analogues.[1] The insensitivity of these structures to the electronic properties of the ligand X (and hence the electronic properties of the Zr center[10]) suggests that the steric difference between the C_5Me_5 and C_5H_5 ligands is the major effect responsible for the remarkable structural difference between 2 and 3.[12-14]

Acknowledgment. Support from the Department of Energy, Division of Basic Energy Sciences, is gratefully acknowledged.

Registry No. 1, 84303-39-9; 3, 88657-67-4; Cp_2ZrCl_2, 1291-32-3; $K[CpFe(CO)_2]$, 60039-75-0; $Cp_2Zr(I)[Fe(CO)_2Cp]$, 88657-68-5; $Cp_2Zr[Fe(CO)_2Cp]_2$, 88657-69-6; $Cp_2Zr(Cl)[Ru(CO)_2Cp]$, 84303-40-2; $Cp_2[(CH_3)_3CO]Zr–Fe(CO)_2Cp$, 84303-42-4; Cp_2ZrI_2, 1298-41-5; $K[CpRu(CO)_2]$, 84332-45-6; $Cp_2Zr(I)Ru(CO)_2Cp$, 88657-70-9.

Supplementary Material Available: Details of the X-ray structure solution, listings of fractional coordinates, thermal parameters, bond distance, bond angles, and structure factors (27 pages). Ordering information is given on any current masthead page.

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(10) Marsella, J. A.; Moloy, K. G.; Caulton, K. G. *J. Organomet. Chem.* **1980**, *201*, 389.

(11) Skora, D. J.; Rausch, D. J.; Rogers, R. D.; Atwood, J. L. *J. Am. Chem. Soc.*, **1981**, *103*, 1265 and references therein.

(12) Martin and Moise have noted that the degree of substitution of the cyclopentadienyl rings Cp^1 strongly affects the nature of the V–Co complexes formed in the reaction of Cp^1_2V with $Co_2(CO)_8$.[13] Vanadocenes with unsubstituted or monosubstituted Cp^1 rings gave as initial products V–CO complexes formulated as $Cp^1_2V–Co(CO)_4$ on the basis of their IR spectra. Vanadocenes with peralkylated Cp^1 rings gave as initial products species with low νCO's (1755 cm^{-1}) indicative of V–OC interactions, possibly of the type observed in $(C_5Me_5)_2Yb(THF)OCCo(CO)_3$.[14]

(13) Martin, J.; Moise, C. *J. Organomet. Chem.* **1982**, *232*, C55.

(14) Tilley, T. D.; Anderson, R. A. *J. Chem. Soc., Chem. Commun.* **1981**, 985.

Synthesis and Crystal Structure of *syn*,*syn*-Bis(η^3-pentadienyl)bis(trimethylphosphine)iron

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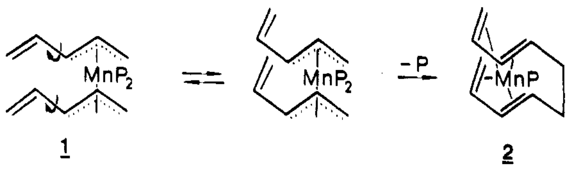
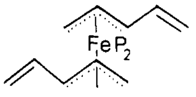
Received October 8, 1983

Summary: Reaction of $FeCl_2[P(CH_3)_3]_2$ with potassium pentadienide results in the formation of *syn*,*syn*-bis(η^3-pentadienyl)bis(trimethylphosphine)iron (**3**). The crystal structure of **3**, as determined by a single-crystal X-ray diffraction study, is reported. Unlike the analogous manganese system, coupling of the pentadienyl ligands is not observed. This stability with respect to coupling is thought to derive from the staggered orientation of the two pentadienyl ligands.

Recently, we reported the stereoselective coupling of two acyclic pentadienyl ligands on a manganese center and the isolation of a manganese–trimethylphosphine complex of the coupled product (2, Scheme I).[1] The stereochemistry of the coupled product, *trans*,*trans*-1,3,7,9-decatetraene, led us to postulate *syn*,*syn*-bis(η^3-pentadienyl)bis(trimethylphosphine)manganese (1, Scheme I) as the critical intermediate. The two η^3-pentadienyl ligands in 1 are required to have the eclipsed orientation shown. We now report the isolation and full structural characterization of *syn*,*syn*-bis(η^3-pentadienyl)bis(trimethylphosphine)iron (3),[2] the first structurally characterized mononuclear *syn*-(η^3-pentadienyl)metal complex.[3,4] 3 differs from the postulated coupling intermediate in the manganese system (1) in that the two pentadienyl ligands have a staggered orientation. Apparently, the barrier associated with rearrangement from this staggered orientation to the required eclipsed one is sufficient to stabilize 3 with respect to pentadienyl ligand coupling.[5]

Scheme I





3

The reaction of $FeCl_2[P(CH_3)_3]_2$[6] with potassium pentadienide[7] in tetrahydrofuran at −78 °C, followed by warming to room temperature, produced red, pentane-soluble 3 in high yield.[8,10] A single-crystal X-ray diffraction study of 3 was carried out.[11] An ORTEP drawing

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(1) Bleeke, J. R.; Kotyk, J. J. *Organometallics* **1983**, *2*, 1263.

(2) The simple allyl analogue of 3, bis(η^3-allyl)bis(trimethylphosphine)iron, has not been reported.

(3) An unusual dinuclear complex, bis(pentadienyl)dinickel, has W-shaped pentadienyl ligands which are coordinated to two nickel atoms: Rienäcker, R.; Yoshiura, H. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 677.

(4) We recently synthesized and carried out a single-crystal X-ray diffraction study of η^3-2,4-dimethylpentadienyltris(trimethylphoshine)cobalt, the first example of a complex possessing an *anti*-η^3-pentadienyl ligand: Bleeke, J. R.; Peng, W.-J., submitted for publication.

(5) 3 decomposes to iron metal and unidentified organic products upon heating for several hours at 50 °C in benzene.

(6) Harris, T. V.; Rathke, J. W.; Muetterties, E. L. *J. Am. Chem. Soc.* **1978**, *100*, 6966.

(7) Yasuda, H.; Ohnuma, Y.; Yamauchi, M.; Tani, H.; Nakamura, A. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 2036.

(8) In a typical reaction, 1.89 g (1.5×10^{-2} mol) of $FeCl_2$ and 2.28 g (3.0×10^{-2} mol) of $P(CH_3)_3$ were refluxed in tetrahydrofuran for 1 h to form a pale green solution of $FeCl_2[P(CH_3)_3]_2$. This solution was added to 3.42 g (4.5×10^{-2} mol) of $P(CH_3)_3$, and the mixture was cooled to −78 °C; 4.46 g (2.5×10^{-2} mol) of potassium pentadienide–tetrahydrofuran ($KC_5H_7 \cdot C_4H_8O$) was then added over a period of 25 min, producing a dark reddish brown solution. This solution was stirred for 3 h while warming to room temperature, filtered through Celite, and evaporated to dryness. The dark red product, 3, was extracted with pentane and crystallized from pentane at −30 °C; yield (based on limiting reagent, $KC_5H_7 \cdot C_4H_8O$) 3.85 g (90%). Alternatively, 3 can be synthesized by adding $P(CH_3)_3$ to a solution of bis(pentadienyl)iron[9] at −78 °C and warming to room temperature. In a typical reaction, 1.78 g (1.0×10^{-2} mol) of $KC_5H_7 \cdot C_4H_8O$ in 30 mL of tetrahydrofuran was added dropwise to a slurry of 0.75 g (5.92×10^{-3} mol) of $FeCl_2$ in 30 mL of tetrahydrofuran at −78 °C, producing a red solution. After stirring at −78 °C for 20 min, a solution of 0.80 g (1.0×10^{-2} mol) of $P(CH_3)_3$ in 10 mL of tetrahydrofuran was added dropwise. The mixture was warmed to room temperature and stirred for 3 h. The resulting dark reddish brown solution was filtered through Celite and evaporated to dryness. 3 was extracted with pentane and crystallized from pentane at −30 °C; yield (based on limiting reagent, $KC_5H_7 \cdot C_4H_8O$) 1.2 g (70%).

(9) (a) The synthesis of bis(η^5-pentadienyl)iron has been reported.[9b] However, the species which is formed at −78 °C in our reaction system may be bis(η^3-pentadienyl)iron. (b) Wilson, D. R.; Ernst, R. D.; Cymbaluk, T. H. *Organometallics* **1983**, *2*, 1220.

(10) ^1H NMR (22 °C, benzene-d_6, 100 MHz) δ 0.86–0.98 (m, 9, $P(CH_3)_3$), 1.09–1.31 (m, 4, allylic H's), 5.02–5.23 (m, 3, vinylic H's); $\{^1H\}^{13}C$ NMR (22 °C, benzene-d_6, 25.14 MHz) δ 145.08 (C_4), 106.82 (C_5), 86.85 (C_2), 55.69 (C_3), 36.38 (C_1), 18.60 ($P(CH_3)_3$); IR (toluene) 1607 (C=C stretch), 937, 949 cm^{-1} (P—C stretch). Anal. Calcd for $FeP_2C_{16}H_{32}$: C, 56.14; H, 9.44. Found: C, 55.84; H, 9.24.

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Table I. Selected Bond Distances (Å) and Bond Angles (deg) with Estimated Standard Deviations for *syn,syn*-Bis(η^3-pentadienyl)bis(trimethylphosphine)iron (3)

Bond Distances

Fe-P	2.211 (1)	C1-C2	1.397 (3)	P-C1M	1.837 (3)
Fe-C1	2.115 (2)	C2-C3	1.406 (3)	P-C2M	1.835 (3)
Fe-C2	2.034 (2)	C3-C4	1.457 (3)	P-C3M	1.836 (3)
Fe-C3	2.226 (2)	C4-C5	1.302 (3)		

Bond Angles

P-Fe-P′	96.36 (4)	P-Fe-C2′	111.87 (6)	C3-Fe-C3′	105.1 (1)
P-Fe-C1	83.29 (6)	P-Fe-C3′	86.17 (6)	C1-C2-C3	120.5 (2)
P-Fe-C2	116.99 (6)	C1-Fe-C1′	177.7 (1)	C2-C3-C4	121.7 (2)
P-Fe-C3	151.37 (6)	C1-Fe-C3	68.14 (8)	C3-C4-C5	127.3 (3)
P-Fe-C1′	98.28 (7)	C1-Fe-C3′	110.33 (8)		

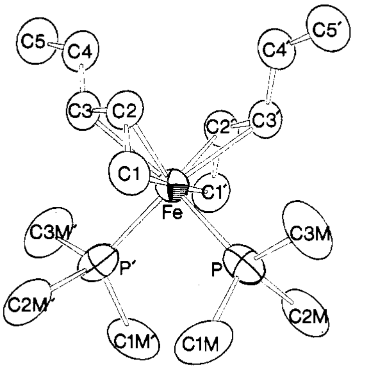
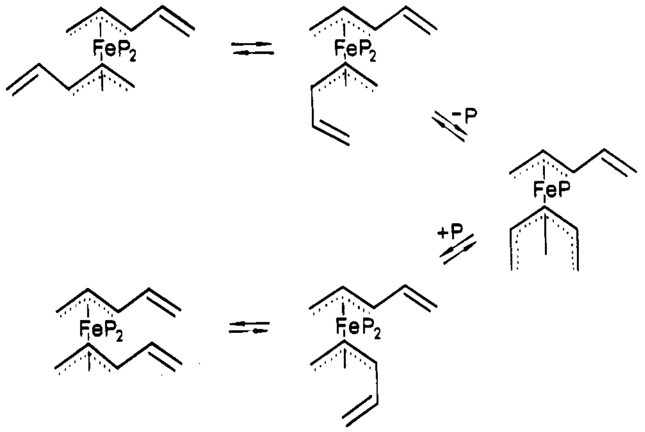


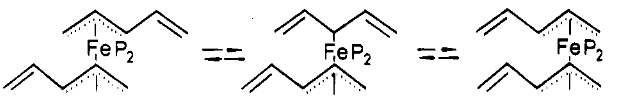
Figure 1. ORTEP drawing for *syn,syn*-bis(η^3-pentadienyl)bis(trimethylphosphine)iron (3). Atoms are represented by thermal vibration spheres drawn to encompass 50% of the electron density. All hydrogen atoms are omitted for clarity.

of the molecular structure is shown in Figure 1, and selected bond distances and angles are given in Table I. The molecular geometry is pseudooctahedral; the six coordination sites around the iron atom are occupied by the two C_1 atoms and two C_3 atoms of the pentadienyl ligands and the two P atoms of the mutually cis $P(CH_3)_3$ ligands.[12,13] The central iron atom resides on a crystallographically imposed C_2 axis which bisects the P–Fe–P angle. The two trimethylphosphine ligands and the two pentadienyl ligands are symmetry related by this 2-fold rotation axis.

Scheme II



Scheme III



The pentadienyl ligands are oriented so that the mouths of their allylic (iron-bound) moieties face $P(CH_3)_3$ ligands (i.e., the mouth made by C_1, C_2, and C_3 faces P′).[14] C_1 of one pentadienyl ligand is trans to C_1 of the other pentadienyl ligand, while the two C_3 atoms are trans to phosphorus atoms. As a result of the trans influence exerted by the trimethylphosphine ligands, Fe–C_3 is significantly longer than Fe–C_1 (2.226 (2) vs. 2.115 (2) Å).[15] Fe–C_2 is the shortest of the Fe–(allylic carbon) bonds.[16] The η^3-pentadienyl ligands are W-shaped, i.e., C_1 is anti to C_4, and C_2 is anti to C_5. C_1, C_2, C_3, and C_4 are coplanar, while C_5 lies 0.26 Å out of the plane away from the iron atom. The dihedral angle between plane C_1–C_2–C_3 and plane C_3–C_4–C_5 is 16.7°. The C–C bond distances within the allylic moiety of the pentadienyl ligand are 1.397 (3) Å for C_1–C_2 and 1.406 (3) Å for C_2–C_3. Bond C_3–C_4, which is a C–C single bond, has a length of 1.457 (3) Å, while bond C_4–C_5, a C–C double bond, has a length of 1.302 (3) Å. Angles C_1–C_2–C_3 and C_2–C_3–C_4 are very near the ideal of 120° (120.5 (2) and 121.7 (2)°, respectively). Angle C_3–C_4–C_5

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[11] Crystals suitable for X-ray diffraction were grown from a saturated pentane solution at −30 °C. The single crystals were monoclinic, space group $C2/c$ (No. 15), with a = 14.746 (4) Å, b = 9.201 (3) Å, c = 14.021 (3) Å, β = 92.66 (2)°, V = 1900.3 Å^3, and Z = 4. X-ray diffraction data were collected at room temperature on a Nicolet P3 diffractometer, using graphite monochromated Mo Kα radiation. A total of 3696 independent reflections with 3° < 2θ < 50° were collected, by employing the ω scanning technique and a variable scan rate of 3.0–29.3°/min. All of the data reduction and structure refinement was done with a modified Enraf-Nonius structure determination package (modified by B. A. Frenz and Associates, Inc., College Station, TX) on a VAX 11/780 computer; 1958 of the reflections were systematically absent and only the 1501 independent reflections with intensities greater than three times their esd's were used in the least-squares refinements. An absorption correction was not made. The iron atom was located from a three-dimensional Patterson map; it resided on the 2-fold rotation axis. Two cycles of least-squares refinement of the iron atom position, followed by a difference Fourier map, revealed the locations of the phosphorus atom and the three allylic carbon atoms of the pentadienyl ligand. After two further least-squares refinement cycles, a difference Fourier map revealed the positions of the remaining two pentadienyl carbon atoms and the three trimethylphosphine carbon atoms. The positions and isotropic thermal parameters of the 10 unique non-hydrogen atoms were refined by several additional least-squares cycles to give agreement indices of R = 0.109 and R_w = 0.166. Refinement of anisotropic thermal parameters for the 10 non-hydrogen atoms produced agreement indices of R = 0.0567 and R_w = 0.0999. A difference Fourier map at this point revealed the positions of the molecule's 16 unique hydrogen atoms. The positions of the hydrogen atoms were refined, while their isotropic thermal parameters were fixed at β = 5.0 Å^2. The convergence values of the agreement indices were R = 0.0312 and R_w = 0.0422. A final difference Fourier map showed no peaks with electron density greater than 0.3 e$^-$/Å^3.

[12] The coordination geometries of allyl–metal complexes are, in general, best described by treating the allyl group as a bidentate ligand: Putnik, C. F.; Welter, J. J.; Stucky, G. D.; D'Aniello, M. J., Jr.; Sosinsky, B. A.; Kirner, J. F.; Muetterties, E. L. *J. Am. Chem. Soc.* **1978**, *100*, 4107.

[13] The octahedral L–M–L angles are distorted somewhat because of the small bite angles of the η^3-pentadienyl ligands.

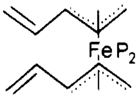
[14] A similar orientation has been observed for the two allyl groups in the related compound, bis(η^3-2-methylallyl)bis(trimethyl phosphite)ruthenium: Marsh, R. A.; Howard, J.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1973**, 778.

[15] A similar weakening of the M–(allyl C) bonds trans to phosphite ligands has been observed in bis(η^3-2-methylallyl)bis(trimethyl phosphite)ruthenium: see ref 14.

[16] In allyl-metal complexes, it is common for the M–(terminal C) distances to be longer than the M–(internal C) distances: see ref 12.

is somewhat larger, 127.3 (3)°.

The hypothetical coupling of the pentadienyl groups in **3** to produce the iron analogue of **2** requires an eclipsed orientation for the two *syn*-η^3-pentadienyl ligands. A simple rotation of one pentadienyl group about an axis drawn from the center of the allylic moiety to the iron atom will not bring the two pentadienyl ligands in **3** into register, neither will the twist mechanism proposed by Green et al.[17] to account for the observed left-to-right exchange process in bis(η^3-2-methylallyl)bis(trimethyl phosphite)ruthenium.



3 after rotation about
Fe-(allyl group) axis

However, several mechanisms which will enable the two pentadienyl ligands to assume the eclipsed configuration can be envisaged. The first (Scheme II) commences with a *syn*-η^3- → *anti*-η^3-pentadienyl ligand isomerization. Subsequent loss of a phosphine ligand enables the uncomplexed double bond (C_4–C_5) of the *anti*-η^3-pentadienyl ligand to coordinate to the iron atom, producing an (η^5-pentadienyl)(η^3-pentadienyl)(trimethylphosphine)iron intermediate. Dissociation of C_1–C_2 (η^5-pentadienyl ligand) from the iron atom, recoordination of $P(CH_3)_3$, and isomerization of the *anti*-η^3-pentadienyl ligand back to the syn form produce *syn,syn*-bis(η^3-pentadienyl)bis(trimethylphosphine)iron with the desired eclipsed geometry. A second mechanism (Scheme III) involves a $\pi \rightarrow \sigma$ pentadienyl isomerization, affording a C_3-bound σ-pentadienyl ligand. Coordination of the C_4–C_5 double bond then yields *syn,syn*-bis(η^3-pentadienyl)bis(trimethylphosphine)iron with eclipsed pentadienyl ligands. A variation on this mechanism involves sliding the Fe atom in a concerted fashion from one end of a pentadienyl ligand (C_1, C_2, C_3) to the other end (C_3, C_4, C_5). In this case, the iron atom would remain π-bonded to the pentadienyl ligand throughout.[18] The stability of **3** with respect to pentadienyl coupling suggests that none of these postulated mechanisms for rearranging the pentadienyl ligands is facile in the iron system.[19] In the manganese system, on the other hand, a low-energy mechanism for bringing the pentadienyl ligands into register does exist and is responsible for the observed coupling reaction.

We are continuing to study this and other pentadienylmetal–phosphine reaction systems.

Acknowledgment. We thank the Research Corporation for providing funding for an inert-atmosphere drybox. Additional support was provided by the donors of the Petroleum Research Fund, administered by the American Chemical Society, and by BRSG S07 RR07054-17, awarded by the Biomedical Research Support Grant Program, Division of Research Resources, National Institues of Health. We thank Professor G. G. Stanley for assistance with the single-crystal X-ray diffraction study of **3** and Dennis Moore for synthetic help.

Registry No. **3**, 88765-93-9; $FeCl_2[P(CH_3)_3]_2$, 55853-16-2; KC_5H_7, 51391-25-4; $FeCl_2$, 7758-94-3; $P(CH_3)_3$, 594-09-2; bis(pentadienyl)iron, 74910-62-6.

Supplementary Material Available: A complete listing of final atomic coordinates, thermal parameters, bond lengths, bond angles, and observed and calculated structure factor amplitudes, as well as a table of several significant least-squares planes including subtended dihedral angles (15 pages). Ordering information is given on any current masthead page.

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[17] Cooke, M.; Goodfellow, R. J.; Green, M.; Parker, G. *J. Chem. Soc. A* **1971**, 16.

[18] Other mechanisms, such as those involving initial formation of a C_1-bound σ-pentadienyl–metal intermediate, can be envisaged.

[19] ^1H and ^{13}C NMR studies give no indication that either process is occurring up to the decomposition temperature of **3**.

Oxidative Addition of Rhodium to Alkane C–H Bonds: Enhancement in Selectivity and Alkyl Group Functionalization

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Received January 11, 1984

Summary: UV irradiation of (η^5-C_5Me_5)$RhPMe_3H_2$ (**2**) in alkanes below −30 °C results in the formation of (η^5-C_5Me_5)$RhPMe_3$(R)(H) (**4**) with significantly greater selectivity toward different C–H bonds than the iridium analogue. Treatment of the thermally labile complexes **4** with $CHBr_3$ gave the corresponding halides (η^5-C_5Me_5)$RhPMe_3$(R)(Br) (**5**); reaction of **5** with Br_2 at 25 °C results in the formation of (η^5-C_5Me_5)$RhPMe_3Br_2$ (**7**) and bromoalkane.

Recently several examples of homogeneous oxidative addition of alkane C–H bonds to iridium centers have been discovered.[1] Jones and Feher[2] recently reported the use of the rhodium complex (η^5-C_5Me_5)$Rh(PMe_3)H_2$ (compound **2** in Scheme I) to activate the C–H bonds in benzene and *n*-propane. We have been independently examining this rhodium system, in order to compare its generality, selectivity, and functionalizing ability with those of the iridium system we reported earlier.[1a,c] Accordingly, we have irradiated **2** in a number of liquid hydrocarbons. As in the Ir case, the reaction is quite general, and no hydrocarbon has yet been found whose C–H bonds are unreactive. Our results demonstrate that the selectivity of the Rh system is greater than that of the Ir system and that at least one alkane functionalization method is more effective. In addition, we have obtained several haloalkylrhodium derivatives of the C–H activation products in analytically pure form and have succeeded in determining the structure of one of these by X-ray diffraction.

Dihydride **2** was prepared[3,4] in 85% yield and analytical purity as shown in Scheme I. Irradiation of **2** at room temperature resulted in loss of H_2 and formation of a dark, as yet unidentified, product (presumably a cluster complex), but no new hydrides. However, when irradiation was carried out below −30 °C, the formation of new alkyl hydrides **4** (Scheme I) was observed by ^1H NMR. Cyclopropane is an especially efficient substrate despite the very high dissociation energy (106 kcal/mol)[5] of its C–H bonds.

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[1] (a) Janowicz, A. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1982**, *104*, 352. (b) Hoyano, J. K.; Graham, W. A. G. *Ibid.* **1982**, *104*, 3723. (c) Janowicz, A. H.; Bergman, R. G. *Ibid.* **1983**, *105*, 3929.

[2] Jones, W. D.; Feher, F. J. *Organometallics* **1983**, *2*, 562.

[3] Spectral data on this material have also been reported in ref 2 and by: Isobe, K.; Bailey, P. M.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1981**, 2003.

[4] Supplementary information provided with this paper includes (a) low-temperature ^1H NMR data for hydridoalkylrhodium complexes **4a**, **4b**, and **4c**; (b) spectral and analytical data for complexes **2**, **5a**, **5b**, and **5c**; and (c) details of the X-ray structure determination of complex **5c**.

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