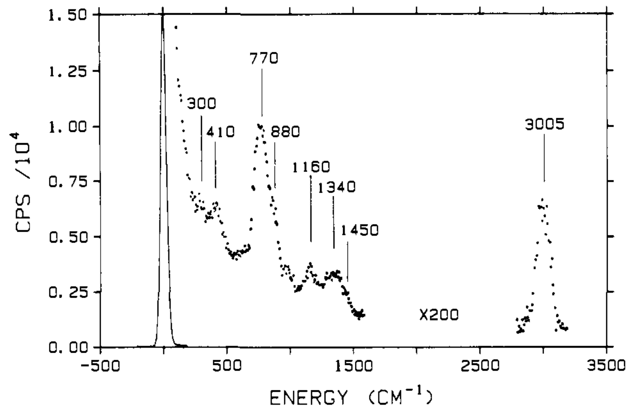

Figure 1. High-resolution electron energy loss spectrum of adsorbed layer after procedure described in text. The spectrum was measured 8° away from the specular angle at an incident electron energy of 3.5 V with $\Delta E = 50$ cm^{-1} and at a surface temperature of 40 K. The features marked are assigned to modes of C_6H_6: 3005 cm^{-1} to ν_1, ν_5, ν_{12}, and ν_{15}; 1450 cm^{-1} to ν_{13}; 1340 cm^{-1} to ν_9; 1160 cm^{-1} to ν_{10} and ν_{17}; 880 cm^{-1} to ν_2, 770 cm^{-1} to ν_4; 410 cm^{-1} to ν_{20}; 300 cm^{-1} to the Ni–C_6H_6 mode.

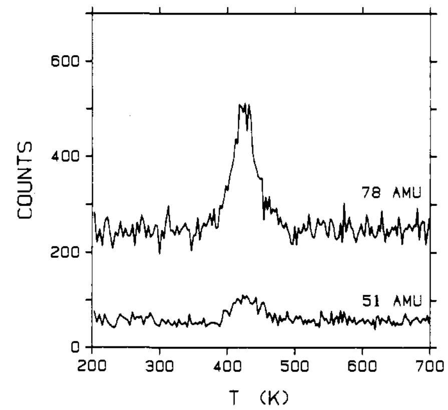

Figure 2. Thermal desorption spectrum from adsorbed layer prepared as described in text. The relative partial pressures at masses 78 and 51 are plotted as a function of crystal temperature. Mass 51 is a fragment ion from the cracking of C_6H_6 after electron-impact ionization. Benzene desorbs at 425 K for a heating rate of 17 K s^{-1}.

a saturated layer of physisorbed CH_4 (0.33 CH_4/Ni) is maintained.[1,2] A monoenergetic Kr beam with a translational energy of 88 kcal/mol, produced by the high-pressure expansion of a 0.3% mixture of Kr in He from a nozzle at 898 K, impinges on the CH_4-covered surface at normal incidence for 45 s. At this energy, the Kr flux is 5×10^{14} cm^{-2} s^{-1} and the cross section for CH_4 dissociation by collision with Kr is 1.9 Å^2 in the limit of zero chemisorbed carbon coverage. After the ambient CH_4 is pumped away, the crystal is heated to and held at 395 K for 30 s, which results in the thermal desorption of all the unreacted CH_4, the recombinative desorption of H_2, and formation of C_2H_2. The C_2H_2 coverage is increased to 0.25 ML by repeating this procedure 12 times. As the C_2H_2 coverage nears 0.25 ML, adsorbed benzene forms and partially desorbs during the annealing to 395 K. Figure 1 shows a vibrational spectrum, measured at 40 K, of the adsorbed layer after this sequence. The majority of the loss features are assigned to the vibrational modes of molecular C_6H_6, as indicated in the figure caption. This spectrum is very similar to one measured after adsorption of 0.14 ML of C_6H_6 on Ni(111) and annealing to 395 K[6] and to one measured in a previous study of the reactions of C_2H_2 on Ni(111).[5] The features that are not attributable to C_6H_6, 1250 cm^{-1}, 970 cm^{-1}, and 650 cm^{-1}, are assigned to modes of C_4 species, C_8 species, or partially dehydrogenated benzene. The crystal, with the adsorbed layer so prepared, is now heated at 17 K s^{-1} while the ambient pressure of masses 78 and 51 is monitored with the mass spectrometer. The resulting thermal desorption spectra are shown in Figure 2. The fragmentation pattern observed for the reaction product is that of benzene. No desorption of other hydrocarbons is detected. The desorption yield of 0.2 ± 0.04%, which is calculated from the thermal desorption spectrum, is a lower limit because as much as 85% of the C_6H_6 formed has already desorbed during the multiple annealings to 395 K. The upper limit for the desorption yield is estimated as 1.5%. The remaining adsorbed benzene and hydrocarbon fragments dehydrogenate as the temperature is increased above 425 K via a mechanism described elsewhere[6] and ultimately dissolve as carbon into the bulk of Ni. These data show conclusively that C_6H_6 is produced from CH_4 on a Ni(111) surface and desorbs at 425 K. These data also provide mechanistic information useful to the possible extrapolation of this synthesis from molecular beam-UHV environments to more practical conditions.

Acknowledgment. This work is supported by the NSF (CHE-8508734), the Petroleum Research Fund, administered by the American Chemical Society and the Synthetic Fuels Center at MIT.

Registry No. C_6H_6, 71-43-2; CH_4, 74-82-8; Ni, 7440-02-0.

Telluroaldehydes and Telluroketones

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Received June 12, 1989

Studies on the chemistry of organic molecules containing the tellurocarbonyl group have been rather scarce because of the lability of the carbon–tellurium double bond.[1] Telluroesters and -amides, stabilized by resonance delocalization of oxygen and nitrogen lone-pair electrons onto tellurium, and stable tellurocarbonyl compounds coordinated to the transition metals have been reported since 1979,[2-5] whereas generation of "free" telluroaldehydes and -ketones[6] has not been known hitherto and therefore remains a challenge for synthesis. Recently we have described simple and convenient methods for selenoaldehyde[7] and selenoketone[8] generations, in which bis(trimethylsilyl) selenide

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(1) Guziec, F. S., Jr. *The Chemistry of Organic Selenium and Tellurium Compounds*; Patai, S., Ed.; John Wiley & Sons: New York, 1987; Vol. 2, pp 215–273.

(2) For telluroesters: (a) Barrett, A. G. M.; Barton, D. H. R.; Read, R. W. *J. Chem. Soc., Chem. Commun.* **1979**, 645–647. (b) Barrett, A. G. M.; Read, R. W.; Barton, D. H. R. *J. Chem. Soc., Perkin Trans. 1* **1980**, 2191–2195. (c) Severengiz, T.; du Mont, W. W. *J. Chem. Soc., Chem. Commun.* **1987**, 820–821.

(3) For telluroamides: Lerstrup, K. A.; Henriksen, L. *J. Chem. Soc., Chem. Commun.* **1979**, 1102–1103.

(4) For telluroketenes: (a) Bender, S. L.; Haley, N. F.; Luss, H. R. *Tetrahedron Lett.* **1981**, *22*, 1495–1496. (b) Lakshmikantham, M. V.; Cava, M. P.; Albeck, M.; Engman, L.; Carroll, P. *Ibid.* **1981**, *22*, 4199–4200. (c) Lakshmikantham, M. V.; Cava, M. P.; Albeck, M.; Engman, L.; Bergman, J.; Wudl, F. *J. Chem. Soc., Chem. Commun.* **1981**, 828–829.

(5) For metal complexes: (a) Lappert, M. F.; Martin, T. R.; McLaughlin, G. M. *J. Chem. Soc., Chem. Commun.* **1980**, 635–637. (b) Fischer, H.; Zeuner, S. *J. Organomet. Chem.* **1983**, *252*, C63–C65. (c) Fischer, H.; Gerbing, U. *Ibid.* **1986**, *299*, C7–C10. (d) Fischer, H.; Pashalidis, I. *Ibid.* **1988**, *348*, C1–C4. (e) Headford, C. E. L.; Roper, W. R. *Ibid.* **1983**, *244*, C53–C56. (f) Hill, A. F.; Roper, W. R.; Waters, J. M.; Wright, A. H. *J. Am. Chem. Soc.* **1983**, *105*, 5939–5940. (g) Herrmann, W. A.; Weichmann, J.; Serrano, R.; Blechschmitt, K.; Pfisterer, H.; Ziegler, M. L. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 314–315. (h) Paul, W.; Werner, H. *Ibid.* **1983**, *22*, 316–317. (i) Wolf, J.; Zolk, R.; Schubert, U.; Werner, H. *J. Organomet. Chem.* **1988**, *340*, 161–178.

(6) The IUPAC nomenclature suggested for the functional groups of these compounds is "-tellural" and "telluroxo-". See ref 1, p 217.

(7) (a) Segi, M.; Nakajima, T.; Suga, S.; Murai, S.; Ryu, I.; Ogawa, A.; Sonoda, N. *J. Am. Chem. Soc.* **1988**, *110*, 1976–1978. (b) Segi, M.; Takahashi, M.; Nakajima, T.; Suga, S.; Murai, S.; Sonoda, N. *Tetrahedron Lett.* **1988**, *29*, 6965–6968.

(8) Segi, M.; Koyama, T.; Nakajima, T.; Suga, S.; Murai, S.; Sonoda, N. *Tetrahedron Lett.* **1989**, *30*, 2095–2098.

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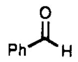
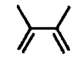
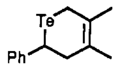
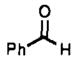
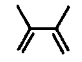
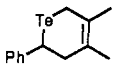
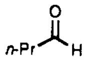
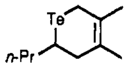
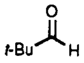
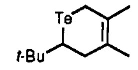
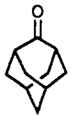
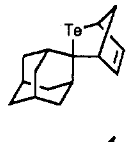
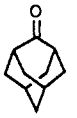
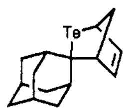
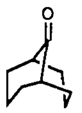
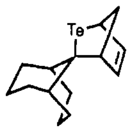
Table I. Generation and Cycloaddition of Telluroaldehydes and Telluroketones

entry	substrate	solvent	condtns (°C, h)	diene	cycloadduct	yield[a] (%)
1		dioxane	100, 2.0			49
2		THF	66, 2.0			26
3		dioxane	100, 2.0			44
4		dioxane	100, 3.0			62
5		dioxane	100, 3.0			55
6		THF	66, 3.0			24
7		dioxane	100, 2.0			52

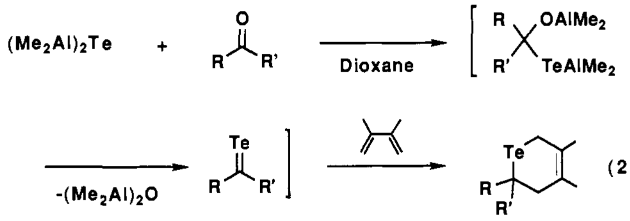
[a] Isolated yield.

($Me_3SiSeSiMe_3$) and bis(dimethylaluminum) selenide ($Me_2AlSeAlMe_2$) were used as selenating reagents, respectively. The tellurium analogue of the former, however, was by no means effective for generation of tellurocarbonyl compounds. Now we have found that bis(dimethylaluminum) telluride ($Me_2AlTeAlMe_2$, **1**) can serve as an efficient tellurating reagent for the direct conversion of aldehydes and ketones to telluroaldehydes and -ketones. While this work was in progress, Erker and Hock reported generation of tellurobenzaldehyde using the reaction of a phosphorus ylide with tellurium. They described only one example, with low yield (11%).[9] In this communication we report the first general method for the generation of both telluroaldehydes and telluroketones.

The preparation of a new tellurating reagent **1** was initially attempted by the reaction of bis(trimethylsilyl) telluride[10] with dimethylaluminum chloride. Unfortunately, **1** obtained via this Si–Al metal exchange was not effective for the telluration of aldehydes or ketones, and immediate deposition of elemental tellurium was observed. The difficulty would be due to trimethylsilyl chloride formed at the stage of transmetalation. We chose then a Sn–Al metal exchange for the synthesis of **1**. Thus, **1** was synthesized by the transmetalation reaction of bis(tributyltin) telluride with 2.0 equiv of trimethylaluminum in toluene, as shown in eq 1. Quantitative formation of tetramethyltin was

$$Bu_3SnTeSnBu_3 + 2Me_3Al \xrightarrow[90\ ^\circ C]{Toluene} \underset{\mathbf{1}}{Me_2AlTeAlMe_2} + 2Bu_3SnMe \quad (1)$$

shown by ^1H NMR measurement for the run using bis(trimethyltin) telluride. The reagent **1** in toluene was likely to exist in aggregated form since the reaction mixture turned into an opaque suspension. This suspension reacted with aldehydes only very slowly. So, after the removal of toluene, dioxane was added as a solvent to result in a homogeneous system. The reaction of **1** with aldehydes or ketones was carried out in refluxing dioxane in the presence of a diene (eq 2).



(2)

Heating **1** with benzaldehyde in the presence of excess 2,3-dimethyl-1,3-butadiene in refluxing dioxane for 6 h afforded the Diels–Alder adduct of the corresponding tellurobenzaldehyde in 49% yield.[11] This indicates that the telluroaldehyde is efficiently formed in situ. Further examples of the reaction of **1** with aldehydes or ketones are summarized in Table I. For telluroketone synthesis, the success depended upon a structural factor. When moderately sterically hindered ketones such as adamantanone and bicyclo[3.3.1]nonan-9-one were used, the efficient trapping of the corresponding telluroketones by cyclopentadiene was observed (entries 5 and 7). All cycloadducts obtained were not very sensitive to air and light, but decomposed under acidic conditions with deposition of elemental tellurium.

The reaction temperature of refluxing dioxane is essential for the generation of tellurocarbonyl compounds by the use of **1** compared with entries 2 and 6 using THF. This reaction may

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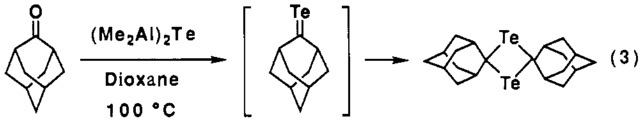
(9) Erker, G.; Hock, R. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 179–180.
(10) Detty, M. R.; Seidler, M. D. *J. Org. Chem.* **1982**, *47*, 1354–1356.

(11) A typical experimental procedure is exemplified by the synthesis of a tellurobenzaldehyde cycloadduct. Trimethylaluminum (1.0 M solution in hexane, 1.4 mL, 1.4 mmol) was added to a solution of bis(tributyltin) telluride (424 mg, 0.6 mmol), bp 165–168 °C/0.2 Torr, easily prepared by the reaction of Li_2Te and *n*-Bu_3SnCl, in toluene (10 mL) under argon, and the mixture was stirred for 15 h at 90 °C. After the removal of toluene carefully under reduced pressure, dioxane (15 mL) as solvent, 2,3-dimethyl-1,3-butadiene (246 mg, 3.0 mmol), and benzaldehyde (106 mg, 1.0 mmol) were added in that order. The mixture was subsequently heated under reflux for 6 h and poured into water. The usual workup followed by flash column chromatography on alumina (hexane:dichloromethane = 5:1) furnished the Diels–Alder adduct of tellurobenzaldehyde in 49% yield.

involve the initial coordination of aluminum of **1** to carbonyl oxygen followed by intramolecular transfer of the tellurium group to the electropositive carbonyl carbon center. Thermodynamically stable Al–O–Al bond formation then leads to the construction of the carbon–tellurium double bond.

In the absence of a diene, **1** reacted with adamantanone to give a dimer of telluroadamantanone in 28% yield (eq 3). The mass



(3)

spectrum of this compound supported the dimeric molecular formula of $C_{20}H_{28}Te_2$ with a molecular ion at m/e = 528 (^{130}Te) having the expected isotope pattern for Te_2.

Thus, it becomes possible for the first time to study the chemistry of telluroaldehydes and -ketones.

Acknowledgment. This work was supported in part by a Grant-in-Aid for Scientific Research (63750830) from the Ministry of Education, Science and Culture of Japan. We also thank Professors Noboru Sonoda and Shinji Murai (Osaka University) for their helpful discussions and comments.

Supplementary Material Available: IR, ^1H and ^{13}C NMR, and mass spectral data for all cycloadducts described (4 pages). Ordering information is given on any current masthead page.

A Reactive Organometallic Oxo Intermediate, $Cp^*_2Zr{=}O$: Generation and Subsequent Trapping Reactions Forming Alkyne and Nitrile Addition Products

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The metal oxo linkage (M=O) in high-valent group 5–8 metal complexes is relatively well-known[1] but is normally quite robust.[2] The apparent lack of monomeric group 4 oxometallocene species ((η^5-C_5R_5)$_2$M=O, M = Ti, Zr, Hf) in the literature led us to believe that if these could be generated they would indeed display greater reactivity than that of metal oxo species already known. In addition, the recent successful isolation and characterization of a reactive monomeric zirconium imido complex, Cp_2(THF)-Zr=N(t-Bu) (Cp = η^5-C_5H_5), in these laboratories[3,4] indicated to us that perhaps the isoelectronic Zr=O complex could be generated in a similar α-elimination reaction.[5] We report here evidence supporting the successful generation of $Cp^*_2Zr{=}O$ (Cp* = η^5-C_5Me_5), its subsequent trapping with various unsaturated organic molecules, and the unusual rearrangement reactions of some of these trapped products.

The chemistry observed is outlined in Scheme I. Heating $Cp^*_2ZrPh(OH)$[6] (**1**) in toluene or benzene at 160 °C in the presence of 3–4 equiv of diphenyl- or di-p-tolylacetylene leads to loss of benzene (observed by ^1H NMR spectrometry) and generation of the orange zirconium oxametallacycles **2** (68% isolated yield;[7] 92% yield by ^1H NMR) and **3** (78% isolated yield), respectively. Isolation of **3** indicates that the phenyl group initially bound to Zr in **1** is liberated (vide infra). Complex **2** has been characterized by X-ray diffraction;[8] an ORTEP diagram is included in Scheme I and clearly shows that the phenyl ring is ortho-metalated.

Heating **1** in the presence of excess 1,4-diphenyl-1,3-butadiyne leads to the formation of a deep red compound, **4** (84% isolated yield), in which a Cp* ligand is now bonded to the coordinated enolate (see Scheme I). A single-crystal X-ray diffraction study[8] confirmed this description of **4**; an ORTEP diagram is included in Scheme I. Heating **1** at 160 °C in the presence of 3–4 equiv of benzonitrile (PhCN) provides an isolable compound that we formulate as the PhCN insertion product, **5**, in 74% yield. Here 2 equiv of PhCN have added to give the six-membered metallacycle, as illustrated in Scheme I. Once again, an X-ray structure determination of **5** was carried out[8] and confirms the proposed connectivity.

The following experiments provide information about the mechanism of thermal decomposition of hydroxyphenylzirconium complex **1**. (1) GC–MS analysis of the volatile materials formed upon separate thermolysis of $Cp^*_2ZrPh(OH)$ and $Cp^*_2ZrPh(OD)$[9] (160 °C in toluene in the presence of PhCCPh) indicates that C_6H_6 and C_6H_5D, respectively, are the exclusive (≥97%)[10] elim-

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(1) (a) Nugent, W. A.; Mayer, J. A. *Metal-Ligand Multiple Bonds*; Wiley-Interscience: New York, 1988. (b) Holm, R. H. *Chem. Rev.* **1987**, *87*, 1401 and references therein.

(2) Apparent exceptions among organometallic oxo compounds include certain Cp*Re oxo complexes (Herrmann, W. A. *J. Organomet. Chem.* **1986**, *300*, 111) and the recently reported $Cp^*_2W{=}O$ (Parkin, G.; Bercaw, J. E. *J. Am. Chem. Soc.* **1989**, *111*, 391).

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

(4) For a related zirconium imido complex, see: Cummins, C. C.; Baxter, S. M.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1988**, *110*, 8731.

(5) Pertinent references concerning α-elimination to generate isolobal alkylidene complexes include the following: (a) McDade, C.; Green, J. C.; Bercaw, J. E. *Organometallics* **1982**, *1*, 1629. (b) Bulls, A. R.; Schaefer, W. P.; Serfas, M.; Bercaw, J. E. *Organometallics* **1987**, *6*, 1219. (c) Gibson, C. P.; Dabbagh, G.; Bertz, S. H. *J. Chem. Soc., Chem. Commun.* **1988**, 603. (d) Bertz, S. H.; Dabbagh, G.; Gibson, C. P. *Organometallics* **1988**, *7*, 563.

(6) Schock, L. E.; Marks, T. J. *J. Am. Chem. Soc.* **1988**, *110*, 7701.

(7) Compounds **2–5** were fully characterized by ^1H and $^{13}C\{^1H\}$ NMR, IR, and EI mass spectrometry and elemental analysis; data are provided as supplementary material. All yields are for recrystallized complexes.(7) The X-ray diffraction studies were carried out at the University of California, Berkeley, X-ray diffraction facility (CHEXRAY) with Mo Kα (I = 0.71073 Å) radiation at 25 °C. Crystal data for **2**: $P2_1/n$, V = 2908.9 (9) Å^3, μ = 3.9 cm^{-1}, D_{calcd} = 1.27 g cm^{-3}, a = 9.4243 (10) Å, b = 18.7513 (17) Å, c = 16.8210 (17) Å, β = 101.882 (9)°, Z = 4; the final residuals for 325 variables refined against the 3169 data for which $F^2 > 3\sigma(F^2)$ were R = 0.0272, R_w = 0.0398, and GOF = 2.05. The R value for all 3797 data was 4.81%. Crystal data for **4**: $P2_1/n$, V = 2974.8 (12) Å^3, μ = 3.8 cm^{-1}, D_{calcd} = 1.24 g cm^{-3}, a = 9.6706 (17) Å, b = 10.2703 (11) Å, c = 30.132 (3) Å, β = 96.285 (12)°, Z = 4; the final residuals for 343 variables refined against 3176 data for which $F^2 > 3\sigma(F^2)$ were R = 2.82%, R_w = 3.96%, and GOF = 1.99. The R value for all 3882 data was 4.13%. Crystal data for **5**·$^1/_2C_6H_5CH_3$: $P2_1/c$, V = 3330.1 (17) Å^3, μ = 3.5 cm^{-1}, D_{calcd} = 1.26 g cm^{-3}, a = 9.4840 (20) Å, b = 17.5041 (19) Å, c = 20.670 (1) Å, β = 103.960 (15)°, Z = 4; the final residuals for 389 variables refined against 3598 data for which $F^2 > 3\sigma(F^2)$ were R = 3.13%, R_w = 4.25%, and GOF = 2.09. The R value for all 4337 data was 4.28%. The six-membered metallacycle in **5** is disordered about a pseudo-two-fold axis containing the zirconium atom and the central nitrogen atom of the ring. Details of the structure determinations are included as supplementary material.

(8) The X-ray diffraction studies were carried out at the University of California, Berkeley, X-ray diffraction facility (CHEXRAY) with Mo Kα (I = 0.71073 Å) radiation at 25 °C. Crystal data for **2**: $P2_1/n$, V = 2908.9 (9) Å^3, μ = 3.9 cm^{-1}, D_{calcd} = 1.27 g cm^{-3}, a = 9.4243 (10) Å, b = 18.7513 (17) Å, c = 16.8210 (17) Å, β = 101.882 (9)°, Z = 4; the final residuals for 325 variables refined against the 3169 data for which $F^2 > 3\sigma(F^2)$ were R = 0.0272, R_w = 0.0398, and GOF = 2.05. The R value for all 3797 data was 4.81%. Crystal data for **4**: $P2_1/n$, V = 2974.8 (12) Å^3, μ = 3.8 cm^{-1}, D_{calcd} = 1.24 g cm^{-3}, a = 9.6706 (17) Å·, b = 10.2703 (11) Å, c = 30.132 (3) Å, β = 96.285 (12)°, Z = 4; the final residuals for 343 variables refined against 3176 data for which $F^2 > 3\sigma(F^2)$ were R = 2.82%, R_w = 3.96%, and GOF = 1.99. The R value for all 3882 data was 4.13%. Crystal data for **5**·$^1/_2C_6H_5CH_3$: $P2_1/c$, V = 3330.1 (17) Å^3, μ = 3.5 cm^{-1}, D_{calcd} = 1.26 g cm^{-3}, a = 9.4840 (20) Å, b = 17.5041 (19) Å, c = 20.670 (3) Å, β = 103.960 (15)°, Z = 4; the final residuals for 389 variables refined against 3598 data for which $F^2 > 3\sigma(F^2)$ were R = 3.13%, R_w = 4.25%, and GOF = 2.09. The R value for all 4337 data was 4.28%. The six-membered metallacycle in **5** is disordered about a pseudo-two-fold axis containing the zirconium atom and the central nitrogen atom of the ring. Details of the structure determinations are included as supplementary material.

(9) $Cp^*_2ZrPh(OD)$ was prepared analogously to $Cp^*_2ZrPh(OH)$ (ref 6) with D_2O used in place of H_2O. Integration (^1H NMR) of the residual OH versus the Cp* or phenyl resonances indicated that $Cp^*_2ZrPh(OD)$ was ca. 98% deuterated.

(10) The percentage is based on a comparison of the GC–MS data (fragmentation patterns and peak heights) of these products with those of authentic samples of C_6H_6 and C_6H_5D (the latter prepared from PhLi and D_2O).

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