11584 *J. Am. Chem. Soc.* **1994,** *116,* 11584−11585

Dihydrogen Complexes of Tetraammineosmium(II) with Carbene as Coligand: Facile Hydrogen Transfer from Cyclic Ethers to the Metal Center

Zai-Wei Li and Henry Taube*

*Department of Chemistry, Stanford University
Stanford, California 94305*

Received April 4, 1994

Since the announcement by Kubas[1] and co-workers of the discovery of dihydrogen complexes, reports on additional examples of this class have appeared at a rapid pace.[2] We recently reported[3] a series of tetraammineosmium dihydrogen complexes $[Os^{II}N_4(\eta^2\text{-}H_2)L]$ (N_4 = en$_2$ or $(NH_3)_4$; L is a variable ligand) which can be formed by facile substitution of a suitable oxygen donor ligand by a wide variety of N, S, or O donors and described some aspects of their reactivity. With certain strong π acids as donors, however, H_2 gas is released.

The precursors to this series of dihydrogen complexes are prepared by the reduction of suitable tetraammineosmium(III) species by Zn/Hg in protic solvents. By the simple variation of using a cyclic ether rather than water or methanol as reaction medium, we have found that reduction of $Os^{III}(NH_3)_4(CF_3SO_3)_3$ (**1**)[4] leads to a dihydrogen complex which has as coligand in the cis position a carbene derived from the cyclic ether.

When **1** (100 mg) is reduced in THF (3 mL) at room temperature (25 °C) with granular Zn/Hg, the solution develops a yellow color. By treating the solution with ether, after 15 min a yellow solid (74 mg) is obtained (yield 84%). The ^1H NMR spectrum of the product, **2**, shows three broadened ammine peaks at 4.33 (3H), 3.93 (6H), and 3.44 (3H) ppm and the hydridic peak at −6.29 (2H) ppm (Figure 1a). The dihydrogen undergoes H−D exchange in acetone-d_6 ($t_{1/2}$ = ca. 36 h, unacidified) to give a clear 1:1:1 triplet with J_{HD} = 22.7 Hz (Figure 1b). (Exchange in the absence of acid also takes place in D_2O, CD_3OD, or CD_3CN, but more slowly than in acetone-d_6.) The values of T_1 (20 °C, 200 MHz) and T_1(min) (−36 °C, 400 MHz) for H_2 were measured as 65 and 21 ms, respectively. The cis geometry[5] of **2** and the presence of η^2-H_2 as ligand are therefore strongly suggested by the ^1H NMR evidence. The signals of the THF residue appear as the characteristic first-order triplet, triplet, and quintet patterns at 4.61 (2H), 2.69 (2H), and 1.92 (2H) ppm, respectively, which indicates a cyclic carbene ligand of the Fischer type.[6a] The ^{13}C NMR spectrum (acetone-d_6), in which the signal of carbene carbon appears at low field (264.4 ppm), far away from the signals of other carbon atoms (80.2, 61.3, and 24.0 ppm) of the ring, is also typical of a cyclic carbene.[6b] A ^1H NOE experiment provided further evidence for the cis geometry. When the H_2 resonance is irradiated, only the resonance at 4.61 ppm ($-OCH_2-$) shows enhancement. On the basis of the NMR evidence and analytical results,[7] we formulate **2** as shown below.

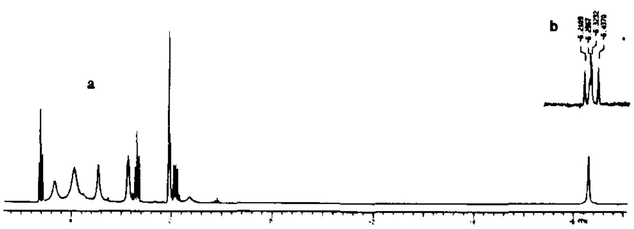
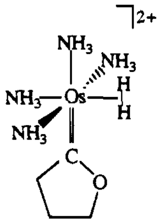


Figure 1. (a) ^1H NMR spectrum of the carbene dihydrogen complex **2** in acetone-d_6 (200 MHz, the peak at 2.85 ppm is from water in the solvent). (b) The Os−(η^2-HD) peak of **2** after H−D exchange in acetone-d_6 (24 h, 25 °C).



To follow the reaction stages, reduction of **1** (0.030 M) was carried out at −20 °C in a medium in which the ratio of THF-d_8 to THF was 17. Under these conditions the cation $[Os(NH_3)_4(CF_3SO_3)_2]^+$ remains intact, and despite being paramagnetic, it shows a prominent broad peak at 9.90 ppm which we assign to ammine protons. With time this shifts to 5.5 ppm and diminishes in intensity. During this phase a new set of peaks in a 1:1:2 ratio develops at 6.52, 5.70, and 5.48 ppm. After 1 h these are replaced by the peaks of the final product (5.48, 4.72, 4.37, 3.78 ppm) in a 1:1:1:1 ratio.[8] Despite the low symmetry suggested by four peaks, δ for η^2-H_2 in THF-d_8 is −6.10 ppm, close to that observed, −6.29 ppm, on dissolving the $CF_3SO_3^-$ salt of **2** in $(CD_3)_2CO$. We interpret the shift in the early reaction phase to rapid electron transfer between trans forms of $Os^{III}(NH_3)_4(CF_3SO_3)_2^+$ and $Os^{II}(NH_3)_4(CF_3SO_3)_2$, the latter isomerizing to a cis form (1:1:2 pattern). No signals attributable to coordinated THF are observed at any reaction stage. While this could be taken to imply reaction of THF by an outer-sphere mode, it is more likely that substitution by THF is a precondition for product formation, but that formation of the final product follows very rapidly on entry of THF into the coordination sphere.

At 25 °C when **2** is dissolved in CD_3CN, the original peaks in the ^1H NMR spectrum decrease with time, yielding to a new set of peaks in the same pattern near the original one.[9] After 2 days the two forms reach equilibrium in the ratio of 1.3:1 (new form to the original). The rate constant of the isomerization

---

[1] Kubas, G. J.; Ryan, R. R.; Swanson, B. I.; Vergamini, P. J.; Wasserman, H. J. *J. Am. Chem. Soc.* **1984**, *106*, 451.

[2] (a) Kubas, G. J. *Acc. Chem. Res.* **1988**, 21, 120. (b) Crabtree, R. H. *Acc. Chem. Res.* **1990**, *23*, 95. (c) Morris, J. H.; Jessop, P. G. *Coord. Chem. Rev.* **1992**, *121*, 155. (d) Heinekey, D. M.; Oldham, W. J., Jr. *Chem. Rev.* **1993**, *93*, 913.

[3] (a) Li, Z.-W.; Taube, H. *J. Am. Chem. Soc.* **1991**, *113*, 8946. (b) Li, Z.-W.; Taube, H. *Science* **1992**, *256*, 210. (c) Li. Z.-W.; Yeh, A.; Taube, H. *J. Am. Chem. Soc.* **1993**, *115*, 10384. (d) Li, Z. -W.; Taube, H. *J. Am. Chem. Soc.* **1994**, *116*, 9506. (e) Li, Z.-W.; Yeh, A.; Taube, H. *Inorg. Chem.* **1994**, *33*, 2874.

[4] Li, Z.-W.; Harman, W. D.; Lay, P. A.; Taube, H. *Inorg. Chem.* **1994**, *33*, 3635.

[5] Because the 1:2:1 pattern of the ammine protons is retained, we believe that trans−cis isomerization as the change in question is unlikely. For a trans configuration to show the 1:2:1 pattern for the ammine protons, the carbene plane must be coplanar with a pair of ammine ligands, a structural feature not found in the two cases thus far reported[5a,b] nor when the coligands are CO.[5c] Moreover, if, as seems likely, for reaction to occur the cyclic ether must be ligated to the metal, it is difficult to see how a trans disposition of fragments derived from it would arise. See: (a) Sundberg, R. J.; Bryan, R. F.; Taylor, I. F.; Taube, H. *J. Am. Chem. Soc.* **1974**, *96*, 381. (b) Krentzien, H. J.; Clarke, M. J.; Taube, H. *Bioinorg. Chem.* **1975**, *4*, 143. (c) Lappert, M. F.; Pye, P. L. *J. Chem. Soc., Dalton Trans.* **1981**, 701 and ref 10.

[6] (a) Casey, C. P. *Chem. Commun.* **1970**, 1220. (b) Bruce, M. I.; Swincer, A. G.; Thomson, B. J.; Wallis, R. C. *Aust. J. Chem.* **1980**, *33*, 2605.

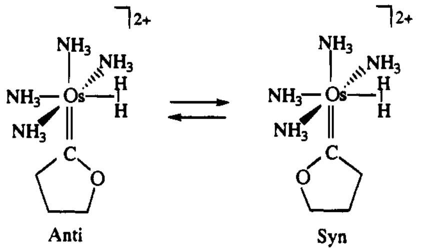
[7] Anal. Calcd for $(NH_3)_4Os(H_2)(CCH_2CH_2CH_2O)(CF_3SO_3)_2$: C, 11.46; H, 3.18; N, 8.91. Found: C, 11.32; H, 3.20; N, 8.61.

[8] The solid recovered from THF reaction solution, when dissolved in $(CD_3)_2CO$, CD_3CN, CD_3OD, or D_2O shows only three ammine peaks in 1:2:1 ratio. The changes in symmetry may arise from distortions which affect the planarity of the carbene ring. See footnote 17.

[9] ^1H NMR data of the isomers of **2** in CD_3CN (ppm). (a) For the original isomer: δ 4.60 (t, 2H, OCH_2), 2.56 (t, 2H, CCH_2), 1.97 (q, 2H, $CH_2CH^*{}_2CH_2O$), 3.72 (s, br, 3H, NH_3), 3.21 (s, br, 6H, $2NH_3$), 2.87 (s, br, 3H, NH_3), −6.69 (s, 2H, Os-H_2). (b) For second isomer: δ 4.67 (t, 2H, OCH_2), 2.65 (t, 2H, CCH_2), 1.94 (q, 2H, $CH_2CH^*{}_2CH_2O$), 3.74 (s, br, 3H, NH_3), 3.20 (s, 6H, $2NH_3$), 3.09 (s, 3H, NH_3), −6.32 (s, 2H, Os-H_2).

0002-7863/94/1516-11584$04.50/0

Scheme 1



was measured as 2.8 × 10^{-5} s^{-1}. By the use of variable temperature ^1H NMR, $\Delta H^{\ddagger}_{298}$ and $\Delta S^{\ddagger}_{298}$ for this process were measured as 21.3 ± 0.4 kcal mol^{-1} and −8.0 ± 0.3 cal mol^{-1} K^{-1}, respectively. (H−D exchange for η^2-H_2 is at least 10 times slower than isomerization). We infer[5] that the net change being observed involves geometric isomerization of **2** in which the carbene plane rotates around the Os=C bond. There are two possible conformational arrangements[10a] in the complex in which the carbene is coplanar with either two cis ammine ligands or the dihydrogen ligand. Studies[10b] of the *cis*-$L(CO)_4M$-carbene systems have shown that the former is more stable. In our system, however, the former can be excluded because rotation by 180° does not yield a new species. The carbene ring in our case is very likely coplanar with the *cis*-H_2 in both isomers and an isomerization from the anti form to the syn form is proposed (Scheme 1). The rotation barrier, $\Delta G^{\ddagger}$, of the carbene ligand was estimated as 23.9 ± 0.5 kcal mol^{-1}. The value we find is in the range of other reported carbene complexes of third-row transition metals[11] and is much higher than that for first-row transition metal complexes.[12]

The first cyclic ether carbene complex was synthesized[13] and structurally characterized[5] 2 or 3 decades ago. The synthesis was indirect, and the direct synthesis from cyclic ethers is unusual. As catalyzed by some transition metal complexes, cyclic ethers commonly undergo α, β hydrogen transfer with the formation of olefins[14] rather than α hydrogen transfer. Very recently Carmona[15] and co-workers reported the first example of the preparation of cyclic carbene complexes by direct α hydrogen activation of cyclic ethers. In their reaction system, however, higher temperature (60 °C) and longer reaction time (8−95 h) were needed than suffice in ours. In contrast, we find that the reductions of **1** in presence of tetrahydropyran[16] and dioxane[17] also take place at room temperature (20−25 °C) and are complete in less than 1 h, giving the α-carbon-coordinated carbene−dihydrogen complexes in good yield (70−80%). Similar experiments with tetrahydrothiophene failed to yield a carbene complex. This failure is ascribable to the high stability of the precursor Os(II) complexes of thioether ligands, which act as π acids. With cyclic amines, paramagnetic products result.

2 is stable in acetonitrile for several days, but in D_2O or CD_3OD it undergoes slow decomposition to paramagnetic species. Most low-valent metal carbene complexes have mainly unsaturated coligands. The carbene in **2**, with ammine and H_2 as coligands, can be expected to lead to novel reaction chemistry. Studies of these complexes are in progress.

Acknowledgment. Support of this work by National Institutes of Health Grant GM13638-27 is gratefully acknowledged.

---

(10) (a) Schubert, U. In *Transition Metal Carbene Complexes*; Dötz, K. H., Fischer, H., Hofmann, P., Kreissl, F. R., Schubert, U., Weiss, K., Eds.; Verlag Chemie: Weinheim, 1983; p 81. (b) Hofmann, P. In *Transition Metal Carbene Complexes*; Dötz, K. H., Fischer, H., Hofmann, P., Kreissl, F. R., Schubert, U., Weiss, K., Eds.; p 113.

(11) (a) Schrock, R. R.; Messerle, L. W.; Wood, C. D.; Guggenberger, L. J. *J. Am. Chem. Soc.* **1978**, *100*, 3793. (b) Toreki, R.; Schrock, R. R.; Davis, W. M. *J. Am. Chem. Soc.* **1992**, *114*, 3367. (c) Kiel, W. A.; Lin, G.-Y.; Constable, A. G.; McCormick, F. B.; Strouse, C. E.; Eisenstein, O.; Gladysz, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 4865.

(12) (a) Brookhart, M.; Tucker, J. R.; Flood, T. C.; Jensen, J. *J. Am. Chem. Soc.* **1980**, *102*, 1203. (b) Kegley, S. E.; Brookhart, M.; Husk, G. R. *Organometallics* **1982**, *1*, 760.

(13) (a) King, R. B. *J. Am. Chem. Soc.* **1963**, *85*, 1922. (b) Casey, C. P. In *Transition Metal Organometallics in Organic Synthesis*; Alper, H., Ed.; Academic Press: New York, 1976; Vol. 1, p 190.

(14) (a) Nishiguchi, T.; Tachi, K.; Fukuzumi, K. *J. Am. Chem. Soc.* **1972**, *94*, 8916. (b) Kolomnikov, I. S.; Kukolev, V. P.; Vol'pin, M. E. *Russ. Chem. Rev.* **1974**, *43*, 399. (c) Johnstone, R. A.; Wilby, A. H. *Chem. Rev.* **1985**, *85*, 129.

(15) (a) Boutry, O.; Gutiérrez, E.; Monge, A.; Nicasio, M. C.; Perez, P.; Carmona, E. *J. Am. Chem. Soc.* **1992**, *114*, 7288. (b) Gutiérrez, E.; Monge, A.; Nicasio, M. C.; Poveda, M. L.; Carmona, E. *J. Am. Chem. Soc.* **1994**, *116*, 791.

(16) ^1H NMR data for the reaction product of **1** with tetrahydropyran (acetone-d_6, ppm): δ 4.49 (t, 2H, OCH_2), 4.28 (s, br, 3H, NH_3), 4.00 (s, br, 6H, $2NH_3$), 3.33 (s, br, 3H, NH3), 2.87 (t, 2H, CCH_2), 1.87 and 1.64 (q, 2H, $CH_2CH^*{}_2CH^*{}_2CH_2$), −6.02 (s, 2H, Os-H_2). J_{HD} = 22.6 Hz, T_1= 56 ms (Os-H_2, 20 °C, 200 MHz).

(17) ^1H NMR data for the reaction product of **1** with dioxane (acetone-d_6, ppm): δ 4.53 (t, 2H, OCH_2), 4.34 (s, br, 3H, NH_3), 4.20 (s, 2H, CCH_2), 4.03 (s, br, 6H, $2NH_3$), 3.93 (t, 2H, OCH_2), 3.46 (s, br, 3H, NH_3), −6.27 (s, 2H, Os-H_2). J_{HD} = 22.2 Hz, T_1 = 54 ms (Os-H_2, 20 °C, 200 MHz). Same product in dioxane-d_8: δ 5.90 (s, br, 3H, NH_3), 5.21 (s, br, 3H, NH_3), 4.68 (s, br, 3H, NH_3), 3.65 (s, br, 3H, NH_3).