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Contribution from the Department of Chemistry,
Princeton University, Princeton, New Jersey 08544

Synthesis and Characterization of Dimeric Zirconium(III) Complexes. Structure of "Zirconocene"

KERRIE I. GELL, THOMAS V. HARRIS, and JEFFREY SCHWARTZ*

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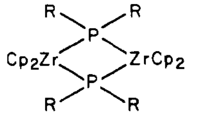
Dimeric Zr(III) complexes have been prepared by thermolysis of $(\eta^5\text{-}C_5H_5)_2Zr^{II}$–bis(phosphine) compounds. These dimeric Zr(III) complexes can also be prepared by treating "zirconocene" with phosphines. The structure of these dimeric Zr(III) complexes has been determined spectroscopically to contain $(\eta^5\text{-}C_5H_5)(\mu\text{-}[\eta^1{:}\eta^5\text{-}C_5H_4])Zr$ units. "Zirconocene" is proposed to contain similar units. Oxidation of these Zr(III) compounds by secondary phosphines, by O_2, and by I_2 is described.

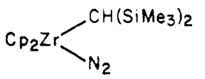
Introduction

Low-valent complexes of the group 4 transition metals are implicated in the polymerization of olefins, in C–H bond activation, and in the stoichiometric fixation and reduction of molecular nitrogen.[1] However, in its isolable organometallic complexes, Zr is almost invariably in the formal oxidation state +4 (d^0).[1] Recently, several low-valent Zr complexes have been characterized, and, as well as enabling systematic studies of the role of reduced Zr in catalytic and stoichiometric processes, these complexes are promising synthetic intermediates.[2–5]

Whereas the formal oxidation state +3 is common for Ti[1,6] and mild reductants will effect the conversion of Ti(IV) to Ti(III), organometallic complexes of Zr(III) are rare.[1,7] The only well-characterized species are the phosphido-bridged dimer **1**,[8a] a dinitrogen complex **2**,[8b] containing the bulky bis(trimethylsilyl)methyl ligand, the radical anions, **3**,[8c] and a bridged naphthyl species.[8d]



1a, R = Et
b, R = *n*-Bu



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Cp = $\eta^5\text{-}C_5H_5$

$[Na(THF)_x]^+[(C_2H_4R')_2MR_2]^-$

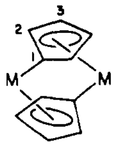
3

R′ = H, Me

R = Ph_2CH, $(Me_3Si)_2CH$

In this paper we report a facile synthesis of dimeric Zr(III) complexes from Zr(II)–bis(phosphine) complexes.[5] The chemistry of these dimers indicates that, under appropriate circumstances, Zr(III) is a readily accessible and synthetically useful oxidation state.

Our study of these complexes also provides some insights into the structure of zirconocene ("Cp_2Zr"), a poorly characterized species which results from reduction of suitable Zr(IV) precursors by various methods.[9] In general, determination of the structure of the group 4 metallocenes has proven difficult, principally because none of these compounds forms crystals suitable for X-ray analysis. Numerous studies of titanocene have established that, at least in its stable form, it is not a simple sandwich compound but a metal hydride containing bridging C_5H_4 units.[10] Two bridging arrangements (**4**, **5**) for this ligand have been identified in other compounds.[10b,11,12]



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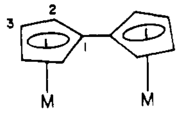

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By indirect means, green stable titanocene has been identified as $[\{(\eta^5\text{-}C_5H_5)Ti(\mu\text{-}H)\}_2\text{-}\mu\text{-}(\eta^5{:}\eta^5\text{-}C_{10}H_8)]$, a Ti(III) hydride dimer, containing the $\eta^5{:}\eta^5$-fulvenalide ligand, **5**.[12b,13] Although it has been assumed that zirconocene is isostructural with titanocene, our results suggest that this is not the case and that, in zirconocene, $\eta^1{:}\eta^5\text{-}C_5H_4$ ligands **4** are found.

Results

Preparation and Characterization of $[\{(\eta^5\text{-}C_5H_5)(\mu\text{-}[\eta^1{:}\eta^5\text{-}C_5H_4])ZrL\}_2]$ (7). Thermal decomposition of bis(η^5-cyclopentadienyl)bis(tertiary phosphine)zirconium(II) complexes

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(1) Wailes, P. C.; Coutts, R. S. P.; Weigold, H. "Organometallic Chemistry of Titanium, Zirconium, and Hafnium"; Academic Press: New York, 1974.

(2) Manriquez, J. M.; Bercaw, J. E. *J. Am. Chem. Soc.* **1974**, *96*, 6229.

(3) (a) Demerseman, B.; Bouquet, G.; Bigorne, M. *J. Organomet. Chem.* **1976**, *107*, C19. (b) Thomas, J. L.; Brown, K. T. *Ibid.* **1976**, *111*, 297. (c) Demerseman, B.; Bouquet, G.; Bigorne, M. *Ibid.* **1977**, *132*, 223.

(4) (a) Cloke, F. G. N.; Green, M. L. H. *J. Chem. Soc., Chem. Commun.* **1979**, 127. (b) Datta, S.; Wreford, S. S.; Beatty, R. P.; McNeese, T. J. *J. Am. Chem. Soc.* **1979**, *101*, 1053.

(5) (a) Gell, K. I.; Schwartz, J. *J. Chem. Soc., Chem. Commun.* **1979**, 244. (b) Gell, K. I.; Schwartz, J., manuscript in preparation.

(6) Clark, R. J. H.; Moorhouse, S.; Stockwell, J. A. *J. Organomet. Chem. Libr.* **1977**, *3*, 223.

(7) In part, this reflects the relative thermodynamic stabilities; Ti(III) is stable in aqueous solution with a reduction potential $E° = 0.1$ V for $TiO^{2+}(aq) + 2H^+ + e^- \rightarrow Ti^{3+} + H_2O$. No reduction potentials for Zr(IV) to Zr(III) or Zr(II) have been measured; zirconium(III) halides are produced from Zr(IV) compounds under vigorous reducing conditions and are most certainly unstable in aqueous solution. Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 3rd ed.; Wiley: New York, 1972.

(8) (a) Issleib, K.; Häckert, H. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1966**, *21B*, 519. (b) Gyanne, M. J. S.; Jeffrey, J.; Lappert, M. F. *J. Chem. Soc., Chem. Commun.* **1978**, 34. (c) Lappert, M. F.; Riley, P. I.; Yarrow, P. I. W. *Ibid.* **1979**, 305. (d) Pez, G. P.; Putnik. C. F.; Suib, S. L.; Stucky, G. D. *J. Am. Chem. Soc.* **1979**, *101*, 6933. Several other Zr(III) compounds have been postulated on the basis of analytical data only.[1]

(9) (a) Watt, G. W.; Drummond, F. O., Jr. *J. Am. Chem. Soc.* **1970**, *92*, 826. (b) Wailes, P. C.; Weigold, H. *J. Organomet. Chem.* **1970**, *24*, 713. (c) Wailes, P. C.; Weigold, H. *Ibid.* **1971**, *28*, 91. (d) Wailes, P. C.; Weigold, H.; Bell, A. P. *Ibid.* **1972**, *43*, C32. (e) Alt, H.; Rausch, M. D. *J. Am. Chem. Soc.* **1974**, *96*, 5936.

(10) (a) Salzmann, J.; Mosimann, P. *Helv. Chim. Acta* **1967**, *50*, 1831. (b) Brintzinger, H. H.; Bercaw, J. E. *J. Am. Chem. Soc.* **1970**, *92*, 6182. (c) Calderazzo, F. *J. Organomet. Chem.* **1973**, *53*, 179 and references therein.

(11) For examples of compounds containing one or two bridging $\eta^1{:}\eta^5\text{-}C_5H_4$ ligands (**4**): (a) Tebbe, F. N.; Parshall, G. W. *J. Am. Chem. Soc.* **1971**, *93*, 3793. (b) Guggenberger, L. J.; Tebbe, F. N. *Ibid.* **1971**, *93*, 5924. (c) Guggenberger, L. J. *Inorg. Chem.* **1973**, *12*, 294. (d) Hoxmeier, R.; Deubzer, B.; Kaesz, H. D. *J. Am. Chem. Soc.* **1971**, *93*, 536. (e) Tebbe, F. N.; Gugenberger, L. J. *J. Chem. Soc., Chem. Commun.* **1973**, 227. (f) Baker, E. C.; Raymond, K. N.; Marks, T. J.; Wachter, W. A. *J. Am. Chem. Soc.* **1974**, *96*, 7586. (g) Pez, G. P. *Ibid.* **1976**, *98*, 8072 and ref 12c.

(12) For examples of compounds containing a bridging $\eta^5{:}\eta^5\text{-}C_{10}H_8$ (fulvenalide) ligand (**5**): (a) Guggenberger, L. J.; Tebbe, F. N. *J. Am. Chem. Soc.* **1973**, *95*, 7870. (b) Tebbe, F. N.; Guggenberger, L. J. *Ibid.* **1976**, *98*, 4137. (c) Cooper, N. J.; Green, M. L. H.; Couldwell, C.; Prout, K. *J. Chem. Soc., Chem. Commun.* **1977**, 145. (d) Smart, J. C.; Curtis, C. J. *Inorg. Chem.* **1978**, *17*, 3290 and references therein. (e) Smart, J. C.; Curtis, C. J. *J. Am. Chem. Soc.* **1977**, *99*, 3518.

(13) Davison, A.; Wreford, S. S. *J. Am. Chem. Soc.* **1974**, *96*, 3017.

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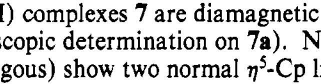
(Cp_2ZrL_2) (**6**)[5] in aromatic solvents produces dark red Zr(III) compounds (**7**) in 60–70% yield and releases hydrogen (ca. 1 equiv on the basis of **7**) (reaction 1). In contrast, Zr(II)

$$\underset{\substack{\mathbf{6a},\ L = PMe_2Ph\\ \mathbf{6b},\ L = PMePh_2}}{Cp_2ZrL_2} \xrightarrow[45-50\ ^\circ C,\ 36\ h]{\text{excess L, toluene}} \underset{\mathbf{7}}{0.5[\{(\eta^5\text{-}C_5H_5)(\mu\text{-}[\eta^1{:}\eta^5\text{-}C_5H_4])ZrL\}_2]} + 0.5H_2 \quad (1)$$

complexes of bis(tertiary phosphines) (L_2 = dmpe, dppe) are stable for several days at 60 °C. The yield of **7** is higher if **6** is decomposed in solutions containing several equivalents of free phosphine; at low phosphine concentration **6** decomposes rapidly, but the product is contaminated with impurities, giving broad absorptions at approximately δ 6–6.5 in the ^1H NMR.

These Zr(III) complexes **7** are diamagnetic and dimeric in benzene (cryoscopic determination on **7a**). NMR spectra of **7a** (**7b** is analogous) show two normal η^5-Cp ligands and two bridging C_5H_4 ligands. In the ^1H NMR the η^5-Cp resonance is a doublet (δ 5.28) from coupling to phosphorus with $^3J_{PH} \simeq 1.5$ Hz.[14] The protons of the C_5H_4 ligand are inequivalent, indicating that the bridge is unsymmetrical, and appear as broad multiplets (ABCD, $J_{obsd} \simeq 1.8$ Hz, $\nu_{1/2} \simeq 7$ Hz) at δ 6.05, 5.50, 5.24, and 3.97. The methyl groups on phosphorus are diastereotopic (δ 1.46, $^2J_{PH} = 5.2$ Hz; δ 1.20, $^2J_{PH} = 5.6$ Hz),[15] and the phosphorus atoms are equivalent (^{31}P, δ 10.4). Irradiation at this phosphorus collapses the ^1H NMR spectrum as required by the coupling constant assignments.

In the $^{13}C\{^1H\}$ NMR spectrum the five carbons of the bridging ligand are inequivalent. The secondary carbon resonances are singlets (no detectable ^{31}P–^{13}C coupling) in the normal region for η^5-Cp ligands on group 4 metals,[13,16] and the quaternary carbon, which resonates at very low field (δ 190.4), is coupled to phosphorus (d, $^2J_{PC} \simeq 7.3$ Hz, confirmed from ^{13}C spectra at 25.2 and 20.16 MHz). These data establish conclusively that the bridging arrangement in these compounds is **4**, $\eta^1{:}\eta^5$-C_5H_4;[17] the low-field chemical shift of the quaternary carbon (C_1) could result from carbene character **8** at this center.[16] The large value of $^2J_{PC}$ for C_1 compared with that found for C_2 and C_3 may then be explained by more direct bonding of C_1 to Zr.[18] In compounds containing structure **5**, C_1 is shifted downfield of C_2 and C_3, but only by 20–30 ppm,[13,19] compared to the shift of 80–90 ppm observed in **7**. Furthermore, the magnitude of $^2J_{PC}$ should be similar for all carbons of this bridging ligand.



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The stereochemistry of **7** cannot be determined from these data. However, the structure of the dimer of niobocene[11a] (**9**), which is isoelectronic with **7**, has recently been reported.[11b,c] The Nb(IV) centers are bridged by $\eta^1{:}\eta^5$-C_5H_4 ligands (**4**), and the complex contains a Nb(IV)–Nb(IV) bond. This structure has been explained[11c] with use of the three frontier molecular orbitals at the metal centers of bent sandwich compounds[20] and bonding in several structurally analogous compounds;[21] e.g., $[\{(\eta^5\text{-}C_5H_5)(HAlEt_2)Ti(\mu\text{-}[\eta^1{:}\eta^5\text{-}C_5H_4])\}_2]$[11e] can also be rationalized in this way. Since in similar ligand environments the bonding orbitals at Zr(III) resemble those at Nb(IV) and Ti(III), **7** may be isostructural with **9**, with phosphine replacing the terminal hydride; a Zr(III)–Zr(III) bond would then result in the observed diamagnetism.[22]

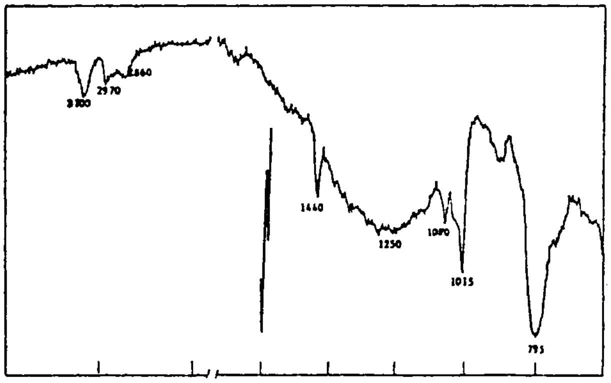

Figure 1.

Preparation of "Zirconocene". Reaction with Dimethylphenylphosphine. (Cyclohexane)methylbis(η^5-cyclopentadienyl)hydridozirconium(IV) (**10**)[23] decomposes at room temperature in toluene solution, producing methylcyclohexane (ca. 1 equiv) and a dark purple compound, a "zirconocene" (**11**). This material is moderately soluble, and a fine purple powder slowly precipitates from toluene solutions of the compound. NMR spectra of **11** in aromatic solvents or tetrahydrofuran (THF) are not diagnostic. In the ^1H NMR at room temperature, broad featureless resonances between δ 6.5–5.5 are seen; the $^{13}C\{^1H\}$ spectrum is a broad envelope centered at approximately δ 101. The IR spectrum of this purple solid shows, in addition to normal metallocene bands (1015, 795 cm^{-1}),[24] a very broad absorption centered at 1300 cm^{-1}. IR samples are rapidly oxidized in air to yellow products; the band at 1300 cm^{-1} is absent from the spectra of these oxidation products, and a broad, strong absorption at 760–730 cm^{-1}, attributable to the Zr–O–Zr unit, appears.[1,24,25]

"Zirconocene" **12**, prepared by reduction of Cp_2ZrCl_2 with excess sodium amalgam[26] in THF, has similar spectral properties. A broad absorption, although centered at a slightly lower frequency (1250 cm^{-1}), is seen in the IR (Figure 1)

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[14] Coupling of similar magnitude is found in many bent sandwich compounds, for example: Benfield, F. W. S.; Green, M. L. H. *J. Chem. Soc., Dalton Trans.* **1974**, 1324 and ref 5.

[15] For other examples of diastereotopic methyl groups on phosphorus: (a) Shaw, B. L.; Smithies, A. C. *J. Chem. Soc. A.* **1968**, 2784. (b) Brunner, H.; Schmidt, E. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 616.

[16] Chisholm, M. H.; Godleski, S. *Prog. Inorg. Chem.* **1976**, *20*, 299.

[17] ^{13}C NMR data have been reported for several compounds containing the μ-$\eta^1{:}\eta^5$-C_5H_4 ligand. However, the quaternary carbon has not been located, so that no direct comparison with the data for **7** can be made.

[18] The carbons of the η^5-Cp ligands on zirconium–phosphine species, e.g., in **7** and in $Cp_2Zr(dmpe)$,[5] are not observably coupled to phosphorus. However, in the methylene complex $Cp_2Zr(CH_2)(PMePh_2)$, $^2J_{PC}$ for the methylene carbon is 14 Hz. Gell, K. I.; Schwartz, J. *J. Organomet. Chem.* **1980**, *184*, C1.

[19] This chemical shift difference is normally observed between a quaternary carbon (bearing a carbon substituent) and a secondary carbon of an η^5-Cp ligand.[16]

[20] Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729 and references therein.

[21] An analogous Mo(III) complex $[\{(\eta^5\text{-}C_5H_5)(\mu\text{-}[\eta^1{:}\eta^5\text{-}C_5H_4])Mo\}_2]$ which is thought to contain a Mo–Mo bond may also have this bonding scheme. Berry, M.; Davies, S. G.; Green, M. L. H. *J. Chem. Soc., Chem. Commun.* **1978**, 99.

[22] Apparent diamagnetism of **7** is a poor criterion for a Zr(III)–Zr(III) bond; indirect magnetic interactions through the bridging ligands can have the same effect. Meyer, T. J. *Prog. Inorg. Chem.* **1975**, *19*, 1.

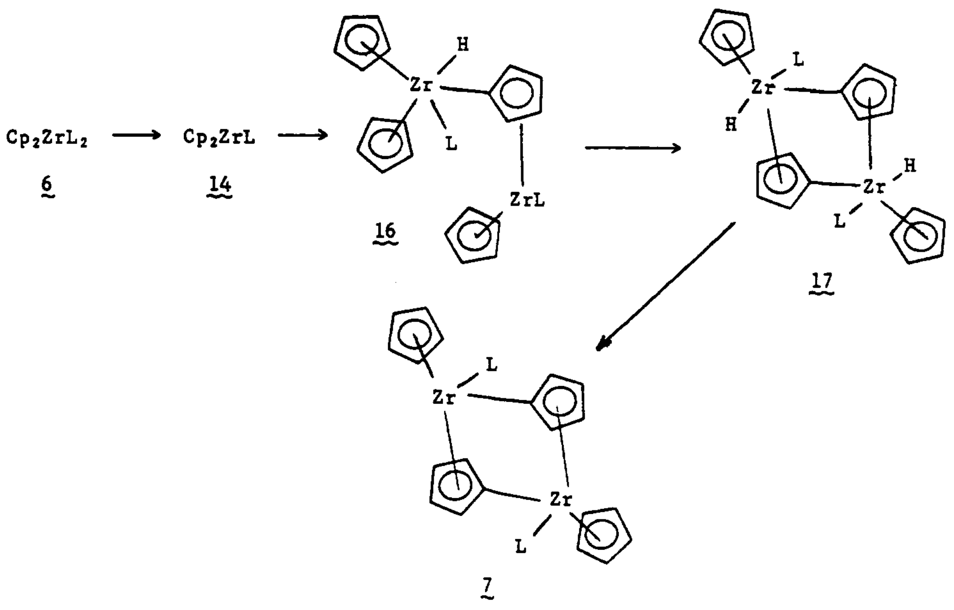
[23] Gell, K. I.; Schwartz, J. *J. Am. Chem. Soc.* **1978**, *100*, 3246.

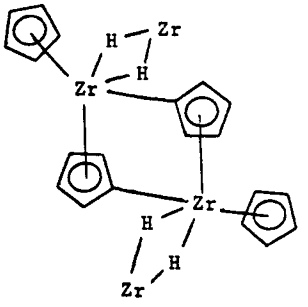
[24] Maslowsky, E., Jr. "Vibrational Spectra of Organometallic Compounds"; Wiley: New York, 1977.

[25] Samuel, E. *Bull. Soc. Chim. Fr.* **1966**, 3548.

[26] Compounds having the stoichiometry of zirconocene have been prepared by various methods: (a) reduction of Cp_2ZrCl_2 with sodium naphthalide;[9a] (b) decomposition of $Cp_2Zr(alkyl)_2$ compounds;[9d] (c) photolysis of Cp_2ZrMe_2.[9e] Sodium amalgam reduction, which was used successfully for reduction of $(\eta^5\text{-}C_5Me_5)_2ZrCl_2$,[2] avoids the possibility of forming naphthalene containing products as in method a.

Scheme I. Proposed Route for the Formation of $\{(\eta^5\text{-}C_5H_5)(\mu\text{-}[\eta^1:\eta^5\text{-}C_5H_4])ZrL\}_2$ (7)





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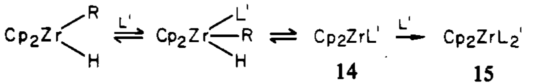
together with all of the normal metallocene bands (3100, 1440, 1015, 795 cm^{-1}).[24] These "zirconocenes" react rapidly with aqueous sulfuric acid, forming yellow solids and evolving hydrogen (approximately 1 equiv).

Toluene or THF solutions of **11** or **12** react with excess PMe_2Ph at 50–60 °C. Hydrogen is steadily evolved over 60 h with isolation of the dimer **7a** in yields of 30–50% (on the basis of Zr). In general, 1–1.5 equiv of hydrogen per dimer **7a** isolated are produced. The yield of **7a** depends on the solubility of the "zirconocene" starting material, with very insoluble fractions producing low yields of **7a** and of hydrogen.

Discussion

We have demonstrated that a variety of donor ligands (L′), including tertiary phosphines, promote reductive elimination of alkane from the Zr(IV) alkyl hydride complex **10**, giving in some cases an isolable Zr(II) product **15** (reaction 2).[5,27]



$$Cp_2Zr\begin{smallmatrix}R\\H\end{smallmatrix} \overset{L'}{\rightleftharpoons} Cp_2Zr\begin{smallmatrix}L'\\R\\H\end{smallmatrix} \rightleftharpoons Cp_2ZrL' \xrightarrow{L'} Cp_2ZrL_2' \qquad (2)$$

10 13 14 15

(6, L′ = mono-(tertiary phosphine))

$R = \overline{CH_2(CH_2)_4CH}CH_2\text{-}$

L′ = tertiary phosphine, acetylene, CO

We have suggested that electronically saturated Cp_2Zr^{IV} complexes are thermodynamically unfavorable and that C–H reductive elimination from the high-energy saturated Zr(IV) intermediate **13** competes effectively with ligand dissociation (to regenerate **10**), especially when the donor ligand (L′) can stabilize the incipient Zr(II) center in the transition state, leading to **14**.[28] Whereas reductive elimination of alkane (sp^3 C–H bond) is apparently irreversible, we have shown that **6**, presumably via **14**, readily inserts reversibly into sp^2 C–H bonds.[5]

An extension of these ideas to a dinuclear system explains the formation of the Zr(III) dimer **7** by a series of oxidative additions of activated (sp^2) C–H bonds and a reductive elimination of hydrogen, which interconvert the +2, +3, and +4 oxidation states for zirconium (Scheme I). The active species in this decomposition is suggested to be the unsaturated (16-electron) Zr(II) intermediate **14**.[5] Free phosphine retards the formation of **7**, perhaps by reducing the concentration of **14**; $Cp_2Zr(dmpe)$, which is stabilized by chelation, resists decomposition to the dimeric species. An intermolecular C–H insertion by **14** into an sp^2 C–H bond of a Cp ligand would give formally mixed-valent species **16**. Phosphine loss, followed by an intramolecular C–H oxidative addition, would produce **17**, a Zr(IV) dimer with the framework of the product **7**. In the presence of phosphine, these C–H oxidative additions may be reversible; reductive elimination of hydrogen (which is apparently irreversible under the reaction conditions[29]) gives

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[27] (a) Yoshifuji, M.; Gell, K. I.; Schwartz, J. *J. Organomet. Chem.* **1978**, *153*, C15. (b) Gell, K. I.; Schwartz, J. *Ibid.* **1978**, *162*, C11.

[28] These ideas are more fully discussed in ref 5b.

[29] Hydrogen elimination is probably irreversible under the reaction conditions. At hydrogen pressures up to 4 atm, no net hydrogenation of 7 is detected.

7 (elimination of H_2 may occur in a dinuclear process[30]). The formal Zr(III) centers in **7** are believed to be stabilized by spin pairing[31a] in a Zr–Zr bond.

The formation of **7** by C–H oxidative additions and subsequent reductive elimination of hydrogen highlights an interesting parallel between the early transition metallocenes. Reactive 16-electron analogues of **14**,[32] which are generated by hydrogen elimination in the thermolysis of Cp_2MH_3 (M = Nb, Ta)[11a] or by photolysis of Cp_2MH_2 (M = Mo, W),[21] are proposed as the active species in C–H insertion reactions leading to the formation of stable dimers with the same framework as **7**: hydrogen elimination from the analogue of **17** occurs thermally for the Nb and Ta species and under photolytic conditions for Mo.

"Zirconocenes" **11** and **12** evolve hydrogen on treatment with PMe_2Ph or $PMePh_2$ and give variable yields of **7**. We suggest that these "zirconocenes" are polymeric Zr(IV) compounds containing hydride and η^1:η^5-C_5H_4 bridges (e.g., **18**). Several qualitative observations on the properties of **11** and **12** support the hypothesis that they are nonuniform polymers. Solutions of these "zirconocenes" slowly precipitate solids which cannot be redissolved, and the approximate correlation that higher yields of **7** are obtained from more soluble fractions of **11** and **12** suggests that phosphine reaction with soluble oligomers is more efficient than with insoluble polymers. The band centered at 1250–1300 cm^{-1} in the IR of **11** and **12**, which disappears instantly on oxidation, is in the correct region for the vibration of bridging hydride ligands on Zr. This band is very broad compared with that in dimeric or polymeric Zr complexes containing double hydride bridges, e.g., $(Cp_2ZrH_2)_2$,[33] and is consistent with a polymeric structure in which vibrations arise from hydride ligands in nonequivalent environments.[34,35]

We believe, then, that "zirconocene" is not isostructural with the green, stable form of "titanocene" nor does it remain in solution as a metastable species, as do the titanocenes.[36] The difference in behavior of these two systems can probably be explained by the relative ease of reduction of Ti(IV) to Ti(III).[7]

Some Reactions of the Zr(III) Dimers 7. These dimers are novel examples of Zr(III) complexes, but it is perhaps more significant that they bind two reduced metal centers in close proximity, providing the potential for bifunctional activation of substrates. In addition to the possibility of reaction at the (real or formal) Zr(III)–Zr(III) bond, a vacant site for reaction at each metal center can be created by phosphine dissociation. For example, phosphine ligands on **7** can be displaced by other phosphines, by carbon monoxide, and by ethylene, although these reaction products have not been fully characterized.

Both ligand displacement and oxidation of the complex are observed in the reaction of **7b** with 2 equiv of PPh_2H, which gives two major products, **19** and **1c** (Scheme II). Simple ligand replacement presumably leads to **19**, whereas oxidation of the formal metal–metal bond, followed by C–H reductive elimination, perhaps promoted by a phosphine ligand, gives the bridge-opened product **1c**. Two analogues (**1a**, **1b**) of this compound have previously been prepared by the reaction of Cp_2ZrCl_2 with a lithium dialkylphosphide.[8a] Treatment of "Cp_2Zr" with PPh_2H also yields **1c**.

Preliminary investigations of the reaction of **7b** with oxygen and with iodine indicate that **7b** can act as a stoichiometric two-electron reductant.

Oxygen. A white yellow solid, **20**, which is insoluble in all common solvents, is formed in the controlled oxidation of **7b** with oxygen (1 equiv). Methyldiphenylphosphine is not oxidized in this reaction, nor is it incorporated in the product, **20**. The IR spectrum of **20** shows metallocene bands (3090, 1440, 1015, 800 cm^{-1})[24] and a broad strong absorption at 740 cm^{-1}, attributable to a Zr–O–Zr stretching vibration[1,25] or to a Zr–O bend.[37a] The absence of strong absorptions in the 1150–1100 cm^{-1} region suggests that oxygen has not inserted into the Zr–C bond of the η^1:η^5-C_5H_4 ligand.[37]

The solid **20** slowly dissolves in acetone solutions of tetra-*n*-butylammonium iodide, releasing iodine. This observation and the reaction stoichiometry (reaction 3) suggest that **20**

$$2Zr^{III} + O_2 \rightarrow Zr^{IV}\text{–}O_2\text{–}Zr^{IV} \qquad (3)$$

may be a polymeric Zr–peroxy species. A similar observation has been made for titanocene, which reacts with 1 equiv of oxygen per dimer, giving an insoluble product thought to be a titanium peroxide.[38]

Iodine. Characterization of the Oxidation Product. Slow addition of iodine (1 equiv) to a dark red toluene solution of **7b** at −78 °C forms a yellow-green mixture which darkens to purple-red above −50 °C. From this solution a dark purple crystalline complex $[\{(\eta^5\text{-}C_5H_5)(C_5H_4)ZrI\}_n]$ (**21**), which is at least dimeric ($n \geq 2$), can be isolated.[39] Methyldiphenylphosphine is quantitatively released in the reaction, although, if small excesses of iodine are present, some oxidation to the yellow, insoluble $PMePh_2I_2$[40] occurs.

The diamagnetic complex **21**[41] contains two η^5-Cp ligands and two bridging C_5H_4 ligands. In the ^1H NMR the η^5-Cp is a singlet (δ 5.61) and the protons of the C_5H_4 unit appear as two pseudotriplets ($J_{obsd} \simeq 2.8$ Hz) at δ 4.58 and 4.16.[42]

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(30) (a) Braterman, P. S.; Cross, R. J. *Chem. Soc. Rev.* **1973**, *2*, 271. (b) For an example of dinuclear elimination of hydrogen: Evans, J.; Norton, J. R. *J. Am. Chem. Soc.* **1974**, *96*, 7577.

(31) (a) Manzer, L. E. *J. Am. Chem. Soc.* **1978**, *100*, 8068. In niobocene,[11a] the Nb(IV) centers are stabilized compared with their mononuclear analogues. (b) Elson, I. H.; Kochi, J. K.; Klabunde, U.; Manzer, L. E.; Parshall, G. W.; Tebbe, F. N. *Ibid.* **1974**, *96*, 7374.

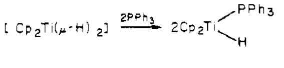
(32) Parshall, G. W. *Catalysis* **1977**, *1*, 335 and references therein.

(33) (a) Weigold, H.; Bell, A. P.; Willing, R. I. *J. Organomet. Chem.* **1974**, *73*, C23. (b) Wailes, P. C.; Weigold, H. *Ibid.* **1970**, *24*, 405.

(34) IR bands from terminal zirconium hydride ligands have been reported at approximately 1550 cm^{-1}: Manriquez, J. M.; McAlister, D. R.; Sanner, R. D.; Bercaw, J. E. *J. Am. Chem. Soc.* **1978**, *100*, 2716. Asymmetric ring vibrations for ZrHZrH are found at approximately 1300 cm^{-1}.[23,33] Coupling of vibrations in a polymer chain will lower the frequency and broaden the absorption. Such observations have been made for the violet titanocene hydride $[\{Cp_2Ti(\mu\text{-}H)\}_2]$, which shows a bending mode for TiHTiH at 1450 cm^{-1}. On polymerization to $[\{Cp_2Ti(\mu\text{-}H)\}_n]$ this band is broadened and shifted to 1140 cm^{-1}.[36]

(35) The IR spectrum is not diagnostic for the presence of η^1:η^5-C_5H_4 ligands, a fact which has led some previous investigators to conclude that zirconocene has a normal metallocene structure. The IR spectra of **11** and **12** show only bands (though somewhat broadened) from a normal metallocene structure, and it has been noted[11a] that even compounds of a well-defined structure containing an η^1:η^5-C_5H_4 ligand have a normal metallocene spectrum. Vibrational data for other well-defined dimers such as niobocene have not been reported, and unfortunately the IR spectrum of **7a** is complicated by absorption bands from PMe_2Ph, preventing extraction of useful information on the vibrational bands of the bridging ligand.

(36) Breaking of hydride bridges by phosphine has been demonstrated in an unsaturated group 4 system:



$$[Cp_2Ti(\mu\text{-}H)_2] \xrightarrow{2PPh_3} 2Cp_2Ti(PPh_3)(H)$$

(a) Bercaw, J. R.; Marvich, R. H.; Bell, L. G.; Brintzinger, H. H. *J. Am. Chem. Soc.* **1972**, *94*, 1219. (b) Bercaw, J. E. *Ibid.* **1974**, *96*, 5087.

(37) (a) Gray, D. R.; Brubaker, C. H., Jr. *Inorg. Chem.* **1971**, *10*, 2143. (b) Blackburn, T. F.; Labinger, J. A.; Schwartz, J. *Tetrahedron Lett.* **1975**, 3041.

(38) IR characterization of this product as a peroxy species is unconvincing. Salzmann, J.-J. *Helv. Chim. Acta* **1968**, *51*, 903.

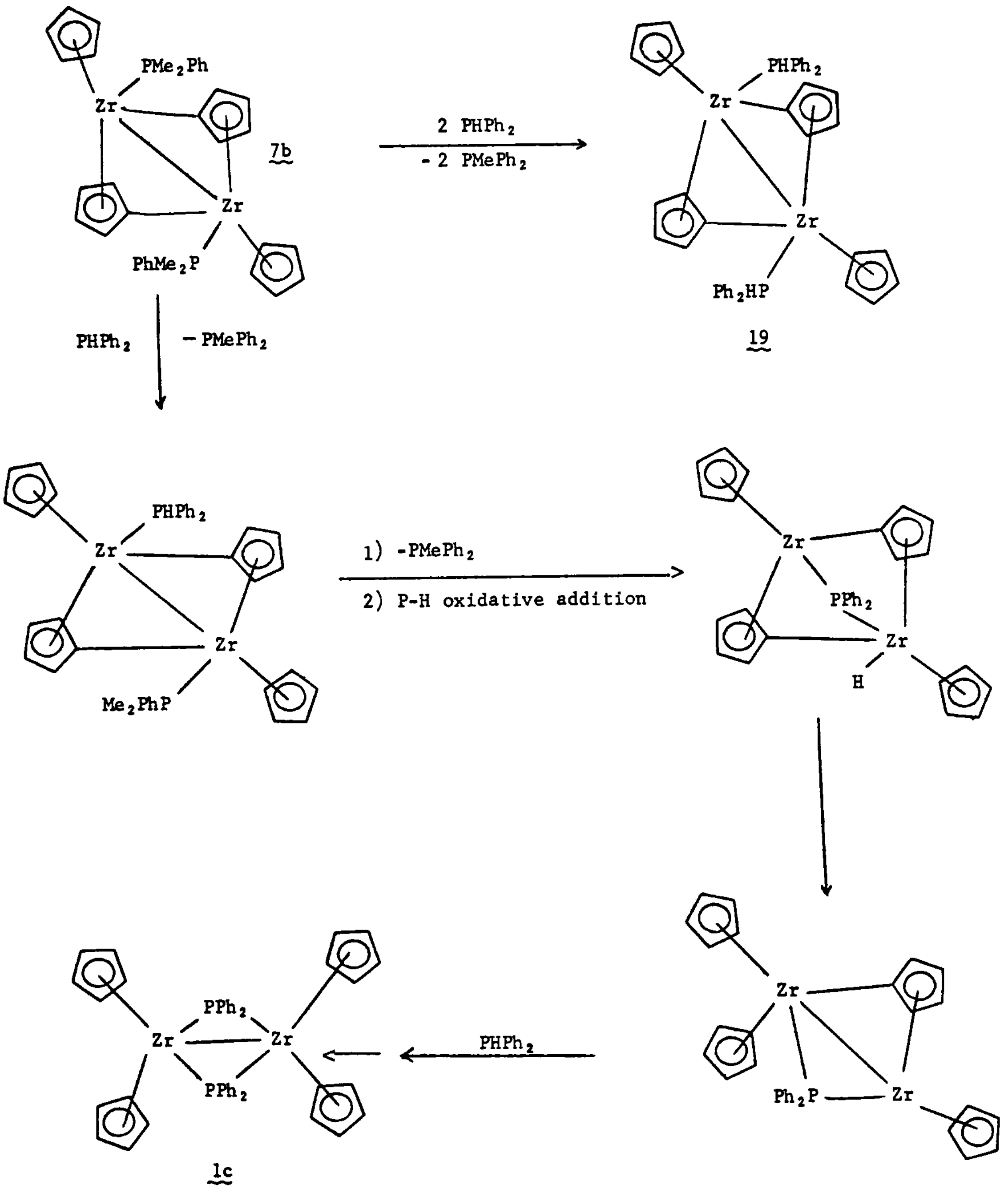
(39) In a cryoscopic molecular weight determination, evidence for a concentration-dependent oligomerization of **32** is obtained.

(40) Hellwinkel, D. In "Organic Phosphorus Compounds"; Kosolapoff, G. M., Maier, L., Eds.; Wiley: New York, 1972; Vol. 3, Chapter 5B.

(41) The complex is apparently diamagnetic, but the only criterion so far applied is sharpness of the ^1H NMR spectrum at room temperature.

(42) The system is a "deceptively simple" AA'BB' spin system which gives approximate A_2B_2 spectra ($J_{obsd} \simeq J_{AB} \simeq J_{AB'}$). Bovey, F. A. "Nuclear Magnetic Resonance Spectroscopy"; Academic Press: New York, 1969.

Scheme II. Proposed Route for the Reaction of $\{(\eta^5\text{-}C_5H_5)(\mu\text{-}[\eta^1{:}\eta^5\text{-}C_5H_4])Zr(PMePh_2)\}_2$ (**7b**) with Diphenylphosphine



In the ^{13}C NMR the η^5-Cp resonance is at δ 101.4 ($^1J_{CH}$ = 173 Hz) and the secondary carbons (C_2, C_3) of the bridging ligand occur at δ 102.4 ($^1J_{CH}$ = 173 Hz) and 98.6 ($^1J_{CH}$ = 173 Hz). Although no signal unequivocally assignable to the quaternary carbon (C_1) has been observed, the small chemical shift difference (3.8 ppm) between the secondary carbons C_2 and C_3 suggests that the C_5H_4 groups in **21** are coupled as the $\eta^5{:}\eta^5$-$C_{10}H_8$ ligand **5**. This criterion has been used in previous studies to distinguish between structures **4** and **5**.[43]

The AA'BB' pattern in the ^{1}H NMR for the protons of the C_5H_4 bridge and the observation of only two secondary carbon resonances in the ^{13}C NMR are evidence for an average plane of symmetry equivalencing the sides of the $C_{10}H_8$ ligand. The average structure of the dimeric unit **21** is then analogous to that of green, stable titanocene,[44] and the sides of the $C_{10}H_8$ ligand in **21** are equivalenced by bridging iodides.

This structural assignment implies a reaction sequence proceeding by net oxidation of the formal Zr(III)–Zr(III) bond to give the Zr(IV) dimer **22** followed by a slower skeletal rearrangement by C–C reductive elimination to give **21** (Scheme III).[12c] In contrast, "zirconocene", which we have suggested is initially structurally analogous to **22**, does not undergo C–C reductive elimination. In the absence of phosphine it polymerizes, sequestering its hydride ligands in bridging positions; in the presence of phosphine it may undergo reversible C–H reductive elimination, but ultimately it loses hydrogen.

Whereas hydride can only act as a two-electron donor ligand, iodide may behave as a four-electron ligand and as an intramolecular nucleophile, resulting in electronic saturation

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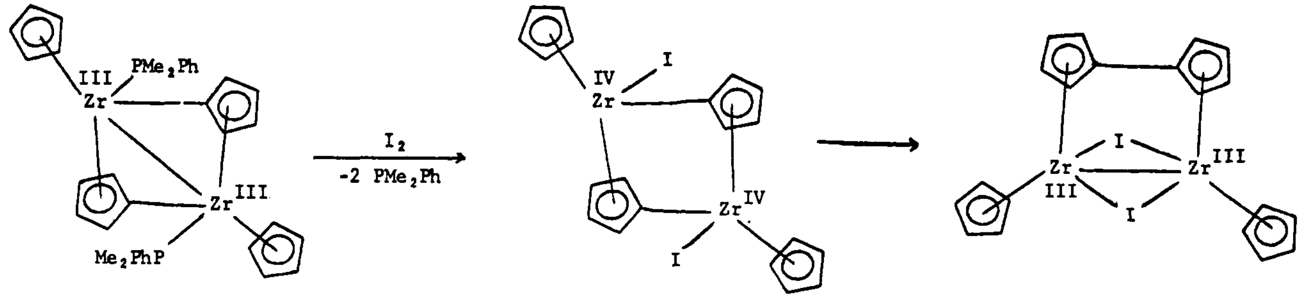
(43) In structure **4** the chemical shift difference between C_2 and C_3 is large (ca. 20 ppm) whereas in structure **5** smaller differences (ca. 2 ppm) have been found.[13]

(44) The ^{13}C{^{1}H} NMR parameters of **24** are very similar to those of **20**.[13] ^{13}C{^{1}H} NMR (tetrahydrofuran-d_8): δ 122.6 (s, C_1), 104.6 (s, η^5-Cp), 102.7 (s, C_2), 100.4 (s, C_3). C_2 and C_3 assignments could be reversed.

Scheme III. Proposed Route for the Reaction of $\{(\eta^5\text{-}C_5H_5)(\mu\text{-}[\eta^1{:}\eta^5\text{-}C_5H_4])Zr(PMePh_2)\}_2$ (7b) with I_2



7b

of the Zr(IV) centers. For **22** C–C reductive elimination may provide a means of collapsing from a state which we have suggested is unfavorable for Zr(IV).

Conclusions

We have suggested that in mononuclear systems the electron count on Zr is an important determinant of reactivity.[5b] Reductive elimination of a C–H bond from **10** to give a 16-electron Zr(II) species is promoted by a suitable donor ligand and is a means of collapsing from a thermodynamically disfavored 18-electron Zr(IV) intermediate.

This idea appears to be valid in dinuclear systems. Reversbile mononuclear C–H reductive elimination in the proposed precursor of **7** may occur. However, in this system *dinuclear* elimination of hydrogen, which may be irreversible under the reaction conditions, is a collapse mechanism for the electronically saturated intermediate and effects a net two-electron reduction of the dimer to the average oxidation state +3. Reductive elimination of an H–H bond rather than an alternative reduction by C–C elimination is observed in this system. However, when no alternative reduction pathway is available, as in the iodide dimer **22**, C–C reductive elimination *may* occur.

Experimental Section

General Procedure and Techniques. Reactions were performed under purified argon with use of standard Schlenk techniques[45] on a high-vacuum line or in a nitrogen-filled Vacuum Atmospheres Corp. drybox. Solvents were distilled from sodium benzophenone ketyl under nitrogen. Nuclear magnetic resonance (NMR) solvents (benzene-d_6, toluene-d_8) were vacuum distilled from lithium aluminum hydride. Dichlorobis(η^5-cyclopentadienyl)zirconium(IV) (Boulder Scientific), 1,2-bis(diphenylphosphino)ethane (dppe) (Pressure chemicals), and 1,2-bis(dimethylphosphino)ethane (dmpe) (Strem) were used without purification. Methyldiphenylphosphine and dimethylphenylphosphine (Strem; Pressure) were vacuum distilled from calcium hydride. Sodium mercury amalgam (2% sodium) was prepared by a literature method and stored under nitrogen.[46] The preparation and characterization of $[\{Cp_2Zr(CH_2CH(CH_2)_4CH_2)(\mu\text{-}H)\}_2]$,[23] Cp_2ZrL_2[5] (L = tertiary phosphine), and $Cp_2Zr(dmpe)$[5] have been described. Proton (100 MHz), ^{13}C, and ^{31}P NMR spectra were recorded on a Varian XL-100 spectrometer. Proton NMR (60 MHz) spectra were measured on a Varian A-60 or A-60A spectrometer. Chemical shifts (^1H, ^{13}C NMR) are reported in units of δ referenced to tetramethylsilane and are calculated from the position of solvent absorption. Phosphorus chemical shifts are reported in units of δ referenced to external H_3PO_4 (85%) and are positive to low field. When important resonances were obscured by aromatic solvents, ^{13}C NMR spectra were obtained with use of 1,2-dimethoxyethane (DME) as a solvent and chloroform-d, contained in a concentric tube, as a locking solvent. Infrared (IR) spectra were obtained on a Perkin-Elmer PE-283 instrument; pellets were prepared in the drybox with use of KBr which had been dried at 120 °C for 24 h under high vacuum. Gas chromatography/mass spectral (GC/MS) analysis was performed on a Du Pont 21-490 GC mass spectrometer. Gas chromatographic (GC) analysis for hydrogen was performed on a Perkin-Elmer PE-3920 thermal conductivity instrument using argon as a carrier gas on Porapak QS, 20 ft × 0.125 in. at 25 °C. For other GC analyses a Hewlett-Packard 402 flame ionization instrument and a Carbowax 20 M, 20 ft × 0.25 in. column at 50 °C, were used. Mass spectra were obtained on an AEI MS-9 instrument using a probe which was loaded in the drybox. Elemental analyses were performed by Alfred Bernhardt with use of drybox sampling techniques. Cryoscopic molecular weights were determined under argon in a jacketed cell fitted with a calibrated thermocouple.[47]

Preparation of Zr(III)–Phosphine Dimers (7). A. Synthesis of $[\{(\eta^5\text{-}C_5H_5)(\mu\text{-}[\eta^1{:}\eta^5\text{-}C_5H_4])Zr(PMe_2Ph)\}_2]$ (7a) by Decomposition of $Cp_2Zr(PMe_2Ph)_2$ (6a). Dimethylphenylphosphine (0.7 mL, 5 mmol, 2.5 equiv) was added to a stirred solution of **10** (0.64 g, 2 mmol) in toluene (30 mL) at 0 °C. The solution immediately turned dark purple-brown, with the formation of **6a**. It was warmed to room temperature and stirred for 15 h and then heated at 45–50 °C. After 7 h and 30 min, ^1H NMR showed a small amount of **6a** remained, so the solution was heated for a further 6 h and then cooled to room temperature. Hydrogen (ca. 0.5 mmol, GC determination) was produced during the reaction. The volatiles were pumped off, and excess PMe_2Ph was partially removed under high vacuum. The resulting dark red solid was dissolved in toluene (15 mL), hexane (10 mL) was slowly added, and the mixture was refrigerated. Dark red microcrystals of **7a** (0.3 g, 0.42 mmol, 42%) which formed were filtered off, washed with hexane, and dried. Recrystallization from toluene–hexane gave an analysis sample.

Anal. Calcd for $C_{23}H_{22}PZr$: C, 65.68; H, 5.27. Found: C, 65.43; H, 5.09.

Molecular weight (cryoscopic, 4.8 mg mL^{-1} benzene) 733 ± 70 (calculated for dimer 712). The compound was diamagnetic (Evans' method).[48]

^1H NMR (100 MHz) (benzene-d_6): δ 7.62 (br, 2, ortho protons of PPh), 7.12 (br, 3, meta- and para protons of PPh), 6.05 (br, 1, $\eta^1{:}\eta^5\text{-}C_5H_4$), 5.50 (br, 1, $\eta^1{:}\eta^5\text{-}C_5H_4$), 5.28 (d, 5, $\eta^5\text{-}C_5H_5$, $^3J_{PH}$ = 1.5 Hz), 5.24 (br, 1, $\eta^1{:}\eta^5\text{-}C_5H_4$), 3.97 (br, 1, $\eta^1{:}\eta^5\text{-}C_5H_4$), 1.46 (d, 3, PMe, $^2J_{PH}$ = 5.2 Hz), 1.20 (d, 3, PMe, $^2J_{PH}$ = 5.6 Hz). The resonances from the protons of the $\eta^1{:}\eta^5\text{-}C_5H_4$ group (ABCD spin system) are poorly resolved multiplets ($\nu_{1/2} \simeq$ 7 Hz).

^{31}P NMR (benzene-d_6): δ 10.4 (m, $\nu_{1/2}$ = 26 Hz). $^{31}P\{^1H\}$ NMR: δ 10.4 (s).

$^{13}C\{^1H\}$ NMR (25.2 MHz) (benzene-d_6): δ 190.43 (d, ZrC of $\eta^1{:}\eta^5\text{-}C_5H_4$, $^2J_{PC}$ = 7.3 Hz), 140.24 (d, PC (phenyl), $^1J_{PC}$ = 20.6 Hz), 131.86 (d, ortho carbons of Ph, $^2J_{PC}$ = 11.1 Hz), 128.90 (s, para carbon of Ph)*, 128.17 (d, meta carbons of Ph, $^3J_{PC}$ = 8.8 Hz)*, 111.18 (s, $\eta^1{:}\eta^5\text{-}C_5H_4$), 109.70 (s, $\eta^1{:}\eta^5\text{-}C_5H_4$), 104.92 (s, $\eta^1{:}\eta^5\text{-}C_5H_4$), 100.90 (s, $\eta^1{:}\eta^5\text{-}C_5H_4$), 99.36 (s, $\eta^5\text{-}C_5H_5$), 18.40 (d, PMe, $^1J_{PC}$ = 17.5 Hz), 16.40 (d, PMe, $^1J_{PC}$ = 15.6 Hz); asterisks indicate resonances partially obscured by benzene-d_6; in DME all of the phenyl signals were located. In a $^{13}C\{^1H\}$ NMR spectrum at 20.16 MHz, the resonance at δ 190.43 remained a doublet (7.1-Hz separation). IR (KBr; NaCl windows

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(46) Fieser, L. F.; Feiser, M. "Reagents for Organic Synthesis"; Wiley: New York, 1967; Vol. 1, p 1030.

(47) (a) Extine, M. E. Ph.D. Dissertation, Princeton University, Princeton, New Jersey, 1976. (b) Shoer, L. I. Ph.D. Dissertation, Princeton University, Princeton, New Jersey, 1978.

(48) Evans, D. F. *J. Chem. Soc.* **1959**, 2003.

on die): 3080, 2970, 2910, 1485, 1435 (m), 1340, 1295, 1280, 1265, 1100 (m), 1015 (m), 945, 920, 905 (s), 795 (s), 770 (m), 740 (m), 695 (m) cm^{-1}. Mass spectrum: compound **7a** decomposed (probe; source 100–150 °C); only fragments from PMe_2Ph were identified.

B. $[\{(\eta^5\text{-}C_5H_5)(\mu\text{-}\{\eta^1:\eta^5\text{-}C_5H_4\})Zr(PMePh_2)\}_2]$ (7b). (a) Synthesis, Purification, and Determination of Hydrogen Evolved. Methyldiphenylphosphine (0.78 mL, 4.2 mmol, 3.5 equiv) was added dropwise to a stirred solution of **10** (0.38 g, 1.2 mmol) in toluene (25 mL) at −30 °C. This mixture, which rapidly turned dark purple, was degassed (three freeze–thaw cycles), warmed to room temperature, and stirred for 12 h. The purple-red solution was then stirred at 50 °C for 36 h. Hydrogen (0.41 mmol) was collected via Toepler pump and identified by GC. The crimson solution was concentrated, DME (50 μL, 0.48 mmol) was added, and ^{1}H NMR showed **7b** (0.53 mmol) in 83% yield (on the basis of Zr). The yield of hydrogen was 68% (on the basis of one hydride per Zr) or 82% on the basis of **7b**. The solvent was removed under vacuum, leaving a dark crimson oil which solidified after trituration with hexane. The hexane suspension was cooled (−30 °C), and the crimson solid (0.4 g, 0.48 mmol, 80% on the basis of Zr) was collected by filtration, washed with hexane, and dried. Although often sufficiently pure for use in subsequent reactions, **7b** was sometimes contaminated by "zirconocene" impurities (broad resonances in the ^{1}H NMR δ 6.2–6.0). These impurities were less soluble than **7b** in toluene; purification was effected by extraction with octane containing 5–10% toluene, followed by concentrating and cooling. The product **7b** is insoluble in hexane but is solubilized by phosphine. Very pure product was sometimes obtained by slow evaporation of this initial filtrate.

^{1}H NMR (benzene-d_6): δ 7.6–6.7 (br, 10, Ph), 5.90 (br, 1, $\eta^1:\eta^5\text{-}C_5H_4$)*, 5.52 (br, 1, $\eta^1:\eta^5\text{-}C_5H_4$)*, 5.22 (d, 5, $\eta^5\text{-}C_5H_5$, $^3J_{PH}$ = 1.5 Hz), 5.12 (br, 1, $\eta^1:\eta_5\text{-}C_5H_4$)*, 3.20 (br, 1, $\eta^1:\eta^5\text{-}C_5H_4$)*, 1.56 (d, 3, PMe, $^2J_{PH}$ = 5 Hz); asterisks indicate $\nu_{1/2}$ = 5 Hz. $^{31}P\{^1H\}$ NMR (benzene-d_6): δ 32.5.

(b) Determination of Hydrogen Evolved Using Gas Chromatography. In several experiments the yield of hydrogen was determined by GC using nitrogen as an internal standard. The response factor for hydrogen compared with nitrogen was independently determined. The above reaction was repeated [**11** (0.31 g, 1 mmol), $PMePh_2$ (0.63 mL, 3.5 mmol, 3.5 equiv), toluene (10 mL)]. Hydrogen was evolved steadily, and after 36 h at 50 °C the ratio of hydrogen to nitrogen was constant (successive samples separated by 4 h 30 min). The yield of hydrogen was 0.29 mmol (60% on the basis of one hydride per Zr) and the yield of **7b** was determined by ^{1}H NMR (DME internal standard) as 0.27 mmol (55% on the basis of Zr). The yield of hydrogen on the basis of **7b** was 110%.

C. Rearrangement of $Cp_2Zr(dmpe)$. A solution of $Cp_2Zr(dmpe)$ in toluene-d_8 (concentration 0.1 M) was sealed in a 5-mm NMR tube and heated at 65 °C. The ^{1}H NMR spectrum did not change over 24 h.

Preparation and Characterization of the "Zirconocenes" 11 and 12. A. Decomposition of 10 and Spectral Characterization of a "Zirconocene" 11. Toluene (33 mL) containing octane (0.25 mL) was vacuum distilled from $LiAlH_4$ onto **10** (0.82 g, 2.6 mmol) contained in a Schlenk flask (100 mL) fitted with a vacuum adapter. The solution was placed under argon, and a sample (0.3 mL) was taken and hydrolyzed (1 M sulfuric acid) for GC analysis to determine the ratio of methylcyclohexane to octane at complete decomposition. Another sample (0.3 mL) was sealed in a 5-mm NMR tube to follow the progress of the decomposition. Nitrogen (2.1 mmol) was added as an internal standard, and the system was sealed.

The solution was stirred at room temperature, and the color changed from pink to red to purple over several days. After 24 h, purple solid began to coat the flask. The atmosphere was periodically sampled during the decomposition. No hydrogen was detected by GC. After 48 h little starting material was present (^{1}H NMR). The solution was sampled, and the sample (0.3 mL) was evaporatively distilled. Methylcyclohexane (80%) was detected by GC. The mixture was left for a further 48 h to complete the decomposition, when a large amount of purple solid was present. The solvent volume was reduced to approximately 10 mL, and hexane (30 mL) was distilled from $LiAlH_4$ onto the purple suspension. This caused the precipitation of more solid. The suspension was filtered in the drybox, and the purple solid **11** (0.3 g, 1.34 mmol, calculated as "Cp_2Zr", 50% on the basis of Zr) was washed with hexane, dried, and stored under nitrogen. ^{1}H NMR (toluene): broad resonance between δ 6.0–5.5. $^{13}C\{^1H\}$ NMR: several attempts to obtain $^{13}C\{^1H\}$ NMR spectra of these purple solids at room temperature were unsuccessful and gave only broad absorptions (tetrahydrofuran-d_8 as solvent) with maxima at δ 104.2, 102.1, and 98.2.

Table I. Hydrogen Evolved in Reaction of 11 with PMe_2Ph

time			amt of hydrogen,
h	min	$H_2:N_2$[a]	mmol
	0	0.2	0.03[b]
1	10	0.5	0.08
2	30	0.7	0.12
3	50	1.5	0.25
13	20	1.7	0.28
24	50	2.7	0.44
37	50	2.8	0.46
42	35	3.0	0.48

[a] Uncorrected. [b] Adventitious hydrolysis.

IR (Nujol mull): 1300 (br), 1015, 800 (s), 730 cm^{-1}. The mull was oxidized in air. It rapidly turned from purple to yellow. Ir (Nujol mull): 1260, 1070 (br), 1015 (m), 890, 800 (s), 730 (br sh, s) cm^{-1}.

B. Decomposition of 10 and Reaction of the Decomposition Product 11 with PMe_2Ph. A sample of **10** (0.8 g, 2.8 mmol) in toluene (45 mL) was decomposed in an analogous way. After 4 days the yield of methylcyclohexane was quantitative (on the basis of the hydrolysate). The purple slurry was filtered with difficulty, and the fine solid (0.11 g) was washed with hexane and dried. This toluene insoluble residue was soluble in tetrahydrofuran (THF).

The deep purple filtrate was collected in a tared Schlenk flask (50 mL) and pumped down thoroughly. This residue (0.5 g) was extracted with toluene (35 mL) until the extracts were colorless. A small amount was insoluble.

(a) Reaction of the Soluble Fraction with PMe_2Ph. The purple toluene solution was degassed (three freeze–thaw cycles) and placed under argon. Nitrogen (2.05 mmol) was added as a GC standard. Dimethylphenylphosphine (1 mL, 7 mmol) was added, and a gas sample was immediately taken to determine the composition of the atmosphere before reaction. The mixture was heated at 50 °C, and the atmosphere was periodically sampled. Hydrogen (0.48 mmol, 43% on the basis of one hydride per Zr) was evolved over a period of 40 h (Table I).

An aliquot (5 mL) of the solution was taken for hydrolysis. The solvent was evaporated from the remainder, and the red residue was taken up in benzene (10 mL). ^{1}H NMR showed **7a** (0.34 mmol, 30% on the basis of Zr, octamethyldisiloxane internal standard). On the basis of **7a**, the yield of hydrogen was 140%.

Control Reaction: Hydrolysis. An aliquot (5 mL) of the crude PMe_2Ph reaction mixture (in toluene, total volume 35 mL) was sealed in a vessel containing nitrogen (1.8 mmol). The purple-red solution was hydrolyzed (aqueous hydrochloric acid, 6 M, 1 mL) and turned brown and then yellow, with the formation of a heavy yellow precipitate. Hydrogen (0.1 mmol, GC determination) was evolved.

(b) Reaction of the Toluene-Insoluble Fraction with PMe_2Ph. A sample of the toluene-insoluble residue (34 mg, 0.15 mmol) was suspended in toluene (2 mL) under nitrogen (0.64 mmol). Dimethylphenylphosphine (70 μL, 0.46 mmol) was added. The atmosphere was sampled for hydrogen arising from adventitious hydrolysis. The purple suspension was heated at 50 °C for 10 h. It remained nonhomogeneous, but the solution had turned purple-red. A small amount of hydrogen (ca. 0.01 mmol, 10% on the basis of one hydride per Zr) was evolved. Most of the solvent was pumped off, nitrogen (0.64 mmol) was added, and the residue was dissolved in THF (2 mL). After the mixture was heated at 50 °C for 36 h, little hydrogen had formed. The total hydrogen yield was approximately 0.01 mmol (15%). A ^{1}H NMR spectrum showed **7a** had formed, but the yield was low and was not accurately measured.

Control Reaction: Hydrolysis. A sample of the toluene insoluble residue (76 mg, 0.34 mmol) was suspended in toluene (2 mL) under nitrogen (1.5 mmol). It was hydrolyzed (aqueous sulfuric acid, 2 M) and turned yellow from purple, with gas evolution. Hydrogen was identified by GC in 70% yield on the basis of "Cp_2Zr".

C. Preparation of "Zirconocene" 12 and Reaction with PMe_2Ph. A solution of Cp_2ZrCl_2 (0.77 g, 2.6 mmol) in THF (50 mL) was stirred vigorously at room temperature with 2% sodium amalgam (15 g, 14 mmol of sodium, 5 equiv). The solution immediately turned brown, and after 6 h, it was dark red-brown and homogeneous. No hydrogen

Table II. Hydrogen Evolved in the Reaction of **12** with PMe_2Ph

time			amt of hydrogen, mmol
h	*min*	$H_2:N_2$[a]	
	0	0.1	0.02[b]
2	30	0.5	0.08
3	45	0.6	0.10
11	25	1.5	0.25
22	30	2.0	0.33
36	15	2.4	0.39
60	15	2.8	0.46

[a] Uncorrected. [b] Adventitious hydrolysis.

was detected by GC. After 22 h the solution was purple and homogeneous, and a trace of hydrogen had been formed. No Cp_2ZrCl_2 remained after 24 h, and only a broad resonance between δ 6.10–5.30 (referred to the α-CH_2 of THF as δ 3.58) was seen. The solution was decanted via cannula from the amalgam and passed through a filter into a Schlenk flask, where it remained at room temperature for 24 h. The total volume of the solution was 45 mL. An aliquot (20 mL) was degassed (three freeze–thaw cycles) and placed under argon. Nitrogen (2.05 mmol) and PMe_2Ph (0.5 mL, 3.5 mmol) were added. The atmosphere was immediately sampled to account for hydrolysis, and the mixture was heated at 50–55 °C. The atmosphere was periodically sampled (Table II). After 60 h, the amount of hydrogen was constant, and was estimated as 0.46 mmol (77% on the basis of Cp_2ZrCl_2).

The solvent was evaporated and the crimson residue was extracted with benzene (15 mL). Some purple solid was insoluble. The red solution was concentrated, and **7a** (0.31 mmol, 50% on the basis of Cp_2ZrCl_2) was identified by ^1H NMR. The yield of hydrogen relative to **7a** was 150%.

Control Reaction: Hydrolysis. An aliquot (5 mL) of the THF *solution of "zirconocene"* **12** *was placed in a Schlenk flask under argon* and connected to a 10-mL gas buret. The solution was hydrolyzed (aqueous sulfuric acid, 2 M, 0.25 mL), and the solution turned yellow from purple with vigorous evolution of hydrogen (8.25 mL, 0.34 mmol, 117% on the basis of Zr).

IR Spectrum. An aliquot (ca. 20 mL) of this THF solution of "zirconocene" **12** was pumped down, and the purple residue was extracted with toluene (40 mL). Most of solid **12** was insoluble; it was filtered off and dried. IR (KBr, NaCl windows on die): 3100, 2970, 2860, 1440, 1250 (v br, m), 1070, 1015 (m), 795 (s), 740 (sh) cm^{-1}. The mull was air oxidized, and it rapidly turned yellow from purple. IR (Nujol mull): 1265, 1070, 1015 (m), 890, 795 (s), 730 (br sh, s) cm^{-1}.

Oxidation Reactions. A. Reaction with Hydrogen. A Fischer-Porter bottle was flushed thoroughly with hydrogen and charged with a toluene solution of **7a** (5 mL, concentration 20 mM) which contained 0.5 equiv of free PMe_2Ph. The solution was stirred under hydrogen (4 atm) for 24 h. No color change occurred. The solution was transferred via cannula to a Schlenk flask, and the solvent was removed. ^1H NMR showed no reaction had occurred.

B. Reaction with Hydrogen Chloride. A solution of **7a** in benzene-d_6 (concentration 30 mM) was placed in a 5-mm NMR tube under nitrogen and sealed with a serum cap. Small aliquots (ca. 0.5 mL) of gaseous hydrogen chloride were added via syringe to the sample which was cooled (0 °C) during the addition. After each aliquot was added, the mixture was warmed to room temperature and shaken vigorously, and a ^1H NMR was taken. The dark red solution lightened after each addition.

Cp_2ZrCl_2 [^1H NMR (benzene-d_6): δ 5.95] was the major product of the reaction (60% on the basis of Zr). The other major Cp-containing compound [^1H NMR (benzene-d_6): δ 6.10] was formed in 20% yield but was not unequivocally identified. Dimethylphenylphosphine (80% on the basis of Zr) was produced; oxidation of free PMe_2Ph did not occur at a substantial rate while **7a** remained.

C. Reaction with Oxygen. Oxygen (0.15 mmol, 1 equiv) was introduced into a degassed solution of **7b** (0.13 g, 0.15 mmol) in toluene (10 mL) at −78 °C. The mixture was stirred, and occasional shaking produced a white solid on the walls of the vessel. After 40 min, the dark red solution was warmed to 0 °C. It slowly lightened, precipitating a solid. After 2 h it was pale orange, and it was warmed to room temperature over several hours.

After 7 h, the solution was almost colorless and contained a yellow precipitate. The reactor was attached to the Toepler pump. No noncondensible gases were collected.

The mixture was filtered, and the pale yellow solid (60 mg) was washed with hexane and dried. It was insoluble in benzene, toluene, acetone, THF, and methylene chloride but appeared to react slowly with dimethyl sulfoxide.

IR (KBr): 3090, 2960, 2920, 1495, 1440, 1370, 1265, 1070 (sh), 1015 (m), 895, 800 (s), 740 (m), 660 (m) cm^{-1}.

The insoluble residue was suspended in acetone, and a solution of tetra-*n*-butylammonium iodide in acetone was added. No iodine was visible after 1 h. (The corresponding reaction with *m*-chloroperbenzoic acid was instantaneous.) The solid slowly dissolved and the acetone darkened. After 12 h the solution was homogeneous and dark red-brown, suggesting that iodine had formed.

The filtrate from the initial reaction was evaporated to a brown oil, which was taken up in benzene-d_6. ^1H NMR showed $PMePh_2$ *in quantitative yield (DME internal standard).*

D. Reaction with Iodine. (a) A solution of iodine (39 mg, 0.15 mL) in toluene (5 mL) was added dropwise over 30 min to a rapidly stirred solution of **7b** (0.13 g, 0.15 mmol) in toluene (30 mL) at −78 °C. The dark red solution was warmed to −50 °C, and it turned green-yellow in 5 min. Upon warming above −50 °C, the solution rapidly turned red, and within 5 min it was dark purple. The solvent was removed, leaving a purple residue, which was triturated with hexane, filtered off, washed with hexane, and dried. This compound, $[\{(\eta^5\text{-}C_5H_5)(C_5H_4)ZrI\}_n]$ (**21**), was contaminated with Cp_2ZrI_2 (5%) [^1H NMR (benzene-d_6): δ 6.0].

^1H NMR (90 MHz) (benzene-d_6): δ 5.61 (s, 5, Cp), 4.58 (t, 2, J_{obsd} = 2.8 Hz), 4.16 (t, 2, J_{obsd} = 2.8 Hz).

^{13}C NMR (benzene-d_6): δ 102.2 (d*, $^1J_{CH}$ = 173 Hz), 101.4 (d*, η^5-Cp, $^1J_{CH}$ = 173 Hz), 98.6 (d*, $^1J_{CH}$ = 173 Hz); asterisks indicate doublets of poorly resolved multiplets.

An attempt to obtain a mass spectrum was unsuccessful (probe; 100–150 °C).

(b) Here we discuss the observation of an intermediate compound **22** in the iodination of **7b**. A solution of **7b** (30 mg, 0.04 mmol) in toluene-d_8 (2 mL) was placed in a reaction flask to which a 10-mm NMR tube was connected. Iodine (40 mg, 0.16 mmol) was dissolved in toluene-d_8 (1 mL). The reaction tube was cooled (−78 °C), and the iodine solution (0.25 mL, ca. 1.2 equiv) was slowly dripped into the stirred solution of **7b**. The reaction tube was then warmed to −50 °C and the reaction mixture was red-brown. The NMR tube and connecting bend were cooled to −78 °C, and the reaction mixture was tipped into the NMR tube. The tube was cooled (−196 °C) and sealed under vacuum.

The sample was warmed to −78 °C, and the small amount of solid which had formed was centrifuged (at −78 °C) to the sealed end of *the tube.* ^1H NMR *spectra of the sparingly soluble material were* recorded at −50 °C.

^1H NMR (100 MHz) (toluene-d_8, −50 °C): δ 7.4–6.9 (br, Ph), 6.8 (br, 32), 6.6 (br, 35), 5.8 (s, 265), 5.6 (s, 51), 5.4 (br, 30), 4.5 (br, 18), 4.1 (br, 18), 4.0 (br, 35), 1.32 (d, PMe, $^2J_{PH}$ = 5 Hz) (integrations rather than intensities reported).

When this sample was warmed above −50 °C, the resonances at δ 6.8, 6.6, 5.8, 5.4, and 4.0 disappeared, and only those from **21** remained.

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