proteolysis are not due to severely different substrate binding modes but instead to the association of the scissile carbonyl with either zinc or Arg-127, respectively. In addition, there may also be different rate-determining steps[4] or an altogether different mechanism for sterically hindered substrates.[6]

The synthetic reaction catalyzed by CPA[10,11] recently has been exploited toward the observation of chemical intermediates.[12] The binding mode observed in the ternary complex reported is one which may be mistaken for such an intermediate, and this mode may occur under conditions of excess substrate or product. This binding mode may also occur under conditions of low temperature,[20] where product diffusion may be hindered due to viscosity of the cryobuffer. Nevertheless, such a binding mode could easily confound spectroscopic attempts to identify catalytic intermediates involving a ligand-saturated metal ion.[21]

(20) Kuo, L. C.; Makinen, M. W. *J. Am. Chem. Soc.* **1985**, *107*, 5255–5261.

(21) We thank the National Institutes of Health for Grant GM-06920 in support of this research and also W. R. Grace & Co. for their financial support. Additonally, D.W.C. thanks AT&T Bell Laboratories for a doctoral fellowship.

Selective O-Atom Transfer from Nitrous Oxide to Hydride and Aryl Ligands of Bis(pentamethylcyclopentadienyl)hafnium Derivatives

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One of today's greatest chemical challenges is the selective oxidation of organic substrates.[1] Reagents energetically capable of effecting useful oxidations are often so reactive that indiscriminate attack of the substrate results; others produce byproducts that subsequently become involved in undesirable side reactions. In this light, an attractive oxidant for oxygen-transfer reactions is nitrous oxide, $N=N=O$, a molecule unstable with respect to its constituent elements ($\Delta G_f° = 25$ kcal/mol) and therefore a thermodynamically potent oxidant, yet one possessing impressive kinetic inertness, reflected in a 59-kcal/mol activation barrier for its thermal decomposition (a unimolecular, spin-forbidden process).[2] Importantly, O-atom-transfer reactions involving N_2O could be very clean since the sole byproduct is N_2. With very few exceptions,[3] when N_2O reacts with transition-metal complexes, nitrogen is extruded and oxo complexes are formed (eq 1).[4] It

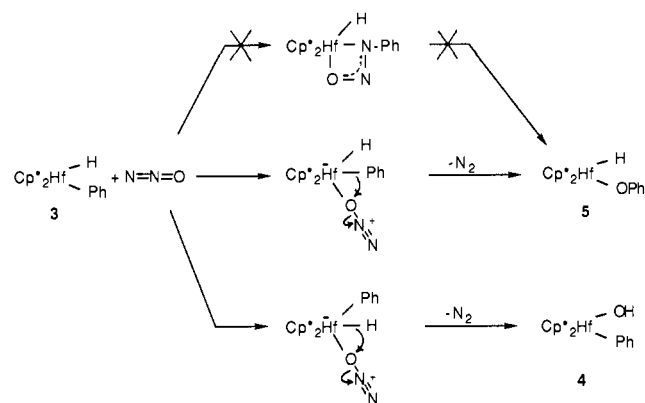$$M^n + N_2O \rightarrow O=M^{n+2} + N_2 \qquad (1)$$
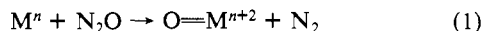
(1) Sheldon, R. A.; Kochi, J. K. *Metal-Catalyzed Oxidations of Organic Compounds*; Academic: New York, 1981.

(2) Jolly, W. L. *The Inorganic Chemistry of Nitrogen*; W. A. Benjamin: New York, 1964; pp 70–71.
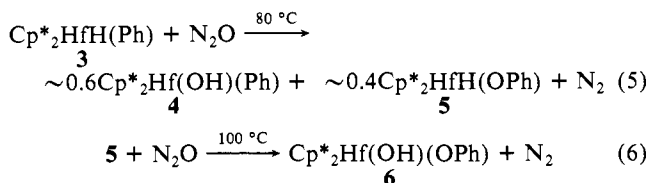
(3) (a) Armor, J. N.; Taube, H. *J. Am. Chem. Soc.* **1969**, *91*, 6874. (b) Armor, J. N.; Taube, H. *Ibid.* **1971**, *93*, 6476. (c) Pu, L. S.; Yamamoto, A.; Ikeda, S. *Chem. Commun.* **1969**, 189. (d) Yamamoto, A.; Kitazume, S.; Pu, L. S.; Ikeda, S. *J. Am. Chem. Soc.* **1971**, *93*, 371. (e) Schrauzer, G. N.; Kiefer, G. W.; Doemeny, P. A.; Kisch, H. *Ibid.* **1973**, *95*, 5582. (f) Sellmann, D.; Kleinschmidt, E. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1977**, *32B*, 795. (g) Cooper, J. N.; Green, M. L. H.; Couldwell, C.; Prout, K. *J. Chem. Soc., Chem. Commun.* **1977**, 145. (h) Banks, R. G. S.; Henderson, R. J.; Pratt, J. M. *J. Chem. Soc. A* **1968**, 2886.

(4) (a) Bottomley, F.; Brintzinger, H. *J. Chem. Soc., Chem. Commun.* **1978**, 234. (b) Bottomley, F.; White, P. S. *Ibid.* **1981**, 28. (c) Bottomley, F.; Lin, I. J. B.; White, P. S. *J. Am. Chem. Soc.* **1981**, *103*, 703. (d) Bottomley, F.; Lin, I. J. B.; Mukaida, M. *Ibid.* **1980**, *102*, 5238. (e) Bottomley, F.; Paez, D. E.; White, P. S. *Ibid.* **1981**, *103*, 5581. (f) Bottomley, F.; Paez, D. E.; White, P. S. *Ibid.* **1982**, *104*, 5651. (g) Liu, H.-F.; Liu, R.-S.; Liew, K. Y.; Johnson, R. E.; Lunsford, J. H. *Ibid.* **1984**, *106*, 4117. (h) Many reports describe chemisorption and catalytic decomposition of N_2O on metal surfaces. For a recent example, see: Tan, S. A.; Grant, R. B.; Lambert, R. M. *J. Catal.* **1987**, *104*, 156.

Scheme I

was our thought that, since the transformation depicted in eq 1 results in an increase in the formal oxidation state of the metal by +2, interesting reactivity between N_2O and coordinated ligands might be observed in d° systems where oxidation at the metal center is precluded. It has been previously shown that organoazides ($N=N=NR$)[5] and diazoalkanes ($N=N=CR_2$),[6] molecules isoelectronic with nitrous oxide, react cleanly with many Group 4 d° metallocene derivatives; we now report that N_2O can be used under mild conditions to selectively oxidize hydrido (to hydroxy) and aryl (to aryloxy) ligands in these systems.

Nitrous oxide reacts at −78 °C with toluene solutions of $Cp*_2HfH_2$ (1)[7] ($Cp* \equiv \eta\text{-}C_5Me_5$) in a 1:1 stoichiometry to afford N_2 and $Cp*_2HfH(OH)$ (2)[8] quantitatively (eq 2).[9] Interestingly,

$$Cp*_2HfH_2 + N=N=O \xrightarrow{-78\ °C} Cp*_2HfH(OH) + N_2 \qquad (2)$$
$$\mathbf{1} \qquad\qquad\qquad\qquad \mathbf{2}$$

no intermediates were detected (^{1}H NMR) for this $1 \rightarrow 2$ conversion, in contrast to the analogous reactions of arylazides with 1 that yield isolable insertion products that subsequently lose N_2 to afford amido species (eq 3).[5a] Diazoalkanes likewise react with 1 but give stable insertion products that are *not* prone to N_2 extrusion (eq 4).[6c] Kinetic measurements (VT ^{1}H NMR) show

$$1 + RN_3 \xrightarrow{0\ °C} Cp*_2HfH(NHNNR) \xrightarrow{80\ °C}$$
$$Cp*_2HfH(NHR) + N_2 \quad (3)$$

$$1 + R_2CN_2 \rightarrow Cp*_2HfH(\eta^2\text{-}NHN=CR_2) \qquad (4)$$

that the reaction in eq 2 is a second-order process with $d[2]/dt \propto [1][N_2O]$; an Eyring plot using data obtained under pseudo-first-order conditions ($[N_2O] \gg [1]$) yielded activation parameters of $\Delta H^\ddagger = 11.7 \pm 0.5$ kcal/mol and $\Delta S^\ddagger = -12 \pm 2$ eu.[9,10] Comparison of these data with measurements on $Cp*_2HfD_2$ ($1\text{-}d_2$) indicated a modest kinetic deuterium isotope effect (at −70 °C, $k_H/k_D = 1.6$ (1)) for the reaction. With an excess of N_2O at higher temperatures (80 °C), 2 reacts further to give a complex mixture containing $Cp*_2Hf(OH)_2$ (~40%).

Treatment of solutions of $Cp*_2HfH(Ph)$ (3)[7] with N_2O (80 °C, 2 h) results in N_2 evolution and competitive oxidation of the hydride and phenyl ligands of 3, cleanly yielding $Cp*_2Hf(OH)(Ph)$ (4) and $Cp*_2HfH(OPh)$ (5) (with no spectroscopically observed intermediates) in a molar ratio of 4:5 = 3:2 (eq 5).[11] At higher

(5) (a) Hillhouse, G. L.; Bercaw, J. E. *Organometallics* **1982**, *1*, 1025. (b) Chiu, K. W.; Wilkinson, G.; Thornton-Pett, M.; Hursthouse, M. B. *Polyhedron* **1984**, *3*, 79.

(6) (a) Gambarotta, S.; Basso-Bert, M.; Floriani, C.; Guastini, C. *J. Chem. Soc., Chem. Commun.* **1982**, 374. (b) Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Inorg. Chem.* **1983**, *22*, 2029. (c) Moore, E. J. Ph.D. Thesis, California Institute of Technology, Pasadena, CA, 1984.

(7) Roddick, D. M.; Fryzuk, M. D.; Seidler, P. F.; Hillhouse, G. L.; Bercaw, J. E. *Organometallics* **1985**, *4*, 97.

(8) Alternatively, 2 can be prepared from 1 and water. Hillhouse, G. L.; Bercaw, J. E. *J. Am. Chem. Soc.* **1984**, *106*, 5472.

(9) Experimental procedures, spectral data, elemental analyses, and kinetic data are given in the Supplementary Material.

(10) The rate was shown to have an approximate first-order dependence on [N_2O], but an exact determination of this was prevented because of the difficulty in quantifying the concentration of nitrous oxide in solution.

temperatures (100 °C) or longer reaction times (12 h) **5** reacts with N_2O to give N_2 and the mixed hydroxyphenoxy complex $Cp*_2Hf(OH)(OPh)$ (**6**),[11] shown in eq 6, but **4** *does not* react with

$$Cp*_2HfH(Ph) + N_2O \xrightarrow{80\ °C}$$
$$\mathbf{3}$$
$$\sim0.6Cp*_2Hf(OH)(Ph) + \sim0.4Cp*_2HfH(OPh) + N_2 \quad (5)$$
$$\mathbf{4} \qquad\qquad\qquad \mathbf{5}$$

$$\mathbf{5} + N_2O \xrightarrow{100\ °C} Cp*_2Hf(OH)(OPh) + N_2 \quad (6)$$
$$\mathbf{6}$$

N_2O below its decomposition temperature (140 °C).[12] The oxidation of the phenyl and hydride ligands of **3** at comparable rates argues against an insertion mechanism for N_2O activation analogous to that seen for RN_3 and R_2CN_2 (eq 3 and 4). While the intermediacy of $[Cp*_2Hf(ONNH)(Ph)]$ in the formation of **4** is plausible, $[Cp*_2HfH(ONNPh)]$ *is not* a reasonable precursor to **5** because of the high activation barrier expected for the required phenyl migration from nitrogen (owing to the multiple bond character inherent in such N–Ph linkages).[13] A more likely mechanism consistent with these data involves initial O-coordination of N_2O to the coordinatively unsaturated Hf center followed by rate-determining hydride (or aryl) migration with concomitant loss of N_2 (Scheme I).[14] The apparent differing modes of interaction for these isoelectronic molecules (N_2O vs. RN_3, R_2CN_2) with Group 4 metallocene derivatives may well be attributable to steric factors.

Since oxygen-transfer reactions using Group 4, d° metals with the common oxidants O_2[15] and *t*-BuOOH (TBHP)[16,17] comprise an important, well-studied class,[18] it is worth noting an interesting feature of these reactions (that contrasts with ours using N_2O): they proceed via intermediate *alkylperoxy ligands and, often, derived radicals*.[15,16] Furthermore, the thermal generation of radicals in these systems can limit their synthetic utility: TBHP converts many $Cp*_2HfR_2$ complexes to the corresponding $Cp*_2Hf(OR)(O-t-Bu)$ but is ineffectual in oxidizing the aryl ligand of **3** due to O–O homolysis of the isolable $Cp*_2Hf(OO-t-Bu)(Ph)$ intermediate to give **4** (compare this with eq 5).[16a]

In summary, these findings are significant because they demonstrate a fundamentally new mode of nitrous oxide reactivity with transition-metal complexes: *direct O-atom transfer from N_2O to metal–ligand bonds* instead of the commonly observed O-abstraction to form metal–oxo species.[4] We are currently exploring the scope of the reactivity of nitrous oxide with other d° organometallic complexes, and these studies will be the topic of future reports.

Supplementary Material Available: Tables of analytical, NMR, and IR data; synthetic and experimental details; and kinetic data (4 pages). Ordering information is given on any current masthead page.

The First Structural Characterization of a Dimeric Lithium Ketone Enolate–Lithium Diisopropylamide Complex

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While attempting to obtain information concerning the effects of chelation on the aggregation state of lithium ketone enolates, we discovered a new dimeric, lithium enolate–lithium amide base complex. We obtained the structure of this dimeric complex by X-ray diffraction analysis. This dimeric complex may occur commonly in solution; hence, the general structure of the dimer is likely to have mechanistic implications in the reaction of ketones with lithium amide bases.

When a heptane solution of the ketone **1** is added to a suspension of freshly prepared lithium diisopropylamide (LDA) in the same solvent, a homogenous solution is formed after only 0.5 equiv of the ketone has been added. If the addition of ketone to the base is stopped after the homogenous solution is obtained and if the reaction mixture is subsequently placed in a freezer maintained at −20 °C, large transparent crystals are obtained. In an alternative procedure, we added a full stoichiometric amount of ketone to the amide base, followed by addition of a second full equivalent of *n*-BuLi. This procedure also yields crystals of the same composition. We carried out low-temperature ($\sim$ −100 °C) diffraction analysis of these crystals according to our standard protocol.[1] The structure of a dimeric, enolate–LDA complex was obtained.[2] This is depicted in Figure 1 as the aggregate **2**.

Two computer generated plots of the dimer are shown in Figure 1 in order to emphasize its stereochemistry. The perspective of the molecule differs by 90° rotation about a horizontal axis in the two plots. In the top plot, the seven-membered chelate rings, made up of an enolate oxygen, a lithium atom, and the silyl ether oxygen, are clearly discernible. In the bottom plot, the slight curvature of the fused, four-membered ring skeleton of the dimer is apparent. It is noteworthy that the silyl ether oxygens coordinate with lithium atoms despite the steric bulk of the *tert*-butyldimethylsilyl group. This coordination is contrary to recent observations that silyl ethers are poor electron donors.[3]

(11) **4**, **5**, and **6** can be prepared independently: $3 + H_2O \rightarrow 4$; $1 + HOPh \rightarrow 5$; $5 + H_2O \rightarrow 6$. See ref 9 for details.

(12) Thermal decomposition with loss of benzene occurs on heating **4** to 140 °C.

(13) (a) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University: Ithaca, NY, 1960; pp 280, 296. (b) Streitwieser, A., Jr.; Heathcock, C. H. *Introduction to Organic Chemistry*, 3rd ed.; Macmillan: New York, 1985; p 691ff.

(14) As pointed out by a referee, there is no precedent for O-coordinated N_2O, but it is reasonable that highly oxophilic early-metal d° centers would promote this binding mode.[14a,b] Nevertheless, initial N-coordination and rearrangement or concerted rearrangement/insertion should be considered as a mechanistic possibility. Attempts to measure an isotope effect using $Cp*_2Hf(D)(Ph)$ resulted in scrambling of the deuterium into the aryl positions *before* O-insertion occurred, suggesting a possible benzyne intermediate in the reaction shown in eq 5.[14c] (a) Tuan, D. F.-T.; Hoffmann, R. *Inorg. Chem.* **1985**, *24*, 871. (b) Bottomley, F.; Brooks, W. V. F. *Ibid.* **1977**, *16*, 501. (c) Vaughan, G. A.; Hillhouse, G. L.; Buchwald, S. L., manuscript in preparation.

(15) (a) Lubben, T. V.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1985**, *107*, 701. (b) Lubben, T. V.; Wolczanski, P. T. *Ibid.* **1987**, *109*, 424. (c) Brindley, P. B.; Scotton, M. J. *J. Chem. Soc., Perkin Trans. 2* **1981**, 419. (d) Blackburn, T. F.; Labinger, J. A.; Schwartz, J. *Tetrahedron Lett.* **1975**, 3041.

(16) (a) van Asselt, A.; Santarsiero, B. D.; Bercaw, J. E. *J. Am. Chem. Soc.* **1986**, *108*, 8291. (b) Sharpless, K. B.; Woodard, S. S.; Finn, M. G. *Pure Appl. Chem.* **1983**, *55*, 1823. (c) Also, ref 18.

(17) Shell process for propylene epoxidation: (a) Sheldon, R. A. In *Aspects of Homogeneous Catalysis*; Ugo, R., Ed.; Reidel: Dordrecht, 1981; Vol. 4, p 3. (b) Shell Oil Br. Patent 1 249 079, 1971. Shell Oil U.S. Patent 3 923 843, 1975.

(18) Applications in organic synthesis: (a) Finn, M. G.; Sharpless, K. B. In *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic: New York, 1985; Vol. 5, p 247. (b) Sharpless, K. B.; Behrens, C. H.; Katsuki, T.; Lee, A. W. M.; Martin, V. S.; Takatani, M.; Viti, S. M.; Walker, F. J.; Woodard, S. S. *Pure Appl. Chem.* **1983**, *55*, 589. (c) Sharpless, K. B.; Verhoeven, T. R. *Aldrichim. Acta* **1979**, *12*, 63.

(1) Williard, P. G.; Carpenter, G. B. *J. Am. Chem. Soc.* **1986**, *108*, 462.

(2) The enolate–LDA complex underwent spontaneous resolution and crystallized in the noncentrosymmetric, monoclinic space group $P2_1$ with unit cell parameters $a = 12.282$ (3) Å, $b = 10.911$ (3) Å, $c = 17.606$ (8) Å, and $\beta = 92.67$ (3)°. The unit cell contained two asymmetric units of molecular formula $[(C_{13}H_{27}SiO_2Li)\cdot(C_6H_{14}NLi)]_2$ in a volume of 2356.8 (1.3) Å^3. This produces a calculated density of 1.01 g·cm^{-3}. A total of 4100 reflections were recorded by using the θ:2θ scan routine and graphite monochromated Mo Kα radiation in the range 3.5° $\leq$ 2θ $\leq$ 45°. The final agreement factors are $R = 0.0414$ and $R_w = 0.0493$ for 450 parameters and 3557 unique, observed reflections. A complete description of the crystallographic parameters is submitted as Supplementary Material.