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Unsymmetrical Tren-Based Ligands: Synthesis and Reactivity of Rhenium Complexes

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Reaction of bis(2-aminoethyl)(3-aminopropyl)amine with C_6F_6 and K_2CO_3 in DMSO yields unsymmetrical $\{(C_6F_5)HNCH_2CH_2\}_2NCH_2CH_2CH_2NH(C_6F_5)$ ($[N_3N]H_3$). The tetraamine acts as a tridentate ligand in complexes of the type $H[N_3N]Re(O)X$ (X = Cl **1**, Br **2**) prepared by reacting $Re(O)X_3(PPh_3)_2$ with $[N_3N]H_3$ and an excess of NEt_3 in THF. Addition of 1 equiv of $TaCH(CMe_2Ph)Br_3(THF)_2$ to **1** gives the dimeric compound $H[N_3N]ClReOReBrCl[N_3N]H$ (**3**) in quantitative yield that contains a Re(V)═O—Re(IV) core with uncoordinated aminopropyl groups in each ligand. Addition of 2 equiv of $TaCH(CMe_2Ph)Cl_3(THF)_2$ to **1** leads to the chloro complex $[N_3N]ReCl$ (**4**) with all three amido groups coordinated to the metal, whereas by addition of 2 equiv of $TaCH(CMe_2Ph)Br_3(THF)_2$ to **2** the dibromo species $H[N_3N]ReBr_2$ (**5**) with one uncoordinated amino group is isolated. Reduction of **4** under an atmosphere of dinitrogen with sodium amalgam gives the dinitrogen complex $[N_3N]Re(N_2)$ (**6**). Single-crystal X-ray structure determinations have been carried out on complexes **1**, **3**, **5**, and **6**.

Introduction

Sterically hindered triamidoamine ligands with a C_3 symmetrical tren-based backbone (tris(2-aminoethyl)amine, tren) have been shown to coordinate to a variety of transition metals stabilizing unusual complexes thereby allowing exceptional reactivities.[1−47] Prominent examples include the activation of dinitrogen,[18−24] alkylidyne formation by α,α-dehydrogenation of alkyl compounds or by C,C-bond cleavage of cyclic alkyls,[25−27] as well as the preparation of terminal phosphido and arsenido compounds.[28−30] One of the major reasons for the reactivity found is the symmetry and energy of the three frontier metal orbitals (one σ and two π), an ideal arrangement for the formation of metal ligand triple bonds. A second requirement for the stabilization of such

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compounds is the three sterically demanding groups attached to the amido substituents. While most research focused on ligands containing $SiMe_3$ groups, chemists have been ingenious in synthesizing tren ligands with other substituents such as Me,[31,32] Et,[33] ^{i}Pr,[34−37] $SiMe_2tBu$,[18,22,38−42] C_6F_5,[19,20,43−45] and very recently also Ar (e.g., Ar = 3,5-$Me_2C_6H_3$ or 3,5-$Ph_2C_6H_3$).[23,24,46,47] In comparison, almost no research was directed toward the influence of the tren backbone. This is surprising, because the coordination chemistry of the unsubstituted, unsymmetrical tren homologues such as bis(2-aminoethyl)(3-aminopropyl)amine (baep) or (2-aminoethyl)-bis(3-aminopropyl)amine (abap) with late transition metals has been thoroughly investigated.[48,49] In these systems, the insertion of additional CH_2 groups has profound structural as well as chemical consequences. In addition, such ligands are thought to model the active site of metalloenzymes. By the controlled variation of the ligand geometry, the elucidation of principles governing biological reactions might be possible.

Here, we report the synthesis of a C_6F_5 substituted unsymmetrical triamidoamine ligand along with the preparation of two rhenium(V) oxo compounds **1** and **2**, of which **1** is crystallographically characterized. Furthermore, we have studied their stepwise reduction by preparing several Re(IV) and Re(III) species. The molecular structures of μ-oxo bridged, mixed-valent dirhenium compound **3**, mononuclear Re(IV) dibromide **5**, and Re(III) dinitrogen complex **6** are reported. The data are compared with previously prepared tren-based symmetrical rhenium complexes.[11,20]

Experimental Section

General Remarks. All manipulations were performed under a nitrogen atmosphere using standard Schlenk technique or a vacuum atmosphere drybox. The solvents were dried by standard methods. $Re(O)X_3(PPh_3)_2$ (X = Cl, Br)[50] and $TaCH(CMe_2Ph)X_3(THF)_2$ (X = Cl, Br)[51] were prepared by published methods. Diethylenetriamine, phthalic anhydride and *N*-(3-bromopropyl)phthalimide were purchased from commercial sources and used as received. NMR spectra were recorded with Bruker Avance 200 and Bruker Avance 500 spectrometers at ∼22 °C. Chemical shifts were referenced to the following standards: ^{1}H and ^{13}C NMR, $Si(CH_3)_4$ at 0 ppm; ^{19}F NMR, C_6F_6 at 0 ppm. IR samples were prepared as mineral oil mull, taken between KBr plates on a Bio-Rad FTS7 spectrometer. Mass spectra were recorded on a Finnigan MAT 8200 or MAT 95 spectrometer. Elemental analysis were performed on a Heraeus CHN-O-RAPID analyzer in our institute.

Synthesis of Bis(2-aminoethyl)(3-aminopropyl)amine (baep). To 47.4 g (0.32 mol) of hot phthalic anhydride (∼180 °C) was added 18.0 g (0.17 mol) of diethylenetriamine by syringe. Elimination of water was immediately apparent. The melt was stirred for 2 h, cooled to room temperature, ground to a powder, and recrystallized from hot DMSO yielding 50.0 g (87%) of the diphthalimide as slightly yellow microcrystals. They were mixed with 43.1 g (0.16 mol) of *N*-(3-bromopropyl)phthalimide and heated under stirring to ∼180 °C for 2 h resulting in a light brown melt. Cooling to room temperature afforded a brown glassy material, which was ground to a powder. This yellow material was suspended in 600 mL of 10 M HCl(aq), stirred under reflux overnight, and cooled to 0 °C, and the thus formed phthalic acid was removed by filtration. After addition of 40 g of NaOH, the filtrate was concentrated to a minimum to give an oily mixture of sodium phthalate, NaOH, $H_2NCH_2CH_2OH$, and the product. The volatile materials were separated from the solid residues by distillation, and subsequent fractional distillation at 95 °C and 0.01 bar gave the pure tetraamine baep as a colorless liquid (11.2 g, 44%). Analytical data are identical to previously reported values.[52]

Synthesis of $[N_3N]H_3$. To a solution of 2.78 g (17.3 mmol) of baep in 20 mL of DMSO were added 11.7 g (62.9 mmol) of C_6F_6 and 8.3 g (60.1 mmol) of K_2CO_3. The resulting white suspension was stirred at 70 °C for 24 h. After cooling to room temperature and hydrolysis with 150 mL of H_2O, the product was extracted with 3 × 50 mL of $CHCl_3$ and dried over $MgSO_4$. The solvent was removed under reduced pressure. The brown residue was extracted with 200 mL of Et_2O and filtered over basic alumina. Evaporation of the solvent gave 11.0 g (94.8%) of the ligand $[N_3N]H_3$ as a orange oil, which was used without further purification. ^{1}H NMR ($CDCl_3$): δ 4.05 (br s, 2 H, NH), 3.68 (br s, 1 H, NH), 3.37 (m, 6 H, $C_6F_5NHC\mathit{H}_2$), 2.71 (t, 4 H, J = 6 Hz, $C_6F_5NHCH_2C\mathit{H}_2N$), 2.61 (t, 2 H, J = 7 Hz, $C_6F_5NHCH_2CH_2C\mathit{H}_2N$), 1.73 (quint, 2 H, J = 7 Hz, $C_6F_5NHCH_2C\mathit{H}_2CH_2N$). ^{13}C NMR ($CDCl_3$): δ 138.10 (C_{ortho} and C_{meta}, $^1J_{CF}$ = 239 Hz), 133.56 (C_{para}, $^1J_{CF}$ = 243 Hz), 123.85 (C_{ipso}, $\mathit{C}NHCH_2CH_2N$), 123.72 (C_{ipso}, $\mathit{C}NHCH_2CH_2CH_2N$), 53.97 ($NHCH_2\mathit{C}H_2N$), 51.40 ($NHCH_2CH_2\mathit{C}H_2N$), 44.55 ($NH\mathit{C}H_2CH_2CH_2N$), 43.58 ($NH\mathit{C}H_2CH_2N$), 28.24 ($NHCH_2\mathit{C}H_2CH_2N$). ^{19}F NMR ($CDCl_3$): 1.67 (m, 6 F, F_{para}), −2.52 (m, 6 F, F_{meta}), −9.75 (m, 3 F, F_{ortho}).

Synthesis of H[N_3N]Re(O)Cl (1). To a suspension of 0.81 g (0.97 mmol) of $Re(O)Cl_3(PPh_3)_2$ in THF (50 mL) was added a solution of 0.64 g (0.97 mmol) of $[N_3N]H_3$ and 2 mL (excess) of NEt_3 in THF (20 mL) at room temperature. The dark mixture was stirred for 5 h, evaporated to 10 mL, cooled to −10 °C, and filtered through Celite. The solvent was removed under reduced pressure, and the solid was washed with Et_2O (3 × 20 mL) to remove PPh_3

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and a brown unidentified impurity resulting in a light green powder. Recrystallization from hot CH_3CN gave 0.65 g (75%) of H[N_3N]-Re(O)Cl as green crystals suitable for X-ray analysis. Mp 185 °C. ^{1}H NMR (THF-d_8): δ 5.41 (br s, 1 H, NH), 4.17 (m, 2 H), 3.77 (m, 2 H), 3.47 (m, 6 H), 3.27 (m, 2 H), 2.25 (m, 2 H, $NHCH_2CH_2$-CH_2N). ^{13}C NMR (THF-d_8): δ 142.75−135.13 (m, ArF), 134.35 ($ReNC_{ipso}$), 131.12 (HNC_{para}, ^1J_F = 242 Hz), 122.75 (m, HNC_{ipso}), 66.83 ($ReNCH_2$), 62.34 ($HNCH_2CH_2CH_2$), 58.26 ($ReNCH_2CH_2$), 41.44 ($NHCH_2$), 23.69 ($CH_2CH_2CH_2$). ^{19}F NMR (THF-d_8): δ 14.78 (m, 4 H, $ReNC_6F_{ortho}$), 2.89 (m, 2 F, HNC_6F_{meta}), 1.03 (t, 2 F, $^3J_{FF}$ = 21 Hz, HNC_6F_{ortho}), −2.1 to −2.9 (m, 6 F, $ReNC_6F_{para}$ and $ReNC_6F_{meta}$), −11.28 (tt, 1 F, $^3J_{FF}$ = 22 Hz, $^4J_{FF}$ = 7 Hz, HNC_6F_{para}). IR (cm^{-1}): 3352 (NH), 911 (ReO). Anal. Calcd for $C_{25}H_{15}N_4ClF_{15}ORe$: C, 33.59; H, 1.69; N, 6.27. Found: C, 33.34; H, 1.80; N, 6.15.

Synthesis of H[N_3N]Re(O)Br (2). The compound was prepared analogously to **1** employing 0.79 g (1.14 mmol) of $Re(O)Br_3(PPh_3)_2$, 0.79 g (1.20 mmol) of [N_3N]H$_3$, and 1 mL (excess) NEt_3. Yield: 0.63 g (59%). ^{1}H NMR (THF-d_8): δ 5.46 (br s, 1 H, NH), 4.20 (m, 2 H), 3.73 (m, 2 H), 3.55−3.32 (m, 6 H), 3.22 (m, 2 H), 2.24 (m, 2 H, $NHCH_2CH_2CH_2N$). ^{13}C NMR (THF-d_8): δ 146.08−137.19 (m, ArF), 133.65 (HNC_{para}, ^1J_F = 242 Hz), 125.28 (t, ^3J_F = 12 Hz, HNC_{ipso}), 69.69 ($ReNCH_2$), 65.06 ($HNCH_2CH_2CH_2$), 60.56 ($ReNCH_2CH_2$), 43.97 ($NHCH_2$), 26.17 ($CH_2CH_2CH_2$). ^{19}F NMR (THF-d_8): δ 15.08 (m, 4 H, $ReNC_6F_{ortho}$), 2.90 (d, 2 F, HNC_6F_{meta}), 1.12 (t, 2 F, $^3J_{FF}$ = 21 Hz, HNC_6F_{ortho}), −2.26 (t, 2 F, $^3J_{FF}$ = 20 Hz, $ReNC_6F_{para}$), −2.60 (m, 4 F, $ReNC_6F_{meta}$), −11.31 (t, 1 F, $^3J_{FF}$ = 21 Hz, HNC_6F_{para}). IR (cm^{-1}): 3353 (NH), 911 (ReO). Anal. Calcd for $C_{25}H_{15}N_4BrF_{15}ORe$: C, 31.99; H, 1.61; N, 5.97; Br, 8.51. Found: C, 31.73; H, 1.78; N, 5.77; Br, 8.54.

Synthesis of H[N_3N]ClReOReBrCl[N_3N]H (3). To a cooled (−20 °C) green suspension of **1** (1.08 g, 1.21 mmol) in toluene (15 mL) was slowly added by cannula a solution of 0.84 g (1.2 mmol, 1 equiv) of $TaCH(CPhMe_2)Br_3(THF)_2$ in toluene (15 mL). The reaction color turned gradually darker, and the product precipitated as fine needles, which were filtered at low temperature. Drying in vacuo gave 1.06 g (95%) of the product as deep blue powder. Crystals suitable for X-ray analysis were obtained by recrystallization from a mixture of CH_2Cl_2 and hexane at −20 °C giving almost black crystals. MS(EI): *m*/*z* (%) 921 (100, [N_3N]-$ReBr^+$); 894 (20, [N_3N]Re(O)Cl); 877 (80, [N_3N]ReCl). Anal. Calcd for $C_{50}H_{30}N_8BrCl_2F_{30}ORe_2$·2toluene: C, 37.75; H, 2.28; N, 5.50. Found: C, 37.97; H, 2.31; N, 5.45.

Synthesis of [N_3N]ReCl (4). To a cooled (−20 °C) green suspension of **1** (1.10 g, 1.23 mmol) in toluene (15 mL) was slowly added by cannula a solution of 1.46 g (2.59 mmol, 2.1 equiv) of $TaCH(CPhMe_2)Cl_3(THF)_2$ in toluene (15 mL). The reaction color turned darker, and initially dark green-blue needles precipitated. After addition of the tantalum reagent, the reaction mixture was stirred at room temperature for 2 h during which the precipitate disappeared and a clear orange-brown solution was formed. The solvent was removed under reduced pressure to a volume of 5 mL and stored at −20 °C. The yellow microcrystals were filtered and washed with a minimum amount of cold toluene and dried under reduced pressure. Yield: 0.75 g, (70%). Mp 292 °C (dec). MS-(EI): *m*/*z* 877 (M^+). ^{19}F NMR (C_6D_6): δ 34.80 (br s, 2 F), 21.13 (br s, 2 F), 16.46 (br s, 2 F), 13.05 (br s, 2 F), 9.23 (br s, 2 F), 8.06 (s, 1 F), 7.11 (s, 2 F), 4.65 (br s, 2 F) Anal. Calcd for $C_{25}H_{14}N_4$-$ClF_{15}Re$: C, 34.24; H, 1.61; N, 6.39. Found: C, 34.27; H, 1.69; N, 6.30. An attempted X-ray crystal structure analysis confirms the connectivity.

Synthesis of H[N_3N]$ReBr_2$ (5). The compound was prepared in a fashion analogous to **4** employing 0.43 g (0.45 mmol) of **2** and 0.70 g (1.01 mmol) of $TaCH(CPhMe_2)Br_3(THF)_2$. Yield: 0.21 g (47%). MS(EI): *m*/*z* (%) 921 (M^+ − HBr). Anal. Calcd for $C_{25}H_{15}N_4Br_2F_{15}Re$: C, 29.95; H, 1.56; N, 5.59. Found: C, 30.18; H, 1.56; N, 5.57.

Synthesis of [N_3N]Re(N_2) (6). To a mixture of 0.24 g (0.23 mmol) of **4** and 0.064 g Na (3.01 g of 0.28% Na/Hg) was added 30 mL of precooled THF (−20 °C), and the mixture was stirred for 1 h resulting in a deep red suspension. The mixture was allowed to warm to room temperature and stirred for an additional hour during which the color changed gradually to orange. The suspension was filtered over Celite, and the solvent was removed under reduced pressure. The orange solid was extracted with toluene and filtered and the volume reduced to 5 mL and cooled to −25 °C affording 0.1 g (42%) of the orange product. Crystals suitable for X-ray analysis were obtained from a layered mixture of CH_2Cl_2/hexane. ^{1}H NMR (C_6D_6): δ 3.63 (m, 2 H), 3.10 (m, 4 H), 1.99 (m, 4 H), 1.75 (m, 2 H), 1.36 (m, 2 H). ^{13}C NMR (C_6D_6): δ 143.4 (C_{Ar}), 141.4 (C_{Ar}), 139.6 (C_{Ar}), 138.8 (C_{Ar}), 137.6 (C_{Ar}), 136.7 (C_{Ar}), 133.3 (C_{Ar}), 61.3 ($CH_2CH_2CH_2NAr$), 60.9 (CH_2CH_2NAr), 59.1 (CH_2CH_2-NAr), 55.7 ($CH_2CH_2CH_2NAr$), 28.2 ($CH_2CH_2CH_2NAr$). ^{19}F NMR (C_6D_6): δ 11.4−10.8 (m, 4 F, $CH_2CH_2NCF_{ortho}$ and $CH_2CH_2CH_2$-NCF_{ortho}), 9.85−9.40 (m, 2 F, $CH_2CH_2NCF_{ortho}$), 2.12 (t, 2 F, $^3J_{FF}$ = 22 Hz, $CH_2CH_2NCF_{para}$), 1.32 (t, 1 F, $^3J_{FF}$ = 22 Hz, CH_2CH_2-CH_2NCF_{para}), −1.04 to −1.48 (m, 6 F, $CH_2CH_2NCF_{meta}$ and CH_2-$CH_2CH_2NCF_{meta}$). IR (cm^{-1}): 2010 (N≡N). Anal. Calcd for $C_{25}H_{14}F_{15}N_6Re$: C, 34.53; H, 1.62; N, 9.66. Found: C, 34.66; H, 1.70; N, 9.46.

Crystal Structure Analysis. The crystals were mounted on a glass fiber in a rapidly cooled perfluoropolyether.[53] Diffraction data were collected on a Stoe-Siemens-Huber four-circle diffractometer coupled to a Siemens CCD area detector with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at 133 K, performing φ- and ω-scans. The structures were solved by direct methods using SHELXS-97[54] and refined against F^2 on all data by full-matrix least-squares with SHELXL-97.[55] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms bound to carbon atoms were included in the model at geometrically calculated positions and refined using a riding model, while all hydrogen atoms bound to nitrogen atoms were refined using distance restraints. Some of the CH_2Cl_2 molecules in **3** are disordered about two positions. They were refined with distance restraints and restraints for the anisotropic displacement parameters.

Results

Synthesis of the Ligand. The parent amine (baep) was synthesized according to a modified method published for the ligand (2-aminoethyl)bis(3-aminopropyl)amine (abap) as shown in Scheme 1.[56−58] The tetraamine was isolated in 44% overall yield as a colorless oil (bp 95 °C, 0.01 bar). The synthesis of baep has been published before employing a fundamentally different method by reduction of the corresponding trinitrile (overall yield 37%).[52] Introduction of the three C_6F_5 groups was performed according to a published procedure for the analogous symmetrical ligand by nucleo-

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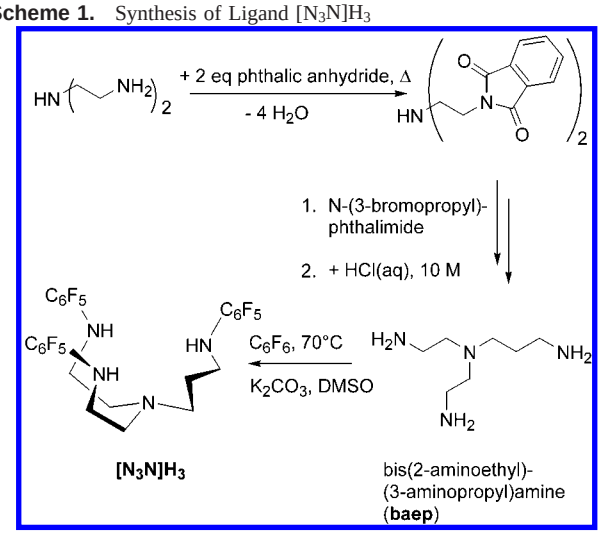
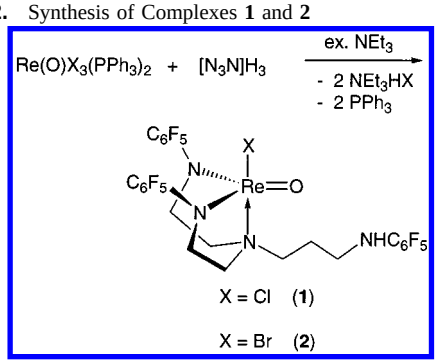
Scheme 1. Synthesis of Ligand $[N_3N]H_3$



Scheme 2. Synthesis of Complexes **1** and **2**



philic substitution by the amine on hexafluorobenzene giving $\{(C_6F_5)HNCH_2CH_2\}_2NCH_2CH_2CH_2NH(C_6F_5)$ ($[N_3N]H_3$) in high yield.[19] The orange oil obtained after evaporation of solvents was generally used without further purification.

Synthesis of Rhenium Oxo Halides. The triaminoamine ligand $[N_3N]H_3$ reacted with $Re(O)X_3(PPh_3)_2$ (X = Cl, Br)[50] in the presence of a slight excess of NEt_3 in THF at room temperature yielding dark brown reaction mixtures within 2 h. After filtration, the solvent was removed under reduced pressure to give dark residues that contain, aside from the product, triphenylphosphine and unidentified impurities. The latter two were removed by extraction with Et_2O yielding the 90% pure products. Recrystallization from hot acetonitrile gave the rhenium oxo halides $[HN_3N]Re(O)X$ (**1**, X = Cl; **2**, X = Br) as green crystalline solids. The compounds are highly soluble in most common polar solvents such as THF, acetonitrile, or CH_2Cl_2, but not Et_2O. NMR spectra show signals indicating the ligand to coordinate in the fashion shown in Scheme 2. Both ethylene substituted amido groups are bound to the metal center while the larger aminopropyl substituent is not, indicated by the broad NH resonance at 5.4−5.6 ppm in the ^1H NMR spectrum as well as the NH stretch at approximately 3350 cm^{-1} in the IR spectrum. The Re−O frequency is assignable to the signal at 911 cm^{-1} by comparison with the spectrum of the monochloride $[N_3N]$-ReCl (vide infra) that lies in the normal range for this moiety.[59]

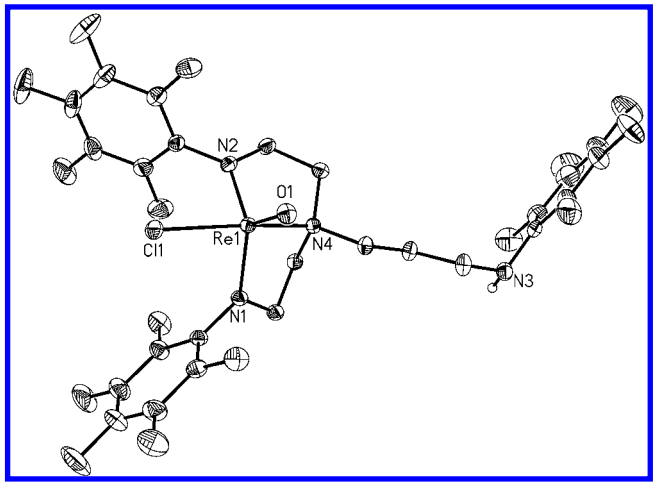


Figure 1. ORTEP plot of $[N_3N]Re(O)Cl$ (**1**).

An X-ray study of **1** confirmed the tridentate coordination of the ligand. An ORTEP plot of the structure is shown in Figure 1. Table 1 contains crystallographic data, while Table 2 contains selected bond lengths and angles. Compound **1** crystallizes in the space group $P\bar{1}$ with one molecule of noncoordinating acetonitrile. The geometry at the metal center is distorted trigonal bipyramidal with two nitrogen atoms and one oxygen atom in the equatorial plane and with the chlorine being trans to the apical nitrogen. Presumably because of the large electron density of the oxo ligand, the N4−Re1−Cl1 angle with 159.59(5)° significantly deviates from linearity. Interestingly, the conformation of the free aminopropyl substituent allows no interaction with the metal or the oxygen atom. However, an *inter*molecular hydrogen bond is formed between N3 and O1 of the next unit cell leading to the formation of chains (N3−H3 0.825(2) Å, H3···O1 2.286(2) Å, N3···O1 3.087(3) Å, N3−H3···O1 164-(3)°).

This situation is presumably analogous to the compound involving the C_3 symmetrical ligand, but a comparison is not possible as no X-ray crystal structure was reported. However, a recently reported rhenium complex displays a similar structure to **1** except for the free amino arm at the apical nitrogen, for which a methyl group has been introduced ($[\{(C_6F_5)NCH_2CH_2\}_2NMe]Re(O)Cl$).[60] Both structures show the same coordination at the metal center with very similar bond lengths and angles.

Reaction with 1 equiv of a Tantalum Alkylidene Reagent. The exchange of the oxo ligand by halides in **1** and **2**, respectively, was realized by the reaction with a tantalum alkylidene compound $Ta(CHR)X_3(THF)_2$ (X = Cl, Br).[51] This unusual reaction has previously been employed in the symmetrical system.[20] As attempts to replace the oxo functionality by more convenient methods failed, such as refluxing in the presence of PPh_3 or reduction with Na/Hg, we proceeded accordingly: by the addition of 1 equiv of $TaCH(CPhMe_2)Br_3(THF)_2$ to **1** at −20 °C in toluene, the deep blue colored compound $H[N_3N]ClReOReBrCl[N_3N]H$ (**3**) precipitated as shown in Scheme 3 in quantitative yield.

(59) Adam, D. M. *Metal−Ligand and Related Vibrations*; Edward Arnold Ltd.: London, 1967.

(60) Cochran, F. V.; Bonitatebus, P. J., Jr.; Schrock, R. R. *Organometallics* **2000**, *19*, 2414.

Table 1. Crystallographic Details of the Structures

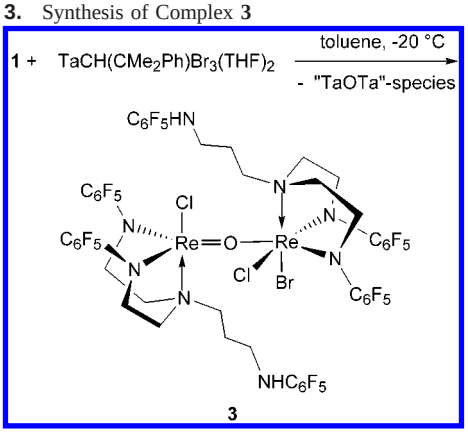
	1	3	5	6
empirical formula	$C_{25}H_{15}ClF_{15}N_4ORe{\cdot}CH_3CN$	$C_{50}H_{30}BrCl_2F_{30}N_8ORe_2{\cdot}6CH_2Cl_2$	$C_{25}H_{15}Br_2F_{15}N_4Re$	$C_{25}H_{14}F_{15}N_6Re$
fw	935.11	2361.59	1002.43	869.62
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a, Å	7.912(2)	13.316(2)	13.797(2)	9.409(2)
b, Å	14.281(3)	17.316(2)	13.959(2)	11.554(2)
c, Å	14.801(3)	18.332(2)	15.722(2)	13.180(3)
α, deg	72.20(3)	76.00(2)	80.86(2)	91.66(3)
β, deg	74.91(3)	81.54(2)	86.87(2)	93.04(3)
γ, deg	89.59(3)	68.25(2)	77.18(2)	109.18(3)
V, Å^3	1532.6(6)	3801.7(8)	2914.4(7)	1349.7(5)
Z	2	2	4	2
ρ_{calcd}, Mg m^{-3}	2.026	2.063	2.285	2.140
μ, mm^{-1}	4.176	4.319	7.034	4.636
cryst size, mm^3	0.2 × 0.2 × 0.1	0.5 × 0.3 × 0.1	0.5 × 0.3 × 0.2	0.2 × 0.1 × 0.1
θ range, deg	2.44−28.28	1.84−27.56	2.15−27.85	1.87−27.93
no. reflns collected	11982	102817	43858	22326
no. independent reflns (R_{int})	7583 (0.0239)	17483 (0.0658)	13657 (0.0731)	6343 (0.0399)
no. data	7583	17483	13657	6343
no. params	457	1103	854	425
no. restraints	1	320	1	0
GOF	1.061	1.135	1.035	1.131
final R1 indices[a] [$I > 2\sigma(I)$] (wR2)	0.0189 (0.0474)	0.0421 (0.0815)	0.0488 (0.1151)	0.0261 (0.0611)
R1 indices, all data (wR2)	0.0204 (0.0482)	0.0531 (0.0849)	0.0742 (0.1263)	0.0285 (0.0619)
extinction coeff	0.00208(19)	0.00035(6)	0.00133(11)	0.0022(3)
largest diff peak and hole (e Å^{-3})	0.497 and −0.595	2.147 and −2.173	3.172 and −2.809	1.336 and −0.912

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR1 = [\sum w(|F_o^2| - |F_c^2|)^2/\sum|F_o^2|^2]^{1/2}$.

Table 2. Selected Bond Lengths (Å) and Angles (deg) of **1**

Re1−O1	1.6991(2)	Re1−Cl1	2.3536(9)
Re1−N1	1.9544(2)	Re1−N2	1.9454(2)
Re1−N4	2.1473(2)		
N4−Re1−Cl1	159.59(5)	N1−Re1−N2	117.87(8)
N1−Re1−O1	121.17(8)	N2−Re1−O1	119.50(8)
N1−Re1−N4	80.21(7)	N1−Re1−Cl1	89.22(6)
N2−Re1−N4	79.49(8)	N2−Re1−Cl1	90.33(7)
O1−Re1−N4	98.13(8)	O1−Re1−Cl1	102.28(6)

Scheme 3. Synthesis of Complex **3**



The interpretation of NMR spectra (in CD_2Cl_2) proved to be challenging because of the presence of a paramagnetic center in combination with an apparently complex structural situation. This is a general problem in the unsymmetrical Re(IV) systems described here that hampered the investigation in solution, and therefore, all the compounds described so far were characterized by X-ray crystal structure analysis. Multiple signals in the ^{19}F NMR spectrum of **3** also did not give insight into structural features. However, it allowed the conclusion that more than one [N_3N] ligand is involved and that the compound contains uncoordinated NHC_6F_5 groups because of a signal at δ −8.7 ppm. This is consistent with the finding that the IR spectrum shows a NH stretch at 3381 cm^{-1}, whereas no classical Re═O stretch is detectable in the usual 900−1000 cm^{-1} range. The mass spectrum shows *m*/*z* peaks corresponding to H[N_3N]Re(O)Cl (894), [N_3N]-ReBr (921), and [N_3N]ReCl (877).

Crystallization of **3** in a mixture of CH_2Cl_2 and hexane over several days at −20 °C yielded dark crystals that were suitable for X-ray crystal structure analysis. An ORTEP plot is shown in Figure 2, while selected bond lengths and angles are listed in Table 3. The crystal structure analysis revealed a dinuclear species with a Re═O─Re core and mixed-valent rhenium centers. The structure is best described as a rhenium-

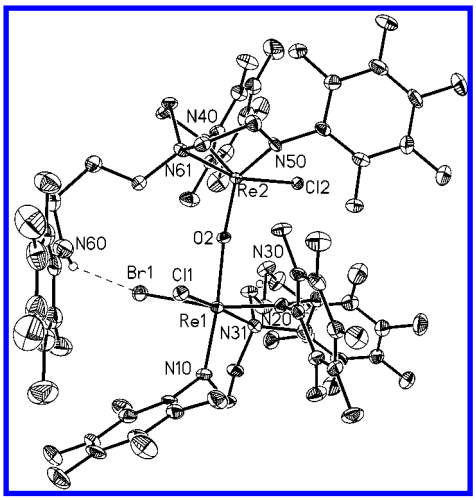


Figure 2. ORTEP plot of H[N_3N]ClReOReBrCl[N_3N]H (**3**).

Table 3. Selected Bond Lengths (Å) and Angles (deg) of **3**

Re1−N20	1.931(4)	Re1−N10	1.936(4)
Re1−O2	2.038(3)	Re1−N31	2.192(4)
Re1−Cl1	2.3800(1)	Re1−Br1	2.5688(6)
Re2−O2	1.756(3)	Re2−N(50)	1.919(4)
Re2−N40	1.932(4)	Re(2)−N(61)	2.144(4)
Re2−Cl2	2.3863(1)		
N20−Re1−N10	101.80(2)	N20−Re1−O2	87.32(1)
N10−Re1−O2	167.88(2)	N20−Re1−N31	81.18(2)
N10−Re1−N31	80.96(2)	O2−Re1−N31	92.73(1)
N20−Re1−Cl1	92.68(1)	N10−Re1−Cl1	95.04(1)
O2−Re1−Cl1	92.45(9)	N31−Re1−Cl1	171.77(1)
N20−Re1−Br1	167.70(1)	N10−Re1−Br1	89.27(1)
O2−Re1−Br1	80.99(9)	N31−Re1−Br1	95.48(1)
Cl1−Re1−Br1	91.65(4)	O2−Re2−N50	120.33(2)
O2−Re2−N40	122.80(2)	N50−Re2−N40	115.57(2)
O2−Re2−N61	97.87(1)	N50−Re2−N61	80.31(2)
N40−Re2−N61	79.95(2)	O2−Re2−Cl2	99.99(1)
N50−Re2−Cl2	90.94(1)	N40−Re2−Cl2	90.03(1)
N61−Re2−Cl2	162.13(1)	Re2−O2−Re1	170.77(2)

(IV) species that is coordinated by the oxo group of an additional molecule of **1**. The Re2 center with the formal oxidation state V is five-coordinate in a distorted trigonal-bipyramidal geometry, whereas the Re1 center with the oxidation state IV displays a distorted six-coordinated octahedron. In both ligands, the propylamino groups are not in coordinating contact to any metal. *Inter*molecular hydrogen bonds are formed between N30 and Br1 (N30−H30 0.74(4) Å, H30···Br1 2.86(5) Å, N30···Br1 3.513(5) Å, N30−H30···Br1 148(5)°) leading to dimers. Additionally, weak *intra*molecular hydrogen bonds between N60 and Br1 are observed (N60−H60 0.74(4) Å, H60···Br1 3.23(5) Å, N60···Br1 3.906(5) Å, N60−H60···Br1 152(7)°).

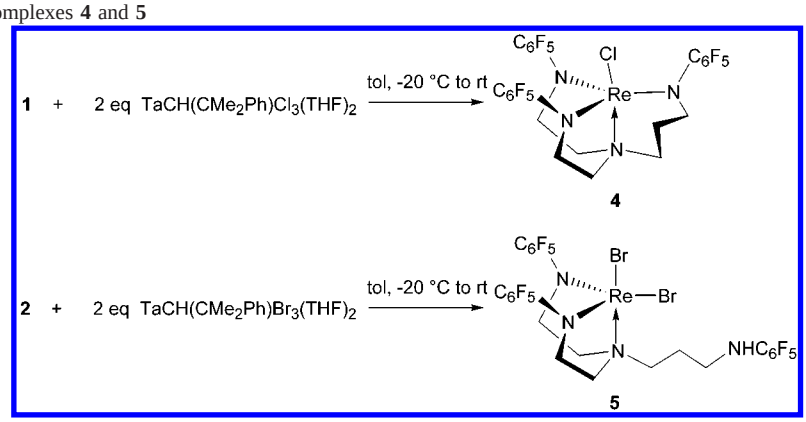
The Re1−O2−Re2 bond angle slightly deviates from linearity (170.8(2)°) with two significantly different Re−O bond distances (Re2−O2 1.756(3) and Re1−O2 2.038(3) Å) indicating a double bond character for Re2−O2 and a coordinating bond for Re1−O2. The Re2−O2 bond length in **3** is elongated in comparison to **1** (from 1.6991(2)° to 1.753(3)°), presumably because of the coordination to Re1. The Re1−O2 bond length is in the normal range for a Re−O single bond.[59] The amido ligands are coordinated in a way that the two apical nitrogen atoms are in transoid position to each other and trans to the chlorine atoms. The N−Re−N angle is smaller at the higher coordinated Re1 in comparison to the Re2 center (N10−Re1−N20 101.8(2)°, N40−Re1−N50 115.6(2)°). The bromide is located in cis position to the chloride ligand.

The structure of **3** is quite unusual, because a Cambridge structural database search revealed only few Re(IV) species containing Re−O−Re units with a single μ-oxo bridge. One of these compounds, $[L_2Re_2Cl_4(\mu\text{-O})][ZnCl_4]$[61] (L = *N*-methylated 1,4,7-triazacyclononane) is centrosymmetric with an inversion center on the (μ-O) atom showing a strictly linear Re−O−Re linkage, whereas $[L_2Re_2Me_2(O)_2(\mu\text{-O})]$[62] (L = η^2-2-butyne) and $[Cp_2Re_2Br_2(\mu\text{-O})][BF_4]_2$[63] involve bent groups due to metal−metal bond interaction. The Re−O bond distance in $[L_2Re_2Cl_4(\mu\text{-O})][ZnCl_4]$ is 1.878(1) Å indicating single bonds with considerable double bond character. This value is between Re1−O2 and Re2−O2 distances in **3** pointing to the different bonding situation. The bonding is therefore best described as a donor−acceptor interaction between the lone pair of the oxo ligand and the Re(IV) center.

Reaction with 2 equiv of the Tantalum Reagent. The addition of 2 equiv of $TaCH(CPhMe_2)Cl_3(THF)_2$ to **1** gave paramagnetic compound **4** in good yield as shown in Scheme 4. We propose complex **4** to be the species with all three amido substituents coordinated to the metal center, which has also been found in the symmetric analogue.[11] The ^{19}F NMR spectrum shows eight broad signals between δ 5 and 35 ppm consistent with a species with a mirror plane between the two aminoethyl groups. Elemental analysis gave correct values for complex **4**. In addition, an attempted crystal structure analysis unambiguously confirmed the connectivity, but the structure was severely disordered about three positions, each with an occupancy of $^1/_3$ pretending the 3-fold axis of the C_3 symmetrical tren ligand. The disorder can be modeled, but of course, all bond lengths and angles are not precise enough to be discussed.

As shown in Scheme 4, by the analogous reaction employing **2** and 2 equiv of $TaCH(CPhMe_2)Br_3(THF)_2$, red-brown $H[N_3N]ReBr_2$ (**5**) could be isolated. Recrystallization from a mixture of CH_2Cl_2 and hexane at room temperature gave red crystals suitable for an X-ray analysis that confirmed the formation of the dibromide (**5**). This is in contrast to the formation of **4**, where the final product is isolated after elimination of HCl. Possibly, differences in the stability of the Re−Br versus the Re−Cl bond prevent such a reactivity in **5** and/or the increased steric requirement of the bromide ligand impedes the coordination of the bulky NC_6F_5 substituent.

Scheme 4. Synthesis of Complexes **4** and **5**



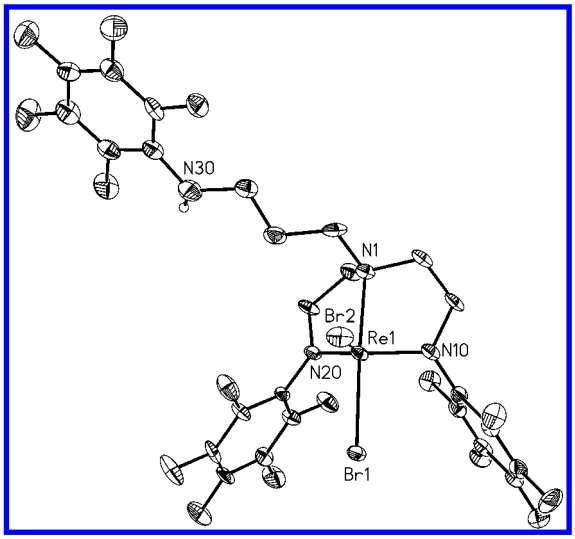


Figure 3. ORTEP plot of $H[N_3N]ReBr_2$ (**5**).

Table 4. Selected Bond Lengths (Å) and Angles (deg) of **5**

Re1−N20	1.891(6)	Re1−N10	1.904(6)
Re1−N1	2.168(6)	Re1−Br2	2.4203(8)
Re1−Br1	2.5143(9)	Re2−N50	1.895(6)
Re2−N60	1.910(6)	Re2−N2	2.162(6)
Re2−Br4	2.4166(8)	Re2−Br3	2.5165(9)
N20−Re1−N10	112.7(3)	N20−Re1−N1	81.9(2)
N10−Re1−N1	81.0(2)	N20−Re1−Br2	127.87(2)
N10−Re1−Br2	118.06(2)	N1−Re1−Br2	94.53(2)
N20−Re1−Br1	93.69(2)	N10−Re1−Br1	94.51(2)
N1−Re1−Br1	171.84(2)	Br2−Re1−Br1	93.59(3)
N50−Re2−N60	116.1(2)	N50−Re2−N2	80.7(2)
N60−Re2−N2	80.9(2)	N50−Re2−Br4	116.09(2)
N60−Re2−Br4	126.27(2)	N2−Re2−Br4	95.71(2)
N50−Re2−Br3	95.29(2)	N60−Re2−Br3	94.73(2)
N2−Re2−Br3	171.95(2)	Br4−Re2−Br3	92.32(3)
N1−C5−C6−C7	−178.0(6)	N2−C44−C45−C46	164.7(6)
C5−C6−C7−N30	168.7(6)	C44−C45−C46−N70	−65.8(8)

An ORTEP plot of the structure is given in Figure 3; selected bond lengths and angles are given in Table 4. The unit cell contains two independent molecules, which differ only in the conformation of the free aminopropyl group. The bond distances and angles at the Re(IV) center are in both molecules almost identical; therefore, the following discussion only deals with molecule **1**. The geometry is distorted trigonal bipyramidal with the two coordinated amido substituents and one bromide ligand in the equatorial positions. As expected according to VSEPR, the Re1—Br1 bond length (2.5143(9) Å) in the axial position is slightly longer compared to Re1—Br2 (2.4203(8) Å). The geometry is comparable to that of **1** with the exception that the Re═O double bond leads to a more pronounced distortion from a perfect trigonal bipyramid. For example, the N1—Re1—Br1 angle in **5** with 171.8(2)° is almost linear whereas the corresponding angle in **1** is 159.59(5)°. Surprisingly, the equatorial Re(IV)—N bonds (Re1—N10 1.904(6) Å, Re1—N20 1.891(6) Å) are shorter than the Re(V)—N bonds in **1** (Re1—N1 1.954(2) Å, Re1—N2 1.945(2) Å). Five-coordinate rhenium(IV) species are rare.[64,65] Like other d^3 ions, the rhenium(IV) ion normally adopts an octahedral geometry, as in the case of compound **3**, where the metal center is six-coordinate. It is therefore surprising that the aminopropyl group of the ligand does not bind to the metal. An *inter*molecular hydrogen bond is observed between N70 and Br1 connecting the two independent molecules to form a dimer (N70—H70 0.76(7) Å, H70···Br1 2.91(7) Å, N70···Br1 3.666(7) Å, N70—H70···Br1 172(8)°), while the other NH group only forms a weak *intra*molecular hydrogen bond to F31 (N30—H30 0.76(7) Å, H30···F31 2.30(9) Å, N30···F31 2.689(9) Å, N30—H30···F31 113(8)°).

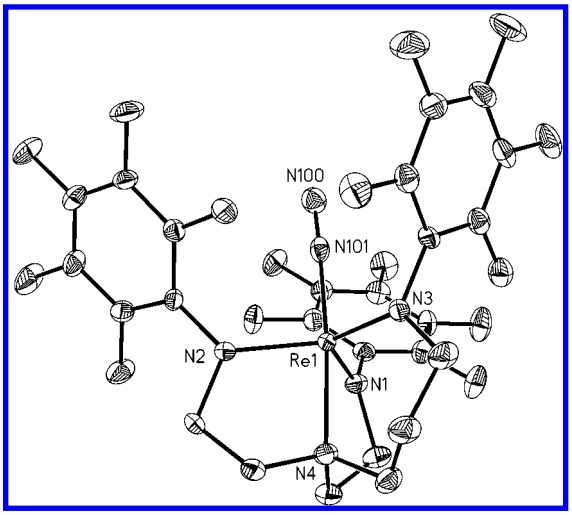
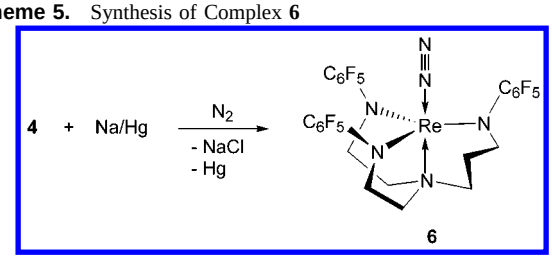


Figure 4. ORTEP plot of $[N_3N]Re(N_2)$ (**6**).

Scheme 5. Synthesis of Complex **6**



Reduction of $[N_3N]ReCl$ under Dinitrogen. The reduction of **4** under an atmosphere of dinitrogen with Na/Hg gave $[N_3N]Re(N_2)$ (**6**) in good yield (Scheme 5). The reaction time of 2 h should not be exceeded; otherwise, the yields decrease significantly as side reactions start to compete. Other reduction methods were not successful. The orange complex is soluble in most common organic solvents. NMR and IR spectroscopy are consistent with the structure shown in Scheme 5, and the data are similar to the reported symmetrical one.[11]

The end-on coordination of the N_2 molecule to the diamagnetic Re(III) center was confirmed by X-ray crystallography. Figure 4 shows an ORTEP plot of the complex, and bond lengths and angles are given in Table 5. The N≡N bond length is 1.087(4) Å, corresponding to a normal value

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(63) Carfagna, C.; Carr, N.; Deeth, R. J.; Dossett, S. J.; Green, M.; Mahon, M. F.; Vaughan, C. *J. Chem. Soc., Dalton Trans.* **1996**, 415.
(64) Hambley, T. W.; Knott, R. K.; Jackson, T. W.; Kojima, M.; Lambrecht, R. M. *Acta Crystallogr., Sect. C* **1995**, *51*, 203.
(65) Masood, M. A.; Sullivan, B. P.; Hodgson, D. J. *Inorg. Chem.* **1999**, *38*, 5425.

Table 5. Selected Bond Lengths (Å) and Angles (deg) of **6**

N100−N101	1.087(4)	Re1−N101	1.943(3)
Re1−N1	1.929(3)	Re1−N2	1.941(3)
Re1−N3	1.943(3)	Re1−N4	2.178(3)
N100−N101−Re1	177.7(3)	N101−Re1−N4	173.81(1)
N1−Re1−N2	114.60(1)	N1−Re1−N3	120.12(1)
N2−Re1−N3	123.87(1)	N1−Re1−N4	82.55(1)
N2−Re−N4	81.11(1)	N3−Re1−N4	94.00(1)
N1−Re1−N101	94.73(1)	N3−Re1−N101	92.18(1)
N2−Re1−N101	95.06(1)		

for a triple bond. The geometry at the metal center is trigonal bipyramidal with a slightly smaller N1−Re1−N2 angle (114.6(1)°) than the other two trigonal angles (120.1(1)°, 123.9(1)°). As expected, the six-membered metallacycle formed by the coordinated amidopropyl group has a larger N−Re−N angle (N3−Re1−N4 94.0(1)° compared to N1−Re1−N4 82.55(1)° and N2−Re1−N4 81.11(1)°) as well as a larger Re−N−C angle (129.(1)° compared to 118.7(2)° and 116.4(2)°), leading to a tilting of the C_6F_5 ring toward the metal center. The thus imposed steric effect on the apical ligand is apparently small as there is almost no tilting of the N_2 molecule between the two other C_6F_5 groups (N4−Re1−N101 173.8(1)° and Re1−N101−N100 177.7(3)°).

Discussion

The here described system allows significant insights into the unusual reaction of the tantalum alkylidene reagent with the metal oxide. Such reactions have previously been shown to transfer entire alkylidene groups by metathesis with a metal oxide.[66] Here, this reaction does not take place, but rather, a halogen atom is transferred. The choice of two different halogen precursors (rhenium chloride and tantalum bromide) in the reaction forming **3** allows the conclusion that only one halogen atom is transferred forming intermediates of the type $H[N_3N]ReX_2$. Depending on the nature of the X ligand, these dihalogenides eliminate HX which is obvious by a slow gas evolution thereby forming the monohalogenides $[N_3N]ReX$. The nature of the tantalum species formed is unclear; however, the stoichiometry of the reactions (1 equiv of the Ta reagent for **3** and 2 equiv for **4** and **5**) points to the formation of a Ta−O−Ta species. Oxo-bridged dinuclear tantalum compounds with other ligands have been structurally characterized.[67−69] After separation of the products, NMR spectra of the remaining reaction mixtures are complex but show no alkylidene signals. Therefore, we assume that the electrons necessary for the formation of the reduced Re(IV) complex stem from dimerization of the alkylidene group.

The systematic study on complexes with the unsubstituted symmetrical and unsymmetrical tren-type ligands has shown the significant influence of the size of the chelate rings toward the basicity of the ligand as well as the geometry of the complexes.[48,49] With this in mind, we set our goal to influence the geometry and thereby provoke unusual reactivities in rhenium complexes that contain triamidoamine ligands having symmetries other than trigonal. The introduction of an additional CH_2 group in the ligand either leads to complexes with a six-membered chelate ring or to tri- instead of tetradentate coordination of the ligand. This variability of the ligand system caused by the decreased stability of the larger chelate ring allows the isolation of unusual intermediates not traceable with the symmetrical ligand. However, once the ligand coordinates in a tetradentate manner, the complexes show minute differences in comparison to the symmetrical one. This is interesting in the view that such ligands are thought to model the nitrogen-rich active site of metalloenzymes. The investigation of controlled changes in the ligand geometry thereby retaining the donor atom set might eventually prove useful in the understanding of principles governing the activation of biological substrates.

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Supporting Information Available: X-ray crystallographic files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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