could dictate gross changes in the polarization ratios while producing only small changes in the state energies. Our basic description based on trigonal symmetry with a substantial amount of spin–orbit coupling included in the core Hamiltonian may only be adequate to rationalize properties related to energy. A definitive answer to the question of the electronic symmetry awaits the measurement of more indicators, particularly polarization ratios, on more molecules with subtle, progressive changes in symmetry.

Preparation of Zirconium(II) Complexes by Ligand-Induced Reductive Elimination. Bis(η^5-cyclopentadienyl)bis(phosphine)zirconium(II) Complexes and Their Reactions

Kerrie I. Gell and Jeffrey Schwartz*

Contribution from the Department of Chemistry, Princeton University, Princeton, New Jersey 08544. *Received August 14, 1980*

Abstract: Bis(η^5-cyclopentadienyl)bis(phosphine)zirconium(II) complexes were prepared by ligand-induced reductive elimination of alkane from bis(η^5-cyclopentadienyl)chloroalkylzirconium(IV) precursors. Reactions of these species with H_2, CO, other phosphines, acetylenes, olefins, arenes, and organic halides are described.

The group 4 metallocenes are electron-deficient (14-electron) coordinatively unsaturated species which are kinetically and thermodynamically unstable to oxidation.[1] Two-electron reduction of the metallocene dichlorides with use of alkali metals or aromatic anions,[2] Grignard reagents,[3] or electrochemical methods[4] may initially yield a simple metallocene, but under the reaction conditions it deactivates by intermolecular insertions into activated C–H bonds, giving dimers, polymers, or species incorporating exogenous ligands.[5]

Intermolecular, and ultimately irreversible, deactivation of titanocene is suppressed in permethylated cyclopentadienyl derivatives which undergo *reversible* intramolecular C–H insertion and react preferentially with most substrates from the low-valent Ti(II) tautomer.[5b,6] With the use of this system, the role of reduced Ti in molecular nitrogen fixation has been clearly defined, and extensions of this work have shown that the chemistry of low-valent Zr is equally interesting.[7]

Apart from the results of these investigations, the chemistry of low-valent Zr is poorly understood. The lack of readily accessible low-valent Zr compounds restricts the range of available synthetic transformations to manipulation of ligands on a Zr(IV) d^0 center.[1] Catalytic cycles employing lower oxidation states of Zr or the synthesis of new Zr compounds by the oxidative processes commonly used for other transition-metal complexes are rare. A practical example of this limitation is that Zr(IV) alkyl and alkenyl compounds, which are useful intermediates in organic synthesis,[8] are accessible only by hydrozirconation or by alkylation of Zr(IV) compounds with a suitable main-group organometallic.[1,8]

Kinetic stabilization of low-valent Zr can be achieved in electronically saturated (18-electron) complexes of π-acceptor ligands, as recent syntheses of bis(η^6-arene)$(PMe_3)Zr^0$ (ref 9), $(\eta^5\text{-}C_6H_8)(dmpe)_2(H)Zr^{II}$ (ref 10), and bis(η^4-C_4H_6)(dmpe)-$(PMe_3)Zr^0$ (ref 10) have demonstrated.[7] The simple metallocene derivative $Cp_2Zr(CO)_2$ has been prepared by reduction of Cp_2ZrCl_2 under carbon monoxide,[11] but this complex is remarkably unreactive.[11c]

We have found that certain donor ligands induce reductive elimination of alkane from alkylbis(η^5-cyclopentadienyl)hydrozirconium(IV) complexes.[12] With use of tertiary phosphines in this reaction, bis(η^5-cyclopentadienyl)bis(phosphine)zirconium(II) complexes are produced in high yield with alkane as the only byproduct. This synthetic method may be successful because it avoids direct generation of the 14-electron metallocene, Cp_2Zr. A preliminary account of this work has appeared,[12c] and we now report details for the preparation of these Zr(II) bis(phosphine) complexes and some of their simple synthetic applications, which demonstrate their utility as highly reactive functional equivalents of monomeric "zirconocene".

Results and Discussion

Preparation and Characterization of Zr(II) Bis(phosphine) Complexes. (Cyclohexylmethyl)bis(η^5-cyclopentadienyl)hydrozirconium(IV) (**1a**) reacts rapidly with tertiary phosphines to

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

(2) (a) Watt, G. W.; Braye, L. J.; Drummond, F. O., Jr. *J. Am. Chem. Soc.* **1966**, *88*, 1138. (b) Watt, G. W.; Drummond, F. O., Jr. *Ibid.* **1966**, *88*, 5926. (c) Salzmann, J.; Mosimann, P. *Helv. Chim. Acta* **1967**, *50*, 1831. (d) Watt, G. W.; Drummond, F. O., Jr. *J. Am. Chem. Soc.* **1970**, *92*, 826. (e) Pez, G. P. *Ibid.* **1976**, *98*, 8072.

(3) (a) Shikatu, K.; Nishino, K.; Azuma, K.; Takegami, Y. *Kogyo Kagaku Zasshi* **1965**, *68*, 358. (b) Vol'pin, M. E.; Shur, V. B. *Nature (London)* **1966**, *209*, 1236.

(4) Dessy, R. E.; King, R. B.; Waldrop, M. *J. Am. Chem. Soc.* **1966**, *88*, 5112.

(5) (a) Brintzinger, H. H.; Bercaw, J. E. *J. Am. Chem. Soc.* **1970**, *92*, 6182. (b) Bercaw, J. E.; Marvich, R. H.; Bell, L. G.; Brintzinger, H. H. *Ibid.* **1972**, *94*, 1219.

(6) (a) Bercaw, J. E.; Brintzinger, H. H. *J. Am. Chem. Soc.* **1971**, *93*, 2045. (b) Bercaw, J. E. *Ibid.* **1974**, *96*, 5087.

(7) (a) Manriquez, J. M.; Bercaw, J. E. *J. Am. Chem. Soc.* **1974**, *96*, 6229. (b) Manriquez, J. M.; McAlister, D. R.; Sanner, R. D.; Bercaw, J. E. *Ibid.* **1976**, *98*, 6733. (c) Manriquez, J. M.; McAlister, D. r.; Sanner, R. D.; Bercaw, J. E. *Ibid.* **1978**, *100*, 2716.

(8) (a) Schwartz, J. In "New Applications of Organometallic Reagents in Organic Synthesis"; Seyferth, D., Ed.; Elsevier: Amsterdam, 1976. (b) Carr, D. B.; Schwartz, J. *J. Am. Chem. Soc.* **1979**, *101*, 3521. (c) Loots, M. J.; Schwartz, J. *Ibid.* **1977**, *99*, 8045.

(9) Cloke, F. G. N.; Green, M. L. H. *J. Chem. Soc., Chem. Commun.* **1979**, 127.

(10) For examples, see: Fischer, M. B.; James, E. J.; McNeese, T. J.; Nyburg, S. C.; Posin, B.; Wong-Ng, W.; Wreford, S. S. *J. Am. Chem. Soc.* **1980**, *102*, 4941.

(11) (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. (d) Fachinetti, G.; Fochi, G.; Floriani, C. *J. Chem. Soc., Chem. Commun.* **1976**, 230.

(12) (a) Yoshifuji, M.; Gell, K. I.; Schwartz, J. *J. Organomet Chem.* **1978**, *153*, C15. (b) Gell, K. I.; Schwartz, J. *Ibid.* **1978**, *162*, C11. (c) Gell, K. I.; Schwartz, J. *J.* Chem. *Soc., Chem Commun.* **1979**, 244.

0002-7863/81/1503-2687$01.25/0

produce methylcyclohexane (80–90%) and high yields of bis(η^5-cyclopentadienyl)bis(phosphine)zirconium(II) complexes (Cp_2ZrL_2) **2** (reaction 1). An alternative synthesis of **2c** is by

$$\underset{\textbf{1a,b}}{Cp_2Zr(R)X} + 2L \rightarrow \underset{\textbf{2a–d}}{Cp_2ZrL_2} + \text{methylcyclohexane} \quad (1)$$

1a, R = $CH_2(CH_2)_4CHCH_2$-, X = H
1b, R = $CH_2(CH_2)_4CDCH_2$-, X = D

2a, L = $PMePh_2$
2b, L = PMe_2Ph
2c, L_2 = dmpe
2d, L_2 = dppe

sodium amalgam reduction of Cp_2ZrCl_2 in a toluene solution of dmpe, but the analogous reaction fails for the complexes **2a,b** which have monophosphine ligands.

These Zr(II) bis(phosphine) complexes have been characterized by their spectral properties and are proposed to have a simple bent sandwich structure. The Bis(tertiary phosphine) complex, Cp_2Zr(dmpe) **2c** is a thermally stable, air- and moisture-sensitive black-green crystalline material. Its mass spectrum shows a molecular ion and successive fragmentation of the dmpe ligand to a base peak at *m/e* 220, corresponding to the metallocene fragment, Cp_2Zr. There is no NMR or IR spectral evidence for a hydride ligand which could have arisen by metallation of the dmpe ligand.[13]

In the ^1H NMR the Cp ligand resonance (δ 4.80), a triplet ($^3J_{PH}$ = 1.6 Hz)[14] from coupling to two equivalent phosphorus ligands, is shifted upfield by more than 1 ppm from its position in Zr(IV) complexes.[1,8b,15] The complex ^1H NMR pattern for the dmpe ligand (spin system $AA'X_6X'_6Y_6Y'_6$) resembles that in other compounds which have one chelating dmpe ligand.[16] The ^{31}P resonance (δ 60.9) is broad ($\nu_{1/2}$ = 29 Hz); coupling of the phosphorus nuclei to the protons of the Cp ligands prevents determination of the phosphorus–phosphorus coupling constant ($J_{XX'}$). Proton irradiation collapses the phosphorus signal to a sharp singlet ($\nu_{1/2}$ = 7.8 Hz), and, conversely, irradiation at this phosphorus collapses the signals in the ^1H NMR as required by the spectral assignments.

The $^{13}C\{^1H\}$ NMR supports the conclusions from the ^1H and ^{31}P NMR. The Cp ligands (δ 88, no detectable ^{13}C–^{31}P coupling[17]) are strongly shielded compared with Cp groups bound to Zr(IV)[15,18] which resonate downfield of δ 100. The methyl and methylene carbons of the dmpe ligand each belong to an AXY spin system and give rise to apparent triplets.[19]

The complexes **2a,b** of monophosphines are nonisolable, as they decompose in the absence of external phosphine ligands. The spectral properties of these complexexes and of **2c** are analogous, suggesting similar structures. They show the characteristic triplet ($^3J_{PH}$ = 1.6 Hz) for the Cp ligand in the ^1H NMR, and their phosphine methyl groups form part of an $AA'X_nX'_n$ (for **2a**, *n* = 3; **2b**, *n* = 6) spin system, with intermediate ^{31}P–^{31}P ($^2J_{AA'}$) coupling.[20]

In practice, **2a** and **2b** are prepared in an aromatic solvent or cyclohexane and used in situ for subsequent reactions. The crude reaction mixture contains only the desired compound **2**, methylcyclohexane, an inert byproduct, and a suitable excess of free phosphine. In fact, these complexes are produced in good yield only if **1a** is treated with an excess of the appropriate phosphine.

Table I. Composition (%) of the Mixture of Deuterated Methylcyclohexanes Produced in the Reaction of **1b** with Tertiary Phosphines

phosphine (L)	equiv	solvent	[1b], mM	% composition d_1	$d_1{}^0$	$d_1{}'$	d_2
$PMePh_2$	4.7	toluene	50	1	4	19	74
$PMePh_2$	4.7	cyclohexane	50[b]	6	(d_1 = 14)		80
$PMePh_2$	2.5	toluene	50	3	4	26	67

[a] 1-(Z'-Methyl)-1-Z-cyclohexane: d_0, Z = Z' = H; $d_1{}^0$, Z = H, Z' = D; $d_1{}'$, Z = D, Z' = H; d_2, Z = Z' = D. The estimated accuracy of these determinations is 5%.[15] [b] Suspension of **1b** (50 mmol mL^{-1}) in cyclohexane. [c] $d_1 = d_1{}^0 + d_1{}'$; interference in the mass spectrum from the solvent parent peak with the (P – Me) peaks of methylcyclohexane prevented determination of $d_1{}^0$ and $d_1{}'$.

Polymeric material, arising partly from rapid secondary reactions of **2** with **1a**, contaminates the product if a stoichiometric amount of phosphine is used. Furthermore, the phosphine ligands of **2a** and **2b** are in equilibrium with free phosphine. Several equivalents of free phosphine are necessary to stabilize the complexes by retarding their decomposition to dimeric Zr(III) complexes **3** (see below) and "zirconocene" polymers.

Mechanistic Investigation. In a previous study[15] we observed that **1** decomposes over several days at room temperature to methylcyclohexane and polymeric "zirconocenes". In the decomposition of **1b** the complex mixture of deuterated methylcyclohexanes which forms has incorporated protons from the Cp ligands. In contrast, treatment of **1b** with a tertiary phosphine gives **2** and methylcyclohexane which is largely methylcyclohexane-*1*,α-d_2 (Table I). The rate of methylcyclohexane formation is approximately 10^3 times faster than that in the autodecomposition of **1b**.[15] This rate of acceleration and the specific labeling pattern of the methylcyclohexane demonstrate that **2** is the product of a simple C–H reductive elimination.[21] The small amount of (<20%) of proton which is incorporated in the methylcyclohexane produced from phosphine treatment of **1b** originates from the Cp ligands and not from the solvent. When **1a** is treated with $PMePh_2$ in toluene-d_8, the methylcyclohexane product is undeuterated. In addition, the reaction of **1b** with phosphine in an inert solvent such as cyclohexane gives only a slightly higher percentage of methylcyclohexane-*1*,α-d_2 than does the corresponding reaction in toluene.

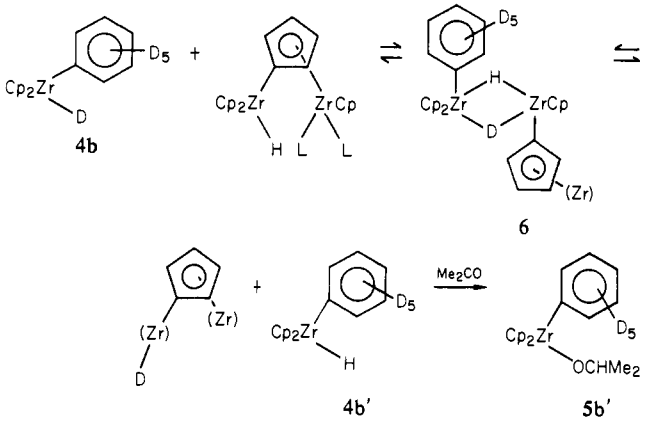
A probable mechanism by which label from the Cp ligands is incorporated into the methylcyclohexane is analogous to that suggested in Scheme I. The Zr(II) product of reductive elimination inserts into the C–H bonds of Cp ligands (see below), generating Zr hydrides. Exchange with deuterides on unreacted **1b** gives new Zr(IV) alkyl hydrides which react with phosphine to produce methylcyclohexane-*1*-d_1 ($d_1{}'$ isomer, Table I). Other experimental evidence supports this exchange mechanism. Larger amounts of phosphine increase the specificity of labeling in the methylcyclohexane, probably by increasing the rate of disappearance of **1** and by reducing the concentration of the active species in C–H insertions (see below). We have observed[12] that other donor ligands promote reductive elimination from **1**. With use of acetylenes,[12a] this reaction is slower than that for phosphines, and unless the acetylene is present in large excess, a significant amount of label scrambling is observed in the methylcyclohexane product.

Insertions into sp^2 Hybridized C–H Bonds. Whereas complexes **2c** or **2d** are stable at 60 °C for 24 h, solutions of **2a** and **2b** evolve hydrogen over several days, and dimeric Zr(III) complexes **3** are produced (reaction 2). The structure of these dimers has been

$$\underset{\textbf{2a}, L = PMePh_2;\ \textbf{2b}, L = PMe_2Ph}{Cp_2ZrL_2} \rightarrow 0.5[((\eta^5\text{-}C_5H_5)(\mu\text{-}[\eta^1\text{:}\eta^5\text{-}C_5H_4])ZrL)_2] + \underset{\textbf{3}}{} \quad 0.5H_2 \quad (2)$$

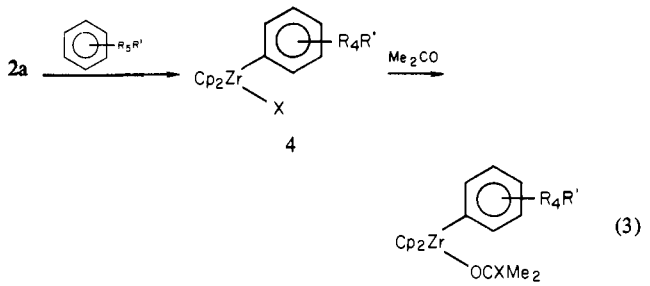
(13) (a) Chatt, J.; Davidson, J. M. *J. Chem. Soc. A* **1965**, 843. (b) Cotton, F. A.; Frenz, B. A.; Hunter, D. L. *J. Chem. Soc., Chem. Commun.* **1974**, 755.
(14) This coupling constant is typical for bent sandwich Cp_2MX_2 complexes; for example: (a) Benfield, F. W. S.; Green, M. L. H. *J. Chem. Soc., Dalton Trans* **1974**, 1324. (b) Lucas, C. R. *Inorg. Synth.* **1976**, *16*, 107.
(15) Gell, K. I.; Schwartz, J. *J. Am. Chem. Soc.* **1978**, *100*, 3246.
(16) Akhtar, M.; Ellis, P. D.; MacDiarmid, A. G.; Odom, J. D. *Inorg. Chem.* **1972**, *11*, 2917.
(17) The phosphine complex **3a** also shows no detectable coupling ($^2J_{PC}$) of the phosphorus ligand to the carbons of the Cp ligand: Haris, T. V.; Gell, K. I.; Schwartz, J. *Inorg. Chem.* **1981**, *20*, 481.
(18) Chisholm, M. H.; Godleski, S. *Prog. Inorg. Chem.* **1976**, *20*, 299.
(19) Because of the ^{13}C isotope effect on the chemical shift of the adjacent ^{31}P, this spin system is not AXX' but is more correctly defined as AXY.[16]
(20) (a) Harris, R. K. *Can. J. Chem.* **1964**, *42*, 2275. (b) Finer, E. G.; Harris, R. K. *Prog. Nucl. Magn. Reson. Spectros.* **1971**, *6*, 1.
(21) (a) Braterman, P. S.; Cross, R. J. *Chem. Soc. Rev.* **1973**, *2*, 271. (b) Abis, L.; Sen, A.; Halpern, J. *J. Am. Chem. Soc.* **1978** *100*, 2915. (c) Norton, J. R.. *Acc. Chem. Res.* **1979**, *12*, 139.

Scheme I



discussed;[17] the presence of η^1:η^5-C_5H_4 bridging ligands was established conclusively from spectral data. The dimer **3** must form by successive insertions of Zr(II) into the C–H bonds of Cp ligands, followed by reductive elimination of hydrogen.[17]

The insertion of Zr(II) into an sp^2 C–H bond of an η^5-C_5H_5 ligand, which produces the bridging arrangement in **3**, is a specific example of a more general reaction. Zirconium(IV) aryl hydride complexes **4**, although not directly observable by ^{1}H NMR, are detected in solutions of **2a** in aromatic solvents, by a trapping reaction with acetone.[22] If **2a** is stirred in benzene or toluene containing several equivalents of acetone, Zr(IV) aryl isopropoxide complexes **5** are formed in high yield (70–80%) (reaction 3).

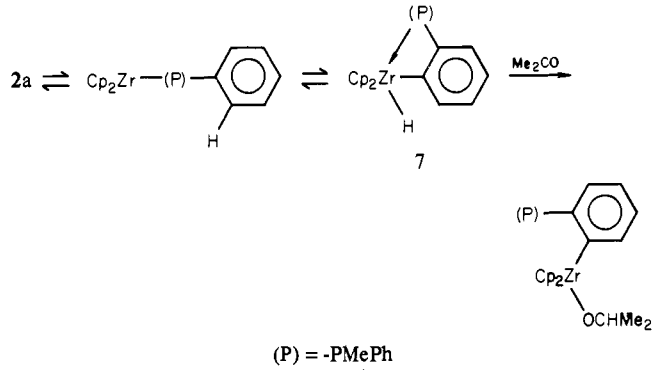


(3)

5a, R = R′ = X = H
5b, R = R′ = D; X = D
5b′, R = R′ = D; X = H
5c, R = H, R′ = Me; X = H
5d, R = D, R′ = CD_3; X = D
5d′, R = D, R′ = CD_3; X = H

Labeling experiments show that the Zr(IV) aryl hydrides are formed by insertion of Zr(II) into a C–H bond of the arene solvent. In benzene-d_6 the product **5b** contains deuterium (80%) at the α-carbon of the isopropoxy ligand. In toluene-d_8 the deuterium incorporation at this position is somewhat lower (ca. 60%), and the cyclopentadiene formed on hydrolysis (aqueous sulfuric acid) of this crude reaction mixture contains some (ca. 5%) deuterium.[23] The proton which is observed at the hydride position of the insertion product (**4b′**,**d′**) from these reactions with deuterated solvents originates from the Cp ligands. One possible mechanism which accomplishes exchange with these ligands is shown in Scheme I and is likely to proceed through the mixed bridged species **6**. The product from the reaction of **2a** with toluene-d_8 is a mixture of meta (74%) and para (26%) isomers (**5d**,**d′**), and no attack on the methyl group of toluene is observed. Approximately equal amounts of meta and para attack (1.3:1) indicate a nonselective insertion which may be primarily determined by steric factors.[24] The same major product forms from solutions

Scheme II



(P) = -PMePh

of **2a** in mesitylene, cyclohexane, or methylcyclohexane containing acetone. Therefore, these solvents do not participate directly in the reaction; in particular, the methyl groups of mesitylene are inert to attack by **2a** under these conditions. Although this product has not been fully characterized, preliminary evidence suggests that the Cp ligands have reacted with acetone. In the ^{1}H NMR spectrum, the protons of the Cp ligands show an ABCD pattern which is consistent with a substituted η^5-Cp ligand and an unsymmetrically substituted Zr center.[25] Mass spectral data support this suggestion, as the major compound in the hydrolysates of these reaction mixtures has a base peak corresponding to 6,6-dimethylfulvene (*m/e* 106).

It is noteworthy that **2a** activates sp^2 C–H bonds in *inter*molecular processes,[26] but that *net intra*molecular metalation of a phosphine ligand, a more common reaction for low-valent metal complexes,[27] is not detected. A metallated species **7** (Scheme II) is probably present in these mixtures, but because it has an *intra*molecularly bound phosphorus nucleophile, its lifetime should be significantly shorter than that of **4**. For rapid reduction, acetone precoordination cis to the hydride ligand may be required; acetone may compete ineffectively *inter*molecularly with the *intra*molecular phosphorus nucleophile for a site on Zr(IV).[28]

Ligand Displacement and Oxidative Coupling Reactions. Displacement of phosphine from **2a** or **2b** by other donor ligands produces new Zr(II) complexes which in some cases oxidatively cyclize[29] to Zr(IV) compounds (Scheme III). The reactions with carbon monoxide and dppe give substitutionally inert complexes and thus perturb the equilibrium between coordinated and free $PMePh_2$ in solutions of **2a**. At room temperature over 4 h, carbon monoxide is absorbed by a solution of **2a** containing 2 equiv of $PMePh_2$ to give, at equilibrium, a mixture of $Cp_2Zr(CO)_2$[11] (40%) and $Cp_2Zr(CO)(PMePh_2)$ (ν_{CO} = 1840 cm^{-1}) (60%).[30] Because of the stability of the resulting chelate, dppe completely displaces $PMePh_2$ to produce **2d**.

The Zr(II) bis(phosphine) complexes are useful intermediates for the synthesis of Zr^{IV}–C bonds directly from unsaturated units, and cyclization of acetylenes and dienes by **2a** gives Zr(IV)

(22) Soluble Zr(IV) alkyl hydride complexes rapidly reduce unhindered ketones such as acetone, even at −30 °C.[15]

(23) Hydrolysis of $Cp_2Zr(R)X$ (R = alkyl or aryl) produces some cyclopentadiene; only under very acidic conditions (e.g., use of gaseous HCl) is cleavage of the Cp ligands prevented.

(24) This analysis assumes that the distribution of the Zr(IV) tolyl isopropoxides accurately reflects the distribution of the Zr(IV) tolyl hydrides; that is, that acetone traps the kinetic insertion products at equal rates.

(25) See, for example: (a) $[((\eta^5\text{-}C_5H_4Me)_2ZrCl)_2O]$: Samuel, E. *Bull. Soc. Chim. Fr.* **1966**, 3548. (b) $[(\eta^5\text{-}C_5H_4R)_2TaI(dialkylacetylene)]$: Labinger, J. A.; Schwartz, J.; Townsend, J. M. *J. Am. Chem. Soc.* **1974**, *96*, 4009. (c) $[(\eta^5\text{-}C_5H_4R)_2Nb(Cl)]_2O$: Broussier, R.; Normand, H.; Gautheron, B. *Tetrahedron Lett.* **1976**, 4077.

(26) For a review of *inter*molecular C–H insertion into sp^2 bonds, see: (a) Parshall, G. W. *Acc. Chem. Res.* **1975**, *8*, 113. For more recent examples, see: (b) Parshall, G. W. *Catalysis (London)* **1977**, *1*, 335. (c) Tolman, C. A.; Ittel, S. D.; English, A. D.; Jesson, J. P. *J. Am. Chem. Soc.* **1979**, *101*, 1742.

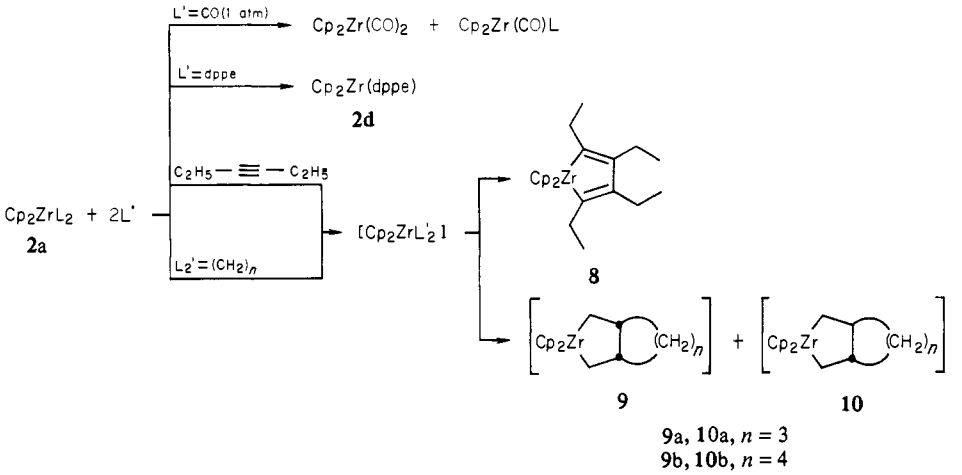
(27) Parshall, G. W. *Acc. Chem. Res.* **1970**, *3*, 139.

(28) (a) Wilkins, J. D. *J. Organomet. Chem.* **1974**, *80*, 357. (b) Labinger, J. A.; Komadina, K. H. *Ibid.* **1978**, *155*, C25.

(29) Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729.

(30) This is a low stretching frequency for a terminal monocarbonyl complex. An analogous compound, $Cp_2Zr(CO)(PMe_3)$, (ν_{CO} = 1852 cm^{-1}) has been prepared by refluxing $Cp_2Zr(CO)_2$ with PMe_3. The second carbon monoxide ligand could not be replaced under these conditions.[11c]

Scheme III[a]



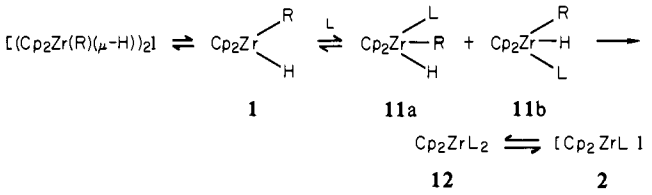
[a] L = $PMePh_2$.

metallacycles. 3-Hexyne reacts rapidly and quantitatively with **2a**, presumably by successive replacement of phosphine ligands, to give the zirconacyclopentadiene complex **8**.[12a] The η^2-acetylene complex assumed to be an intermediate in this reaction is not observed by ^1H NMR at room temperature.[31] There are no other reports of the oxidative cyclization of dialkylacetylenes by group 4 complexes. Activated acetylenes such as diphenylacetylene have been cyclized in trapping reactions for "Cp_2Zr"[32] or in a slow reaction with $Cp_2Zr(CO)_2$.[11c]

1,7-Octadiene is cleanly cyclized by **2a** to a mixture of *cis*- and *trans*-2-bis(η^5-cyclopentadienyl)zirconahydrindans (**9b** and **10b**) which on hydrolysis gives *cis*- and *trans*-1,2-dimethylcyclohexane in a 1:1 ratio. The metallacycles **9b** and **10b** were spectrally characterized but have not been isolated in analytically pure form; they appear to be stable at room temperature. The metallacycles **9** and **10** may be equilibrium with their bis(olefin) precursors. However, it is clear from the results on other hydrindane systems[33] that the stereochemistry of the hydrindan products does not indicate the reversibility of the cyclization. In this case, approximately equal amounts of cis and trans isomers could be the thermodynamic equilibrium mixture or the kinetic products of an indiscriminate cyclization. Although the synthesis of $(\eta^5\text{-}C_5Me_5)_2Zr(CH_2CH_2CH_2CH_2)$ from ethylene has been reported,[7c,34] the only existing method for the synthesis of zirconacyclopentanes with unsubstituted Cp ligands is from Cp_2ZrCl_2 and a 1,4-dilithiobutane or Grignard reagent, a method which has been used successfully for Ti(IV).[35]

Oxidation with Halogenated Compounds. The oxidation of Zr(II) bis(phosphine) complexes by halogenated compounds is a general reaction. Primary alkyl halides react readily with **2a** in toluene solution at room temperature, giving Zr(IV) alkyl halide

Scheme IV



complexes,[8] the products of an oxidative-elimination reaction[36] (reaction 4). For these substrates, a qualitative ordering of

$$Cp_2Zr(PMePh_2)_2 + RX \xrightarrow{-2PMePh_2} Cp_2Zr(R)X + Cp_2ZrX_2 + [PMePh_2R]^+X^- \quad (4)$$

R = Me; X = I, Cl, SO_3F
R = *n*-Bu; X = Cl
R = *t*-$BuCH_2CH_2$; X = Cl, Br

reactivity is RI > RBr > RCl.[37] Small amounts (<10%) of Zr(IV) dihalide complexes are formed in the reactions with methyl iodide and with 1-bromo-3,3-dimethylbutane. The reactive alkyl halides quaternize $PMePh_2$ but do so more slowly than they react with **2a**. A second-order rate constant of 4×10^{-3} M^{-1} s^{-1} (34 °C) is measured for the reaction of 1-chlorobutane with **2a** in benzene solution containing 2 equiv of $PMePh_2$. Approximate data indicate that these reactions are rapid compared with oxidative additions of alkyl halides to other low-valent metal centers.[38] Perhaps because of higher electron density on the metal or because of the lability of a phosphine ligand (see below), **2a** is considerably more reactive than the other group 4 complexes $Cp_2Zr(CO)_2$[39] and $Cp_2Ti(CO)_2$,[40] whose oxidations with alkyl halides have been reported. Secondary and tertiary alkyl halides,[41] acyl halides, and

(31) An intermediate mixed-ligand complex, $Cp_2Ti(\eta^2\text{-PhC}{\equiv}\text{CPh})(CO)$, has been isolated from the reaction of $Cp_2Ti(CO)_2$ with diphenylacetylene.[11d]

(32) Diphenylacetylene has been used to trap "Cp_2Zr" generated from Cp_2ZrCl_2 by reduction with NaNp[2d] or by photolysis of Cp_2ZrMe_2.[32a,b] 1,1-Bis(η^5-cyclopentadienyl)-2,3,4,5-tetraphenylzirconacyclopentadiene has also been prepared from 1,4-dilithio-1,2,3,4-tetraphenyl-1,3-butadiene and Cp_2ZrCl_2.[32c] (a) Alt, H.; Rausch, M. D. *J. Am. Chem. Soc.* **1974**, *96*, 5936. (b) Atwood, J. L.; Hunter, W. E.; Alt, H.; Rausch, M. D. *J. Am. Chem. Soc.* **1976**, *98*, 2454. (c) Braye, E. H.; Hübel, W.; Caplier, I. *Ibid.* **1961**, *83*, 4406.

(33) Several stereochemical preferences have been observed in other hydrindane systems in which reversible metallacycle formation has been demonstrated: (a) Grubbs, R. H.; Miyashita, A. *J. Am. Chem. Soc.* **1978**, *100*, 1300; (b) *Ibid.* **1978**, *100*, 7418. (c) McLain, S. J.; Wood, C. D.; Schrock, R. R. *Ibid.* **1979**, *101*, 4558.

(34) McAlister, D. R; Erwin, D. K.; Bercaw, J. E. *J. Am. Chem. Soc.* **1978**, *100*, 5966.

(35) Zirconacyclopentanes were formed in very low yields (<5%) in trapping reactions with the use of olefins in the LiNp reduction of Cp_2ZrCl_2. Titanocene was trapped, although inefficiently, by ethylene, but 1,7-octadiene gave none of the desired metallacycle. McDermott, J. X.; Wilson, M. E.; Whitesides, G. M. *J. Am. Chem. Soc.* **1976**, *98*, 6529.

(36) Oxidative elimination reactions $M^nX_xL_z + YY' \rightarrow [M^{n+2}X_xYY'L_{z-1}] + L$, involve a formal oxidation of the metal center with elimination of a "two-electron donor", L. The reaction with **2a**, in which two "two-electron donors" are eliminated, falls into this category. (a) Lewis, J.; Wild, S. B. *J. Chem. Soc. A* **1966**, 69. These reactions have also been termed replacement–addition reactions. (b) Green, M. L. H.; Mahtab, R. *J. Chem. Soc., Dalton Trans.* **1979**, 262.

(37) This reactivity series is found for S_N2, electron transfer or halogen abstraction pathways: Parshall, G. W.; Mrowca, J. J. *Adv. Organomet. Chem.* **1968**, *7*, 157.

(38) (a) The reaction rates are comparable to those observed for the "supernucleophiles" of Co(I) (cobaloxime, vitamin B_{12a})[38b] or the Rh(I) macrocyclic complex Rh(DO)(DOH)(pn) and its BF_2 derivatives.[38c,d] (b) Schrauzer, G. N.; Deutsch, E. *J. Am. Chem. Soc.* **1969**, *91*, 3341. (c) Collman, J. P.; Murphy, D. W.; Dolcetti, G. *Ibid.* **1973**, *95*, 2687. (d) Collman, J. P.; MacLaury, M. R. *Ibid.* **1974**, *96*, 3019.

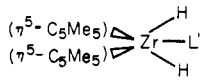
(39) $Cp_2Zr(CO)_2$ reacts with methyl iodide over 4 h at 70 °C, giving $Cp_2Zr(Me)I$.[11c]

(40) Fachinetti, G.; Floriani, C.; Stoeckli-Evans, H. *J. Chem. Soc., Dalton Trans.* **1977**, 2297.

aryl bromides react with **2a**, although not always to give the oxidative-elimination product. For example, at −78 °C, acetyl chloride rapidly oxidizes **2a** to Cp_2ZrCl_2 and neither $Cp_2Zr(COMe)Cl$ nor the corresponding decarbonylated material, $Cp_2Zr(Me)Cl$, is produced.[42] Quaternization of $PMePh_2$ by aryl bromides[43] is promoted by **2a** under mild conditions, which contrasts with those used in most phosphine arylation methods.[44]

General Discussion. Our results suggest that the Zr(IV) alkyl hydride complex **1** reacts with a tertiary phosphine to produce a species which readily undergoes C–H reductive elimination. This coordinatively unsaturated, 16-electron complex[45] **1** should be susceptible to attack by a Lewis base, in this case, a tertiary phosphine. The 18-electron Zr(IV) complexes, **11a** and **11b**, are predicted to be the kinetic products of phosphine attack at the lowest unoccupied molecular orbital of **1**,[29] and, significantly, each contains alkyl and hydride ligands in a cis orientation (Scheme IV).

We suggest that C–H reductive elimination occurs from these Zr(IV) complexes. Although there are numerous examples of coordinatively saturated Cp_2Zr^{IV} complexes,[46] electronically saturated complexes with three simple σ-donor ligands are thermodynamically unstable compared with 16-electron species.[47] The 18-electron adducts **13**, which have been observed below −50 °C, are the only examples of such complexes[7c] and are thought to be stabilized by some π donation from the Zr–H bonds to the acceptor ligand, L′.[48] Ligands which are better σ donors, but poorer π acceptors than CO or PF_3, fail to form spectroscopically detectable adducts. Thus **1** should be favored in the equilibrium with the 18-electron adducts **13**. We propose that an alternative,



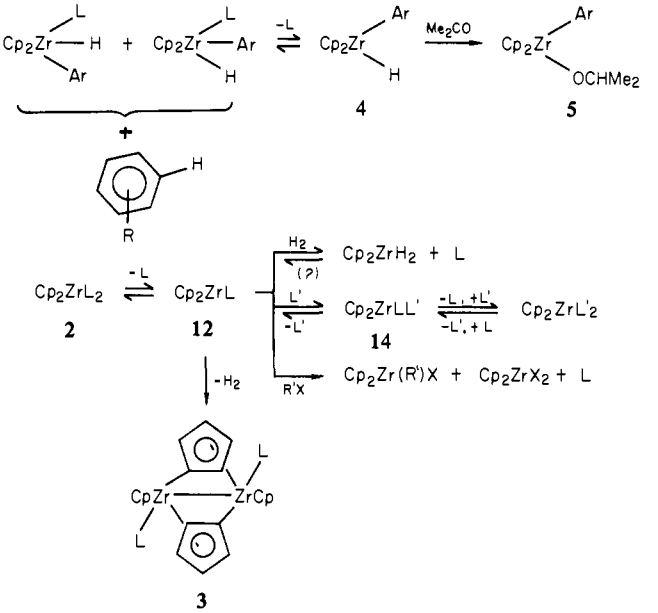
13a, L′ = CO[7c]
13b, L′ = PF_3

accessible reaction pathway for these intermediates is C–H reductive elimination. Irreversible formation of an sp^3 C–H bond drives the equilibrium between **1** and **11** and directly generates a 16-electron Zr(II) species **12** which coordinates another ligand to give the observed product **2**.

Although we have not made a complete study of the types of donor ligands which participate in this reaction, some general trends are clear. Bulky phosphines[49] ($P(c\text{-}Hx)_3$, PPh_3) do not promote methylcyclohexane formation, perhaps because of steric problems preventing their coordination to the relatively hindered molecule **1**. Although acetylenes[12a] and carbon monoxide[12b] promote reductive elimination,[50] pure σ donors (THF, Et_3N),[51] which should coordinate well to the Zr(IV) center in **1**, do not have a dramatic effect on the rate of decomposition of **1**. This suggests that reductive elimination from **11** is facilitated if the donor ligand L is a good ligand for the low-valent metal center. Thus the transition state leading to **12** may resemble the product, and stabilization of the developing Zr(II) center may be important in determining how the intermediate **13** partitions between **1** and **12**.

Most of the reactions (Scheme V) which we have observed for the Zr(II) bis(phosphine) complexes appear to procced through the 16-electron Zr(II) intermediate **12** supporting our suggestion that such a species is energetically accessible, at least from an 18-electron Zr(II) complex. This unsaturated intermediate is probably the active species in C–H bond insertions by **2**. It can be regarded as a group 4 member of a homologous series of low-valent early transition metallocene derivatives, including **15** and **16**, which have been proposed as intermediates in similar C–H bond activation reactions (Scheme VI)[26] and which decompose to give dimers which are structurally analogous to **3**.[55]

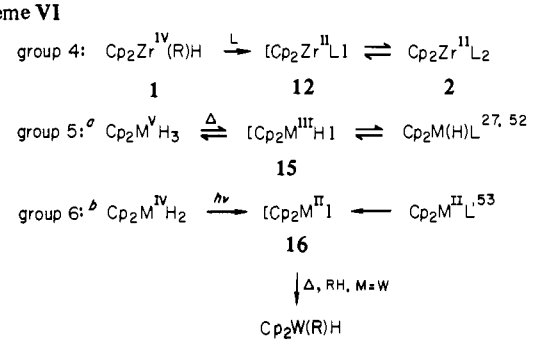
Scheme V[a]



3

[a] L = $PMePh_2$, PMe_2Ph; R = alkyl, aryl, acyl. L′ = L, CO; R′X = alkyl halide.

Scheme VI



[a] M = Ta, Nb. [b] M = Mo, W,[54] R = Me; R = R′CH=CHR′, R′ = EtOCO.

(41) Williams, G. M.; Gell, K. I.; Schwartz, J. *J. Am. Chem. Soc.* **1980**, *102*, 3660.
(42) Acetyl chloride addition to $Cp_2Ti(CO)_2$ gives $Cp_2Ti(COMe)Cl$, although a secondary reaction producing Cp_2TiCl_2 is reported.[40] It is important to note that the reaction $Cp_2Zr(Me)Cl + MeCOCl \rightarrow Me_2CO + Cp_2ZrCl_2$ is slow: Hart, D. W.; Schwartz, J. *J. Am. Chem. Soc.* **1974**, *96*, 8115 and reference 8b.
(43) Gell, K. I.; Schwartz, J., unpublished results.
(44) For a review of methods used to perform phosphine arylation, see: Beck, P. In "Organic Phosphorus Compounds"; Kosolapoff, G. M.; Maier, L., Eds.; Wiley: New York, 1972; Chapter 4.
(45) In solution a monomer–dimer equilibrium appears to be established.[15] the dimer is coordinatively saturated; we suggest that a donor ligand displaces this equilibrium by reacting preferentially with the unsaturated monomer.
(46) (a) Among examples of these complexes note: $Cp_2Zr(BH_4)X$, X = Cl, BH_4,[46b] H;[46c] Cp_2ZrH_2;[46c] $Cp_2Zr(C_3H_5)_2$.[46d] (b) Nanda, R. K.; Wallbridge, M. G. H. *Inorg. Chem.* **1964**, *3*, 1798. (c) James, B. D.; Nanda, R. K.; Wallbridge, M. G. H. *J. Chem. Soc., Chem. Commun.* **1966**, 849. (d) Martin, H. A.; Lemaire, P. J.; Jellinek, F. N. *J. Organomet. Chem.* **1968**, *14*, 149.
(47) Coates, G. E.; Green, M. L. H.; Powell, P.; Wade, K. "Principles of Organometallic Chemistry"; Methuen: London, 1968.
(48) These complexes likely are the thermodynamic products of L′ attack on $(\eta^5\text{-}C_5Me_5)_2ZrH_2$; the reversibility of CO attack has been demonstrated.[7c] π overlap, which apparently is necessary to stabilize these complexes, is maximized with L′ bound at the central orbital. Brintzinger, H. H. *J. Organomet. Chem.* **1979**, *171*, 337.
(49) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.
(50) Elimination of alkane is also promoted by hydrogen; we have suggested[15] that the mechanism of this reaction does not differ greatly from that proposed for two-electron donor ligands.
(51) Cotton, F. A. *Inorg. Chem.* **1964**, *3*, 702.
(52) Tebbe, F. N.; Parshall, G. W. *J. Am. Chem. Soc.* **1971**, *93*, 3793.
(53) Tang Wong, K. L.; Thomas, J. L.; Brintzinger, H. H. *J. Am. Chem. Soc.* **1974**, *96*, 3964.
(54) (a) Green, M. L. H. *Pure Appl. Chem.* **1978**, *50*, 27 and references therein. (b) Berry, M.; Davies, S. G.; Green, M. L. H. *J. Chem. Soc., Chem. Commun.* **1978**, 99.

In other reactions the intermediacy of a 16-electron Zr(II) species is also probable. The oxidation of **2** by alkyl halides shows an inverse phosphine dependence,[41] consistent with ligand dissociation prior to halogen abstraction. In ligand displacement, other donor ligands L′ can trap the 16-electron intermediate **12**, setting up new equilibria which includes the mixed-ligand species **14**, from which a second displacement leads to $Cp_2ZrL'_2$ (Scheme V).

In summary, we suggest that reductive elimination from **1** in the presence of a suitable donor ligand occurs from a relatively high-energy 18-electron Zr(IV) intermediate to give a 16-electron Zr(II) species,[56] which is an important intermediate in the reactions of **2**, and hence is a relatively stable entity. The generality of this reduction process is being examined to determine whether C–C and H–H[57] reductive elimination from Zr(IV) can be promoted in this way.

Experimental Section

General Procedures and Techniques. Reactions were performed under purified argon with use of standard Schlenk techniques[59] 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. Chloroform-d was washed with water and then dried and distilled under vacuum from phosphorus pentoxide. Methylene-d_2 chloride was distilled from calcium hydride.

Methyldiphenylphosphine and dimethylphenylphosphine (Strem Chemical Co.; Pressure Chemicals) were vacuum distilled from calcium hydride; 1,2-bis(dimethylphosphino)ethane (dmpe) (Strem) and 1,2-bis(diphenylphosphino)ethane (dppe) (Pressure) were used as received.

Acetone was dried over molecular sieves (3 Å) for 2 days prior to vacuum distillation; alkyl halides were vacuum distilled from phosphorus pentoxide or calcium hydride. Acetyl chloride was purified by a literature method.[60] Acetylenes and dienes were vacuum distilled from lithium aluminum hydride. Methyl chloride was transferred through a trap at −30 °C.

Dichlorobis(η^5-cyclopentadienyl)zirconium(IV) (Cp_2ZrCl_2) was obtained from Boulder Scientific. The preparation of chlorobis(η^5-cyclopentadienyl)hydridozirconium(IV) ($Cp_2Zr(H)Cl$),[8] (cyclohexylmethyl)-bis(η^5-cyclopentadienyl)hydridozirconium(IV) $Cp_2Zr(CH_2\overline{CH(CH_2)_4CH_2})H$, and the deuterated analogue $Cp_2Zr(CH_2\overline{CD(CH_2)_4CH_2})D$ have been described.[15] Sodium amalgam (2% sodium) was prepared by a literature method[61] and stored under nitrogen.

Celite was dried under vacuum at 200 °C for 24 h. Biobeads (SX-12; Bio-Rad), with a molecular weight exclusion limit of 400, were dried under vacuum at 100 °C and swelled with toluene in the drybox, where column chromatography was performed.

Proton (100 MHz), ^{13}C, and ^{31}P NMR spectra were recorded on a Varian XL-100 spectrometer. Dueterium-decoupled ^1H NMR (100 MHz) spectra were obtained with use of an ^{19}F internal lock on hexafluorobenzene (solvent) or from hexafluorobenzene contained in a capillary tube. Proton NMR (90 MHz) spectra were obtained on a Perkin-Elmer R32 instrument; 60-MHz proton spectra were measured on a Varian A-60 or A-60A spectrometer. Chemical shifts (^1H and ^{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.

Infrared (IR) spectra were obtained on a Perkin-Elmer PE-283 instrument; pellets were prepared in the drybox with use of KBr which has been dried at 120 °C for 24 h under high vacuum. Gas chromatography/mass spectra (GC/MS) analysis was performed on a DuPont 21-490 GC mass spectrometer. Gas chromatographic (GC) analysis for hydrogen was performed on a Perkin-Elmer PE-3920 thermal conductivity instrument with the use of argon as a carrier gas on Porapak QS, (20 ft × 0.125 in. column at 25 °C; for other GC analyses a Hewlett-Packard 402 flame ionization instrument was used. Unless otherwise stated, a Carbowax 20 M 20 ft × 0.25 in. column was used for GC and a Carbowax 20 M, 20 ft × 0.125 in. column for GC/MS analyses. Mass spectra were obtained on an AEI MS-9 instrument with use of a probe which was loaded in the drybox. Elemental analyses were performed by Alfred Bernhardt, West Germany, using drybox sampling techniques.

Preparation of Bis(η^5-cyclopentadienyl)bis(phosphine)zirconium(II) Complexes (2). 1. Complexes of Monotertiary Phosphines (2a,2b). These complexes were prepared in toluene, benzene, or cyclohexane solution and used immediately or stored for short periods (up to 2 days) at −30 °C under nitrogen. Representative procedures are given for the preparation of **2a**; **2b** is prepared in an analogous manner.

(a) Preparation of 2a in Toluene or Benzene. Methyldiphenylphosphine (0.35 mL, 1.9 mmol, 4.7 equiv) was added dropwise to a stirred solution of **1a** (0.13 g, 0.4 mmol) in toluene (7.5 mL) at −30 °C [for benzene reactions the solution was cooled to a slurry (5 °C)]. The solution was allowed to warm during the addition, and it rapidly became dark purple. Octane (37 μL, 0.23 mmol) and 1,2-dimethoxyethane (DME) (34 μL, 0.33 mmol) were added as internal standards. After 1 h and 15 min, an ^1H NMR spectrum showed **2a** (75%, DME standard); some polymeric material (broad ^1H NMR absorptions at ca. δ 6.0) contaminated some preparations.

At this point the solution could be used in subsequent reactions.

Analysis. A sample of the solution was hydrolyzed (aqueous sulfuric acid, 1 M), and the ratio of methylcyclohexane to octane was determined by GC (50 °C). The remainder of the solution was evaporatively distilled, and the distillate contained methylcyclohexane in 85% yield based on Zr (96% based on the methylcyclohexane to octane ratio in the hydrolysate).

(b) Preparation in Cyclohexane. A suspension of **1a** (0.13 g, 0.41 mmol) in cyclohexane (8 mL) containing octane (36 μL, 0.22 mmol) and DME (34 μL, 0.33 mmol) was stirred vigorously as $PMePh_2$ (0.35 mL, 1.9 mmol, 4.7 equiv) was added dropwise at room temperature over several minutes. The solution rapidly turned purple as **1a** dissolved. The complex **2a** was formed (72%, DME standard), and after 30 min, this solution could be used in subsequent reactions. Methylcyclohexane was formed in 90% yield (based on Zr; quantitative based on the hydrolysate).

The complexes **2a,b** were not isolated. Spectral characterization was achieved by direct analysis of the crude reactions with use of benzene-d_6 as the solvent. Resonances of free phosphine and methylcyclohexane are omitted in reporting spectral data.

For **2a**: ^1H NMR (100 MHz) (toluene-d_8, 0 °C) δ 7.6-6.9 (br, m, PPh), 4.86 (t, 10, Cp, $^3J_{PH}$ = 1.5 Hz), 1.22 (m, 6, PMe, 4.5 Hz) (spacing between the outer doublet = $^2J_{PH} + {}^4J_{PH}$) (complex $AA'X_3X'_3$ pattern); ^{31}P NMR (toluene-d_8) δ 60.9 ($\upsilon_{1/2}$ = 22 Hz).

For **2b**: ^1H NMR (benzene-d_6) 7.5–7.1 (br m, PPh), 4.82 (t, 10, Cp, $^3J_{PH}$ = 1.5 Hz), 1.32 (m, 12, PMe, 4.5 Hz) spacing between the outer doublet = $^2J_{PH} + {}^4J_{PH}$) (complex $AA'X_6X'_6$ pattern).

(c) Attempted Isolation of 2b. (i) A solution of **1a** (0.20 g, 0.63 mmol) in toluene (12 mL) contained in an H-filtration tube was cooled to −80 °C. After PMe_2Ph (0.23 mL, 1.6 mmol, 2.5 equiv) had been added, the mixture was thawed and stirred vigorously. It immediately turned pink, and in several minutes it was dark purple-brown. After 1.5 h at room temperature, the solution was frozen and the apparatus was pumped out. The solvent was distilled into the other leg of the H-tube, leaving a dark crimson oily residue which was flashed with toluene and pumped down. Benzene-d_6 (8 mL) was added, and the ^1H NMR spectrum showed **2b**, contaminated with **3b** (10 mol %) and PMe_2Ph (1 equiv). After 14 h at room temperature, the molar ratio of **2b**:**3b** was approximately 5:4.

(ii) $Cp_2Zr(CH_2\overline{CH(CH_2)_4CH_2})H$ (**1a**) (45 mg, 0.14 mmol) was dissolved in toluene-d_8 (1.38 g) containing DME (20 mg, 0.22 mmol). Methyldiphenylphosphine (40 μl, 0.2 mmol, 2 equiv) was added to 1 g of this solution (containing 0.10 mmol Zr) at 0 °C. After 20 h at 0 °C, **1a** had completely reacted but the yield of **2a** was only 50%. Free $PMePh_2$ (ca. 1 equiv) and polymeric "zirconocene" material were present. The remainder of the solution of **1a** was added. It reacted with **2a** rather than with $PMePh_2$ to produce more of the uncharacterized polymeric material.

(d) Reactions of $Cp_2Zr(CH_2\overline{CD(CH_2)_4CH_2})D$ (1b). The volatiles

(55) The group 5 complexes, presumably via **15**, catalyze H–D exchange between D_2 aromatic substrates,[26,52] whereas photolytically or thermally generated tungstenocene **16** irreversibly inserts into sp^2 arene C–H bonds and activated sp^3 C–H bonds.[54] The group 5 complexes, Cp_2MH_3 and $Cp_2M(L)H$ (M = Nb, Ta; L = PEt_3) decompose by a mechanism assumed to involve **15** to give a dimer (niobocene, tantalocene) analogous to **3**.[52] A similar dimer forms on prolonged photolysis of Cp_2MoH_2.[54b]

(56) Reductive elimination of alkane from $(\eta^5\text{-}C_5Me_5)_2Zr(Bu\text{-}i)H$ has recently been reported to be assisted by ethylene.[39] This result may be interpreted by using similar thermodynamic arguments.

(57) The reaction of **2a** with hydrogen gives only low yields of the simple oxidative-elimination product Cp_2ZrH_2. The inefficiency of this oxidation compared with that for other Zr(II) complexes[58] may be partly explained if hydrogenation of **2a** is reversible; phosphine could promote reductive elimination of hydrogen from the monomeric Zr(IV) dihydride.

(58) Bercaw, J. E. *Adv. Chem. Ser.* **1978**, *No. 167*, 136.

(59) Shriver, D. F. "The Manipulation of Air-Sensitive Compounds"; McGraw-Hill: New York, 1969.

(60) Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. "Purification of Laboratory Chemicals"; Pergamon Press: Oxford, 1966.

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

from reaction of **1b** with $PMePh_2$ or PMe_2Ph were examined by GC/MS (50 °C) for the deuterium content of the methylcyclohexane. The mass spectral results were analyzed,[15] and the composition of the deuterated methylcyclohexanes is reported in Table I.

(e) Reduction of Cp_2ZrCl_2 in the Presence of $PMePh_2$. A solution of $PMePh_2$ (2 mL, 10.7 mmol, 3.6 equiv) in toluene (60 mL was added at room temperature to a mixture of Cp_2ZrCl_2 (0.87 g, 2.97 mmol) and sodium amalgam (2% sodium, 26.3 g, tenfold excess). The solution immediately turned brown. After it had been stirred vigorously for 1 h, the red-brown solution was sampled for ^1H NMR analysis. Neither **2a** nor Cp_2ZrCl_2 was present. After 7.5 h the volume of the solution was reduced to 15 mL. A small amount of **3a** was detected by ^1H NMR.

2. Complexes of Bis(tertiary phosphines) (2c, 2d). (a) Reduction of Cp_2ZrCl_2 in the Presence of dmpe. Synthesis of Cp_2Zr(dmpe) (2c). A solution of dmpe (0.58 mL, 3.9 mmol) in toluene (60 mL) was added with stirring to a mixture of Cp_2ZrCl_2 (0.87 g, 2.97 mmol) and sodium amalgam (2% sodium, 26.3 g, tenfold excess). The solution rapidly darkened to red-brown. After 3.25 h, no Cp_2ZrCl_2 remained, and Cp_2Zr(dmpe) (**2c**) was the major compound present (by ^1H NMR).

The solution was decanted from the amalgam and filtered through Celite. The volatiles were removed under high vacuum, and the dark crystalline residue was triturated with hexane to remove residual dmpe. The black-green crystals (0.8 g, 75%) were collected by filtration, washed with cold hexane, dried, and stored under nitrogen. An analysis sample was obtained by recrystallization (twice) from toluene–octane. This compound can be sublimed (110 °C (0.005 torr)) but decomposes extensively to dark-red, nonvolatile insoluble products.

Anal. Calcd for $C_{12}H_{26}P_2Zr$: C, 51.72; H, 7.05; Zr, 24.55. Found: C, 51.41; H, 6.90; Zr, 24.79.

^1H NMR(100 MHz)(benzene-d_6) δ 4.80 (t, 10, Cp, $^3J_{PH}$ = 1.6 Hz), 0.95 (apparent t, 12, PMe, J = 2.5 Hz), 0.60 (m, 4, PCH_2, J = 14 Hz). The pattern for the dmpe ligand is complex: $AA'X_6X'_6Y_6Y'_6$; 2.5 Hz is the separation between the lines of the triplet, 14 Hz is the separation between the wings of the multiplet. $^1H\{^{31}P\}$ NMR(100 MHz)(benzene-d_6) δ 4.80 (s, Cp), 0.95 (s, PMe), 0.60 (br, PCH_2). ^{31}P NMR-(benzene-d_6) δ 60.9 (br s, $\nu_{1/2}$ = 29 Hz). $^{31}P\{^1H\}$ NMR(benzene-d_6) δ 60.9 (s, $\nu_{1/2}$ = 7.8 Hz). $^{13}C\{^1H\}$ NMR(benzene-d_6) δ 88.7 (s, Cp), 33.8 (apparent t, PCH_2, AXY, J_{CP} = 14 Hz), 18.9 (apparent t, BXY, PMe, J_{CP} = 6 Hz); $J_{CP} = {}^1/_2(J_{C_1P_1} + J_{C_1P_2})$.

IR(KBr, NaCl windows on die) 3080, 2940, 2885, 1415 (m), 1275 (m), 1260 (m), 1100 (s), 1005, 990 (m), 930 (s), 910, 890, 800 (s, br), 740, 710 (m), 680, 610 (m) cm^{-1}. Some decomposition occurs if the pellet is not protected from the air.

Mass spectrum(70 eV) m/e (intensity) 370 (M^+, 97), 355 (M – Me, 5), 281 ($Cp_2Zr(PMe_2)$, 62), 235 (Cp_2ZrMe, 14), 220 (Cp_2Zr, 100); the most intense peak [$^{12}C_n{}^1H_m{}^{31}P_x{}^{90}Zr$] in each multiplet is reported; no peaks to higher m/e.

(b) Reaction of Bis(tertiary phosphines) with 1a. dmpe (0.31 mL, 2.1 mmol) was added to a solution of **1a** (1.29 g, 4.1 mmol) in toluene (50 mL) at −78 °C. The solution was warmed slowly to 0 °C with stirring, and as the dmpe thawed, the solution turned brown. It was stirred at 0 °C for 2.5 h and then the reaction was complete. The dark brown solution was filtered at room temperature, and the volume was reduced to 5 mL. Addition of hexane caused precipitation of **2c** as a black microcrystalline compound (0.2 g, 50%). Column chromatography on Biobeads SX-12 (6 in. × 1.25 in.) with use of toluene as an eluant, separated black **2c** from a red polymer which passed rapidly through the column.

A similar reaction with use of dppe (2 equiv) at room temperature produced Cp_2Zr(dppe) (**2d**), but neither fractional crystallization nor chromatography on Biobeads SX-12 (toluene) separated it from excess dppe. With the use of only 1 equiv of dppe in this reaction, **2b** was contaminated with a considerable amount of polymeric material.

^1H NMR(benzene-d_6) δ 4.76 (t, 10, Cp, $^3J_{PH}$ = 1.5 Hz), 2.12 (apparent t, 4, PCH_2, J_{PH} = 4 Hz), phenyl groups of coordinated phosphine obscured by free dppe.

Insertions into sp^2 Hybridized C–H Bonds. (a) Toluene. Acetone (90 μL, 1.4 mmol, 4.5 equiv) was added to a solution of **2a** prepared from **1a** (0.1 g, 0.3 mmol) and $PMePh_2$ (0.23 mL, 1.2 mmol, 4 equiv) in toluene (5 mL). The purple solution was stirred at room temperature. It rapidly turned brown (3 h) and then golden, and after 7.5 h it was very pale orange. The solvent and a volatile yellow compound were removed under vacuum. The residue was taken up in benzene-d_6, and ^1H NMR spectra showed one major Cp-containing compound (74%, DME standard; a small amount of **3** was noted).

The solution was diluted to 10 mL with toluene, cooled (−30 °C), and methyl iodide (0.2 mL, 10 equiv) was added. After 12 h of stirring at room temperature, the precipitate of $(PMe_2Ph_2)^+I^-$ was filtered off, the filtrate was pumped down, and a ^1H NMR spectrum of the residue was taken. The product **5c** was attributed to a mixture of $Cp_2Zr(m$-$MeC_6H_4)(OPr$-$i)$ (72%) and $Cp_2Zr(p$-$MeC_6H_4)(OPr$-$i)$ (28%) based on ^1H NMR spectral data. The composition of this mixture was determined from the tolyl methyl signals; assignments were made by comparing isomer ratios with those determined in the reaction of **2a** with toluene-d_8 [see below (b)]. The identity of the product **5c** was confirmed by analysis (^1H NMR) of a hydrolyzed (aqueous sulfuric acid, 1 M) sample, which showed toluene and 2-propanol in a 1:1 ratio.

^1H NMR(benzene-d_6) δ 7.5–6.9 (complex m, 3, aromatics), 5.83 (s, 10, Cp), 4.11 (septet, 1, $OCHMe_2$, ^3J = 6.5 Hz), 2.45 (br s, m-MePhZr), 2.40 (br s, p-MePhZr), 1.05 (d, 6, $CHMe_2$, ^3J = 6.5 Hz). The resonances at δ 2.45 and 2.40 (ratio 2.6:1) integrated together as three protons.

Similar reactions (identical scale) were performed.

(b) Toluene-d_8. After the reaction mixture had been treated with methyl iodide and filtered, the volatiles were collected and analyzed by GC/MS (50 °C). Methylcyclohexane and acetone were identified and were undeuterated.

The inorganic residue, a mixture of Cp_2Zr(tolyl-d_7)($OCDMe_2$) (**5d**) (58%) and Cp_2Zr(tolyl-d_7)($OCHMe_2$) (**5d′**) (42%)[61] was dissolved in methylene-d_2 chloride and hydrolyzed (aqueous sulfuric acid, 1 M). The organic layer was dried ($MgSO_4$), filtered, evaporatively distilled, and analyzed by $^1H\{^2H\}$ NMR (100 MHz). By analysis of the aromatic region of the spectrum of toluene-d_8 (neat and in methylene-d_2 chloride), and comparison with a literature assignment, the resonances from the ortho, meta, and para protons were identified.[62] Toluene which had formed in the hydrolysis was a mixture of toluene-d_7(m-H) (74%) and toluene-d_7(p-H) (26%).[64] No proton incorporation into the methyl group of toluene-d_8 was detected by NMR.

The tolyl methyl resonances are therefore assignable in the reaction of **2a** with toluene: δ 2.45 (m-MePhZr), 2.40 (p-MePhZr). The cyclopentadiene formed in this hydrolysis was analyzed by GC/MS (40 °C): mass spectrum (78 eV), parent cluster: m/e (intensity) 67 (11.4), 66 (100), 65 (38.7).

Authentic cyclopentadiene: mass spectrum (78 eV), parent cluster: m/e (intensity) 67 (6), 66 (100), 65 (33).

(c) Benzene. Acetone (90 μL, 1.4 mmol, 4.5 equiv) was added to a solution of **2a**, prepared from **1a** (95 mg, 0.3 mmol) and $PMePh_2$ (0.21 mL, 1.1 mmol, 4 equiv) in benzene (5 mL). This mixture was stirred for 12 h, and it changed color from dark purple through orange to clear, pale yellow. At the conclusion of the reaction, the solvent was removed and the residue was redissolved in benzene-d_6 and analyzed by ^1H NMR. Methyldiphenylphosphine and Cp_2Zr(Ph)(OPr-i) (**5a**) (80%) were identified. The solution was treated with methyl iodide to remove $PMePh_2$, and **5a** was obtained as white crystals. Hydrolysis (aqueous sulfuric acid, 1 M) of a solution of **5a** in chloroform-d gave benzene and 2-propanol in a 1:1 ratio (GC identification, 70 °C).

^1H NMR(chloroform-d) δ 7.67–7.16 (m, 5, Ph), 6.22 (s, 10, Cp), 4.49 (septet, 1, OCHMe, ^3J = 6.5 Hz), 1.34 (d, 6, Me, ^3J = 6.5 Hz).

$^{13}C\{^1H\}$ NMR(chloroform-d) δ 183.0 (ZrC of Ph), 139.0 o-C of Ph), 126.3 (m-C of Ph), 124.0 (p-C of Ph), 111.0 (Cp), 74.7 (OCHMe), 26.5 (Me). (The assignments of ortho and meta resonances could be reversed.)

(d) Benzene-d_6. A solution of **2a** was prepared from **1a** (0.11 g, 0.34 mmol) and $PMePh_2$ (0.25 mL, 1.3 mmol, 4 equiv) in benzene-d_6 (5 mL). After 1 h the dark purple solution was halved. Acetone (90 μL, 1.4 mmol, 8 equiv) was added to half of this solution, and after 5 h the solution was pale yellow. The product was isolated as before and analyzed by ^1H NMR. It was a mixture of Cp_2Zr(Ph-d_5)($OCDMe_2$) (**5b**) (80%) and Cp_2Zr(Ph-d_5)($OCHMe_2$) (**5b′**) (20%).

After 7.5 h, an ^1H NMR spectrum was taken of a sample of the second half of the reaction mixture, which had been stirring at room temperature. It showed **2a** contaminated by **3a** (15%). Acetone (90 μL, 1.4 mmol, 8 equiv) was added, and after 5 h, this solution was halved. From half of the solution, **5b** (80%) and **5b′** (20%) were isolated.

After removal of the volatiles at room temperature from the other half of the reaction mixture, $PMePh_2$ was distilled off (70 °C, (0.5 torr)) and analyzed by mass spectrometry (MS-9). No deuterium incorporation in the $PMePh_2$ was observed (comparison with authentic sample).

Ligand Displacement and Oxidative Coupling Reactions. A solution of **2a** was prepared from **1a** (0.51 g, 1.6 mmol) and $PMePh_2$ (1.2 mL, 6.3 mmol, 4 equiv) in benzene (30 mL), containing DME (90 μL, 0.86

(62) The relative amount of **5d** and **5d′** was determined by integration of the methyl signal of the isopropoxy group. This signal is a triplet ($^3J_{HD} \simeq$ 1.5 Hz) in the deuterated compound and a doublet ($^3J_{HH}$ = 6.5 Hz) in the undeuterated compound.

(63) Bovey, F. A.; Hood, F. P., III; Pier, E.; Weaver, H. E. *J. Am. Chem. Soc.* **1965**, *87*, 2060.

(64) The nuclear Overhauser effect in $^1H\{^2H\}$ NMR spectra is small: Noggle, J. H.; Schirmer, R. E. "The Nuclear Overhauser Effect, Chemical Applications"; Academic Press: New York, 1971.

Table II. Carbon Monoxide Uptake by 2a in Benzene Solution

time, min	CO uptake, mmol	equiv of CO[a]
35	0.05	0.14
60	0.12	0.32
75	0.21	0.57
135	0.31	0.84
195	0.43	1.16
240	0.49	1.32
365	0.51	1.38

[a] Based on Zr.

mmol). Aliquots (7.5 mL, 0.37 mmol of Zr) of this solution were used in each of the following reactions.

(a) Carbon Monoxide. A Schlenk flask was connected to a gas buret (25 mL), and this system was filled with carbon monoxide. The benzene solution of **2a** was added via syringe, the buret was leveled, and the mixture was stirred. Carbon monoxide uptake was monitored (Table II) during the reaction. After 4 h the solution was brown-red, and the buret reading remained constant for the next 2 h.

The solution was sampled for ^{1}H NMR analysis, which showed only two Cp-containing products: $Cp_2Zr(CO)_2$ (**10**) (40%) and $Cp_2Zr(CO)(PMePh_2)$ (**11**) (60%) in 83% yield (based on Zr). For this product distribution the expected uptake of carbon monoxide was calculated as 10.5 mL. $Cp_2Zr(CO)_2$ was identified by spectral comparison with an authentic sample prepared by reduction of Cp_2ZrCl_2 with sodium amalgam under carbon monoxide.[11b] For $Cp_2Zr(CO)_2$: ^{1}H NMR(benzene) δ 4.92 (s, Cp); IR(benzene) ν_{CO} 1960, 1870 cm^{-1}. For $Cp_2Zr(CO)(PMePh_2)$: ^{1}H NMR (benzene) δ 4.90 (d, 10, Cp, $^3J_{PH}$ = 1.6 Hz), 1.59 (d, 3, PMe, $^2J_{PH}$ = 5.5 Hz); phenyl groups of the coordinated $PMePh_2$ were obscured by benzene; IR(benzene) ν_{CO} 1840 cm^{-1}.

(b) 3-Hexyne. 3-Hexyne (0.22 mL, 2 mmol, 5 equiv) was added to the benzene solution of **2a**. The mixture was stirred at room temperature, and it slowly turned red-brown from purple. After 12 h an ^{1}H NMR spectrum showed only one Cp-containing compound (90% DME standard). The solvent was removed, and the red-brown oil was redissolved in benzene-d_6. The product, which was contaminated by $PMePh_2$, was identified as 1,1-bis(η^5-cyclopentadienyl)-2,3,4,5-tetraethylzirconacyclopentadiene (**8**) by spectral comparison with an authentic sample.[64]

^{1}H NMR(benzene-d_6) δ 5.9 (s, 10, Cp), 2.3 (q, 4, CH_2Me, ^3J = 7.5 Hz), 2.2 (q, 4, CH_2Me, ^3J = 7.5 Hz), 1.0 (t, 6, CH_2Me, ^3J = 7.5 Hz), 0.9 (t, 6, CH_2Me, ^3J = 7.5 Hz). Assignments of the ethyl groups are not known; signals from $PMePh_2$ are omitted.

Hydrolysis (aqueous sulfuric acid, 1 M) of **8** gave (*E,E*)-4,5-diethyl-3,5-octadiene: GC/MS (78 eV) *m/e* 166, 151, 137, 123; ^{1}H NMR(benzene-d_6) δ 5.3 (t, 2, =CH, ^3J = 7 Hz), 2.1 (overlapping quartets, 8, CH_2Me, ^3J = 7 Hz), 0.95 (t, 6, CH_2Me, ^{3}J = 7 Hz), 0.90 (t, 6, CH_2Me, ^3J = 7 Hz).

(c) 1,7-Octadiene. 1,7-Octadiene (0.29 mL, 2 mmol, 5 equiv) was added to the benzene solution of **2a**, and the mixture was stirred at room temperature. In 4 h it was dark red. After 12 h the volatiles were removed and excess 1,7-octadiene was pumped off under high vacuum overnight. ^{1}H NMR(benzene-d_6) showed one major Cp compound (62%) and several minor compounds. The solvent was again removed, and the residue was redissolved in diethyl ether (2 mL) and hydrolyzed with aqueous sulfuric acid (0.5 mL, 2 M). The solution slowly lightened, and after 4 h it was colorless with a white precipitate. The volatiles were collected and analyzed by GC/MS (60 °C). The two major components were identified by mass spectral comparison (78 eV) with authentic samples as *trans*-1,2-dimethylcyclohexane (shorter GC retention time) and *cis*-1,2-dimethylcyclohexane (1:1 ratio, 60% combined yield based on Zr, methylcyclohexane internal standard).

Hydrogenation of 2a. A solution of **2a** (0.37 mmol) in benzene (7 mL) was sealed under hydrogen (2 atm). The tube was shaken occasionally, and over several days the dark purple solution turned crumson and a pale solid precipitated. After 4 days the solution was filtered. The white precipitate was washed with toluene and then resuspended in toluene (1 mL) and acetone (30 μL) was added. After 30 min the solution was homogeneous and the solvent was removed to leave a white crystalline compound, which was identified as $Cp_2Zr(OPr\text{-}i)_2$ (0.05 mmol, 12%, octamethyldisiloxane standard) by ^{1}H NMR (comparison with authentic sample).

^{1}H NMR(toluene-d_8) δ 6.0 (s, 10, Cp), 4.1 (septet, 2, $OCHMe_2$, ^3J = 6.5 Hz), 1.1 (d, 12, Me, ^3J = 6.5 Hz).

^{1}H NMR of the crimson filtrate showed **3a** in 25% yield (based on Zr, DME standard). Other Cp-containing products were not identified.

Oxidations with Alkyl Halides. (a) Methyl Chloride. Methyl chloride (2.9 mmol, 10 equiv) was condensed (through a trap at −30 °C) into a solution of **2a** prepared from **1a** (91 mg, 0.29 mmol) and $PMePh_2$ (0.21 mL, 1.14 mmol, 4 equiv) in toluene (9 mL). The purple solution was warmed to −78 °C and then to room temperature over 2 h. After 3 h the solution was still purple, but a precipitate was forming, and after 5 h it was brown-red with a heavy precipitate.

After 12 h the solution was filtered and the pale pink precipitate of $(PMe_2Ph_2)^+Cl^-$ (90 mg, 0.36 mmol, 120% based on Zr) was washed with toluene and dried. ^{1}H NMR(D_2O) δ 7.73 (br m, 10, Ph), 2.45 (d, 6, PMe, $^2J_{PH}$ = 14.5 Hz).

The filtrate was pumped down, and the dark red oil was taken up in benzene-d_6. $Cp_2Zr(Me)Cl$ (60%, octamethyldisiloxane internal standard), contaminated by $PMePh_2$, was identified by ^{1}H NMR comparison with an authentic sample prepared by reaction of $(Cp_2ZrCl)_2O$ with Me_3Al.[65] ^{1}H NMR (benzene-d_6) δ 5.76 (s, 10, Cp), 0.37 (s, 3, ZrMe).

(b) 1-Chlorobutane. A solution of **2a** prepared from **1a** (35 mg, 0.11 mmol) and $PMePh_2$ (80 μL, 0.44 mmol, 4 equiv) in toluene-d_8 (1.2 mL) was placed in an NMR tube (5 mm) under nitrogen and sealed with a serum cap. 1-Chlorobutane (56 μL, 0.55 mmol, 5 equiv) was added via syringe, and sequential ^{1}H NMR spectra were recorded at 34 °C.

time, min	% 2a	% $Cp_2Zr(n\text{-}C_4H_9)Cl$
0	100	0
7	56	44
15	16	84
40	00	100

Excess phosphine was removed by reaction with methyl iodide, and the sole product of the reaction, $Cp_2Zr(n\text{-}C_4H_9)Cl$, was identified by ^{1}H NMR comparison with an authentic sample prepared from $Cp_2Zr(H)Cl$ and 1-butene.[8] The identity of the product was confirmed by bromine cleavage of the Zr–C bond, which gave 1-bromobutane (^{1}H NMR identification). For $Cp_2Zr(n\text{-}C_4H_9)Cl$: ^{1}H NMR(benzene-$d_6$) δ 5.77 (s, 10, Cp), 1.70–0.80 (br m, 9, n-C_4H_9).

(c) 1-Chloro-3,3-dimethylbutane. 1-Chloro-3,3-dimethylbutane (0.35 mL, 2.5 mmol, 5 eqiv) was added to a cold solution (−78 °C) of **2a** prepared from **1a** (0.16 g, 0.51 mmol) and $PMePh_2$ (0.38 mL, 2 mmol, 4 equiv) in toluene (16 mL). the solution was warmed to room temperature and stirred for 8 h.

The solvent was removed from the dark red-brown, homogeneous solution, leaving a dark red oil. An ^{1}H NMR spectrum(benzene-d_6) showed $Cp_2Zr(CH_2CH_2Bu\text{-}t)Cl$ (65%) contaminated by $PMePh_2$. The red oil was redissolved in benzene (10 mL) and stirred with methyl iodide (0.12 mL, 2 mmol, 4 equiv) for 12 h, when $(PMe_2Ph_2)^+I^-$ (0.5 g, 1.4 mmol) was removed by filtration. Yellow crystalline $Cp_2Zr(CH_2CH_2Bu\text{-}t)Cl$ (40%) was obtained from the filtrate and identified by ^{1}H NMR comparison with an authentic sample prepared from $Cp_2Zr(H)Cl$ and 3,3-dimethyl-1-butene.[8b] ^{1}H NMR(benzene-d_6) δ 5.83 (s, 10, Cp), 1.44 (m, 2, $CH_2Bu\text{-}t$), 1.00 (m, 2, $ZrCH_2$), 0.92 (s, 9, Me).

(d) Methyl Iodide. A solution of **2a** prepared from **1a** (0.13 g, 0.4 mmol) and $PMePh_2$ (0.35 mL, 1.9 mmol, 4.5 equiv) in cyclohexane (8 mL) was diluted with cyclohexane (20 mL) and cooled to a slurry. Methyl iodide (0.2 mL, 3.2 mmol, 8 equiv) was added dropwise, and the mixture was allowed to warm to room temperature. Large amounts of solid formed in the purple solution which rapidly turned brown. In 30 min the solution was orange and contained a heavy white precipitate. After 3 h the cyclohexane was removed and the residue was extracted with toluene (20 mL). The extract was pumped down, leaving a semicrystalline orange-yellow solid. ^{1}H NMR(benzene-d_6) showed only two products, $Cp_2Zr(Me)I$ [δ 5.80 (s, 10, Cp), 0.12 (s, 3, Me)] and a compound with a Cp resonance at δ 6.0 (consistent with Cp_2ZrI_2) in a 5:1 ratio. The toluene insoluble residue was $(PMe_2Ph_2)^+I^-$.

^{1}H NMR(chloroform-*d*) δ 8.1–7.6 (m, 5, Ph), 2.8 (d, 3, PMe, $^2J_{PH}$ = 14 Hz).

(e) Methyl Fluorosulfonate. $Cp_2Zr(dmpe)$ (**2c**) (30 mg) was dissolved in benzene-d_6 (0.3 mL) and placed under nitrogen in a 5-mm NMR tube sealed with a serum cap. Methyl fluorosulfonate (10 μL, 8 equiv) was added and an instantaneous reaction occurred with precipitation of a heavy pink-white precipitate (not characterized). One major Cp compound, having an ^{1}H NMR spectrum consistent with that expected for $Cp_2Zr(Me)(OSO_2F)$, was formed. ^{1}H NMR(benzene-d_6) δ 5.78 (s, 10, Cp), 0.45 (s, 3, Me).

Oxidation with Acetyl Chloride. Acetyl chloride (0.18 mL, 2.5 mmol, 5 equiv) was added dropwise to a cold (−65 °C) solution of **2a** prepared from **1a** (0.16 g, 0.51 mmol) and $PMePh_2$ (0.38 mL, 2.0 mmol, 4 equiv) in toluene (15 mL). The purple solution immediately turned dark brown-red, and a heavy precipitate formed which made stirring very

(65) Characterized by M. Yoshifuji.
(66) Surtees, J. R. *J. Chem. Soc.* **1965**, 567.

inefficient. The flask was shaken periodically, and the mixture was warmed slowly to room temperature over 2.5 h. The solution was then pale yellow with a cream precipitate.

The mixture was filtered. The yellow filtrate was concentrated and refrigerated after the addition of one volume of hexane. A pale yellow solid was obtained which was filtered off, washed with hexane, and dried. It was identified by ^{1}H NMR analysis by comparison with (in methylene chloride and benzene) an authentic sample, as Cp_2ZrCl_2 (0.1 g, 0.34 mmol, 67% based on Zr). ^{1}H NMR(methylene chloride) δ 6.46 (s, Cp).

The yellow filtrate was pumped down and analyzed by ^{1}H NMR. It contained only $PMePh_2$ and Cp_2ZrCl_2.

The cream precipitate (75 mg, 0.27 mmol, 53% based on Zr), formed in the reaction, had the following spectral properties: ^{1}H NMR(D_2O) δ 8.2–7.5 (m, 10, Ph), 2.7 (d, 3, PMe, $^2J_{PH}$ = 14 Hz), 2.0 (br s, 3). IR(Nujol mull) 1760 (s), 1720, 1590, 1210, 1155 (s), 1020, 920, 820, 750 (m), 725, 690 cm^{-1}. These data are consistent with that expected for [(acetyl)(methyl)(diphenyl)phosphonium]chloride.

Acknowledgment. We acknowledge generous support for this work by the National Science Foundation (Grant No. 79-00996). One of us (K.I.G) also acknowledges support from a University Travelling Scholarship from the Australian National University.

Detailed Mechanism of Thermal Hydrogen Migration in Cyclohexadieneiron Tricarbonyl

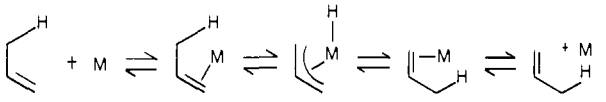
Karin J. Karel, M. Brookhart,* and R. Aumann*

Contribution from the Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina 27514, and the Organisch-Chemisches Institut der Universität, 44 Munster, Orleansring 23, West Germany. *Received June 30, 1980*

Abstract: The thermal isomerization of (cyclohexadiene-*5-exo-h-d*$_1$)iron tricarbonyl (**8**) was examined to obtain detailed information about the general mechanism of 1,5-hydrogen shifts in simple cyclic polyolefin iron tricarbonyl complexes. The isotopically labeled system, as opposed to substituent-labeled systems, was chosen to eliminate substituent effects on the relative rates of formation of intermediates and thus, ultimately, on the kinetically controlled product distributions. Thermolysis of **8** at 134 °C revealed identical initial rates of ^{1}H incorporation into the 1- and 2-positions of the cyclohexadiene ring ($\Delta G^{\ddagger}$ = 33.5 kcal/mol). This result is consistent only with a mechanism involving two simple sequential 1,3-shifts of deuterium endo to the metal. Results rule out several plausible alternative mechanisms, including one in which the intermediate 1,4-cyclohexadiene system is symmetrically bridged by iron.

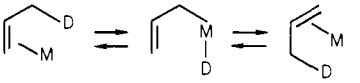
Metal-promoted hydrogen migration is a reaction that often occurs in both the iron carbonyl catalyzed isomerization of olefins and the thermal isomerization of polyolefin–iron tricarbonyl complexes. Because such reactions are of fundamental interest in organometallic chemistry, considerable effort has been made by several research groups to elucidate the detailed mechanisms of iron-catalyzed hydrogen migration in olefins.

Several possible mechanisms for iron carbonyl promoted hydrogen migrations have been suggested. The most common and generally accepted mechanism for metal-catalyzed isomerizations of olefins and stoichiometric isomerizations of diene iron carbonyl complexes involves sequential 1,3-hydrogen migrations which occur via formation of a π-allyliron hydride intermediate as illustrated in a general way below:



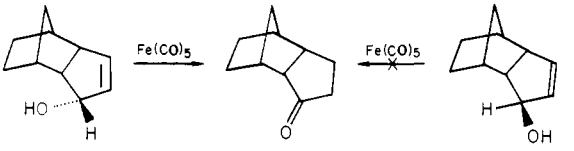
The elements of this mechanism were first proposed by Pettit[1] and Manuel[2] to account for the isomerizations by iron carbonyl compounds of both cyclic olefins (e.g., 1,4-cyclohexadiene and 1,5-cyclooctadiene) and acyclic olefins (e.g., 1-hexene and 2-methyl-1-pentene). More recently, Casey and Cyr[3] have convincingly demonstrated that such a mechanism can account for the $Fe_3(CO)_{12}$-catalyzed isomerization of 3-ethyl-1-pentene-*3-d*. Using a chiral complex as well as deuterium labeling, Whitesides and Neilan[4] have shown that such a mechanism, coupled with dechelation and bond rotation processes, accounts for isomerization of (*cis*-1,5-diphenyl-1,3-pentadiene)iron tricarbonyl to (*trans*-1,5-diphenyl-1,3-pentadiene)iron tricarbonyl.

Several variations of this mechanism have been advanced,[5,6] the most novel of which is a proposal by Green and Hughes that a σ-allyliron tricarbonyl hydride forms directly from an olefin–$Fe(CO)_3$ species (no π-allyl intermediate) and collapses in a different manner, as shown, to yield rearranged product.[7]



This mechanism was advanced to account for the thermal chemistry of [η^4-3-methylene-*endo*-4-vinyldihydrofuran-2(3*H*)-one]iron tricarbonyl.

Suprafacial 1,3-hydrogen shifts might also seem feasible in many systems, but attempts to observe metal-catalyzed suprafacial shifts have been unsuccessful. For example, Cowherd and von Rosenberg[8] found that in a mixture of isomeric alcohols **1** and



1 **3** **2**

2, $Fe(CO)_5$ smoothly catalyzed the conversion of **1** to the isomeric ketone **3**, whereas **2** was recovered unchanged.

*To whom correspondence should be addressed: M.B., University of North Carolina; R.A., Organisch-Chemisches Institute der Universität.

(1) (a) J. E. Arnet and R. Pettit, *J. Am. Chem. Soc.*, **83**, 2954 (1961); (b) G. F. Emerson and R. Pettit, *ibid.*, **84**, 4591 (1962); (c) R. Pettit, G. F. Emerson, and J. Mahler, *J. Chem. Educ.* **40**, 175 (1963).
(2) T. A. Manuel, *J. Org. Chem.*, **27**, 3941 (1962).
(3) C. P. Casey and C. R. Cyr, *J. Am. Chem. Soc.*, **95**, 2248 (1973).
(4) T. Whitesides and J. P. Neilan, *J. Am. Chem. Soc.*, **98**, 63 (1976).
(5) (a) J. C. Barborak, L. W. Dasher, A. T. McPhail, J. B. Nichols, and K. D. Dnan, *Inorg. Chem.*, **17**, 2936 (1978); (b) J. C. Barborak, J. W. Herndon, and J. W. Wong, *J. Am. Chem. Soc.*, **101**, 7430 (1979).
(6) M. A. Schroeder and M. S. Wrighton, *J. Am. Chem. Soc.*, **98**, 551 (1976).
(7) M. Green and R. P. Hughes, *J. Chem. Soc., Dalton Trans.*, 1907 (1976).
(8) F. G. Cowherd and J. L. von Rosenberg, *J. Am. Chem. Soc.*, **91**, 2157 (1969).

0002-7863/81/1503-2695$01.25/0