Inorg. Chem. **2006**, *45*, 8477–8479

Inorganic Chemistry
Communication

An Isolable, Nonreducible High-Valent Manganese(V) Imido Corrolazine Complex

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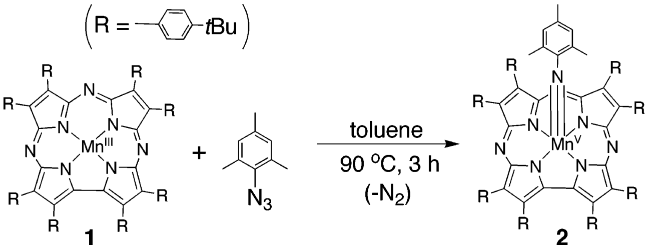
Received May 27, 2006

The manganese(V) imido complex [(TBP$_8$Cz)Mn^V(NMes)] (**2**) was synthesized from the Mn^{III} complex [(TBP$_8$Cz)Mn^{III}] (**1**) and thermolysis of mesityl azide. An X-ray structure of **2** reveals a short Mn–N distance [1.595(4) Å], consistent with the Mn–N triple bond expected for a manganese(V) imido species. This high-valent species is remarkably inert to one- and two-electron reductive processes such as NR group transfer to alkenes or H-atom abstraction from O–H bonds. Electrochemical studies support this lack of reactivity. In contrast, oxidation of **2** is easily accomplished by treatment with [(4-BrC$_6$H$_4$)$_3$N]$^{•+}$SbCl$_6$, giving a π-radical-cation complex.

High-valent Mn complexes have been postulated as the active intermediates in many synthetic and biologically relevant transformations. For example, Mn^V terminal oxo species have been invoked as the key oxidizing intermediates in epoxidations and hydroxylations.[1] However, the direct characterization or isolation of such species has only been accomplished in a few cases.[2] We recently synthesized one example of a stable Mn^V terminal oxo complex by using the corrolazine platform.[3] Even more elusive has been the definitive characterization of an isolectronic manganese(V) imido complex, of which only one example is known, the corrole complex [(tpfc)Mn^V(NMes)] [tpfc = tris(pentafluorophenyl)corrole].[4] Manganese(V) imido and related nitrido species have been implicated as key intermediates in NR group transfer reactions,[5] and thus their direct characterization is of interest. More generally, the synthesis of mid- to late-transition-metal imido complexes has been challenging, and only recently have well-characterized examples appeared.[6] Herein we report the synthesis of the Mn^V terminal imido complex [(TBP$_8$Cz)Mn^V(NMes)] [**2**; TBP$_8$Cz = octakis(*p-tert*-butylphenyl)corrolazinato]. Structural characterization reveals a short, linear Mn–N triple bond for the imido ligand. This complex is remarkably resistant to either one- or two-electron reductive processes, even though it contains a high-valent Mn^V center.

Scheme 1



The synthesis of the manganese(V) imido complex was accomplished by heating mesityl azide with [(TBP$_8$Cz)Mn^{III}] (**1**) in toluene (Scheme 1), following the method established for [(tpfc)Mn^V(NMes)].[4] This method presumably involves

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10.1021/ic0609251 CCC: $33.50
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Published on Web 09/16/2006

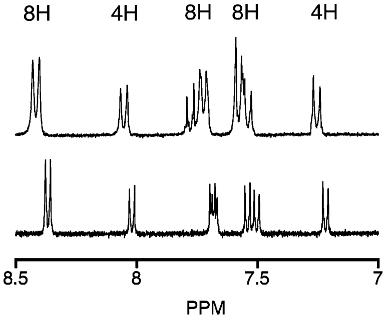

Figure 1. ^{1}H NMR spectra of **2** (bottom) and **3** (top) in CD$_2$Cl$_2$.

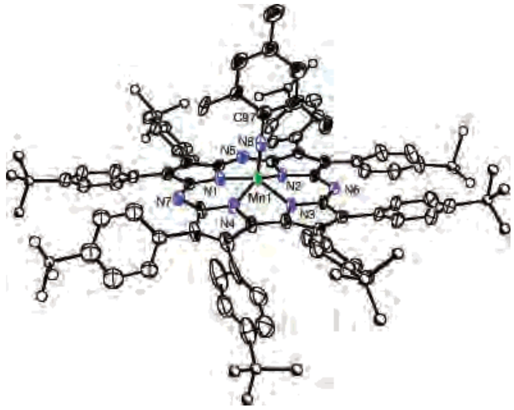

Figure 2. ORTEP diagram of **2** at the 50% probability level. H atoms are not shown for clarity.

capture of a nitrene intermediate by the Mn^{III} complex,[7] resulting in oxidation of the Mn center to Mn^{V} and release of N$_2$. The reaction was easily monitored by thin-layer chromatography and UV−vis, indicating loss of the starting material and production of the manganese(V) imido complex (**2**). After evaporation of the solvent, the resulting dark-brown solid was purified by column chromatography (silica gel, CH$_2$Cl$_2$) and then washed with CH$_3$CN to remove mesitylamine. Complex **2** was obtained as a dark-green solid in 90% yield.

The aromatic region of the ^{1}H NMR spectrum for **2** is shown in Figure 1. The spectrum is clearly diamagnetic, indicative of a low-spin Mn^{V} (d^2) species. The phenyl (5.74 ppm) and *o*-methyl (−0.05 ppm) peaks (not shown) for the NMes ligand are shifted upfield because of ring current effects. The eight doublets appearing between 7.2 and 8.4 ppm are assigned to the four types of inequivalent para-substituted *tert*-butylphenyl substituents. Three sets of doublets overlap, resulting in an integration ratio of 8:4:8:8:4. A similar aromatic pattern of doublets in a 8:4:8:8:4 ratio is found for the isoelectronic manganese(V) oxo complex (**3**; Figure 1). The phenyl protons do not display magnetic inequivalence based upon their orientation with respect to the axial mesitylimido or oxo ligands, implying that there is free rotation about the C(pyrrole)−C(phenyl) bonds in both compounds. Variable-temperature ^{1}H NMR experiments (198−300 K) for **2** reveal only some line broadening at the lowest temperature reached.[8]

In addition to the NMR spectrum, the UV−vis, matrix-assisted laser desorption ionization mass spectrometry, and elemental analysis for **2** are all consistent with the proposed structure. Confirmation of this structure was obtained by X-ray crystallography, and an ORTEP diagram for **2** is shown in Figure 2. The crystal structure contains two independent molecules per asymmetric unit, and only one molecule is shown in Figure 2. The independent molecules are oriented in slipped dimer pairs, with the imido axial ligands pointing away from each other. However, the Mn−Mn distance is 10.0150(11) Å, indicating that the two Cz rings are not in a position for π-stacking interactions. The Mn−N$_{imido}$ distances are 1.595(4) and 1.611(4) Å for the two independent molecules. Such short distances are consistent with a Mn−N triple bond. The corrole complexes (tpfc)Mn^{V}(NMes) and (tpfc)Cr^{V}(NMes)[4] exhibit M−N bond lengths of 1.613(4) and 1.635(2) Å, respectively, both of which are slightly longer than those found for **2**. For [(TBP$_8$Cz)Mn^{V}(O)] (**3**), the Mn−O distance from extended X-ray absorption fine structure data [1.56(2) Å] is slightly shorter than the Mn−N$_{imido}$ distance, as is expected for the less sterically encumbered terminal oxo ligand. The Mn−N$_{imido}$−C angle for **2** [179.7(4)°, 176.9(4)°] is closer to linearity than those for (tpfc)Mn^{V}(NMes) [170.4(4)°] and (tpfc)Cr^{V}(NMes) (169.59(18)°) and, taken together with the slightly shorter Mn−N$_{imido}$ distance in **2**, suggests that there may be stronger π overlap between the terminal imido ligand and the empty metal d$_{xz}$/d$_{yz}$ orbitals for the corrolazine complex. The Mn−N$_{pyrrole}$ distances in **2** range from 1.869(4) to 1.907(4) Å and are similar to the Mn−N$_{pyrrole}$ distances [average = 1.884(7) Å] in the Mn^{III}Cz complex [(TBP$_8$Cz)Mn^{III}(HOMe)],[3b] despite the higher oxidation state for **2**. The Mn−N$_{pyrrole}$ distances for the manganese(v) imido corrole complex [1.891(4)−1.947(4) Å] are longer than those in **2** and likely reflect the larger cavity size of the corrole ligand. The Mn ion sits 0.55 Å above the mean plane of the four pyrrole N atoms in both independent molecules of **2**, which is slightly greater than the displacement of the Mn ion in (tpfc)Mn^{V}(NMes) (Mn−N$_{plane}$ = 0.513 Å).

Attempted reactions of **2** with alkene substrates did not lead to aziridine products. For example, prolonged heating of **2** with excess cyclooctene in toluene afforded only the starting imido complex. Other alkenes (e.g., *cis*-stilbene, styrene) were equally unreactive. The manganese(V) oxo complex **3** shows a similar lack of reactivity toward alkenes to give epoxides, a formal two-electron process. However, we have recently shown that **3** is capable of the one-electron process of abstracting a H atom from O−H bonds (e.g., substituted phenols) and weak C−H bonds (e.g., cyclohexadiene). Kinetic studies of these reactions showed that they proceed through an H-atom transfer (HAT) mechanism.[9] By analogy with **3**, we speculated that the imido complex **2** should be capable of H-atom abstraction even though it does not effect the two-electron oxidation of alkene to aziridine.

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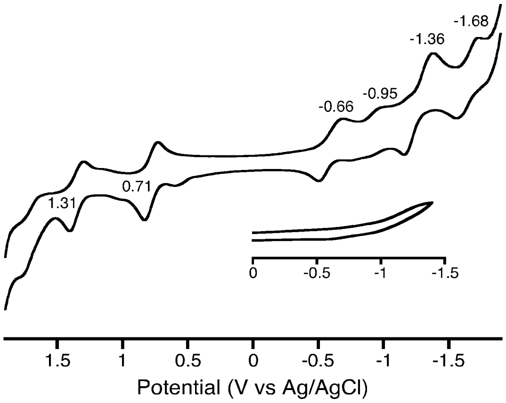

Figure 3. Cyclic voltammogram of **2** in CH_2Cl_2 at a scan rate of 50 mV/s. Inset: First cycle from 0 to −1.4 V.

Interestingly, **2** was found to be completely unreactive toward H-atom donors such as C_6H_5OH, 2,4-di-*tert*-butylphenol, and even TEMPO-H. The latter substrate has an O−H bond dissociation energy (BDE) of 70 kcal/mol,[10] which is even lower than that of the phenol substrates (BDE = 78−83 kcal/mol)[11] and indicates that it is a highly reactive H-atom donor. The absence of reactivity toward TEMPO-H shows that the manganese(V) imido complex is incapable of even weak H-atom abstraction.

To shed more light on this lack of reactivity for **2**, electrochemical measurements were carried out as shown in Figure 3. The cyclic voltammogram reveals two quasi-reversible oxidations centered at 0.71 and 1.31 V and irreversible reductions at −1.36 and −1.68 V. The peaks at −0.66 and −0.49 V appear only after an initial scan is carried out past −1.3 V, indicating that these peaks are not from the original imido complex but rather from one or more species generated by reduction beyond −1.3 V. A clean single sweep between 0 and −1.3 V reveals no electrochemical activity (inset, Figure 3), confirming that complex **2** is not reduced until at least −1.3 V! In support of these results, we have found that **2** does not react with an excess of cobaltocene ($E^{1/2} = -0.95$ V).[12,13] Thus, although **2** is formally a high-valent Mn^V species, it is remarkably resistant to reduction. In contrast, the manganese(V) oxo complex **3** exhibits a Mn^V/Mn^{IV} couple at −0.05 V,[3b,13] and the analogous redox couple for (tpfc)Mn^V(NMes) appears at −0.36 V.[4b] The first irreversible reduction observed at −1.36 V for **2** is assigned to a corrolazine ring reduction, $Cz/Cz^{\bullet -}$, based on electrochemical and spectroelectrochemical data for other metallocorrolazines including manganese(III) and manganese(V) oxo complexes.[3]

The complete absence of H-atom abstraction reactivity for **2** is understandable in light of the electrochemical data because the thermodynamic driving force for this reaction, in part, needs to come from the ease of the Mn^V/Mn^{IV} reduction.[9] Because the Mn^V/Mn^{IV} reduction is not accessible, the thermodynamic affinity of **2** for an H atom is exceedingly low.

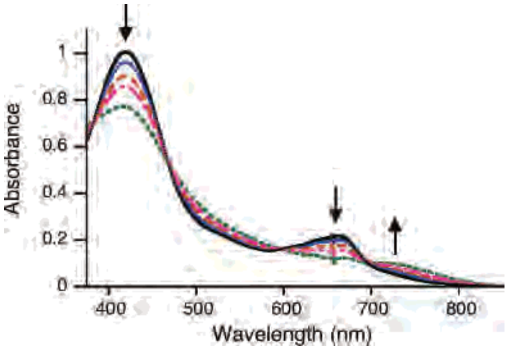

Figure 4. UV−vis spectrum of the reaction between **2** and $[(4\text{-}BrC_6H_4)_3N]^{\bullet +}SbCl_6$.

Although reductive transformations appear to be out of reach for **2**, the cyclic voltammetry data show a reversible oxidation at 0.71 V, indicating that **2** could be reversibly oxidized with an appropriate chemical oxidant. In comparison, the manganese(V) oxo complex **3** is not oxidized until 1.02 V, and (tpfc)Mn^V(NMes) exhibits an oxidation at 1.21 V. Reaction of **2** with the one-electron oxidant $[(4\text{-}BrC_6H_4)_3N]^{\bullet +}SbCl_6$ ($E^{1/2} = 1.16$ V)[12] results in isosbestic conversion of the UV−vis spectrum for **2**, as shown in Figure 4. The original spectrum is restored upon the addition of 1 equiv of Cp_2Co, indicating that the oxidation is fully reversible. Characterization of the oxidized product by EPR spectroscopy (Figure S1 in the Supporting Information) shows a sharp singlet at $g = 2.006$ ($\Delta H = 25$ G) and no hyperfine splitting from Mn. This spectrum is indicative of a corrolazine π-radical-cation ($[(TBP_8Cz^{\bullet +})Mn^V(NMes)]$).

In summary, the first example of a manganese(V) imido corrolazine complex has been synthesized and structurally characterized. The X-ray structure and NMR data show conclusively that **2** is a bona fide high-valent Mn^V (low-spin, d^2) complex. However, **2** is extremely resistant to reduction via electron transfer, NR group transfer, or HAT. It is much more difficult to reduce, and easier to oxidize, than the isoelectronic terminal oxo complex **3**. This discrepancy may arise from significantly better π overlap between the imido ligand and Mn^V as compared to an oxo ligand. Complex **2** is even more difficult to reduce than the corrole analogue, which is surprising because the electron-withdrawing *meso*-N atoms of corrolazines are expected to make Cz complexes *easier* to reduce than their corrole counterparts.[14] In the case of **2**, we suggest that the “pull” effect of the *meso*-N atoms is more than counterbalanced by a strong “push” effect from the π donation of the terminal imido ligand.

Acknowledgment. The NSF (Grants CHE0094095 and CHE0606614) is gratefully acknowledged for support of this work.

Supporting Information Available: Synthetic details and EPR (PDF) and X-ray crystallographic data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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