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A Semibridging Hydrido Zirconium–Rhodium Complex: A Possible Way to Catalytic Hydrogen Transfer on d^0–d^8 Systems

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Zirconium–rhodium complexes are studied with the aim of generating a zirconium–hydrogen bond by rhodium-mediated activation of dihydrogen in order to obtain highly selective catalytic synthesis. By reaction of the bis(phosphinomethyl) complex $Cp_2Zr(CH_2PPh_2)_2$ on $Rh(H)(PPh_3)_4$ we get the bimetallic hydride $Cp_2Zr(CH_2PPh_2)_2Rh(H)(PPh_3)$ (**3**), which was structurally characterized (crystal system monoclinic, space group $P2_1/n$, $a = 12.189$ (2) Å, $b = 21.054$ (3) Å, $c = 17.587$ (2) Å, $\beta = 98.67$ (1)°, $Z = 4$). The most remarkable structural features of **3** are the trans chelating arrangement of the bis[(diphenylphosphino)methyl]zirconium on rhodium together with pentacoordination around zirconium due to a strong interaction of Zr on the Rh–H bond with a Zr···H distance of 2.28 (5) Å. The bimetallic system is an efficient precursor for selective catalytic hydroformylation of 1-hexene.

Introduction

Early-transition-metal complexes are known as useful synthetic tools especially for their very high regioselectivity related to the hydridic character of the d^0 metal–hydrogen bond, one of the best documented examples being Schwartz's reagent $Cp_2Zr(H)Cl$ ($Cp = \eta^5\text{-}C_5H_5$).[2] Still, these reactions are essentially stoichiometric.

Among catalytic applications expected from heterobimetallic complexes associating both early- and late-transition metals, we are especially interested in d^0–d^8 systems with the aim of regenerating the hydridic bond via a hydrogen transfer involving the d^8 transition metal. We report here the first example of a semibridging hydrido rhodium–zirconium moiety where the strong interaction of the zirconium center on the hydrogen atom bonded to rhodium may be considered as a model for a possible hydrogen transfer from rhodium to zirconium as a step to catalytic hydrozirconation. Moreover, this is the first crystal structure of a zirconium–monorhodium complex corresponding to the general formula $Cp_2Zr(CH_2PPh_2)_2RhX(L)$, making possible the interpretation of NMR data on sound arguments.

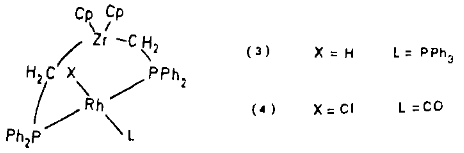
Results and Discussion

The reaction of the bis(phosphinomethyl) complex $Cp_2Zr(CH_2PPh_2)_2$ (**1**)[3] with 1 equiv of $Rh(H)(PPh_3)_4$ (**2**)[4] at room temperature in THF afforded very cleanly the bimetallic complex $Cp_2Zr(CH_2PPh_2)_2Rh(H)(PPh_3)$ (**3**) as shown on the $^{31}P\{^1H\}$ NMR spectrum registered directly on the reaction mixture (Figure 1) following eq 1. The bimetallic species **3** was isolated as orange crystals by addition of heptane in ca. 90% yield.

$$\underset{\mathbf{1}}{Cp_2Zr(CH_2PPh_2)_2} + \underset{\mathbf{2}}{Rh(H)(PPh_3)_4} \rightarrow \underset{\mathbf{3}}{Cp_2Zr(CH_2PPh_2)_2Rh(H)(PPh_3)} + 3PPh_3 \quad (1)$$

To explain the spectroscopic data collected for **3** (Table I) and specifically the AB_2X pattern of the $^{31}P\{^1H\}$ spectrum (Figure 1) and the eight lines of the hydride resonance of the ^1H spectra (see Figure 2), a trans arrangement of the chelating bis[(diphenylphosphino)methyl]zirconium must be assumed, with the remaining PPh_3 in a trans position to the Rh–H bond.

A similar trans chelation has been previously suggested on the basis of cryoscopic measurements and ^{31}P NMR spectroscopy for the various rotamers of the related complex $Cp_2Zr(CH_2PPh_2)_2RhCl(CO)$ (**4**).[5] But as the structure of **4** could not be ascertained by X-ray diffraction technique and as there was no previous report of a five-membered-chain bis(phosphine) spanning trans coordination sites in the square-planar environment of rhodium(I), the proposed arrangement A was still controversial.[6]



(A)

In order to define the structure of this type of bimetallic complexes unambiguously, we performed a single-crystal X-ray analysis of **3**. The crystal data are presented in Table II. Tables III and IV give the atomic coordinates and the bond distances and angles within the bimetallic frame, respectively. Perspective views of the molecule are shown in Figures 3 and 4. As seen in Figure 3, coordination about rhodium is square-planar (the largest deviation from the least-squares plane P(1),P(2),P(3),Rh,H(5) is 0.18 Å for H(5)) with the expected distortion arising from the lack of steric hindrance of the hydride ligand while Rh–P bond distances are very similar to those in $RhH(PPh_3)_3$ (**5**)[7] and $RhH(P(i\text{-}Pr)_3)_3$ (**6**)[8] (see Table V). The

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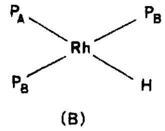
Table I. Spectroscopic Data [IR (ν_{Rh-H}, cm^{-1}) and ^{1}H and ^{31}P{^{1}H} NMR Chemical Shifts (δ) and Coupling Constants (J, Hz)] of $Cp_2Zr(CH_2PPh_2)_2Rh(H)(PPh_3)$ (3) Compared to Those of $RhH(PPh_3)_3$ (5)



(B)

compd	ν_{Rh-H}	^{1}H (hydride) δ_H	^{1}H (hydride) J(Rh–H)	^{31}P (AB$_2$X pattern) $\delta_{P_A(dt)}$	$\delta_{P_B(dd)}$	J(Rh–P$_A$)	J(Rh–P$_B$)	J(P$_A$–P$_B$)
3	*a*	−9.45[c]	24.6	40.4[e]	24.0	151.5	116.2	28
5	1890[b]	−7.8[d]	14	35.9[f]	41.5	145	172	25

[a] No IR absorption could be found in the 2200–1600 cm^{-1} range (terminal hydrides). The bridged hydride range (1200–1000 cm^{-1}) was obscured by ligand absorption. [b] Reference 7b. [c] In CD_2Cl_2 at 20 °C; AB$_2$MX pattern; $J(P_AH) = 85.5$ Hz; $J(P_BH) = 24.6$ Hz. [d] Reference 7a; in toluene-d_8 at 30 °C, coalesced into a doublet. [e] In THF/C_6D_6 (3:1) at 35 °C. [f] Reference 7a; in toluene-d_8 at −78 °C, coalesced into a doublet at 4 °C.

Table II. Crystal Data

empirical formula	$C_{54}H_{50}P_3RhZr$
fw	986.04
cryst system	monoclinic
space group	$P2_1/n$
a, Å	12.189 (2)
b, Å	21.054 (3)
c, Å	17.587 (2)
β, deg	98.67 (1)
V, Å^3	4462
Z	4
cryst size, mm	0.4 × 0.18 × 0.18
μ(Mo Kα), cm^{-1}	7.4
d(calcd), g/cm^3	1.47
temp, °C	20
radiatn	Mo Kα (graphite monochromator)
scan range θ, deg	$0.6 + 0.345 \tan \theta$
2θ range, deg	3–50
scan type	$w/1.66\theta$
standard reflectn(s)	2, 3, −12; 6, 2, 7
reflectns collected	8588 (hkl, $-hkl$)
reflectns merged	8380
reflectns used	4665
criteria	$l \geq 2\sigma(l)$
$R = \sum \lVert F_o\rvert - \lvert F_c \rVert / \sum \lvert F_o \rvert$	0.0352
$R_w = \{\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\sum w F_o^2\}^{1/2}$	0.0392
final shift/error max (av)	0.08 (0.03)

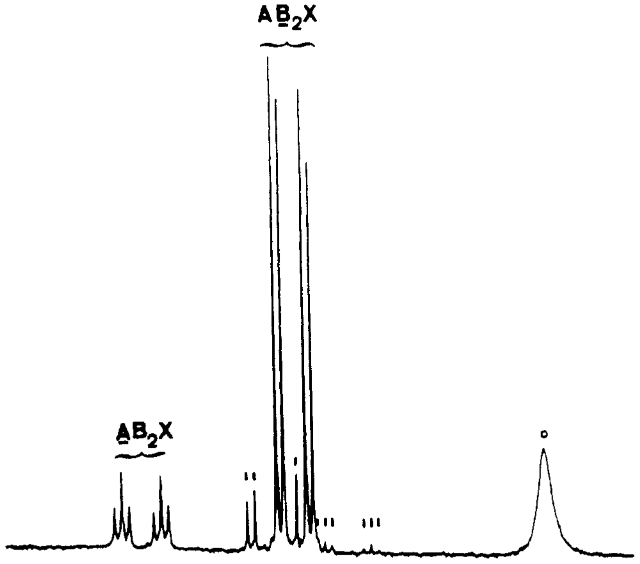


Figure 1. ^{31}P{^{1}H} NMR spectrum of the stoichiometric mixture of $Cp_2Zr(CH_2PPh_2)_2$ and $Rh(H)(PPh_3)_4$ in THF/C_6D_6 (3:1) after 2 h of stirring, showing the AB$_2$X pattern of 3 and the free phosphine PPh_3 (○) liberated (eq 1). Small amounts of an unidentified species (|) give another AB$_2$X pattern.

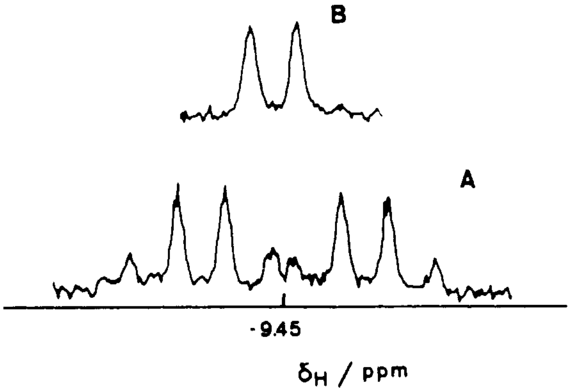


Figure 2. NMR spectra of the hydride proton of 3 in CD_2Cl_2: A, ^{1}H; B, ^{1}H{^{31}P}.

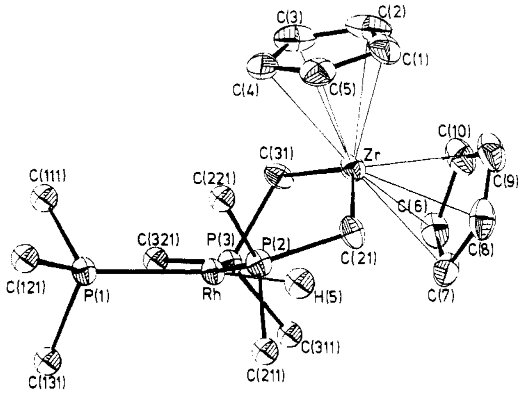


Figure 3. Thermal ellipsoid diagram (30% probability) and labeling scheme for 3. Phenyl groups are omitted for clarity.

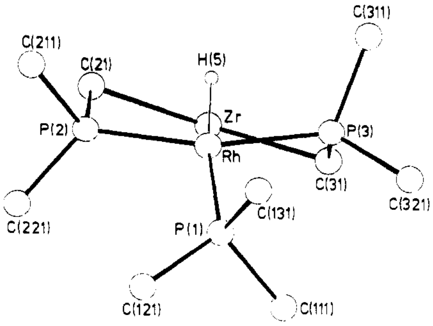


Figure 4. View of the molecule of 3 along the Rh–Zr axis. C atoms of phenyl and Cp rings are omitted for clarity.

P(2)–Rh–P(3) angle of 150.13 (5)° is to be compared to the values 151.7 (2)° in 5 and 141.53 (3)° in 6, confirming definitely the trans chelating arrangement of the [(diphenylphosphino)methyl]zirconium on rhodium, proposed on the basis of NMR spectroscopy. Moreover, the phosphorus–hydride coupling constants may now be assigned

Table III. Fractional Atomic Coordinates with Esd's in Parentheses

atom	*x/a*	*y/b*	*z/c*
Rh(1)	0.49049 (3)	0.10411 (2)	0.19182 (2)
Zr(2)	0.60978 (4)	0.08039 (2)	0.36052 (2)
C(1)	0.7304 (6)	0.0109 (4)	0.4568 (4)
C(2)	0.8034 (5)	0.0479 (4)	0.4210 (4)
C(3)	0.7943 (5)	0.0272 (3)	0.3452 (3)
C(4)	0.7150 (5)	−0.0194 (3)	0.3342 (3)
C(5)	0.6744 (5)	−0.0298 (3)	0.4043 (4)
C(6)	0.5965 (7)	0.1887 (3)	0.4238 (4)
C(7)	0.4893 (6)	0.1734 (3)	0.3937 (3)
C(8)	0.4566 (5)	0.1224 (3)	0.4324 (3)
C(9)	0.5463 (6)	0.1043 (3)	0.4868 (3)
C(10)	0.6312 (6)	0.1471 (5)	0.4806 (4)
P(1)	0.4013 (1)	0.18098 (6)	0.11092 (7)
P(2)	0.3667 (1)	0.04625 (6)	0.24788 (7)
C(21)	0.4534 (4)	0.0110 (2)	0.3296 (3)
P(3)	0.66726 (9)	0.13611 (6)	0.18775 (6)
C(31)	0.7058 (4)	0.1528 (2)	0.2874 (3)
H(5)	0.565 (4)	0.054 (2)	0.234 (3)
C(111)	0.4556 (4)	0.2613 (2)	0.1340 (3)
C(112)	0.4793 (5)	0.2756 (3)	0.2122 (4)
C(113)	0.5113 (7)	0.3352 (4)	0.2372 (5)
C(114)	0.5230 (7)	0.3824 (4)	0.1844 (6)
C(115)	0.5057 (8)	0.3684 (4)	0.1094 (6)
C(116)	0.4704 (6)	0.3086 (3)	0.0831 (4)
C(121)	0.2512 (4)	0.1977 (3)	0.0978 (3)
C(122)	0.2067 (5)	0.2490 (3)	0.1322 (3)
C(123)	0.0925 (7)	0.2567 (4)	0.1246 (5)
C(124)	0.0234 (6)	0.2150 (5)	0.0846 (6)
C(125)	0.0665 (7)	0.1654 (5)	0.0504 (7)
C(126)	0.1798 (5)	0.1555 (3)	0.0561 (4)
C(131)	0.4184 (4)	0.1652 (3)	0.0109 (3)
C(132)	0.4740 (5)	0.1113 (3)	−0.0053 (3)
C(133)	0.4914 (6)	0.0983 (4)	−0.0807 (5)
C(134)	0.4531 (7)	0.1381 (5)	−0.1396 (4)
C(135)	0.3950 (8)	0.1895 (5)	−0.1236 (4)
C(136)	0.3745 (6)	0.2033 (3)	−0.0497 (4)
C(211)	0.2978 (4)	−0.0206 (2)	0.1923 (3)
C(212)	0.2545 (5)	−0.0118 (3)	0.1153 (3)
C(213)	0.2010 (6)	−0.0603 (4)	0.0718 (4)
C(214)	0.1891 (5)	−0.1183 (3)	0.1047 (4)
C(215)	0.2335 (6)	−0.1279 (3)	0.1790 (4)
C(216)	0.2871 (5)	−0.0795 (3)	0.2232 (3)
C(221)	0.2484 (4)	0.0801 (2)	0.2882 (3)
C(222)	0.2241 (5)	0.1431 (3)	0.2805 (3)
C(223)	0.1369 (6)	0.1695 (3)	0.3130 (4)
C(224)	0.0753 (5)	0.1319 (4)	0.3538 (4)
C(225)	0.0985 (5)	0.0687 (4)	0.3612 (4)
C(226)	0.1836 (5)	0.0427 (3)	0.3284 (3)
C(311)	0.7630 (4)	0.0754 (2)	0.1615 (3)
C(312)	0.7266 (5)	0.0166 (3)	0.1366 (3)
C(313)	0.8004 (6)	−0.0301 (3)	0.1208 (4)
C(314)	0.9105 (6)	−0.0170 (4)	0.1288 (4)
C(315)	0.9489 (5)	0.0422 (4)	0.1528 (4)
C(316)	0.8758 (4)	0.0882 (3)	0.1691 (3)
C(321)	0.7095 (4)	0.2029 (2)	0.1315 (3)
C(322)	0.7011 (4)	0.1982 (3)	0.0523 (3)
C(323)	0.7247 (5)	0.2495 (3)	0.0085 (4)
C(324)	0.7569 (6)	0.3055 (3)	0.0437 (4)
C(325)	0.7684 (6)	0.3104 (3)	0.1210 (4)
C(326)	0.7443 (5)	0.2595 (3)	0.1648 (3)

unambiguously as $^2J_{\text{H-P(cis)}} = 24.6$ Hz and $^2J_{\text{H-P(trans)}} = 85.5$ Hz together with $^1J_{\text{H-Rh}} = 24.6$ Hz.

Coordination about zirconium is characterized by a C(21)–Zr–C(31) angle of 134.3 (2)°, a much larger value than in the uncomplexed bis[(diphenylphosphino)methyl]zirconium $Cp_2Zr(CH_2PPh_2)_2$ (100.2°),[9] which is indicative of a pentacoordinated zirconocene moiety, Cp_2ZrX_3, as previously reported for $Cp_2Zr(H_2O)_3^{2+}$ (145.2°),[10] $Cp_2ZrCl(S_2CNEt_2)$ (137.5°),[11] and more recently $Cp_2Zr(CH_2PPh_2)_2[Rh(S\text{-}t\text{-}Bu)(CO)]_2$ (134.2°)[12] (where a sulfur atom completes the zirconium environment to pentacoordination). In strong contrast, the cis complex $Cp_2Zr(CH_2PPh_2)_2Cr(CO)_4$ obtained by Schore[9] displayed a C–Zr–C angle of 93.5° for the pseudotetrahedral zirconium atom (Table VI).

Table IV. Bond Distances (Å) and Bond Angles (deg) within Coordination Sphere of Metal and Phosphorus Atoms[a]

	Bond Distances		
Rh(1)–P(1)	2.315 (1)	P(1)–C(131)	1.834 (5)
Rh(1)–P(2)	2.276 (1)	P(2)–C(21)	1.810 (5)
Rh(1)–P(3)	2.269 (1)	P(2)–C(211)	1.842 (5)
Zr(2)–H(5)	2.28 (5)	P(2)–C(221)	1.843 (5)
Zr(2)–C(21)	2.398 (5)	P(3)–C(31)	1.780 (5)
Zr(2)–C(31)	2.408 (5)	P(3)–C(311)	1.836 (5)
P(1)–C(111)	1.839 (5)	P(3)–C(321)	1.837 (5)
P(1)–C(121)	1.843 (5)	Rh(1)–H(5)	1.51 (4)
	Bond Angles		
P(2)–Rh(1)–P(1)	111.08 (4)	C(211)–P(2)–C(21)	105.9 (2)
P(3)–Rh(1)–P(1)	97.67 (4)	C(221)–P(2)–Rh(1)	124.6 (2)
P(3)–Rh(1)–P(2)	150.13 (5)	C(221)–P(2)–C(21)	104.5 (2)
C(31)–Zr(2)–C(21)	134.3 (2)	C(221)–P(2)–C(211)	100.3 (2)
C(111)–P(1)–Rh(1)	112.7 (2)	P(2)–C(21)–Zr(2)	106.2 (2)
C(121)–P(1)–Rh(1)	125.2 (2)	C(31)–P(3)–Rh(1)	97.9 (2)
C(121)–P(1)–C(111)	99.8 (2)	C(311)–P(3)–Rh(1)	116.4 (2)
C(131)–P(1)–Rh(1)	110.6 (2)	C(311)–P(3)–C(31)	107.5 (2)
C(131)–P(1)–C(111)	106.8 (2)	C(321)–P(3)–Rh(1)	126.1 (2)
C(131)–P(1)–C(121)	99.7 (2)	C(321)–P(3)–C(31)	109.0 (2)
C(21)–P(2)–Rh(1)	102.6 (2)	C(321)–P(3)–C(311)	99.0 (2)
C(211)–P(2)–Rh(1)	117.3 (2)	P(3)–C(31)–Zr(2)	108.9 (2)

[a] Esd's in parentheses refer to the last significant digit.

It has long been known that in pentacoordinated zirconocenes, the fifth ligand is located on the median line of the X–Zr–X angle. In the title compound, the Rh atom as well as H(5) are roughly in a position suitable for an interaction with zirconium: they lie on the bissecting plane of the C(21)–Zr–C(31) angle (C(21)–Zr–H(5) 64.0°, C(31)–Zr–H(5) 72.6°; C(21)–Zr–Rh 69.1°, C(31)–Zr–Rh 65.7°), but they both deviate from the C(21)–Zr–C(31) plane with the Rh atom 0.46 Å above this plane and H(5) 0.75 Å below. With reference to classical models two cases can be considered: (i) there is a Rh→Zr dative bond, or (ii) H(5) is bridging Rh and Zr.

In the first case, the Rh→Zr dative bond would complete the Zr surrounding to 18-valence electrons. However, the intermetallic rhodium–zirconium distance of 3.141 Å is slightly over 3.088 Å, a value observed in another dinuclear Rh–Zr complex, $Cp_2Zr(\mu\text{-}PPh_2)_2Rh(\eta\text{-indenyl})$,[13] in which Zr is described as pseudotetrahedral with 16-valence electrons and with no direct metal–metal interaction. Furthermore, it is worth pointing out that the Zr atom is 1.87 Å out of the Rh surrounding square plane and that P(1)–Rh–Zr angle is 143.1°; such values do not favor a direct metal–metal interaction.

On the other hand, the Zr–H(5) distance of 2.28 Å and the Rh–H(5)···Zr angle of 109.9° compare well with the semibridging arrangement described in $(Cp_2ZrH)_2(\mu\text{-}\eta^2\text{-}OCHMe)$[14] where bridging distances are 1.98 and 2.15 Å (mean value) and the angle at H is 113° (mean value). In $[(C_5H_4CH_3)_2ZrH(\mu\text{-}H)]_2$,[15] a non fully symmetrical bridge is reported: Zr–H = 2.05 and 1.94 Å with a Zr–H–Zr angle

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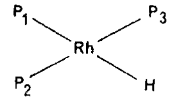
Table V. Bond Distances (Å) and Angles (deg) around the Rhodium Atom in $Cp_2Zr(CH_2PPh_2)_2Rh(H)(PPh_3)$ (3) Compared to Those in $Rh(H)(PPh_3)_3$ (5) and $Rh(H)(P(i\text{-}Pr)_3)_3$ (6)



(C)

compd	Rh-P_1	Rh-P_2	Rh-P_3	Rh-H	P_1-Rh-P_2	P_1-Rh-P_3	P_2-Rh-P_3
3	2.315 (1)	2.276 (1)	2.269 (1)	1.51 (4)	111.08 (4)	97.67 (4)	150.13 (5)
5[a]	2.316 (6)	2.274 (6)	2.262 (5)	*a*	104.0 (2)	102.4 (2)	151.7 (2)
6[b]	2.330 (1)	2.297 (1)	2.291 (1)	1.58 (2)	109.32 (3)	109.15 (3)	141.52 (3)

[a] Reference 7a. The hydride ligand was not located. [b] Reference 8.

Table VI. Bond Distances (Å) and Angles (deg) around the Zirconium Atom in $Cp_2Zr(CH_2PPh_2)_2Rh(H)(PPh_3)$ (3) Compared to Those in $Cp_2Zr(CH_2PPh_2)_2$ (1) and to Those in the Related Complexes $Cp_2Zr(CH_2PPh_2)_2Cr(CO)_4$ (7) and $Cp_2Zr(CH_2PPh_2)_2[Rh(S\text{-}t\text{-}Bu)(CO)]_2$ (8)

compd	Zr-C(CH_2)	Zr-Cp[a]	P-C(CH_2)	(CH_2)C-Zr-C(CH_2)	Cp-Zr-Cp
3	2.398, 2.408	2.249, 2.257	1.780, 1.810	134.3	122.9
1[b]	2.284, 2.340	*c*	1.808, 1.813	100.2	*d*
7[b]	2.292, 2.329	*e*	1.816, 1.817	93.5	*d*
8[f]	2.413, 2.423	2.242, 2.271	1.808, 1.809	134.2	124.8

[a] Distance to the centroid of the C_5H_5 ring. [b] Reference 9. [c] Zr-C range = 2.460–2.560 Å. [d] Not available. [e] Zr-C range = 2.504–2.570 Å. [f] Reference 12.

Table VII. Catalytic Performances of $Rh(H)(PPh_3)_4$ (2) and $Cp_2Zr(CH_2PPh_2)_2Rh(H)(PPh_3)$ (3) for Hydroformylation of 1-Hexene[a]

precursor	reactn time,[b] min	activity: *n*-heptanal produced,[c] %	selectivity: linear/branched aldehyde
2	150	38	1.1
2 + $2PPh_3$	135	52	1.9
3	95	61	2.2
2 + $Cp_2Zr(CH_2PPh_2)_2$	40	67	2.9

[a] Reaction conditions: 20 bar; 80 °C; H_2/CO, 1:1; olefin/catalyst = 400:1; solvent, THF. [b] For about 90% conversion. [c] Referring to initial 1-hexene.

of 120°. The larger difference observed for compound 3, Rh-H(5) = 1.51 Å and Zr-H(5) = 2.28 Å, may be explained by the fact that both metal atoms are chemically and structurally different.[16] Finally, let us mention the 2.21 Å Zr-H distance found recently by Erker, who described an "agostic" interaction of zirconium with a C-H olefinic bond.[17] It is worth pointing out that this H(5) atom was easily located on a difference Fourier map (0.08 e/Å^3) and refined quite well with a low isotropic temperature factor (U = 0.030 (2) Å).

Considering all these features, a semibridging Rh-H-(5)···Zr is preferred even if, taking the risk of going beyond classical models, it could be described as (the first example of) an agostic interaction of the zirconium atom on a Rh-H bond.

It is noteworthy that sensitivity of the zirconium moiety toward alcoholysis (and hydrolysis) is dramatically decreased in the bimetallic complex since crystals of 3 can be washed with ordinary alcohol (95% vol) for hours without detectable decomposition while this reagent rapidly decomposes uncomplexed $Cp_2Zr(CH_2PPh_2)_2$ into CH_3PPh_2 and oxygenated derivatives of zirconium.

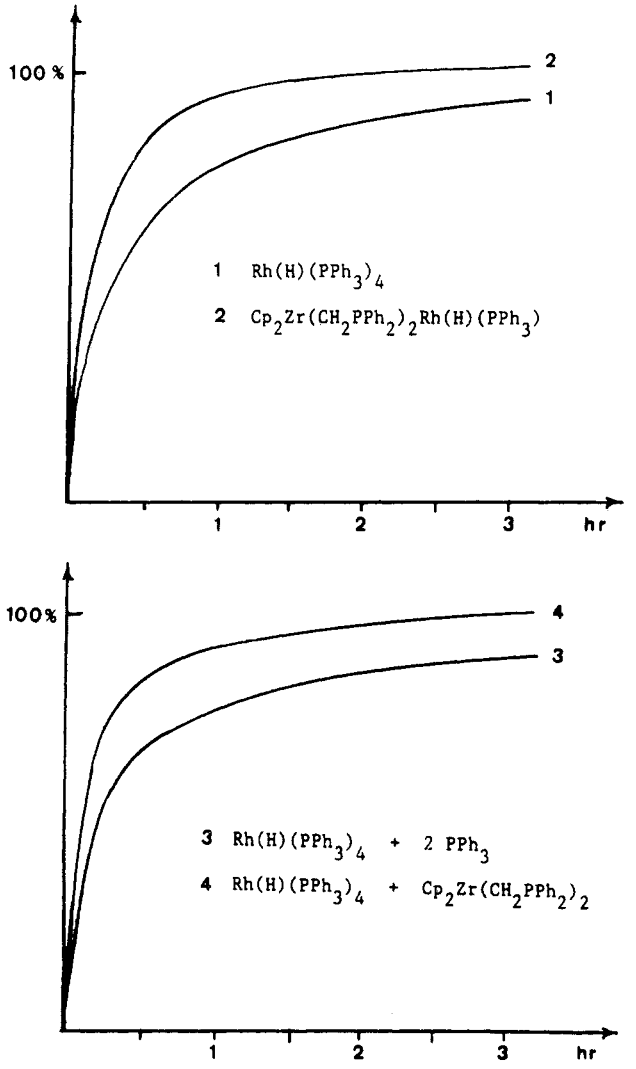


Figure 5. Conversion of 1-hexene (%) vs. time (h) (reaction conditions as in Table VII).

The same is true concerning sensitivity to aldehydes since the bimetallic species, either isolated or generated "in situ", may be used as a catalyst for hydroformylation

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(16) The distance Rh-H (1.51 (4) Å) is shorter than other previously reported values not only for bridged but also for terminal rhodium(I) hydrides; for instance 1.58 (2) Å was found for Rh(H) $(P(i\text{-}Pr)_3)_3$.[8] But in many cases including $Rh(H)(PPh_3)_3$[7] the hydrogen atom could not be located precisely, and it was not possible to compare our data with those of any other complex containing PPh_3 in the transposition of hydrogen in a square-planar coordination around rhodium(I).

(17) Erker, G.; Frömberg, W.; Angermund, K.; Schlund, R.; Krüger, C. *J. Chem. Soc., Chem. Commun.* **1986**, 372–374.

of 1-hexene. A preliminary account of the catalytic results has already been published.[18] The results are summarized in Table VII and Figure 5 where the catalytic performances of the bimetallic complex **3** isolated (curve 2) or generated "in situ" (curve 4) are compared to those of the rhodium hydride **2** without any phosphine added (curve 1) or in the presence of two molecules of triphenylphosphine per molecule of **2** (curve 3). As in a previous work concerning the system obtained by addition of the bis(phosphinomethyl)complex $Cp_2Zr(CH_2PPh_2)_2$ on $Rh_2(\mu\text{-S-}t\text{-Bu})_2(CO)_4$[12,19] the bimetallic complex is significantly more active than the rhodium complex in the absence of zirconium, but in this case enhanced selectivity toward *n*-heptanal is also observed, probably as a consequence of the enhanced polarity of the rhodium–hydride bond. These first results concerning hydroformylation may be described as catalysis by rhodium assisted by zirconium. Our current interest is devoted to catalytic hydrozirconation assisted by rhodium, the latter metal making possible the regeneration of the Zr–H bond by activation of H_2 on rhodium and hydrogen transfer from rhodium to zirconium. With this aim reactions are now in progress on catalytic hydrogenation and hydroformylation of internal olefins and alkynes.

Experimental Section

All preparations were carried out under argon by using Schlenk techniques. All solvents were dried and distilled from sodium benzophenone ketyl under argon and degassed before use. The bis(phosphinomethyl) complex $Cp_2Zr(CH_2PPh_2)_2$ may be prepared either as previously reported by Schore[9] or by the procedure used for $Cp_2Ti(CH_2PPh_2)_2$.[20] $RhH(PPh_3)_4$ was prepared as previously reported.[24]

^1H and ^{31}P NMR spectra were recorded on Bruker WH90 and WM250 spectrometers. Values of ^{31}P chemical shifts are positive downfield from external 85% H_3PO_4 in D_2O. The catalytic experiments were carried out in a 100-mL stainless-steel autoclave at constant pressure (20 bars). Temperature was maintained at 80 °C (through circulation of oil in a double jacket). The mixture of gas (H_2/CO, 1:1) was prepared in a gas tank that is connected to the autoclave, and the drop of pressure in the tank was followed with a pressure gauge connected to an electronic unit for measurement and recording.

The GPC tests were performed on an Intersmat IGC 121 apparatus, using a Carbowax M20 (10%; 2 m) and a SE 30 (10%; 3 m) column.

Preparation of $Cp_2Zr(CH_2PPh_2)_2Rh(H)(PPh_3)$ (3). A solution of the bis(phosphinomethyl)complex $Cp_2Zr(CH_2PPh_2)_2$ (0.433 g, 0.70 mmol) in THF (20 mL) was added slowly at room temperature to a solution of $Rh(H)(PPh_3)_4$ (0.806 g, 0.70 mmol) in THF (40 mL). The mixture was stirred for 2 h and then reduced to 10 mL. Heptane (40 mL) was added to give after 12 h orange crystals that were filtered, washed with pentane, and dried under vacuum; yield 0.61 g (88%).

X-ray Structural Determination. Preliminary unit- cell dimensions and symmetry informations were derived from precession photographs; the selected crystals was then set up on a Nonius CAD4 automatic diffractometer. Accurate cell dimensions and orientation matrix were obtained from least-squares refinements of the setting angles of 25 well-centered reflections ($24 < 2\theta < 28$).

Crystals data and data collection parameters are listed in Table II. Intensities of two standard reflections were monitored every hour; they showed no change during data collection. Corrections were made for Lorentz and polarization effects. In view of the low absorption coefficient and of the psi scan curves that showed no significant intensity variations, absorption correction was not applied.

Computations were performed by using the CRYSTALS system[21] adapted on a VAX 11/725. Atomic scattering factors for neutral Rh, Zr, P, C, and H were taken from ref 22; dispersion for Rh and Zr atoms was taken into account.

The positions of Rh and Zr atoms were determined by Harker vector analysis of a three-dimensional Patterson map. All remaining non-hydrogen atoms were found by successive electron density maps calculations. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located on difference electron density map and included as fixed contribution at their calculated idealized positions (C–H = 0.96 Å). They were assigned isotropic thermal parameter of 0.05. These idealized positions were recalculated after each cycle. Atomic coordinates of H atom attached to the rhodium were introduced with a fixed overall isotropic thermal parameter in the last cycles of refinement. Refinement was by least squares with a large-block approximation to the normal matrix. The derivatives of the positional parameters and the U_{ii} and U_{ij} components were contained in four distinct blocks. In the last stages of the refinement, each reflection was assigned a weight, $W = 1/\sum_{r=1}^{n} A_r T_r(X)$, where n is the number of coefficients A_r, for a Chebyshev series, for which X if $F_o/F_o(\max)$.[23] Three coefficients, A_r, were used with values of 3.63, −1.471, and 2.646. The criteria for a satisfactory completed analysis were the ratio of the parameter shifts to standard deviations (Table II) and no significant features in the final difference map.

Tables of observed structure amplitudes and structure factors calculated from the final atomic parameters, anisotropic thermal parameters, and hydrogen atomic coordinates are available as supplementary material. Atomic coordinates are given in Table III and selected bond lengths and bond angles in Table IV.

General Procedure for Catalytic Experiments. In a typical run, a solution of $Cp_2Zr(CH_2PPh_2)_2Rh(H)(PPh_3)$ (**3**) (79 mg, 8.0×10^{-5} mol) in 16 mL of THF and 4 mL of 1-hexene (32×10^{-3} mol) was syringed into the preheated (80 °C) autoclave, and the syn-gas was immediately introduced. Samples for GPC analysis were syringed off during the course of the catalytic reaction.

Registry No. 1, 74395-16-7; 2, 18284-36-1; 3, 107556-17-2.

Supplementary Material Available: Complete listings of positional parameters and anisotropic thermal parameters for 3 (4 pages); a listing of observed and calculated structure factors for 3 (27 pages). Ordering information is given on any current masthead page.

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