nance in the ^{125}Te{^{1}H} NMR spectrum at 370.1 ppm. The ^{125}Te NMR spectrum of a sample of LiTePh in THF gave a resonance in the ^{125}Te{^{1}H} NMR spectrum at 133.9 ppm. Anal. Calcd for $C_{32}H_{54}Ga_2Te_2$: C, 46.12; H, 6.53. Found: C, 46.41; H, 6.63. IR (Nujol, cm^{-1}): 3070 (vw), 3055 (vw), 1571 (m), 1430 (m), 1358 (m), 1232 (m), 1133 (m), 1099 (m), 1062 (vw), 1055 (vw), 1011 (m), 999 (w, sh), 994 (m), 795 (vw, br), 740 (w), 720 (s), 648 (w), 618 (m), 449 (w).

Crystallography. A colorless crystal of $(Me_3CCH_2)_2GaTePh$ was selected and sealed in a glass capillary under an argon atmosphere for examination by X-ray diffraction procedures. Data were collected on an Enraf-Nonius CAD-4 diffractometer by using graphite-monochromated Mo Kα radiation. Table III summarizes the unit cell data and the refinement parameters. Unit cell dimensions were determined by least-squares refinement of 25 reflections ($20.0° < 2\theta < 26.8°$). Three standard reflections were remeasured after every 1 h of X-ray exposure. The data were corrected for a slow, steady decrease of intensity over time. The maximum correction was 1.230 on *I*. An empirical absorption correction[21] was applied. Correction factors ranged from 0.85 to 1.31.

The structure of $(Me_3CCH_2)_2GaTePh$ was solved by direct methods with use of MULTAN 11/82.[22] An E-map phased with the best phase set gave the four heavy-atom positions. Subsequent difference electron density maps allowed location of the remaining atoms. All hydrogen atoms were included in the refinement, except that those on methyl groups were fixed at calculated positions riding on the parent carbon atoms. Positional parameters, excluding those for the hydrogen atoms, are given in Table IV.

Acknowledgment. This work was supported in part by the Office of Naval Research and by a generous grant from Eastman Kodak Co.

Supplementary Material Available: Tables of refined temperature factors for $[(Me_3CCH_2)_2GaTePh]_2$, hydrogen atom positional parameters, and carbon–carbon bond distances and angles (7 pages); a table of structure factors (29 pages). Ordering information is given on any current masthead page.

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[21] Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 159.

[22] Programs used in this study were from the Structure Determination Package: SDP-PLUS; Enraf-Nonius: Delft, Holland, 1985; Version 3.0.

Substituted Cyclopentadienyl Phosphinomethyl Complexes of Zirconium. Synthesis, Chemical Characteristics, Complexation with Rhodium Complexes, and Catalytic Properties. Molecular and Crystal Structure of $(\eta^5\text{-}t\text{-}BuC_5H_4)_2Zr(CH_2PPh_2)_2[Rh_2(\mu\text{-}S\text{-}t\text{-}Bu)_2(CO)_2]$†

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Summary: The synthesis of $Cp'_2Zr(CH_2PPh_2)_2$ (**1**) and $Cp'_2ZrCl(CH_2PPh_2)$ (**2**) ($Cp' = \eta^5\text{-}t\text{-}BuC_5H_4$) is reported. The ^{1}H NMR spectrum of **2** shows four separate ring proton absorptions, unambiguously assigned by decoupling experiments and simulated spectra. Reduction of **2** with Na/Hg produces a paramagnetic Zr(III) species formulated as $Cp'_2Zr(CH_2PPh_2)$ (**3**). Reduction of **1** with sodium naphthalenide leads to the monocyclopentadienyl $Cp'Zr(CH_2PPh_2)_2$ species **6** characterized by EPR features and simulated spectra. Evolution of **6** gives the hydridozirconium(III) species **7** able to hydrogenate, in a catalytic way, various olefins. Reactions of **1** with the cationic rhodium complex $Rh(COD)(PPh_3)_2BPh_4$ and the neutral dinuclear complex $Rh_2(\mu\text{-}S\text{-}t\text{-}Bu)_2(CO)_4$ produces the bimetallic complexes $Cp'_2Zr(CH_2PPh_2)_2[Rh(COD)]BPh_4$ (**8**) and $Cp'_2Zr(CH_2PPh_2)_2[Rh_2(\mu\text{-}S\text{-}t\text{-}Bu)_2(CO)_2]$ (**9**), respectively. The X-ray structure of **9** was determined, giving the following crystal data: space group $P2_1/n$, $a = 14.320$ (2) Å, $b = 19.488$ (3) Å, $c = 19.405$ (2) Å, $\beta = 95.08$ (2)°, $V = 5394$ Å^3, $Z = 4$. The crystal structure displays relatively normal Zr and Rh geometric environments. Results for the catalytic hydroformylation of 1-hexene with **9** can be related to the *t*-Bu electronic effect.

We are interested in ((diphenylphosphino)methyl)zirconium and -titanium chemistry, and our previous results have shown that (i) the cyclometalated Zr(III) species $Cp_2Zr(CH_2PPh_2)$ ($Cp = \eta^5\text{-}C_5H_5$) (or $CpM(CH_2PPh_2)_2$ with M = Ti, Zr) is an active precursor in the catalytic hydrogenation of olefins.[1,2] and (ii) d^0–d^8 [Zr,Rh] and [Ti,Rh] bimetallic systems,[3-7] synthesized due to the ability of the zirconium diphosphine (or titanium diphosphine) to complex rhodium compounds, were demonstrated to be efficient hydroformylation catalysts.[5,8-10]

The aim of the present work is to determine whether the introduction of an R group on the cyclopentadienyl ligand makes it possible to achieve a different catalytic behavior. We have focused our attention on new substi-

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† Dedicated to the memory of Professor D. Gervais.

[1] Choukroun, R.; Basso-Bert, M.; Gervais, D. *J. Chem. Soc., Chem. Commun.* **1986**, 1317.

[2] Choukroun, R.; Delaveau, B.; Raoult, Y.; Gervais, D. Unpublished results.

[3] Choukroun, R.; Gervais, D. *J. Organomet. Chem.* **1984**, *266*, C37.

[4] Etienne, M.; Choukroun, R.; Basso-Bert, M.; Dahan, F.; Gervais, D. *Nouv. J. Chim.* **1984**, *8*, 531.

[5] Choukroun, R.; Gervais, D.; Jaud, J.; Kalck, P.; Senocq, F. *Organometallics* **1986**, *5*, 67.

[6] Choukroun, R.; Gervais, D.; Kalck, P.; Senocq, F. *J. Organomet. Chem.* **1987**, *335*, C9.

[7] Choukroun, R.; Iraqi, A.; Gervais, D.; Daran, J. C.; Jeannin, Y. *Organometallics* **1987**, *6*, 1197.

[8] Senocq, F.; Randrianalimanana, C.; Thorez, A.; Kalck, P.; Choukroun, R.; Gervais, D. *J. Chem. Soc., Chem. Commun.* **1984**, 1376.

[9] Choukroun, R.; Iraqi, A.; Gervais, D. *J. Organomet. Chem.* **1986**, *311*, C60.

[10] Senocq, F.; Randrianalimanana, C.; Thorez, A.; Kalck, P.; Choukroun, R.; Gervais, D. *J. Mol. Catal.* **1986**, *35*, 213.

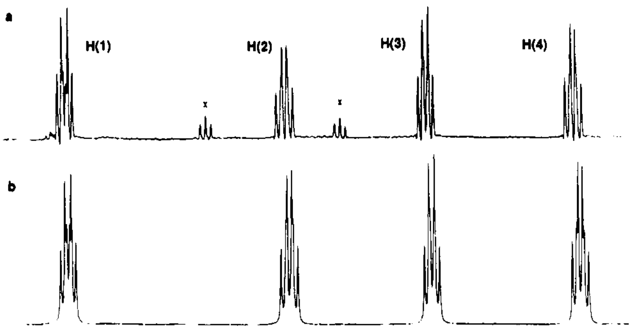

Figure 1. NMR spectra of $(\eta^5\text{-}t\text{-}BuC_5H_4)_2ZrCl(CH_2PPh_2)$ (**2**): (a) experimental spectrum (absorptions marked × are for $(\eta^5\text{-}t\text{-}BuC_5H_4)_2ZrCl_2$); (b) simulated spectrum.

tuted-cyclopentadienyl complexes, $(\eta^5\text{-}C_5H_4R)_2Zr(CH_2PPh_2)_2$ (**1**) and $(\eta^5\text{-}C_5H_4R)_2ZrCl(CH_2PPh_2)_2$ (**2**), with R = *t*-Bu as an electron-donating group in attempts to modify the basicity of the phosphorus atom that could govern the catalytic process. A comparison of the X-ray structure and hydroformylation catalytic data of $(\eta^5\text{-}t\text{-}BuC_5H_4)_2Zr(CH_2PPh_2)_2[Rh_2(\mu\text{-}S\text{-}t\text{-}Bu)_2(CO)_2]$ (**9**) with those of the nonsubstituted-cyclopentadienyl homologue will be discussed on the basis of the *t*-Bu influence.

Results and Discussion

Synthesis, Spectroscopic Characterization, and Reactivity of 1 and 2. Although the basic synthetic methodology used to prepare $(\eta^5\text{-}t\text{-}Bu\text{-}C_5H_4)_2Zr(CH_2PPh_2)_2$ (**1**) and $(\eta^5\text{-}t\text{-}Bu\text{-}C_5H_4)_2ZrCl(CH_2PPh_2)$ (**2**) is the same as that for the nonsubstituted-cyclopentadienyl zirconium homologues,[11-15] the reaction time and temperature conditions vary substantially due to the steric effect of the *tert*-butyl group. Attempts to improve the synthesis of **2** by redistribution reaction between **1** and $(\eta^5\text{-}t\text{-}BuC_5H_4)_2ZrCl_2$ or Me_3SiCl unfortunately gave a mixture of complexes, including the starting materials. Introduction of a substituent onto a cyclopentadienyl ring results in the remaining protons being magnetically nonequivalent. Thus, in **1**, the ring gives rise to two pseudotriplets of an A_2B_2 system in the ^1H NMR spectra, in agreement with the ^{13}C NMR spectra showing the nonequivalence of C(2), C(5) and C(3), C(4) bearing the hydrogen atoms of the ring. In complex **2**, the ^1H NMR spectrum shows for the cyclopentadienyl rings four separated proton absorptions (labeled H(1)–H(4); Figure 1a) as an AA′BB′ system. Irradiation of each of them clearly establishes that the four ring protons are magnetically nonequivalent. The $^1H\{^{31}P\}$ NMR spectrum results in a simplification of the H(1) and H(2) signals with $J(H(1)\text{–}P) = J(H(2)\text{–}P) = 0.8$ Hz, and from the analysis of these decoupling experiments, specific coupling constants were determined and given in Figure 2, in agreement with the simulated NMR spectrum (Figure 1b).

The reactivity of **1** toward CO and CO_2 was explored in THF and toluene solutions at room temperature under atmospheric pressure. No reaction with CO was observed under our experimental conditions. With CO_2, the carboxylate complex $(\eta^5\text{-}t\text{-}BuC_5H_4)_2Zr(O_2CCH_2PPh_2)_2$ (**3**) was obtained as an oily product, by CO_2 insertion into the metal–carbon bonds.[13]

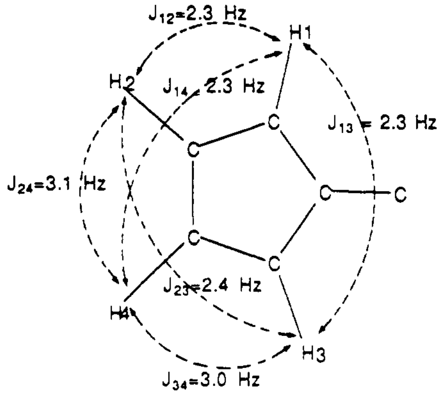

Figure 2. Coupling constant data for **2**.

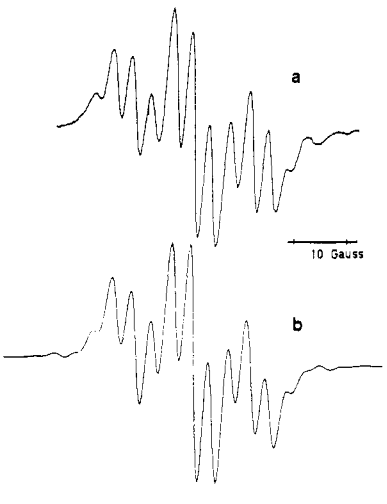

Figure 3. ESR spectra for **6**: (a) experimental spectrum, (b) simulated spectrum ($a(^1H) = 3.5$ G; $a(^{31}P) = 11.0$ G).

Reaction of **1** with CH_3I has been performed to give $(\eta^5\text{-}t\text{-}BuC_5H_4)_2ZrI_2$ (**4**) as a standard in order to trap and characterize paramagnetic species.[14]

Zirconium(III) Species: Chemical Reduction of 1 and 2 and Hydrogenation Catalysis. The chemical reduction of **2** with Na/Hg in THF gives an intense EPR signal, stable in THF solution, allowing the formulation $(\eta^5\text{-}t\text{-}BuC_5H_4)_2\overline{Zr(CH_2P}Ph_2)$ (**5**) by comparison with the species $Cp_2\overline{Zr(CH_2P}Ph_2)$ observed by Schore,[15] under the same experimental conditions. The ESR spectrum consists of a doublet, centered at $g = 1.982$, with $a(^{31}P) = 17.5$ G. No observable $a(^1H)$ value involving the methylene protons could be detected, in agreement with other data on the dicyclopentadienyl zirconium(III) species $Cp_2\overline{M(CH_2P}Ph_2)$ (M = Zr, Ti).[13,16]

The chemical reduction of **1** with sodium naphthalenide (Na(np)) in tetrahydrofuran solution recently reported in a preliminary study[14] can be described by the equations

$$1 + Na(np) \rightarrow \underset{\mathbf{6}}{(\eta^5\text{-}t\text{-}BuC_5H_4)\overline{Zr(CH_2P}Ph_2)_2} + NaCp' + np$$

$$6 \xrightarrow{\text{room temp}} \underset{\mathbf{7}}{(\eta^5\text{-}t\text{-}BuC_5H_4)\overline{ZrH(CH_2P}Ph_2)} + PPh_2Me$$

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(11) Schore, N. E.; Young, S. J.; Olmstead, M.; Hofmann, P. *Organometallics* **1983**, *2*, 1769.

(12) Choukroun, R.; Iraqi, A.; Rifai, C.; Gervais, D. *J. Organomet. Chem.* **1988**, *353*, 45.

(13) Etienne, M.; Choukroun, R.; Gervais, D. *J. Chem. Soc., Dalton Trans.* **1984**, 915.

(14) Choukroun, R.; Gervais, D.; Rifai, C. *J. Organomet. Chem.* **1989**, *368*, C11.

(15) Schore, N. E.; Hope, H. *J. Am. Chem. Soc.* **1980**, *102*, 4251.

(16) Young, S. J.; Olmstead, M.; Knudsen, M.; Schore, N. E. *Organometallics* **1985**, *4*, 1432.

Table I. Catalytic Hydrogenation of Olefins and Diolefins[a] with the Hydride Species 7

substrate	reacn time, min	% conversion	product obtained
1,5-cyclooctadiene[b]	120	100	88% cyclooctene, 12% cyclooctane
cyclooctene	240	43	cyclooctane
cyclohexene	40	45	cyclohexane
1-hexene	25	100	hexane
1,5-hexadiene	380	100	hexane

[a] Experimental conditions: 80 °C; 40 bar (H_2); solvent THF; [substrate]/[catalyst] = 300. [b] Intermediate formation of the 1,3-diene is detected.

Computer simulation was used to determine the isotropic magnetic parameters of 6 (Figure 3) with two equivalent phosphorus nuclei and four equivalent hydrogen nuclei ($a(^1H) = 3.5$ G; $a(^{31}P) = 11.0$ G; $a(^{91}Zr) = 21.0$ G).

The value $a(^{31}P) = 11$ G obtained for 6 could be compared to the value 11.6 G for $Cp_2Zr[P(C_6H_5)_2]^-$,[17] which contains a fully covalent Zr–P linkage.

The mechanism of the evolution 6 → 7 is unresolved, although recent mechanistic considerations on $Cp_2Zr(CH_2PPh_2)$ were recently reported by Schore,[18] but the formulation of 7 is unquestionably determined by comparison of its ESR signal (doublet of doublets; $a(^1H) = 6.0$ G; $a(^{31}P) = 25.5$ G) with those of other Zr(III) hydrides previously published[19-22] and by the evolution of methane and formation of the phosphonium salt PPh_2EtMeI when 7 is reacted with CH_3I as a trapping reagent.[14] It is worthy of note that the same chemical reduction was obtained in the presence of totally deuteriated naphthalene (C_8D_{10}) in THF-d_8 as solvent, which precludes their participation in the evolution of 6 to 7.[23]

Catalytic tests for the hydrogenation of olefins and diolefins were carried out with the hydride species 7 (checked by ESR spectroscopy before the catalytic runs). From the data collected in Table I, it appears that hydrogenation is quite rapid, but the selectivity for the formation of cyclooctene from 1,5-COD (1,5-cyclooctadiene) via isomerization of 1,3-COD is lost and partial hydrogenation of cyclooctene into cyclooctane can occur, in contrast with previous results obtained with $Cp_2ZrH(CH_2PPh_2)$ and $Cp_2Zr(CH_2PPh_2)$,[1,24] where 100% production of cyclooctene was reached.[1]

Bimetallic Complexes [Zr,Rh]: Synthesis and Catalytic Activity in Hydroformylation. Structure of $(\eta^5\text{-}t\text{-}BuC_5H_4)_2Zr(CH_2PPh_2)_2[Rh_2(\mu\text{-}S\text{-}t\text{-}Bu)_2(CO)_2]$ (9). With the goal of discussing the steric and electronic effects of the *t*-Bu group attached to the cyclopentadienyl ligand on the formation of bimetallic systems and the catalytic activity of these systems in hydroformylation of 1-hexene, we have reacted 1 with different rhodium complexes such as $RhH(PPh_3)_4$, $RhH(CO)(PPh_3)_3$, $[Rh_2(\mu\text{-}S\text{-}t\text{-}Bu)_2(CO)_4]$, and $Rh(COD)(PPh_3)_2BPh_4$. Only the last two compounds gave bimetallic systems according to the reactions

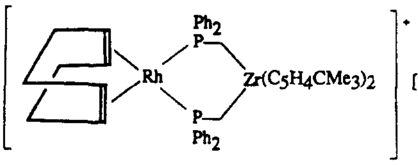

Figure 4.

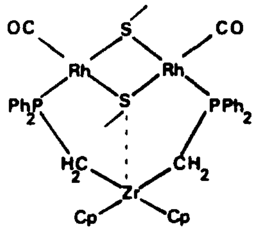

Figure 5.

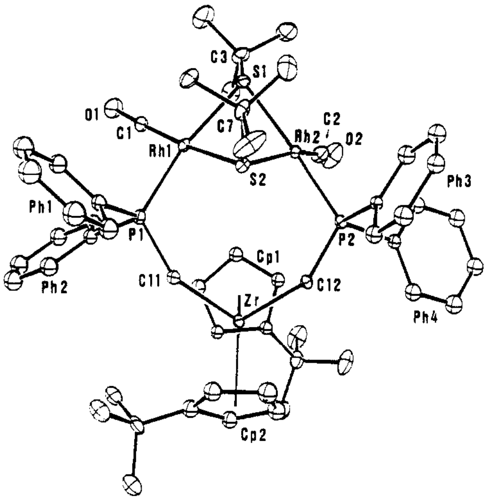

Figure 6. ORTEP diagram and atom-labeling scheme for 9.

$$1 + Rh(COD)(PPh_3)_2BPh_4 \rightarrow \underset{8}{[(\eta^5\text{-}t\text{-}BuC_5H_4)_2Zr(CH_2PPh_2)_2Rh(COD)]BPh_4} + 2PPh_3$$

$$1 + [Rh_2(\mu\text{-}S\text{-}t\text{-}Bu)_2(CO)_4] \rightarrow \underset{9}{(\eta^5\text{-}t\text{-}BuC_5H_4)_2Zr(CH_2PPh_2)_2[Rh_2(\mu\text{-}S\text{-}t\text{-}Bu)_2(CO)_2]} + 2CO$$

Complex 8 has a remarkable structure: the cis position of COD on the rhodium center forced the cis chelation of the zirconium diphosphine 1[25] (Figure 4).

Keeping in mind that 11 shows a strong interaction between one of the sulfur atoms and the zirconium atom together with a pentacoordinated arrangement around the zirconium atom, demonstrated by an X-ray structure determination[5] (Figure 5), we have ascertained the structure of 9 by X-ray diffraction techniques. An ORTEP plot of the molecular structure of 9 is shown in Figure 6. Selected bond lengths and angles for 9 are given in Table II. Both rhodium atoms show the expected square-planar coordination geometry, which is by no means perfect. The conformation of the dirhodium core Rh_2S_2 is roughly comparable to that of the previously reported Rh_2S_2.[5,26]

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(17) Kenworth, J. G.; Myatt, J.; Todd, P. E. *J. Chem. Soc. D* **1969**, 263.

(18) Blandy, C.; Locke, S.; Young, S. J.; Schore, N. E. *J. Am. Chem. Soc.* **1988**, *110*, 7540.

(19) Hudson, A.; Lappert, M. F.; Pichon, R. J. *J. Chem. Soc., Chem. Commun.* **1983**, 374.

(20) Jons, S. B.; Petersen, J. L. *J. Am. Chem. Soc.* **1983**, *105*, 5504.

(21) Choukroun, R.; Gervais, D. *J. Chem. Soc., Chem. Commun.* **1985**, 225.

(22) Samuel, E. *Inorg. Chem.* **1983**, *22*, 2967.

(23) Pez, G. P.; Putnik, C. F.; Suib, S. L.; Stucky, G. D. *J. Am. Chem. Soc.* **1979**, *101*, 6933.

(24) Choukroun, R.; Raoult, Y.; Gervais, D. Unpublished results.

(25) Anderson, M. P.; Pignolet, L. H. *Inorg. Chem.* **1981**, *20*, 4101.

(26) Kalck, P.; Randrianalimanana, C.; Ridmy, M.; Thorez, A.; Tom Dieck, H.; Ehlers, J. *Nouv. J. Chim.* **1988**, *12*, 679.

Table II. Selected Bond Lengths (Å) and Angles (deg) for 9 with Estimated Standard Deviations in Parentheses

Rh(1)–C(1)	1.796 (4)	Rh(2)–C(2)	1.790 (5)
Rh(1)–P(1)	2.277 (1)	Rh(2)–P(2)	2.275 (1)
Rh(1)–S(1)	2.365 (1)	Rh(2)–S(1)	2.356 (1)
Rh(1)–S(2)	2.408 (1)	Rh(2)–S(2)	2.394 (1)
C(1)–Rh(1)–P(1)	95.0 (2)	C(2)–Rh(2)–P(2)	94.4 (2)
C(1)–Rh(1)–S(1)	97.6 (2)	C(2)–Rh(2)–S(1)	99.7 (2)
C(1)–Rh(1)–S(2)	171.5 (1)	C(2)–Rh(2)–S(2)	165.0 (2)
P(1)–Rh(1)–S(1)	167.19 (4)	P(2)–Rh(2)–S(1)	165.85 (4)
P(1)–Rh(1)–S(2)	87.02 (4)	P(2)–Rh(2)–S(1)	85.28 (4)
S(1)–Rh(1)–S(2)	80.80 (4)	S(1)–Rh(2)–S(2)	81.28 (4)
C(1)–O(1)	1.158 (6)	C(2)–O(2)	1.167 (7)
Rh(1)–C(1)–O(1)	174.0 (4)	Rh(2)–C(2)–O(2)	176.1 (5)
S(1)–C(3)	1.853 (5)	S(2)–C(7)	1.867 (5)
Rh(1)–S(1)–Rh(2)	80.28 (3)	Rh(1)–S(2)–Rh(2)	78.68 (3)
Rh(1)–S(1)–C(3)	117.9 (2)	Rh(1)–S(2)–C(7)	110.2 (1)
Rh(2)–S(1)–C(3)	118.8 (2)	Rh(2)–S(2)–C(7)	118.0 (2)
Zr–C(11)	2.344 (4)	Zr–C(12)	2.340 (4)
P(1)–C(11)–Zr	136.8 (2)	P(2)–C(12)–Zr	133.6 (2)
Zr–Cp(1)[a]	2.213 (3)	Zr–Cp(2)	2.276 (3)
Cp(1)–Zr–Cp(2)	131.4 (1)	Cp(2)–Zr–C(11)	102.3 (1)
Cp(1)–Zr–C(11)	109.0 (1)	Cp(2)–Zr–C(12)	102.5 (1)
Cp(1)–Zr–C(12)	109.3 (1)	C(11)–Zr–C(12)	97.0 (1)

[a] Cp = centroid of the cyclopentadienyl ring.

The Rh(1)S(1)Rh(2) and Rh(1)S(2)Rh(2) angles (80.28 and 78.68°, respectively) and the distances Rh(1)–Rh(2) (3.034 Å) are of the same magnitude as those of $[Rh_2(\mu\text{-S-}t\text{-Bu})_2(CO)_2P_2]$[26] ($P_2$ = 1,4-bis(diphenylphosphino)butane) but lower than those of 11[5] (90.63 and 89.66°, Rh(1)–Rh(2) = 3.391 Å).

The geometry around the zirconium atom is quite similar to that of the uncomplexed analogue $Cp_2Zr(CH_2PPh_2)_2$[11] or those of other mononuclear Zr complexes[27,28] (C(11)ZrC(12) = 97°, CpZrCp = 131.4°) but different from the zirconium environment in 11 (C(11)ZrC(12) = 134.2°, CpZrCp = 124.8°). In this latter case, such a C(11)ZrC(12) angle is described by pentacoordination around the zirconium atom, which is supported by an interaction of one sulfur atom with the zirconium atom (Zr–S(2) = 2.995 Å). This distance is much shorter than in 9 (Zr–S(2) = 4.365 Å).

The absence of a zirconium–sulfur interaction allows us to understand the geometric arrangement of the eight-membered ring formed by the zirconium diphosphine bridging the Rh–S–Rh segment, i.e. a pseudotetrahedral environment for the zirconium atom and a $[Rh_2S_2]$ core quite similar to that of the starting material.

The catalytic activity of 8 and 9 in the hydroformylation of 1-hexene was tested at 80 °C under a 20-bar atmosphere of H_2/CO (1/1) and compared to that of the nonsubstituted-cyclopentadienyl parents 10 and 11.

As we previously noted,[12] the introduction of a *t*-Bu group in 8 does not change drastically the catalytic results obtained for 10 (Figure 7, Table III), and there is no improvement of the catalytic performances in comparison with that of the cationic rhodium complex.

In the same way, the catalytic activities of 9 and 11 are quite similar (Figure 8, Table III). The 1-hexene conversion is achieved in about 2 h with a high selectivity (100% in aldehydes), and the linear to branched isomer ratio is roughly the same for both complexes ($n \approx 2$), but the bimetallic complex **9** (or **11**) is significantly more active than $Rh_2(\mu\text{-S-}t\text{-Bu})_2(CO)_2$dppb (dppb = bis(diphenylphosphino)propane).[10]

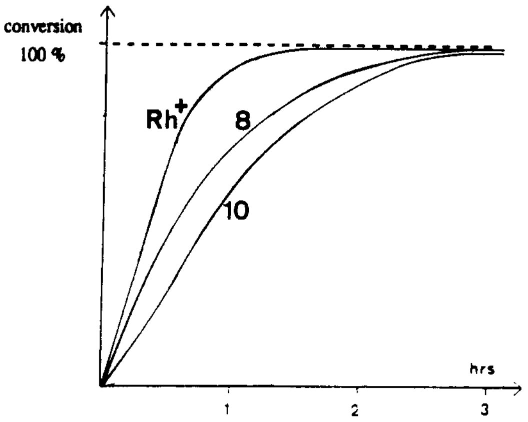

Figure 7. Plot of the conversion of 1-hexene (%) versus time (h) (reaction conditions as in Table III).

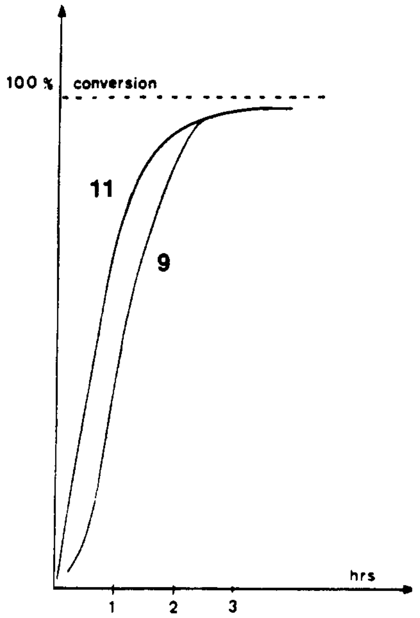

Figure 8. Plot of the conversion of 1-hexene (%) versus time (h) (reaction conditions as in Table III).

Table III. Catalytic Performances of 8 and 9 and Related Derivatives in the Hydroformylation of 1-Hexene[a]

precursor	reacn time, min	% conversion	selectivity n[b]
$[(\eta^5\text{-}t\text{-BuC}_5H_4)_2Zr(CH_2PPh_2)_2Rh(COD)]BPh_4$ (**8**)	80	79	2.2
	160	98	2.1
$[Cp_2Zr(CH_2PPh_2)_2(Rh(COD))]BPh_4$ (**10**)	50	33	2.3
	135	93	2.1
$[Rh(COD)(PPh_3)_2]^+$	30	74	2.7
	90	97	2.6
$(\eta^5\text{-}t\text{-BuC}_5H_4)_2Zr(CH_2PPh_2)_2[Rh_2(\mu\text{-S-}t\text{-Bu})_2(CO)_2]$ (**9**)	70	38	2.2
	140	97	1.8
$Cp_2Zr(CH_2PPh_2)_2[Rh_2(\mu\text{-S-}t\text{-Bu})_2(CO)_2]$ (**11**)	65	56	2.1
	115	96	2.0

[a] Experimental conditions: 80 °C; 20 bar (H_2/CO, 1:1); [olefin]:[catalyst] = 400:1; solvent THF. [b] n = ratio of linear to branched aldehyde.

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(27) Lappert, M. F.; Riley, P. I.; Yarow, P. I. W. *J. Chem. Soc., Dalton Trans.* **1981**, 818.

(28) Howie, R. A.; McQuillan, g. P.; Thompson, D. W.; Lock, G. A. *J. Organomet. Chem.* **1986**, *303*, 213.

Conclusion

The chemical reduction of 1 and 2 and bimetallic systems with rhodium were investigated toward hydrogenation and hydroformylation catalysis, respectively.

The modification of the cyclopentadienyl ligand by addition of an electron-donating group such as *t*-Bu does not change drastically the chemistry of 1 and 2. Chemical reduction of 2 and 1 gives the expected Zr(III) species 5 and 6, respectively, but the rapid formation of the hydridozirconium(III) species 7 in connection with the presence of a *t*-Bu group is unusual. (No ESR evolution was observed with $CpZr(CH_2PPh_2)_2$ under the same experimental conditions.) The generation of 7 could be a model for catalytic hydrogenation performed with $CpM(CH_2PPh_2)_2$ (M = Ti, Zr) under H_2.[2] The structure of the bimetallic complex 9 is different from that of its parent 11, but the same catalytic hydroformylation activity is found in both cases. The absence of a Zr–S interaction in 9 is counterbalanced by the *t*-Bu group effect, which, when the electron density on the Zr atom is increased, prevents Zr–S interaction. Considering the tetrahedral geometry around the zirconium atom, both rhodium atoms are maintained in proximity with each other and a cooperative effect could be favored in the catalytic cycle, to give finally the same catalytic results as 11.

We hope that appropriate modification of the R group of the C_5H_4R cyclopentadienyl ligand will achieve high conversion and full selectivity of the conversion of alkenes into the corresponding aldehydes.

Experimental Section

General Data. All compounds are extremely air-sensitive, and manipulations were carried out by using Schlenk and vacuum-line techniques under argon. Solvents were distilled from Na/benzophenone ketyl. $(\eta^5\text{-}t\text{-}BuC_5H_4)_2ZrCl_2$,[29] $LiCH_2PPh_2{\cdot}TMEDA$,[30] and the rhodium complexes $Rh_2(\mu\text{-}S\text{-}t\text{-}Bu)_2(CO)_4$[31] and $Rh(COD)(PPh_3)BPh_4$[32] were prepared by following published procedures.

IR spectra were recorded on a Perkin-Elmer Model PE 983 instrument. All NMR experiments were performed on WH90 and WH250 NMR spectrometers. Spectra are referenced to C_6D_6 (δ 7.15 ppm) or CD_2Cl_2 (δ 5.32 ppm). ^{13}C NMR chemical shift were referenced to C_6D_6 (δ 127.96 ppm) or CD_2Cl_2 (δ 53.6 ppm).

$^{31}P\{^1H\}$ NMR spectra were determined in THF/C_6D_6 solvent (3/1) and referenced to H_3PO_4 in D_2O.

ESR spectra were recorded on a Brucker 200 TT spectrometer. Elemental analyses were performed by the Service Central de Microanalyses du CNRS.

Preparation of $(\eta^5\text{-}t\text{-}BuC_5H_4)_2Zr(CH_2PPh_2)_2$ (1). $(\eta^5\text{-}t\text{-}BuC_5H_4)_2ZrCl_2$ (2.5 g, 6.2 mmol) was suspended in tetrahydrofuran (20 mL). $LiCH_2PPh_2{\cdot}TMEDA$ (3.9 g, 12.4 mmol) was added at room temperature, and the mixture was stirred for 4 days. The solution was reduced to 5 mL and layered with pentane (30 mL). After diffusion, the remaining solid was filtered and dissolved in toluene (40 mL) and the solution filtered through Celite to remove LiCl. The yellow solution was concentrated under vacuum layered with pentane. Microcrystals of 1 were separated by filtration. ^1H NMR (C_6D_6, δ): 6.2, 5.66 (virtual t, $^1J_{CH}$ = 2.6 Hz, C_5H_4), 1.19 (s, *t*-Bu), 1.03 (s, $^2J_{PH}$ = 3.2 Hz, CH_2). ^{31}P NMR (δ): 0.16. ^{13}C NMR (C_6D_6, δ): 140.40 (s, substituted C, C_5H_4), 111.55, 109.02 (d, $^1J_{CH}$ = 166.0 and 162.6 Hz, C_5H_4), 45.11 (dd, $^1J_{CH}$ = 115.9, $^1J_{CP}$ = 47.2 Hz, CH_2), 33.34 (s, $C(CH_3)_3$), 32.02 (d, $^1J_{CH}$ = 125 Hz, $C(CH_3)_3$). Yield: 3 g (70%). Anal. Calcd for $C_{44}H_{50}P_2Zr$: C; 72.20; H, 6.83; P, 8.48; Zr, 12.47. Found: C; 72.35; H, 7.00; P, 8.39; Zr, 12.52.

Preparation of $(\eta^5\text{-}t\text{-}BuC_5H_4)_2ZrCl(CH_2PPh_2)$ (2). The same experimental procedure was followed as described above $(\eta^5\text{-}t\text{-}BuC_5H_4)_2ZrCl_2$ 7 g, 17.3 mmol; $LiCH_2PPh_2{\cdot}TMEDA$, 5.5 g, 17.3 mmol), but the product was always contaminated by varying amounts of the starting material $(\eta^5\text{-}t\text{-}BuC_5H_4)_2ZrCl_2$. This was eliminated to some extent by dissolving the mixture in toluene and cooling the solution to −30 °C for 24 h. Crystals of $(\eta^5\text{-}t\text{-}BuC_5H_4)_2ZrCl_2$ were filtered, and the remaining solution was layered with pentane to afford 2. ^1H NMR (C_6D_6, δ): 6.60, 6.14, 5.86, 5.55 (m, see coupling constants in Figure 2, C_5H_4), 2.06 (d, $^2J_{PH}$ = 3.2 Hz, CH_2), 1.26 (s, *t*-Bu). ^{31}P NMR (δ): 0.12 ^{13}C NMR (C_6D_6, δ): 144.0 (s, substituted C, C_5H_4), 116.10, 113.80, 108.22, 106.71 (respectively dd ($^1J_{CH}$ = 116.4, J_{CP} = 5.5 Hz); dd ($^1J_{CH}$ = 168.0, J_{CP} = 7.3 Hz), d ($^1J_{CH}$ = 165.0 Hz), and d ($^1J_{CH}$ = 165 Hz), C_5H_4), 45.11 (dd, $^1J_{CH}$ = 117.9, $^1J_{CP}$ = 44.3 Hz, CH_2), 33.44 (s, *t*-Bu), 31.40 (d, $^1J_{CH}$ = 125.8 Hz). Yield: 2 g (20%). Anal. Calcd for $C_{31}H_{38}PClZr$: C, 65.50; H, 6.70; P, 5.46; Zr, 16.03. Found: C, 63.44; H, 6.63; P, 5.55; Zr, 16.15.

Me_3SiCl (0.019 g 0.175 mmol) in THF (5 mL) was added to 1 (0.128 g, 0.175 mmol) in THF (5 mL). After it was stirred for 1 day at room temperature, the solution was concentrated to dryness. The residue was washed with pentane, and ^1H NMR spectroscopy showed the presence of 2 along with the presence of $(\eta^5\text{-}t\text{-}BuC_5H_4)_2ZrCl_2$.

To a suspension of $(\eta^5\text{-}t\text{-}BuC_5H_4)_2ZrCl_2$ (70 mg, 0.173 mmol) in THF (5 mL) was added 1 (128 mg, 0.175 mmol) in THF (5 mL). The mixture was stirred for 12 h at room temperature and evaporated to dryness; the ^1H NMR spectrum of the residue shows the presence of 2, along with unreacted starting materials.

Preparation of $(\eta^5\text{-}t\text{-}BuC_5H_4)_2Zr(O_2CCH_2PPh_2)_2$ (3). 1 (0.200 g, 0.27 mmol) was dissolved in toluene (5 mL), and CO_2 was introduced. The yellow solution became colorless after is was stirred for 2 h at room temperature. The solution was vacuum-dried and the viscous liquid remaining washed with pentane. ^1H NMR (C_6D_6, δ): 6.89, 6.14 (virtual triplet, $^1J_{CH}$ = 2.7 Hz, C_5H_4), 3.18 (broad s, CH_2), 1.18 (s, *t*-Bu). ^{31}P NMR (δ): −20.6 IR: ν_{CO_2} = 1570, 1370 cm^{-1}. Yield: 0.180 g (80%). Anal. Calcd for $C_{46}H_{50}P_2O_4Zr$: C, 67.38; H, 6.10. Found: C, 68.08; H, 6.17.

Preparation of $(\eta^5\text{-}t\text{-}BuC_5H_4)_2ZrI_2$ (4). Excess CH_3I (0.387 g, 2.730 mmol) was added to 1 (0.200 g, 0.273 mmol) in THF (5 mL) at −30 °C. After the mixture was stirred for 15 min, a yellow precipitate was formed. After evaporation under vacuoum, 4 was extracted from the residue by toluene and identified by its mass spectrum (*m/e* 586) and by ^1H NMR spectroscopy.

The phosphonium salt PPh_2MeEtI, produced in the reaction and extracted from the residue with $CHCl_3$, was identified by ^1H NMR spectroscopy by comparison with an authentic sample.

Reduction of 1 and 2. All experiments were performed in a Vacuum Atmospheres Dri-Lab. In the general procedure, 0.080 g (0.11 mmol) of 1 in 0.5 mL of THF-d_8 was treated with 1 equiv of a THF-d_8 solution of sodium naphthalenide (prepared from a mixture of 0.014 g (0.11 mmol) of naphthalene and excess sodium in 0.5 mL of THF-d_8 that was stirred 2 h). The brown-red solution was stirred for 5 min and placed in a ^1H NMR tube. The tube was sealed and the solution monitored by NMR spectroscopy and ESR techniques. Solutions of 7 in sealed tubes are stable for months, but attempts to isolate 7 failed. Several additional experiments were carried out at higher and lower concentrations of Na(np) and the hydridozirconium(III) species 7 was always obtained. At this stage, the ESR tube was placed in a Schlenk tube; the Schlenk tube was filled with a THF solution of CH_3I (10 equiv) and connected to a Toepler pump. After the tube containing the sample was broken, at −30 °C, evolution of CH_4 was measured (75–85% according to different experiments) and identified by IR spectroscopy. The remaining solution was vacuum-dried and the residue extracted with toluene and chloroform to give $(\eta^5\text{-}t\text{-}BuC_5H_4)_2ZrI_2$ and the phosphonium salts PPh_2MeEtI and PPh_2Me_2I.

The chemical reduction of 2 with Na/Hg(s) was complete in less than $^1/_2$ h at room temperature.

Preparation of $(\eta^5\text{-}t\text{-}BuC_5H_4)_2Zr(CH_2PPh_2)_2Rh(COD)BPh_4$ (8). 1 (1.0 g 0.95 mmol) was dissolved in THF (20 mL) and the solution added at room temperature to $Rh(COD)(PPh_3)_2BPh_4$ (0.7 g 0.95 mmol) in THF (20 mL). After it was stirred for 6 h, the solution was concentrated and pentane added. The resulting orange solid was filtered, dried, and dissolved in THF/pentane

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(29) Tainturier, G.; Gautheron, B.; Renaut, P.; Etieviant, P. *C.R. Seances Acad. Sci., Ser. C* **1975**, *281*, 1035.

(30) Schore, N. E.; Benner, L. S.; La Belle, B. E. *Inorg. Chem.* **1981**, *20*, 3200.

(31) Kalck, P.; Poilblanc, R. *Inorg. Chem.* **1975**, *14*, 2779.

(32) Schrock, R. R.; Osborn, J. A. *J. Am. Chem. Soc.* **1971**, *93*, 2397.

Table IV. Crystallographic Data for $(\eta^5\text{-}t\text{-BuC}_5H_4)_2Zr(CH_2PPh_2)_2[Rh_2(\mu\text{-S-}t\text{-Bu})_2(CO)_2]$ (9)

formula	$C_{54}H_{68}O_2P_2S_2Rh_2Zr$	λ(Mo Kα)	0.710 73 Å
fw	1172.24	ρ(calc)	1.443 g cm^{-3}
cryst syst	monoclinic	μ	9.5 cm^{-1}
space group	$P2_1/n$ (No. 14)	transmissn coeff	0.80–1.00
		no. of unique rflns	9412
a	14.320 (2) Å	no. of obsd rflns	4965
b	19.488 (3) Å	no. of params	344
c	19.405 (2) Å	refined	344
β	95.08 (2)°	$R(F_o)$	
V	5394 Å^3	R_w	0.032
Z	4		

to give yellow crystals. ^{1}H NMR (C_6D_6, δ): 5.90, 5.45 (virtual t, $^1J_{CH}$ = 2.6 Hz, C_5H_4), 1.34 (d, $^2J_{PH}$ = 9.1 Hz, CH_2), 4.05, 2.36–2.06 (m, COD). ^{31}P NMR (δ): 47.5 (J_{RhP} = 146 Hz). Yield: 1.46 g (85%). Anal. Calcd for $C_{76}H_{82}P_2ZrRhB$: C, 72.30; H, 6.50; P, 4.90. Found: C, 71.35; H, 6.72; P, 4.45.

Preparation of $(\eta^5\text{-}t\text{-BuC}_5H_4)_2Zr(CH_2PPh_2)_2[Rh_2(\mu\text{-S-}t\text{-Bu})_2(CO)_2]$ (9). $Rh_2(\mu\text{-S-}t\text{-Bu})_2(CO)_4$ (0.300 g, 0.60 mmol) was dissolved in THF (20 mL), and 1 (0.422 g, 0.6 mmol) in THF (20 mL) was added slowly at room temperature. The resulting solution was stirred for 2 h and evaporated to 5 mL. Pentane was added to give a yellow precipitate. ^{1}H NMR (C_6D_6, δ): 7.84–6.22, 6.02, 5.73 (virtual t, $^1J_{CH}$ = 2.7 Hz, C_5H_4), 1.84, 1.44 (m, CH_2), 1.03, 0.58 (s, C_5H_4-*t-Bu*), 2.10, 1.07 (s, S-*t*-Bu). ^{31}P NMR (δ): 45.8 (J_{RhP} = 141 Hz). ^{13}C NMR (CD_2Cl_2, δ): 141.9 (s, substituted C, C_5H_4), 115.2, 113.1, 109.3, 108.9 (d, $^1J_{CH}$ = 170 Hz, C_5H_4), 33.2, 32.7 (s, *C*(CH_3)$_3$), 31.9, 31.0 (d, $^1J_{CH}$ = 126 Hz, C(CH_3)$_3$), 50.7, 44.1 (s, S-*C*-C), 38.0, 34.7 (s, S-C-*C*), 194.2 (dd, $^2J_{PC}$ = 11 Hz, $^1J_{RhC}$ = 77 Hz, CO) (CH_2–P is not observed[5]). IR: ν_{CO} = 1947, 1930 cm^{-1}. Yield: 80%. Anal. Calcd for $C_{54}H_{68}Rh_2ZrO_2P_2S_2$: C, 53.32; H, 5.80; P, 5.29; Zr, 7.78; Rh, 17.58. Found: C, 55.10; H, 5.99; P, 5.46; Zr, 8.23; Rh, 16.95.

Recrystallization from a CH_2Cl_2/pentane solution gives orange crystals suitable for X-ray analysis.

X-ray Crystal Structure Determination for $(\eta^5\text{-}t\text{-BuC}_5H_4)_2Zr(CH_2PPh_2)_2[Rh_2(\mu\text{-S-}t\text{-Bu})_2(CO)_2]$ (9). Collection and Reduction of X-ray Data. A yellow parallelepipedic crystal of size 0.50 × 0.25 × 0.15 mm was mounted on a glass fiber in an Enraf-Nonius CAD4 diffractometer. Systematic absences were found for $0k0$ reflections for which $k \neq 2n$ and $h0l$ reflections for which $h + l \neq 2n$. Cell parameters were determined from a least-squares fit of 25 accurately centered reflections ($22 < 2\theta < 29.5°$). These parameters are summarized in Table IV. Data were collected at 20 °C in a $\omega/2\theta$ scan mode (scan width $(1.10 + 0.35 \tan \theta)°$, scan range $3 < 2\theta < 50°$, scan speed 1.2–8.3° min^{-1}). Three intense reflections were monitored every 2 h. Intensities of these reflections decreased 27%, gradually during the course of the experiment. Data were corrected for Lorentz, polarization, and decay effects by using SDP.[33] Empirical absorption[34] corrections were applied. A total of 9412 unique reflections were collected ($+h,+k,\pm l$); 4965 were considered observed ($I > 3\sigma(I)$) and used for structure refinement.

Solution and Refinement. Atoms were located by use of SHELX 86.[35] Refinement and Fourier difference calculations were made with SHELX 76.[36] H atoms were included in calculated positions (C–H = 0.97 Å) in structure factor calculations with an assigned U value of 0.08 Å^2 for phenyl and cyclopentadienyl H and 0.10 Å^2 for methyl H. Methylenic H atoms were included at their found positions with an assigned U value of 0.06 Å^2. H parameters were not refined. Phenyl rings were refined as isotropic rigid groups (C–C = 1.397 Å), as were both cyclopentadienyl rings (C–C = 1.420 Å). Anisotropic temperature factors were refined for all other atoms.

Scattering factors for H were obtained from Stewart et al.[37] and for other atoms were taken from ref 38. In the last full-matrix least-squares cycle the greatest shift/esd was 0.5 on the thermal parameters and the final R value was 0.031. $[\sum w(|F_o|-|F_c|)^2/(n-m)]^{1/2}$ was equal to 1.1 with n = 4965 observations and m = 344 variables. A final Fourier difference map showed a residual electron density of 0.7 e Å^{-3}. Final positional parameters are shown in the supplementary material for non-hydrogen atoms; all calculations were performed on a DEC VAX 11/730 computer.

General Procedure for Catalytic Experiments. Catalytic tests were carried out in a 75-cm^3 autoclave. The temperature was maintained at 80 °C through oil circulation in a double jacket. The gas was admitted from a 125-cm^3 gas tank, and the drop of pressure in the tank was followed with a pressure gauge connected to an electron measurement and recording unit.

Samples for GPC analysis were syringed off during the course of the catalytic reaction.

Registry No. 1, 123669-83-0; 2, 126821-86-1; 3, 126821-87-2; 4, 125754-29-2; 5, 126821-88-3; 6, 125754-27-0; 7, 125754-28-1; 8, 125984-42-1; 9, 126923-02-2; $(\eta^5\text{-}t\text{-BuC}_5H_4)_2ZrCl_2$, 32876-92-9; $LiCH_2PPh_2$, 62263-69-8; $Rh(COD)(PPh_3)_2BPh_4$, 31761-02-1; $Rh_2(\mu\text{-S-}t\text{-Bu})_2(CO)_4$, 122742-03-4; PPh_2MeEtI, 1017-88-5; PPh_2Me_2I, 1661-08-1; sodium naphthalenide, 3481-12-7.

Supplementary Material Available: Listings of ^{1}H, ^{31}P, and ^{13}C NMR and ESR data, fractional atomic parameters, thermal parameters, all bond lengths and angles, and least-squares plane equations (16 pages); a table of observed and calculated structure factors (24 pages). Ordering information is given on any current masthead page.

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[33] Frenz, B. A. SDP Structure Determination Package; Enraf-Nonius: Delft, Holland, 1982.

[34] North, A. C. T.; Phillips, D. C.; Matthews, F. S. *Acta Crystallogr.* **1968**, *A24*, 351.

[35] Sheldrick, G. M. SHELX 86: Program for Crystal Structure Solution; University of Göttingen: Göttingen, FRG, 1986.

[36] Sheldrick, G. M. SHELX 76: Program for Crystal Structure Determination: University of Cambridge: Cambridge, England, 1976.

[37] Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

[38] *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV.