High Oxidation State Rhenium Cp* Complexes Containing Hydrazine, Hydrazido, Ammonia, and Amido Ligands

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Received March 18, 1991

Summary: Paramagnetic ReCp*Me$_4$ reacts with triflic acid to give ReCp*Me$_3$(OTf) (**1**) in 90% yield. Hydrazine reacts with **1** to give diamagnetic [ReCp*Me$_3$(NH$_2$NH$_2$)]$^+$OTf$^-$ (**2**), which is deprotonated to give ReCp*Me$_3$(NHNH$_2$) (**3**) in good yield. **1** also reacts with ammonia to give [ReCp*Me$_3$(NH$_3$)$_2$]$^+$OTf$^-$ (**4**), which is deprotonated to give ammonia and ReCp*Me$_3$(NH$_2$) (**5**). Addition of triflic acid to **5** yields [ReCp*Me$_3$(NH$_3$)]$^+$OTf$^-$ (**6**). Reduction of **2** in the presence of 2,6-lutidine hydrochloride in THF yields 1.20 equiv of ammonia, using zinc amalgam, and 1.46 equiv of ammonia, using 0.5% sodium amalgam. In the absence of protons, reduction of **2** by zinc amalgam gives 1.00 equiv of ammonia.

We have shown recently that (i) addition of one electron to d^1 complexes of the type [MCp*Me$_3$(η^2-NH$_2$NH$_2$)]$^+$ (M = Mo or W; Cp* = η^5-C$_5$Me$_5$) results in the splitting of the N–N bond, (ii) reduction of these complexes in the presence of protons gives 1.85 equiv of ammonia, and (iii) hydrazine can be reduced catalytically to ammonia in the presence of protons in yields between 80 and 95%.[1] In order to determine whether this chemistry is unique to W and Mo (and therefore of special relevance to the reduction of dinitrogen by Mo nitrogenases), and in order to observe and characterize by NMR spectroscopy types of species that are paramagnetic in the Mo and W systems, we sought to synthesize several isostructural Re complexes.

ReCp*Me$_4$[2] reacts with triflic acid in diethyl ether to give yellow ReCp*Me$_3$(OTf) (1) in greater than 90% yield.[3] Unlike paramagnetic d^2 ReCp*Me$_4$, 1 is diamagnetic with an unusually low field resonance (in toluene-d_8) for the methyl protons at 7.8 ppm (Cp* protons at 1.3 ppm). At −95 °C the methyl resonance is shifted and split into two broadened resonances at 3.0 and 2.5 ppm in a ratio of 1:2, consistent with inequivalent methyl groups in a square pyramid or a trigonal bipyramid possessing an apical methyl ligand. Similar behavior is observed in CD$_2$Cl$_2$. We speculate that the large temperature dependence of the chemical shifts of the methyl groups can be ascribed to a thermally populated paramagnetic state; the species also may be fluxional on the NMR time scale, or triflate may be dissociating, even in toluene. Comparison of IR data for cationic complexes in which OTf is the counterion with those for group VI complexes[4] that contain covalently bound triflate suggests that the absorption for ionic triflate is found 80–100 cm^{-1} toward higher energy than when the triflate is covalent. By this criterion the IR spectrum of 1 is consistent with covalently bound triflate, at least in the solid state.

Hydrazine reacts with 1 in ether as shown in eq 1.[5] The ^{1}H NMR spectrum in CD$_2$Cl$_2$ of pale orange diamagnetic 2 contains broadened singlet resonances for the hydrazine

$$1 \xrightarrow{N_2H_4} \underset{75\%\ \text{yield}}{[\text{ReCp*Me}_3(\text{NH}_2\text{NH}_2)]^+\text{OTf}^-\ (2)} \xrightleftharpoons[\text{HOTf}]{\text{DBU}} \underset{80\%\ \text{yield}}{\text{ReCp*Me}_3(\text{NHNH}_2)\ (3)} \quad (1)$$

protons at 5.7 ppm and 6.4 ppm. On the basis of these data alone we cannot discriminate between the η^1 and η^2 binding modes or, if it is bound in an η^2 manner, determine which of two possible pseudooctahedral structures is correct. The IR spectrum of 2 is identical with structurally characterized [WCp*Me$_3$(η^2-N$_2$H$_4$)]OTf,[1] in which one nitrogen atom in the hydrazine ligand is trans to the Cp* ring. It should be noted that although 2 contains two d electrons it does not undergo N–N bond cleavage to give hypothetical [ReCp*Me$_3$(NH)]$^+$ and ammonia (cf. the proposed mechanism of N–N bond cleavage in d^2 WCp*Me$_3$(η^2-NH$_2$NH$_2$) to produce WCp*Me$_3$(NH) and ammonia[1]). Deprotonation of 2 by DBU yields dimagnetic ReCp*Me$_3$(NHNH$_2$) (3) in good yield.[6] Decomposition of 2 over a period of several hours at room temperature in dichloromethane also yields 3 in <50% yield. (No other product of this reaction has been observed by NMR spectroscopy.) 3 displays a 1:2 pattern of proton resonances characteristic of a hydrazido(1−) ligand[7] at 8.2 and 6.0 ppm, respectively, in CD$_2$Cl$_2$ at room temperature, and is protonated by HOTf to give 2.

The reaction between 1 and ammonia yields 4 (eq 2),[8] which can be deprotonated by triethylamine to give 5.[9] The fact that the ammonia ligands in 4 are equivalent (δ 2.8 ppm) at 25 °C and at −95 °C suggests either that they

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[1] Schrock, R. R.; Glassman, T. E.; Vale, M. G. *J. Am. Chem. Soc.* **1991**, *113*, 725.

[2] (a) Floel, M.; Herdtweck, E.; Wagner, W.; Kulpe, J.; Haerter, P.; Herrmann, W. W. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 787. (b) Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1297.

[3] ReCp*Me$_4$ (0.830 g, 2.18 mmol) was dissolved in 50 mL of ether at −40 °C in the dark. Triflic acid (0.193 mL, 2.18 mmol) was added directly to the stirred solution. Gas evolution was evident. After 30 min the dark orange-yellow solution was filtered and the filtrate was cooled to −40 °C for several hours. The yellow microcrystalline solid was filtered off, and the mother liquor was concentrated and cooled to −40 °C to give additional crops; total yield 1.03 g (1.99 mmol, 91%).

[4] Glassman, T. E.; Vale, M. G.; Schrock, R. R. *Organometallics*, submitted for publication.

[5] ReCp*Me$_3$(OTf) (0.300 g, 0.572 mmol) was dissolved in 20 mL of ether at room temperature to form a dark orange solution. Hydrazine (0.018 mL, 0.570 mmol) was added directly to the stirred solution. A light orange precipitate formed within 30 s. After 5 min a pale orange solid was isolated from the reaction mixture by filtration. It was washed with ether and dried in vacuo; yield 0.235 g (0.429 mmol, 75%).

[6] [ReCp*Me$_3$(N$_2$H$_4$)][OTf] (0.300 g, 0.548 mmol) was suspended in 20 mL of cold ether. DBU (78 μL, 0.522 mmol) was added to the stirred solution. The reaction mixture immediately turned dark yellow-orange. After 15 min the reaction mixture was filtered and the solvent was removed in vacuo from the dark orange filtrate to yield a tan-orange solid, which was washed with cold pentane. An orange solution was decanted off and the tan solid was dried in vacuo; yield 0.170 g (0.428 mmol, 82%).

[7] Liu, A. H.; O'Regan, M. B.; Finch, W. C.; Payack, J. F.; Schrock, R. R. *Inorg. Chem.* **1988**, *27*, 3574.

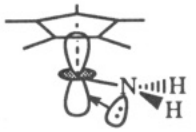
[8] ReCp*Me$_3$(OTf) (0.600 g, 1.17 mmol) was dissolved in 50 mL of ether. The solution was subjected to three freeze–pump–thaw cycles on a high-vacuum line and then frozen in liquid nitrogen. Ammonia (4.66 mmol) was condensed into the reaction flask, which was then warmed to room temperature while the solution was stirred vigorously. A yellow precipitate appeared within 30 s. After 5 min the solvent was removed in vacuo to give a yellow solid. The reaction flask was brought into the drybox where the solid was washed with ether, collected by filtration and dried in vacuo; yield 0.516 g (0.938 mmol, 81%).

[9] [ReCp*Me$_3$(NH$_3$)$_2$][OTf] (0.415 g, 0.903 mmol) was dissolved in 50 mL of THF at −40 °C, and triethylamine (0.503 mL, 3.61 mmol) was added. The reaction mixture was stirred for 1.5 h, and the solvent was then removed in vacuo from the green-yellow reaction mixture. The residue was extracted with pentane and filtered. Solvent was removed from the green filtrate in vacuo to give a green powder that was recrystallized from pentane; yield 0.211 g (0.640 mmol, 71%).

0276-7333/91/2310-1661$02.50/0

$$1 \xrightarrow{2NH_3} \underset{80\%\ \text{yield}}{[ReCp^*Me_3(NH_3)_2]^+OTf^-}\ (4) \xrightarrow[-NEt_3\cdot HOTf,\ -NH_3]{NEt_3} \underset{70\%\ \text{yield}}{ReCp^*Me_3(NH_2)}\ (5) \quad (2)$$

are equivalent in pseudooctahedral **4** or (less likely) that they are exchanging rapidly on the NMR time scale, even at −95 °C. If the former explanation is correct then the structure would not be analogous to that known for $[WCp^*Me_3(\eta^2\text{-}N_2H_4)]OTf$.[1] The amido protons in **5** at −80 °C are equivalent. They would be inequivalent if the lone pair on nitrogen were donated into an empty orbital ($\sim d_{xy}$) that points between the ligands in a square pyramid.[10] Perhaps the d_{xy} orbital contains the two d electrons and the lone pair is donated into what is approximately a d_{z^2} orbital, viz.



It is also possible that the π bond is especially weak, regardless of how it is formed, and rotation about the Re–N bond therefore rapid on the NMR time scale under all conditions employed. Addition of triflic acid to **5** in ether yields $[ReCp^*Me_3(NH_3)]OTf$ (**6**).[11] The proton NMR spectrum of **6** in CD_2Cl_2 shows an unusual temperature-dependent paramagnetic contribution to the chemical shifts, a situation related to that noted above for **1**; resonances are found (at 20 °C in CD_2Cl_2) at 16.02 (Me), 14.60 (2 Me), 10.20 (NH_3), and 2.15 ppm (Cp*) and (at −80 °C) at 5.00 (NH_3), 4.30 (Me), 2.90 (2 Me), and 1.70 ppm (Cp*).

Reduction of **2** by 87% zinc amalgam in the presence of 2,6-lutidine hydrochloride in THF reproducibly yields 1.20 equiv of ammonia. Reduction of **2** using 0.5% sodium amalgam (in the presence of lut·HCl) produced 1.46 equiv of ammonia, while reduction using zinc amalgam in the absence of protons produced 1.00 equiv of ammonia. These experiments suggest that the N–N bond can be cleaved in neutral d^3 $ReCp^*Me_3(NH_2NH_2)$ but that the resulting $ReCp^*Me_3(NH)$ is not efficiently protonated and reduced to give the second equivalent of ammonia under conditions employed so far.

We conclude that high-oxidation complexes containing the $ReCp^*Me_3$ core and NH_x or N_2H_y ligands are reasonably stable and that N–N bond cleavage in $ReCp^*Me_3(NH_2NH_2)$ may be a controlled reaction, as it is in $MCp^*Me_3(\eta^2\text{-}NH_2NH_2)$ (M = Mo, W).[1] Future studies will be aimed at expanding chemistry that is relevant to the reduction of dinitrogen and comparing and contrasting it with analogous chemistry of complexes containing the MCp^*Me_3 core where M = Mo or W.[1,7,12]

Acknowledgment. R.R.S. thanks the National Institutes of Health for support through Grant GM 31978, and M.G.V. thanks the National Science Foundation for a predoctoral fellowship and C.C. Cummins for valuable discussions.

Supplementary Material Available: Textual description of syntheses, IR and NMR data, and analytical data (3 pages). Ordering information is given on any current masthead page.

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[10] Kubacek, P.; Hoffmann, R.; Havlas, Z. *Organometallics* **1982**, *1*, 180.

[11] $ReCp^*Me_3(NH_2)$ (0.150 g, 0.392 mmol) was dissolved in 10 mL of ether at −40 °C. Triflic acid (0.035 mL, 0.392 mmol) was added directly to the stirred dark green solution. A yellow precipitate formed immediately. After 10 min the yellow solid was filtered off, washed with ether, and dried in vacuo; yield 0.125 g (0.230 mmol, 60%).

[12] O'Regan, M. B.; Liu, A. H.; Finch, W. C.; Schrock, R. R.; Davis, W. M. *J. Am. Chem. Soc.* **1990**, *112*, 4331. (c) Schrock, R. R.; Kolodzieg, R. M.; Liu, A. H.; Davis, W. M.; Vale, M. G. *J. Am. Chem. Soc.* **1990**, *112*, 4338.

Site-Selective Oxidative-Addition Reactions in a Heterometallic Octanuclear Carbido Cluster Compound. A Reactivity Parallel with Mononuclear Indenyliridium Complexes

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Received February 26, 1991

Summary: The reactions of triphenylsilane and allyl bromide with $[PPN]_2[Re_7C(CO)_{21}Ir(C_8H_{14})(CO)]$ in refluxing THF afforded products in which the substrates were added selectively to the iridium center. The products $[PPN]_2[Re_7C(CO)_{21}Ir(H)(CO)(SiPh_3)]$ (**1**) (77%) and $[PPN][Re_7C(CO)_{21}Ir(\eta^3\text{-}C_3H_5(CO)]$ (**2**) (40%) were characterized by analytical and spectroscopic data. The analogous reactions in refluxing cyclohexane with the indenyl complex $(\eta^5\text{-}C_9H_7)Ir(C_8H_{14})(CO)$ yielded $(\eta^5\text{-}C_9H_7)Ir(H)(CO)(SiPh_3)$ (**3**) (78%) and $[(\eta^5\text{-}C_9H_7)Ir(\eta^3\text{-}C_3H_5)(CO)]Br$ (**4**) (86%), respectively, which were similarly characterized. No reactions with the cyclopentadienyl complex $(\eta^5\text{-}C_5H_5)Ir(C_8H_{14})(CO)$ were observed under similar or more severe conditions.

There is an isolobal analogy between the cyclopentadienide ion and a triangular face of a polyhedral metal cluster in terms of their coordination by a metal complex fragment.[1] Motivated by this concept, we have prepared compounds of the formula $[Re_7C(CO)_{21}ML_n]^{2-}$,[2] which are complexes between the metal fragments $[ML_n]^+$ and the carbide cluster compound $[Re_7C(CO)_{21}]^{3-}$,[3] that

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[1] (a) Mingos, D. M. P.; Wales, D. J. *Introduction to Cluster Chemistry*; Grimes, R. N., Ed.; Prentice Hall: Englewood Cliffs, NJ, 1990. (b) Mingos, D. M. P.; Forsyth, M. I. *J. Chem. Soc., Dalton Trans.* **1977**, 610.

[2] (a) Henly, T. J.; Shapley, J. R. *Organometallics* **1989**, *8*, 2729. (b) Henly, T. J.; Shapley, J. R.; Rheingold, A. L.; Geib, S. J. *Organometallics* **1988**, *7*, 441. (c) Henly, T. J.; Wilson, S. R.; Shapley, J. R. *Inorg. Chem.* **1988**, *27*, 2551. (d) Henly, T. J.; Shapley, J. R.; Rheingold, A. L. *J. Organomet. Chem.* **1986**, *310*, 55.

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