greater ease of isolation of **1d** may be due in part to the lower basicity of phenyl-substituted amido groups. Also, preliminary data show that **1f** and other secondary amido complexes dissociate PPh_3 at appreciably faster rates than the primary amido complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)\{NHCH(CH_3)C_6H_5\}$ (relative rates: $\geq 10^3$; 0°C)[18]. This likely explains the more ready formation of a bridging bis(amido) complex from **1f**. Many other terminal amido complexes undergo similar dimerizations with loss of a spectator ligand[34].

Our data do not establish whether the stereoselective formation of *cis*-**4f** is under kinetic or thermodynamic control. However, based upon literature precedent with related bimetallic complexes, *cis*-**4f** is likely to be the more stable isomer. For example, several cyclopentadienyl iron carbonyl complexes of the formula $(\eta^5\text{-}C_5H_5)(CO)Fe(\mu\text{-}CO)(\mu\text{-}L)Fe(CO)(\eta^5\text{-}C_5H_5)$ have been synthesized (L = CO, CH_2)[35].

Both *cis* and *trans* isomers can be observed, and interconvert in solution. Although the equilibrium constants are solvent- and temperature-dependent, the *cis* isomers predominate under all conditions. Analogous trends are generally found for similar diruthenium complexes[36].

6. Conclusion

Our data establish that transition-metal complexes containing pyramidal organoamido ligands may be more common than previously recognized. However, this ligand geometry will likely be restricted to cases where the metal is coordinatively saturated, and the nitrogen bears simple alkyl or aryl substituents. In all cases, extremely low nitrogen inversion barriers can be anticipated. At the same time, the nitrogen basicities and nucleophilicities should be enhanced relative to organic analogs. Additional physical and chemical properties of **1** will be described in future reports.

We thank the *NSF* for support of this research, and *J. Bakke* for helpful exploratory observations.

Experimental

General: Experimental procedures, and reagent and solvent purifications were identical to those given in a previous paper[15], with the following additons: [D$_8$]THF: vacuum-transferred from CaH_2; hexane (in crystallizations): distilled from Na/benzophenone and stored over 3-Å molecular sieves; *n*BuLi (Aldrich): standardized prior to use[37]; CH_3OTf and $(CH_3)_3SiCH_2OTf$ (Aldrich): used as received; $(CH_3CH_2)_3NH^+$ TfO^- [38]: isolated as a precipitate from the reaction of $(CH_3CH_2)_3N$ and TfOH in hexane; $(CH_3)_4N^+$ TfO^- [39]: isolated as a precipitate from the reaction of $(CH_3)_3N$ and CH_3OTf in $CHCl_3$. Variable-temperature NMR data were acquired as described earlier[10]. Mass spectra were obtained with a Finnigan MAT-95 instrument with a VG data system 2000.

Isolation of (*η^5-C_5H_5)Re(NO)(PPh$_3$)(NHC$_6$H$_5$)* (**1d**): A Schlenk flask was charged with **2d** (0.099 g, 0.13 mmol)[15], THF (3 ml), and a stir bar and cooled to −80°C. Then *n*BuLi (0.074 ml, 0.13 mmol, 1.73 M in cyclohexane) was added with stirring. The cold bath was removed, and the solution was concentrated to ca. 1.5 ml under oil-pump vacuum and frozen in liquid N_2. Hexane (ca. 8 ml) was then added by vacuum transfer. The frozen mass was carefully thawed, giving a colorless hexane layer above a red THF solution. Over the course of three days, the two layers mixed and orange plates were formed. These were collected in a glove box and dried under oil-pump vacuum to give **1d** (0.050 g, 63%), dec.p. 194−195°C.

$C_{29}H_{26}N_2OPRe$ (635.7) Calcd. C 54.79 H 4.12
Found C 54.50 H 4.32

Generation of (*η^5-C_5H_5)Re(NO)(PPh$_3$)(NR'R")* (**1**): The following procedure is representative. Complex **2a** (0.0393 g, 0.0544 mmol)[15], THF (4 ml), and *n*BuLi (0.031 ml, 0.054 mmol, 1.73 M in cyclohexane) were combined in a procedure analogous to that given for **1d**. After 15 min, the cold bath was removed and an oil-pump vacuum applied. The residue was dried under vacuum for 1 h, cooled to −80°C, and extracted with [D$_8$]THF. The extract was transferred by cannula to a 5-mm NMR tube. The spectroscopically pure product **1a** was characterized by NMR at −20°C. Data: Table 1.

Alkylation of (*η^5-C_5H_5)Re(NO)(PPh$_3$)(NH$_2$)* (**1a**): Complex **2a** (0.176 g, 0.249 mmol), THF (10 ml), and *n*BuLi (0.149 ml, 0.294 mmol, 1.73 M in cyclohexane) were combined in a procedure analogous to that given for the generation of **1**. After 10 min, $(CH_3)_3SiCH_2OTf$ (0.056 ml, 0.298 mmol) was added. The cold bath was removed, and the solution was allowed to warm to room temperature. After 1.5 h, hexane (50 ml) was slowly added with stirring. An orange powder precipitated, which was collected by filtration and extracted with CH_2Cl_2 (20 ml). The extract was filtered and the resulting orange solution layered with hexane (100 ml). After 48 h, clusters of orange prisms formed. These were collected by filtration, washed with hexane, and dried under oil-pump vacuum to give **2c** (0.077 g, 62%), m.p. 185−187°C (ref.[15] 186−189°C).

$C_{28}H_{33}F_3N_2O_4PReSSi$ (795.9) Calcd. C 42.25 H 4.18
Found C 42.33 H 4.18

Table 2. Summary of crystallographic data for complex **1d**

Molecular formula: $C_{29}H_{26}N_2OPRe$; molecular mass: 635.717; crystal system: orthorhombic; space group: *Pbca* (♯61); cell dimensions (16°C): $a = 16.303(1)$, $b = 18.272(1)$, $c = 16.547(1)$ Å; $V = 4929.16$ Å^3; $Z = 8$; $d_{calcd.}$ (16°C) = 1.71 g/cm^3; d_{found} (22°C) = 1.70 g/cm^3; crystal dimensions: 0.30 × 0.28 × 0.09 mm; diffractometer: Syntex $P\bar{1}$; radiation: Mo K_α ($\lambda = 0.71073$ Å); data collection method: $\Theta-2\Theta$; scan speed: 2.0 °/min; reflections measured: 4946; *h*, *k*, *l* range: 0/19; 0/21, 0/19; scan range: $K_{\alpha1}$ −1.3 to $K_{\alpha2}$ +1.6; 2Θ limit: 2.0−50.0°; no. of reflections between standards: 98; observed data [$I > 3\sigma(I)$]: 2855; $\mu = 50.85$ cm^{-1}; min./max. absorption correction: 57.80/99.90; no of variables: 308; goodness of fit: 1.08; $R = \Sigma \| F_o | - | F_c \| / \Sigma | F_o | = 0.0354$; $R_w = \Sigma w(\| F_o | - | F_c \|) w^{1/2} / \Sigma w | F_o | w^{1/2} = 0.0459$; $\Delta/\sigma(\max) = 0.001$; $\Delta(\max) = 1.330$ e/Å^3 (0.928 Å from Re)

Table 3. Atomic coordinates and equivalent isotropic thermal parameters for **1d**[a]

Atom	x	y	z	B(Å²)
Re	0.01936(2)	0.17300(1)	0.07699(1)	2.607(5)
P	-0.0281(1)	0.1504(1)	0.2090(1)	2.46(3)
O	0.0939(4)	0.3157(3)	0.1177(3)	4.5(1)
N1	0.0665(3)	0.2544(3)	0.1040(3)	2.8(1)
N2	0.1084(4)	0.0947(3)	0.1007(4)	4.0(1)
C1	0.0029(6)	0.1830(5)	-0.0619(4)	4.2(2)
C2	-0.0580(5)	0.2231(4)	-0.0224(4)	4.0(2)
C3	-0.1076(5)	0.1738(4)	0.0245(5)	4.2(2)
C4	-0.0757(6)	0.1012(4)	0.0097(4)	4.5(2)
C5	-0.0087(6)	0.1078(5)	-0.0418(5)	4.6(2)
C6	-0.1028(4)	0.2157(3)	0.2486(4)	2.5(1)
C7	-0.0992(4)	0.2883(4)	0.2229(4)	3.4(2)
C8	-0.1497(5)	0.3407(4)	0.2569(5)	4.1(2)
C9	-0.2038(5)	0.3219(4)	0.3169(4)	3.9(2)
C10	-0.2090(5)	0.2507(4)	0.3427(4)	3.6(2)
C11	-0.1576(4)	0.1972(4)	0.3096(4)	2.9(1)
C12	0.0460(4)	0.1493(4)	0.2917(4)	2.7(1)
C13	0.0274(4)	0.1202(4)	0.3669(4)	3.4(2)
C14	0.0812(5)	0.1263(4)	0.4316(4)	3.8(2)
C15	0.1549(5)	0.1628(5)	0.4203(4)	4.5(2)
C16	0.1754(4)	0.1937(5)	0.3463(5)	4.0(2)
C17	0.1210(4)	0.1866(4)	0.2815(4)	3.2(2)
C18	-0.0780(4)	0.0618(4)	0.2169(4)	2.7(1)
C19	-0.0344(5)	-0.0008(4)	0.2375(4)	3.6(2)
C20	-0.0715(6)	-0.0689(4)	0.2324(5)	4.3(2)
C21	-0.1500(6)	-0.0754(4)	0.2061(5)	5.1(2)
C22	-0.1948(6)	-0.0143(5)	0.1851(5)	4.8(2)
C23	-0.1590(5)	0.0540(4)	0.1908(5)	3.9(2)
C24	0.1837(4)	0.0854(4)	0.0651(4)	3.3(2)
C25	0.2137(5)	0.1306(4)	0.0039(4)	3.7(2)
C26	0.2911(5)	0.1194(5)	-0.0284(5)	5.1(2)
C27	0.3403(5)	0.0627(5)	-0.0018(5)	5.9(2)
C28	0.3111(6)	0.0168(5)	0.0582(5)	5.4(2)
C29	0.2356(5)	0.0282(5)	0.0913(5)	4.6(2)
H21*	0.084	0.049	0.104	5.0

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$; the starred atom was located but its position was not refined.

Alkylation of $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)\{N(CH_3)_2\}$ (**1f**): Complex **2f** (0.142 g, 0.192 mmol)[15], CH_2Cl_2 (20 ml), and *n*BuLi (0.111 ml, 0.192 mmol, 1.73 M in cyclohexane) were combined in a procedure analogous to that given for the generation of **1**. After 10 min, CH_3OTf (0.065 ml, 0.576 mmol) was added. The cold bath was removed and the mixture allowed to warm to room temperature. Some product precipitated. After 0.5 h, hexane (50 ml) was added to complete precipitation. The resulting powder was collected by filtration and extracted with CH_2Cl_2 (250 ml). The extract was filtered and concentrated by rotary evaporation. The resulting orange powder was collected by filtration, washed with hexane, and dried under oil-pump vacuum to give **2i** (0.081 g, 56%), m.p. 187–189 °C (ref.[15] 187–189 °C).

$C_{27}H_{29}F_3N_2O_4PReS$ (751.8) Calcd. C 43.14 H 3.89
Found C 42.88 H 3.79

Isolation of cis-$[(\eta^5\text{-}C_5H_5)Re(NO)\{\mu\text{-}N(CH_3)_2\}]_2$ (*cis*-**4f**): Complex **2f** (0.123 g, 0.167 mmol), THF (8 ml), and *n*BuLi (0.0984 ml, 0.167 mmol, 1.73 M in cyclohexane) were combined in a procedure analogous to that given for **1d**. An identical workup was attempted. Crystallization (layered hexane/THF) gave, over the course of 3 d, a mixture of purple rectangular cubes and needles – a close examination showed the absence of single crystals – which were collected by filtration and dried under oil-pump vacuum to give *cis*-**4f** (0.019 g, 35%), m.p. >250 °C. – MS (17 eV, ^{187}Re): *m/z* (%) = 652 (4) [M^+], 326 (31) [$M^+/2$].

$C_{14}H_{22}N_4O_2Re_2$ (650.8) Calcd. C 25.84 H 3.41 N 8.61
Found C 26.06 H 3.44 N 8.52

Crystal Structure of **1d**: The structure of **1d** was solved in a manner identical to that of amine complex **2f**[15]. Full details are given elsewhere[40]. Hydrogen atom positions were calculated, except for H21 which was located. All hydrogen atom locations were added to the structure-factor calculations, but their positions were not refined.

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[1] [1a] M. F. Lappert, P. P. Power, A. R. Sanger, R. C. Srivastava, *Metal and Metalloid Amides,* Wiley, New York, **1979**. – [1b] M. H. Chisholm, I. P. Rothwell in *Comprehensive Coordination Chemistry* (Eds.: G. Wilkinson, R. D. Gillard, J. A. McCleverty), Pergamon, New York, **1987**, vol. II, chapter 13.4.

[2] [2a] D. C. Bradley, M. H. Chisholm, *Acc. Chem. Res.* **1976**, *9*, 273. – [2b] H. E. Bryndza, W. Tam, *Chem. Rev.* **1988**, *88*, 1163. – [2c] M. D. Fryzuk, C. D. Montgomery, *Coord. Chem. Rev.* **1989**, *95*, 1.

[3] Selected examples: [3a] R. L. Cowan, W. C. Trogler, *Organometallics* **1987**, *6*, 2451. – [3b] W. A. Nugent, D. W. Ovenall, S. J. Holmes, *Organometallics* **1983**, *2*, 161. – [3c] R. R. Schrock, T. E. Glassman, M. G. Vale, *J. Am. Chem. Soc.* **1991**, *113*, 725.

[4] R. Koelliker, D. Milstein, *Angew. Chem.* **1991**, *103*, 724; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 707; *J. Am. Chem. Soc.* **1991**, *113*, 8524.

[5] [5a] A. Rauk, L. C. Allen, K. Mislow, *Angew. Chem.* **1970**, *82*, 453; *Angew. Chem. Int. Ed. Engl.* **1970**, *9*, 400. – [5b] C. L. Perrin, J. D. Thoburn, S. Elsheimer, *J. Org. Chem.* **1991**, *56*, 7034. – [5c] R. Cervellati, A. D. Esposti, D. G. Lister, P. Palmieri, *J. Mol. Struct. (Theochem)* **1985**, *122*, 173.

[6] K. W. Chiu, W.-K. Wong, G. Wilkinson, A. M. R. Galas, M. B. Hursthouse, *Polyhedron* **1982**, *1*, 37.

[7] [7a] M. D. Fryzuk, K. Joshi, S. J. Rettig, *Polyhedron* **1989**, *8*, 2291. – [7b] M. D. Fryzuk, K. Joshi, R. K. Chadra, S. J. Rettig, *J. Am. Chem. Soc.* **1991**, *113*, 8724.

[8] [8a] R. L. Cowan, W. C. Trogler, *J. Am. Chem. Soc.* **1989**, *111*, 4750. – [8b] H. E. Bryndza, W. C. Fultz, W. Tam, *Organometallics* **1985**, *4*, 939; see Cambridge Structural Database Refcod DAMBAU. – [8c] D. T. Eadie, A. Pidcock, S. R. Stobart, E. T. Brennan, T. S. Cameron, *Inorg. Chim. Acta.* **1982**, *65*, L111.

[9] [9a] G. L. Hillhouse, A. R. Bulls, B. D. Santarsiero, J. E. Bercaw, *Organometallics* **1988**, *7*, 1309. – [9b] J. Feldman, J. C. Calabrese, *J. Chem. Soc., Chem. Commun.* **1991**, 1042.

[10] [10a] W. E. Buhro, B. D. Zwick, S. Georgiou, J. P. Hutchinson, J. A. Gladysz, *J. Am. Chem. Soc.* **1988**, *110*, 2427. – [10b] W. E. Buhro, J. A. Gladysz, *Inorg. Chem.* **1985**, *24*, 3505 and B. D. Zwick, M. A. Dewey, D. A. Knight, W. E. Buhro, A. M. Arif, J. A. Gladysz, *Organometallics,* submitted for publication.

[11] I. Saura-Llamas, J. A. Gladysz, *J. Am. Chem. Soc.* **1992**, *114*, in press, and references therein.

[12] S. K. Agbossou, C. Roger, A. Igau, J. A. Gladysz, *Inorg. Chem.* **1992**, *31*, 419, and references therein.

[13] [13a] B. E. R. Schilling, R. Hoffmann, J. W. Faller, *J. Am. Chem. Soc.* **1979**, *101*, 592. – [13b] S. Georgiou, J. A. Gladysz, *Tetrahedron* **1986**, *42*, 1109. – [13c] P. T. Czech, J. A. Gladysz, R. F. Fenske, *Organometallics* **1989**, *8*, 1806. – [13d] D. L. Lichtenberger, A. R. Rai-Chaudhuri, M. J. Seidel, J. A. Gladysz, S. K. Agbossou, A. Igau, C. H. Winter, *Organometallics* **1991**, *10*, 1355.

[14] [14a] M. A. Dewey, J. M. Bakke, J. A. Gladysz, *Organometallics* **1990**, *9*, 1349. – [14b] M. A. Dewey, A. M. Arif, J. A. Gladysz, *J. Chem. Soc., Chem. Commun.* **1991**, 712.

[15] M. A. Dewey, D. A. Knight, D. P. Klein, A. M. Arif, J. A. Gladysz, *Inorg. Chem.* **1991**, *30*, 4995.

[16] For example, the powders were extracted with dry toluene at −20 °C. In all cases, some Li^+ TfO^- also solubilized. Further manipulations often resulted in reprotonation to amine complexes, and attempted chromatographic separations failed.

[17] J. Sandström, *Dynamic NMR Spectrometry,* Academic Press, New York, **1982**.

[18] M. A. Dewey, J. A. Gladysz, *Organometallics* **1990**, *9*, 1351.

[19] R. M. Silverstein, G. C. Bassler, T. C. Morrill, *Spectrometric Identification of Organic Compounds,* 4th ed., Wiley, New York, **1981**, p. 200–205.

[20] F. L. Joslin, M. P. Johnson, J. T. Mague, D. M. Roundhill, *Organometallics* **1990**, *10*, 11; *ibid.* **1990**, *10*, 2781.

[21] D. A. Knight, M. A. Dewey, A. M. Arif, J. A. Gladysz, manuscript in preparation.

[22] G. C. Martin, J. M. Boncella, E. J. Wucherer, *Organometallics* **1991**, *10*, 2804.

[23] [23a] D. G. Lister, J. K. Tyler, J. H. Høg, N. W. Larsen, *J. Mol. Struct.* **1974**, *23*, 253. – [23b] J. Kao, *J. Comput. Chem.* **1988**, *9*, 905.

[24] D. M. Dalton, J. M. Fernández, K. Emerson, R. D. Larsen, A. M. Arif, J. A. Gladysz, *J. Am. Chem. Soc.* **1990**, *112*, 9198.

[25] Some lead references: [25a] J. H. Merrifield, C. E. Strouse, J. A. Gladysz, *Organometallics* **1982**, *1*, 1204. – [25b] G. S. Bodner, A. T. Patton, D. E. Smith, S. Georgiou, W. Tam, W.-K. Wong, C. E. Strouse, J. A. Gladysz, *Organometallics* **1987**, *6*, 1954. – [25c] C. H. Winter, W. R. Veal, C. M. Garner, A. M. Arif, J. A. Gladysz, *J. Am. Chem. Soc.* **1989**, *111*, 4766. – [25d] S. K. Agbossou, G. S. Bodner, A. T. Patton, J. A. Gladysz, *Organometallics* **1990**, *9*, 1184. – [25e] K. E. Lee, A. M. Arif, J. A. Gladysz, *Organometallics* **1991**, *10*, 751.

[26] For a summary of similar distortions in cationic σ-ketone, -aldehyde, and -ester complexes, see: I. Saura-Llamas, D. M. Dalton, A. M. Arif, J. A. Gladysz, *Organometallics* **1992**, *11*, 683.

[27] [27a] M. J. Chetcuti, M. H. Chisholm, K. Folting, D. A. Haitko, J. C. Huffman, J. Janos, *J. Am. Chem. Soc.* **1983**, *105*, 1163. – [27b] H. E. Brynzda, P. J. Domaille, R. A. Paciello, J. E. Bercaw, *Organometallics* **1989**, *8*, 379. – [27c] D. M. Lunder, E. B. Lobkovsky, W. E. Streib, K. G. Caulton, *J. Am. Chem. Soc.* **1991**, *113*, 1837.

[28] F. M. Conroy-Lewis, A. D. Redhouse, S. J. Simpson, *J. Organomet. Chem.* **1990**, *399*, 307.

[29] M. A. Dewey, A. M. Arif, J. A. Gladysz, *J. Organomet. Chem.* **1990**, *384*, C29; M. A. Dewey, D. A. Knight, A. M. Arif, J. A. Gladysz, *Z. Naturforsch. B: Anorg. Chem., Org. Chem.*, in press.

[30] Additional crystal structures of amido complexes that would be coordinatively saturated in the absence of π bonding are given in ref.[6] (Re) and [22] (Ru). However, these are severely disordered, and the amido ligand geometry could not be ascertained.

[31] [31a] T. Fjeldberg, *J. Mol. Struct.* **1984**, *112*, 159. – [31b] D. W. H. Rankin, A. G. Robiette, G. M. Sheldrick, W. S. Sheldrick, B. J. Aylett, I. A. Ellis, J. J. Monaghan, *J. Chem. Soc. A* **1969**, 1224.

[32] M. Zipprich, H. Pritzkow, J. Jander, *Angew. Chem.* **1976**, *88*, 225; *Angew. Chem. Int. Ed. Engl.* **1976**, *15*, 225.

[33] N. Quirós Méndez, A. M. Arif, J. A. Gladysz, *Organometallics* **1991**, *10*, 2199.

[34] S. Park, A. L. Rheingold, D. M. Roundhill, *Organometallics* **1991**, *10*, 615.

[35] [35a] A. R. Manning, *J. Chem. Soc. A* **1968**, 1319. – [35b] J. G. Bullitt, F. A. Cotton, T. J. Marks, *J. Am. Chem. Soc.* **1970**, *92*, 2155. – [35c] C. P. Casey, P. J. Fagan, W. H. Miles, *J. Am. Chem. Soc.* **1982**, *104*, 1134. – [35d] C. P. Casey, K. P. Gable, D. M. Roddick, *Organometallics* **1990**, *9*, 221.

[36] R. E. Colborn, D. L. Davies, A. F. Dyke, S. A. R. Knox, K. A. Mead, A. G. Orpen, J. E. Guerchais, J. Rouś, *J. Chem. Soc., Dalton Trans.* **1989**, 1799 and references therein.

[37] M. R. Winkle, J. M. Lansinger, R. C. Ronald, *J. Chem. Soc., Chem. Commun.* **1980**, 87.

[38] T. Gramstad, R. N. Haszeldine, *J. Chem. Soc.* **1957**, 4069.

[39] V. Beyl, H. Niederprum, P. Voss, *Justus Liebigs Ann. Chem.* **1970**, *731*, 58.

[40] M. A. Dewey, Ph. D. Thesis, University of Utah, **1991**.

[464/91]

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1a: 139236-38-7 / **1b**: 139101-70-5 / **1d**: 135320-29-5 / **1f**: 139236-39-8 / **1h**: 139101-71-6 / **2a**: 126136-35-4 / **2b**: 126136-37-6 / **2c**: 137623-75-7 / **2d**: 135320-28-4 / **2f**: 126136-39-8 / **2h**: 126136-41-2 / **2i**: 137541-58-3 / *cis*-**4f**: 139101-72-7 / $(CH_3)_3SiCH_2OTf$: 64035-64-9