

# Reactivity of the Coordinated $\eta^2$ -Ketone in the Tropocoronand Complex $[\text{Hf}(\text{TC-3,5})(\eta^2\text{-OC}(\text{CH}_2\text{Ph})_2)]: \text{N-C Coupling, C-C Coupling, and Insertion into the C-O Bond}$

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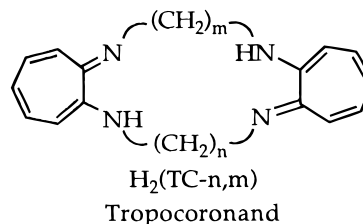
The reactions of  $[\text{Hf}(\text{TC-3,5})(\eta^2\text{-OC}(\text{CH}_2\text{Ph})_2)]$  (**1**) with a variety of substrates are described. Molecules containing conjugated terminal nitrogen atoms, specifically arylazides and diazoalkanes, insert into the metalloxirane unit in a 1,1-fashion to form four-membered chelate rings  $\text{Hf-O-C-N}$  via N-C coupling. Enones and phenyl-substituted ketones react by C-C, pinacolic-type coupling to give the 1,2-addition product of the ketone moiety across the metal-carbon bond,  $\text{Hf-O-C-C-O}$ . Reaction of **1** with simple ketones is notably more complex. With acetone, the product contains a six-membered  $\text{Hf-O-C=C-C-O}$  chelate ring, possibly derived by a  $\beta$ -hydrogen transfer from the  $\eta^2$ -ketone to form the metal hydride, which reacts with substrate to achieve C-C coupling accompanied by loss of  $\text{H}_2$ . Substrates containing nitro groups insert a single oxygen atom into the metalloxirane unit, forming an equivalent of nitrosoalkane or nitrosoarene. In the presence of nitrosoarenes, the resulting four-membered oxametallacycle can react further, undergoing a retro  $[2 + 2]$  cycloaddition to generate an unusual  $\mu\text{-}\eta^2\text{:}\eta^2$  nitrosoarene-bridged dinuclear species. Phenyl isocyanate attacks the C-O bond of the  $\eta^2$ -ketone ligand in **1** giving rise to a coordinated carbamate, perhaps by means of a  $[2 + 2]$  cycloaddition. The products of the reactions were characterized by X-ray crystallography, and plausible mechanisms are suggested for all the coupling reactions.

## Introduction

With the continual improvement of exploration and extraction technologies, the supply of hydrocarbons today is considerably greater than in the "gas crisis" era of the early 1970s.<sup>1</sup> As a consequence, research into the organometallic chemistry of readily available precursors such as CO and  $\text{CO}_2$  has waned in recent years. Nevertheless, the reactions of these  $\text{C}_1$  substrates remains of fundamental interest for many reasons, among them being the need to delineate how they are incorporated as synthons for biomolecules.<sup>2,3</sup> Moreover, the rate of human consumption of hydrocarbons will inevitably exceed that supplied by fossil fuels,<sup>1</sup> and strategies will be required for the manufacture of larger constructs from such simple starting materials. Of particular interest from a synthetic point of view are insertion, coupling, and ligand-migration reactions involving carbon monoxide.<sup>4,5</sup>

In the present article, we have investigated several

insertion and coupling reactions of the metalloxirane core of  $[\text{Hf}(\text{TC-3,5})(\eta^2\text{-OC}(\text{CH}_2\text{Ph})_2)]$  (**1**), where TC-3,5 is the tetraazamacrocyclic tropocoronand depicted below.



Compound **1** forms in nearly quantitative yield by insertion of a single molecule of CO into the two metal-alkyl bonds of  $[\text{Hf}(\text{TC-3,5})(\text{CH}_2\text{Ph})_2]$ . As described previously, dichloromethane, isocyanides, and enones attack the coordinated ketone in **1** to afford a variety of organic fragments (Scheme 1).<sup>6</sup> Further elaboration of this chemistry, described here, includes some remarkable and unprecedented examples of an  $\eta^2$ -ketone ligand

(1) A summary of the supply and regulation of petroleum products in the United States is available on the Internet from Petroleum Supply Monthly at [http://eiainfo.eia.doe.gov/oil\\_gas/psm/psm.html](http://eiainfo.eia.doe.gov/oil_gas/psm/psm.html), and a profile of energy consumption can be found at <http://www.eia.doe.gov/fueloverview.html>.

(2) Holm, R. H.; Kennepohl, P.; Solomon, E. I. *Chem. Rev.* **1996**, *96*, 2239–2314 and references therein.

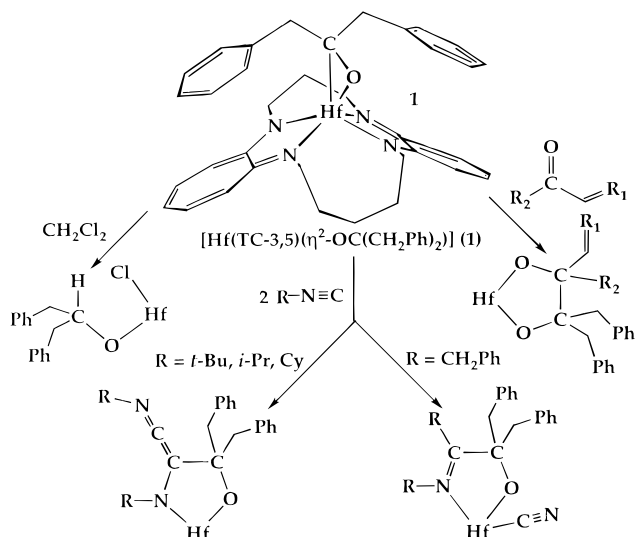
(3) Lippard, S. J.; Berg, J. M. *Principles of Bioinorganic Chemistry*; University Science Books: Mill Valley, CA, 1994.

(4) *Applied Homogenous Catalysis with Organometallic Complexes*; Cornils, B., Hermann, W. A., Eds.; VCH: Weinheim, Germany, 1996.

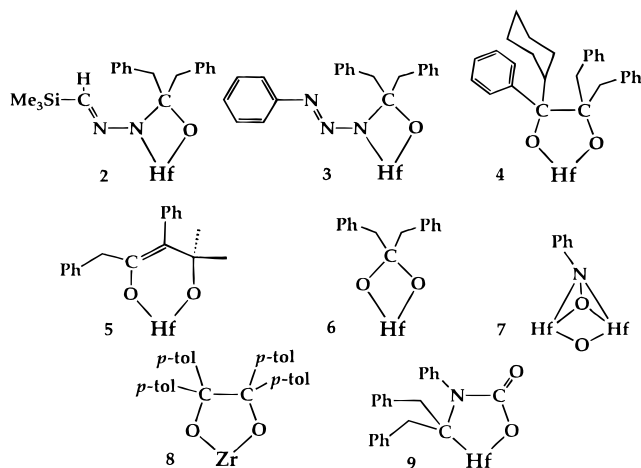
(5) Collmann, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987.

(6) Scott, M. J.; Lippard, S. J. *J. Am. Chem. Soc.* **1997**, *119*, 3411–3412.

Scheme 1



Scheme 2



coupling to acetone, isocyanates, and nitro groups. Scheme 2 depicts the newly obtained fragments and the numbering scheme adopted in this paper.

## Experimental Section

**General Procedures.** The ligand  $\text{H}_2(\text{TC-3,5})^7$  and starting material **1**<sup>6</sup> were prepared as described. All manipulations, excluding ligand preparations, were conducted under a pure dinitrogen or argon atmosphere using standard Schlenk and glovebox techniques. Solvents were dried according to established protocols and were degassed prior to use. Unless otherwise specified, all reagents were obtained from commercial suppliers and were thoroughly degassed and dried before use. NMR spectra were recorded on a Bruker AM-250 at room temperature. Owing to the thermal instability of the tropocoronand complexes in solution at room temperature and their sparing solubility at low temperatures, <sup>13</sup>C NMR data could not be obtained. All compounds were characterized by crystallographic chemical analysis (CCA), and elemental analyses were obtained on representative species. Product yields are reported for the isolated, crystalline materials and were not optimized.

**[(TC-3,5)HfOC(CH<sub>2</sub>Ph)<sub>2</sub>N(N=CHSiMe<sub>3</sub>)] (2).** A 2 M solution of (trimethylsilyl)diazomethane (0.200 mmol) in hex-

ane was added dropwise to a solution of 30 mg (0.041 mmol) of **1** in 1.5 mL of chlorobenzene. As the temperature was raised to 35 °C, the color of the solution slowly turned from red-brown to orange-yellow, and after 30 min the mixture was filtered through Celite. Several volume equivalents of ether were diffused into the filtrate over 48 h at -30 °C, yielding long, feathery crystals. The solid was collected, washed with ether, and dried to afford 14 mg (40%) of product. <sup>1</sup>H NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  7.18 (m, 4H), 6.99 (m, 4H), 6.85 (s, 1H,  $\text{N}_2\text{CHSi}$ ), 6.71 (m, 4H), 6.53 (m, 8H), 4.81 (d of t,  $J = 3.8, 14.7$  Hz, 2H), 3.35 (m, 8H), 2.64 (d,  $J = 12.9$  Hz, 2H,  $\text{CH}_2\text{Ph}$ ), 2.09 (m, 4H), 1.42 (m, 2H), 0.98 (m, 2H), 0.22 (s, 9H,  $\text{SiCH}_3$ ). IR (KBr,  $\text{cm}^{-1}$ ): 2931 m, 1592 vs, 1509 vs, 1472 w, 1437 w, 1423 m, 1389 m, 1346 w, 1328 w, 1275 s, 1229 s, 1186 m, 1112 w, 1028 m, 992 w, 979 w, 934 m, 903 w, 887 w, 846 m, 833 m, 767 w, 723 s, 699 m, 658 w, 613 w, 518 w, 473 m. Anal. Calcd for  $\text{C}_{41}\text{H}_{50}\text{N}_6\text{HfOSi}$ : C, 57.97; H, 5.93; N, 9.89. Found: C, 58.27; H, 5.50; N, 9.36.

**[(TC-3,5)HfOC(CH<sub>2</sub>Ph)<sub>2</sub>N(N=NPh)] (3).** A rapidly stirred solution of 40 mg (0.054 mmol) of **1** in dichloromethane was treated with 19.3 mg (0.162 mmol) of phenylazide. Upon heating to 35 °C, the color of the solution gradually turned yellow and the temperature was maintained for 1 h. After the mixture was cooled to room temperature, the solution was filtered and ether was diffused into the saturated solution at -30 °C over the course of several days. The product was collected from the reaction mixture and washed with ether and pentane to afford 11 mg (24%) of yellow needle-like crystals. <sup>1</sup>H NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  7.57 (m, 1H), 7.40 (t,  $J = 7.5$  Hz, 1H), 7.22 (m, 8H), 6.90 (m, 6H), 6.63 (m, 2H), 6.52 (m, 6H), 6.28 (t,  $J = 7.4$  Hz, 1H), 4.86 (d of t,  $J = 3.7, 14.0$  Hz, 2H), 4.17 (d,  $J = 12.5$  Hz, 1H), 3.74 (m, 3H), 3.54 (m, 4H), 3.19 (m, 1H), 2.85 (d,  $J = 12.5$  Hz, 1H), 2.61 (d,  $J = 12.5$  Hz, 2H), 2.06 (m, 2H), 1.43 (m, 2H), 0.96 (m, 2H). IR (KBr,  $\text{cm}^{-1}$ ): 2931 m, 1593 vs, 1511 vs, 1471 w, 1438 w, 1424 m, 1387 w, 1375 w, 1341 w, 1327 w, 1304 w, 1276 m, 1239 m, 1207 w, 1137 w, 1114 w, 1082 w, 1044, 1029 m, 979 w, 936 w, 887 w, 865 w, 766 m, 741 m, 720 m, 700 m, 473 m.

**[(TC-3,5)HfOC(CH<sub>2</sub>Ph)<sub>2</sub>C(Cy)(Ph)O] (4).** A solution of 30 mg (0.0408 mmol) of **1** in 1.5 mL of dichloromethane was treated with 15.4 mg (0.0817 mmol) of solid cyclohexyl phenyl ketone at -30 °C. The solution rapidly turned from red-brown to bright yellow, and the mixture was allowed to warm to room temperature. The reaction was filtered, and several volume equivalents of ether were diffused into the filtrate at -30 °C over the course of several days. The resulting yellow material was collected, washed with ether, and dried to afford of 11 mg (29%) of blocklike crystals of **4**. <sup>1</sup>H NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  7.34 (t,  $J = 7.4$  Hz, 2H), 7.25 (m, 4H), 7.01 (s, br, 5H), 6.88 (m, 2H), 6.80 (m, 4H), 6.60 (m, 2H), 6.55 (m, 2H), 6.51 (m, 2H), 5.70 (m, 1H), 5.24 (m, 1H), 4.24 (m, 1H), 3.90 (d,  $J = 16$  Hz, 2H), 3.62 (m, 6H), 2.97 (d,  $J = 14.1$  Hz, 1H), 2.67 (d,  $J = 13.4$  Hz, 1H), 2.51 (m, br, 1H), 2.10 (m, br, 2H), 1.86 (m, br, 3H), 1.67 (m, br, 2H), 1.43 (m, br, 2H), 1.23 (m, br, 2H), 0.99 (m, br, 2H), 0.82 (m, br, 2H), 0.53 (m, br, 2H). IR (KBr,  $\text{cm}^{-1}$ ): 3079 w, 3054 w, 3023 w, 2921 m, 2847 m, 2593 s, 1509 s, 1472 m, 1425 s, 1381 m, 1355 m, 1337 w, 1318 m, 1277 m, 1229 m, 1206 w, 1168 w, 1137 w, 1096 m, 1066 w, 1026 m, 995 w, 978 w, 934 w, 887 w, 823 w, 748 w, 729 m, 707 m, 627 w, 611 w, 565 w, 546 w, 465 m. Anal. Calcd for  $\text{C}_{50}\text{H}_{56}\text{N}_4\text{HfO}_2$ : C, 65.03; H, 6.11; N, 6.07. Found: C, 65.11; H, 6.04; N, 6.34.

**[(TC-3,5)HfOC(CH<sub>2</sub>Ph)<sub>2</sub>C(Ph)C(Me)<sub>2</sub>O] (5).** At -30 °C, a red-brown slurry of 75 mg (0.102 mmol) of **1** in 2 mL of tetrahydrofuran was treated with 15  $\mu\text{L}$  (0.204 mmol) of acetone and allowed to warm to room temperature. Over the course of several minutes, the solution became bright yellow and homogenous. After 30 min, the mixture was filtered and several volume equivalents of pentane were diffused into the solution at -30 °C resulting in the formation of large,

(7) Zask, A.; Gonnella, N.; Nakanishi, K.; Turner, C. J.; Imajo, S.; Nozoe, T. *Inorg. Chem.* **1986**, *25*, 3400-3406.

irregularly shaped yellow crystals. The crystals were collected, washed with ether, and dried to afford 31 mg (39%) of product. The crystals contained two tetrahydrofuran solvate molecules, as confirmed by  $^1\text{H}$  NMR spectroscopy, elemental analysis, and CCA.  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  7.18 (m, 8H), 6.72 (d, br,  $J$  = 11.3 Hz, 8H), 6.50 (t,  $J$  = 9.2 Hz, 4H), 4.7 (s, br, 2H), 3.84 (m, br, 4H), 3.50 (m, br, 4H), 3.14 (s, 2H), 2.16 (s, br, 2H), 1.35 (s, br, 2H), 1.20 (s, 6H,  $\text{CH}_3$ ), 0.95 (s, br, 2H). IR (KBr,  $\text{cm}^{-1}$ ): 2968 m, 2919 m, 2854 m, 1609 m, 1592 vs, 1509 vs, 1471 w, 1438 m, 1426 m, 1383 m, 1351 w, 1321 w, 1278 m, 1244 w, 1229 w, 1198 w, 1113 w, 1067 w, 1027 w, 1003 w, 978 w, 962 w, 937 w, 887 w, 826 w, 718 s, 650 w, 611 w, 564 w, 536 w, 469 m. Anal. Calcd for  $\text{C}_{48}\text{H}_{60}\text{N}_4\text{HfO}_4$ : C, 61.63; H, 6.46; N, 5.99. Found: C, 61.69, H, 6.41; N, 6.15.

**[(TC-3,5)HfOC(CH<sub>2</sub>Ph)<sub>2</sub>O] (6).** Upon addition of 12  $\mu\text{L}$  (0.099 mmol) of nitrocyclohexane, a red-brown solution of 35 mg (0.048 mmol) of **1** in 1.5 mL of dichloromethane rapidly turned bright yellow and a precipitate formed. The mixture was filtered through Celite, and ether was diffused into the solution over 48 h. The solid was collected and washed with ether and pentane, and the product was isolated as large yellow-orange blocklike crystals (17 mg, 47%). The crystalline material contained one ether solvate molecule, as confirmed by elemental analysis and CCA.  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  7.16 (m, 4H), 7.07 (m, 4H), 6.68 (t,  $J$  = 7.45 Hz, 4H), 6.53 (m, 4H), 6.41 (m, 4H), 4.58 (d of t,  $J$  = 4.1, 14.7 Hz, 2H), 3.85 (m, 2H), 3.58 (m, 2H), 3.42 (m, 4H), 2.87 (s, 4H,  $\text{CH}_2\text{Ph}$ ), 2.14 (m, br, 2H), 1.46 (m, br, 2H), 0.98 (m, 2H). IR (KBr,  $\text{cm}^{-1}$ ): 2029 m, 1592 s, 1511 s, 1495 w, 1472 w, 1451 w, 1438 w, 1422 m, 1389 m, 1354 w, 1340 w, 1321 w, 1300 w, 1276 s, 1229 m, 1141 m, 1114 m, 1089 w, 1054 w, 1044 w, 1028 m, 980 w, 937 w, 887 w, 857 w, 822 w, 798 w, 768 w, 725 m, 706 s, 699 m, 661 w, 517 w, 475 m. Anal. Calcd for  $\text{C}_{41}\text{H}_{50}\text{N}_4\text{HfO}_3$ : C, 59.66; H, 6.11; N, 6.79. Found: C, 59.80; H, 6.19; N, 6.28.

**[Hf(TC-3,5)<sub>2</sub>( $\mu$ , $\eta^2$ : $\eta^2$ -ONPh)( $\mu$ -O) (7).** A mixture of 26  $\mu\text{L}$  (0.252 mmol) of nitrobenzene and 92 mg (0.125 mmol) of **1** in 2 mL of dichloromethane was stirred at room temperature for 15 min. Addition of an additional 27 mg (0.252 mmol) of PhNO induced a further color change from yellow to yellow-orange. After 30 min of additional stirring, the mixture was filtered and several volume equivalents of ether were diffused into the filtrate over the course of 48 h at  $-30^\circ\text{C}$ . The product was collected by filtration, washed with ether and pentane, and dried to afford 12 mg (21%) of material. In an alternative procedure, 11.7  $\mu\text{L}$  (0.114 mmol) of nitrobenzene added to a dichloromethane solution of 40 mg (0.057 mmol) of  $[\text{Hf}(\text{TC-3,5})(\text{CH}_2\text{Ph})_2]_2$ <sup>8</sup> induced a rapid color change from red-orange to orange yellow. Several volume equivalents of ether were diffused into the solution over 72 h at  $-30^\circ\text{C}$  to afford 8 mg (27%) of orange blocks. The material was isolated by removal of the supernatant followed by washing with copious amounts of ether.  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  7.05 (m, br, 4H), 6.86 (m, 2H), 6.64 (m, vbr, 6H), 6.34 (m, br, 4H), 6.01 (m, br, 6H), 5.50 (m, 1H), 5.01 (m, 2H), 4.37 (m, 2H), 4.14 (m, 2H), 3.50 (m, vbr, 6H), 3.14 (m, 2H), 2.56 (m, 2H), 2.08 (m, 2H), 1.51 (m, br, 6H), 1.0 (m, br, 2H). IR (KBr,  $\text{cm}^{-1}$ ): 2918 m, 2855 m, 1591 vs, 1508 vs, 1472 m, 1427 d, 1385 m, 1352 w, 1337 w, 1319 w, 1273 m, 1228 m, 1113 w, 1026 m, 978 w, 938 w, 887 w, 823 w, 724 s, 630 s, 519 w, 473 m.

**[(TC-3,3)ZrOC(*p*-tol)<sub>2</sub>C(*p*-tol)<sub>2</sub>O] (8).** Addition of 7  $\mu\text{L}$  (0.068 mmol) of nitrobenzene to a red solution of 20 mg (0.034 mmol) of  $[\text{Zr}(\text{TC-3,3})(\eta^2\text{-OC}(\textit{p}\text{-tol})_2)]_2$ <sup>9</sup> in dichloromethane induced a rapid color change to orange. The mixture was stirred for 15 min and filtered through Celite, and several volume equivalents of ether were diffused into the reaction mixture

at  $-30^\circ\text{C}$ . After several days, a fine yellow powder and large orange crystals formed in the reaction vessel. The single orange crystals of **8** were manually separated from the mixture and characterized by CCA. Since multiple products were formed in the reaction media, no attempt was made to optimize the synthesis of **8**.

**[(TC-3,5)HfOC(=O)N(Ph)C(CH<sub>2</sub>Ph)<sub>2</sub>] (9).** In 2 mL of chlorobenzene a red-brown slurry of 107 mg (0.146 mmol) of **1** and 32  $\mu\text{L}$  (0.294 mmol) of phenyl isocyanate was stirred at  $35^\circ\text{C}$  for 30 min, and the resulting orange-brown solution was filtered through Celite. Over the course of several days, pentane was diffused into the filtrate at  $-30^\circ\text{C}$ . The subsequent orange crystalline mass was collected, washed with pentane, and dried to afford 39 mg (31%) of product.  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  7.24 (m, 11H), 7.06 (m, 2H), 6.88 (d,  $J$  = 11.6 Hz, 2H), 6.75 (m, 6H), 6.49 (t,  $J$  = 7.3 Hz, 2H), 6.36 (d,  $J$  = 11.3 Hz, 2H), 5.56 (m, 2H), 4.05 (d, br, 2H), 3.57 (m, br, 6H), 3.00 (m, 1H), 2.75 (d,  $J$  = 17.5 Hz, 2H), 2.34 (m, br, 1H), 2.05 (m, br, 2H), 1.58 (m, br, 2H), 0.91 (m, br, 2H). IR (KBr,  $\text{cm}^{-1}$ ): 2931 m, 1645 vs, 1592 vs, 1509 vs, 1492 w, 1472 w, 1443 w, 1424 m, 1378 m, 1364 w, 1349 m, 1336 w, 1318 w, 1281 m, 1274 m, 1131 m, 1116 w, 1086 w, 1026 m, 983 w, 936 m, 886 w, 859 w, 826 w, 784 w, 759 w, 725 s, 694 m, 520 w, 469 m. Anal. Calcd for  $\text{C}_{44}\text{H}_{45}\text{N}_5\text{HfO}_2$ : C, 61.86; H, 5.31; N, 8.20. Found: C, 61.32; H, 5.53; N, 8.07.

**Collection and Reduction of X-ray Data.** Crystals were typically obtained by vapor diffusion of ether or pentane into a saturated solution of the complexes at  $-30^\circ\text{C}$  as described above. Single crystals were coated with Paratone-N oil, selected under a microscope, attached to a glass fiber, and transferred rapidly to a Siemens CCD X-ray diffraction system controlled by a Pentium-based PC running the SMART software package.<sup>10</sup> The program SADABS<sup>11</sup> was utilized for absorption corrections. Data were collected by following the standard procedures reported in detail elsewhere.<sup>12</sup>

The structures were solved by direct methods using SIR-92<sup>13</sup> or SHELXS and refined by full-matrix least-squares and Fourier techniques using the SHELXTL-PLUS program package.<sup>14</sup> Space groups were determined from an examination of the systematic absences in the data confirmed by the successful solution and refinement of the structures. When a complex crystallized in a polar space group, both enantiomers were refined, and the structure presented is that yielding the lowest-weighted residual and smaller value for the Flack parameter.<sup>15</sup> Except in the cases where disorder was apparent, all non-hydrogen atoms were refined anisotropically. Hydrogen atoms were assigned idealized locations and given a thermal parameter equal to 1.2 times that of the carbon atom to which it was attached.

The asymmetric units of both **2** and **4** contain one complete complex; in compound **3** the Hf atom lies on a mirror plane. The phenyl group derived from the azide substrate is disordered across this mirror plane. The azide nitrogen atoms, the ipso carbon atom, and one meta carbon atom all lie on the mirror plane, but the phenyl ring is canted approximately  $30^\circ$  with respect to this plane in two orientations, each having a site occupancy of 0.5. The disordered carbon atoms were refined isotropically, and the hydrogen atoms on the ring were omitted from the final refinement. Compound **5** crystallized

(10) SMART: Version 4.0; Siemens Industrial Automation, Inc.: Madison, WI, 1994.

(11) SADABS was obtained from Prof. George Sheldrick at the University of Göttingen. The program corrects data collected on Siemens CCD and Multiwire detectors for absorption and decay.

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(14) SHELXTL: Structure Analysis Program; Siemens Industrial Automation, Inc.: Madison, WI, 1995.

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(8) Scott, M. J.; Lippard, S. J. *Inorg. Chim. Acta* **1997**, *263*, 287–299.

(9)  $[\text{Zr}(\text{TC-3,3})(\eta^2\text{-OC}(\textit{p}\text{-tol})_2)]_2$  was prepared from  $[\text{Zr}(\text{TC-3,3})(\textit{p}\text{-tol})_2]$  (ref 8) following the procedures outlined for the formation of **1** (ref 6).

**Table 1. Crystallographic and Selected Metric Parameters of Products from the Reaction of 1 with TMSCHN<sub>2</sub> (2) and PhN<sub>3</sub> (3)**

compound	<b>2</b>	<b>3</b>
formula	C <sub>41</sub> H <sub>50</sub> HfN <sub>6</sub> O <sub>Si</sub>	C <sub>43</sub> H <sub>45</sub> HfN <sub>7</sub> O
fw	849.45	854.35
cryst syst	orthorhombic	orthorhombic
space group	<i>Pca</i> 2 <sub>1</sub>	<i>Cmc</i> 2 <sub>1</sub>
<i>a</i> (Å)	26.8228(8)	18.0841(5)
<i>b</i> (Å)	13.8639(4)	20.7913(5)
<i>c</i> (Å)	10.2644(3)	10.0864(2)
<i>V</i> (Å <sup>3</sup> )	3817.0(2)	3792.4(2)
<i>Z</i>	4	4
<i>T</i> , K	188	188
<i>R</i> (%) <sup>a</sup>	5.68	3.36
<i>wR</i> <sup>2</sup> (%) <sup>b</sup>	6.65	7.59
Hf(1)–O(1) Å	1.998(4)	2.005(6)
Hf(1)–N(1) Å	2.190(6)	2.193(6)
Hf(1)–N(2) Å	2.211(6)	2.181(6)
Hf(1)–N(3) Å	2.202(5)	2.195(7)
Hf(1)–N(4) Å	2.201(6)	
Hf(1)–N(5) Å	2.151(6)	
Hf(1)–N–N (deg)	140.5(6)	141.1(6)
O(1)–Hf(1)–N(5) (deg)	63.9(2)	
O(1)–Hf(1)–N(3) (deg)	62.8(3)	

$$^a R = \sum ||F_o| - |F_c|| / \sum |F_o|, \quad ^b wR^2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)] \}^{1/2}.$$

with two tetrahydrofuran solvent molecules, which were refined anisotropically despite their high degree of thermal motion. Compound **6** was well-ordered on a mirror plane, but the ether solvate molecule exhibited a large amount of thermal motion across this symmetry element. Since the structure refined to a low residual value, no attempt was made to model the disorder rigorously and hydrogen atoms on the disordered carbon atoms were omitted. In the structure of **7**, both bridging ligands lie in the mirror plane as do two dichloromethane solvate molecules, one of which had one chlorine atom disordered across this plane. An additional dichloromethane molecule crystallized on a general position in two orientations with site occupancies of 0.75 and 0.25, respectively. These atoms were refined isotropically, and hydrogen atoms were not included in the refinement of the solvate molecules. The asymmetric units of both **8** and **9** contain one complete complex, but **8** also crystallized with a dichloromethane molecule in the lattice. The ether was badly disordered, and its electron density was modeled with partially occupied carbon atoms. Crystallographic data and selected metrical parameters are reported in Tables 1–4, and additional experimental details are available as Supporting Information.

## Results and Discussion

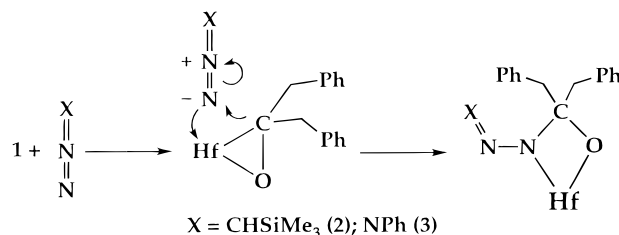
**1,1-Insertions Forming C–N Bonds.** At 35 °C, (trimethylsilyl)diazomethane and phenylazide both react with **1** by formal 1,1-insertion into the Hf–C bond to afford **2** and **3**, respectively (Scheme 3). ORTEP diagrams of the products from these reactions are displayed in Figures 1 and 2, and selected geometric parameters are available in Table 1. The Hf–O bond lengths of 1.998(4) Å in **2** and 2.005(6) Å in **3** are indistinguishable from the analogous distance of 1.993(5) Å in **1**, and the two Hf–N distances are marginally inequivalent, 2.151(6) and 2.195(7) Å, respectively. These substrates typically insert into group 4 metal–hydride or metal–carbon bonds to afford either  $\eta^2$ -hydrazone<sup>6,16,17</sup> or  $\eta^2$ -triazene<sup>18,19</sup> com-

**Table 2. Crystallographic and Selected Metric Parameters of the Products from the Reaction of 1 with CyPhCO (4) and Acetone (5)**

compound	<b>4</b>	<b>5</b> ·2C <sub>4</sub> H <sub>8</sub> O
formula	C <sub>50</sub> H <sub>56</sub> HfN <sub>4</sub> O <sub>2</sub>	C <sub>48</sub> H <sub>60</sub> HfN <sub>4</sub> O <sub>4</sub>
fw	923.48	935.49
cryst syst	triclinic	Triclinic
space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> (Å)	11.0942(8)	10.9645(4)
<i>b</i> (Å)	13.0632(10)	11.7043(4)
<i>c</i> (Å)	15.1685(11)	18.4183(6)
$\alpha$ (deg)	78.5990(10)	87.9380(10)
$\beta$ (deg)	75.885(2)	89.2560(10)
$\gamma$ (deg)	72.773(2)	65.5680(10)
<i>V</i> (Å <sup>3</sup> )	2017.5(3)	2150.60(13)
<i>Z</i>	2	2
<i>T</i> , K	188	188
<i>R</i> (%) <sup>a</sup>	6.95	4.69
<i>wR</i> <sup>2</sup> (%) <sup>b</sup>	9.71	7.76
Hf(1)–O(1) Å	2.001(5)	1.962(3)
Hf(1)–O(2) Å	2.038(5)	2.039(3)
Hf(1)–N(1) Å	2.244(6)	2.185(4)
Hf(1)–N(2) Å	2.206(6)	2.238(4)
Hf(1)–N(3) Å	2.253(6)	2.212(4)
Hf(1)–N(4) Å	2.166(6)	2.230(4)
O(1)–C(23) Å	1.406(8)	1.354(6)
O(2)–C(38) Å	1.408(9)	1.404(5)
C(23)–C(31) Å		1.335(6) <sup>c</sup>
C(23)–C(38) Å	1.612(10)	
C(31)–C(38) Å		1.545(6)
O(1)–Hf(1)–O(2) (deg)	76.0(2)	80.91(13)

$$^a R = \sum ||F_o| - |F_c|| / \sum |F_o|, \quad ^b wR^2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)] \}^{1/2}.$$

<sup>c</sup> The angles (deg) at C(23) and C(31) are as follows: C(31)–C(23)–O(1), 125.0(4); C(31)–C(23)–C(24), 123.6(4); O(1)–C(23)–C(24), 111.3(4); C(23)–C(31)–C(32), 120.6(4); C(23)–C(31)–C(38), 123.4(4); C(23)–C(31)–C(38), 115.8(4).

**Scheme 3**

plexes, although 1,1-additions occur, [Cp\*<sub>2</sub>Zr( $\eta^2$ -C<sub>2</sub>Ph<sub>2</sub>)] inserting both *p*-tolylazide and diazoalkanes via this pathway.<sup>20</sup> In the latter systems, the steric requirements of the Cp\* ligand were suggested to block coordination of a second nitrogen atom from the incoming substrate. In both **2** and **3**, the coordination sphere of the metal is relatively unencumbered. Instead, the strongly electron-donating tropocoronand ligand reduces the electrophilicity of the Hf atom, reducing its ability to bind a second nitrogen atom. Attempts to extrude dinitrogen from **2** and **3** at elevated temperatures resulted in the formation of complex product mixtures.

**1,2-Insertions Forming C–C Bonds.** As described previously, enones add across the metal–carbon bond of **1** in a 1,2-fashion forming five-membered metallacycles (Scheme 1).<sup>6</sup> Although simple ketones attack the metallocene unit in **1**, the reaction is more complicated and slow, even at elevated temperatures. When a

(18) Hillhouse, G. L.; Bercaw, J. E. *Organometallics* **1982**, *1*, 1026–1029.

(19) Chiu, K. W.; Wilkinson, G.; Thornton-Pett, M.; Hursthouse, M. B. *Polyhedron* **1984**, *3*, 79–85.

(20) Vaughan, G. A.; Hillhouse, G. L.; Rheingold, A. L. *J. Am. Chem. Soc.* **1990**, *112*, 7994–8001.

(16) Gambarotta, S.; Basso-Bert, M.; Floriani, C.; Guastini, C. *J. Chem. Soc., Chem. Commun.* **1982**, 374–375.

(17) Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Inorg. Chem.* **1983**, *22*, 2029–2034.

**Table 3. Crystallographic and Selected Metric Parameters for Products from the Reaction of CyNO<sub>2</sub> (6) and PhNO<sub>2</sub> (7) with 1 and [Zr(TC-3,3)( $\eta^2$ -OC(Ph)<sub>2</sub>)] with PhNO<sub>2</sub> (8)**

compound	<b>6</b> ·Et <sub>2</sub> O	<b>7</b> ·4CH <sub>2</sub> Cl <sub>2</sub>	<b>8</b> ·CH <sub>2</sub> Cl <sub>2</sub>
formula	C <sub>41</sub> H <sub>50</sub> HfN <sub>4</sub> O <sub>3</sub>	C <sub>54</sub> H <sub>65</sub> Cl <sub>8</sub> Hf <sub>2</sub> N <sub>9</sub> O <sub>2</sub>	C <sub>51</sub> H <sub>52</sub> Cl <sub>2</sub> N <sub>4</sub> O <sub>3</sub> Zr
fw	825.34	1512.73	931.09
cryst syst	orthorhombic	orthorhombic	orthorhombic
space group	<i>Cmc2</i> <sub>1</sub>	<i>Pnma</i>	<i>P2</i> <sub>1</sub> <i>2</i> <sub>1</sub> <i>2</i> <sub>1</sub>
<i>a</i> (Å)	17.4362(4)	14.9933(2)	9.7421(2)
<i>b</i> (Å)	21.7256(4)	21.6572(5)	20.4331(5)
<i>c</i> (Å)	9.7862(2)	18.1929(4)	23.7925(1)
<i>V</i> (Å <sup>3</sup> )	3707.13(13)	5907.5(2)	4736.2(2)
<i>Z</i>	4	4	4
<i>T</i> , K	188	188	188
<i>R</i> (%) <sup>a</sup>	1.66	3.55	7.40
<i>wR</i> <sup>2</sup> (%) <sup>b</sup>	3.62	9.19	15.47
M–O(1) Å	2.018(2)	2.161(3)	2.024(5)
M–O(2) Å	2.045(2)	1.975(3)	2.043(5)
M–N <sub>trop</sub> (avg) Å	2.203(5)	2.24(2)	2.21(2)
M–N(5) Å		2.218(4)	
O(1)–M–O(2) (deg)	67.37(9)	78.92(13)	75.3(2)
O(1)–N(5) Å		1.500(7)	
Hf(1)–O(1)–Hf(1') (deg)		93.7(2)	
Hf(1)–N(5)–Hf(1') (deg)		90.7(2)	
Hf(1)–O(2)–Hf(1') (deg)		106.1(2)	
C(21)–C(36) Å			1.627(12)

<sup>a</sup>  $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ . <sup>b</sup>  $wR^2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$ .

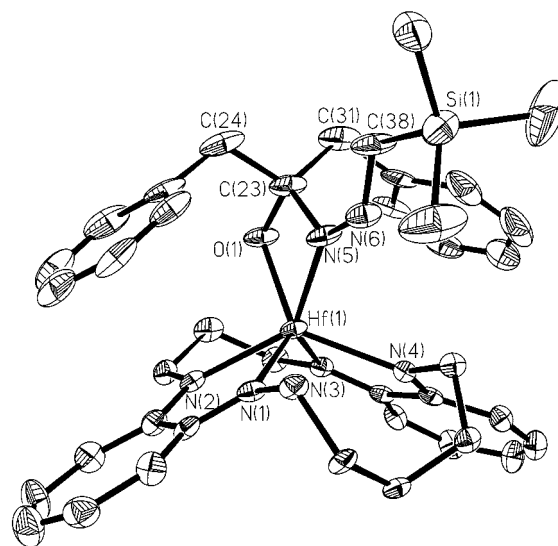
**Table 4. Crystallographic and Selected Metric Parameters for Products from the Reaction of 1 with PhNCO (9)**

compound	<b>9</b>
formula	C <sub>44</sub> H <sub>45</sub> HfN <sub>5</sub> O <sub>2</sub>
fw	854.34
cryst syst	orthorhombic
space group	<i>Pbca</i>
<i>a</i> (Å)	12.1883(2)
<i>b</i> (Å)	14.9260(2)
<i>c</i> (Å)	38.7591(3)
<i>V</i> (Å <sup>3</sup> )	7051.2(2)
<i>Z</i>	8
<i>T</i> , K	193
<i>R</i> (%) <sup>a</sup>	4.20
<i>wR</i> <sup>2</sup> (%) <sup>b</sup>	7.26
Hf(1)–O(1) Å	2.050(3)
Hf(1)–N(4) Å	2.200(4)
Hf(1)–N(1) Å	2.207(4)
Hf(1)–N(2) Å	2.210(4)
Hf(1)–N(3) Å	2.214(3)
Hf(1)–C(23) Å	2.439(4)
O(1)–C(44) Å	1.306(5)
O(2)–C(44) Å	1.222(5)

<sup>a</sup>  $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ . <sup>b</sup>  $wR^2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$ .

phenyl group is present, the reactivity is enhanced and a 1,2-insertion into the metalloxirane occurs, as depicted in Scheme 4.

Coupling reactions of this type are common with group 4 metal centers, as illustrated by the insertion of acetophenone into [Cp<sub>2</sub>Zr( $\eta^2$ -CO(CH<sub>3</sub>)<sub>2</sub>( $\mu$ -Cl)Al(CH<sub>3</sub>)<sub>2</sub>)]<sup>21</sup> Moreover, treatment of reduced cyclopentadienyl-ligated group 4 metal centers with either ketones or aldehydes will afford saturated diolate complexes, but typically, in these systems, two equivalent substrates are coupled to give a symmetric ligand.<sup>22,23</sup> With the tropocoronand complexes, however, asymmetric diolate complexes can be prepared in a stepwise manner (Scheme 4). The structure of [(TC-3,5)HfOC(CH<sub>2</sub>Ph)<sub>2</sub>C(Cy)(Ph)O] (**4**) is

**Figure 1.** ORTEP diagram of **2** showing 50% ellipsoids and atom-labeling scheme. Selected distances and angles are contained in Table 1.

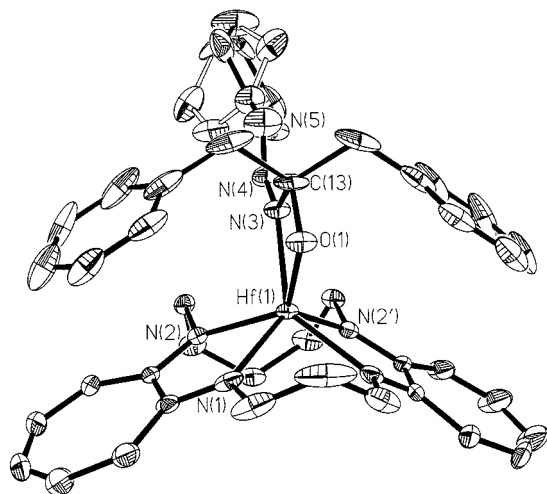
illustrated in Figure 3 and selected crystallographic parameters are contained in Table 2. This transformation is general for tropocoronand complexes with disparate macrocycles and auxiliary groups, as illustrated by the reaction of [Zr(TC-3,3)( $\eta^2$ -OC(*p*-tol)<sub>2</sub>)] outlined below.

Whereas both enones and phenyl-substituted ketones react with **1** in a manner analogous to pinacol coupling,<sup>22</sup> acetone induces the formation of a diolate product having distinctive characteristics, including a new olefinic stretch in the infrared spectrum at 1609 cm<sup>-1</sup>. Figure 4 depicts the structure of the product, **5**, isolated from the reaction mixture upon recrystallization. Selected metrical parameters are contained in Table 2, from which the C(23)=C(31) bond can be identified. The two Hf–O bond lengths are inequivalent (2.039(3), 1.962(3) Å) and span the values of 1.999(7) and 2.009(7) Å observed in the diolate product obtained from the reaction of **1** with cyclohexenone (1.999(7) and 2.009(7) Å).<sup>6</sup> This result is ascribed to the presence of

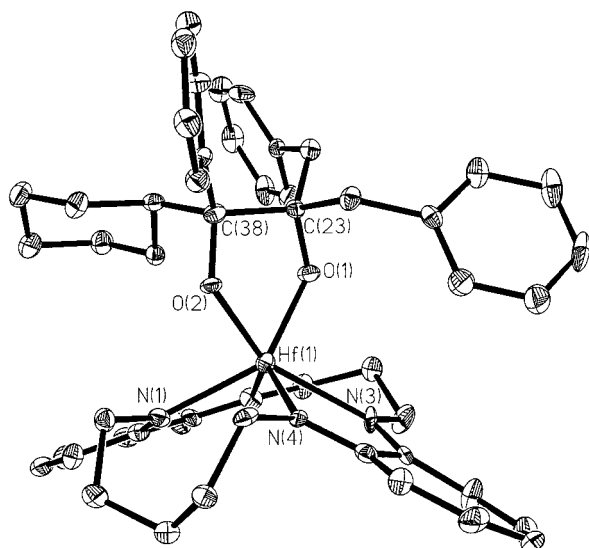
(21) Waymouth, R. M.; Clauser, K. R.; Grubbs, R. H. *J. Am. Chem. Soc.* **1986**, *108*, 6385–6387.

(22) McMurry, J. E. *Acc. Chem. Res.* **1983**, *16*, 405–411.

(23) Fürstner, A.; Bogdanovic, B. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2442–2469 and references therein.

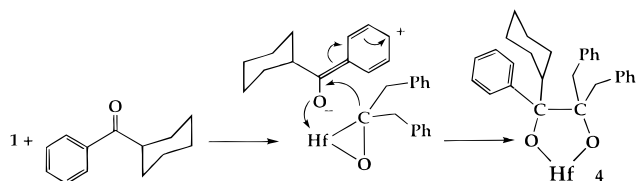


**Figure 2.** ORTEP diagram of **3** showing 30% ellipsoids, atom-labeling scheme, and both orientations of the disordered phenyl group. Primed and unprimed atoms are related by an mirror plane. Selected distances and angles are contained in Table 1.



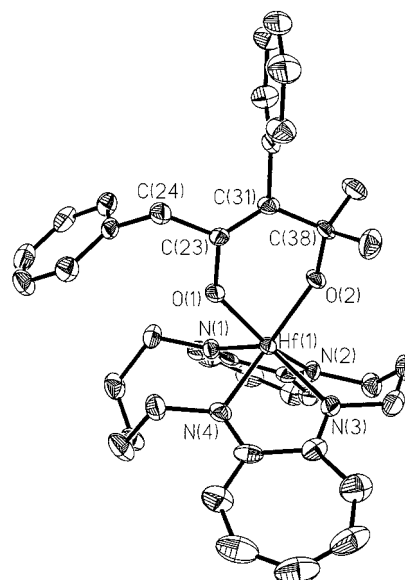
**Figure 3.** ORTEP diagram of **4** showing 30% ellipsoids and atom-labeling scheme. Selected distances and angles are contained in Table 2.

#### Scheme 4



the double bond. The spectroscopic and structural data indicate that, during the formation **5**, two hydrogen atoms were lost from one benzylic position of the coordinated  $\eta^2$ -ketone, a reaction accomplished by formation of a bond to the central carbon atom of the acetone substrate. Group 4 metal centers can abstract  $\beta$ -hydrogen atoms from coordinated transient  $\eta^2$ -ketone ligands to form metal-hydride/enolate species,<sup>24,25</sup> suggesting that **5** may form through such an intermediate.

(24) Manriquez, J. M.; McAlister, D. R.; Sanner, R. D.; Bercaw, J. E. *J. Am. Chem. Soc.* **1978**, *100*, 2716–2724.



**Figure 4.** ORTEP diagram of **5** showing 30% ellipsoids and atom-labeling scheme. Selected distances and angles are contained in Table 2.

Addition of acetone to the resulting enolate with the accompanying rearrangement and loss of dihydrogen would afford **5**, as illustrated in Scheme 5.

**O-Atom Transfer from Nitroalkanes.** The met-alloxirane unit in **1** reacts rapidly with nitroalkanes, excising one of the N–O bonds to afford the diolato-ligated tropocoronand complex  $[(TC-3,5)HfOC(CH_2-Ph)_2O]$  (**6**). The structure is illustrated in Figure 5 and selected geometric information is contained in Table 3. Concomitant with the formation of **6**, 1 equiv of nitrosoalkane would be generated, but attempts to detect this material in the reaction were unsuccessful. In **6**, the resulting four-membered chelate ring has a O–Hf–O angle of  $67.37(9)^\circ$ , smaller than that in **4**, and shorter Hf–O distances of 2.018(2) and 2.045(2) Å, which reflect the greater charge accumulation. Although reagents such as  $[TiCl_2(O-i-Pr)_2]$  can catalyze the cycloaddition of olefins and nitroalkanes,<sup>26</sup> evidently little attention has been paid to the interaction of nitroalkanes with group 4 metals. Hydrolysis of **6** affords dibenzyl ketone and the di( $\mu$ -oxo) complex  $[Hf(TC-3,5)(\mu-O)]_2$ ,<sup>27,28</sup> presumably through dimerization of transient terminal oxo species.<sup>29</sup>

**Formal Retrocycloaddition Chemistry.** Nitroarenes also react with **1** to afford complex reaction mixtures having  $^1H$  NMR spectra revealing several species present in solution. Nevertheless, after careful purification by recrystallization, the dominant product **7**, a dinuclear complex in which two Hf atoms are bridged by both oxo and a  $\eta^2$ : $\eta^2$ -nitroso groups, was isolated. Addition of

(25) Hessen, B.; Blenkins, J.; Teuben, J. H.; Helgesson, G.; Jagner, S. *Organometallics* **1989**, *8*, 2809–2812.

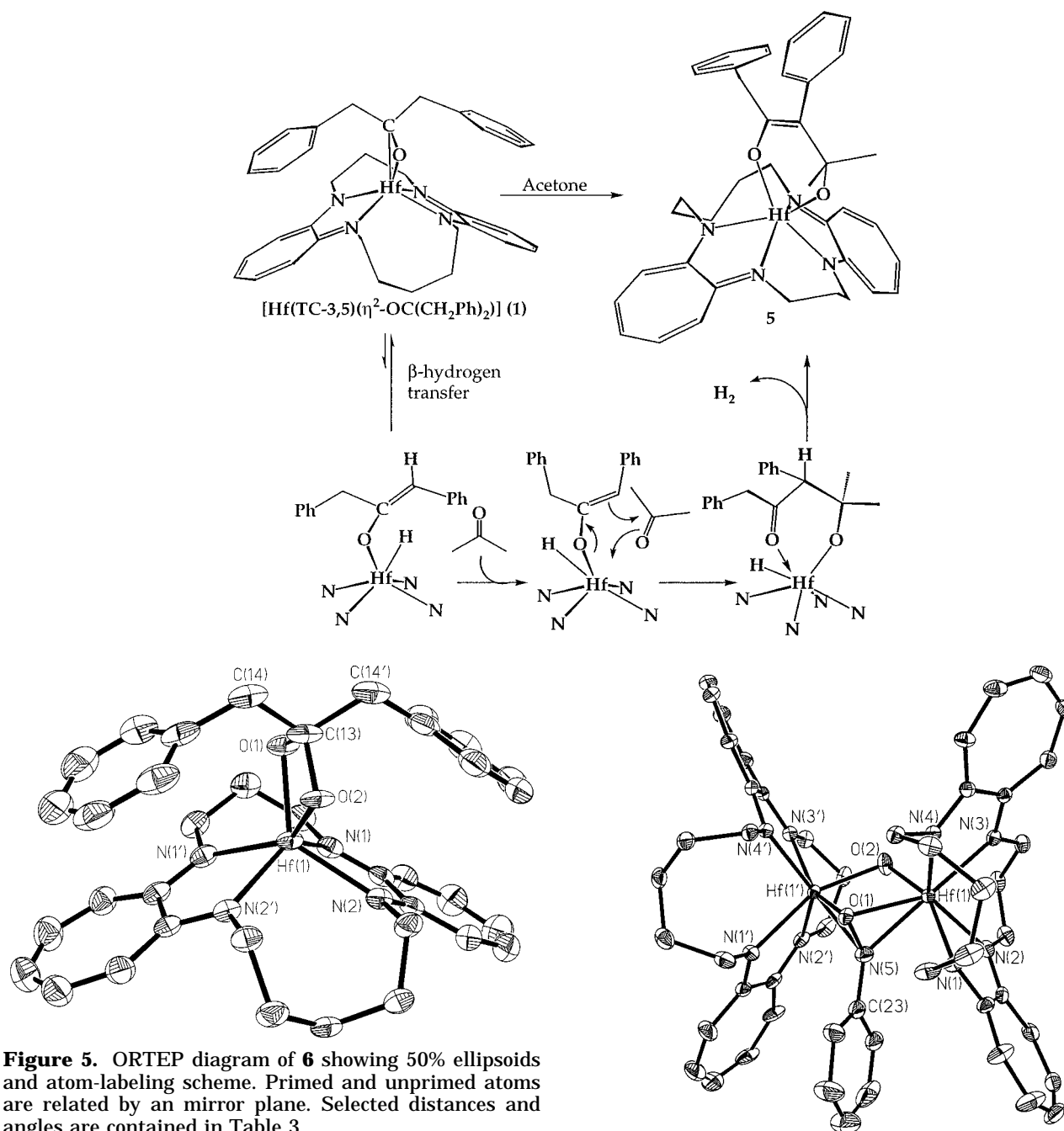
(26) Denmark, S. E.; Thorarensen, A. *Chem. Rev.* **1996**, *96*, 137–165.

(27)  $[Hf(TC-3,5)(\mu-O)]_2$ :  $C2/c$ ,  $a = 15.9674(5)$  Å,  $b = 19.0350(6)$  Å,  $c = 14.7935(3)$  Å,  $\beta = 97.644(1)^\circ$ ,  $Z = 4$ ,  $R = 3.05\%$ ,  $wR^2 = 6.74\%$ . Relevant distances: Hf–O 1.971(4), 1.983(4) Å. Complete structural details are available in the Supporting Information.

(28) Dibenzylketone was detected in the reaction mixture by GC/MS.

(29) Hey-Hawkins, E. *Chem. Rev.* **1994**, *94*, 1661–1717 and references therein.

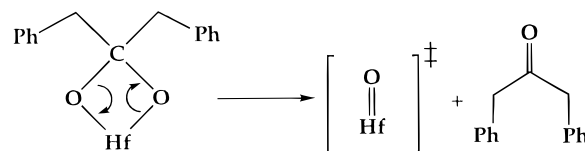
Scheme 5



excess nitrosobenzene to the crude reaction mixture increases the yield of **7**. Figure 6 presents an ORTEP diagram of the product, and Table 3 contains selected geometric information. Compound **7** is a rare example of the  $\eta^2:\eta^2$ -nitrosoarene bridging motif,<sup>30</sup> in which the nitrogen and oxygen atoms link the two metal centers with elongated metal–ligand distances of 2.218(4) and 2.161(3) Å, respectively. The N–O distance of 1.500(7) Å in the nitrosoarene bridge is markedly longer than the comparable distance of 1.422(4) Å in the only other structurally characterized example of the  $\mu\text{-}\eta^2:\eta^2$  bonding mode,  $[(\text{Cp}^+\text{Rh})_2(\mu\text{-Cl})(\mu,\eta^2\text{-}\eta^2\text{-ONPh})](\text{BF}_4)$ ,<sup>30</sup> indicating significant reduction in bond order. The Hf–O distance of 1.975(3) Å in the ( $\mu$ -oxo)dihafnium-(IV) is normal.<sup>27</sup>

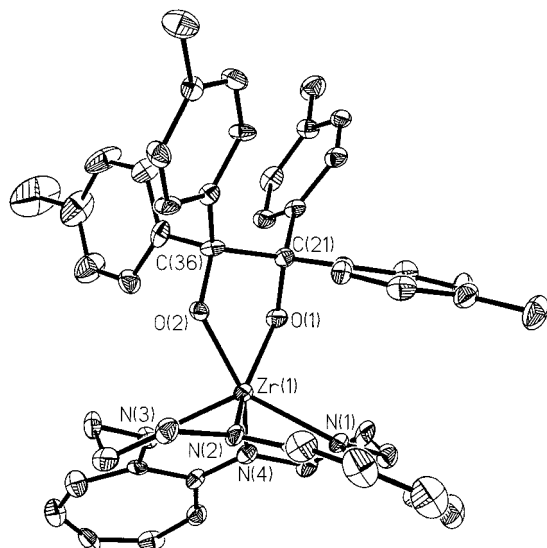
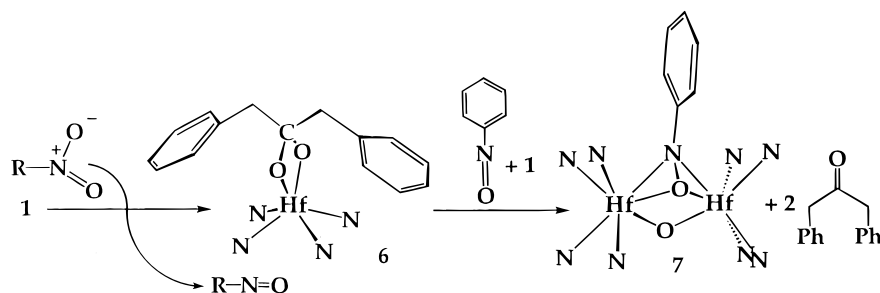
(30) Hoard, D. W.; Sharp, P. R. *Inorg. Chem.* **1993**, *32*, 612–620.

Scheme 6



On the basis of the products isolated, we suggest that the nitrosobenzene generated by excision of oxygen from nitrobenzene (vide supra) may induce **6** to react further, probably by a retro [2 + 2] cycloaddition, as depicted in Scheme 6. Such a reaction would afford a transient terminal oxo complex and 1 equiv of dibenzyl ketone.

Scheme 7

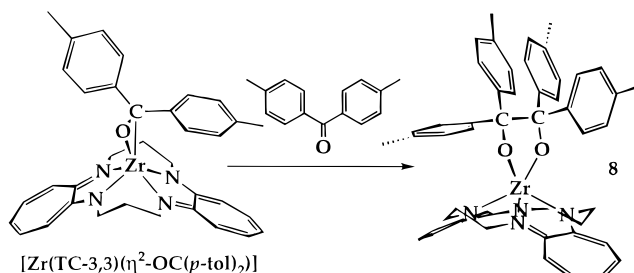


**Figure 7.** ORTEP diagram of **8** showing 50% ellipsoids and atom-labeling scheme. Primed and unprimed atoms are related by an mirror plane. Selected distances and angles are contained in Table 3.

The latter was detected in the reaction mixture by GC-MS. In the presence of unreacted **1**, the terminal oxo complex can react with nitrosoarene to afford **7**, as pictured in Scheme 7.

Several observations lend credence to this proposal. Electron-deficient ketones undergo reversible cycloadditions with oxotitanium tetraazaannulene complexes.<sup>31</sup> Addition of PhNO to the reaction mixture increased the yield of **7**, consistent with the postulated mechanism. Finally, the diolate complex  $[\text{Zr}(\text{TC-3,3})(\eta^2\text{-OC}(p\text{-tol})_2)]$  (**8**) (Figure 7; Table 3) was isolated from the reaction of  $[\text{Zr}(\text{TC-3,3})(\eta^2\text{-OC}(p\text{-tol})_2)]$  with PhNO<sub>2</sub>, albeit from a mixture complicated by the presence of multiple products. The manner by which **8** might form would be consistent with the postulated mechanism for **7** formation. With *p*-tol substituents, the ketone liberated by a retro [2 + 2] cycloaddition (Scheme 6) is activated by the phenyl rings. It could, in turn, attack unreacted  $[\text{Zr}(\text{TC-3,3})(\eta^2\text{-OC}(p\text{-tol})_2)]$ , as outlined in Scheme 8, presumably by a mechanism similar to that postulated for the formation of **4** (Scheme 4). As indicated previously,<sup>6</sup> enones form coupled products in this manner. In reactions of **1**, the released dibenzyl ketone is inert, preventing such coupling chemistry and allowing isolation of the bridged nitrosoarene complex **7**.

Scheme 8



Although the  $\mu\text{-}\eta^2\text{:}\eta^2$  binding of nitrosoarenes is exceedingly uncommon, such a motif readily assembles with group 4 tropocoronand complexes. Most dialkyl-substituted Zr(IV) and Hf(IV) tropocoronand complexes react with nitrobenzene as well as other nitroalkanes to afford either  $\mu\text{-}\eta^2\text{:}\eta^2$ -nitrosoarene- or -nitrosoalkane-bridged compounds in moderate yield. Several examples have been structurally characterized from reaction mixtures containing nitromethane,<sup>32</sup> nitropropane,<sup>33</sup> and nitrotoluene.<sup>34</sup> In comparison to **1**, the mechanism by which this structural type forms from dialkyl complexes could be more complicated, perhaps involving protonation of the nitroalkane substrate by the nitronic acid tautomer.<sup>26</sup>

**C–O Bond Scission with Phenyl Isocyanate and the  $\eta^2$ -Ketone.** In contrast to reactions of **1** discussed above, phenyl isocyanate does not attack the Hf–C bond of the metalloxirane unit. Rather unexpectedly, this substrate preferentially inserts into the carbon–oxygen bond, generating the carbamate moiety **9** (Figure 8; Table 4). This reaction differs dramatically from that of ( $\eta^2$ -formaldehyde)zirconocene, which reacts by 1,2-addition to insert the C–O fragment from isocyanates into the metal–carbon bond, forming a five-membered metallacycle.<sup>35,36</sup> A simple [2 + 2] cycloaddition reaction between the N–C bond of the phenyl isocyanate and the C–O bond of the  $\eta^2$ -ketone in **1** would account for the observed carbamate functionality (Scheme 9), but other mechanisms are possible.

Without any perceptible alteration in the Hf–N distances, the metal–carbon distance in **9** has increased considerably to 2.439(4) Å. The Hf–O distance of

(32)  $[\text{Hf}(\text{TC-3,5})_2\{\mu\text{-}\eta^2\text{:}\eta^2\text{-ON}(\text{CH}_2\text{CH}_2\text{Ph})\}(\mu\text{-O})]$ :  $P2_1/c$ ,  $Z = 4$ ,  $a = 23.5409(4)$  Å,  $b = 11.9600(2)$  Å,  $c = 19.3407(3)$  Å,  $\beta = 109.709(1)^\circ$ ,  $V = 5126.35(8)$  Å<sup>3</sup>.

(33)  $[\text{Zr}(\text{TC-3,3})_2\{\mu\text{-}\eta^2\text{:}\eta^2\text{-ON}(i\text{-Pr})\}(\mu\text{-O})]$ :  $Pnma$ ,  $Z = 4$ ,  $a = 10.0703(9)$  Å,  $b = 24.146(2)$  Å,  $c = 17.8020(16)$  Å,  $V = 4328(1)$  Å<sup>3</sup>.

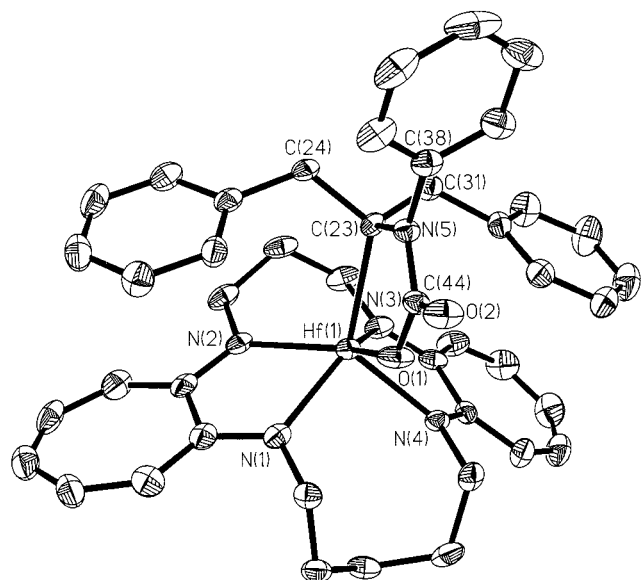
(34)  $[\text{Zr}(\text{TC-3,5})_2\{\mu\text{-}\eta^2\text{:}\eta^2\text{-ON}(o\text{-MePh})\}(\mu\text{-O})]$ :  $Pnma$ ,  $Z = 4$ ,  $a = 14.811(6)$  Å,  $b = 21.96(1)$  Å,  $c = 18.143(9)$  Å,  $V = 5903(2)$  Å<sup>3</sup>.

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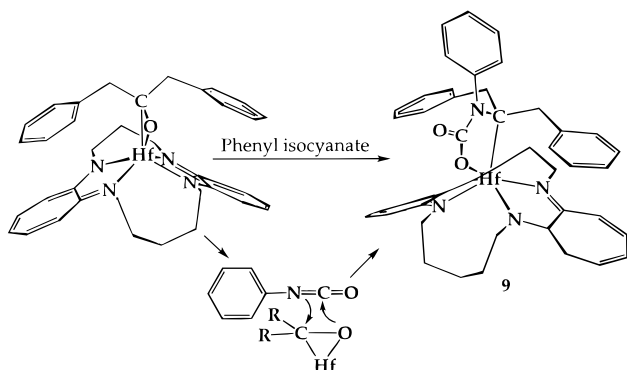
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**Figure 8.** ORTEP diagram of **9** showing 50% ellipsoids and atom-labeling scheme. Selected distances and angles are contained in Table 4.

**Scheme 9**



2.050(3) Å is not unusually short, despite differences in the bound (1.306(5) Å) and terminal (1.222(5) Å) C–O bond lengths, which implies some delocalization of the carbamate double bond, potentially contributing additional electron density to the metal center. The carbamate ligand exhibits a single C–O stretching band at 1645 cm<sup>−1</sup> in the infrared spectrum, slightly lower in energy compared to the values of 1660 and 1651 cm<sup>−1</sup> in a somewhat related dinuclear zirconafuranone com-

plex.<sup>37</sup> Attempts to isolate products from the reaction of **1** with substrates comparable to phenyl isocyanate, among them PhCH<sub>2</sub>NCO and PhNCS, were unsuccessful. In the polar solvent media required for these reactions, compound **1** slowly decomposed at elevated temperatures, forming [Hf(TC-3,5)(OCH(CH<sub>2</sub>Ph)<sub>2</sub>)Cl]<sup>6</sup> as well as other unidentified species.

## Conclusions

The coordinated η<sup>2</sup>-ketone ligand in the tropocoronand complex **1** reacts with several substrates to afford interesting organic moieties. Metal-mediated transformations include 1,1-additions, pinacolic coupling, and C–H and C–O bond scission from which a variety of complicated constructs have been assembled incorporating one of the simplest of starting materials, carbon monoxide. As exemplified by the insertion of phenyl isocyanate into a C–O bond derived from carbon monoxide, these metal-mediated conversions can proceed through unprecedented pathways. These bond-forming reactions allow for the incorporation of isotopically labeled substrates into larger molecules and potentially could contribute to synthetic organic methodology. During the course of this research, metal complexes with a diverse set of organic ligands have been isolated (Scheme 2), which, following hydrolysis, could be detached. The reactivity described here is due at least in part to the electronic and steric properties of the (TC-*n,m*)<sup>2−</sup> tetraazamacrocycle compared to more conventional organometallic ligands such as cyclopentadienyl.

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**Supporting Information Available:** Tables of anisotropic thermal parameters, hydrogen atom parameters, and complete bond distances and angles and ORTEP diagrams for all compounds (81 pages). Ordering information is given on any current masthead page.

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