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Supplementary Material Available: Tables of crystal data en-

compassing data collection and solution/refinement, atomic coordinates, isotropic and anisotropic temperature factors, hydrogen atom coordinates, bond lengths, and bond angles (10 pages); tables of observed and calculated structure factors (36 pages). Ordering information is given on any current masthead page.

Syntheses, Structures, and Reactivities of Unusual Four-Membered Metallacycles Formed in Insertion Reactions of $\text{N}=\text{N}=\text{O}$, $\text{N}=\text{N}=\text{NR}$, and $\text{N}=\text{N}=\text{CR}_2$ with $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Zr}(\text{C}_2\text{Ph}_2)$

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Abstract: Nitrous oxide reacts with $\text{Cp}^*_2\text{Zr}(\text{C}_2\text{Ph}_2)$ (**1**, $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$) to afford an organometallic product in which N_2O has been incorporated *without* loss of dinitrogen. This adduct, $\text{Cp}^*_2\text{Zr}\{\text{N}(\text{O})\text{NCP}(\text{CPh})\}$ (**2**), is isolable yet thermally unstable with respect to loss of dinitrogen at ambient temperature to give the monomeric diphenyloxametallacyclobutene derivative $\text{Cp}^*_2\text{Zr}(\text{OCPh}=\text{CPh})$ (**3**). **3** crystallizes from toluene solution in the monoclinic space group $P2_1/n$ with $a = 9.194$ (2) Å, $b = 19.422$ (4) Å, $c = 16.642$ (4) Å, $\beta = 104.60$ (2)°, and $Z = 4$. The least-squares refinement converged to $R(F) = 0.051$ and $R(wF) = 0.058$ for the 1849 unique data with $F_o > 4\sigma(F_o)$. Salient metrical parameters of the four-membered oxametallacycle include the following: $\text{Zr}\cdots\text{C}(1)$, 2.543 (6) Å; $\text{Zr}-\text{C}(2)$, 2.219 (7) Å, $\text{Zr}-\text{O}$, 2.065 (5) Å; $\text{C}(1)-\text{C}(2)$, 1.348 (12) Å; $\text{O}-\text{C}(1)$, 1.440 (10) Å. **3** reacts with H_2 to give the enolate hydride $\text{Cp}^*_2\text{Zr}(\text{H})(\text{OCPh}=\text{CHPh})$ (**8**) and with HCl to give $\text{Cp}^*_2\text{ZrCl}_2$ and deoxybenzoin. Substrates with acidic hydrogens (H_2O , PhOH , $\text{O}=\text{CMe}_2$, $\text{HC}\equiv\text{CH}$, $\text{HC}\equiv\text{CPh}$, and $\text{HC}\equiv\text{C}^t\text{Bu}$) react with **3** to give enolate derivatives $\text{Cp}^*_2\text{Zr}(\text{X})(\text{OCPh}=\text{CHPh})$ (**9**, $\text{X} = \text{OH}$; **10**, $\text{X} = \text{OPh}$; **11**, $\text{X} = \text{OC}(\text{CH}_2)\text{Me}$; **12**, $\text{X} = \text{C}\equiv\text{CH}$; **13**, $\text{X} = \text{C}\equiv\text{CPh}$; **14**, $\text{X} = \text{C}\equiv\text{C}^t\text{Bu}$), respectively. In contrast, insertion reactions into the $\text{Zr}-\text{C}$ bond of **3** are observed for $(\text{O}=\text{CH}_2)_x$, $\text{O}=\text{CHTol}$, $\text{O}=\text{CH}(n\text{-Hex})$, ToIN_3 , Ph_2CN_2 , CO , and $^t\text{BuN}\equiv\text{C}$, affording the 5- and 6-membered metallacycles $\text{Cp}^*_2\text{Zr}(\text{OCPh}=\text{CPhCH}_2\text{O})$ (**15**), $\text{Cp}^*_2\text{Zr}(\text{OCPh}=\text{CPhCHTolO})$ (**16**), $\text{Cp}^*_2\text{Zr}\{\text{OCPh}=\text{CPhCH}(n\text{-Hex})\text{O}\}$ (**17**), $\text{Cp}^*_2\text{Zr}\{\text{OCPh}=\text{CPhN}(\text{N}=\text{NTol})\}$ (**18**), $\text{Cp}^*_2\text{Zr}\{\text{OCPh}=\text{CPhN}(\text{N}=\text{CPh}_2)\}$ (**19**), $\text{Cp}^*_2\text{Zr}\{\text{OCPh}=\text{CPhC}(=\text{O})\}$ (**20**), and $\text{Cp}^*_2\text{Zr}\{\text{OCPh}=\text{CPhC}(=\text{N}^t\text{Bu})\}$ (**21**), respectively. *p*-Tolyl azide and diphenyldiazomethane react with **1** to afford $\text{Cp}^*_2\text{Zr}\{\text{N}(\text{N}_2\text{-}p\text{-C}_6\text{H}_4\text{CH}_3)\text{CPh}=\text{CPh}\}$ (**4**) and $\text{Cp}^*_2\text{Zr}\{\text{N}(\text{N}=\text{CPh}_2)\text{CPh}=\text{CPh}\}$ (**5**), respectively; these complexes do not cleanly lose N_2 on thermolysis. **4** crystallizes from benzene solution in the monoclinic space group $P2_1/c$ with $a = 9.912$ (4) Å, $b = 30.919$ (9) Å, $c = 13.583$ (5) Å, $\beta = 98.97$ (2)°, and $Z = 4$. The least-squares refinement converged to $R(F) = 0.067$ and $R(wF) = 0.064$ for the 2439 unique data with $F_o > 3\sigma(F_o)$. Important metrical parameters of the planar four-membered azametallacycle include the following: $\text{Zr}-\text{C}(21)$, 2.285 (8) Å; $\text{Zr}-\text{N}(1)$, 2.173 (8) Å; $\text{C}(21)-\text{C}(22)$, 1.373 (16) Å; $\text{C}(22)-\text{N}(1)$, 1.423 (12) Å; $\text{N}(1)-\text{N}(2)$, 1.341 (12) Å; $\text{N}(2)-\text{N}(3)$, 1.305 (12) Å. Water adds across a $\text{Zr}-\text{C}$ bond of **1** to give the hydroxy vinyl species $\text{Cp}^*_2\text{Zr}(\text{OH})(\text{CPh}=\text{CHPh})$ (**6**), but H_2O adds across the $\text{Zr}-\text{N}$ bond of **5** to yield $\text{Cp}^*_2\text{Zr}(\text{OH})\{\text{CPh}=\text{CPhNH}(\text{N}=\text{CPh}_2)\}$ (**7**).

Introduction

During the course of our investigations on the use of nitrous oxide ($\text{N}=\text{N}=\text{O}$) as an oxygen atom transfer reagent in organometallic systems, we have been especially interested in studying its reactivity toward early metal (group 4), d^0 complexes.^{2,3} The impetus for focusing our initial work on this area has been 2-fold. First, since d^0 complexes are in their highest oxidation states, oxidation of such complexes by N_2O to give metal oxo derivatives is precluded,⁴ and any oxo-transfer reaction from

N_2O will necessarily involve oxidation at a ligand site. Second, it has been previously shown that organoazides ($\text{N}=\text{N}=\text{NR}$)⁵ and diazoalkanes ($\text{N}=\text{N}=\text{CR}_2$),⁶ molecules isoelectronic with

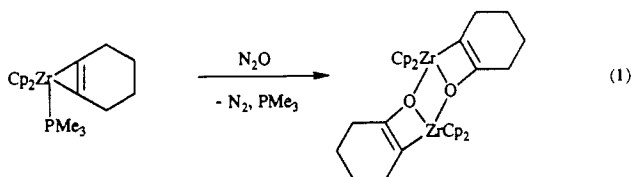
(4) Other workers have exploited N_2O as a reagent for preparing unusual transition-metal oxides and oxo clusters according to the general reaction $\text{M}^+ + \text{N}_2\text{O} \rightarrow \text{O}=\text{M}^{+2} + \text{N}_2$. (a) Bottomley, F.; Sutin, L. *Adv. Organomet. Chem.* **1988**, *28*, 339. (b) Bottomley, F.; Brintzinger, H. *J. Chem. Soc., Chem. Commun.* **1978**, 234. (c) Bottomley, F.; White, P. S. *Ibid.* **1981**, 28. (d) Bottomley, F.; Lin, I. J. B.; White, P. S. *J. Am. Chem. Soc.* **1981**, *103*, 703. (e) Bottomley, F.; Egharevba, G. O.; Lin, I. J. B.; White, P. S. *Organometallics* **1985**, *4*, 550. (f) Bottomley, F.; Lin, I. J. B.; Mukaida, M. *J. Am. Chem. Soc.* **1980**, *102*, 5238. (g) Bottomley, F.; Paez, D. E.; White, P. S. *Ibid.* **1981**, *103*, 5581. (h) Bottomley, F.; Paez, D. E.; White, P. S. *Ibid.* **1982**, *104*, 5651. (i) Bottomley, F.; Paez, D. E.; White, P. S. *Ibid.* **1985**, *107*, 7226. (j) Bottomley, F.; Drummond, D. F.; Paez, D. E.; White, P. S. *J. Chem. Soc., Chem. Commun.* **1986**, 1752. (k) Berg, D. J.; Burns, C. J.; Andersen, R. A.; Zalkin, A. *Organometallics* **1989**, *8*, 1865.

(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.

(1) (a) The University of Chicago. (b) University of Delaware.
 (2) For a recent review of oxo-transfer reactions, see: Holm, R. H. *Chem. Rev.* **1987**, *87*, 1401.
 (3) (a) Vaughan, G. A.; Rupert, P. B.; Hillhouse, G. L. *J. Am. Chem. Soc.* **1987**, *109*, 5538. (b) Vaughan, G. A.; Hillhouse, G. L.; Lum, R. T.; Buchwald, S. L.; Rheingold, A. L. *J. Am. Chem. Soc.* **1988**, *110*, 7215. (c) Vaughan, G. A.; Sofield, C. D.; Hillhouse, G. L.; Rheingold, A. L. *J. Am. Chem. Soc.* **1989**, *111*, 5491.

nitrous oxide, react cleanly with many group 4 metallocene complexes, so this seemed to be an attractive, logical starting point.

We recently demonstrated that a new, simple ligand type, an oxametallacyclobutene, could be accessed by formal insertion of an oxygen atom (from nitrous oxide) into a Zr-C bond of the coordinated alkyne in $\text{Cp}_2\text{Zr}(\text{PMe}_3)(\text{cyclohexyne})$ ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$) as shown in eq 1.^{3b} We were intrigued by the synthetic possibilities



offered by this unique ligand (essentially an enolate anion), but our efforts to explore its reaction chemistry were thwarted by the dimeric nature of the complex that rendered it (a) relatively insoluble in common solvents and (b) effectively coordinatively and electronically saturated at the metal center. In an attempt to inhibit dimerization and enhance solubility, we have turned to the sterically more encumbered bis(pentamethylcyclopentadienyl) alkyne derivative $\text{Cp}^*\text{Zr}(\text{C}_2\text{Ph}_2)$ (**1**; $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$). Herein we report the preparation of a monomeric diphenyloxametallacyclobutene complex (from the reaction of **1** with N_2O) and its reactivity toward a number of small molecules. Additionally, the reactivities of organoazides and diazoalkanes toward **1** have been explored, and the results of these studies are also presented. Some of these results have been previously communicated in preliminary form.^{3c}

Experimental Section

General Considerations. Reactions were carried out by using standard high-vacuum and Schlenk techniques with dry, air-free solvents;⁷ gas evolution experiments were carried out with a Toepler apparatus. ^1H NMR spectra were recorded at 500 MHz in C_6D_6 solution. In all cases the coupling between aromatic protons is $J = 7 \pm 1$ Hz. ^{13}C NMR spectra were recorded at 125.77 or 75.57 MHz in C_6D_6 solution. For the aromatic carbons $^1J_{\text{CH}} = 160 \pm 5$ Hz. In some cases aryl or vinyl signals are obscured by the solvent signals or accidental overlap with another peak. Infrared data (Nujol mulls, KBr plates) were measured by using a Nicolet 20SXB instrument. Elemental analyses were performed by Desert Analytics (Tucson, AZ). Nitrous oxide from a lecture bottle (Matheson) was condensed at liquid nitrogen temperature and residual noncondensable gases were removed under vacuum; boil-off N_2O (bp -90°C) was used in subsequent experiments. Nitrous oxide labeled with 99% ^{15}N at the terminal position ($^{15}\text{N}=\text{N}=\text{O}$) was used as purchased from MSD Isotopes. *p*-Tolyl azide⁸ and diphenyldiazomethane⁹ were prepared by literature procedures. $\text{Cp}^*\text{Zr}(\text{C}_2\text{Ph}_2)$ (**1**) was prepared by reacting diphenylacetylene with $\{\text{Cp}^*\text{Zr}(\text{N}_2)\}_2(\mu\text{-N}_2)$ according to the procedure of Bercaw and Threlkel.¹⁰

Preparation of $\text{Cp}^*\text{Zr}[\text{N}(\text{O})\text{NCPH}=\text{CPh}]$ (2**).** Petroleum ether (10 mL) was vacuum transferred onto 0.120 g (0.222 mmol) of **1** in a 25-mL recovery flask attached to a needle-valve adapter. Stirring the cooled (-78°C) solution under nitrous oxide (1 atm) resulted in the immediate precipitation of pale orange solids. The solvent was removed under vacuum into a cold trap, and a Toepler experiment showed that only 0.04 equiv of N_2/Zr had been evolved. The yield of residual solids was 0.095 g (73%) of **2**. Storage of **2** for 24 h at ambient temperature in a nitrogen-filled glovebox resulted in decomposition with loss of dinitrogen (see below). Thus, characterization of **2** required maintaining both its solutions and solid samples at low temperature, and for this reason elemental analyses of solid samples were generally low in nitrogen. Anal. Calcd for $\text{C}_{34}\text{H}_{40}\text{N}_2\text{OZr}$: C, 69.94; H, 6.90; N, 4.80. Found: C, 69.91; H, 7.14; N, 2.80. ^1H NMR δ 1.77 (s, $\text{C}_5(\text{CH}_3)_5$, 30 H), 6.83 (d, *o*-Ph, 2 H), 6.89

(t, *p*-Ph, 1 H), 7.01 (t, *m*-Ph, 2 H), 7.07 (t, *p*-Ph, 1 H), 7.17 (t, *m*-Ph, 2 H), 7.84 (d, *o*-Ph, 2 H). ^{13}C NMR δ 190.1 (s), 148.4 (s), 145.3 (s), 138.5 (s, in ^{15}N -**2**: d, $|^1J_{\text{N}^{15}\text{C}}| = 7$ Hz), 130.6 (d, Ph), 130.2 (d, Ph), 128.4 (d, Ph), 127.6 (d, Ph), 127.1 (d, Ph), 124.5 (d, Ph), 121.1 (s, $\text{C}_5(\text{CH}_3)_5$), 11.5 (q, $\text{C}_5(\text{CH}_3)_5$, $J = 126$ Hz). $\text{Cp}^*\text{Zr}[\text{N}(\text{O})\text{NCPH}=\text{CPh}]$ (^{15}N -**2**) was prepared analogously except that only 1 equiv of $^{15}\text{N}=\text{N}=\text{O}$ was used; alternatively, solutions of ^{15}N -**2** for NMR studies could be prepared cleanly in C_7D_8 or C_6D_6 solution.

Preparation of $\text{Cp}^*\text{Zr}(\text{OCPh}=\text{CPh})$ (3**).** (a) Toluene (10 mL) was vacuum transferred onto 0.165 g (0.306 mmol) of **1** in a 25-mL recovery flask attached to a needle-valve adapter. The solution was stirred for 48 h under nitrous oxide (1 atm) at ambient temperature. The solvent was removed from the deep red solution under vacuum, and the residual gases were collected in a Toepler experiment yielding 0.96 equiv of N_2/Zr . Recrystallization of the residue from cold petroleum ether gave 0.145 g (85%) of red **3**. Anal. Calcd for $\text{C}_{34}\text{H}_{40}\text{OZr}$: C, 73.46; H, 7.25; N, 0.00. Found: C, 73.78; H, 7.43; N, 0.00. ^1H NMR δ 1.81 (s, $\text{C}_5(\text{CH}_3)_5$, 30 H), 6.95 (t, *p*-Ph, 2 H), 7.08 (t, *p*-Ph, 2 H), 7.18 (m, Ph, 6 H), 7.99 (d, *o*-Ph, 2 H). ^{13}C NMR δ 158.6 (s), 144.1 (s), 136.8 (s), 136.0 (s), 129.2 (d, Ph), 127.4 (d, Ph), 122.7 (d, Ph), 120.6 (s, $\text{C}_5(\text{CH}_3)_5$), 11.2 (q, $\text{C}_5(\text{CH}_3)_5$, $J = 127$ Hz).

(b) Alternatively, **3** may be prepared in the solid state by gently agitating solid **1** under an atmosphere of N_2O for 15 h, yielding **3** quantitatively.

Reaction of **3 with HCl.** A 20-mg (0.036 mmol) sample of **3** was placed in a 5-mm NMR tube along with 0.4 mL of C_6D_6 . The tube was placed on a vacuum line via a needle-valve adapter, the contents were frozen at -196°C , and then anhydrous HCl (0.078 mmol) was condensed from a calibrated volume onto the frozen solution. The tube was sealed with a torch and the contents were allowed to thaw at room temperature, during which time the solution decolorized from red to pale yellow. The products, as determined by ^1H NMR, were deoxybenzoin ($\text{PhCH}_2\text{C}(\text{O})\text{Ph}$, by comparison to an authentic sample) and Cp^*ZrCl_2 (the only Zr-containing product).

Reaction of $^{14}\text{N}=\text{N}=\text{O}$ with ^{15}N -2**.** A C_6D_6 solution sample of ^{15}N -**2** was prepared in a 5-mm NMR tube as described above, using 57 mg (0.106 mmol) of **1** and 0.107 mmol of $^{15}\text{N}=\text{N}=\text{O}$. The sample was frozen and the volatile gasses were removed under vacuum. Into the sample tube was condensed (-196°C), via a calibrated volume, enough $^{14}\text{N}=\text{N}=\text{O}$ to give about 1 atm at 10°C . The solution was thawed at 10°C and placed in a precooled (20°C) ^{13}C NMR spectrometer probe. The ^{13}C resonance corresponding to the carbon atom attached to nitrogen was monitored over a period of several hours. During that time, a singlet at δ 138.50 corresponding to **2** grew as a shoulder on the doublet due to ^{15}N -**2** (δ 138.53, $|^1J_{\text{N}^{15}\text{C}}| = 7$ Hz).

Preparation of $\text{Cp}^*\text{Zr}[\text{N}(\text{N}=\text{NTol})\text{CPh}=\text{CPh}]$ (4**).** A 25-mL 2-necked flask fitted with a rubber septum was charged with 0.165 g (0.306 mmol) of **1** and attached to a filter-frit apparatus. The apparatus was evacuated and toluene (10 mL) was condensed into the reaction flask at -78°C . An inert atmosphere was established, and 0.340 mmol of *p*-tolyl azide (0.41 mL of a 0.83 M petroleum ether solution) was added via syringe. The cold bath was removed and the solution was stirred for 1 h, and then the volume was reduced to 5 mL, the green solution was filtered, and the remaining solvent was removed under vacuum. Heptane (3 mL) was transferred onto the residue, and the mixture was briefly stirred and then filtered. The bright green precipitate was washed with a small portion of heptane, yielding 0.145 g (71%) of **4**. Anal. Calcd for $\text{C}_{41}\text{H}_{47}\text{N}_3\text{Zr}$: C, 73.17; H, 7.04; N, 6.24. Found: C, 72.60; H, 7.08; N, 5.43. ^1H NMR δ 1.89 (s, $\text{C}_5(\text{CH}_3)_5$, 30 H), 2.16 (s, $\text{C}_6\text{H}_4\text{CH}_3$, 3 H), 6.78 (d, *o*-Ph, 2 H), 6.85 (t, *p*-Ph, 1 H), 7.04 (m, *m*-Ph/Tol, 4 H), 7.14 (t, *p*-Ph, 1 H), 7.26 (t, *m*-Ph, 2 H), 7.43 (d, Tol', 2 H), 7.70 (d, *o*-Ph, 2 H). ^{13}C NMR δ 173.4 (s), 151.4 (s), 143.5 (s), 135.0 (s), 133.2 (s), 131.3 (d, aryl), 130.5 (d, aryl), 129.7 (d, aryl), 128.4 (d, aryl), 127.7 (d, aryl), 127.4 (d, aryl), 123.5 (d, aryl), 122.8 (s, $\text{C}_5(\text{CH}_3)_5$), 119.9 (d, aryl), 21.1 (q, $\text{C}_6\text{H}_4(\text{CH}_3)$, $J = 126$ Hz), 12.0 (q, $\text{C}_5(\text{CH}_3)_5$, $J = 127$ Hz).

Preparation of $\text{Cp}^*\text{Zr}[\text{N}(\text{N}=\text{CPh}_2)\text{CPh}=\text{CPh}]$ (5**).** Toluene (8 mL) was vacuum transferred into a 25-mL flask charged with 0.216 g (0.389 mmol) of **1** and 0.079 g (0.407 mmol) of diphenyldiazomethane in a filter-frit assembly. The solution was stirred for 90 min and filtered, and the solvent was removed under vacuum. Heptane (3 mL) was transferred onto the green-brown residue, and the mixture was briefly stirred and then filtered. The green precipitate was washed with a small portion of heptane, yielding 0.229 g (78%) of **5**. Anal. Calcd for $\text{C}_{47}\text{H}_{50}\text{N}_2\text{Zr}$: C, 76.89; H, 6.86; N, 3.82. Found: C, 76.71; H, 7.06; N, 3.63. ^1H NMR δ 1.78 (s, $\text{C}_5(\text{CH}_3)_5$, 30 H), 6.85–7.30 (m, Ph, 18 H), 7.58 (d, *o*-Ph, 2 H). ^{13}C NMR δ 172.2 (s), 144.3 (s), 144.1 (s), 141.6 (s), 140.0 (s), 138.8 (s), 133.8 (s), 131.2 (d, Ph), 130.4 (d, Ph), 129.1 (d, Ph), 128.4 (d, Ph), 128.0 (d, Ph), 127.3 (d, Ph), 126.8 (d, Ph), 126.6 (d, Ph), 126.3 (d, Ph),

(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, 1984.

(7) For a general description of the equipment and techniques used in carrying out this chemistry, see: Burger, B. J.; Bercaw, J. E. In *Experimental Organometallic Chemistry*; Wayda, A. L., Darensbourg, M. Y., Eds.; ACS Symposium Series 357; American Chemical Society: Washington, DC, 1987; pp 79–98.

(8) Noelting, E.; Michel, O. *Ber. Dtsch. Chem. Ges.* **1893**, *26*, 86.

(9) Miller, J. B. *J. Org. Chem.* **1959**, *24*, 560.

(10) Threlkel, R. S. Ph.D. Thesis, California Institute of Technology, 1980.

122.6 (d, Ph), 121.2 (s, $C_5(CH_3)_5$), 12.2 (q, $C_5(CH_3)_5$, $J = 126$ Hz).

Preparation of $Cp^*_2Zr(OH)(CPh=CHPh)$ (6). A 25-mL 2-necked flask fitted with a rubber septum was charged with 0.135 g (0.242 mmol) of **1** and attached to a needle valve adapter. Toluene (10 mL) was condensed into the reaction flask at $-78^\circ C$, and then 4.5 μL (0.250 mmol) of water was added to the stirred solution via syringe followed by removal of the cold bath. The dark-red solution became yellow in color over a period of 30 min, at which time the volume of the solution was reduced to 5 mL, the solution was filtered, and the volatiles were removed under vacuum. Addition of heptane (4 mL) and vigorous stirring caused the formation of pale-yellow solids which were isolated by filtration, yielding 0.095 g (68%) of **6**. Anal. Calcd for $C_{34}H_{42}OZr$: C, 73.19; H, 7.59. Found: C, 73.64; H, 7.61. 1H NMR δ 1.84 (s, $C_5(CH_3)_5$, 30 H), 4.91 (s, OH, 1 H), 5.76 (s, $=CHPh$, 1 H), 6.94 (t, *p*-Ph, 1 H), 6.97 (t, *p*-Ph, 1 H), 7.0 (t, *m*-Ph, 2 H), 7.14 (t, *m*-Ph, 2 H), 7.22 (m, *o*-Ph, 4 H). ^{13}C NMR δ 195.0 (s), 151.7 (s), 140.0 (s), 132.4 (d, $=CHPh$, $J = 148$ Hz), 129.1 (d, Ph), 128.3 (d, Ph), 127.6 (d, Ph), 125.3 (d, Ph), 123.9 (d, Ph), 119.4 (s, $C_5(CH_3)_5$), 11.7 (q, $C_5(CH_3)_5$, $J = 126$ Hz). IR $\nu(OH) = 3634$ (s) cm^{-1} .

Preparation of $Cp^*_2Zr(OH)\{CPh=CPhNH(N=CPh_2)\}$ (7). A 25-mL 2-necked flask fitted with a rubber septum was charged with 0.042 g (0.057 mmol) of **5** and attached to a vacuum adapter. The apparatus was evacuated and toluene (8 mL) was condensed into the reaction flask at $-78^\circ C$. An Ar atmosphere was established and 1.2 μL (0.067 mmol) of water was added via syringe to the stirred solution followed by removal of the cold bath. The dark-green solution became orange in color within 30 min, at which time the volatiles were removed under vacuum. The residues were extracted with 5 mL of heptane and filtered, and the volume was reduced to 1 mL to precipitate 0.035 g (81%) of pure **7** as a yellow powder that was collected by filtration. Anal. Calcd for $C_{47}H_{52}N_2OZr$: C, 75.05; H, 6.97; N, 3.72. Found: C, 75.34; H, 7.02; N, 3.86. 1H NMR δ 1.71 (s, $C_5(CH_3)_5$, 30 H), 4.06 (s, OH, 1 H), 6.75 (d, *o*-Ph, 2 H), 6.81 (t, *p*-Ph, 1 H), 6.90 (m, Ph, 1 H), 6.97 (m, Ph, 4 H), 7.08 (m, Ph, 1 H), 7.18 (t, *m*-Ph, 2 H), 7.27 (t, *m*-Ph, 2 H), 7.37 (d, *o*-Ph, 2 H), 7.51 (d, *o*-Ph, 2 H), 7.56 (d, *o*-Ph, 2 H), 9.91 (s, N-H, 1 H). ^{13}C NMR δ 158.9 (s), 149.3 (s), 147.6 (s), 141.0 (s), 140.0 (s), 138.4 (s), 137.3 (s), 132.5 (d, Ph), 131.7 (d, Ph), 131.1 (d, Ph), 129.2 (d, Ph), 128.2 (d, Ph), 127.8 (d, Ph), 127.3 (d, Ph), 126.9 (d, Ph), 126.6 (d, Ph), 126.1 (d, Ph), 126.0 (d, Ph), 122.0 (d, Ph), 120.1 (s, $C_5(CH_3)_5$), 11.7 (q, $C_5(CH_3)_5$, $J = 129$ Hz). IR $\nu(OH) = 3650$ (s) cm^{-1} , $\nu(NH) = 3176$ (m, br) cm^{-1} .

Preparation of $Cp^*_2Zr(H)(OCPh=CHPh)$ (8). (a) A 25-mL flask was charged with 0.235 g (0.423 mmol) of **3**, and then toluene (15 mL) was vacuum transferred onto the solids at $-78^\circ C$. An atmosphere of dihydrogen (400 Torr) was admitted into the reaction flask, causing a color change from dark red to yellow over a period of 10 min. The volume of the solvent was reduced under vacuum to 5 mL, during which the solution darkened to a green-brown color (reestablishment of the H_2 atmosphere caused the color to revert to yellow). The solution was filtered, and the remaining solvent was removed under vacuum. Heptane (2 mL) was vacuum transferred onto the solids, and the mixture was vigorously stirred under H_2 (400 Torr) to afford a pale-yellow solid that was isolated by filtration to yield 0.055 g (23%) of **8**. Anal. Calcd for $C_{34}H_{42}OZr$: C, 73.20; H, 7.59. Found: C, 73.06; H, 7.64. 1H NMR δ 1.96 (s, $C_5(CH_3)_5$, 30 H), 5.92 (s, 1 H), 6.26 (s, 1 H), 6.91 (t, *p*'-Ph, 1 H), 7.04 (m, *m*'-*p*-Ph, 3 H), 7.0 (t, *m*-Ph, 2 H), 7.19 (d, *o*'-Ph, 2 H), 7.60 (d, *o*-Ph, 2 H). ^{13}C NMR δ 159.0 (s), 139.9 (s), 139.4 (s), 129.6 (d, Ph), 129.1 (d, Ph), 128.4 (d, Ph), 128.1 (d, Ph), 124.8 (d, Ph), 118.6 (s, $C_5(CH_3)_5$), 107.0 (d, $=CHPh$, $J = 151$ Hz), 11.8 (q, $C_5(CH_3)_5$, $J = 126$ Hz).

(b) Alternatively, 0.06 g (0.104 mmol) of **3** was placed into a tared vial attached to a 22.2-mL calibrated volume. After evacuation, 240 Torr (0.290 mmol) of hydrogen was admitted to the volume, which was isolated and opened to the solid **3**. Over a period of several hours, the color of the solids changed from red to yellow, yielding **8** quantitatively. A Toepler analysis indicated 0.8 equiv of H_2/Zr was consumed.

Preparation of $Cp^*_2Zr(OH)(OCPh=CHPh)$ (9). A 25-mL 2-necked flask fitted with a rubber septum was charged with 0.223 g (0.401 mmol) of **3** and attached to a needle-valve adapter. The apparatus was evacuated and petroleum ether (20 mL) was condensed into the reaction flask at $-78^\circ C$. An Ar atmosphere was established and 7.5 μL (0.040 mmol) of water was added via syringe to the stirred solution. The cold bath was removed, and the dark-red solution became yellow in color as the solution slowly warmed to ambient temperature (30 min). The solvent was removed to yield 0.149 g (64%) of **9** as a tacky-yellow foam. Anal. Calcd for $C_{34}H_{42}O_2Zr$: C, 71.15; H, 7.38. Found: C, 71.07; H, 7.52. 1H NMR δ 1.85 (s, $C_5(CH_3)_5$, 30 H), 4.46 (s, OH, 1 H), 6.02 (s, $=CHPh$, 1 H), 6.93 (t, *p*-Ph, 1 H), 7.05–7.20 (m, Ph, 5 H), 7.23 (d, *o*-Ph, 2 H), 7.63 (d, *o*-Ph, 2 H). ^{13}C NMR δ 159.9 (s), 141.1 (s), 139.8 (s), 129.7 (d, Ph), 128.8 (d, Ph), 128.3 (d, Ph), 128.0 (d, Ph), 127.8 (d, Ph), 124.2

(d, Ph), 120.0 (s, $C_5(CH_3)_5$), 106.0 (d, $=CHPh$, $J = 150$ Hz), 11.1 (q, $C_5(CH_3)_5$, $J = 126$ Hz). IR $\nu(OH) = 3672$ (s) cm^{-1} .

Reaction of **8 with H_2O .** Titration of a C_6D_6 solution of **8** in a screw-capped NMR tube (monitored by 1H NMR spectroscopy) with 0.5- μL aliquots of H_2O resulted in gas (H_2) evolution and the clean formation of **9**. The addition of a second equivalent of water cleanly produced $Cp^*_2Zr(OH)_2$ and $PhC(O)CH_2Ph$, identified by comparison to authentic samples. (Moreover, it was also observed that samples of **8** stored in non-oven-dried vials were converted over a period of several weeks to **9** by adsorbed water.)

Preparation of $Cp^*_2Zr(OPh)(OCPh=CHPh)$ (10). A 25-mL flask was charged with 0.103 g (0.185 mmol) of **3** and 0.023 g (0.244 mmol) of PhOH and was attached to a filter-frit apparatus. Toluene (6 mL) was vacuum transferred into the flask at $-78^\circ C$. The cold bath was removed from the stirred solution, and the color of the solution changed from deep red-orange to pale pink. Under an argon counterflow, an additional crystal of PhOH (ca. 0.002 g) was added to the mixture via a side-arm on the frit to complete the bleaching of the color. The yellow solution was filtered and the solvent removed under vacuum. The resulting yellow oil was taken up in petroleum ether (3 mL), which was removed cold under vacuum to yield 0.096 g (82%) of **10** as a white foam. Anal. Calcd for $C_{40}H_{46}O_2Zr$: C, 73.91; H, 7.13. Found: C, 73.89; H, 7.36. 1H NMR δ 1.91 (s, $C_5(CH_3)_5$, 30 H), 6.08 (s, $=CHPh$, 1 H), 6.71 (d, *o*-Ph, 2 H), 6.80 (t, *p*-Ph, 1 H), 6.91 (t, *p*-Ph, 1 H), 7.05 (t, *m*-Ph, 2 H), 7.13 (t, *p*-Ph, 1 H), 7.19 (m, *m*-Ph, 6 H), 7.63 (d, *o*-Ph, 2 H). ^{13}C NMR δ 163.8 (s), 160.2 (s), 141.2 (s), 139.2 (s), 129.7 (d, Ph), 129.4 (d, Ph), 128.6 (d, Ph), 128.5 (d, Ph), 128.3 (d, Ph), 128.0 (d, Ph), 124.4 (d, Ph), 121.8 (s, $C_5(CH_3)_5$), 120.2 (d, Ph), 118.1 (d, Ph), 107.5 (d, $=CHPh$, $J = 150$ Hz), 11.6 (q, $C_5(CH_3)_5$, $J = 128$ Hz).

Preparation of $Cp^*_2Zr\{OC(=CH_2)Me\}(OCPh=CHPh)$ (11). Toluene (15 mL) was vacuum transferred into a 25-mL flask charged with 0.110 g (0.196 mmol) of **3**. The solution was frozen to $-196^\circ C$, and then 1.0 mmol of dry acetone was condensed into the flask from a calibrated volume. The solution was thawed and stirred at $65^\circ C$ for 5 h, during which time the color of the solution changed from red to yellow. The volatiles were removed under vacuum, and the residue was dissolved in petroleum ether (4 mL). After removal of the solvent, 0.060 g (50%) of tacky, yellow oil was isolated. A 1H NMR analysis showed that the product mixture contained **11** (75%) and several inseparable impurities, including **9** (10%). 1H NMR δ 1.87 (s, $C(=CH_2)CH_3$, 3 H), 1.95 (s, $C_5(CH_3)_5$, 30 H), 4.07 (s, $=CH_2$, 1 H), 4.09 (s, $=CH_2$, 1 H), 6.04 (s, $=CHPh$, 1 H), 6.92 (t, *p*-Ph, 1 H), 7.06–7.18 (m, Ph, 7 H), 7.58 (d, *o*-Ph, 2 H).

Preparation of $Cp^*_2Zr(C\equiv CH)(OCPh=CHPh)$ (12). Acetylene (0.297 mmol) was transferred from a calibrated volume onto a frozen solution of 0.100 g (0.180 mmol) of **3** in toluene (8 mL). The dark-red solution was thawed and stirred for 18 h, gradually changing color from red to golden yellow. The solution was filtered and the solvent removed under vacuum to give a golden oil. Petroleum ether (3 mL) was condensed onto the oil, stirred, and evaporated at reduced temperature to afford **12** (0.065 g, 62% yield) as a tacky yellow oil. Anal. Calcd for $C_{36}H_{42}OZr$: C, 74.30; H, 7.27. Found: C, 74.22; H, 7.37. 1H NMR δ 1.95 (s, $C_5(CH_3)_5$, 30 H), 3.06 (s, $C\equiv CH$, 1 H), 6.10 (s, $=CHPh$, 1 H), 6.92 (t, *p*-Ph, 1 H), 7.06 (m, Ph, 3 H), 7.15 (m, Ph, 2 H), 7.24 (d, *o*-Ph, 2 H), 7.65 (d, *o*-Ph, 2 H). ^{13}C NMR δ 159.1 (s), 139.6 (s), 139.5 (s), 139.2 (s), 129.9 (d, Ph), 129.0 (d, Ph), 128.3 (d, Ph), 128.0 (d, Ph), 127.9 (d, Ph), 124.7 (d, Ph), 120.7 (s, $C_5(CH_3)_5$), 107.0 (d, $=CHPh$, $J = 157$ Hz), 103.4 (d, $C\equiv CH$, $J = 222$ Hz), 11.9 (q, $C_5(CH_3)_5$, $J = 126$ Hz). IR $\nu(C\equiv CH) = 3270$ (m) cm^{-1} , $\nu(C\equiv C) = 1943$ (w) cm^{-1} .

Preparation of $Cp^*_2Zr(C\equiv CPh)(OCPh=CHPh)$ (13). A 25-mL 2-necked flask fitted with a rubber septum was charged with 0.100 g (0.180 mmol) of **3** and attached to a filter-frit apparatus. Toluene (8 mL) was condensed into the reaction flask by vacuum transfer. Under an argon counterflow, 22.5 μL (0.205 mmol) of phenylacetylene was added to the cold ($-78^\circ C$), stirred solution. The cold bath was removed, and the dark-red solution became pale red-orange in color over the course of an hour, at which time an additional 3- μL portion (0.027 mmol) of phenylacetylene was added to the reaction mixture and stirring was continued for 60 min more. The yellow solution was then filtered and the solvent was removed under vacuum. The addition of petroleum ether (5 mL) to the residue resulted in the formation of yellow solids which, after reduction of the solvent volume to about 3 mL, were isolated by filtration affording 0.076 g (64%) of **13**. Anal. Calcd for $C_{42}H_{46}OZr$: C, 76.66; H, 7.05. Found: C, 76.88; H, 6.98. 1H NMR δ 1.98 (s, $C_5(CH_3)_5$, 30 H), 6.10 (s, $=CHPh$, 1 H), 6.91 (t, *p*-Ph, 1 H), 7.04 (m, Ph, 6 H), 7.17 (t, *m*-Ph, 2 H), 7.23 (d, *o*-Ph, 2 H), 7.64 (d, *o*-Ph, 2 H), 7.67 (d, *o*-Ph, 2 H). ^{13}C NMR δ 159.2 (s), 147.1 (s), 139.5 (s), 139.2 (s), 131.4 (d, Ph), 129.9 (d, Ph), 129.0 (d, Ph), 128.5 (d, Ph), 128.3 (d, Ph), 128.0 (d, Ph), 127.3 (s), 126.7 (d, Ph), 124.7 (d, Ph), 120.6 (s, $C_5(CH_3)_5$), 117.7 (s), 106.9 (d, $=CHPh$, $J = 151$ Hz), 11.8 (q, $C_5(C$

H₃), $J = 125$ Hz). IR $\nu(\text{C}=\text{C}) = 2072$ (w) cm^{-1} .

Preparation of Cp*₂Zr(C≡C^tBu)(OCPh=C^tPh) (14). *tert*-Butylacetylene (0.283 mmol) was condensed from a calibrated gas volume onto a frozen solution of 0.123 g (0.221 mmol) of **3** in 8 mL of toluene. The dark-red solution was thawed and stirred for 3 h, taking on a pale flesh color. An additional 0.103-mmol portion of *tert*-butylacetylene was condensed onto the solution, and stirring was continued for another 60 min, at which time the reaction mixture was yellow. The solution was filtered and the solvent was removed under vacuum. Addition of heptane (2 mL) produced yellow solids which, after reducing the solvent volume to 1 mL, were isolated by filtration to yield 0.44 g (32%) of **14** from the precipitate and 0.057 g (40%) of **14** from the filtrate. Anal. Calcd for C₄₀H₅₀OZr: C, 75.30; H, 8.12. Found: C, 74.68; H, 7.88. ¹H NMR δ 1.44 (s, C(CH₃)₃, 9 H), 1.96 (s, C₅(CH₃)₅, 30 H), 6.10 (s, =CHPh, 1 H), 6.92 (t, *p*-Ph, 1 H), 7.07 (t, *m*-Ph, 2 H), 7.17 (m, *p'*, *m'*-Ph, 3 H), 7.26 (d, *o*-Ph, 2 H), 7.63 (d, *o'*-Ph, 2 H). ¹³C NMR δ 159.3 (s), 139.9 (s), 139.6 (s), 132.3 (s), 129.8 (d, Ph), 129.0 (d, Ph), 128.3 (d, Ph), 127.9 (d, Ph), 125.8 (s), 124.6 (d, Ph), 120.2 (s, C₅(CH₃)₅), 106.7 (d, =CHPh, $J = 151$ Hz), 32.2 (q, C(CH₃)₃, $J = 126$ Hz), 28.7 (s, C(CH₃)₃), 11.9 (q, C₅(CH₃)₅, $J = 126$ Hz). IR $\nu(\text{C}=\text{C}) = 2082$ (m) cm^{-1} .

Preparation of Cp*₂Zr(OCPh=CPhCH₂O) (15). Toluene (10 mL) was vacuum transferred at -78 °C onto 0.213 g (0.383 mmol) of **3** and 0.015 g (0.401 mmol) of paraformaldehyde in a 25-mL flask attached to a filter-frit apparatus. The cold bath was removed and the solution was stirred for 3 h, during which time the color of the solution bleached from deep red-orange to pale orange. The mixture was filtered and the volatiles were removed under vacuum. The remaining pale solids were vigorously stirred with 2 mL of hexamethyldisiloxane, isolated by filtration, and washed twice with small portions of hexamethyldisiloxane, yielding 0.116 g (52%) of **15**. Anal. Calcd for C₃₅H₄₂O₂Zr: C, 71.75; H, 7.22. Found: C, 71.46; H, 7.23. ¹H NMR δ 1.90 (s, C₅(CH₃)₅, 30 H), 5.30 (s, CH₂, 2 H), 6.94 (t, *p*-Ph, 1 H), 6.98 (t, *p*-Ph, 1 H), 7.07 (t, *m*-Ph, 4 H), 7.23 (d, *o*-Ph, 2 H), 7.56 (d, *o*-Ph, 2 H). ¹³C NMR δ 153.1 (s), 143.1 (s), 141.5 (s), 131.3 (d, Ph), 129.6 (d, Ph), 128.5 (d, Ph), 127.4 (d, Ph), 126.4 (d, Ph), 125.8 (d, Ph), 120.9 (s, C₅(CH₃)₅), 113.1 (s), 76.2 (t, CH₂, $J = 142$ Hz), 11.0 (q, C₅(CH₃)₅, $J = 128$ Hz).

Preparation of Cp*₂Zr(OCPh=CPhCHTolO) (16). A 25-mL 2-necked flask fitted with a rubber septum was charged with 0.103 g (0.185 mmol) of **3** and attached to a reaction filter-frit assembly. Toluene (8 mL) was condensed into the reaction flask at -78 °C, and 22.5 μL (0.191 mmol) of *p*-tolualdehyde was added via syringe under an argon counterflow. The cold bath was removed and the stirred solution bleached in color from dark-red to pale red-orange over the course of 90 min, at which time an additional 2 μL (0.017 mmol) of *p*-tolualdehyde was added. The solution was stirred at ambient temperature for 12 h longer and filtered, and the solvent was removed under vacuum. The addition of heptane (4 mL) resulted in the formation of white solids that were separated from the rose-colored solution by filtration, affording 0.065 g (52%) of **16**. Anal. Calcd for C₄₂H₄₈O₂Zr: C, 74.62; H, 7.16. Found: C, 74.66; H, 7.16. ¹H NMR δ 1.89 (s, C₅(CH₃)₅, 15 H), 1.96 (s, C₅(CH₃)₅, 15 H), 2.05 (s, C₆H₄CH₃, 3 H), 6.72 (s, CH(Tol), 1 H), 6.77 (t, *p*-Ph, 1 H), 6.90 (t, *m*-Ph, 2 H), 6.95 (m, *p'*-Ph/Tol, 3 H), 7.08 (m, *o*, *m'*-Ph, 4 H), 7.40 (d, Tol, 2 H), 7.56 (d, *o'*-Ph, 2 H). ¹³C NMR δ 156.8 (s), 143.9 (s), 143.4 (s), 141.8 (s), 135.5 (s), 132.0 (d, aryl), 129.9 (d, aryl), 129.4 (d, aryl), 128.4 (d, aryl), 127.9 (d, aryl), 127.4 (d, aryl), 126.3 (d, aryl), 125.1 (d, aryl), 121.3 (s, C₅(CH₃)₅), 121.2 (s, C₅(CH₃)₅), 114.0 (s), 85.2 (d, CH(Tol), $J = 140$ Hz), 21.1 (q, C₆H₄CH₃, $J = 125$ Hz), 11.4 (q, C₅(CH₃)₅, $J = 126$ Hz), 11.2 (q, C₅(CH₃)₅, $J = 126$ Hz).

Preparation of Cp*₂Zr(OCPh=CPhCH(*n*-Hex)O) (17). A 0.113-g (0.203 mmol) sample of **3** and 30.0 μL (0.223 mmol) of heptaldehyde were allowed to react by following an analogous procedure to that for **16** (above), affording 0.087 g (64%) of **17** as a tacky yellow oil. Anal. Calcd for C₄₁H₅₄O₂Zr: C, 73.49; H, 8.12. Found: C, 73.80; H, 8.33. ¹H NMR δ 0.86–1.86 (m, *n*-Hex, 13 H), 1.95 (s, C₅(CH₃)₅, 15 H), 1.99 (s, C₅(CH₃)₅, 15 H), 5.56 (m, CH(*n*-Hex), 1 H), 6.91 (t, *p*-Ph, 1 H), 6.96 (t, *p*-Ph, 1 H), 7.07 (m, *m*-Ph, 4 H), 7.20 (d, 2 H, *o*-Ph), 7.52 (d, *o*-Ph, 2 H). ¹³C NMR δ 126.1 (d, Ph), 125.5 (d, Ph), 120.8 (s, C₅(CH₃)₅), 120.7 (s, C₅(CH₃)₅), 115.4 (s), 83.1 (d, CH(*n*-Hex), $J = 141$ Hz), 38.8 (t, CH₂, $J = 125$ Hz), 32.5 (t, CH₂, $J = 125$ Hz), 29.8 (t, CH₂, $J = 125$ Hz), 27.8 (t, CH₂, $J = 125$ Hz), 23.1 (t, CH₂, $J = 125$ Hz), 14.3 (q, (CH₂)₃CH₃, $J = 124$ Hz), 11.5 (q, C₅(CH₃)₅, $J = 126$ Hz), 11.2 (q, C₅(CH₃)₅, $J = 126$ Hz).

Preparation of Cp*₂Zr(OCPh=CPhN(N=NTol)) (18). A 25-mL 2-necked flask fitted with a rubber septum was charged with 0.265 g (0.477 mmol) of **3** and attached to a filter-frit assembly. Toluene (5 mL) was condensed into the reaction flask at -78 °C, and 0.498 mmol of *p*-tolyl azide (0.83 M solution in petroleum ether) was added via syringe under an argon counterflow. The cold bath was removed, and the

dark-red solution became deep purple after being stirred at ambient temperature for 3 h. The volatiles were removed under vacuum, 2 mL of heptane was added, and the mixture was cooled to -78 °C. The cold supernatant was cannula filtered off of the residue. Another 2-mL portion of heptane was added to the solids, which were filtered and dried under vacuum to yield 0.143 g (44%) of **18** as a royal purple powder. Anal. Calcd for C₄₁H₄₇N₃OZr: C, 71.47; H, 6.88; N, 6.10. Found: C, 70.58; H, 7.11; N, 5.13. ¹H NMR δ 1.87 (s, C₅(CH₃)₅, 30 H), 2.20 (s, C₆H₄CH₃, 3 H), 7.02 (m, aryl, 3 H), 7.11 (m, aryl, 3 H), 7.23 (m, aryl, 4 H), 7.60 (d, aryl, 2 H), 7.76 (d, aryl, 2 H). ¹³C NMR δ 154.1 (s), 147.4 (s), 139.2 (s), 134.0 (s), 130.8 (d, aryl), 130.3 (s), 129.2 (d, aryl), 128.7 (d, aryl), 128.4 (d, aryl), 127.8 (d, aryl), 127.1 (d, aryl), 127.0 (d, aryl), 126.4 (s), 120.8 (s, C₅(CH₃)₅), 118.2 (d, aryl), 20.9 (q, C₆H₄(CH₃), $J = 126$ Hz), 11.7 (q, C₅(CH₃)₅, $J = 127$ Hz).

Preparation of Cp*₂Zr(OCPh=CPhN(N=CPh₂)) (19). Toluene (8 mL) was vacuum transferred at -78 °C onto 0.105 g (0.189 mmol) of **3** and 0.037 g (0.190 mmol) of diphenyldiazomethane in a 25-mL flask attached to a filter-frit assembly. The cold bath was removed and the solution was stirred for 45 min at ambient temperature, during which time the color of the solution changed from deep red-orange to orange-brown. The solution was then filtered and the solvent removed under vacuum. Petroleum ether (2 mL) was added to the residue, the mixture was vigorously stirred, and then the solvent was removed under vacuum to afford 0.127 g (94%) of **19** as a foamy, dry, red-brown solid. Anal. Calcd for C₄₇H₅₀N₂OZr: C, 75.25; H, 6.72; N, 3.73. Found: C, 74.80; H, 7.18; N, 3.86. ¹H NMR δ 1.85 (s, C₅(CH₃)₅, 30 H), 6.80–7.21 (m, Ph, 10 H), 7.61 (m, Ph, 8 H), 8.19 (d, *o*-Ph, 2 H). ¹³C NMR δ 197.5 (s), 168.1 (s), 167.6 (s), 142.5 (s), 137.9 (s), 137.8 (s), 132.7 (d, Ph), 130.3 (d, Ph), 129.2 (d, Ph), 128.9 (d, Ph), 128.7 (d, Ph), 128.5 (d, Ph), 128.4 (d, Ph), 128.2 (d, Ph), 128.1 (d, Ph), 127.9 (d, Ph), 127.4 (d, Ph), 120.3 (s), 118.0 (s, C₅(CH₃)₅), 12.0 (q, C₅(CH₃)₅, $J = 126$ Hz).

Preparation of Cp*₂Zr(OCPh=CPhC(=O)) (20). A 25-mL flask was charged with 0.201 g (0.362 mmol) of **3** dissolved in 5 mL of toluene. To the stirred solution was added 0.600 mmol of dry CO via a calibrated volume. The red solution of **3** became purple within 5 min after exposure to the carbon monoxide, and after stirring for 20 min at ambient temperature, the noncondensable gases were passed through two liquid nitrogen cooled traps and collected in a Toepler pump which indicated that 0.8 equiv of CO had been consumed. Collection of the purple solids yielded 0.184 g (87%) of **20**. Anal. Calcd for C₃₅H₄₀O₂Zr: C, 71.99; H, 6.91. Found: C, 71.51; H, 6.98. ¹H NMR δ 1.81 (s, C₅(CH₃)₅, 30 H), 6.96 (m, *p'*-Ph, 1 H), 7.01 (m, *m'*-Ph, 2 H), 7.07 (t, *p*-Ph, 1 H), 7.24 (t, *m*-Ph, 2 H), 7.42 (d, *o*-Ph, 2 H), 7.67 (d, *o'*-Ph, 2 H). ¹³C NMR δ 282.6 (s, C=O), 139.9 (s), 138.4 (s), 131.0 (d, Ph), 129.5 (d, Ph), 128.7 (d, Ph), 128.3 (d, Ph), 127.9 (d, Ph), 127.7 (d, Ph), 125.7 (d, Ph), 121.1 (s, C₅(CH₃)₅), 112.4 (s), 11.1 (q, C₅(CH₃)₅, $J = 126$ Hz). IR $\nu(\text{CO}) = 1534$ (s) cm^{-1} . Cp*₂Zr(OCPh=CPh¹³C(=O)) (¹³C-**20**) was analogously prepared by using ¹³CO (92% ¹³C). IR $\nu(\text{CO}) = 1520$ cm^{-1} .

Preparation of Cp*₂Zr(OCPh=CPhC(=N^tBu)) (21). A 25-mL 2-necked flask fitted with a rubber septum was charged with 0.072 g (0.130 mmol) of **3** and attached to a filter-frit assembly. Toluene (5 mL) was condensed into the reaction flask, and the contents were allowed to warm to ambient temperature. To the stirred solution was added via syringe, over the course of 15 min under an argon counterflow, a petroleum ether solution containing 0.136 mmol of *tert*-butyl isocyanide, causing the dark-red solution to turn yellow in color. Removal of the solvent under vacuum left an orange oil which, upon dissolution in and removal of 1.5 mL of petroleum ether, gave a dry orange foam that was recrystallized from cold heptane to yield 0.079 g (95%) of **21** as an orange powder. Anal. Calcd for C₃₉H₄₉NOZr: C, 73.30; H, 7.73; N, 2.19. Found: C, 73.54; H, 7.77; N, 2.18. ¹H NMR δ 1.25 (s, C(CH₃)₃, 9 H), 1.90 (s, C₅(CH₃)₅, 30 H), 6.99 (t, *p'*-Ph, 1 H), 7.06 (m, *p'*, *m*-Ph, 3 H), 7.20 (t, *m'*-Ph, 2 H), 7.38 (d, *o'*-Ph, 2 H), 7.91 (d, *o*-Ph, 2 H). ¹³C NMR δ 192.0 (s), 143.0 (s), 140.9 (s), 132.1 (d, Ph), 129.8 (d, Ph), 128.9 (d, Ph), 128.9 (s), 128.7 (d, Ph), 127.6 (d, Ph), 126.0 (d, Ph), 116.5 (s, C₅(CH₃)₅), 108.5 (s), 59.4 (s, C(CH₃)₃), 32.5 (q, C(CH₃)₃, $J = 126$ Hz), 11.7 (q, C₅(CH₃)₅, $J = 126$ Hz).

Crystal Structure Determinations of **3 and **4**.** A specimen of Cp*₂Zr(OCPh=CPh) grown from a heptane/toluene mixture was mounted and sealed in a glass capillary and found from photographic evidence and systematic absences in the diffraction data to belong to the monoclinic space group *P*₂₁/*n*. Crystallographic data for **3** and **4** are summarized in Table I. No correction for decay of absorption was necessary. The Zr atom was located from a Patterson synthesis. All non-hydrogen atoms were anisotropically refined, all hydrogen atoms were treated as idealized contributions, and the two phenyl rings were constrained as rigid planar hexagons. Table II (Supplementary Material) contains the atomic coordinates and Table III a list of selected bond distances and angles. A

Table I. Crystallographic Data for **3** and **4**

	3	4
(a) Crystal Parameters		
formula	C ₃₄ H ₄₀ OZr	C ₄₁ H ₄₇ N ₃ Zr·C ₆ D ₆
formula wt	555.95	757.11
cryst system	monoclinic	monoclinic
space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> , Å	9.194 (2)	9.912 (4)
<i>b</i> , Å	19.422 (4)	30.919 (9)
<i>c</i> , Å	16.642 (4)	13.583 (5)
β , deg	104.60 (2)	98.97 (2)
<i>V</i> , Å ³	2875.8 (12)	4111.8 (22)
<i>Z</i>	4	4
μ (Mo, K α), cm ⁻¹	4.0	2.6
temp, K	293	294
<i>D</i> (calcd), g·cm ⁻³	1.28	1.22
(b) Data Collection		
radiation	Mo K α	Mo K α
scan limits, deg	4 ≤ 2 θ ≤ 48	4 ≤ 2 θ ≤ 45
rflns colltd	3113	5055
indepdt rflns	2992	4723
obs rflns	1849, 4 σF_o	2439, 3 σF_o
<i>R</i> (int), %	1.6	2.1
std rflns	3 stds/197 rflns	3 stds/97 rflns
decay, %	<1	~40
(c) Refinement		
<i>R</i> (<i>F</i>), %	5.12	6.65
<i>R</i> (<i>wF</i>), %	5.76	6.42
GOF	1.270	1.318
Δ/σ (final)	0.077	0.028
$\Delta(\rho)$ (max), e·Å ⁻³	0.74	0.42
<i>N</i> _o / <i>N</i> _v	6.14	7.84

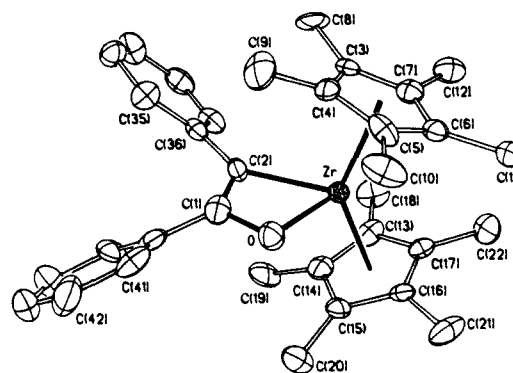
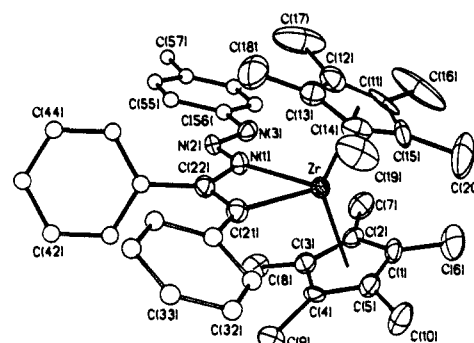
Table III. Selected Bond Distances and Angles for Cp*₂Zr(OCPh=CPh) (**3**)

(a) Bond Distances (Å)			
Zr–CNT(1) ^a	2.242 (10)	Zr–C(2)	2.219 (7)
Zr–CNT(2)	2.255 (10)	C(1)–C(2)	1.348 (12)
Zr–O	2.065 (5)	O–C(1)	1.440 (10)
Zr···C(1)	2.543 (6)		
(b) Bond Angles (deg)			
CNT(1)–Zr–CNT(2)	139.6 (3)	Zr–O–C(1)	91.3 (4)
CNT(1)–Zr–O	105.6 (3)	O–C(1)–C(46)	111.5 (6)
CNT(1)–Zr–C(2)	106.1 (4)	O–C(1)–C(2)	114.5 (7)
CNT(2)–Zr–O	106.6 (3)	O–Zr–C(2)	66.3 (3)
CNT(2)–Zr–C(2)	108.8 (4)	C(1)–C(2)–C(36)	125.6 (6)
Zr–C(2)–C(36)	146.3 (5)	C(2)–C(1)–C(46)	133.7 (8)
Zr–C(2)–C(1)	87.4 (5)		
(c) Dihedral Angles (deg)			
[CNT(1), Zr, CNT(2)] to [Zr, C(2), C(1), O]	90.9		
[Zr, C(2), C(1), O] to [C(31)–C(36)]	42.1		
[Zr, C(2), C(1), O] to [C(41)–C(46)]	35.1		
[C(1), C(2), C(36)] to [C(1), C(2), C(46)]	19.4		

^a CNT(1) = centroid C(3)–C(7); CNT(2) = centroid C(13)–C(17).

perspective view of the complex along with the atom numbering scheme is shown in Figure 1.

Crystals of Cp*₂Zr{N(N₂-*p*-C₆H₄CH₃)CPh=CPh}·C₆D₆ were grown from benzene-*d*₆ and affixed to a glass fiber with epoxy cement that was additionally used to prevent loss of the cocrystallized solvent. Photographic evidence showed the crystal to belong to the monoclinic space group *P*2₁/*c*. Even with the epoxy coating, radiation-exposed crystals rapidly deteriorated, necessitating the use of three crystals to complete the data collection. Unexposed specimens left for comparable periods under epoxy resin showed no visible deterioration, whereas exposed crystals became opaque after several hours' exposure. Interlayer scale factors and corrections for decay were applied before merging the individual data sets. No correction for absorption was required. The structure was solved by heavy-atom methods and completed by difference Fourier syntheses. Due to the limited data available, the two unsubstituted phenyl rings were constrained to rigid hexagons, and the carbon atoms of these rings and the tolyl group were refined isotropically. The remaining non-hydrogen atoms were refined anisotropically. Table IV (Supplementary Material) contains the atomic coordinates, and Table

**Figure 1.** The molecular structure and atom numbering scheme for Cp*₂Zr(OCPh=CPh) (**3**). The hydrogen atoms have been omitted for clarity.**Figure 2.** The molecular structure and atom numbering scheme for Cp*₂Zr{N(N=NTol)CPh=CPh} (**4**). The hydrogen atoms have been omitted for clarity.**Table V.** Selected Bond Distances, Angles, and Deviations from Least-Squares Planes for Cp*₂Zr{N(N₂-Tol)CPh=CPh}·C₆D₆ (**4**)

(a) Bond Distances (Å)			
Zr–CNT(1) ^a	2.252 (9)	C(22)–N(1)	1.423 (12)
Zr–CNT(2)	2.250 (9)	N(1)–N(2)	1.341 (12)
Zr–C(21)	2.285 (8)	N(2)–N(3)	1.305 (12)
Zr–N(1)	2.173 (8)	Zr···C(22)	2.677 (10)
C(21)–C(22)	1.373 (16)		
(b) Bond Angles (deg)			
CNT(1)–Zr–CNT(2)	140.0 (3)	Zr–N(1)–C(22)	93.9 (6)
CNT(1)–Zr–C(21)	107.6 (3)	C(21)–C(22)–N(1)	58.6 (5)
CNT(2)–Zr–C(21)	106.2 (3)	C(22)–N(1)–N(2)	116.4 (8)
CNT(1)–Zr–N(1)	107.2 (3)	Zr–N(1)–N(2)	149.0 (6)
CNT(2)–Zr–N(1)	106.9 (3)	N(1)–N(2)–N(3)	110.1 (8)
N(1)–Zr–C(21)	62.9 (4)	N(2)–N(3)–C(56)	113.3 (8)
Zr–C(21)–C(22)	90.6 (6)		
(c) Least-Squares Planes (dev in Å)			
(1) Zr	-0.006	C(22)	-0.014
C(21)	0.010	N(1)	0.010
(2) Zr	-0.004	N(3)	-0.006
C(21)	-0.042	C(36)	0.023
C(22)	-0.006	C(46)	-0.051
N(1)	0.072	C(56)	-0.035
N(2)	0.020		

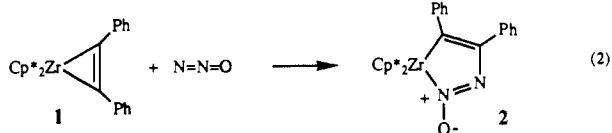
^a CNT(1) = centroid C(1)–C(5); CNT(2) = centroid C(11)–C(15).

V contains a list of selected bond distances and angles. A perspective view of the complex along with the atom numbering scheme is shown in Figure 2. All software used in the solution and refinement of the structures is contained in the SHELXTL (5.1) program library (G. Sheldrick, Nicolet XRD, Madison, WI).

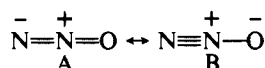
Results and Discussion

Reactions of Cp*₂Zr(C₂Ph₂) with N₂O, N₃R, and N₂CR₂. Treatment of hydrocarbon solutions of Cp*₂Zr(C₂Ph₂) (**1**) with nitrous oxide at -78 °C results in the facile insertion of N₂O into one of the Zr–C(alkyne) bonds to afford orange, thermally

unstable $\text{Cp}^*_2\text{Zr}\{\text{N}(\text{O})\text{NCPH}=\text{CPh}\}$ (**2**) in good isolated yield (eq 2). This unusual metallacycle has been characterized by

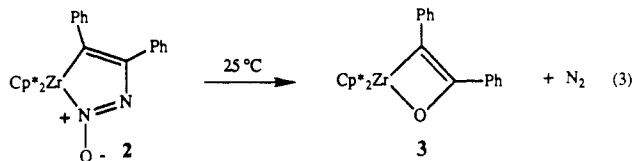


standard spectroscopic data which are similar in all respects to data obtained for a Ti derivative that has been structurally characterized by X-ray diffraction methods.^{3c,11} The appearance of a doublet (δ 138.5; $|^1J_{\text{N-C}}| = 7$ Hz) in the ^{13}C NMR spectrum of [^{15}N]-**2** (prepared from $^{15}\text{N}=\text{N}=\text{O}$) provides clear evidence that the terminal nitrogen atom of nitrous oxide has been covalently attached to one of the non-aryl carbons of the C_2Ph_2 ligand (the resonance is a singlet in **2**).¹² If one considers the formal similarities between an alkyne and the resonance structure of N_2O depicted in B, below, then formation of **2** could be envisaged as being analogous to the well-established coupling reactions of two alkynes at transition-metal centers to give metallacyclopentadiene moieties.¹³



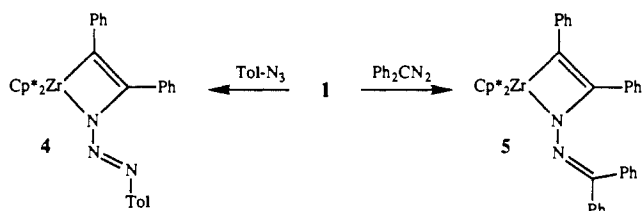
The reaction depicted in eq 2 is an interesting one from two perspectives. First, it is somewhat surprising that the oxygen atom of **2** is not bound to the oxophilic Zr center.¹⁴ Second, insertion of N_2O into a metal–ligand bond is unprecedented; indeed, any reaction between N_2O and a metal complex in which N_2 is not extruded is exceedingly rare. Nitrous oxide forms a coordination complex in $[\text{Ru}(\text{N}_2\text{O})(\text{NH}_3)_5]^{2+}$, but the weak ligation of N_2O has prevented its characterization by X-ray structural methods,^{15,16} and a thermally unstable intermediate (that does not lose N_2 at -78 °C) has been observed in the reaction of N_2O with Cp_2V that yields $\text{Cp}_5\text{V}_5(\mu_3\text{-O})_6$.^{4h}

Stirring solutions of **2** at ambient temperature for several hours results in extrusion of dinitrogen (0.96 equiv of N_2/Zr) and formation of the red diphenyloxametallacyclobutene complex $\text{Cp}^*_2\text{Zr}(\text{OCPh}=\text{CPh})$ (**3**), illustrated in eq 3. Solid samples of **2** also undergo N_2 loss at ambient temperature, and thus the most



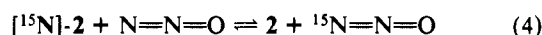
convenient route to **3** is a remarkable reaction in which solid **1**, upon exposure to a nitrous oxide atmosphere for 12–15 h, is quantitatively converted to spectroscopically and analytically pure **3** in the absence of solvent! **3** has been completely characterized by standard spectroscopic, analytical, and single-crystal X-ray

Scheme 1



diffraction techniques, as well as by its substantial reaction chemistry (the solid-state structure and reactivity of **3** are described in detail, below).

Kinetic measurements monitored by ^1H NMR spectroscopy over the temperature range of 30–60 °C show the decomposition of **2** to have a first-order dependence on [**2**] and to be independent of $[\text{N}_2\text{O}]$, with $\Delta H^\ddagger = 19.3 \pm 0.5$ kcal/mol and $\Delta S^\ddagger = -10.1 \pm 1$ eu. The negative entropy of activation suggests that N_2 loss from **2** to give **3** is not a concerted process, with it perhaps involving a rate-determining ligand rearrangement (e.g., ring expansion with formation of a Zr–O bond) before N_2 extrusion occurs. Extensive mechanistic speculation is unwarranted, however, since external nitrous oxide is observed to undergo exchange with the N_2O moiety of **2** (see eq 4) during the course of the solution synthesis of **3**.



To assess the scope of this chemistry, we have also investigated the action of the isoelectronic *p*-tolyl azide and diphenyldiazomethane molecules on **1**. Insertion reactions (that do not involve loss of N_2) of organoazides^{5,17} and diazoalkanes^{6,18} with metal complexes are common, even though they have not been observed for nitrous oxide. **1** reacts cleanly with 1 equiv of ToIN_3 to effect insertion of the terminal N atom of the azide into one of the Zr–alkyne bonds, giving green, crystalline $\text{Cp}^*_2\text{Zr}\{\text{N}(\text{N}_2\text{-}p\text{-C}_6\text{H}_4\text{CH}_3)\text{CPh}=\text{CPh}\}$ (**4**) in excellent yield (Scheme I), and diphenyldiazomethane (1 equiv) reacts with solutions of **1** in an analogous fashion to give $\text{Cp}^*_2\text{Zr}\{\text{N}(\text{N}=\text{CPh}_2)\text{CPh}=\text{CPh}\}$ (**5**) as green crystals. Spectroscopic and analytical data are consistent with the formulation of **4** and **5** as *azametallacyclobutene* derivatives, and this was confirmed for **4** by a single-crystal X-ray diffraction study (discussed below in detail). The azametallacyclobutenes **4** and **5** bear a close resemblance to the product of the reaction of $\text{Cp}_2\text{Zr}(\text{N}^i\text{Bu})$ with diphenylacetylene, $\text{Cp}_2\text{Zr}(\text{N}^i\text{BuCPh}=\text{CPh})$, as reported by Bergman et al.¹⁹ The differences in reactivity toward **1** found for ToIN_3 and Ph_2CN_2 compared with N_2O (i.e., formation of 4- vs 5-membered metallacycles) might be a consequence of steric factors. It is noteworthy that neither **4** nor **5** is prone to thermally induced N_2 loss. They decompose at temperatures >40 °C, without nitrogen evolution, to give a complex mixture of products.

It is essential to use rigorously anhydrous reagents (ToIN_3 and Ph_2CN_2) and oven-baked glassware in the reactions shown in Scheme I to avoid the competitive addition of H_2O across a Zr–C bond to give a hydroxo–vinyl complex. To characterize this water addition product, pure samples were prepared by allowing **1** and H_2O to react in hydrocarbon solvent, giving $\text{Cp}^*_2\text{Zr}(\text{OH})(\text{CPh}=\text{CHPh})$ (**6**) in good yield (eq 5). Additionally, both **4** and **5** were observed to react cleanly with atmospheric moisture, and

(17) (a) Hillhouse, G. L.; Haymore, B. L. *J. Organomet. Chem.* **1978**, *162*, C23. (b) Hillhouse, G. L.; Goeden, G. V.; Haymore, B. L. *Inorg. Chem.* **1982**, *21*, 2064. (c) Hillhouse, G. L.; Haymore, B. L. *Ibid.* **1987**, *26*, 1876. (d) Burgess, K.; Johnson, B. F. G.; Lewis, J.; Raithby, P. R. *J. Organomet. Chem.* **1982**, *224*, C40.

(18) (a) Hillhouse, G. L.; Haymore, B. L.; Herrmann, W. A. *Inorg. Chem.* **1979**, *18*, 2423. (b) Arnold, J.; Tilley, T. D. *J. Am. Chem. Soc.* **1987**, *109*, 3318. (c) Arnold, J.; Tilley, T. D.; Rheingold, A. L.; Geib, S. J. *J. Chem. Soc., Chem. Commun.* **1987**, 793. (d) Churchill, M. R.; Wasserman, H. J. *Inorg. Chem.* **1981**, *20*, 2905. (e) Burgess, K.; Johnson, B. F. G.; Lewis, J.; Raithby, P. R. *J. Chem. Soc., Dalton Trans.* **1982**, 263.

(19) Walsh, P. J.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 8729.

(11) The metrical parameters of the structure of $\text{Cp}^*_2\text{Ti}\{\text{N}(\text{O})\text{NCPH}=\text{CPh}\}$ are most consistent with a planar five-membered metallacycle containing approximately localized C–C and N–N double bonds, thus it is best described as an azoxy derivative (as shown for **2** in eq 2), with the heteroatomic distances being comparable to the corresponding distances found in *p*-azoxyanisole.^{3c}

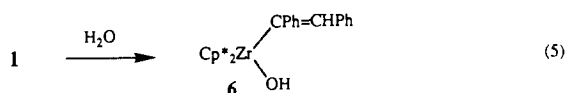
(12) Levy, G. C.; Lichter, R. L. *Nitrogen-15 Nuclear Magnetic Resonance Spectroscopy*; Wiley: New York, 1979; p 119.

(13) Collman, 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.

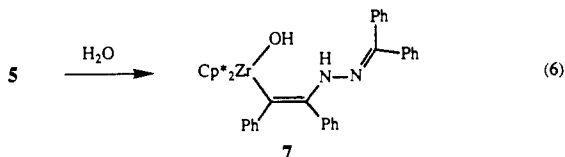
(14) Kinetically controlled nitrogen attack of N_2O at the metal is, however, consistent with calculations that suggest that interactions of nitrous oxide with metal complexes should occur preferentially via the terminal N atom. Tuan, D. F.-T.; Hoffmann, R. *Inorg. Chem.* **1985**, *24*, 871.

(15) (a) Armor, J. N.; Taube, H. *J. Am. Chem. Soc.* **1969**, *91*, 6874. (b) Armor, J. N.; Taube, H. *Ibid.* **1970**, *92*, 2560. (c) Armor, J. N.; Taube, H. *Ibid.* **1971**, *93*, 6476. (d) Armor, J. N.; Taube, H. *J. Chem. Soc., Chem. Commun.* **1971**, 287. (e) Diamantis, A. A.; Sparrow, G. J. *Ibid.* **1969**, 469. (f) Diamantis, A. A.; Sparrow, G. J. *Ibid.* **1970**, 819.

(16) (a) Bottomely, F.; Crawford, J. R. *J. Chem. Soc., Chem. Commun.* **1971**, 200. (b) Bottomely, F.; Crawford, J. R. *J. Am. Chem. Soc.* **1972**, *94*, 9092. (c) Bottomely, F.; Brooks, W. V. *F. Inorg. Chem.* **1977**, *16*, 501. (d) Bottomely, F. *Inorg. Synth.* **1976**, *16*, 75.

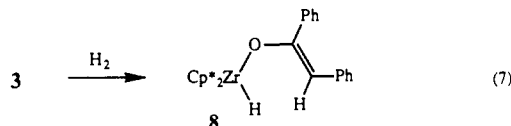


the nature of the hydrolysis was examined in detail for **5**. Water (1 equiv) adds specifically across the Zr–N bond of **5** (not the Zr–C bond of the metallacycle) to give the air-stable N-protonated hydroxy derivative $\text{Cp}^*_2\text{Zr}(\text{OH})\{\text{CPh}=\text{CPhNH}(\text{N}=\text{CPh}_2)\}$ (**7**), as shown in eq 6. The regioselectivity of the water addition is in accord with the previously noted preference for N-protonation in the reaction of H_2O with $\text{Cp}^*_2\text{Hf}(\text{H})(\text{NH}_2)$ that gives $\text{Cp}^*_2\text{Hf}(\text{H})(\text{OH})$ and NH_3 (not $\text{Cp}^*_2\text{Hf}(\text{OH})(\text{NH}_2)$ and H_2).²⁰

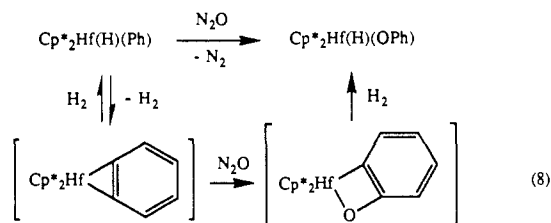


Reactivity of $\text{Cp}^*_2\text{Zr}(\text{OCPh}=\text{CPh})$. In contrast to the relatively unreactive, dimeric oxametallacyclobutene complex $[\text{Cp}_2\text{Zr}(\text{OC}_6\text{H}_5)_2]_2$ shown in eq 1,^{3b} monomeric **3** exhibits a rich reaction chemistry. We have surveyed the reactivity of **3** toward a number of simple substrates, and unlike the hydrolysis of the azametallacycle **5** shown in eq 6, reactions of **3** occur exclusively at the Zr–C bond of the metallacycle.

Dihydrogen (400 Torr, 25 °C) rapidly adds across the Zr–C bond of **3** to cleanly afford the enolate hydride complex $\text{Cp}^*_2\text{Zr}(\text{H})(\text{OCPh}=\text{CHPh})$ (**8**, eq 7). The observation of the facile hydrogenation of **3** → **8** is significant because it provides

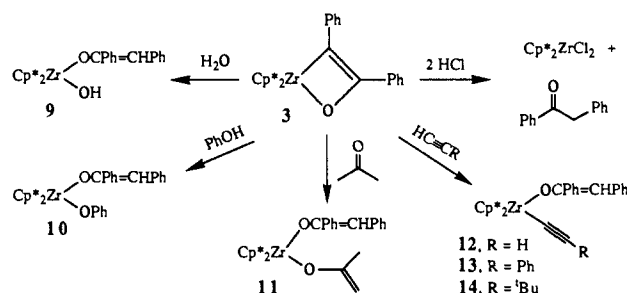


precedence for a postulated key mechanistic step in the N_2O oxidation of $\text{Cp}^*_2\text{Hf}(\text{H})(\text{Ph})$ to $\text{Cp}^*_2\text{Hf}(\text{H})(\text{OPh})$ (shown in eq 8), the hydrogenation of an intermediate oxametallacyclobutene derivative to afford a hydrido phenoxide complex.²¹

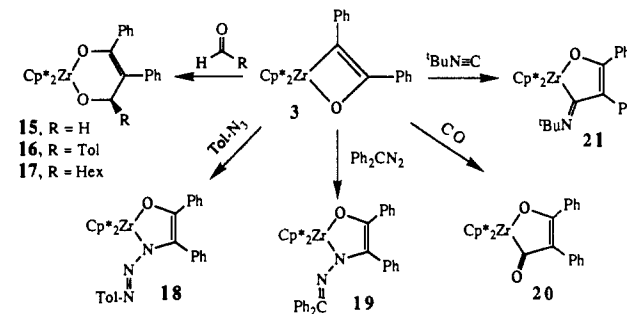


Although the enolate ligand of **8** is depicted with cis-disposed Ph groups, the spectroscopic data do not allow definitive differentiation between cis and trans isomers. In related systems that yield enolate products (e.g., Bercaw's $\text{Cp}^*_2\text{Zr}/\text{Hf}$ CO-reduction chemistry),²² minor changes in reaction conditions can dramati-

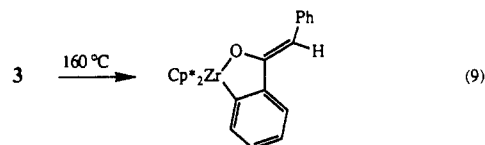
Scheme II



Scheme III



ically affect the geometry about the C–C bond for the resultant enolates. However, it seems very likely that the cis geometry of **3** is maintained in **8** (a) for steric reasons and (b) because radical intermediates would likely be involved in a cis → trans isomerization, and such a stilbenyl radical would likely give an isomeric mixture, not the observed single product.²³ It should be noted, however, that Bergman et al. have reported that **3** undergoes clean thermolysis at 160 °C to give an orthometalated metallacycle having a trans arrangement of the two aromatic substituents (see eq 9),²⁴ so such a cis → trans isomerism for our enolate products is a possibility although our Zr–C bond cleavage reactions are carried out under much milder thermal conditions.



A variety of substrates that possess acidic protons react with **3** to effect cleavage of the Zr–C bond of the metallacycle according to the generalized reaction given in eq 10; specific examples are illustrated in Scheme II. Thus, anhydrous HCl (2 equiv) reacts with **3** to give $\text{Cp}^*_2\text{ZrCl}_2$ and deoxybenzoin, while water and phenol react with **3** to give $\text{Cp}^*_2\text{Zr}(\text{OH})(\text{OCPh}=\text{CHPh})$ (**9**) and $\text{Cp}^*_2\text{Zr}(\text{OPh})(\text{OCPh}=\text{CHPh})$ (**10**), respectively. Acetone reacts with **3** at 65 °C, via its enol tautomer, to give the mixed bis-

(enolate) complex $\text{Cp}^*_2\text{Zr}(\text{OC}(\text{CH}_2)\text{Me})(\text{OCPh}=\text{CHPh})$ (**11**) along with about 10% of **9** as an inseparable contaminant. Terminal alkynes ($\text{HC}\equiv\text{CR}$, R = H, Ph, ^tBu) react with **3** to give the zirconium acetylides $\text{Cp}^*_2\text{Zr}(\text{C}\equiv\text{CR})(\text{OCPh}=\text{CHPh})$ (**12**, R = H; **13**, R = Ph; **14**, R = ^tBu), but internal alkynes (2-butyne, diphenylacetylene) do not react with **3**. Here again, the geometries of the enolate products have not been unambiguously determined, but the phenyl groups are probably in a cis configuration for the reasons outlined above.

A variety of small, unsaturated molecules were observed to insert into the Zr–C bond of **3** to give 5- and 6-membered me-

(20) Hillhouse, G. L.; Bercaw, J. E. *J. Am. Chem. Soc.* **1984**, *106*, 5472.

(21) As previously noted, in the reaction of $\text{Cp}^*_2\text{Hf}(\text{D})(\text{Ph})$ with N_2O , the deuterium label scrambles into the phenyl hydrogen positions (at about 40 °C) well before the onset of the reaction between N_2O and the Hf complex (that gives $\text{Cp}^*_2\text{Hf}(\text{OH})(\text{Ph})$ and $\text{Cp}^*_2\text{Hf}(\text{H})(\text{OPh})$ at about 80 °C).^{3a,b} and in the light of related zirconocene^{21a-c} and tantalocene^{21d-h} chemistry, an intermediate benzyne complex is strongly implicated in the scrambling process. Moreover, we have demonstrated that strained-ring metallacycles (like the postulated benzyne intermediate) undergo reaction with N_2O to give oxametallacyclobutene complexes.³ However, prior to this work there was no precedent for the final postulated step in the formation of $\text{Cp}^*_2\text{Hf}(\text{H})(\text{OPh})$, the hydrogenation of the intermediate oxametallacyclobutene complex. (a) Miller, F. D.; Sanner, R. D. *Organometallics* **1988**, *7*, 818. (b) Buchwald, S. L.; Watson, B. T.; Huffman, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 7411. (c) Buchwald, S. L.; Watson, B. T.; Lum, R. T.; Nugent, W. A. *Ibid.* **1987**, *109*, 7137. (d) Erker, G. J. *J. Organomet. Chem.* **1977**, *134*, 189. (e) Erker, G.; Kropp, K. *J. Am. Chem. Soc.* **1979**, *101*, 3629. (f) Kropp, K.; Erker, G. *Organometallics* **1982**, *1*, 1246. (g) McLain, S. J.; Schrock, R. R.; Sharp, P. R.; Churchill, M. R.; Youngs, W. J. *J. Am. Chem. Soc.* **1979**, *101*, 263. (h) Parkin, G.; Bunel, E.; Burger, B. J.; Trimmer, M. S.; van Asselt, A.; Bercaw, J. E. *J. Mol. Catal.* **1987**, *41*, 21.

(22) (a) Wolcanski, P. T.; Bercaw, J. E. *Acc. Chem. Res.* **1980**, *13*, 121. (b) Roddick, D. M.; Fryzuk, M. D.; Seidler, P. F.; Hillhouse, G. L.; Bercaw, J. E. *Organometallics* **1985**, *4*, 97.

(23) Smith, M. R., III; Hillhouse, G. L. *J. Am. Chem. Soc.* **1989**, *111*, 3764.

(24) Carney, M. J.; Walsh, P. J.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 8751.

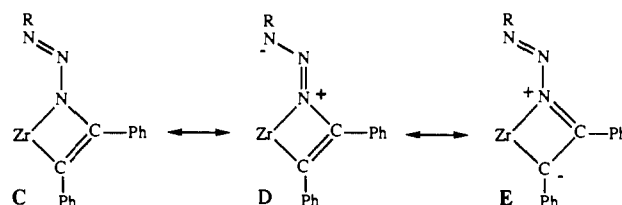
tallacycles (see Scheme III). Paraformaldehyde undergoes a 1,2-insertion reaction with formation of a new Zr–O bond, giving $\text{Cp}^*_2\text{Zr}\{\text{OCPh}=\text{CPhCH}_2\text{O}\}$ (**15**). The unsymmetrical aldehydes *p*-tolualdehyde and heptaldehyde react with **3** in a similar fashion to afford $\text{Cp}^*_2\text{Zr}\{\text{OCPh}=\text{CPhCHTolO}\}$ (**16**) and $\text{Cp}^*_2\text{Zr}\{\text{OCPh}=\text{CPhCH}(n\text{-Hex})\text{O}\}$ (**17**), respectively. Both **16** and **17** possess diastereotopic Cp^* rings, consistent with their formulation as shown in Scheme III. Although excess nitrous oxide will not oxidize the remaining Zr–C metallacycle bond of **3** to give the enediolate, *p*-tolyl azide and diphenyldiazomethane undergo clean 1,1-insertion reactions with **3** (without N_2 loss) to give the 5-membered azametallacycles $\text{Cp}^*_2\text{Zr}\{\text{OCPh}=\text{CPhN}(\text{N}=\text{NTol})\}$ (**18**) and $\text{Cp}^*_2\text{Zr}\{\text{OCPh}=\text{CPhN}(\text{N}=\text{CPh}_2)\}$ (**19**), respectively. Analogous 1,1-insertions are observed for the reactions of carbon monoxide and *tert*-butyl isocyanide with **3** that yield purple $\text{Cp}^*_2\text{Zr}\{\text{OCPh}=\text{CPhC}(=\text{O})\}$ (**20**) and orange $\text{Cp}^*_2\text{Zr}\{\text{OCPh}=\text{CPhC}(=\text{N}^t\text{Bu})\}$ (**21**), but nitriles (like benzonitrile and pivalonitrile) do not react with **3** over the course of weeks at room temperature, although acetonitrile causes the slow decomposition of **3** to give a complex mixture.

Molecular Structure of $\text{Cp}^*_2\text{Zr}(\text{OCPh}=\text{CPh})$. The monomeric nature of dark-red **3** was confirmed by an X-ray diffraction study, and a perspective view of the complex along with the atom-labeling scheme is shown in Figure 1. The most interesting features of the structure are those associated with the novel oxametallacyclobutene ring. The four atoms of the metallacycle lie approximately in the wedge between the two Cp^* rings, with a slight puckering of the metallacycle: the $\{\text{Zr}, \text{O}, \text{C}(2)\}$ to $\{\text{O}, \text{C}(1), \text{C}(2)\}$ dihedral angle is 8.0° , and C(1) is displaced from the $\{\text{Zr}, \text{O}, \text{C}(2)\}$ plane by 0.105 \AA . There is not pyramidalization at C(1) or C(2), with the sums of angles about these atoms equal to 360° and 359° (see Table III for selected metrical parameters), but the ipso carbons of the phenyl groups are substantially displaced out of the $\{\text{Zr}, \text{O}, \text{C}(1), \text{C}(2)\}$ least-squares plane (C(36), 0.26 \AA ; C(46), -0.31 \AA). This results in a significant $\{\text{C}(1), \text{C}(2), \text{C}(36)\}$ to $\{\text{C}(1), \text{C}(2), \text{C}(46)\}$ dihedral angle of 19.4° . The two phenyl groups are twisted out of the metallacycle plane by 35° and 42° , respectively, diminishing their conjugation with the C–C double bond of the metallacycle.

Noteworthy differences are apparent when comparing the metrical parameters of the oxametallacycle of **3** with those in dimer $\{\text{Cp}_2\text{Zr}(\text{OC}_6\text{H}_8)\}_2$.^{3b} The Zr–O bond is significantly shorter in **3** ($2.065(5) \text{ \AA}$) than in the dimer ($2.227(7) \text{ \AA}$), probably reflecting increased electron deficiency at Zr in **3** (hence a stronger Zr–O interaction) in the absence of the stabilizing donation from the O atom of a neighboring metallacycle (as found in the dimer). Moreover, the Zr–C(1) cross-ring interaction in **3** at $2.543(6) \text{ \AA}$ is much shorter than the corresponding distance in $\{\text{Cp}_2\text{Zr}(\text{OC}_6\text{H}_8)\}_2$ ($2.702(10) \text{ \AA}$), and it is comparable to the Zr–to- Cp^* ring carbon distances of **3** ($\sim 2.53\text{--}2.58 \text{ \AA}$) and the Zr–C(allyl) bond distances found in η^3 -allyl derivatives of Zr(IV) (that range from ~ 2.48 to 2.53 \AA).²⁵ Finally, the C(1)–C(2) bond ($1.348(12) \text{ \AA}$ in **3**) is somewhat longer than the corresponding double bond of $\{\text{Cp}_2\text{Zr}(\text{OC}_6\text{H}_8)\}_2$ ($1.309(17) \text{ \AA}$). These data, taken as a whole, seem consistent with some degree of donation from the C₂ fragment of the metallacycle to the electronically unsaturated Zr center.

Molecular Structure of $\text{Cp}^*_2\text{Zr}\{\text{N}(\text{N}=\text{NTol})\text{CPh}=\text{CPh}\}$ (18**).** The molecular structure of **4** (see Figure 2) clearly shows that *p*-tolyl azide has undergone a 1,1-insertion into one of the Zr–C(alkyne) bonds of **1** in an analogous fashion to the observed reactions of RN_3 with other group 4 M–H and M–R bonds⁵ and, specifically, *not* in a 1,2-manner as observed for nitrous oxide.

The azametallacyclobutene moiety is planar (see Table V) and lies in the wedge between the Cp^* rings. From the viewpoint of the azide fragment, the insertion reaction has effectively formed a triazenido (RN_3R^-) unit, and this is reflected in a highly conjugated ToIN_3C_2 system. All of the non-hydrogen atoms of **4**, with the exception of the Cp^* and Ph carbon atoms, are essentially coplanar. Moreover, the N–N, N–C, and C–C bond distances in the ToIN_3C_2 system are typical of resonance averaged contributions having intermediate (between 1 and 2) bond orders, illustrated below for the canonical structures C, D, and E.



Because of orbital symmetry constraints, N(1) cannot effectively π -donate to Zr in this complex (via the lone pair on nitrogen, structure C).²⁶ Consequently, the Zr–N(1) bond length of $2.173(8) \text{ \AA}$ is $\sim 0.16 \text{ \AA}$ longer than in $\text{Cp}_2\text{Zr}(\text{N}=\text{CHPh})\text{Cl}$, where $\text{N} \rightarrow \text{Zr} \pi$ -donation is allowed and $\text{Zr}=\text{N} = 2.013(5) \text{ \AA}$.²⁷ The electronic unsaturation about Zr in **4** (it is formally a 16-electron complex) could be satisfied by coordination of the pendent NTol group, but this is not observed ($\text{Zr}\cdots\text{N}(3) \sim 3.7 \text{ \AA}$), possibly owing to steric congestion at the metal center.

Conclusions

Nitrous oxide has been shown to react with $\text{Cp}^*_2\text{Zr}(\text{C}_2\text{Ph}_2)$ (**1**) in a different manner than its isoelectronic cousins *p*-tolyl azide and diphenyldiazomethane (possibly due to steric factors). For ToIN_3 and Ph_2CN_2 , 1,1-insertion into a Zr–C bond of **1** is observed, affording azametallacyclobutene products, $\text{Cp}^*_2\text{Zr}\{\text{N}(\text{N}=\text{N}(p\text{-C}_6\text{H}_4\text{CH}_3)\text{CPh}=\text{CPh})\}$ (**4**) and $\text{Cp}^*_2\text{Zr}\{\text{N}(\text{N}=\text{CPh}_2)\text{CPh}=\text{CPh}\}$ (**5**), that are not susceptible to subsequent N_2 extrusion reactions. An X-ray diffraction study of **4** was carried out, verifying the structural assignment. In contrast, N_2O participates in a 1,2-insertion reaction with **1**, giving a 5-membered azoxy metallacycle $\text{Cp}^*_2\text{Zr}\{\text{N}(\text{O})\text{NCPH}=\text{CPh}\}$ (**2**) that eliminates N_2 upon mild thermolysis to afford a monomeric oxametallacyclobutene, $\text{Cp}^*_2\text{Zr}(\text{OCPh}=\text{CPh})$ (**3**), that was also structurally characterized by X-ray diffraction methods. The extensive reaction chemistry of **3** can be divided into two distinct classes: (a) formal "addition" of X–H (dihydrogen, hydrochloric acid, water, alcohols, terminal alkynes, and enolizable ketones) across the Zr–C bond of the metallacycle of **3** to give diphenylenolate derivatives $\text{Cp}^*_2\text{Zr}(\text{X})(\text{OCPh}=\text{CHPh})$ and (b) insertion (in a 1,1- or 1,2-fashion) of unsaturated small molecules (aldehydes, carbon monoxide, *tert*-butyl isocyanide, *p*-tolyl azide, and diphenyldiazomethane) into the Zr–C bond of the metallacycle of **3** to give 5- and 6-membered zirconacycles.

Acknowledgment. Financial support from the National Science Foundation (CHE-8818607), an Alfred P. Sloan Foundation Research Fellowship (1989–1991), and a Union Carbide Innovation Recognition Program Award (1990) are sincerely appreciated by G.L.H. The NMR facilities were supported in part by PHS Grant No. 5 P30 CA 14599-17 and an instrumental grant from the National Science Foundation.

Supplementary Material Available: Tables of bond angles, bond distances, anisotropic thermal parameters, hydrogen atom coordinates, and atomic coordinates for **3** and **4** (16 pages); observed and calculated structure factors for **3** and **4** (26 pages). Ordering information is given on any current masthead page.

(25) (a) Erker, G.; Engel, K.; Dorf, U.; Atwood, J. L.; Hunter, W. E. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 914. (b) Erker, G.; Berg, K.; Angermund, K.; Krüger, C. *Organometallics* **1987**, *6*, 2620. (c) Larson, E. J.; Van Dori, P. C.; Dailey, J. S.; Lakanen, J. R.; Pederson, L. M.; Silver, M. E.; Huffman, J. C.; Russo, S. O. *Ibid.* **1987**, *6*, 2141.

(26) For a discussion of ligand-to-metal π -bonding in related $\text{Cp}^*_2\text{M}(\text{NR}_2)\text{X}$ complexes, see: Hillhouse, G. L.; Bulls, A. R.; Santarsiero, B. D.; Bercaw, J. E. *Organometallics* **1988**, *7*, 1309.

(27) Erker, G.; Fromberg, W.; Atwood, J. L.; Hunter, W. E. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 68.