Rhenium(III) and Rhenium(V) Complexes That Contain the ($C_6F_5NCH_2CH_2)_3N$ Ligand

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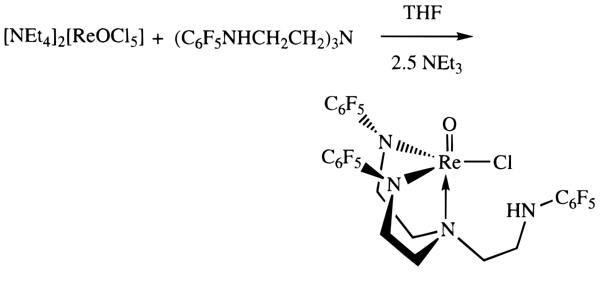
*Summary: The reaction between $[Et_4N]_2[ReOCl_5]$ and $(C_6F_5NHCH_2CH_2)_3N$ in THF at room temperature in the presence of NEt_3 yielded air-stable emerald green diamagnetic $[(C_6F_5NCH_2CH_2)_2NCH_2CH_2NHC_6F_5]Re(O)Cl$ (**1**). The reaction between **1** and $Ta(CH\text{-}t\text{-}Bu)(THF)_2Br_3$ gave paramagnetic $\{[(C_6F_5NCH_2CH_2)_3N]ReBr\}Br$ (**2**). Reduction of **2** by methyllithium under dinitrogen gave diamagnetic $[(C_6F_5NCH_2CH_2)_3N]Re(N_2)$, under carbon monoxide gave $[(C_6F_5NCH_2CH_2)_3N]Re(CO)$, under dihydrogen gave $[(C_6F_5NCH_2CH_2)_3N]ReH_2$, and under ethylene gave $[(C_6F_5NCH_2CH_2)_3N]Re(C_2H_4)$.*

We recently reported the synthesis of tris(2-((pentafluorophenyl)amino)ethyl)amine, $(C_6F_5NHCH_2CH_2)_3N$, and several molybdenum complexes containing its trianion, including two that contain dinitrogen.[1] The complex that yielded structurally characterized diamagnetic $[(C_6F_5NCH_2CH_2)_3N]MoN{=}NSi(i\text{-}Pr)_3$ upon treatment with $(i\text{-}Pr)_3SiCl$ was proposed to be a sodium salt of the d^4 "Mo(II)" species, $\{[(C_6F_5NCH_2CH_2)_3N]Mo(N_2)\}^-$, or "$[(C_6F_5NCH_2CH_2)_3N]MoN{=}NNa$". Since we were not able to confirm the nature of the sodium salt via an X-ray study, we became interested in the possibility that a neutral d^4 Re(III) analog of $\{[(C_6F_5NCH_2CH_2)_3N]Mo(N_2)\}^-$ could be prepared. Therefore, we began to search for entries into the chemistry of Re complexes containing the $(C_6F_5NCH_2CH_2)_3N$ ligand. We report our preliminary findings here.

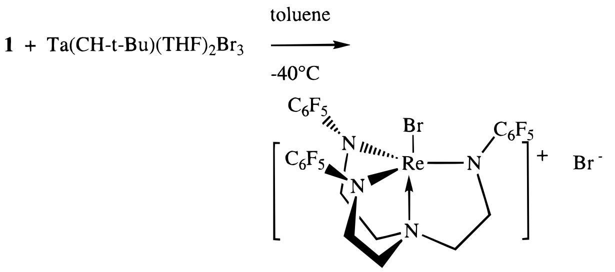
The reaction between $[Et_4N]_2[ReOCl_5]$[2,3] and $(C_6F_5NHCH_2CH_2)_3N$ in THF at room temperature in the presence of NEt_3 gave emerald green diamagnetic **1** (eq 1). An attempted X-ray study confirmed the connectivity, but full solution and refinement were not successful. (Details will be reported later.) NMR spectra of **1** are entirely consistent with the mirror symmetry shown and reveal a broad resonance for the NH proton between 2.15 and 4.70 ppm. The NH resonance disappears upon addition of D_2O, although **1** is stable in air as a solid and in a mixture of THF and water for at least 2 days. Many attempts to remove HCl with a variety of bases have not been successful. We speculate that 3-fold symmetric, d^2 $[(C_6F_5NCH_2CH_2)_3N]Re{=}O$ would be a high-energy species, since no π donation from the oxo ligand into one of the three orbitals available in the apical site (d_{xz}, d_{yz}, and a σ orbital along the Re═O (z) axis) is possible as a consequence of two d electrons being present in the remaining π type orbital.



(1)

1

An attempt to exchange the oxo ligand[4,5] in **1** with the neopentylidene ligand in $Ta(CH\text{-}t\text{-}Bu)(THF)_2Br_3$[6] gave olive green $[(C_6F_5NCH_2CH_2)_3N]ReBr_2$ (**2**; 60−85% yield) instead. This reaction is formally an exchange of the oxo ligand in **1** with Br_2 on tantalum plus removal of HCl from Re; no attempt to isolate and identify the tantalum product (hypothetically "$Ta(O)(CH_2\text{-}t\text{-}Bu)BrCl(THF)_x$") was made. The paramagnetism of **2** is consistent with the ionic formulation, since the two d electrons should then occupy the degenerate d_{xz}/d_{yz} orbital set. The unexceptional structure of **2** has been confirmed in an X-ray study,[7] details of which will be published later.



(2)

2

An attempt to form a Re(V) methyl complex by treating **2** with methyllithium under dinitrogen yielded a sparingly soluble, diamagnetic, orange crystalline complex with the formula $[(C_6F_5NCH_2CH_2)_3N]Re(N_2)$ (**3**) in good yield.[8] Treatment of **2** with methyllithium under $^{15}N_2$ yielded the analogous complex $[(C_6F_5NCH_2CH_2)_3N]Re(^{15}N_2)$ (**3-^{15}N$_2$**). IR spectra of **3** (ν_{NN} 2004 cm^{-1}) and **3-^{15}N$_2$** ($\nu_{^{15}N^{15}N}$ 1935 cm^{-1}) are consistent with

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[⊗] Abstract published in *Advance ACS Abstracts*, December 1, 1995.

(1) Kol, M.; Schrock, R. R.; Kempe, R.; Davis, W. M. *J. Am. Chem. Soc.* **1994**, *116*, 4382.

(2) This compound was prepared in a manner analogous to that for the known tetramethylammonium salt.[3]

(3) Grove, D. E.; Wilkinson, G. *J. Chem. Soc. A* **1966**, 1224.

(4) Recently it has been possible to exchange the oxo ligand in Os(VI) complexes with the neopentylidene ligand in Ta(V) complexes; see ref 5.

(5) LaPointe, A. M.; Schrock, R. R.; Davis, W. M. *J. Am. Chem. Soc.* **1995**, *117*, 4802.

(6) Rupprecht, G. A.; Messerle, L. W.; Fellmann, J. D.; Schrock, R. R. *J. Am. Chem. Soc.* **1980**, *102*, 6236.

(7) Reid, S. M., Davis, W. M. Unpublished results.

(8) An ether solution of methyllithium (0.357 mmol) was added to a stirred solution of **2** (167 mg, 0.17 mmol) in 5 mL of THF under an atmosphere of dinitrogen. The green-brown solution turned dark purple immediately and then faded to orange-brown over a period of 1 h. The solvent was evaporated in vacuo, and the oily orange residue was dissolved in a minimum amount of methylene chloride. The extract was filtered, pentane was added, and the mixture was cooled to −40 °C to yield orange cubes; yield 104 mg (0.12 mmol, 72%).

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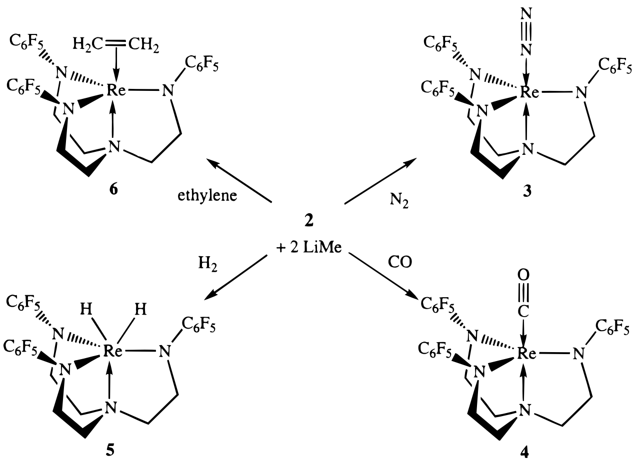
Scheme 1. Reductions of 2 with Methyllithium



an end-on mode of dinitrogen binding, as is the ^{15}N NMR spectrum of **3-^{15}N$_2$**, which reveals two doublet resonances at 281.3 and 332.0 ppm with $^1J_{NN} = 5.5$ Hz. Exposure of **3-^{15}N$_2$** to ^{14}N$_2$ (22 °C, 1 atm) does not lead to exchange of ^{15}N$_2$ for ^{14}N$_2$. **3** also is formed upon treating **2** with phenyl-, butyl-, or neopentyllithium under dinitrogen. Attempts to synthesize **3** by reducing **2** with Zn dust or sodium amalgam under dinitrogen so far have not been successful. Purple intermediates are formed rapidly in all reactions involving lithium reagents, but attempts to identify any such intermediate have been hampered by their extreme sensitivity to air and moisture and their apparent paramagnetism (according to NMR studies).

Addition of methyllithium to **2** under an atmosphere of CO, dihydrogen, or ethylene led to the sparingly soluble diamagnetic compounds **4**, **5**, and **6**, respectively, in good yields (Scheme 1).[9] The IR spectrum of **4** has a CO band at 1875 cm^{-1} that shifts to 1830 cm^{-1} in the ^{13}CO analog. A sharp resonance for the hydrides in **5** is found at −0.89 ppm in the proton NMR spectrum in CD$_2$Cl$_2$, but no peak could be located in the IR spectrum. A T_1 measurement at 21 °C yielded a value of 138 ms for the hydrides, a possibly nonminimal value that would favor **5** being a classical dihydride complex.[10−12] On the other hand, the J_{HD} coupling constant in **5-d_1** (15 Hz) is more consistent with **5** being a dihydrogen complex (typically $J_{HD} = 30 \pm 4$ Hz).[10−12] Therefore, at this stage we cannot state with certainty which description, if either,[13] is the most appropriate. Proton NMR spectra of **6** in THF-d_8 show a broad resonance at 2.61 ppm, consistent with a intermediate rate of "rotation" of the ethylene with respect to the (C$_6$F$_5$NCH$_2$CH$_2$)$_3$N ligand. An X-ray study of **6** has shown it to have the expected structure in which the ethylene lies in the same plane as one of the Re−N bonds;[7] details will be published later.

The results presented here suggest that a variety of Re(III)/Re(V) complexes that contain the [(C$_6$F$_5$NCH$_2$CH$_2$)$_3$N] ligand should be accessible. Future efforts will be directed toward synthesizing such species by more direct methods and preparing analogous complexes that contain other types of triamidoamine ligands, such as [(Me$_3$SiNCH$_2$CH$_2$)$_3$N]$^{3-}$.[14−21]

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Supporting Information Available: Text giving experimental details for the synthesis of compounds **1**−**6** (4 pages). Ordering information is given on any current masthead page.

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[9] A THF solution of **2** (10 mL of THF per 100 mg) and MeLi (in 10 mL of ether per 2.1 equiv) were separately degassed three times by freeze−pump−thaw cycles. The reaction vessel was then filled with the desired gas, and the solutions were combined. The rapidly formed dark purple color that was generated in the case of **5** and **6** faded over a period between 1 h and 3 days. The product was isolated in a manner analogous to the isolation of **3**.

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