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. $Bis(\eta^5$ -cyclopentadienyl)bis(phosphine)zirconium(II) Complexes and Their Reactions

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Abstract: Bis(η^5 -cyclopentadienyl)bis(phosphine)zirconium(II) complexes were prepared by ligand-induced reductive elimination of alkane from $bis(\eta^5$ -cyclopentadienyl)chloroalkylzirconium(IV) precursors. Reactions of these species with H₂, 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 methods⁴ 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.³

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)d⁰ 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 $bis(\eta^6-arene)(PMe_3)Zr^0$ (ref 9), $(\eta^5 - C_6 H_8)(dmpe)_2(H)Zr^{II}$ (ref 10), and bis $(\eta^4 - C_4 H_6)(dmpe)$ - $(PMe_3)Zr^0$ (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 $alkylbis(\eta^5$ -cyclopentadienyl)hydrozirconium(IV) complexes.¹² With use of tertiary phosphines in this reaction, $bis(\eta^5$ -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^{2} -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. 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) Marriquez, 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.
(11) (a) Demerseman, B.; Bouquet, G.; Bigorne, M. 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.

produce methylcyclohexane (80-90%) and high yields of bis- $(\eta^{5}$ -cyclopentadienyl)bis(phosphine)zirconium(II) complexes (Cp_2ZrL_2) 2 (reaction 1). An alternative synthesis of 2c is by

Cp₂Zr(R)X + 2L
$$\rightarrow$$
 Cp₂ZrL₂ + methylcyclohexane (1)
1a,b 2a-d
1a, R = CH₂(CH₂)₄CHCH₂- 2a, L = PMePh₂
X = H 2b, L = PMe₂Ph
2c, L₂ = dmpe
1b, R = CH₂(CH₂)₄CDCH₂- 2d, L₂ = dppe
X = D

sodium amalgam reduction of Cp₂ZrCl₂ 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, Cp₂Zr. 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} = $1.6 \text{ Hz})^{14}$ 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 ³¹P resonance (δ 60.9) is broad ($v_{1/2}$ = 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 ($v_{1/2} = 7.8$ Hz), and, conversely, irradiation at this phosphorus collapses the signals in the ¹H NMR as required by the spectral assignments.

The ¹³C¹H NMR supports the conclusions from the ¹H and ³¹P NMR. The Cp ligands (δ 88, no detectable ¹³C-³¹P coupling¹⁷) 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 $({}^{3}J_{PH} = 1.6 \text{ Hz})$ for the Cp ligand in the ${}^{1}\text{H}$ 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 ³¹P-³¹P (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.

(14) This coupling constant is typical for bent sandwich Cp₂MX₂ 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.

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

phosphine			[1h]	% composition				-
(L)	equiv	solvent	mM	\overline{d}_1	d_1^0	<i>d</i> ₁ ′	$\overline{d_2}$	
PMePh ₂ PMePh ₂ PMePh ₂	4.7 4.7 2.5	toluene cyclohexane toluene	50 50 ^b 50	1 6 3	$\begin{array}{c} 4\\ (d_1\\ 4\end{array}$	19 = 14) 26	74 80 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 study¹⁵ 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- $1, \alpha$ - d_2 (Table I). The rate of methylcyclohexane formation is approximately 10³ 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 $I_1\alpha - d_2$ 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 observed¹² 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 sp² 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

 $\begin{array}{l} Cp_2 ZrL_2 \rightarrow 0.5[((\eta^5 - C_5 H_5)(\mu - [\eta^1 : \eta^5 - C_5 H_4])ZrL)_2] + \\ \textbf{2a}, \ L = PMePh_2 \\ \textbf{2b}, \ L = PMe_2Ph \end{array}$

 $0.5H_2$ (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.

⁽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 $({}^{2}J_{PC})$ (17) The prosprine complex 3a also shows no detectable coupling (³P_C) 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 ¹³C isotope effect on the chemical shift of the adjacent ³¹P, this spin system is not AXX' but is more correctly defined as AXX¹⁶ (20) (a) Harris, R. K. Can. J. Chem. 1964, 42, 2275. (b) Finer, E. G.; Harris, P. K. Prog. Nucl. Magn. Pasaro, Spacetore, 1971. 6.1

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 $\eta^{1}:\eta^{5}\cdot C_{5}H_{4}$ 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 sp² C–H bond of an η^5 -C₅H₅ 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 ¹H 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).



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



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 ¹H 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 sp² 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 cyclize²⁹ 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 PMePh₂ in solutions of 2a. At room temperature over 4 h, carbon monoxide is absorbed by a solution of 2a containing 2 equiv of PMePh₂ to give, at equilibrium, a mixture of Cp₂Zr(CO)₂¹¹ (40%) and Cp₂Zr(CO)(PMePh₂) ($\nu_{CO} = 1840 \text{ cm}^{-1}$) (60%).³⁰ Because of the stability of the resulting chelate, dppe completely displaces PMePh₂ 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 $^{\circ}C.^{15}$

⁽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) $[((\eta^5-C_5H_4Me)_2ZrCI)_2O]$: Samuel, E. Bull. Soc. Chim. Fr. 1966, 3548. (b) $[(\eta^5-C_5H_4R)_2TaI(dialkylacetylene)]$: Labinger, J. A.; Schwartz, J.; Townsend, J. M. J. Am. Chem. Soc. 1974, 96, 4009. (c) $[(\eta^5-C_5H_4R)_2Nb(CI)]_2O$: Broussier, R.; Normand, H.; Gautheron, B. Tetrahedron Lett. 1976, 4077.

⁽²⁶⁾ For a review of *inter*molecular C-H insertion into sp² 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, $Cp_2Zr(CO)(PMe_3)$, ($\nu_{CO} = 1852 \text{ cm}^{-1}$) has been prepared by refluxing $Cp_2Zr(CO)_2$ with PMe₃. The second carbon monoxide ligand could not be replaced under these conditions.^{11e}

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 "Cp₂Zr"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 systems³³ 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 $(\eta^5-C_5Me_5)_2Zr(CH_2CH_2CH_2CH_2)$ from ethylene has been reported,^{7c,34} the only existing method for the synthesis of zirconacyclopentanes with unsubstituted Cp ligands is from Cp₂ZrCl₂ 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

$$[(C_{p_2}Z_r(R)(\mu-H))_2] \rightleftharpoons C_{p_2}Z_r \bigwedge_{H}^{R} \rightleftharpoons C_{p_2}Z_r \bigwedge_{H}^{L} + C_{p_2}Z_r \bigcap_{L}^{R} + C_{p_2}Z_r \bigcap_{L}$$

complexes,⁸ the products of an oxidative-elimination reaction³⁶ (reaction 4). For these substrates, a qualitative ordering of

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

$$R = Me; X = I, Cl, SO_3F$$

$$R = n-Bu; X = Cl$$

$$R = t-BuCH_2CH_2; X = Cl, Br$$

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 PMePh₂ 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 PMePh₂. 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, $Cp_2Ti(\eta^2-PhC==CPh)(CO)$, 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^2 -cyclopentadienyl)-2,3,4,5-tetraphenylzirconacyclopentadiene has also been prepared from 1,4-dilithio-1,2,3,4-tetraphenyl-1,3-butadiene and Cp₂ZrCl₂.^{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 dem-onstrated: (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 Cp2ZrCl2. Titanocene was trapped, although inefficiently, by ethylene, but 1,7-octadiene ve 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 $M^n X_x L_z + YY' \rightarrow [M^{n+2} X_x YY' L_{z-1}]$ + 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

¹⁹⁶⁸, 7, 157. (38) (a) The reaction rates are comparable to those observed for the "supernucleophiles" of Co(I) (cobaloxime, vitamin B_{12h})^{38b} or the Rh(I) macrocyclic complex Rh(DO)(DOH)(pn) and its BF₂ 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. (20) Co. Terc(Co.) acret with method individual data of the term of te

⁽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 Cp₂ZrCl₂ and neither Cp₂Zr-(COMe)Cl nor the corresponding decarbonylated material, Cp₂Zr(Me)Cl, is produced.⁴² Quaternization of PMePh₂ by aryl bromides⁴³ 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 complex⁴⁵ 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 PF₃, 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,

$$(\pi^{5-}C_{5}Me_{5})$$
 Z_{r} L'
 $(\pi^{5-}C_{5}Me_{5})$ Z_{r} L'
H
13a, L' = CO⁷c
13b, L' = PF₃

accessible reaction pathway for these intermediates is C-H reductive elimination. Irreversible formation of an sp³ 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 phosphines⁴⁹ (P(c-Hx)₃, PPh₃) 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, Et₃N),⁵¹

(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} $Cp_2Zr(L_3H_5)_2$.^{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*, 140. 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 $(\eta^5 - C_5 Me_5)_2 ZrH_2$; 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.

Scheme Va



^a $L = PMePh_2$, PMe_2Ph ; R = alkyl, aryl, acyl. L' = L, CO;R'X = alkyl halide.

Scheme VI

group 4:
$$Cp_2Zr^{IV}(R)H \xrightarrow{L} (Cp_2Zr^{IL}L) \rightleftharpoons Cp_2Zr^{IL}L_2$$

1 12 2
group 5: $^{\sigma}Cp_2M^{V}H_3 \stackrel{\Delta}{\Rightarrow} (Cp_2M^{II}H_1) \rightleftharpoons Cp_2M(H)L^{27, 52}$
15
group 6: $^{\rho}Cp_2M^{IV}H_2 \stackrel{h_{\nu}}{\longrightarrow} (Cp_2M^{II}) \stackrel{C}{\longleftarrow} Cp_2M^{II}L^{53}$
16
 $\downarrow^{\Delta, RH, M:W}$
 $Cp_2W(R)H$

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 proceed 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

⁽⁴¹⁾ Williams, G. M.; Gell, K. I.; Schwartz, J. J. Am. Chem. Soc. 1980, 102, 3660.

⁽⁵⁰⁾ Elimination of alkane is also promoted by hydrogen; we have suggested¹⁵ 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-H⁵⁷ 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 techniques⁵⁹ on a highvacuum 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 1,2bis(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) (Cp₂ZrCl₂) was obtained from Boulder Scientific. The preparation of $chlorobis(\eta^5-cyclo$ pentadienyl)hydridozirconium(IV) (Cp₂Zr(H)Cl),⁸ (cyclohexylmethyl)-

Cp₂Zr(CH₂CHbis(η^5 -cyclopentadienyl)hydridozirconium(IV) $(CH_2)_4CH_2)H$, and the deuterated analogue $Cp_2Zr(CH_2CD-$ (CH₂)₄CH₂)D have been described.¹⁵ Sodium amalgam (2% sodium) was prepared by a literature method⁶¹ 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), ¹³C, and ³¹P NMR spectra were recorded on a Varian XL-100 spectrometer. Dueterium-decoupled ¹H NMR (100 MHz) spectra were obtained with use of an ¹⁹F 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 13C NMR) are reported in units of δ referenced to tetramethylsilane and are calculated from the position of solvent absorption. Phosphorus chemical

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) complexes⁵⁸ 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.

shifts are reported in units of δ referenced to external H₃PO₄ (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 \times 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 $Bis(\eta^5$ -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 $^{\circ}$ 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 μ L, 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 hydrolvsate).

(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 μ L, 0.33 mmol) was stirred vigorously as PMePh₂ (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, ${}^{3}J_{PH} = 1.5$ Hz), 1.22 (m, 6, PMe, 4.5 Hz) (spacing between the outer doublet ${}^{2}J_{PH} + {}^{4}J_{PH}$) (complex AA'X₃X'₃ pattern); ³¹P NMR (toluene- d_{8}) δ 60.9 ($v_{1/2} = 22$ Hz). For **2b**: ¹H NMR (benzene- d_{6}) 7.5–7.1 (br m, PPh), 4.82 (t, 10, Cp,

 ${}^{3}J_{\rm PH}$ = 1.5 Hz), 1.32 (m, 12, PMe, 4.5 Hz) spacing between the outer doublet = ${}^{2}J_{\rm PH}$ + ${}^{4}J_{\rm PH}$) (complex AA'X₆X'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 PMe₂Ph (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 PMe2Ph (1 equiv). After 14 h at room temperature, the molar ratio of 2b:3b was approximately 5:4.

(ii) Cp₂Zr(CH₂CH(CH₂)₄CH₂)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 PMePh₂ (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 PMePh₂ to produce more of the uncharacterized polymeric material.

(d) Reactions of Cp₂Zr(CH₂CD(CH₂)₄CH₂)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 series to the series of the s (M = Nb, Ta; L = PEt₃) decompose by a mechanism assumed to involve 15 to give a dimer (niobocene, tantalocene) analogous to 3.5^2 A similar dimer forms on prolonged photolysis of Cp₂MoH₂.^{54b} (56) Reductive elimination of alkane from (η^5 -C₅Me₅)₂Zr(Bu-*i*)H has recently been reported to be assisted by ethylene.³⁹ This result may be

from reaction of **1b** with PMePh₂ or PMe₂Ph 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 PMePh₂. A solution of PMePh₂ (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, ³ J_{PH} = 1.6 Hz), 0.95 (apparent t, 12, PMe, J = 2.5 Hz), 0.60 (m, 4, PCH₂, J = 14 Hz). The pattern for the dmpe ligand is complex: AA'X₆X'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, PCH₂). ³¹P NMR-(benzene- d_6) δ 60.9 (br s, $v_{1/2} = 29$ Hz). ³¹P{}^{1}H} NMR(benzene- d_6) δ 88.7 (s, Cp), 33.8 (apparent t, PCH₂, AXY, $J_{CP} = 14$ Hz), 18.9 (apparent t, BXY, PMe, $J_{CP} = 6$ Hz); $J_{CP} = \frac{1}{2}(J_{C1P1} + J_{C1P2})$.

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 (Cp₂Zr(PMe₂), 62), 235 (Cp₂ZrMe, 14), 220 (Cp₂Zr, 100); the most intense peak [${}^{12}C_{n}{}^{1}H_{m}{}^{31}P_{x}{}^{90}Zr$] 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. \times 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, ³ J_{PH} = 1.5 Hz), 2.12 (apparent t, 4, PCH₂, J_{PH} = 4 Hz), phenyl groups of coordinated phosphine obscured by free dppe.

Insertions into sp² Hybridized C-H Bonds. (a) Toluene. Acetone (90 μ L, 1.4 mmol, 4.5 equiv) was added to a solution of 2a prepared from 1a (0.1 g, 0.3 mmol) and PMePh₂ (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 **5**c 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 ('H NMR) of a hydrolyzed (aqueous sulfuric acid, 1 M) sample, which showed toluene and 2-propanol in a 1:1 ratio.

¹H NMR(benzene- \hat{d}_6) δ 7.5-6.9 (complex m, 3, aromatics), 5.83 (s, 10, Cp), 4.11 (septet, 1, OCHMe₂, ³J = 6.5 Hz), 2.45 (br s, *m*-MePhZr), 2.40 (br s, *p*-MePhZr), 1.05 (d, 6, CHMe₂, 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 (MgSO₄), filtered, evaporatively distilled, and analyzed by ¹H₁²H₁ 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- $d_7(m-H)$ (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: $\delta 2.45$ (*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 μ L, 1.4 mmol, 4.5 equiv) was added to a solution of 2a, prepared from 1a (95 mg, 0.3 mmol) and PMePh₂ (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 Cp₂Zr(Ph)(OPr-*i*) (5a) (80%) were identified. The solution was treated with methyl iodide to remove PMePh₂, 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, ³*J* = 6.5 Hz), 1.34 (d, 6, Me, ³*J* = 6.5 Hz). ¹³C{¹H} NMR(chloroform-*d*) δ 183.0 (ZrC of Ph), 139.0 *o*-C of Ph),

¹³C¹H 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 PMePh₂ (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 μ L, 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 Cp₂Zr(Ph- d_5)(OCDMe₂) (5b) (80%) and Cp₂Zr(Ph- d_5)(OCHMe₂) (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 μ L, 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, PMePh₂ was distilled off (70 °C, (0.5 torr)) and analyzed by mass spectrometry (MS-9). No deuterium incorporation in the PMePh₂ 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 PMePh₂ (1.2 mL, 6.3 mmol, 4 equiv) in benzene (30 mL), containing DME (90 μ L, 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 $({}^{3}J_{\rm HD} \simeq 1.5 \text{ Hz})$ in the deuterated compound and a doublet $({}^{3}J_{\rm HH} = 6.5 \text{ Hz})$ 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 ¹H NMR analysis, which showed only two Cp-containing products: Cp₂Zr(CO)₂ (10) (40%) and Cp₂Zr-(CO)(PMePh₂) (11) (60%) in 83% yield (based on Zr). For this product distribution the expected uptake of carbon monoxide was calculated as 10.5 mL. Cp₂Zr(CO)₂ was identified by spectral comparison with an authentic sample prepared by reduction of Cp₂ZrCl₂ with sodium amalgam under carbon monoxide.^{11b} For Cp₂Zr(CO)₂: ¹H NMR-(benzene) δ 4.92 (s, Cp); IR(benzene) ν_{CO} 1960, 1870 cm⁻¹. For Cp₂Zr(CO)(PMePh₂): ¹H 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 PMePh₂ 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 ¹H 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 PMePh₂, was identified as 1,1-bis(η^5 -cyclopentadienyl)-2,3,4,5-tetraethylzirconacyclopentadiene (8) by spectral comparison with an authentic sample.⁶⁴

¹H NMR(benzene- d_6) δ 5.9 (s. 10, Cp), 2.3 (q. 4, CH₂Me, 3J = 7.5 Hz), 2.2 (q. 4, CH₂Me, 3J = 7.5 Hz), 1.0 (t, 6, CH₂Me, 3J = 7.5 Hz), 0.9 (t, 6, CH₂Me, 3J = 7.5 Hz). Assignments of the ethyl groups are not known; signals from PMePh₂ 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; ¹H NMR(benzene- d_6) δ 5.3 (t, 2, ==CH, ³J = 7 Hz), 2.1 (overlapping quartets, 8, CH₂Me, ³J = 7 Hz), 0.95 (t, 6, CH₂Me, ³J = 7 Hz), 0.90 (t, 6, CH₂Me, 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. ¹H 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 (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 μ L) was added. After 30 min the solution was homogeneous and the solvent was removed to leave a white crystalline compound, which was identified as Cp₂Zr(OPr-*i*)₂ (0.05 mmol, 12%, octamethyldisiloxane standard) by ¹H NMR (comparison with authentic sample).

¹H NMR(toluene- d_8) δ 6.0 (s, 10, Cp), 4.1 (septet, 2, OCHMe₂, ³J = 6.5 Hz), 1.1 (d, 12, Me, ³J = 6.5 Hz).

¹H 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 PMePh₂ (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. ¹H NMR(D₂O) 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 . Cp₂Zr(Me)Cl (60%, octamethyldisiloxane internal standard), contaminated by PMePh₂, was identified by ¹H NMR comparison with an authentic sample prepared by reaction of (Cp₂ZrCl)₂O with Me₃Al.⁶⁵ ¹H 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 PMePh₂ (80 μ L, 0.44 mmol, 4 equiv) in toluene-d₈ (1.2 mL) was placed in an NMR tube (5 mm) under nitrogen and sealed with a serum cap. 1-Chlorobutane (56 μ L, 0.55 mmol, 5 equiv) was added via syringe, and sequential ¹H NMR spectra were recorded at 34 °C.

time, min	% 2 a	$% \operatorname{Cp}_{2}\operatorname{Zr}(n-\operatorname{C}_{4}\operatorname{H}_{9})\operatorname{C}$
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, $Cp_2Zr(n-C_4H_9)Cl$, was identified by ¹H 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 (¹H NMR identification). For $Cp_2Zr(n-C_4H_9)Cl$: ¹H 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 $(-78 \ ^{\circ}C)$ of 2a prepared from 1a (0.16 g, 0.51 mmol) and PMePh₂ (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 ¹H NMR spectrum(benzene- d_6) showed Cp₂Zr(CH₂CH₂Bu-t)Cl (65%) contaminated by PMePh₂. 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 (PMe₂Ph₂)⁺I⁻ (0.5 g, 1.4 mmol) was removed by filtration. Yellow crystalline Cp₂Zr(CH₂CH₂Bu-t)Cl (40%) was obtained from the filtrate and identified by ¹H NMR comparison with an authentic sample prepared from Cp₂Zr-(H)Cl and 3,3-dimethyl-1-butene.^{8b} ¹H NMR(benzene- d_6) δ 5.83 (s, 10, Cp), 1.44 (m, 2, CH₂Bu-t), 1.00 (m, 2, ZrCH₂), 0.92 (s, 9, Me).

(d) Methyl Iodide. A solution of 2a prepared from 1a (0.13 g, 0.4 mmol) and PMePh₂ (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. ¹H NMR(benzene-d₆) showed only two products, Cp₂Zr(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 Cp₂ZrI₂) in a 5:1 ratio. The toluene insoluble residue was (PMe₂Ph₂)⁺I⁻.

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

(e) Methyl Fluorosulfonate. Cp₂Zr(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 μ L, 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 ¹H NMR spectrum consistent with that expected for Cp₂Zr(Me)(OSO₂F), was formed. ¹H 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 PMePh₂ (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 ¹H NMR analysis by comparison with (in methylene chloride and benzene) an authentic sample, as Cp₂ZrCl₂ (0.1 g, 0.34 mmol, 67% based on Zr). ¹H NMR(methylene chloride) δ 6.46 (s, Cp).

The yellow filtrate was pumped down and analyzed by ¹H NMR. It contained only PMePh₂ and Cp₂ZrCl₂.

The cream precipitate (75 mg, 0.27 mmol, 53% based on Zr), formed in the reaction, had the following spectral properties: ${}^{1}H NMR(D_{2}O)$ 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.

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Detailed Mechanism of Thermal Hydrogen Migration in Cyclohexadieneiron Tricarbonyl

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Abstract: The thermal isomerization of (cyclohexadiene-5-exo-h- d_7) 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 ¹H incorporation into the 1- and 2-positions of the cyclohexadiene ring (ΔG^{4} = 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:

$$\bigcirc^{H} + \mathsf{M} \rightleftharpoons \bigcirc^{H} \swarrow \bigcirc^{H} \rightleftharpoons \bigcirc^{H} \overset{H}{\Longrightarrow} \overset{H}{\longleftarrow} \overset{H}{\longleftarrow} \overset{H}{\Longrightarrow} \overset{H}{\longleftarrow} \overset{H}{\longrightarrow} \overset{H}{\to$$

The elements of this mechanism were first proposed by Pettit¹ and Manuel² 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 2methyl-1-pentene). More recently, Casey and Cyr³ 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 Neilan⁴ 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.



This mechanism was advanced to account for the thermal chemistry of $[\eta^4-3-methylene-endo-4-vinyldihydrofuran-2(3H)-one]$ 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 Rosenberg⁸ found that in a mixture of isomeric alcohols 1 and



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

(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) L. C. Bacbarzk L. W. Dasher, A. T. McBhail, L. B. Nichols and

- (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).

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