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Synthesis of Cationic Oxorhenium Salen Complexes via μ-Oxo Abstraction and Their Activity in Catalytic Reductions

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Cationic oxorhenium salen complexes are prepared by the abstraction of bridging oxo ligands with $[Et_3Si][B(C_6F_5)_4]$ and $[Ph_3C][B(C_6F_5)_4]$. These complexes catalyze the reduction of 2-butanone with Et_3SiH under ambient conditions.

Rhenium complexes incorporating tetradentate bis(salicylideneamine) ligands, salenes, have been known for some time and have been developed primarily as catalysts for oxygen atom transfer reactions.[1−5] The cationic oxorhenium oxazoline complex $[Re(O)(hoz)_2(CH_3CN)][B(C_6F_5)_4]$ (**1**) was recently employed by our group for the dehydrogenative oxidation of organosilanes[6] and hydrosilation of aldehydes and ketones.[7] Struck by the similarity of the oxazoline ligand in **1** to commonly employed salen ligands, we attempted to synthesize oxorhenium salen complexes that could similarly be used for hydrosilation reactions and other metal-catalyzed reductions.

Cationic complexes of transition metals are widely used in catalytic processes. A classic example is the use of cationic group 4 complexes in olefin polymerization reactions. These complexes are typically generated when transition-metal alkyls or hydrides are abstracted with salts of weakly coordinating borate anions, such as $B(C_6F_5)_4^-$, or with Lewis acids, such as $B(C_6F_5)_3$.[8] Recently, the generation of iridium and rhenium cations with $[Et_3Si][B(C_6F_5)_4]$ was reported by Heinekey and co-workers.[9−11] For this reaction, the silylium cation is generated in situ and the driving force is the formation of the Si−Cl bond. This method was also employed by us in order to generate the cationic oxorhenium catalyst **1**.[6,7]

During the course of our studies, we discovered that complex **1** can also be generated by the direct abstraction of a chloride with $[Ph_3C][B(C_6F_5)_4]$ (Scheme 1). To date and to the best of our knowledge, the use of a trityl cation in the abstraction of transition-metal halides has not been reported. Consequently, we were interested in the use of this strategy for the generation of new cationic oxorhenium complexes.

In this Communication, we report the generation of oxorhenium cationic complexes via abstraction of bridging oxo ligands from μ-oxorhenium dimers. This reaction as well as the chloride extraction reaction described above presents a facile synthetic strategy for the generation of transition-metal cations from both trityl and silylium salts. Furthermore, this discovery potentially extends the chemistry of transition-metal μ-oxo complexes that were generally thought to be unreactive because of the inertness of the M−O−M bond.[12]

Dimeric oxorhenium complexes have been well documented.[12] The rhenium oxo dimers $Re_2O_3(salen)_2$ (**3**) and $Re_2O_3(salpd)_2$ (**4**) were synthesized in moderate yields by refluxing $ReOCl_3(PPh_3)_2$ in EtOH or MeOH with the appropriate ligand and 2.2 equiv of lutidene (Scheme 2). Contrary to a previous report,[13a] we did not observe the formation of rhenium alkoxy species. Further, NMR, mass

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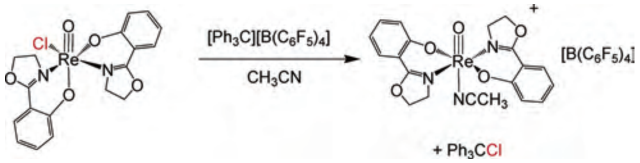
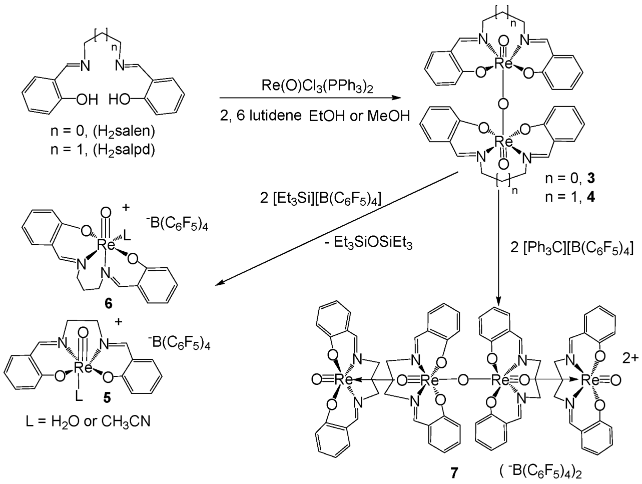
Scheme 1



Scheme 2



spectrometry, elemental analysis, and X-ray crystallography are all consistent with the formation of **3** and **4**.

Treatment of these complexes with 2 equiv of $[Et_3Si][B(C_6F_5)_4]$ results in the abstraction of the bridging oxo ligand and the formation of $Et_3SiOSiEt_3$ and the new oxorhenium cationic complexes $[ReO(salen)(L)][B(C_6F_5)_4]$ (**5**) and $[ReO(salpd)(L)][B(C_6F_5)_4]$ (**6**), where L = H_2O or CH_3CN (Scheme 2).

While complexes incorporating salen ligands are well-known, complexes **5** and **6** are the first examples of cationic group 7 metal complexes with these ligands. The stereochemistry of these complexes depends on the nature of the bridging group.[14] Complex **6** shows ^1H NMR resonances at 8.37 (s, 1H, *H*C═N) and 8.14 (s, 1H, *H*C═N) ppm in addition to five resonances for the propyl bridge. Broad signals were observed for the methylene protons α to the C═N group at 4.79 (1H), 4.53 (1H), 4.41 (1H), and 3.95 (1H) ppm. A broad signal at 2.48 ppm (2H) was observed for the central methylene protons. These assignments suggest that the molecule possesses C_1 symmetry in solution, with a coordinating solvent molecule occupying a coordination site cis to the Re═O bond (Scheme 2). In contrast, complex **5** shows a single ^1H NMR resonance at 8.71 ppm (s, 2H, *H*C═N) and a resonance for the ethyl bridge at 4.42 ppm (br s, 4H). Thus, unlike complex **6**, the coordinating solvent molecule in **5** occupies a coordination site trans to the Re═O bond. The difference in these two geometries presumably arises from the inability of the parent salen ligand with an ethyl bridge to adopt the cis conformation (Scheme 2).

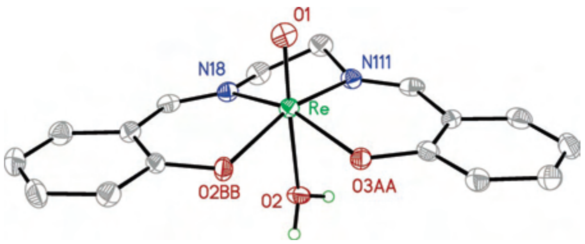


Figure 1. X-ray crystal structure for **5**. The anion and hydrogen atoms are removed for clarity; 50% ellipsoids are shown on selected atoms. Selected bond lengths (Å) and angles (deg): Re−O(1), 1.664(3); Re−O(2), 2.276(3); Re−N(18), 2.050(3); Re−N(111), 2.041(3); O(1)−Re−O(2), 175.82(11); O(1)−Re−O(3AA), 100.98(12); O(1)−Re−N(18), 102.04(13).

Our assignment of the geometry for **5** was confirmed by an X-ray molecular structure determination. X-ray-quality crystals were obtained by slow diffusion of hexanes into a concentrated CH_2Cl_2 solution of complex **5** at room temperature (Figure 1). The geometry of **5** is that of a distorted octahedron, with the salen ligand occupying the equatorial plane. The Re═O bond length [Re−O(1) 1.664(3) Å] is consistent with a Re−O multiple bond.[15] The Re−OH_2 bond is long [Re−O(2) 2.276(3) Å], reflecting the strong trans influence of the oxo ligand. In contrast, the Re−O bonds to the salen ligand are 1.976(2) Å [Re−O(2BB)] and 1.999(2) Å [Re−O(3AA)].

Treatment of **4** with 2 equiv of $[Ph_3C][B(C_6F_5)_4]$ in methylene chloride resulted in the dicationic complex $[Re_4O_5(salpd)_4][B(C_6F_5)_4)_2]$ (**7**; Figure 2 and Scheme 2). X-ray-quality crystals of this compound were obtained by slow evaporation of a concentrated CH_2Cl_2 solution at room temperature. Complex **7** features two $[ReO(salpd)]^+$ monomeric cations that are bridged by the oxorhenium dimer **4**. The central O(2)═Re(2)−O(3)−Re(2)═O(2) unit consists of short Re═O(2) bonds [1.753(2) Å] and long Re(2)−O(3) bonds [1.884(1) Å]. These bonds are within the normal range for Re complexes possessing the O═M−O−M═O core.[15] The terminal Re═O(1) bonds [1.676(3) Å] are also within the normal range for multiply bonded rhenium oxo complexes. However, the Re(1)$\leftarrow$O(2) bonds are long [2.122(2) Å], which is consistent with the description of two cationic Re═O monomers bridged by a O═Re−O−Re═O dimer.

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(14) Synthesis and characterization of **5** and **6**. $[ReO(salen)(L)][B(C_6F_5)_4]$ (**5**): Et_3SiH (8.4 μL, 0.05 mmol) was added to an acetonitrile solution of $[Ph_3C][B(C_6F_5)_4]$ (0.048 g, 0.05 mmol). This solution was added to an acetonitrile solution of **3** (0.025 g, 0.026 mmol), and the mixture was stirred for 30 min. The organic products, $Et_3SiOSiEt_3$ and Ph_3CH, were extracted with hexanes, and their presence was confirmed by gas chromatography/mass spectrometry (GC/MS). The solvent from the residual green solution was removed in vacuo to yield **5** as a brown precipitate in 95% yield. ^1H NMR (300 MHz, CD_2Cl_2): δ 8.71 (s, 2H, HC═N), 7.82 (br, 2H, aromatic C−H), 7.62 (br, 2H, aromatic C−H), 7.37 (br, 2H, aromatic C−H), 7.18 (br, 2H, aromatic C−H), 4.42 (br s, 4H, ethyl bridge). HRMS (ESI$^+$). Calcd for $C_{16}H_{14}N_2O_3Re$: 467.0534. Found: 467.0532. $[ReO(salpd)(L)][B(C_6F_5)_4]$ (**6**): Et_3SiH (6.39 μL, 0.04 mmol) was added to an acetonitrile solution of $[Ph_3C][B(C_6F_5)_4]$ (0.037 g, 0.04 mmol). This solution was added to an acetonitrile solution of **4** (0.020 g, 0.020 mmol), and the mixture was stirred for 30 min. The organic products, $Et_3SiOSiEt_3$ and Ph_3CH, were extracted with hexanes, and their presence was confirmed by GC/MS. The solvent from the residual green solution was removed in vacuo to yield **6** as a brown precipitate in 95% yield. ^1H NMR (300 MHz, CD_2Cl_2): δ 8.37 (s, 1H, HC═N), 8.14 (s, 1H, HC═N), 7.86 (br, 1H, aromatic C−H), 7.60 (br, 3H, aromatic C−H), 7.35 (br, 2H, aromatic C−H), 7.15 (br, 2H, aromatic C−H), 4.79 (br, 1H, α-CH_2), 4.53 (br, 1H, α-CH_2), 4.41 (br, 1H, α-CH_2), 3.95 (br, 1H, α-CH_2) 2.48 (br, 2H, β-CH_2). HRMS (ESI$^+$). Calcd for $C_{17}H_{16}N_2O_3Re$: 481.0691. Found: 481.0690.

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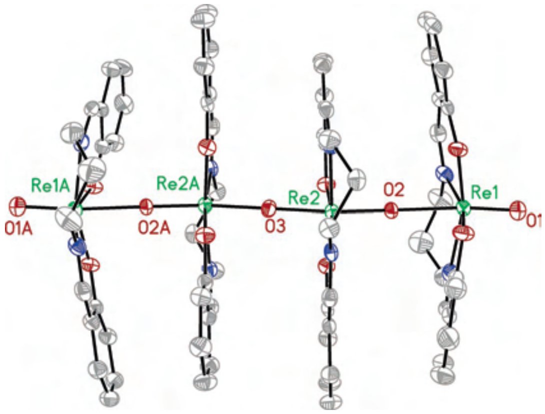
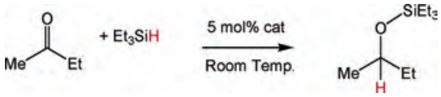


Figure 2. Structure of **7**. The anions and hydrogen atoms are removed for clarity; 50% ellipsoids are shown on selected atoms. Selected bond lengths (Å): Re(1)−O(1), 1.676(3); Re(1)−O(2), 2.122(2); Re(2)−O(2), 1.753(2); Re(2)−O(3), 1.884(1).

Scheme 3



Analysis of the organic products of the reaction described in the synthesis of **7** (Scheme 2) revealed the presence of benzophenone, triphenylmethanol, and phenol. These products result from the abstraction of the bridging oxo ligand.

As noted earlier, we have recently reported on the catalytic activity of **1** for the hydrosilation of aldehydes and ketones.[7,16] We examined the potential of the rhenium(V) oxo complexes **3**−**7** as catalysts for the hydrosilation of 2-butanone with Et_3SiH using 5 mol % catalyst loading under ambient conditions (Scheme 3). The results of the catalytic hydrosilation of 2-butanone with complexes **3**−**7** are summarized in Table 1. The neutral dimeric complexes **3** and **4** are not active. This result demonstrates the need for an open coordination site on rhenium for catalysis and suggests that Si−H activation via addition across the Re═O bond is not applicable in these systems.[7,16c] However, complexes **5**−**7** are effective hydrosilation catalysts. The most effective catalyst from the group appears to be the propyl-bridged salen complex **6**. The tetrameric complex **7** shows activity, as would be expected because it contains the monomeric cation $Re(O)(salpd)^+$. The activity of **7** is less than those of the monomeric complexes **5** and **6** because this tetramer contains the inactive dimer **4** (vide supra). Thus, in solution, the bridging dimer **4** likely dissociates from the monomeric cation $Re(O)(salpd)^+$, providing an open coordination site for catalysis.

Table 1. Catalytic Hydrosilation of 2-Butanone with Et_3SiH^a

catalyst	% conversion	time/h
$Re_2O_3(salen)_2$ (**3**)	NR	6
$Re_2O_3(salpd)_2$ (**4**)	NR	6
$[ReO(salen)(L)][B(C_6F_5)_4]$ (**5**)	100	6
$[ReO(salpd)(L)][B(C_6F_5)_4]$ (**6**)	100	0.5
$[Re_4O_5(salpd)_4{}^2][(B(C_6F_5)_4)_2]$ (**7**)	66	0.5

[a] Conditions: 0.05 mmol of 2-butanone, 1.5 equiv of Et_3SiH, 5 mol % catalyst in 0.65 mL of CD_2Cl_2 at ambient temperature. NR = no reaction. L = H_2O or CH_3CN. Yields of $H_3CC(H)(OSiEt_3)CH_2CH_3$ were quantitative (100%).

In conclusion, we have demonstrated a new synthetic method for the preparation of cationic oxorhenium hydrosilation catalysts by the abstraction of chloride and bridging oxo ligands with $[Ph_3C][B(C_6F_5)_4]$ as well as with $[Et_3Si][B(C_6F_5)_4]$. The latter reaction extends the chemistry of transition-metal μ-oxo complexes that were generally thought to be unreactive because of the inertness and stability of the M−O−M bond. Using this method, monomeric cationic complexes of other transition metals that are prone to forming μ-oxo complexes, such as Fe, Mn, and Mo, might become accessible.[3,5,12,17]

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Supporting Information Available: Synthesis and characterization for compounds **3**−**7**, full X-ray experimental details, ORTEP diagrams, tables of bond lengths and angles, and CIF files for **5** and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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