Reactivity of Rhenium Complexes Containing a Triamidoamine Ligand Toward Samarium Diiodide

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Received February 18th, 2005.

Dedicated to Professor Herbert W. Roesky on the Occasion of his 70th Birthday

Abstract. The reaction of $[(HN_3N)ReOCI]$ (1) that contains the unsymmetric tren-based ligand $HN_3N = (\{C_6F_5NCH_2CH_2\}_2 NCH_2CH_2CH_2NHC_6F_5\}^{2-}$ with samarium diiodide leads to the formation of the iodide compounds $[(N_3N)ReI]$ (2) and $[(HN_3N)ReOI]$ (3). The reduction reaction also generates the unusual rhenium(IV) compound $[(HN_3N^*)ReX]$ (4, X = 0.35 % F and 0.65 % I,), where the amine ligand $HN_3N^* = (\{C_6F_5NCH_2CH_2\}_2$

Introduction

Not only since Schrock's seminal discovery in 2003 that dinitrogen can be catalytically reduced under mild conditions [1-3], complexes containing ligands with a tris(2-aminoethyl)amine (tren) backbone have held prominence in coordination and organometallic chemistry. In particular, derivatives with sterically demanding substituents at the amido nitrogen atom led to a wide variety of main group, transition and lanthanide metals complexes [4-20], that allow for example activation of dinitrogen [1, 3, 21, 22], alkylidyne formation by α, α -dehydrogenation of alkyl compounds or by C,C-bond cleavage of cyclic alkyls [23, 24], and preparation of terminal phosphido and arsenido compounds [25-27]. Both, the C_3 symmetry and the stability of the chelate-5-rings imposed by such ligands are fundamental requirements for the found reactivity. Triamidoamine ligands with variable substituents attached to the central nitrogen atom breaking the symmetry should therefore lead to other reactivities. The coordination chemistry of 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, where the insertion of additional CH₂ groups has profound structural and chemical consequences [28 - 30].

We investigated the baep-based ligand with the sterically demanding substituent C_6F_5 at the amido nitrogen atom $(C_6F_5NHCH_2CH_2)_2NCH_2CH_2CH_2NHC_6F_5$ (H₃N₃N) employing an additional CH₂ group in the backbone and found considerably less stable chelate rings leading to com $NCH_2CH_2CH_2NHC_6F_4)^{3-}$ is involved in an intramolecular C-F bond activation. The larger 6-membered metallacycle formed by the propylene amido substituent facilitates *ortho* metallation. All compounds have been characterized by single crystal X-ray analyses.

Keywords: Metallacycles; N ligands; Rhenium; Samarium

plexes with an uncoordinated propylene substituent (Scheme 1) [31], which is in contrast to the symmetrical tren-based system [32, 33]. However, depending on the metal ligand bond that needs to be cleaved, the N₃N ligand was also found to coordinate tetradentate. For example, $[(N_3N)ReCl]$ is formed with the ligand in its trianionic form, whereas in [(HN₃N)ReBr₂] the ligand is dianionic and two bromine atoms remain at the metal center. These rhenium complexes are formed by the unusual reaction of the rhenium oxide [(HN₃N)ReOX] with tantalum alkylidene complexes of the type $[TaCHCMe_2PhX_3(THF)_2]$ (X = Cl, Br) [34], whereby oxygen transfer to tantalum and reduction to rhenium(IV) occurs. The intended transfer of an alkylidene group from tantalum to rhenium was not observed rendering the tantalum compound as unusual reducing agent. More common reducing agents such as sodium amalgam, magnesium or zinc did not yield in any products. In the search for a suitable reducing agent, we investigated the reactivity of samarium diiodide toward [(HN₃N)ReOX]. The divalent lanthanide reagent has attracted much interest in organic transformations as a mild one-electron reducing



Scheme 1

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Scheme 2 Synthesis of [(N₃N)ReI] (2)

agent [35-37]. In addition to the reducing capability, we figured that the oxophilicity of the lanthanide metal should facilitate oxygen transfer from rhenium to samarium.

Here, we describe the reaction of samarium diiodide with [(HN₃N)ReOCl] [31] producing several rhenium complexes in the oxidation states III to V. Moreover, in one of them the ligand is involved in an intramolecular C-F bond activation producing a complex with a rhenium fluorine bond.

Results and Discussion

Treatment of a THF solution of green [(HN₃N)ReOX] (1) with excess samarium diiodide (0.1 M in THF) at room temperature for 12 hours gave a brown solution. After evaporation of the solvent and extraction of the resulting brown powder, red crystals of $[(N_3N)ReI]$ (2) could be isolated in 17 % yield (Scheme 2). The compound is paramagnetic analogous to previously described [(N₃N)ReCl], which was prepared employing the tantalum compound [TaCHCMe₂PhCl₃(THF)₂] [31]. Due to the paramagnetism and the unsymmetric ligand, characterization of compound 2 by NMR spectroscopy proved to be difficult. However, mass spectrometry showing a peak at m/z= 969 with the correct isotopic pattern for [M]⁺ and CHN analysis confirm the formation of the iodide. In addition, storage of a toluene solution of 2 at $-25 \,^{\circ}\text{C}$ produced single crystals suitable for X-ray diffraction analysis allowing the determination of its molecular structure.

In the formation of complex 2, SmI_2 plays presumably a twin role by reducing the rhenium center and by acting as



Figure 1 Molecular view of $[(N_3N)ReI]$ (2). Hydrogen atoms have been omitted for clarity.

the oxygen acceptor. The redox reaction was apparent by the initial disappearance of the typical blue color of Sm^{II} solutions. Samarium diiodide has been widely used in organic synthesis employing ketones and other oxygen containing reagents in reductive cross-coupling reactions [35–37].

The molecular structure of **2** is shown in Figure 1, while selected bond lengths and angles are given in Table 1 and crystallographic data in Table 2. The structure is similar to $[\{(C_6F_5NCH_2CH_2)_3N\}ReX]$ (X = 40 % Cl, 60 % Br) that contains the symmetrical tren ligand [33]. The influence of the additional CH₂ group in **2** on the geometry at the metal center is negligible as shown by the bond lengths and angles listed in Table 1, even though the six-membered metallacy-cle formed by the coordinated propylene amido group has an expected larger N_{ax} -Re- N_{eq} angle (N2-Re1-N4 89.9(4)° compared to N1-Re1-N4 84.3(4)° and N3-Re1-N4 80.9(3)°). The Re1-I2 bond length is with 2.723(1) Å in a similar range as in the few other crystallographically analyzed rhenium(IV) complexes that contain a Re-I bond [38, 39].

We further investigated the reaction shown in Scheme 2 by varying the amount of added samarium diiodide as well as the reaction time. Thus, treatment of a THF solution of





Figure 2 Molecular view of compound [(HN₃N)ReOI] (3).

[(HN₃N)ReOCl] with one equivalent SmI₂ at room temperature for one hour gave also a brown solution. However, after work up a mixture of a brown paramagnetic and a green diamagnetic compound was obtained. The former proved to be complex **2**, whereas the green species analyzed as [(HN₃N)ReOI] (**3**) as shown in Scheme 3. ¹H and ¹⁹F NMR spectroscopy data are consistent with the formulation of **3** and are similar to those of **1**. Moreover, the green needles proved to be suitable for single crystal X-ray diffraction analysis confirming the proposed structure.

The smaller amount of SmI_2 leads only to partial reduction. The oxo iodide compound **3** represents the substitution product, where the chlorine is replaced by an iodine atom delivered by the samarium reagent. The electron impact mass spectrum shows the molecular ions of **2** and **3**, respectively, but gives no indication of unreacted **1**. This is intriguing as substitution reaction at the Re^V=O center are kinetically hindered [40]. This has been verified by refluxing **1** with excess NaI in acetonitrile, the inorganic analogue

to the Finkelstein reaction [41]. After one week, ¹H NMR spectroscopy revealed still only 85% conversion to **3**. Therefore, in the reaction involving samarium(II) a redox process is presumably involved catalyzing the substitution reaction. Separation of complexes **2** and **3** by crystallization was not possible as they always co-crystallized in various solvent mixtures. However, by exposing samples containing mixtures of **2** and **3** to the laboratory atmosphere, pure **3** could be isolated after work up (Scheme 3).

The molecular structure of **3** determined by X-ray structure analysis shows the metal atom in a trigonal bipyramidal environment with the iodide and the central nitrogen N4 in the apical position thereby forcing the oxygen atom in the equatorial position preventing coordination of the third substituent (Figure 2). Analogous structural situations are found in the structures of **1** as well as of $[{(C_6F_5NCH_2CH_2)_2NMe}ReOCI]$ [31, 42]. The Re–I bond distance compares well with previously reported lengths of this type [43, 44].

Table 1 Selected Bond Lengths/Å and Angles/° of Compounds $[(N_3N)ReI]$ (2), $[\{(C_6F_5NCH_2CH_2)_3N\}ReX](X = Cl \ 0.6, Br \ 0.4)[33]$ and $[(HN_3N)ReOI]$ (3).

| [(N ₃ N)ReI] (2) | | [{(C ₆ F ₅ NCH ₂ CH ₂) ₃ N}ReX] [33] | [(HN ₃ N)ReOI] (3) | |
|--------------------------------------|----------|--|-------------------------------|------------|
| Re1-I2 | 2.723(1) | | Re-I | 2.684(1) |
| Re1-N1 | 1.913(8) | 1.940(8) | Re-N1 | 1.958(3) |
| Re1-N2 | 1.945(8) | 1.913(8) | Re-N2 | 1.954(3) |
| Re1-N3 | 1.930(7) | 1.917(8) | Re-N4 | 2.161(3) |
| Re1-N4 | 2.147(9) | 2.173(8) | Re-O1 | 1.694(3) |
| N1-Re1-N2 | 118.7(3) | 117.1(3) | N1-Re-N2 | 118.58(14) |
| N1-Re1-N3 | 117.5(3) | 116.0(3) | N2-Re-N4 | 79.23(12) |
| N3-Re1-N2 | 121.6(3) | 120.2(4) | N1-Re-N4 | 80.13(12) |
| N1-Re1-N4 | 84.3(4) | | O1-Re-N4 | 98.60(12) |
| N2-Re1-N4 | 89.9(4) | | O1-Re-I | 99.80(9) |
| N3-Re1-N4 | 80.9(3) | | N4-Re-I | 161.60(8) |
| N4-Re1-I2 | 175.7(3) | | | |

Table 2 Crystallographic Data and Structure Refinement of 2, 3 and 4

| | 2 | 3.0.5 C-H. | 4 |
|---|-------------------------------|---------------------------|--|
| М | 1244.90 | 1031.58 | 1003.60 |
| Formula | $C_{46}H_{38}F_{15}IN_4Re$ | C_{28} 5H19F15IN4ORe | $C_{32}H_{22}F_{14} {}_{35}I_{0} {}_{65}N_4Re$ |
| <i>T</i> /K | 133(2) | 133(2) | 133(2) |
| Crystal system | monoclinic | triclinic | monoclinic |
| Space group | $P2_1/c$ | $P\overline{1}$ | $P2_1/c$ |
| alÅ | 11.754(2) | 8.5068(7) | 16.0605(6) |
| b/Å | 17.786(4) | 12.1953(11) | 12.4985(6) |
| c/Å | 22.019(4) | 15.5134(13) | 16.6479(6) |
| α/° | | 86.203(7) | |
| βl° | 100.56(3) | 85.963(7) | 106.512(3) |
| γ/° | | 78.296(7) | |
| $U/Å^3$ | 4525.1(16) | 1569.8(2) | 3204.0(2) |
| Ζ | 4 | 2 | 4 |
| $D_{\rm c}/{\rm mg}{\rm m}^{-3}$ | 1.827 | 2.182 | 2.081 |
| μ/mm^{-1} | 3.468 | 4.976 | 4.532 |
| F(000) | 2420 | 978 | 1922 |
| 20/Range/° | 1.88 to 22.51 | 2.10 to 24.63 | 2.07 to 24.68 |
| Measured reflections | 28421 | 34349 | 97528 |
| Unique reflections | $5899 (R_{\rm int} = 0.0925)$ | $5256 (R_{int} = 0.0761)$ | 5421 ($R_{\rm int} = 0.0765$) |
| Observed reflections | 4004 | 5003 | 5347 |
| $[I > 2\sigma(I)]$ | | | |
| Data / restraints / parameters | 5899 / 0 / 439 | 5256 / 0 / 441 | 5421 / 0 / 477 |
| Goodness-of-fit on F^2 | 0.911 | 1.092 | 1.135 |
| Final <i>R</i> indices $[I > 2\sigma(I)]$ | R1 = 0.0447, wR2 = 0.0877 | R1 = 0.0228, wR2 = 0.0657 | R1 = 0.0313, wR2 = 0.0803 |
| R indices (all data) | R1 = 0.0776, wR2 = 0.0954 | R1 = 0.0241, wR2 = 0.0662 | R1 = 0.0317, wR2 = 0.0805 |
| Largest diff. peak, hole / e $Å^{-3}$ | 1.319 and -0.712 | 1.515 and -1.234 | 1.356 and -0.987 |

In one of several attempts to separate 2 and 3 by crystallisation, few additional red crystals appeared in cold toluene solutions which were shown to be the remarkable rhenium(IV) compound [(HN_3N^*)ReX] (4) (X = 0.35 F, $0.65 \text{ I}; \text{HN}_3\text{N}^* = (\{C_6F_5\text{NCH}_2\text{CH}_2\}_2\text{NCH}_2\text{CH}_2\text{CH}_2\text{NHC}_6$ $(F_4)^{3-}$) as shown in Figure 3. Since we were unable to crystallize further samples of this compound we can offer no corroborative evidence for its formulation, but a brief discussion is included here because of its unusual nature. In the C_6F_5 group attached to the propylene substituent C-F bond activation occurred in ortho position forming a 4membered metallacycle with a metal carbon and a metal nitrogen bond. The hydrogen atom at nitrogen remains bound. Thus, the ligand can be considered trianionic and pentacoordinate. Furthermore, a fluoride ligand, which is partially substituted by iodide is coordinated to the metal atom. Therefore, the formal oxidation state of the metal can be considered Re^{IV}.

The proton attached to N3 was located in difference Fourier maps and refined. Furthermore, the angles about N3 show a pyramidal geometry (see inset in Figure 3) rather than a planar one as for N1 and N2 and the N3-Re bond length (2.279(5) Å) is significantly longer than the amido rhenium bond lengths (1.93 – 1.98 Å). The coordination at the rhenium atom is distorted octahedral with the halide ligand in apical position. The crystal chosen for X-ray crystallography was composed of 35 % [(HN₃N*)ReF] and 65 % [(HN₃N*)ReI], since refinement of the axial position as 0.35 F and 0.65 I gave a structure of high quality. The thus determined bond lengths of Re–F and Re–I are 2.108(13) and 2.688(1)Å, respectively. The Re–F bond is slightly longer than that of [PNP]₂[ReFBr₅] (PNP = Ph₃P= N=PPh₃)⁺, Re–F 1.976(3) Å), the only other X-ray crystal



Figure 3 Molecular structure of $[(HN_3N^*)ReX]$ (4) (X = 0.35 F, 0.65 I) showing both the fluoride and iodide ligand. The inset shows the pyramidal N3 atom within the metallacylce. Hydrogen atoms have been omitted for clarity except the H atom at N3. Selected bond lengths/Å and angles/° of 4:

Re-I 2.688(1), Re-F 2.108(13), Re-N1 1.981(5), Re-N2 1.925(5), Re-N3 2.279(5), Re-N4 2.177(4), Re-C21 2.154(6), N3-Re-C21 62.5(2), N4-Re-I 170.88(13).

structure of a rhenium(IV) compound with a Re-F bond deposited with the Cambridge Crystallographic Data Centre [45]. The Re-C bond lengths is with 2.154(6) Å in the same range as in previously reported rhenium compounds containing a Re-C₆F₅ unit [46, 47].

The mechanism of the C-F bond activation is not clear, but formal oxidative addition of the C-F bond to a reduced rhenium center is likely [48]. Further reactivity involves substitution of the fluoride by iodide, probably due to the abundance of iodide in the reaction solutions. Substitution is probably fast once the rhenium atom is reduced to Re^{IV}. Abstraction of the ortho fluorine atom in a related C₆F₅ substituted amido ligand, (C₆F₅NCH₂CH₂)₂NMe, has previously been observed [42]. By the reaction of $[Mo(NMe_2)_4]$ with $(C_6F_5NHCH_2CH_2)_2NMe$, the molybdenum fluoro complex [{ $(C_6F_4(NMe_2)NCH_2CH_2)_2NMe$ } MoF₂] is formed, where the *ortho* fluorine atom is replaced by a NMe₂ group and the fluorine atom is bound to the metal atom. Thus, the metallacycle formed is 5-membered unlike in 4. The longer propylene substituent in 4 allows the ortho carbon atom to bind to rhenium atom, whereas in the ethylene substituents, the situation would be too strained. In the molybdenum complex, this leads to replacement of the ortho fluorine atom by NMe2. In both cases, the existence of a C-F bond in *ortho* position leads to noninnocent behavior of the ligand, a fact that might be responsible for the obtained low yields of the reactions described in this report and should be taken into consideration for future design of such ligands.

Conclusion

This report demonstrates that excess samarium diiodide reduces [(HN₃N)ReOCl] to [(HN₃N)ReI]. Lower ratios of samarium to rhenium leads to partial reduction and additionally to substitution of the chloride by an iodide ligand forming [(HN₃N)ReOI]. The yields are lowered by side reactions involving C-F bond activation in *ortho* position of the C₆F₅ group attached to the propylene substituent.

Experimental Section

All manipulations were carried out under dry nitrogen using standard Schlenk line or glove box techniques. All solvents were purified by standard methods and distilled under a nitrogen atmosphere immediately prior to use. [(HN₃N)ReOCI] was prepared according to the literature procedure [31]. All other chemicals mentioned were used as purchased from commercial sources.

Samples for mass spectrometry were measured on a BIO-RAD Digilab FTS-7 mass spectrometer with a Finnigan MAT 95 and all NMR spectra on a Bruker Avance 500 or 200. Elemental analyses were performed by the Analytisches-Chemisches Laboratorium des Instituts für Anorganische Chemie, Göttingen.

[(N₃N)ReI] (2). To a solution of 0.44 g (0.5 mmol) of [(HN₃N)Re-OCI] in 15 mL of THF was added by syringe a solution of SmI_2 (0.1 M in THF, 13,3 mL, 1.3 mmol) at room temperature. The solution was stirred for 12 h, whereby the color turned gradually from

green to brown-red. The solvent was evaporated, 50 mL of toluene were added and the solution was filtered through a pad of Celite. The thus obtained brown solution was evaporated to approximately 10 mL and stored at -25 °C. The product crystallized as red needles suitable for X-ray crystal analysis (81 mg, 17 %). – MS(EI): m/z (%) 969 (100, [M]⁺). – Anal. calcd for C₂₅H₁₄F₁₅IN₄Re (968.49): Calcd. C 31.00, H 1.46, N 5.78. Found: C 31.81, H 1.55, N, 5.71.

[(HN₃N)ReOI] (3). To a solution of 0.57 g (0.64 mmol) of [(HN₃N)ReOCI] in 15 mL of THF was added by syringe a solution of SmI₂ (0.1 M in THF, 6.4 mL, 0.64 mmol) at room temperature. The solution was stirred for 1 hour, whereby the color turned gradually from green to brown. The solvent was evaporated, 50 mL of toluene were added and the solution was filtered through a pad of Celite. The thus obtained brown solution was exposed to the laboratory atmosphere for 10 minutes, filtered, evaporated to approximately 10 mL and stored at -25 °C. The product crystallized as green needles, that were suitable for X-ray crystal analysis (Yield: 62 mg, 10 %). C₂₅H₁₅F₁₅IN₄ORe (985.5): Calcd. C 30.47, H 1.53, N 5.69. Found: C 30.65, H 1.53, N 5.53 %.

¹**H NMR** (CD₃CN): δ 4.5 (br s, 1 H, NH), 4.21 (m, 2 H), 3.59 (m, 2 H), 3.34 (m, 6 H), 3.12 (m, 2 H), 2.14 (m, 2 H, NHCH₂CH₂CH₂N). – ¹⁹**F NMR** (CD₃CN): δ 14.9 (m, 4 H, ReNC₆F_{ortho}), 3.75 (m, 2 F, HNC₆F_{meta}), 1.61 (t, 2 F, ³J_{FF} = 21 Hz, HNC₆F_{ortho}), -2.3 – -2.8 (m, 6 F, ReNC₆F_{para} and ReNC₆F_{meta}), -10.56 (tt, 1 F, ³J_{FF} = 22 Hz, ⁴J_{FF} = 7 Hz, HNC₆F_{para}). – **MS(EI)**: *mlz* (%) 986 (100, M⁺).

X-ray crystallographic determinations

Crystals of compounds **2**, **3** and **4** were taken from the solution, covered with oil and mounted on glass fibres at room temperature. Data were collected on a Stoe IPDS II-array detector system instrument with graphite-monochromated Mo-K α radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods using SHELXS-97[49] and refined against F^2 on all data by full-matrix least-squares with SHELXL-97 [50]. All non-hydrogen atoms were refined anisotropically. For **4**, the hydrogen atom H3N was located in difference Fourier maps and refined. All other hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model.

Crystallographic data (excluding structure factors) for the structures have been deposited with the Cambridge Crystallographic Data Centre as a supplementary publication no. CCCD 262729 (2), 262728 (3) and 262727 (4). Copies of the data can be obtained free of charge on application to CCDC, 12 union Road, Cambridge CB21EZ, UK (fax: +(44)1223-336-033; email: deposit@ccdc.cam.ac.uk).

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