collected under argon, and solvent was evaporated under reduced pressure to give 14 mg (69%) of perdeuteriomethyldiphenylphosphine as a clear oil. $^{31}P\{^1H\}$ (CDCl$_3$): δ −36 (s). IR (neat): 2700 (s), 2406 (w), 1926 (w), 1818 (w), 1752 (w), 1568 (w), 1200 (m), 906(w) cm^{-1}. This ligand was bound to palladium in a manner similar to that previously described for diphenylmethylphosphine.

Diperdeuteriomethylpalladium Complexes. Diperdeuteriomethylpalladium complexes were prepared from perdeuteriomethyllithium in a manner analogous to that previously described for the methyllithium metathesis reaction. Perdeuteriomethyllithium was prepared as follows.

To 60 mg (10 mmol) of a 40% dispersion of lithium in mineral oil in a fritted glass Schlenk tube was added 20 mL of dry pentane. The pentane and oil were removed by filtration through the fritted glass with a positive pressure of argon. The positive pressure of argon was then applied to the opposite side of the fritted glass, allowing 5 mL of oxygen-free dry diethyl ether to be added to the lithium powder collected on the fritted glass to form a suspension, which was transferred under argon to a reaction flask. A solution of 0.60 mL (9.5 mmol) of perdeuteriomethyl iodide in 3 mL of oxygen-free dry diethyl ether was added dropwise over a period of 10 min at 25 °C to the stirred lithium–ether suspension. An argon atmosphere was maintained as the mixture was allowed to stir with no external heating or cooling for 36 h. At this time the mixture was filtered in an argon atmosphere to yield a clear, colorless solution of perdeuteriomethyllithium in diethyl ether. The solution was titrated with *tert*-butyl alcohol[46] which indicated a molarity of 0.84.

Analysis of Coupled Products by Mass Spectroscopy. All coupled products submitted for analysis by mass spectroscopy were obtained in a similar manner. Typical mass spectra experiments are described.

(a) A U-tube designed for vacuum transfer was fit to the vacuum manifold, a receiving flask which could be closed off with an air-tight stopcock, and a reaction flask containing 536 mg (1 mmol) of **2a** and 539 mg (1 mmol) of the corresponding diperdeuteriomethylpalladium complex in 5 mL of freshly distilled oxygen-free dimethyl sulfoxide. The reaction flask was cooled with liquid nitrogen, and the apparatus was evacuated under reduced pressure (0.5 μmHg). The reaction flask was then allowed to warm to room temperature. This freeze–pump–thaw sequence was repeated several times. The apparatus was then closed to the pump manifold and to the receiving flask. The reaction flask was heated to 60 °C for 1.5 h. At this point the reaction flask was cooled to −50 °C, and the receiving flask, which was held in a liquid nitrogen Dewar, was open to the system. After 10 min the receiving flask was closed to the system and removed to submit for mass spectral analysis.

(b) To a sample of 266 mg (0.5 mmol) of bis(diphenylperdeuteriomethylphosphine)dimethylpalladium (**4**) dissolved in 2.5 mL of oxygen-free dimethyl sulfoxide was added 90 mg (0.5 mmol) of diphenylacetylene, and the mixture was treated under the conditions described above; only ethane was obtained.

Kinetic Runs. Perdeuteriodimethyl sulfoxide was distilled from barium oxide at reduced pressure (2 mmHg) and stored over highly activated 4-Å molecular sieves for 24 h before use as a solvent in each kinetic run. All samples were dried at reduced pressure (0.5 μmHg) for 16 h and dissolved under an argon atmosphere immediately before placing the sample in the probe. Experiments were performed by varying temperature, time intervals, and solvent system to establish the conditions at which the reaction could be closely followed on the JEOL FX 100 NMR. The reductive elimination reactions were monitored by the appearance of ethane (coupled product) at 0.9 ppm and disappearance of Pd–CH$_3$ resonances which occur in the range 0.2 to 0.7 ppm. The appearance and disappearance of free phosphine could be observed in the ^{31}P spectra on the NT 150 at −17.2 ppm (PPh$_2$Me).

Isolation of Remaining Palladium Species after Coupling. A solution of 536 mg (1 mmol) of **2a** and 178 mg (1 mmol) of diphenylacetylene in 5 mL of dry, oxygen-free dimethyl sulfoxide was heated to 60 °C with stirring for 8 h. The yellow solution obtained was cooled to 0 °C under a flow of argon, followed by addition of 6 mL of oxygen-free benzene and 6 mL of deoxygenated water. The palladium black which precipitated was collected on a filter in an argon atmosphere, and the water layer was removed from the filtrate. The benzene solution was dried over magnesium sulfate under an argon atmosphere for 3 h. The benzene solution was decanted from magnesium sulfate, and 15 mL of dry degassed pentane added to yield 32 mg of a white solid, mp 117–121 °C. ^{13}C NMR (C$_6$D$_6$): δ 17.8 (d, J = 38 Hz), 106.4, 128.1, 133, 137. IR (C$_6$D$_6$): 1764 (w) cm^{-1}. Anal. Calcd for C$_{40}$H$_{36}$P$_2$Pd: C, 69.97; H, 5.25; P, 9.33. Found: C, 70.34; H, 5.61; P, 9.48.

Isolation of the remaining palladium species by the above method in the absence of diphenylacetylene was not successful. A black precipitate was obtained upon washing the benzene–dimethyl sulfoxide solution in water.

Acknowledgments. We wish to thank Dr. Jim Frye and Mr. Rich Bryson, of the Colorado State University Regional NMR Center, who were invaluable in their help with the NMR experiments. Discussions with Professor Jack Norton resulted in a number of helpful suggestions. We also wish to acknowledge stimulating discussions with Professor Roald Hoffman concerning possible pathways for the elimination reaction. The palladium used in this study was provided under the Johnson Matthey Metal Loan Program. The research was supported by a Grant ER-78-S-02-4903.A000 from the U.S. Department of Energy.

Hydrogen-Transfer Reactions Catalyzed by Low-Valent, Tertiary Phosphine Complexes of Zirconium. Molecular Structure of Hydrido(η^5-cyclooctadienyl)bis[1,2-bis(dimethylphosphino)ethane]zirconium

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Abstract: Treatment of ZrCl$_4$(dmpe)$_2$ (dmpe = 1,2-bis(dimethylphosphino)ethane) with Na/Hg and 1,3-cyclohexadiene or 1,3-cyclooctadiene affords ZrH(η^5-cyclohexadienyl)(dmpe)$_2$ or ZrH(η^5-cyclooctadienyl)(dmpe)$_2$, respectively. The crystal structure of ZrH(η^5-C$_8$H$_{11}$)(dmpe)$_2$ was determined and refined to a conventional R factor of 0.066. Although there were several spurious peaks on the ΔF map in the neighborhood of Zr, a peak 1.67 Å from it is assigned to the hydrogen (i.e., hydride) atom. Five carbon atoms of C$_8$H$_{11}$ are sp^2 hybridized, coplanar, and approximately the same distance (2.43–2.47 Å) from Zr. ZrH(η^5-C$_6$H$_7$)(dmpe)$_2$ catalyzes the disproportionation of 1,3-cyclohexadiene to benzene and cyclohexene, as well as a number of related hydrogen-transfer reactions.

The few low-valent group 4 metal complexes known offer enhanced, occasionally unique reactivity. The increased reactivity is, in part, associated with the powerful reducing properties of the lower oxidation states, a feature illustrated by (i) the reversible oxidative addition of the CH bond of the methyl groups of (η-C$_5$Me$_5$)$_2$Ti^{II},[1] (ii) charge transfer to the N$_2$ ligand as shown by

0002-7863/80/1502-4941$01.00/0

formation of hydrazine on protonation of $[(\eta\text{-}C_5Me_5)_2Zr(N_2)]_2(N_2)$,[2] (iii) formation of the metallocyclopentane complex $(\eta\text{-}C_5H_5)_2Ti(CH_2)_4$ from metastable titanocene and ethylene,[3] and (iv) the coupling of carbonyl compounds with elimination of TiO_2 on treatment with low-valent Ti species.[4] Since the thermodynamic parameters controlling these reactions are determined, partially, by the oxidation potential of the complex, ligands which are potent electron donors are expected to enhance reactivity. Excepting recently prepared phosphine derivatives of zirconocene,[5] most low-valent group 4 metal derivatives known prior to our work are based on carbocyclic, relatively electron-withdrawing ligands, e.g., benzene,[6] cyclooctatetraene,[7] cyclopentadienyl ion,[8] substituted cyclopentadienyl ligands,[1,2] and tropylium ion.[9] Recently, we have prepared Zr(0) and Zr(II) complexes of dienes in combination with the powerful electron donor 1,2-bis(dimethylphosphino)ethane (dmpe).[10] In this paper we report the structural and preparative details of complexes of the type $ZrH(\eta^5\text{-enyl})(dmpe)_2$ and their ability to catalyze intramolecular CH transfer reactions.

Experimental Section

Manipulations throughout were performed in vacuo or under an atmosphere of prepurified nitrogen or argon. $ZrCl_4(dmpe)_2$[11] and methylcyclohexadiene[12] were prepared by published procedures. Olefins and methyl iodide were dried by stirring with $LiAlH_4$ or P_5O_5, followed by vacuum distillation. Solvents were purified by distillation from sodium benzophenone ketyl. GLC analyses were performed on a Varian 920 gas chromatograph fitted with an 8 ft × 1/4 in. 1090 Carbowax 20 M column. The 80-MHz ^1H and 32.2-MHz ^{31}P NMR spectra were obtained on a Bruker WP-80 spectrometer. ^{31}P NMR chemical shifts are relative to 85% H_3PO_4, a positive shift being at higher field than the standard. Cryoscopic molecular weights were determined with an apparatus similar to that described by Bercaw.[1] Elemental analyses were performed by Alfred Bernhardt Analytische Laboratorien, West Germany.

$ZrH(\eta^5\text{-}C_6H_7)(dmpe)_2$. To 10.0 g (18.7 mmol) of $ZrCl_4(dmpe)_2$ dissolved in 250 mL of THF was added 4.5 mL (40 mmol) of 1,3-cyclohexadiene and 750 g of 0.75% Na/Hg. The mixture was mechanically shaken overnight, yielding a red-brown solution. The supernatant was decanted, centrifuged, and evaporated to dryness. The solid residue was extracted with 3 × 100 mL of boiling hexane. The pooled extracts were filtered through a layer of Celite, concentrated to 50 mL, and cooled to −20 °C. The resulting red-brown, crystalline product was collected, washed with 2 × 10 mL of cold hexane, and dried in vacuo (4.6 g, 52%): ^{31}P NMR (toluene-d_8) resolved ABCD pattern, δ_A −20.5, δ_B −15.7, δ_C −2.2, δ_D −0.3, $|J_{AB}| = 13.0$, $|J_{AC}| = 22.1$, $|J_{AD}| = 7.4$, $|J_{BC}| = 11.2$, $|J_{BD}| = 17.7$, $|J_{CD}| = 24.2$ Hz; mass spectrum m/e 470 $[^{12}C_{18}{}^1H_{40}{}^{31}P_4{}^{90}Zr]^+$, 320 $[P - dmpe]^+$.

Anal. Calcd for $C_{18}H_{40}P_4Zr$: C, 45.84; H, 8.55. Found: C, 45.63; H, 8.33.

Reactions of $ZrH(\eta^5\text{-}C_6H_7)(dmpe)_2$ with HCl, DCl, and CH_3I. A solution of 685.1 mg (1.45 mmol) of $ZrH(\eta^5\text{-}C_6H_7)(dmpe)_2$ in 4 mL of toluene was cooled to −196 °C, and 6.42 mmol (4.4 equiv/Zr) of HCl was condensed onto the frozen mass. The mixture was warmed to room temperature and stirred for 3 h, resulting in formation of a white suspension. The volatile components were removed by distillation into a −196 °C trap, noncondensable gasses being collected with a Toepler pump. The involatile colorless solid, remaining in the reaction vessel, was identified as $ZrCl_4(dmpe)_2$ by mass spectroscopy. A 1.59-mmol (1.10 equiv/Zr) sample of hydrogen, identified by mass spectroscopy, was collected. The volatile components contained in the −196 °C were analyzed by GLC, using cyclopentane as an internal standard, and shown to contain 1.40 mmol of cyclohexene (0.97 equiv/Zr).

A similar experiment with 58.2 mg (0.12 mmol) of $ZrH(\eta^5\text{-}C_6H_7)(dmpe)_2$ and using 0.96 mmol of DCl resulted in formation of 0.14 mmol of noncondensable gas, identified as HD by mass spectroscopy.

A solution of 44.0 mg (0.093 mmol) of $ZrH(\eta^5\text{-}C_6H_7)(dmpe)_2$ in 2 mL of toluene was treated with 0.15 mmol of CH_3I in a similar manner. Methane (0.092 mmol, 0.99 equiv/Zr) was collected by a Toepler pump and identified by mass spectroscopy.

Thermal Decomposition and Photolytic Decomposition of $ZrH(\eta^5\text{-}C_6H_7)(dmpe)_2$. A 200.8-mg (0.43 mmol) sample of $ZrH(\eta^5\text{-}C_6H_7)(dmpe)_2$ was dissolved in 5 mL of hexane and the solution heated in a sealed glass tube to 130 °C for 18 h. At the end of this period, a black precipitate had formed and the solution was nearly colorless. The vessel was opened, and the contents were distilled into a −196 °C trap; 1.02 mmol of H_2 (identified by mass spectroscopy) was collected with a Toepler pump. GLC analysis of the volatiles contained in the −196 °C trap showed the presence of 0.32 mmol of benzene (0.75 equiv/Zr).

Similar results were obtained by irradiating a hexane solution of $ZrH(\eta^5\text{-}C_6H_7)(dmpe)_2$ in a quartz tube with a low-pressure Hanovia Hg lamp. Thus, 169.4 mg (0.36 mmol) of $ZrH(\eta^5\text{-}C_6H_7)(dmpe)_2$ afforded 0.28 mmol of H_2 and 0.23 mmol of benzene after 1 week of irradiation.

Reaction of $ZrH(\eta^5\text{-}C_6H_7)(dmpe)_2$ with Cyclooctatetraene. $ZrH(\eta^5\text{-}C_6H_7)(dmpe)_2$ (486.4 mg, 1.03 mmol) was treated with 3 mL of C_8H_8. A rapid reaction occurred, as indicated by formation of a red precipitate. The resulting slurry was stirred for 3 h. Removal of the volatile components in vacuo left a red solid weighing 395.5 mg (calcd for quantitative formation of $[(C_8H_8)_2Zr]_2(dmpe)$, 386.3 mg). The product was recrystallized from toluene and identified as $[(C_8H_8)_2Zr]_2(dmpe)$ by analytical and mass spectral data and by comparison with an authentic sample: mass spectrum m/e 298 $[P - dmpe]^+$.

Anal. Calcd for $C_{19}H_{24}PZr$: C, 60.92; H, 6.46; P, 8.27. Found: C, 59.89; H, 6.13; P, 8.02.

$ZrH(\eta^5\text{-}C_8H_{11})(dmpe)_2$. To 6.0 g (11.3 mmol) of $ZrCl_4(dmpe)_2$, dissolved in 125 mL of THF, was added 4.5 mL (36.6 mmol) of 1,3-cyclooctadiene and 400 g of 0.75% Na/Hg. The mixture was shaken vigorously for 90 min, yielding a red-brown solution. The supernatant was decanted, filtered through a pad of Celite, and evaporated to dryness. The solid residue was extracted with 3 × 75 mL of hot hexane. The pooled extracts were filtered, concentrated, and cooled to −20 °C. Decantation of the supernatant from the resulting red-brown crystals and drying in vacuo afforded 2.24 g (4.48 mmol, 40%) of the product: ^{31}P NMR (benzene-d_6) unresolved ABCD pattern, δ_A −17.3, δ_B −6.5, $\delta_{C,D}$ 5.7.

Anal. Calcd for $C_{20}H_{44}P_4Zr$: C, 48.07; H, 8.88; P, 24.80; Zr, 18.26. Found: C, 47.80; H, 8.62; P, 24.44; Zr, 18.55.

Reaction of $ZrH(\eta^5\text{-}C_8H_{11})(dmpe)_2$ with Methyl Iodide. A solution of 81.6 mg (0.163 mmol) of $ZrH(\eta^5\text{-}C_8H_{11})(dmpe)_2$ in 2 mL of benzene-d_6 was cooled to −196 °C and treated with 0.26 mmol of CH_3I. Warming to room temperature and stirring resulted in formation of a green solution. Noncondensable gasses were collected by distillation of volatile components through a −196 °C trap with the aid of a Toepler pump. The gas collected (0.084 mmol, 0.51 equiv/Zr) was analyzed by mass spectroscopy and shown to be pure CH_4; no CH_3D was detected.

Two similar experiments resulted in formation of 0.58 and 0.61 equiv of CH_4/Zr.

Time-Dependent Reductions of $ZrCl_4(dmpe)_2$ and 1,3-Cyclohexadiene. A mixture of 2.5 g of $ZrCl_4(dmpe)_2$, 1 mL of 1,3-cyclohexadiene, 15 mL of 0.75% Na/Hg, and 40 mL of THF was shaken mechanically for 55 min. The supernatant was decanted, centrifuged, and evaporated to dryness. The residue was extracted with 50-mL portions of boiling hexane until the extracts were colorless. The filtered extracts were pooled and evaporated to dryness. ^{31}P NMR analysis of a benzene-d_6 solution of the residue showed the presence of two overlapping ABCD patterns. One was assignable to $ZrH(\eta^5\text{-}C_6H_7)(dmpe)_2$; the other was subsequently shown to be due to $[ZrCl_2(C_6H_8)(dmpe)]_2$. The product ratio was 0.9.

An identical mixture was shaken for 100 min and analyzed similarly. The product ratio was 2.4. A reaction shaken for 18 h had a product ratio 9.3.

Isolation of $[ZrCl_2(C_6H_8)(dmpe)]_2$. A mixture of $ZrH(\eta^5\text{-}C_6H_7)(dmpe)_2$ and $[ZrCl_2(C_6H_8)(dmpe)]_2$ was prepared as described above and, by ^{31}P NMR analysis, shown to have a respective product ratio of 1.5. A solution of 525 mg of this mixture in 8 mL of toluene was cooled to −196 °C and 0.44 mmol of H_2O distilled onto the frozen mass. Warming to room temperature with vigorous stirring resulted in formation of a brown solution containing a white precipitate. Volatile components were removed in vacuo (0.27 mmol of H_2 was collected), and the residue was dissolved in benzene-d_6 and analyzed by ^{31}P NMR. The ratio of $ZrH(\eta^5\text{-}C_6H_7)(dmpe)_2$ to $[ZrCl_2(C_6H_8)(dmpe)]_2$ was 0.9. Similarly, 330 mg of the crude mixture in 5 mL of toluene was stirred overnight

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Table I. Fractional Coordinates (×10⁴) and Temperature Factors (×10²) ($=\exp(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})$) for Nonhydrogen Atoms

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{23}	β_{13}
Zr	2356 (1)	908 (1)	94 (1)	33 (1)	12	17	0	0	1
P(1)	2649 (2)	−411 (2)	449 (2)	49 (2)	15 (1)	29 (1)	4 (1)	1 (1)	−1 (1)
P(2)	3769 (2)	1350 (2)	951 (2)	42 (2)	21 (1)	27 (1)	−5 (1)	−2 (1)	−2 (1)
P(3)	3295 (2)	1774 (2)	−873 (2)	50 (2)	17 (1)	30 (1)	−3 (1)	6 (1)	5 (1)
P(4)	1978 (2)	194 (2)	−1224 (2)	51 (2)	20 (1)	23 (1)	−2 (1)	−1 (1)	−3 (1)
C(1)	1848 (10)	−926 (8)	1004 (9)	87 (9)	20 (5)	42 (7)	3 (6)	8 (6)	6 (5)
C(2)	3704 (11)	−693 (8)	865 (10)	77 (10)	26 (5)	44 (8)	18 (6)	−7 (7)	1 (5)
C(3)	3616 (12)	1895 (10)	1788 (10)	71 (10)	45 (7)	44 (8)	1 (7)	−5 (7)	−21 (5)
C(4)	4639 (10)	798 (9)	1360 (10)	52 (8)	36 (6)	49 (8)	−1 (6)	−10 (6)	11 (6)
C(5)	4504 (10)	1862 (10)	329 (10)	52 (8)	38 (6)	42 (8)	−19 (6)	5 (6)	3 (6)
C(6)	3965 (10)	2297 (8)	−214 (10)	65 (9)	22 (5)	47 (8)	−20 (5)	1 (7)	7 (5)
C(7)	4175 (10)	1513 (9)	−1557 (9)	52 (9)	40 (6)	34 (7)	−8 (6)	13 (6)	−3 (5)
C(8)	2763 (11)	2395 (8)	−1502 (9)	80 (11)	25 (5)	40 (7)	4 (6)	−9 (7)	13 (5)
C(9)	2794 (11)	169 (8)	−1999 (8)	74 (10)	38 (6)	28 (6)	−9 (6)	0 (6)	−15 (5)
C(10)	937 (10)	319 (9)	−1807 (8)	69 (9)	35 (6)	24 (6)	1 (6)	−15 (6)	−3 (5)
C(11)	1870 (13)	−690 (8)	−984 (9)	108 (12)	19 (5)	33 (7)	−11 (6)	−2 (7)	−7 (5)
C(12)	2659 (11)	−891 (7)	−468 (8)	83 (10)	21 (4)	29 (5)	8 (6)	1 (6)	0 (5)
C(13)	1711 (9)	2000 (6)	296 (7)	50 (7)	11 (3)	24 (5)	7 (4)	6 (5)	1 (3)
C(14)	1121 (8)	1640 (7)	−211 (8)	42 (7)	25 (4)	27 (5)	5 (4)	0 (5)	9 (4)
C(15)	717 (8)	1033 (7)	−21 (8)	30 (6)	28 (5)	28 (6)	4 (3)	−1 (5)	−3 (5)
C(16)	902 (8)	595 (7)	619 (9)	31 (6)	18 (4)	40 (7)	−1 (4)	11 (5)	3 (4)
C(17)	1474 (8)	731 (7)	1259 (8)	39 (7)	26 (5)	21 (5)	2 (4)	1 (4)	−5 (4)
C(18)	1228 (10)	1252 (7)	1869 (8)	65 (9)	23 (5)	22 (6)	9 (5)	4 (5)	3 (4)
C(19)	787 (9)	1869 (7)	1557 (8)	55 (8)	22 (5)	25 (6)	12 (5)	8 (5)	1 (4)
C(20)	1372 (9)	2287 (7)	1073 (8)	54 (8)	20 (4)	32 (6)	7 (5)	13 (5)	−1 (4)

in a vessel containing 0.21 mmol of O_2. The mixture was evaporated to dryness, extracted with 2 mL of benzene-d_6, and analyzed by ^{31}P NMR. The product ratio was 1.0.

A 3.0-g sample of a mixture of $ZrH(\eta^5\text{-}C_6H_7)(dmpe)_2$ and $[ZrCl_2(C_6H_8)(dmpe)]_2$ prepared as described above was dissolved in 300 mL of hexane contained in an evacuated 500-mL flask. The flask was briefly opened to the atmosphere and, then, allowed to stand overnight. The solution was filtered and concentrated to 100 mL. Cooling to −20 °C overnight afforded a crop of dark red crystals of $ZrH(\eta^5\text{-}C_6H_7)(dmpe)_2$ mixed with orange crystals. Concentration of the supernatant to 20 mL and cooling overnight afforded a nearly homogeneous second crop of orange crystals. Recrystallization of this solid from hexane afforded 439 mg of pure $[ZrCl_2(C_6H_8)(dmpe)]_2$: ^{31}P NMR (C_6D_6) ABCD pattern, δ_A −12.5, δ_B −2.0, δ_C 6.2, δ_D 9.0, $|J_{AB}| = 34.8$, $|J_{AC}| = 18.9$, $|J_{AD}| = 11.6$, $|J_{BC}| = 9.2$, $|J_{BD}| = 24.4$, $|J_{CD}| = 12.8$ Hz; molecular weight (cryoscopic in benzene) 810 ± 117.

Anal. Calcd for $C_{12}H_{24}Cl_2P_2Zr$: C, 36.73; H, 6.17; Cl, 18.07; P, 15.79. Found: C, 36.40; H, 6.25; Cl, 17.80; P, 15.57.

Disproportionation of 1,2-Dihydronaphthalene Catalyzed by $ZrH(\eta^5\text{-}C_6H_7)(dmpe)_2$. A 6-mm glass tube, fitted with a standard taper joint, was loaded with 20 mg (0.042 mmol) of $ZrH(\eta^5\text{-}C_6H_7)(dmpe)_2$ and 0.25 mL (50 equiv) of 1,2-dihydronaphthalene. The tube was cooled to −196 °C, evacuated, and sealed. Upon being thawed it was immersed in an oil bath at 90 °C for 24 h. The vessel was then cooled and opened, and the contents were analyzed by GLC. Comparison of retention times and coinjection with authentic materials established that the dihydronaphthalene had been completely converted to an equimolar mixture of 1,2,3,4-tetrahydronaphthalene and naphthalene. Product studies of other $ZrH(\eta^5\text{-}C_6H_7)(dmpe)_2$ catalyzed hydrogen-transfer reactions were performed similarly, except for the isomerization of 1-pentene which was followed by ^1H NMR.

Hydrogenation of Octene Catalyzed by $ZrH(\eta^5\text{-}C_6H_7)(dmpe)_2$. A 300-mL flask was charged with 25 mg (0.053 mmol) of $ZrH(\eta^5\text{-}C_6H_7)(dmpe)_2$, 5 mL of hexane, and 0.83 mL (5.34 mmol) of 1-octene. The vessel was cooled to −196 °C, evacuated, and filled with 1 atm of hydrogen. After being warmed to room temperature, the flask was heated to 95 °C for 12 h. After the flask was cooled the contents were analyzed by GLC; 93% conversion to octane had been effected.

Kinetic Studies of $ZrH(\eta^5\text{-}C_6H_7)(dmpe)_2$ Catalyzed Cyclohexadiene Disproportionation. In a volumetric flask 170 mg of $ZrH(\eta^5\text{-}C_6H_7)(dmpe)_2$ was dissolved in 25 mL of hexane, affording a solution 0.014 M in catalyst. To a series of volumetrically calibrated NMR tubes were added measured aliquots of the catalyst solution and 1,3-cyclohexadiene. Hexane was then added to make 1 mL of solution in each tube. The tubes were fitted with vacuum adaptors, cooled to −196 °C, evacuated, and sealed. Upon being thawed, they were immersed in a constant temperature bath. The NMR tubes were withdrawn at timed intervals and their spectra recorded.

Concentrations of benzene, cyclohexadiene, and cyclohexene were determined by measuring the ratio of the peak areas of the vinylic protons of cyclohexadiene and cyclohexene taken together to that of benzene. With the assumption $[C_6H_{10}] = [C_6H_6]$, the ratio, α, is given by

$$\alpha = \frac{4[C_6H_8] + 2[C_6H_{10}]}{6[C_6H_6]} = \frac{2}{3}\frac{[C_6H_8]}{[C_6H_6]} + \frac{1}{3}$$

Since $[C_6H_8] = [C_6H_8]_{\text{initial}} - 2[C_6H_6]$, then $[C_6H_6] = (2/3)[C_6H_8]_{\text{initial}}/(\alpha + 1) = [C_6H_{10}]$ and $[C_6H_8] = [C_6H_8]_{\text{initial}}[(\alpha - {}^1/_3)/(\alpha + 1)]$.

Crystal Structure Analysis of $ZrH(\eta^5\text{-}C_8H_{11})(dmpe)_2$. A red-brown crystal ca. 0.2 × 0.2 × 0.2 mm obtained from hexane solution, as described above, was transferred under an inert atmosphere to a Lindemann glass capillary and sealed in a flame.

X-ray analysis was carried out on an automated four-circle Picker diffractometer using Ni-filtered Cu Kα radiation and pulse-height analyses. Unit cell dimensions were determined from setting angles of eight centered reflections.

Crystal data: fw = 449.45; orthorhombic; space group *Pbcn*; $a = 14.936$ (5), $b = 20.342$ (6), $c = 17.278$ (6) Å; $V = 5249.6$ Å^3; ρ_c (for $Z = 8$) = 1.264 g cm^{-3}; ρ_0 not determined; μ(Cu Kα) = 8.39 cm^{-1}. A total of 4462 reflections were collected in 2θ scan mode at 2° min^{-1} in the range $0 \leq \sin\theta \leq 0.89$. Background counts were for 30 s. The crystal remained stable, as evidenced by the intensity of a standard reflection, remeasured throughout data collection.

The standard deviation in raw intensity $\sigma(I)$ was taken as $(\text{scan} + \sum b)^{1/2}$, where $\sum b$ is the total background count. Reflections with $(\text{scan} - \sum b) < \sigma(I)$ were considered insignificant. $\sigma(F_o)$ was taken as $\{[\sigma(I)\cdot Lp]^2 + 0.02F_o^4\}^{1/2}/2F_o$, Lp being the Lorentz–polarization factor.

The structure was solved by the heavy-atom method. XFLS-3[13] full-matrix least squares was used for refinement, using scattering factors of Cromer and Mann,[14] the anomalous dispersion corrections[15] $\Delta f'$ and $\Delta f''$ for Zr being −0.134 and 2.245 and for P, 0.283 and 0.434. All hydrogen atoms (apart from that associated with the Zr atom) were found on the ΔF map. Location of this hydrogen atom presented some problems as there were a number of spurious peaks in this region. Program HOLE,[16] which finds the positions and extent of "van der Waals holes" (i.e., the space left between local van der Waals radii) in a crystal structure, was used to establish the existence of an extensive hole adjacent to Zr and lying between the four phosphorus atoms. Near the center of this hole there was a peak 2.4 Å from Zr, but we believe that this does not correspond to the hydrogen atom sought; rather, we believe a peak (0.4 e/Å^3) near the edge of the hole ca. 1.7 Å from Zr is the genuine one. This is based on the fact that the hydrides of several other second-row

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(13) "XFLS-3", an extensively modified version of ORFLS, Report ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1962.

(14) Cromer, D. T.; Mann, J. B. *Acta Crystallogr., Sect. A* **1968**, *24*, 321.

(15) "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, p 149.

(16) Nyburg, S. C., local program, unpublished, 1979.

(17) Schultz, A. J.; Steerley, K. L.; Williams, J. M.; Mink, R.; Stucky, G. D. *Inorg. Chem.* **1977**, *16*, 3303.

Table II. Fractional Atomic Coordinates of Hydrogen Atoms

	x	*y*	*z*
H(Zr)	0.340	0.075	−0.020
H(C1)	0.115	−0.094	0.070
H(C1)	0.208	−0.140	0.104
H(C1)	0.178	−0.076	0.155
H(C2)	0.430	−0.050	0.070
H(C2)	0.375	−0.118	0.077
H(C2)	0.367	−0.062	0.144
H(C3)	0.350	0.164	0.232
H(C3)	0.308	0.219	0.168
H(C3)	0.416	0.218	0.184
H(C4)	0.495	0.118	0.175
H(C4)	0.508	0.062	0.097
H(C4)	0.439	0.041	0.167
H(C5)	0.490	0.157	0.002
H(C5)	0.489	0.215	0.067
H(C6)	0.438	0.258	−0.053
H(C6)	0.355	0.259	0.009
H(C7)	0.380	0.135	−0.195
H(C7)	0.457	0.188	−0.172
H(C7)	0.457	0.115	−0.132
H(C8)	0.235	0.210	−0.190
H(C8)	0.320	−0.267	−0.178
H(C8)	0.235	0.269	−0.118
H(C9)	0.342	0.025	−0.180
H(C9)	0.265	0.051	−0.239
H(C9)	0.278	−0.028	−0.225
H(C10)	0.092	−0.010	−0.230
H(C10)	0.095	0.077	−0.205
H(C10)	0.040	0.029	−0.146
H(C11)	0.187	−0.096	−0.147
H(C11)	0.129	−0.077	−0.070
H(C12)	0.324	−0.081	−0.076
H(C12)	0.262	−0.138	−0.035
H(C13)	0.210	0.238	0.005
H(C14)	0.099	0.183	−0.074
H(C15)	0.024	0.087	−0.040
H(C16)	0.068	0.015	0.062
H(C17)	0.170	0.030	0.150
H(C18)	0.179	0.140	0.214
H(C18)	0.082	0.105	0.226
H(C19)	0.024	0.173	0.122
H(C19)	0.053	0.214	0.200
H(C20)	0.106	0.271	0.096
H(C20)	0.192	0.239	0.140

early transition metals show comparable distances. Thus by neutron diffraction, M–H is found to be 1.665 Å in H_2MoCp_2,[17] 1.669 Å in $H_8Re_2(PEt_2Ph)_4$,[18] 1.68 Å in ReH_9^{2-},[19] and 1.59 Å in $HMo[P(OCH_3)_3]_4[O_2CCF_3]$ by X-ray diffraction.[20]

The peak which we regard as spurious, 2.4 Å from Zr, prevented the refinement of the positional and thermal parameters of the authentic hydrogen atoms. Keeping all hydrogen positions fixed, with $B = 6$ Å^2, an anisotropic refinement of the other atoms yielded $R = 0.066$. Bond lengths are given in an ORTEP plot of the molecule in Figure 1, and bond angles are given in Table III. Best least-squares planes of interest are given in Table IV.

Results

Preparation and Chemical Characterization of Zr(II) Pentadienyl Hydrides. Treatment of $ZrCl_4(dmpe)_2$ with Na/Hg in the presence of butadiene affords the dmpe-bridged Zr(0) complex $[Zr(\eta\text{-}C_4H_6)_2(dmpe)]_2(dmpe)$.[10,11] However, when conjugated dienes with allylic CH groups are used, different products are formed. Thus, prolonged shaking of $ZrCl_4(dmpe)_2$, Na/Hg, and 1,3-cyclohexadiene or 1,3-cyclooctadiene yields brown, crystalline solids having the stoichiometry Zr(diene)(dmpe)$_2$ on the basis of analytical and mass spectral data.

Both complexes have ABCD ^{31}P NMR spectra. ^1H NMR spectra are complex and poorly resolved because of ^{31}P couplings.

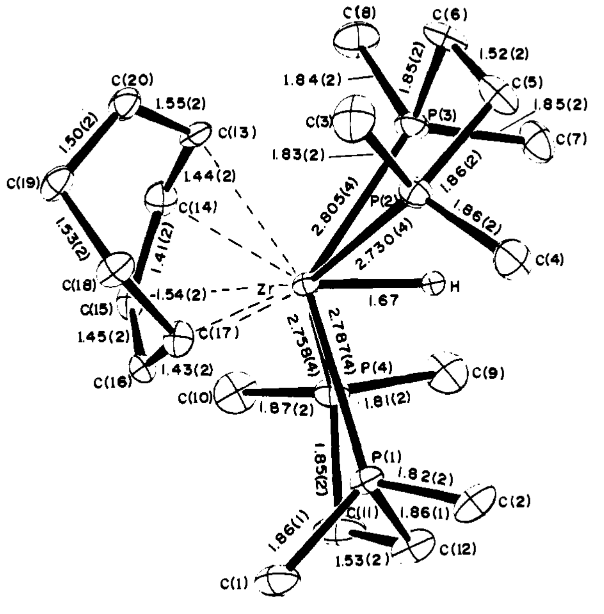


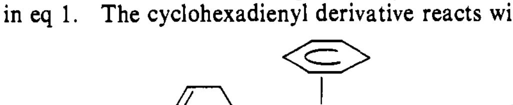
Figure 1. ORTEP plot of a molecule of $ZrH(\eta^5\text{-}C_8H_{11})(dmpe)_2$ (50% probability ellipsoids) showing bond lengths.

Table III. Bond Angles (Deg)

P(1)–Zr–P(3)	131.2 (1)	P(1)–Zr–P(2)	94.4 (1)
P(2)–Zr–P(4)	141.2 (1)	P(2)–Zr–P(3)	74.3 (1)
P(3)–Zr–P(4)	86.6 (1)	P(1)–Zr–P(4)	73.0 (1)
H–Zr–P(1)	74.7	H–Zr–P(3)	58.2
H–Zr–P(2)	60.5	H–Zr–P(4)	80.7
C(1)–P(1)–Zr	123.8 (5)	C(7)–P(3)–Zr	123.8 (5)
C(2)–P(1)–Zr	121.2 (6)	C(8)–P(3)–Zr	124.4 (5)
C(3)–P(2)–Zr	122.0 (6)	C(9)–P(4)–Zr	119.2 (5)
C(4)–P(2)–Zr	123.2 (5)	C(10)–P(4)–Zr	122.9 (5)
P(1)–C(12)–C(11)	105.5 (10)	P(3)–C(6)–C(5)	109.4 (10)
P(2)–C(5)–C(6)	111.8 (11)	P(4)–C(11)–C(12)	109.7 (11)
Zr–P(1)–C(12)	108.5 (5)	Zr–P(3)–C(6)	85.3 (4)
Zr–P(2)–C(5)	85.3 (3)	Zr–P(4)–C(11)	110.2 (6)
C(1)–P(1)–C(2)	100.2 (7)	C(3)–P(2)–C(5)	101.0 (8)
C(3)–P(2)–C(4)	98.8 (8)	C(4)–P(2)–C(4)	98.4 (7)
C(7)–P(3)–C(8)	97.3 (7)	C(7)–P(3)–C(6)	100.0 (7)
C(9)–P(4)–C(10)	99.5 (7)	C(8)–P(3)–C(6)	101.7 (7)
C(1)–P(1)–C(12)	98.6 (7)	C(9)–P(4)–C(11)	101.3 (8)
C(2)–P(1)–C(12)	99.4 (7)	C(10)–P(4)–C(11)	100.4 (7)
C(13)–C(14)–C(15)	124.3 (12)	C(17)–C(18)–C(19)	115.6 (12)
C(14)–C(15)–C(15)	129.4 (12)	C(18)–C(19)–C(20)	113.0 (12)
C(15)–C(16)–C(17)	126.0 (12)	C(19)–C(20)–C(13)	117.9 (12)
C(16)–C(17)–C(18)	121.4 (12)	C(20)–C(13)–C(14)	121.2 (11)

Although neither compound has a clearly identifiable Zr–H ^1H NMR resonance or stretching frequency, they may occur but be obscured by dmpe resonances and vibrational bands, respectively. Precedent exists for the occurence of relatively low-field ^1H NMR resonances;[21] ν_{ZrH} is expected at low frequencies.

Chemical evidence suggests that both compounds contain a ZrH unit and should be formulated as $Zr^{II}H(\text{pentadienyl})(dmpe)_2$, as suggested in eq 1. The cyclohexadienyl derivative reacts with



(1)

HCl and CH_3I to form 1 equiv of H_2 and CH_4, respectively. In the former case $ZrCl_4(dmpe)_2$ and 1 equiv of cyclohexene are formed as well (eq 2). When DCl is substituted, HD is the predominant isotopic component. Evolution of hydrogen or methane on treatment with acids or methyl iodide is a common test for hydridic group 4 metal hydrides.[22] When treated with

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(19) Abrahams, S. C.; Ginsberg, A. P.; Knox, F. *Inorg. Chem.* **1964**, *3*, 558.

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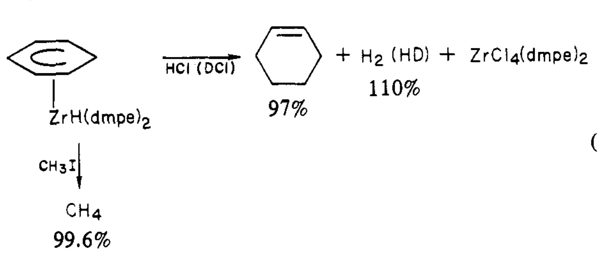
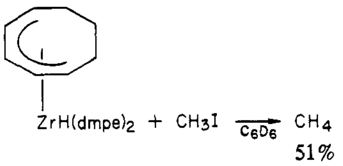
(21) For example, see: Manriquez, J. M.; McAlister, D. R.; Sanner, R. D.; Bercaw, J. E. *J. Am. Chem. Soc.* **1978**, *100*, 2716.



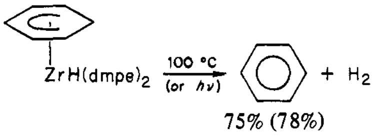
(2)

methyl iodide, the cyclooctadienyl analogue, $ZrH(\eta^5\text{-}C_8H_{11})(dmpe)_2$, gave a less than stoichiometric amount of methane, suggesting a more complex reaction path.[23] The methane is not formed by simple oxidation of methyl iodide and trapping of the resulting methyl radicals, as no CH_3D is produced when C_6D_6 is used as a solvent (see eq 3).

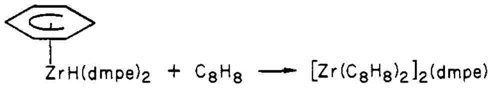


(3)

The cyclohexadienyl methylene hydrogens of $ZrH(\eta^5\text{-}C_6H_7)(dmpe)_2$ are, apparently, labile as heating or irradiation of the complex in alkane solvents affords benzene, hydrogen, and a black deposit, presumed to be zirconium metal (eq 4). Similarly, treatment of the complex with cyclooctatetraene gives a mixture of benzene, cyclohexene, hydrogen, and the dmpe-bridged complex in eq 5. The complex has also been prepared by direct reaction of $Zr(C_8H_8)_2$[7b] with dmpe[24] and is, presumably, structurally analogous to other Lewis base adducts of $Zr(C_8H_8)_2$,[7b] e.g., $Zr(C_8H_8)_2\cdot THF$.[25]



(4)



(5)

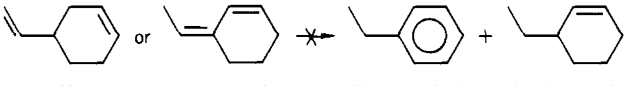
The formation of $ZrH(\eta^5\text{-}C_6H_7)(dmpe)_2$ from $ZrCl_4(dmpe)_2$, Na/Hg, and 1,3-cyclohexadiene involves a detectable intermediate. An additional ABCD spectrum was observed in the ^{31}P NMR spectrum of hexane extracts of reaction mixtures shaken for short periods. Longer reaction periods resulted in an increase of the $ZrH(\eta^5\text{-}C_6H_7)(dmpe)_2$/intermediate ratio. Thus, reaction periods of 1, 2, and 18 h gave ratios of 0.9, 2.4, and 9.3, respectively. Although neither complex survived chromatographic conditions, small samples of the intermediate could be obtained. Reaction of a mixture of the compounds with a deficiency of oxygen or water resulted in a mixture enriched in the intermediate; $ZrH(\eta^5\text{-}C_6H_7)(dmpe)_2$ is degraded more rapidly than the intermediate. Fractional crystallization of the enriched mixture allowed isolation of the pure intermediate. Chemical analysis established the stoichiometry as $Zr(C_6H_8)(dmpe)Cl_2$; we formulate the complex as a dimer, $[Zr(C_6H_8)Cl_2]_2$, on the basis of cryoscopic molecular weight measurements and because an ABCD ^{31}P NMR spectrum is observed.

Structure of $ZrH(\eta^5\text{-}C_8H_{11})(dmpe)_2$. The X-ray data establish that the complex contains an $\eta^5\text{-}C_8H_{11}$ unit. Given the chemical (eq 3) and analytical data above and the diamagnetism of the compound, a hydride ligand must be present. Indeed, a peak in the electron density map in a plausible location was observed. Thus, the structure can be described as a distorted octahedron with the C_8H_{11} moiety occupying a vertex trans to the hydride. There is no molecular symmetry, in accord with the ^{31}P NMR data. Because of the distortion, Zr does not lie in the plane of the four phosphorus atoms but is 1.03 Å from it; in fact, hydrogen is closer at ca. 0.6 Å (see Table II). The Zr–P distances range from 2.730 (4) to 2.805 (4) Å, somewhat longer than those found in other transition-metal dmpe complexes.[26] As a consequence, the "bite" angles P–M–P at 73.0 (1) and 74.3 (1)° are smaller than those found in other complexes.

When acting as a ligand, dmpe can have either of two principal conformations with the carbon atoms on the same or on the opposite sides of the P–M–P plane.[27] In the present case, for both ligand molecules the carbon atoms lie on opposite sides of the P–Zr–P plane. The distances between P(2) and P(3) and the hydrogen atom associated with Zr at 2.40 and 2.39 Å are shorter than the sum of the van der Waals radii ($1.9 + 1.2 = 3.1$ Å), an effect which has been noted elsewhere.[20] Chemical bonding is possible here but a purely electrostatic interaction may be possible. (Alternatively the existence of "polar flattening" of the P atom is a possibility.[28])

Five of the carbon atoms of C_8H_{11} are virtually coplanar (Table IV) and are clearly those of the ring which are sp^2 hybridized. The mean C–C distance for these five C atoms is 1.433 (20) Å. They are virtually all the same distance from Zr, lying in the narrow range 2.43 (1)–2.47 (1) Å. Coplanarity of carbon atoms coordinated to the metal is shown by several complexes of this type. Thus in $Mn(\eta^5\text{-}C_6H_7)(CO)_3$ the five sp^2-hybridized atoms of the ring are strictly coplanar with closely similar Mn–C distances (the sixth C atom is out-of-plane).[29] A situation more closely similar to ours is presented by the crystal structure of $(C_8H_{11})Cr(PF_3)_2H$ to judge by the published ORTEP plot.[30] For complexes $\eta\text{-}C_nH_nM$, all carbon atoms are normally coplanar, sp^2 hybridized, and equidistant from M. See, for example, the vapor-phase electron diffraction study of $(\eta\text{-}C_5H_5)_2ZrCl_2$[31] and X-ray diffraction studies of $[(\eta\text{-}C_5Me_5)_2Zr(N_2)]_2$[32] and of $(\eta\text{-}C_8H_8)ZrCl_2\cdot THF$.[25b] The mean Zr–C distances in these three cases are 2.522, 2.535 and 2.458 (4) Å. As yet there are too few cases to permit any conclusion as to a possible relation between C–C ring and Zr–C distances.

Hydrogen-Transfer Reactions Catalyzed by $ZrH(\eta^5\text{-}C_6H_7)(dmpe)_2$. Heating neat 1,3-cyclohexadiene or benzene or hexane solutions of cyclohexadiene with catalytic amounts of $ZrH(\eta^5\text{-}C_6H_7)(dmpe)_2$ resulted in its conversion to an equimolar mixture of benzene and cyclohexane. No hydrogen was evolved during the reaction. The solutions remained homogeneous during the disproportionation, and the catalyst could be recovered unchanged from the reaction mixture. Related hydrogen-transfer reactions are summarized in Table V. 1,4-Cyclohexadiene is disproportionated more slowly than the 1,3 isomer (reaction 2), suggesting isomerization to the conjugated diene may be required. The complex does catalyze double-bond migration; thus, 1-pentene is slowly isomerized to a mixture of 2-pentenes (reaction 7). Dienes with exocyclic double bonds are not disproportionated or isomerized, as shown in eq 6. Presumably, the catalyst is not capable of effecting migration of the double bond through the tertiary



(6)

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[22] For example, see: Brintzinger, H. H.; Bercaw, J. E. *J. Am. Chem. Soc.* **1970**, *92*, 6182.

[23] For example, a competing reaction involving reductive elimination of cyclooctadiene from the oxidized hydride.

[24] Beatty, R. P.; Wreford, S. S., unpublished results.

[25] (a) Brauer, D. J.; Krüger, C. *J. Organomet. Chem.* **1972**, *42*, 129. (b) *Inorg. Chem.* **1975**, *14*, 3053.

[26] Albright, J. O.; Datta, S.; Dezube, B.; Kouba, J. K.; Marynick, D. S.; Wreford, S. S.; Foxman, B. M. *J. Am. Chem. Soc.* **1979**, *101*, 611.

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[29] Churchill, M. R.; Scholer, F. R. *Inorg. Chem.* **1969**, *8*, 1950.

[30] Given in Figure 9 of: von Gustorf, E. A. K.; Jaenicke, O.; Wolfbeis, O.; Eady, C. R. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 278. Details of the structure analysis by D. J. Brauer, C. Krüger, P. J. Robert, and Y. H. Tsay do not appear to have been published.

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Table IV. Least-Squares Planes

(a) Coefficients of Planes $AX + BY + CZ = D$, Where X, Y, and Z Are Real Orthogonal Coordinates (in Å) with X along x and Z and z^*

plane	descrptn	A	B	C	D
1	P(1), P(2), P(3), P(4)	0.851 (3)	−0.371 (2)	−0.372 (2)	3.279 (2)
2	C(13), C(14), C(15), C(16), C(17)	0.761 (14)	−0.429 (9)	−0.487 (13)	0.005 (7)
3	Zr, P(2), P(3)	0.558 (3)	−0.740 (4)	−0.333 (3)	0.508 (1)
4	Zr, P(1), P(4)	0.952 (6)	0.088 (1)	−0.292 (3)	3.467 (1)

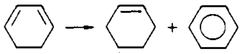
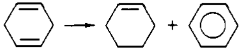
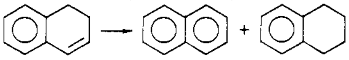
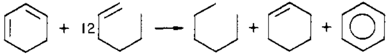
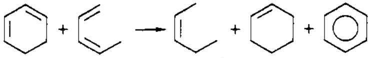
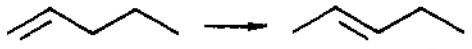
(b) Distances of Atoms to Planes (Å)

plane	atoms	distance	atoms	distance	atoms	distance	atoms	distance
1	C(13)	−0.021 (13)	C(14)	0.049 (13)	C(15)	−0.040 (12)	C(16)	0.013 (13)
	C(17)	0.006 (13)	C(18)	−1.242 (15)	C(19)	−2.042 (14)	C(20)	−1.310 (14)
2	P(1)	0.109 (4)	P(2)	−0.120 (4)	P(3)	0.131 (4)	P(4)	−0.125 (4)
	Zr	−1.030 (1)	H(Zr)	0.605				
3	C(4)	0.179 (17)	C(16)	−0.628 (16)				
4	C(11)	−0.434 (19)	C(12)	0.392 (16)				

(c) Dihedral Angles (Deg)

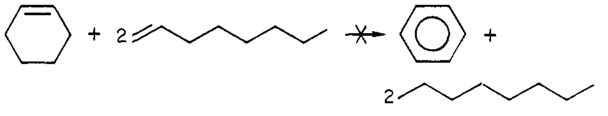
	1	2	3		1	2	3
2	9.03 (7)			4	34.0 (7)	27.6 (2)	55.8 (3)
3	24.1 (7)	28.3 (3)					

Table V. $ZrH(\eta^5\text{-}C_7H_6)(dmpe)_2$ Catalyzed Hydrogen-Transfer Reactions

reaction	substrates → products (yields)[a]	conditns
1	 (0) (0.45) (0.55)	94 °C, 20 h, neat, catalyst/substrate = 1/106
2	 (0.75) (0.11) (0.14)	90 °C, 24 h, neat, catalyst/substrate = 1/50
3	 (0.22) (0.38)[b] (0.39)	same
4	 (0.21) (0.41) (0.38)	same
5	 (0) (0.99)[b] (trace) 0.50 0.50	same, except catalyst/substrate = 1/20
6	 (0) (0)[c] (0.38)[b] (0.33) (0.67)	same
7	 (0.01)[d] (0.99)[d,e]	95 °C, 17 h, benzene solution, catalyst/substrate = 1/20

[a] Unless otherwise stated, yields are determined by GLC and are expressed as mole fraction of the substrate. The figures represent the composition of the mixture when the reaction was analyzed. [b] A mixture of isomers, which were assumed to have the same GLC response factors. [c] A substantial amount of pentadiene was converted to an involatile polymer. [d] Yields determined by NMR. [e] A mixture of isomers.

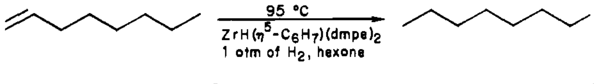
center, as would be required for formation of the conjugated cyclic diene. Substituents on the ring may slow, but do not prevent, disproportionation. Dihydronaphthalene and 1-methylcyclohexadiene are converted to, respectively, mixtures of tetralin and naphthalene and methylcyclohexene and toluene (reactions 3 and 4). Linear olefins are not effective in intercepting the hydrogen transferred. When 1,3-cyclohexadiene is heated with an excess of 1-hexene, only a trace of hexane is formed. Similarly, the catalyst does not operate on cyclohexene. Heating cyclohexene and 1-octene with the Zr complex did not result in hydrogen transfer, although it would be thermodynamically favorable (eq 7). Other conjugated dienes can, however, function as hydrogen acceptor. An equimolar mixture of 1,3-pentadiene and 1,3-cyclohexadiene is converted to benzene, cyclohexene, and 2-pentene (reaction 6).



(7)

$\Delta G° = -34.7$ kcal/mol[37]

$ZrH(\eta^5\text{-}C_6H_7)(dmpe)_2$ functions as a catalyst or a catalyst precursor for the hydrogenation of octene at low pressures. Under the conditions indicated in eq 8 a *minimum* rate of 7.8 turnovers/h was achieved.



(8)

Kinetics of $ZrH(\eta^5\text{-}C_6H_7)(dmpe)_2$ Catalyzed Cyclohexadiene Disproportionation. Reaction 1 (Table V) was monitored by ^1H NMR and the disappearance of cyclohexadiene was found to follow first-order kinetics over the concentration ranges 2.63–0.53 M in 1,3-cyclohexadiene and 0.15–0.0043 M in catalyst. Rate constants, k_{obsd} according to eq 9, are collected in Table VI.

$$-d[C_6H_8]/dt = k_{obsd}[C_6H_8] \qquad (9)$$

Considerable difficulty was encountered in reproducibly preparing dilute stock solutions of the catalyst at known concentrations because of its high air and moisture sensitivity. Rate constants measured for reaction 1 (Table V) with samples prepared from

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(33) Computed from data in: Stull, D. R.; Westrum, E. F., Jr.; Sinke, G. C. "The Chemical Thermodynamics of Organic Compounds"; Wiley: New York, 1969.

Table VI. Rate Constants[a] for the $ZrH(\eta^5\text{-}C_6H_7)(dmpe)_2$ Catalyzed Disproportionation of 1,3-Cyclohexadiene

expt	T, °C	[catalyst], M	$[C_6H_8]_{initial}$, M	$10^5 k_{obsd}$, s^{-1}	$10^3 k$,[b] $M^{-1} s^{-1}$
1[c]	79	0.013	0.53	2.42 ± 0.21	1.86 ± 0.16
2[c]	79	0.0098	0.53	1.75 ± 0.15	1.78 ± 0.15
3[c]	89.5	0.0098	0.53	5.09 ± 0.27	5.19 ± 0.27
4[c]	100	0.0098	0.53	9.16 ± 0.60	9.36 ± 0.61
5[c]	79	0.0072	0.53	1.30 ± 0.07	1.81 ± 0.09
6[c]	79	0.0043	0.53	0.77 ± 0.09	1.79 ± 0.21
7[d]	79	0.0152	2.63	1.87 ± 0.13	1.23 ± 0.09
8[d]	79	0.0152	2.10	1.80 ± 0.09	1.18 ± 0.06
9[d]	79	0.0152	1.58	1.71 ± 0.12	1.12 ± 0.08
10[d]	79	0.0152	1.05	1.84 ± 0.16	1.21 ± 0.11

[a] Errors are the standard error derived from the least-squares fits. [b] Second-order rate constant according to eq 10. [c] Samples prepared from the same catalyst stock solution with [catalyst] = 0.0144 M; see text. [d] Samples prepared from the same catalyst stock solution with [catalyst] = 0.0218 M; see text.

different batches of stock solution varied by as much as a factor of 2. However, samples prepared from the same batch of stock solution gave highly reproducible rates. Consequently, while the accuracy of the rate constants in Table VI is not high, the relative rates of samples prepared from the same stock solution are reliable.

The pseudo-first-order rate constant, k_{obsd}, shows a linear dependence on catalyst concentration and has a zero intercept (eq 10), implying the second-order rate law shown in eq 11. Second-order rate constants, derived according to eq 10 are presented in Table VI. As shown by experiments 7–10, k is independent of $[C_6H_8]$ up to 2.63 M; no evidence for saturation or deviation from second-order kinetics was observed at high concentrations of cyclohexadiene.

$$k_{obsd} = k[ZrH(\eta^5\text{-}C_6H_7)(dmpe)_2] \tag{10}$$

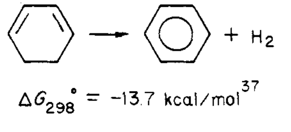
$$\frac{-d[C_6H_8]}{dt} = k[ZrH(\eta^5\text{-}C_6H_7)(dmpe)_2][C_6H_8] \tag{11}$$

A plot of ln k against $1/T$ gives an activation energy of 20.3 ± 3.2 kcal/mol.

Discussion

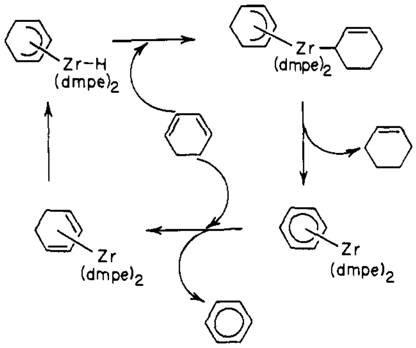
Although the formation of $ZrH(\eta^5\text{-}C_6H_7)(dmpe)_2$ may occur by a complex mechanism, the basic steps presumably involve trapping of a low-valent Zr phosphine complex by cyclohexadiene and insertion into the allylic C–H bond. Numerous examples of addition of transition-metal complexes to the allylic C–H bonds of complexed olefins[34] and dienes[35] are known. For example, cocondensation of 1,3-cyclohexadiene, $P(OMe)_3$, and iron atoms affords $Fe(\pi^4\text{-}C_6H_8)[P(OMe)_3]_3$ and $FeH(\eta^5\text{-}C_6H_7)[P(OMe)_3]_2$.[35] Further, coordinatively unsaturated group 4 complexes appear to be particularly reactive toward sp^3 CH bonds, as suggested by reactions involving insertion into alkyl C–H groups attached to coordinated cyclopentadienyl ligands.[36]

Since thermal decomposition of $ZrH(\eta^5\text{-}C_6H_7)(dmpe)_2$ liberates hydrogen, benzene, and, presumably, a low-valent Zr complex (eq 12), it seemed plausible that decomposition in the presence of cyclohexadiene would allow regeneration of $ZrH(\eta^5\text{-}C_6H_7)(dmpe)_2$ and catalytic dehydrogenation of cyclohexadiene. However, heating $ZrH(\eta^5\text{-}C_6H_7)(dmpe)_2$ with excess 1,3-cyclohexadiene does not result in the evolution of hydrogen; rather, the substrate is disproportionated according to reaction 1 (Table V), $\Delta G_{298}° = -16.4$ kcal/mol.[37] Derivatives of Vaska's compound,[38] $(\eta^4\text{-}C_6H_8)(\eta\text{-}C_5Me_5)Rh$,[39] $[Rh(norbornadiene)_2]BF_4$,[40] and cyclohexadiene complexes of iron[35,41] and ruthenium[42] have also been reported to catalyze cyclohexadiene disproportionation, and likely do so by a mechanism involving an η^5-cyclohexadienyl hydride.[35,39,42]



(12)

Scheme I



A plausible mechanism is shown in Scheme I. The first-order dependence on cyclohexadiene concentration suggests a step involving association of substrate is the slowest. Benzene and cyclohexene are, apparently, eliminated irreversibly and do not effectively compete with cyclohexadiene for coordination sites on the catalyst as no inhibition of disproportionation by these products is observed. This is consistent with the inability of terminal olefins to function as hydrogen acceptors in competition with cyclohexadiene itself. Since no saturation, i.e., deviation from the rate law in eq 9, was observed at the practical upper and lower limits of substrate and catalyst concentrations, respectively, the unimolecular steps proposed in Scheme I could not be kinetically observed.

It is noteworthy that the mechanism proposed in Scheme I operates on a Zr(II)–Zr(0) redox couple and requires a fast, reversible step creating a vacant coordination site prior to association of the substrate. We conclude that reductive elimination from Zr(II) complexes is not necessarily a slow reaction[43] and, consequently, that low-valent group 4 complexes are at least potentially useful catalysts for reactions involving C–H[11] and C–C[44] bond formation. Further, although $ZrH(\eta^5\text{-}C_6H_7)(dmpe)_2$ has at least a kinetically accessible vacant coordination site and reacts readily with ligated C–H bonds, no interaction with unfunctionalized alkanes was observed.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science and Engineering Research Council of Canada for support of this research.

Supplementary Material Available: A listing of observed and calculated structure factor amplitudes (14 pages). Ordering information is given on any current masthead page.

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(34) For example, see: (a) Lukas, J.; Coren, S.; Blom, J. E. *Chem. Commun.* **1969**, 1303. (b) Bonneman, H. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 736. (c) Byrne, J. W.; Blaser, H. U.; Osborn, J. A. *J. Am. Chem. Soc.* **1975**, *97*, 3871.

(35) Ittel, S. D.; Van-Catledge, F. A.; Jesson, J. P. *J. Am. Chem. Soc.* **1979**, *101*, 3874.

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

(37) Janz, G. J. *J. Chem. Phys.* **1954**, *22*, 751.

(38) Lyons, J. E. *Chem. Commun.* **1969**, 564.

(39) Moseley, K.; Maitlis, P. M. *J. Chem. Soc. A* **1970**, 2884.

(40) Green, M.; Kuc, T. A. *J. Chem. Soc., Dalton Trans.* **1972**, 832.

(41) Williams-Smith, D. L.; Wolf, L. R.; Skell, P. S. *J. Am. Chem. Soc.* **1972**, *94*, 4042.

(42) Chaudret, B. N.; Cole-Hamilton, D. J.; Wilkinson, G. *Acta Chem. Scand., Ser. A* **1978**, *32*, 763.

(43) Reductive elimination from Zr(IV) cyclopentadienyl complexes does occur and is assisted by nucleophiles.[5]

(44) Datta, S.; Fischer, M. B.; Wreford, S. S. *J. Organomet. Chem.*, **1980**, *188*, 353.