# Synthesis, NMR Study, and Reactivity of Isomeric Early−Late Heterobimetallic Dihydrides. X-ray Crystal Structure of $(PPh_3)HRu(\mu\text{-}H)(\mu\text{-}PMe_2C_5Me_4)_2(\mu\text{-}Cl)ZrCl$

**Vladimir I. Bakhmutov,*,†,‡ Marc Visseaux,‡ Denise Baudry,*,‡ Alain Dormond,‡ and Philippe Richard§**

Institute of Organo-Element Compounds, Russian Academy of Sciences, 28 Vavilova, Moscow, Russia, and Laboratoire de Synthèse et d'Electrosynthèse Organométallique (URA 1685) and UFR Sciences et Techniques, Faculté des Sciences, 6 Boulevard Gabriel, 21000 Dijon, France

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The new isomeric ruthenium/zirconium dihydrides of the formula $(PPh_3)HRuH(\mu\text{-}PMe_2Cp^*)_2ClZrCl$ (**1**, **2**) ($Cp^* = C_5Me_4$) have been characterized by elemental analysis and NMR ($^1H$, $^{31}P$ and $^1H$ relaxation data). Complex **1**, stabilized by Cl and H bridges, has been isolated from the room temperature reaction between $RuH_2(H_2)(PPh_3)_3$ and $(PMe_2Cp^*)_2ZrCl_2$. The X-ray crystallographic study of **1** revealed a bimetallic complex. The six-coordinate Ru atom and the five-coordinate Zr atom are held together by two bifunctional phosphinocyclopentadienyl ligands and by H and Cl bridges. Crystal data for **1**: monoclinic space group $P2_1/c$, $a = 13.901(2)$ Å, $b = 18.205(6)$ Å, $c = 16.633(3)$ Å, $\beta = 92.43(1)°$, $V = 4206$ Å$^3$, $Z = 4$, $d_{calc} = 1.472$ g cm$^{-3}$, $R(F) = 0.056$, $R_w(F) = 0.058$. Complex **2** with two H bridges and terminal Cl ligands at Ru and Zr has been obtained by an irreversible isomerization of **1** in the presence of $HNEt_3BPh_4$. This transformation has been proposed to occur through slow protonation of one of the phosphorus ligands with the five-coordinate Ru center formed by undergoing rapid pseudorotation. Complexes **1** and **2** do not react with $H_2$, $N_2$, or 3,3-dimethyl-but-1-ene. Treatment of **1** with 1 equiv of $NaHBEt_3$ in $C_6D_6$ gives a mixture of new trihydrides $(PPh_3)HRu(\mu\text{-}Cl)(\mu\text{-}H)(\mu\text{-}PMe_2Cp^*)_2ZrH$ (**3**) and $(PPh_3)HRu(\mu\text{-}H)_2(\mu\text{-}PMe_2Cp^*)_2ZrCl$ (**4**). Complex **3** transforms to **4** upon standing in solution for a period of several days. Under the same conditions, complex **2** leads smoothly to trihydride **4**. Both trihydrides are new and have been characterized by $^1H$, $^{31}P$ NMR, and $^1H$ NMR relaxation data. Complexes **1** and **4** are fluxional in solution at room temperature, showing hydride exchange between the terminal and bridging positions. The variable-temperature $^1H$ NMR spectra allowed determinations of the $\Delta G^‡$ values of 16.4 (313 K, THF-$d_8$) and 13.5 kcal/mol (295 K, toluene-$d_8$) for the exchange in complexes **1** and **4**, respectively. Possible exchange mechanisms have been discussed. Complex **2** is rigid on the NMR time scale.

## Introduction

Heterobimetallic hydride complexes have attracted considerable attention[1] in the hope that these compounds might show unusual stoichiometric or catalytic properties.[2] Many hydride-bridged bimetallic complexes have already been described by the groups of Venanzi,[1a,3a] Muetterties,[3b] Caulton,[1c] Mathieu,[1d] Bergman,[1e] Wakatsuki,[1f] and Andersen.[1g] Among these systems, bimetallic compounds containing electronically different metal centers (an early transition metal (Nb, Zr, for example) and a late transition metal (Ru, Rh, Ir)) seem to be the most interesting because of the presence of both hydridic and acidic hydrogens in such molecules.[2b]

In order to produce some Re/Y and Re/Lu hydride compounds, Alvarez et al. have suggested $\sigma$-bond metathesis reactions of lanthanide alkyls with transition metal hydrides.[3c] The same approach has been used in the synthesis of some Ln/W dihydrides.[3d] The salt elimination reaction between an anionic transition metal hydride and an organometallic halide has been suggested by Caulton et al.[4a] to obtain Zr/Os and Zr/Re dimers. Some new heterobimetallic polyhydride uranium compounds have also been produced by this method.[4b]

Bifunctional cyclopentadienylphosphino ligands are useful structural units for building heterobimetallic early−late complexes.[5a−c] Our group has been working in this area[5d,e] for some years, and we hoped that this approach could be used to replace a phosphido ligand in a ruthenium catalyst for a metallophosphine containing an oxophilic metal.

† Russian Academy of Sciences.

‡ Laboratoire de Synthèse et d'Electrosynthèse Organométallique (URA 1685), Faculté des Sciences.

§ UFR Sciences et Techniques, Faculté des Sciences.

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(1) (a) Venanzi, L. M. *Coord. Chem. Rev.* **1982**, *43*, 251. (b) Casey, C. P.; Whiteker, G. T. *Inorg. Chem.* **1990**, *29*, 876. (c) Alvarez, D.; Lundquist, E. G.; Ziller, J. W.; Evans, W. J.; Caulton, K. G. *J. Am. Chem. Soc.* **1989**, *111*, 8392. (d) He, Z.; Nefedov, S;. Lugan, N.; Neibecker, D.; Mathieu, R. *Organometallics* **1993**, *12*, 3837. (e) Baranger, A. M.; Bergmann, R. G. *J. Am. Chem. Soc.* **1994**, *115*, 3822. (f) Nakajima, T.; Mise, T.; Shimizu, I.; Wakatsuki, Y. *Organometallics* **1995**, *14*, 5598. (g) Schwartz, D. J.; Ball, G. E.; Andersen, R. A. *J. Am. Chem. Soc.* **1995**, *117*, 6027.

(2) (a) Roberts, D. A.; Geoffroy, G. L. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, W. W., Eds.; Pergamon Press: Oxford, U.K., 1982; Chapter 40. (b) Bullock, R. M.; Casey, C. P. *Acc. Chem. Res.* **1987**, *20*, 167. (c) Esteruelas, M. A.; Garcia, M. P.; Lopez, A. M.; Oro, L. A. *Organometallics* **1991**, *10*, 127.

(3) (a) Albinati, A.; Lehner, H.; Venanzi, L. M. *Inorg.Chem.* **1985**, *24*, 1483. (b) Teller, R. G.; Williams, J. M.; Koetzle, T. F.; Burch, R. R.; Gavin, R. M.; Muetterties, E. L. *Inorg. Chem.* **1981**, *20*, 1806. (c) Alvarez, D. A.; Caulton, K. G.; Evans, W. J.; Ziller, J. W. *Inorg. Chem.* **1992**, *31*, 5500. (d) Radu, N. S.; Gantzel, P. K; Tilley, T. D. *J. Chem. Soc., Chem. Commun.* **1994**, 1175.

(4) (a) Bruno, J. W.; Huffman, J. C.; Green, M. A.; Caulton, K. G. *J. Am. Chem. Soc.* **1984**, *106*, 8310. (b) Baudry, D.; Ephritikhine, M. *J. Organomet. Chem.* **1986**, *311*, 189.

(5) (a) Tikkanen, W.; Fujita, Y.; Petersen, J. L. *Organometallics* **1986**, *5*, 888. (b) Deacon, G. D.; Dietrich, A.; Forsyth, C. M.; Schumann, H. *Angew. Chem., Int. Engl.* **1989**, *10*, 1370. (c) Deacon, G. D.; Forsyth, C. M.; Patalinghug, A. H.; White, A. H.; Dietrich, A; Schumann, H. *Aust. J. Chem.* **1992**, *45*, 567 (d) Visseaux, M; Dormond, A.; Kubicki, M. M.; Moïse, C.; Baudry, D.; Ephritikhine, M. *J. Organomet. Chem.*, **1992**, *433*, 95. (e) Baudry, D.; Dormond, A.; Visseaux, M.; Monnot, C.; Chardot, H.; Lin, Y.; Bakhmutov, V. I. *New J. Chem.* **1995**, *19*, 921.

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This work describes the characterization and some properties of the new isomeric Ru/Zr dihydrides of the formula $PPh_3$-$HRuH(\mu\text{-}PMe_2Cp^*)_2ClZrCl$ (**1**, **2**) ($Cp^* = C_5Me_4$). Complex **1** was isolated from the reaction between $Ru(H_2)H_2(PPh_3)_3$ and $(PMe_2Cp^*)_2ZrCl_2$,[5e] whereas dihydride **2** was obtained by an isomerization of **1.** New trihydride derivatives of **1** and **2** are also discussed in this paper.

## Results and Discussion

**Synthesis and X-ray Structure of Complex 1.** Bimetallic complex **1** has been synthesized (eq 1) at room temperature in toluene. Elemental analysis was consistent with the formula

$$RuH_2(H_2)(PPh_3)_3 + (PMe_2Cp^*)_2ZrCl_2 \rightarrow \mathbf{1} + H_2 + 2PPh_3 \quad (1)$$

$[H_2Ru(PPh_3)(PMe_2Cp^*)_2ZrCl_2]$. In the absence of X-ray data, the complex was fully characterized by $^1H$ and $^{31}P$ NMR methods. The data obtained are summarized in Tables 1 and 2.

Strong evidence was obtained for the bimetallic structure of **1** with bifunctional phosphinocyclopentadienyl ligands and two Cl and H bridges. This is now confirmed by the X-ray crystal structure.

**Molecular Structure of $(PPh_3)HRu(\mu\text{-}H)(\mu\text{-}PMe_2Cp^*)_2(\mu\text{-}Cl)ZrCl$.** The molecular structure of **1** is shown in Figure 1, and selected bond lengths and angles are given in Table 3.

The molecular structure of **1** consists of ZrCl and Ru(H)-$PPh_3$ units in which the two metals are bridged by two bifunctional phosphinocyclopentadienyl ligands and by two monoatomic ligands, Cl and H. The molecule includes six-coordinated ruthenium and five-coordinated zirconium atoms.

The coordination sphere of the ruthenium atom can be described as a distorted octahedron consisting of three P, one bridging Cl, and terminal (located in the $^1H$ NMR spectrum, see Table 1) and bridging H atoms. The pseudooctahedral geometry about Ru requires the terminal hydrides to be located in a cis position with respect to the H bridge. The Ru−P distances are shorter than those observed in Ru−$PPh_3$ (2.34 vs 2.37 Å) and Ru−$PMe_2Ph$ (2.34 Å) moieties, while the Ru−Cl(1) bond length value is slightly higher than that reported in the literature (2.43 Å).[6]

The zirconium coordination sphere can be described as a distorted trigonal bipyramid: the H bridge and the terminal Cl ligand occupy two apical positions with the Cl−Zr−H angle close to 158° (Table 3) while vectors Zr−CP (CP is the geometrical center of the cyclopentadienyl ring) and Zr−Cl (bridge) form the base of this bipyramid (the sum of the corresponding angles is equal to 358°).[7−12]

The Zr−Ru distance of 3.130(1) Å in **1** is longer than the direct unsupported Zr−Ru bond lengths observed, for example, in $Cp_2Zr(OtBu)Ru(CO)_2Cp$ (2.910(1) Å)[13] and $Cp_2Zr[Ru(Co)_2Cp]_2$ (2.943(1) Å).[14] However, it should be noted that in

**Table 1.** Room-Temperature $^1H$ NMR Data ($C_6D_6$) for Complexes **1** to **4** ($\delta$, ppm/TMS; *J*, Hz)

| | $\delta$ (*J*) | | | | | | |
|---|---|---|---|---|---|---|---|
| compd | $H_a$ | $H_b$ | $H_c$ | $H_d$ | $PMe_2$[b] | MeCp | $PPh_3$ |
| **1** | −14.09 (q) ($J$(H−$PPh_3$) = 23.0; $J$(H−$PMe_2$) = 19.1) | −10.62 (db) ($J$(H−$PPh_3$) = 46.6; $J$(H−$PMe_2$) = 21.7) | | | 0.84, 1.27 | 1.49, 2.01, 2.29, 2.33 | 7.07 (9 H), 7.93 (6 H) |
| **2** | | −11.89 (db) ($J$(H−$PPh_3$) = 66.0; $J$(H−$PMe_2$) = 20.2; $J$($H_b$−$H_c$) = 3.0) | −18.10 (q) ($J$(H−$PPh_3$) = 18.7; $J$(H−$PMe_2$) = 18.7; $J$($H_c$−$H_b$) = 3.0) | | 1.13, 2.22 | 1.41, 1.62, 2.03, 2.27 | 7.08 (9 H), 7.83 (6 H) |
| **3** | −13.85 (q) ($J$(H−$PPh_3$) = 19.1; $J$(H−$PMe_2$) = 19.1) | −11.10 (db) ($J$(H−$PPh_3$) = 50.2; $J$(H−$PMe_2$) = 25.1; $J$($H_b$−$H_d$) = 10.7) | | 2.90 (d) ($J$($H_d$−$H_b$) = 10.7) | 0.74, 1.44 | 1.56, 2.11, 2.23, 2.40 | 7.11 (9 H), 8.00 (6 H) |
| **4**[a] | −10.70 (m) ($J$(H−$PPh_3$) = 21.9; $J$(H−$PMe_2$) = 21.9; $J$($H_a$−$H_b$) ≤ 3.0; $J$($H_a$−$H_c$) = 12.7) | −12.09 (db) ($J$(H−$PPh_3$) = 48.7; $J$(H−$PMe_2$) = 24.7; $J$($H_b$−$H_a$) ≤ 3.0) | −7.36 (m) ($J$(H−$PPh_3$) = 13.0; $J$(H−$PMe_2$) = 13.0; $J$($H_c$−$H_a$) = 12.7) | | 1.02, 1.80 | 1.50, 1.83, 2.10, 2.29 | 7.08 (9 H), 7.94 (6 H) |

[a] In toluene-$d_8$ at 233 K. [b] Apparent triplets in AA′$X_6$ spin systems.


(6) Orpen, A. G.; Brammer, L.; Allen, F. M.; Kennard, O.; Watson, D. G.; Taylor, R. *J. Chem. Soc., Dalton Trans.* **1989**, *12*, S1.
(7) Silver, M. E.; Eisenstein, O.; Fay, R. C. *Inorg. Chem.* **1983**, *22*, 759.
(8) Tilley, T. D. *Organometallics* **1985**, *4*, 1452.
(9) Lasser, W.; Thewalt, U. *J. Organomet. Chem.* **1986**, *302*, 201.
(10) Gambarotta, S.; Strologo, S.; Floriani, C; Chiesi-Villa, A.; Guastini, C. *J. Am. Chem. Soc.* **1985**, *107*, 6278.
(11) Choukroun, R.; Dahan, F.; Gervais, D. *J. Organomet. Chem.* **1984**, *266*, C33.
(12) Engelhardt, L. M.; Jacobsen, G. E.; Raston, C. L.; White, A. H. *J. Chem. Soc., Chem. Commun.* **1984**, 220.
(13) Casey, C. P.; Jordan, R. F.; Rheingold, A. L. *J. Am. Chem. Soc.* **1983**, *105*, 665.
(14) Casey, C. P.; Jordan, R. F.; Rheingold, A. L. *Organometallics* **1984**, *3*, 504.

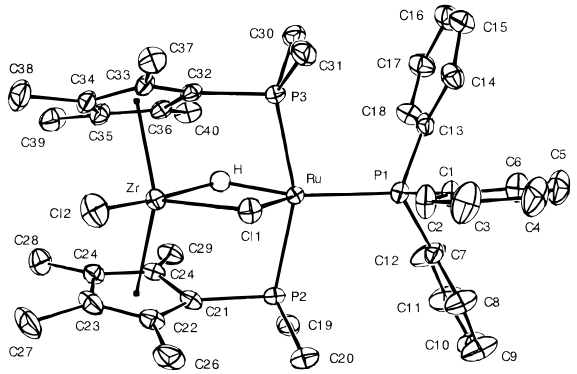



**Figure 1.** ORTEP drawing of **1**. The terminal H atom attached to the Ru atom is not represented.

**Table 2.** Room-Temperature $^{31}P\{^1H\}$ NMR Data ($C_6D_6$) for Complexes **1**−**4** ($\delta$, ppm/$H_3PO_4$; *J*, Hz)

| | $\delta$ | | |
|---|---|---|---|
| complex | $PMe_2$ (multiplicity) | $PPh_3$ (multiplicity) | $^2J$(P−P) |
| **1** | 7.70 (d) | 53.87 (t) | 26.8 |
| **2** | −1.50 (d) | 40.98 (t) | 26.4 |
| **3** | 8.15 (d) | 63.3 (t) | 24.3 |
| **4** | 4.20 (d) | 61.8 (t) | 28.2 |

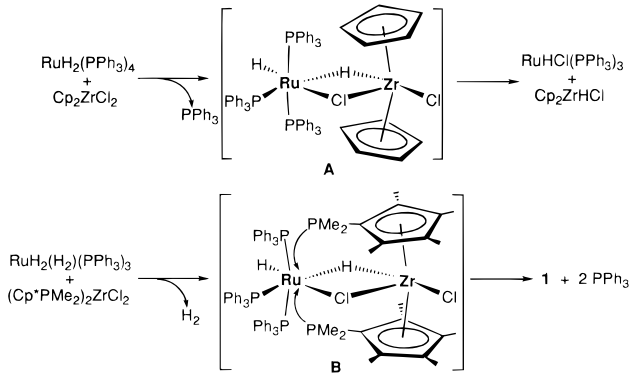
**Table 3.** Selected Bonding Parameters for **1**

| | | | |
|---|---|---|---|
| | Distances (Å) | | |
| Ru−Zr | 3.130(1) | Zr−Cl(1) | 2.566(2) |
| Ru−Cl(1) | 2.493(2) | Zr−Cl(2) | 2.550(3) |
| Ru−P(1) | 2.303(2) | Zr−CP(1) | 2.278 |
| Ru−P(2) | 2.310(2) | Zr−CP(2) | 2.274 |
| Ru−P(3) | 2.324(2) | Zr−H | 1.93 |
| Ru−H | 1.81 | | |
| | Angles (deg) | | |
| Cl(1)−Ru−P(1) | 111.30(8) | Cl(1)−Zr−Cl(2) | 78.03(8) |
| Cl(1)−Ru−P(2) | 86.78(8) | Cl(1)−Zr−CP(1) | 107.6 |
| Cl(1)−Ru−P(3) | 84.41(8) | Cl(1)−Zr−CP(2) | 110.7 |
| Cl(1)−Ru−H | 86. | Cl(1)−Zr−H | 82. |
| P(1)−Ru−P(2) | 103.28(8) | Cl(2)−Zr−H | 158. |
| P(1)−Ru−P(3) | 99.37(8) | Cl(2)−Zr−CP(1) | 99.4 |
| P(1)−Ru−H | 159.96(6) | Cl(2)−Zr−CP(2) | 100.0 |
| P(2)−Ru−P(3) | 157.34(8) | CP(1)−Zr−CP(2) | 139.8 |
| P(2)−Ru−H | 86. | Ru−Cl(1)−Zr | 76.42(6) |
| P(3)−Ru−H | 72. | Ru−H−Zr | 114. |

the latter cases the coordination number of the zirconium atoms is equal to 4. The metal−metal distance observed here is intermediate between the Zr−Zr (3.233(1) Å)[15] and Ru−Ru (2.821(1) Å)[16] bond lengths found in fulvalene bimetallics.

The acute value of the bridging Zr−Cl−Ru linkage (78.42(6) Å) argues for the presence of a direct metal−metal bond or a three-center two-electron bond, including the bridging H ligand. The last description is plausible because the bent metallocenes display three frontier hybrid orbitals in the plane bisecting that of the cyclopentadienyl ligands.[17] These three orbitals could be involved in the bonds with terminal Cl(2), bridging Cl(1), and H atoms. Finally, such a description provides an 18 electron environment for each metal center. Note that the value of the above mentioned Cl−Zr−H angle implies the known position of the bridging hydride ligand. In fact, as described in the Experimental Section, the position of this hydride was poorly located in a difference Fourier map. Nevertheless, the Zr−$\mu$-H (1.93 Å) and Ru−$\mu$-H (1.81Å) distances correspond well to the values reported for Zr[18] and Ru[6] complexes containing H bridges.

**Scheme 1**




The Zr−Cl bond lengths are close to each other (Table 3) and fall in the range observed for five-coordinated zirconocenes (2.52−2.57 Å).[7,10−12] At the same time, these values are significantly higher than those reported for four-coordinated zirconocenes (2.41−2.48 Å).[19]

The CP−Zr−CP angle in **1** is significantly opened (140°). This value is slightly higher than that determined in the titanocene compound $[(C_5Me_4PPh_2)_2TiCl_2Mo(CO)_4]$[20] bearing the $C_5Me_4PPh_2$ ligand (138.4°), while it is generally accepted that a smaller central atom (Ti vs Zr) is more sensitive to the changes of the ligand sizes. Note that the CP−Zr−CP angle in the dinuclear Zr/Mo complex $[(C_5H_4PPh_2)_2ZrCl_2Mo(CO)_4]$ is equal to 130°,[5a] while the difference in these CP−Zr−CP angles could be attributed to steric requirements of the $C_5H_4$-$PPh_2$ and $C_5Me_4PPh_2$ ligands. The magnitude of the above difference (10°) suggests a cooperation of electronic effects in the overall structure.

The zirconium atom in **1** is certainly more electron rich than in $[(C_5H_4PPh_2)_2ZrCl_2Mo(CO)_4]$ ($C_5Me_4PPh_2$ is a better cyclopentadienyl donor than $C_5H_4PPh_2$, and $Ru(H)PPh_3$ is a better donor than $Mo(CO)_4$). Even without a detailed knowledge of the exact distribution of electron density in **1**, a qualitative argument, based on the Lauher and Hoffmann model,[17] suggests some population of the so-called antibonding frontier orbitals of the $Cp_2M$ system. In turn, the population of these orbitals may contribute to the opening of the CP−Zr−CP angle.

**Mechanism of Formation of 1.** The formation of a complex with a trans configuration of the $PMe_2$ groups was unexpected. Chelating ligands usually adopt a cis configuration, as observed in $[Mo(CO_4)][(PMe_2Cp^*)_2ZrCl_2]$ [5e] and more generally in [Ru]L−L compounds.[21] As a working hypothesis, we propose that the mechanism of reaction (eq 1) may involve an H/Cl exchange observed in solutions of $RuH_2(PPh_3)_4$ and $Cp_2ZrCl_2$.[5e] This exchange leads to the hydrochloride $RuHCl(PPh_3)_3$,[22] and therefore formation of an H and Cl bridged transient binuclear species (**A** in Scheme 1) seems to be quite reasonable.

Complex **1** could be formed by a "blocked" exchange process: the first step would result in a similar doubly bridged

(15) Gambarotta, S.; Chiang, M. Y. *Organometallics* **1987**, *6*, 897.
(16) Vollhardt, K. P. C.; Weidman, T. W. *J. Am. Chem. Soc.* **1983**, *105*, 1676.
(17) Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729.
(18) (a) Pez, G. P.; Putnik, C. F.; Suib, S. L.; Stucky, G. D. *J. Am. Chem. Soc.* **1979**, 106, 6933. (b) Jones, S. B.; Petersen, J. L. *Inorg. Chem.* **1981**, *20*, 2889. (c) Kreutzer, K. A.; Fisher, R. A.; Davis, W. M.; Spaltenstein, E.; Buchwald, S. L. *Organometallics* **1991**, *10*, 4031.
(19) Holloway, C. E.; Walker, I. M.; Melnik, M. *J. Organomet. Chem.* **1987**, *321*, 143.
(20) Szymoniak, J.; Kubicki, M. M.; Besançon, J.; Moïse, C. *Inorg. Chim. Acta* **1991**, *180*, 153.
(21) (a) Garrou, P. E. *Chem. Rev.* **1981**, *81*, 229. (b) Jung, C. W., Garrou, P. E. *Organometallics* **1982**, *1*, 658
(22) Hallman, P. S.; McGarvey, B. R.; Wilkinson, G. *J. Chem. Soc. A* **1968**, 3143.

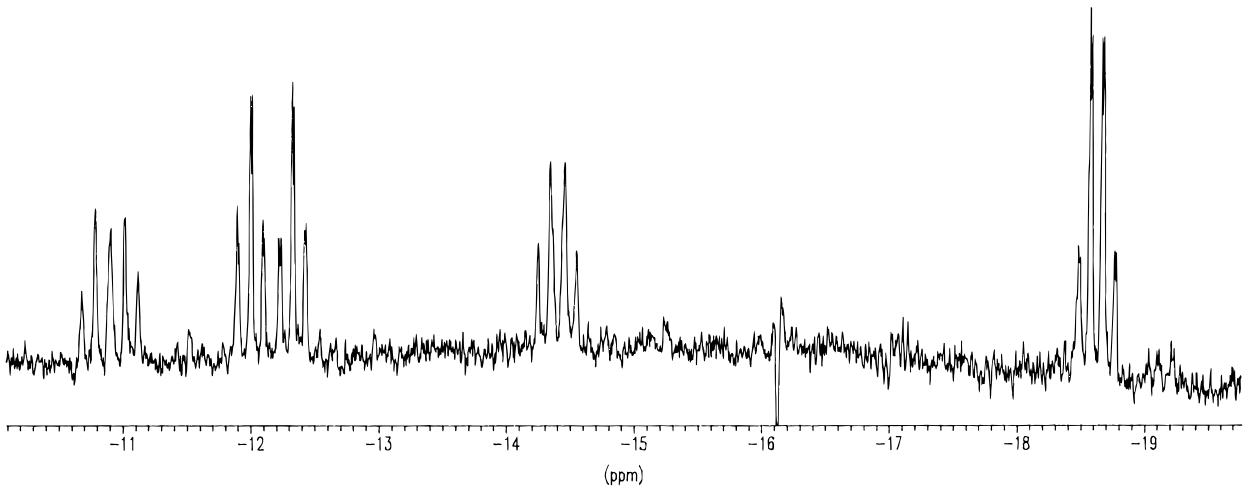



**Figure 2.** Room-temperature $^1$H NMR spectra of the hydride region of the mixture obtained when complex **1** is dissolved in THF-$d_8$ in the presence of 1 equiv of $HNEt_3BPh_4$ (reaction time: 1 h).

binuclear species in which, instead of the H/Cl exchange, the displacement of two $PPh_3$ ligands for the two $PMe_2Cp^*$ moieties would take place (**B** in Scheme 1), leading to the rigid strongly bonded tetrabridged heterobimetallic **1**. We observed that no bimetallic complex analogous to **1** was formed when $(PMe_2Cp^*)_2ZrCl_2$ was mixed with $RuHCl(PPh_3)_3$. At room temperature, no reaction took place, whereas the progressive consumption of the starting material and the formation of unidentified products were observed at 60°C. Thus, it might be possible that the first step of the reaction leading to **1** would not be a simple phosphine displacement.

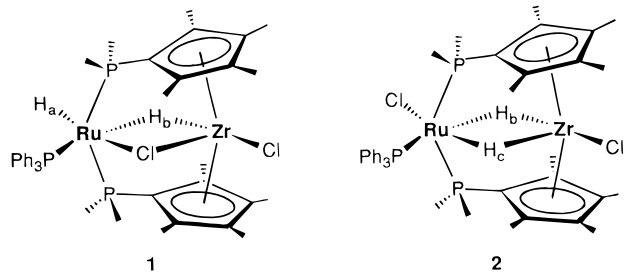
**Acidic Isomerization of 1 and Structure of Complex 2.** As evidenced by NMR and X-ray analysis, **1** is coordinatively and formally electronically saturated. It was found to be unreactive toward dihydrogen, dinitrogen, or olefins. A vacant site could be created by protonation of the ruthenium and $H_2$ elimination.[1d,23] However, no $H_2$ evolution was observed when 1 equiv of the noncoordinating acid $HEt_3NBPh_4$ was added to a $C_6D_6$ solution of **1**. Instead, the acid addition resulted in the isomerization of **1** to **2** (eq 2) which was effective after 30−40 min at 60 °C. No reaction was observed at room temperature.

$$\mathbf{1} \xrightarrow{[Et_3NH]^+[BPh_4]^-} \mathbf{2} \qquad (2)$$

In THF-$d_8$, the transformation, followed by $^1$H NMR spectroscopy (Figure 2), is effective at room temperature after 3 h. This difference of temperature may be attributed to the poor solubility of the acid in benzene. Complex **2** is soluble in aromatic solvents.

The elemental analysis of **1** and **2** revealed the same chemical composition. It is important that complex **2** is also unreactive toward $H_2$, $N_2$, and 3,3-dimethylbut-1-ene. The room-temperature $^1$H and $^{31}$P NMR spectra of **2** were similar to those of **1**. Complex **2** was assumed to possess the same skeleton as **1**, but with a terminal Ru−Cl bond and two H bridges (Chart 1) (we have used the following notations for the H ligands: $H_a$, the terminal ruthenium hydride ligand; $H_b$, the bridging H ligand located trans to the $PPh_3$ group; $H_c$, the bridging H ligand located cis to the $PPh_3$ group; and $H_d$, the terminal zirconium hydride ligand). Unfortunately, it was impossible to obtain crystals suitable for X-ray analysis. Nevertheless, a complete NMR analysis (see below) allows us to propose for **2** the structure of a dihydridochloride.

**Chart 1**




The M−H region of the IR spectrum of dihydride **2** exhibits two absorptions at 1919 and 1784 $cm^{-1}$. Similar bands have already been reported for $(Cp_2ZrCl)(\mu\text{-}H_3)Os(PMe_2Ph)_3$ and were discussed in terms of a splitting caused by symmetric and antisymmetric motions.[4a] Thus, the IR spectrum does not contradict the structural formulation of the dihydride obtained in this work.

To elucidate the mechanism of the above acidic isomerization of **1**, we have carried out NMR experiments in $C_6D_6$ and THF-$d_8$ solutions in the presence of $DEt_3NBPh_4$ and no D bound to Ru (instead H) was found in the $^1$H NMR spectra of the final product **2**. This result contradicts protonation of the hydride ligands of the Ru center of complex **1** to form a fluxional trihydride intermediate. Therefore it is reasonable to suppose protonation of one of the phosphorus atoms with formation of the five-coordinate Ru center which undergoes very rapid pseudorotation. The formalism of the Berry mechanism or of the turnstile rotation[24] allows us to rationalize the isomerization of **1** in **2** when the protonation of one of the $PMe_2Cp^*$ groups takes place.

Finally, in the presence of 1 equiv of $PPh_3$, after addition of an excess of $H^+$ in THF-$d_8$, the bimetallic structure is destroyed. The well-known complexes $RuHCl(PPh_3)_3$ and $Ru(H_2)H_2(PPh_3)_3$, which are formed after consecutive protonation of both $PMe_2Cp^*$ ligands of **1**, were characterized. Appearance of $H_2$ in the reaction solution (to give $RuH_2(H_2)(PPh_3)_3$) is not surprising because protonation of transition metal hydrides often leads to $H_2$ liberation.[25]

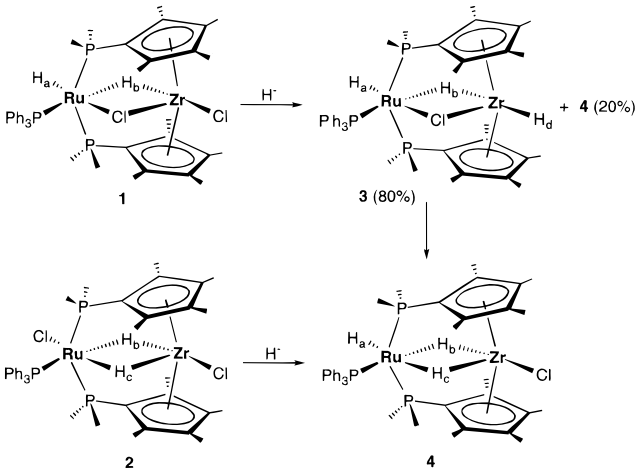
**Reactivity of 1 and 2 toward $H^-$.** Addition of 1 equiv of the soluble hydride $NaHBEt_3$ to a $C_6D_6$ solution of **1** results in formation of two isomeric trihydrides **3** and **4** in a 4:1 molar

(23) Grossman, R. B.; Doyle, R. A.; Buchwald, S. L. *Organometallics* **1991**, *10*, 1501.

(24) Cotton, F. A.; Wilkinson, G. In *Advanced Inorganic Chemistry*, 4th ed.; John Wiley and Sons: New York, 1980; p 1220.

(25) Heinekey, D. M.; Oldham, W. J. *Chem. Rev.* **1993**, *93*, 913.

**Scheme 2**




ratio. However, upon standing in solution for a period of several days, trihydride **3** isomerizes into trihydride **4** (Scheme 2). Under the same conditions, complex **2** gives only one product: trihydride **4**.

The structure of **3** is well-deduced from the $^1$H and $^{31}$P NMR spectra (Tables 1 and 2, see below), and thus, the substitution of the terminal Cl ligand in **1** occurs with complete retention of stereochemistry at the zirconium center leading to trans $H_b$ and $H_d$.

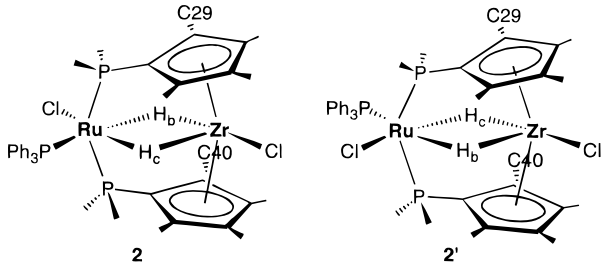
Scheme 2 shows the most probable structure for **4** proposed on the basis of the complete NMR analysis (see below). This trihydride can be envisaged as a product of the substitution of the bridging Cl atom in **1** with retention of the Ru configuration, as is usually observed for an octahedral site.[26] Finally, it should be emphasized that trihydride **4** with two H bridges is more stable than **3** containing the bridging Cl and H ligands.

In contrast to compound **1**, treatment of complex **2** with $NaHBEt_3$ leads to a single compound identified as trihydride **4** by the $^1$H, $^{31}$P{$^1$H} NMR data (see below). The high selectivity of this substitution is chemical evidence for structure **2**, which should be considered as a double ruthenium and zirconium hydridochloride, whereas **1** would be regarded as a ruthenium dihydride−zirconium dichloride. In this context, formation of trihydride **4** from **2** is entirely expected because the displacement of a chloride ligand on the ruthenium moiety by a hydride is effective immediately at room temperature. It is also well-known that if the displacement of the first chlorine atom of a $ZrCl_2$ moiety is easy, the substitution of the second one requires more forcing conditions. These differences of reactivity also explain the preferred formation of **3** from **1**.

**NMR Studies.** The $^{31}$P{$^1$H} NMR parameters of **1**−**4** are very similar (Table 2), showing that the same type of structure is adopted for all of these compounds. Actually, the $J$(P−P) values of ∼25 Hz indicate clearly that the geometry of the $PPh_3$-$Ru(PMe_2Cp^*)_2$ fragment is conserved. All of the $CH_3$ groups are inequivalent in the $^1$H NMR spectra of **1**−**4**.

**Complex 2.** The room-temperature $^{31}$P{$^1$H} NMR spectrum of **2** in $C_6D_6$ exhibits a well-resolved triplet at 40.98 ppm coupled to a doublet at −1.50 ppm with a $^2J$(P−P) value of 26.4 Hz (Table 2). A 1:2 integral ratio was obtained for these lines when delays of 10 s were used between the NMR pulses. Thus, the $PPh_3$ ligand is located cis to the equivalent $PMe_2Cp^*$ groups without significant changes in the corresponding P−Ru−P angles in going from **1** to **2**. Additional splittings observed in the $^{31}$P NMR spectra of **2** with selective decoupling of the $PMe_2$ and $PPh_3$ protons indicate clearly two Ru-bonded hydrogens.

**Chart 2**




These H ligands are well-manifested in the hydride region of the $^1$H NMR spectrum as a doublet of triplets at −11.89 ppm ($J^d$(H−P) = 66.0 Hz, $J^{tr}$(H−P) = 20.2 Hz) with small additional doublet splittings of 3 Hz ($^2J$(H−Ru−H), H/H decoupling resonance experiments) and as a quadruplet at −18.10 ppm ($J$(H−P) = 18.7 Hz) with the same additional splittings. On the basis of the larger doublet H/P coupling, the former resonance can be assigned to the hydride ligand located trans to the $PPh_3$ group.[27] Table 2 shows that the trans $J$(H−P) coupling constant increases when **1** transforms to **2**. Nevertheless the value of 66 Hz remains within the limits corresponding to bridging hydrides.[1d,28]

The quadruplet at −18.10 ppm (a typical value for a RuHCl fragment[22]) with $J$(H−P) = 18.7 Hz, can be assigned to a hydride ligand located cis to all phosphorus ligands of **2**. In accordance with this assignment, the small H−Ru−H coupling of 3 Hz can be well-interpreted as coupling of the two hydrides located cis to one another. Indeed, trans couplings between terminal and bridging RuH ligands are larger: for example, 12.7 Hz in **4** (Table 1) and about 13 Hz in some Ru/Rh dihydrides.[27] The presence of two cis hydrogen ligands, one of them bridging ($H_b$), implies, for a $Ru^{II}$, $Zr^{IV}$ complex with the same type of structure as **1**, the presence of two terminal chloride ligands and of a zirconium−hydrogen ($H_c$) bond involving the empty orbital of the zirconocene moiety.

The $^1$H NMR data can be interpreted in terms of two possible structures: **2** and **2′** (Chart 2), which both contain the coordinatively saturated Ru center. In full accordance with this formulation, no $H_2$ binding (on the basis of the $T_1$ value observed for the $H_2$ signal[29] ) to the Ru center of **2** has been found in THF-$d_8$ and $C_6D_6$ at room temperature under $H_2$ atmosphere.We first used the NOE technique to locate the $H_b$ signal, but no significant results were obtained. Usually, the increase in intensity of the observed resonance is 5−10%,[30] and such a variation of the intensity is not easily recorded for ruthenium hydride signals. We then employed $T_1$ measurements (see below): a shorter relaxation time of the $H_b$ ligand, located trans to the $PPh_3$ group, implies a close proximity of both $C_{29}$ and $C_{40}$ atoms and supports structure **2**.

**Trihydride 3.** The $^{31}$P NMR spectrum with selective decoupling of the $PMe_2$ and $PPh_3$ protons corresponds to two Ru-bonded H ligands.

The hydride region of the $^1$H NMR spectrum shows a multiplet at −11.10 ppm ($H_b$, 1H) which is coupled to the $PPh_3$ ($J$(H−P) = 50.2 Hz) and $PMe_2Cp^*$ ligands ($J$(H−P) = 25.1 Hz). This value compares well with 46.6 Hz found for $H_b$ in

(26) Henderson, R. A. *The Mechanisms of Reactions at Transition Metal Sites*; Oxford University Press: Oxford, U.K., 1993; pp 23−32.
(27) Esteruelas, M. A.; Werner, H. *J. Organomet. Chem.* **1986**, *303*, 221.
(28) Van Der Sluys, L. S.; Kubas, G. J. Caulton, K. G. *Organometallics* **1991**, *10*, 1033.
(29) Hamilton, D. G.; Crabtree, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 4126.
(30) Crabtree, R. H. In *The orgamometallic chemistry of the transition metals*; John Wiley and Sons: New York, 1988; p 230.

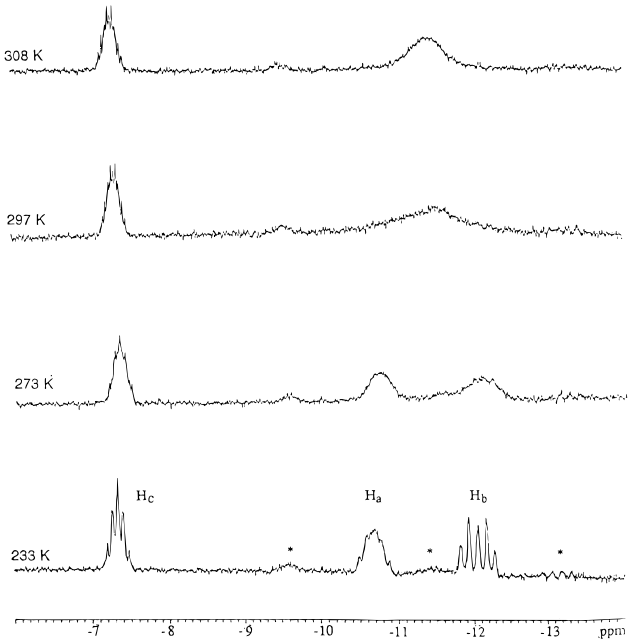



**Figure 3.** Hydride region of the variable-temperature $^1$H NMR spectra of complex **4** dissolved in toluene-$d_8$. (Signals marked with an asterisk, also observed when an excess of $NaHBEt_3$ was added to **4**, are tentatively attributed to a tetrahydride species.)

complex **1**. Such $J$(H−P) magnitudes, observed for trans located $^1$H and $^{31}$P nuclei, correspond to H bridges,[1d,25] whereas terminal trans-HRuP moieties display high values[31] (in agreement with this, $H_b$ has been actually located in the X-ray structure of **1** in the bridging position). As detailed in Table 1, $H_b$ in **3** shows an additional splitting of 10.7 Hz which disappears after $H_d$ irradiation. Thus, $H_b$ is located trans to $H_d$. The $H_d$ resonance was found in the $^1$H NMR spectrum as a broadened doublet at 2.90 ppm that corresponds well to the terminal Zr−H ligands observed usually in the "positive" chemical shift region.[4a,23,32] $H_a$ is manifested as a quadruplet resonance at −13.85 ppm (1H) with $J$(H−P) = 19.1 Hz. It must be emphasized that these hydride chemical shifts are very similar to those found for complex **1** (Table 1), confirming that the same geometry is retained from **1** to **3**.

**Trihydride 4.** The room-temperature $^{31}$P{$^1$H} NMR spectrum of **4** in $C_6D_6$ shows a well-resolved triplet at 61.8 ppm and a doublet at 4.2 ppm with $J$(P−P) = 28.2 Hz (Table 2). The spectrum with selective decoupling of the $PMe_2$ and $PPh_3$ protons corresponds to three Ru-bonded hydrogens.

The room-temperature $^1$H NMR spectrum exhibits a multiplet at −7.36 ppm (1H, $H_c$) and a very broad line at −11 ppm (2H, $H_a$ and $H_b$) which transforms to the well-resolved resonances in toluene-$d_8$ at 233 K (Figure 3), demonstrating complex **4** to be fluxional on the NMR time scale. H/H decoupling experiments at this temperature have allowed determination of all proton−proton and proton−phosphorus coupling constants (Table 1); from these, it is possible to deduce the H positions with respect to the phosphorus sites.

The value of the coupling constant found for the multiplet at −12.09 ppm ($J$(H−$PPh_3$) = 48.7 Hz) shows that trans hydride $H_b$ must be considered as a Ru/Zr bridge[1d,25] (this compares well with the 46.6 Hz found for $H_b$ in complex **1**).

**Chart 3**

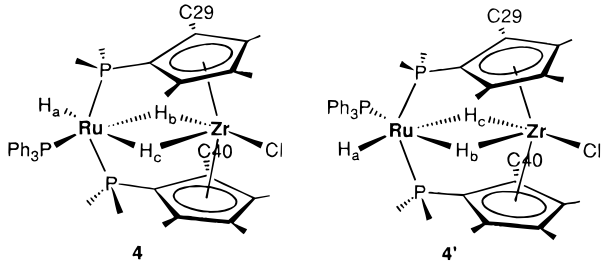



Figure 3 shows that the signal at −7.36 ppm ($H_c$) does not participate in the H/H exchange. This resonance is characterized by the smallest $J$(H−P) magnitude (13 Hz) that can be attributed, in our opinion, to a strong binding of this ligand to the Zr atom. In addition to the zirconium electronic saturation, this is another argument for considering $H_c$ as a bridge between the two metals. According to the data, the trans terminal and bridging hydrides ($H_a$ and $H_c$, respectively) are coupled with $^3J$(H−Ru−H) = 12.7 Hz. The significantly smaller coupling of ≤3 Hz is found for cis $H_a$ and $H_b$, and no H−Ru−H coupling is resolved for the two bridging $H_b$ and $H_c$ hydrides.

As in the case of complex **1**, the $CH_3$ groups of the Cp* and $PMe_2$ ligands of **4** are inequivalent in the $^1$H NMR spectrum (Table 1). Chemical shifts of coordinated methylphosphines are usually found in the range of $\delta$ = 1.4 ppm. The unusually low shift of one of the P−Me groups (0.74 ppm) can be attributed to magnetic anisotropy of the phenyl rings of the $PPh_3$ ligand.

The NMR data presented here can be interpreted in terms of two possible structures **4** and **4′** in Chart 3. On the basis of the $T_1$ data, structure **4** seems to be the most probable (see below).

**$^1$H NMR Relaxation Study.** In recent years, $^1$H $T_1$ relaxation time measurements have often been used in structural studies of transition metal hydride complexes.[33]

In the present work, the $^1$H $T_1$ approach was used in order to obtain additional information, particularly for compounds **2** and **4**.

If complexes **1**−**4** show the same type of structural arrangement, correlation times of their molecular reorientations[34] should be the same. In fact, the very similar (not recorded for **3** which is metastable) $^1$H $T_1$ values (Table 4) for the $CH_3$ protons of the Cp* or $PMe_2$ groups (and moreover the upfield resonance from one of the two nonequivalent $CH_3$ groups in the $PMe_2$ ligands, which is characterized by the shorter $T_1$ magnitude in each complex), demonstrate clearly that these complexes have similar structures.[35]

The hydride relaxation in classical transition metal hydride systems is dominated by dipole−dipole [34] "hydride−hydride" and hydride−bulky proton-rich ligands[36] interactions. According to the X-ray structure (Figure 1), the shortest H···H contacts in complex **1** are observed between $H_b$ and the $CH_3$ groups of

(31) Gusev, D. G.; Vymenits, A. B.; Bakhmutov, V. I. *Inorg. Chim. Acta* **1991**, *179*, 195.
(32) (a) Curtis, C. J.; Haltiwanger, R. C. *Organometallics* **1991**, *10*, 3220. (b) Luinstra, G. A.; Rief, U.; Prosenc, M. H. *Organometallics* **1995**, *14*, 1551.
(33) (a) Farrar, T. C.; Quinting, G. R. *J. Phys. Chem.* **1986**, *90*, 2834. (b) Bautista, M. T.; Earl, K. A.; Maltby, P. A.; Morris, R. H.; Schweitzer, C. T.; Sella, A. *J. Am. Chem. Soc.* **1988**, *110*, 7031. (c) Hamilton, D. G.; Crabtree, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 4126..
(34) (a) Muetterties, E. L. *J. Am. Chem. Soc.* **1968**, *90*, 5097. (b) Hoffman, R.; Howell, J. M.; Rossi, A. R. *J. Am. Chem. Soc.* **1976**, *98*, 2484. (c) Meakin, P.; Guggenberger, L. J.; Jesson, J. P; Gerlach, D. H.; Tebbe, F. N.; Peet, W. G.; Muetterties, E. L. *J. Am. Chem. Soc.* **1970**, *92*, 3482.
(35) Desrosiers, P. J.; Cai, L.; Lin, Z.; Richards, R.; Halpern, J. *J. Am. Chem. Soc.* **1991**, *113*, 4173.
(36) (a) Gusev, D. G.; Vymenits, A. B.; Bakhmutov, V. I. *Inorg. Chem.* **1991**, *30*, 3116. (b) Luo, X.; Lui, H; Crabtree, R. H. *Inorg. Chem.* **1991**, *30*, 4740. (c) Gusev, D. G.; Nietlispach, D.; Vymenits, A. B.; Bakhmutov, V. I.; Berke, H. *Inorg. Chem.* **1993**, *32*, 3270.

**Table 4.** Relaxation Time Measurements $T_1$ (s)[a] for Complexes **1**−**4** Recorded in $C_6D_6$ at 303 K and 80 MHz ($\delta$, ppm/TMS in parentheses)

| | $T_1$ | | | | | |
|---|---|---|---|---|---|---|
| compd | $H_a$ | $H_b$ | $H_c$ | $H_d$ | $PMe_2$ | MeCp |
| **1** | 0.69, 0.17[b] | 0.69, 0.10[b] | | | 0.39 (0.84), 0.62 (1.27) | 0.59 (1.49), 0.64 (2.01), 0.68 (2.29), 0.42 (2.33) |
| **2** | | 0.62 | 0.96 | | 0.44 (1.13), 0.65 (2.22) | 0.63 (1.40), 0.70 (1.62), 0.69 (2.02), 0.60 (2.27) |
| **3** | | 0.17[c] | | 0.53[c] | | |
| **4** | 0.80 | 0.80 | 1.20 | | 0.51 (1.02), *d* (1.80) | 0.60 (1.50), 0.79 (1.83), 0.58 (2.10), 0.66 (2.29) |
| | | 0.20[c] | 0.29[c] | | | |

[a] ±5%. [b] 240 K, THF-$d_8$. [c] 233 K, toluene-$d_8$. [d] Not measurable, the $T_1$ being masked by the nearby peaks.

the Cp* ligands, approximated to this hydride because of the corresponding slope of the cyclopentadienyl rings (the contacts can be estimated to be 2.1−2.3 Å). Therefore for $H_b$ one can expect a shorter $T_1$ time caused by these additional dipole−dipole interactions.

At room temperature the hydride ligands of **1** show equal $T_1$ times of 0.69 s ($C_6D_6$) which is explained by the slow hydride−hydride exchange on the NMR time scale. However, when the temperature is lowered to 240 K (THF-$d_8$), they become quite different. It is important that the shorter $T_1$ value of 0.10 s is measured for the bridging hydride ligand $H_b$ located trans to the $PPh_3$ group (versus 0.17 s obtained for $H_a$). Thus, the structural motive of **1** is manifested in the $T_1$ behavior.

The $^1$H, $^{31}$P NMR characterization of the product of isomerization of **1** does not allow us to make a choice between **2** and **2′** (Chart 2). Indeed, the $^1$H $T_1$ relaxation time measurements support only structure **2**. Actually due to stereochemical rigidity of this complex, the $T_1$ times of the RuH resonances are different even at room temperature ($C_6D_6$): $T_1(H_b) = 0.62$ s and $T_1(H_c) = 0.96$ s.

As mentioned above, the $^1$H, $^{31}$P NMR parameters obtained for the thermodynamic product of the hydride substitution reaction of **1** can be interpreted in terms of two possible structures: **4** and **4′** (Chart 3).

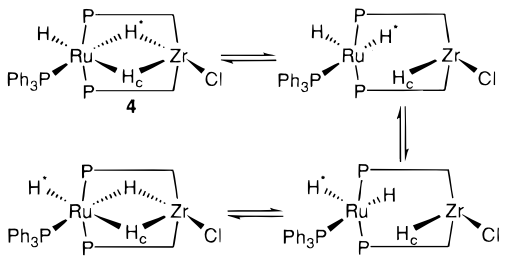
However, the $^1$H $T_1$ relaxation time measurements allow us to distinguish them. According to the measurements at 233 K in toluene-$d_8$, the $H_b$ ligand located trans to the $PPh_3$ group is characterized by the shorter $T_1$ time of 0.20 s vs 0.29 s obtained for the second bridging $H_c$ ligand located cis to the $PPh_3$ ligand. It is obvious that such a situation can be realized only in the case of structure **4**, where $H_b$ undergoes additional dipole-dipole interactions with the corresponding $CH_3$ protons (C(29) and C(40)) of the Cp* ligands. It should be noted that the low-temperature measurements were necessary because of the rapid $H_a/H_b$ exchange observed in **4** at room temperature.

Finally, to be sure that the above representations are correct, we have measured the $T_1$ times for $H_b$ and $H_d$ in complex **3**. The $T_1$ values of 0.53 and 0.17 s observed for the terminal zirconium hydride ($H_d$) and for the bridging hydride ($H_b$), respectively, support our approach.

**Solution Fluxionality of Complexes 1 and 4.** Complex **1** has prevously been found to be fluxional in solution according to the spin saturation transfer detected for the RuH resonances in $C_6D_6$ at room temperature. Similar H/H exchanges have recently been reported for the bridging hydride ligands of some Ru/Ru[28] and Ru/Re[1d] bimetallics.

In this work, we have observed the line broadening effects for these hydride resonances in THF-$d_8$ at 313 K, which allowed determination of a $\Delta G^{\ddagger}$ value[37] of 16.4 kcal/mol for this bridging−terminal hydride exchange.

**Scheme 3**




Complex **3**, which isomerizes in the reaction mixture, has not been isolated, and therefore its fluxional behavior has not been investigated.

According to the above variable-temperature $^1$H NMR spectra (Figure 3), complex **4** is also fluxional on the NMR time scale: the resonances at −12.1 ($H_b$) and −10.7 ppm ($H_a$), observed at 233 K, coalesce at room temperature, giving $\Delta G^{\ddagger} = 13.5$ kcal/mol.[33] Thus, the exchange in **4** is energetically preferable (vs **1**). In both cases the fluxionality is explained by a hydride exchange between the terminal and bridging positions located cis to one another (Figure 3 shows clearly that $H_c$ in **4** does not participate in the exchange).

The exchange between the bridging hydrides in complex $(PPh_3)_2(H)Ru(\mu\text{-}H)_3Ru(PPh_3)_3$ has been explained by a fluxional process, whereby one bridging hydride becomes a terminal hydride and the resultant five-coordinated ruthenium center undergoes pseudorotation.[28] A similar mechanism (Scheme 3) can operate in the case of trihydride **4** when the hydride bridges are opened (that leads $H_c$, which was more strongly bound to the Zr atom, to become a Zr hydride). For complex **1**, this mechanism calls for a similar transformation of the stronger bridging Cl atom, and therefore, the increase of the $\Delta G^{\ddagger}$ value is expected.

Alternative rearrangement pathways have recently been suggested for polyhydride transition metal systems, including H ligand scrambling by $H_2$ ligand formation, with subsequent rotation of this moiety around the M−$H_2$ axis.[38] This mechanism operates only with H movements and seems to be reasonable for complexes **1** and **4** (Scheme 4). In this case, the smaller exchange energy calculated for **4** could be explained by a more stable dihydrogen intermediate with trans location of the $H_2$ and H ligands.[39]

In contrast to complexes **1** and **4**, dihydride **2** with two H bridges was found to be stereochemically rigid on the NMR time scale (in $C_6D_6$ and THF-$d_8$ up to 333 K). In our opinion, this rigidity can be better explained in terms of the last mechanism because the $H_2$ ligand should be bound to both metal centers in such a case. However, among numerous dihydrogen

(37) (a) Oki, M. Applications of Dynamic NMR Spectroscopy to Organic Chemistry. In *Methods in Stereochemical Analysis*; Verkade, J. G., Quin, L. D., Eds.; VCH Publisher: Weinheim, Germany, 1986; Vol. 4. (b) *La spectroscopie de RMN*; H. Günther Publisher: Masson, France, 1994; Chapter 9.

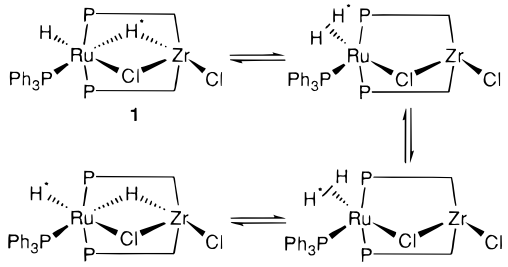
(38) (a) Jessop, P. G.; Morris, R. H. *Coord. Chem. Rev.* **1992**, *121*, 155. (b) Bakhmutov, V. I.; Burgi, T.; Burger, P.; Ruppli, U.; Berke, H. *Organometallics* **1994**, *13*, 4203. (c) Gusev, D. G.; Vymenits, A. B.; Bakhmutov, V. I. *Inorg. Chem.* **1992**, *31*, 1.

(39) (a) Ogasawara, M.; Saburi, M. *J. Organomet. Chem*. **1994,** *482*, 7. (b) Burrow, T.; Sabo-Etienne, S.; Chaudret, B. *Inorg. Chem.* **1995**, *34*, 2470.

**Table 5.** Crystallographic Data for **1**

| | |
|---|---|
| formula | $ZrRuC_{43}P_3Cl_2H_{53}D_3$ |
| fw | 932 |
| cryst syst | monoclinic |
| space group | $P2_1/c$ (No. 14) |
| $a$, Å | 13.901(2) |
| $b$, Å | 18.205(6) |
| $c$, Å | 16.633(3) |
| $\beta$, deg | 92.43(1) |
| $V$, Å$^3$ | 4206 |
| $Z$ | 4 |
| $\rho_{calc}$, g·cm$^{-3}$ | 1.472 |
| $F(000)$ | 1908 |
| radiation ($\lambda$(MoK$\alpha$)), Å | 0.710 73 |
| scan type | $\omega-2\theta$ |
| scan speed min, deg·min$^{-1}$ | 2 |
| scan width, deg | $\Delta\omega = 1.3 + 0.347 \tan\theta$ |
| reflecns measd (*hlk*) | (0 −2 −20)<br>(17 22 20) |
| $\sin(\theta)/\lambda_{max}$, Å$^{-1}$ | 0.624 |
| $\mu$(MoK$\alpha$), cm$^{-1}$ | 8.65 |
| absorpn correcn | semiempirical |
| no. of reflecns measd | 10 392 |
| temp | room temp |
| decay, % | not corrected |
| cut off for obsd data | $I \geq 3\sigma(I)$ |
| no. of unique obsd data ($N_O$) | 4720 |
| no. of variables ($N_V$) | 433 |
| $N_O/N_V$ | 10.9 |
| $R(F)$ | 0.056 |
| $R_w(F)$ | 0.058 |
| weighting scheme | $w = [\sigma^2(F) + 0.001F^2]^{-1}$ |
| G. O. F. | 1.52 |
| $\Delta(\rho)$, e Å$^{-3}$ | +1.9, −1.9 |

**Scheme 4**




complexes, there is only one example containing the Ru−($H_2$)−Ru moiety.[40]

## Conclusions

This work shows that the reaction of $RuH_2(H_2)(PPh_3)_3$ with $(PMe_2Cp^*)_2ZrCl_2$ finally gives a heterobimetallic Ru/Zr complex stabilized by four bridges; the heterobifunctional ligands $C_5Me_4PMe_2$ provide two of them, and additional stabilization results from the Ru−H−Zr and Ru−Cl−Zr bonds. The structure of **1** as the first example of a Zr−($\mu$-H,Cl)−Ru system has been established by the X-ray study.

Dihydride **2**, containing two hydride bridges and two terminal chlorine atoms, is obtained by the acid catalyzed isomerization of **1**. This transformation has been proposed to occur through a slow protonation of one of the $PMe_2$ groups with formation of a five-coordinated Ru center undergoing rapid pseudorotation. This proposition is supported by experiments in the presence of $DEt_3NBPh_4$: no evidence for the Ru−D bond was found in the $^1$H NMR spectra of compound **2**. The structural formulation of **2** has been carried out on the basis of the elemental analysis and $^1$H, $^{31}$P NMR, and $^1$H NMR relaxation data. As in the case of complex **1**, no $H_2$ binding to **2** was found under an $H_2$ atmosphere in THF-$d_8$ or $C_6D_6$ at room temperature. This complex was also unreactive toward dimethyl-3,3-but-1-ene.

The room temperature treatment of **2** with 1 equiv of $NaHBEt_3$ leads smoothly to trihydride **4**, whereas complex **1** gives a mixture of **3** and **4** under the same conditions. The former trihydride seems to be the kinetic product of this reaction because, upon standing in solution for a period of several days, trihydride **3** transforms to trihydride **4**.

The NMR data collected in this work have shown complexes **1** and **4** to be fluxional in solution at room temperature. This fluxionality is manifested as a hydride exchange between the bridging and terminal positions located cis one to another. Complex **2** has been found to be rigid on the NMR time scale.

## Experimental Section

**General Procedures.** All experiments were performed under a dry nitrogen or argon atmosphere using standard Schlenk or glovebox (JACOMEX) techniques. Solvents were stored under argon on sodium−benzophenone and distilled immediately before use. The compounds $H_2(H_2)Ru(PPh_3)_3$,[41] $HClRu(PPh_3)_3$,[22] and $(C_5Me_4PMe_2)_2ZrCl_2$ [5e] were synthesized following published methods.

The $^1$H, $^{31}$P NMR spectra were collected on Bruker AC-200 and AC-80 spectrometers operating for $^1$H at 200 and 80 MHz, respectively. The conventional inversion-recovery method (180-$\tau$-90) was used to determine $T_1$. The calculation of the relaxation times was made by using the nonlinear three-parameters fitting routine of the spectrometers. Durations of the pulses were controlled in each experiment.

IR spectra were recorded on a BRUKER IFS66V spectrophotometer. The elemental analyses have been performed by the Service Central d'Analyses (CNRS Lyon, Gif/Yvette).

The $\Delta G^{\ddagger}$ values for the $H_a-H_b$ exchanges have been determined by the line broadening method (**1**) or by measuring the coalescence temperature (**4**). The error limits are estimated at ±1.5 kcal·mol$^{-1}$.

**Crystal Structure Analysis of 1.** Crystals suitable for X-ray analysis were grown in an NMR tube. This fact explains the presence of a $C_6D_6$ solvate molecule in the formula of the compound. A dark red crystal (approximate dimensions 0.3 × 0.3 × 0.2 mm$^3$) was sealed in a capillary and mounted on an Enraf-Nonius CAD4 diffractometer. The crystal data and data collection parameters are summarized in Table 5. The unit cell was determined and refined from 25 randomly selected reflections obtained by the use of the CAD4 automatic routines. Intensities were corrected for Lorentz and polarization effects, and a semiempirical absorption correction (DIFABS) was performed after the isotropic refinement of the structure. The structure was solved by means of a Patterson search program,[42] difference Fourier synthesis, and full matrix least-squares methods.[43] All non-hydrogens were refined with anisotropic temperature factors. Hydrogen atoms were either located in final difference Fourier synthesis or placed in a calculated position with $B_{iso}$ fixed at the values equal to $1.3B_{eq}$ for the attached atoms. Due to the poor quality of the final difference synthesis, the terminal hydrogen atom bound to the ruthenium atom was not located, while the bridging hydrogen atom was tentatively located in the difference Fourier map but not refined.

A $C_6D_6$ solvate molecule was located on an inversion center and refined as an isotropic rigid group.

(40) Collman, J. P.; Nagenknecht, P. S.; Hutchison, J. E.; Lewis, N. S.; Lopez, M. A.; Guilard, R.; L'Her, M.; Bothner-By, A. A.; Mishra, P. K. *J. Am. Chem. Soc.* **1992**, *114*, 5654.

(41) (a) Harris, R. O.; Hota, N. K.; Sadavov, L.; Yuen, J. M. C. *J. Organomet. Chem.* **1973**, *54*, 259. (b) Linn, D. E.; Halpern, J. *J. Am. Chem. Soc.* **1987**, *109*, 2974. (c) Grushin, V. V.; Vimenits, A. B.; Vol'Pin, M. E. *J. Organomet. Chem.* **1990**, *382*, 185.

(42) Sheldrick, G. M. *SHELXS-86*, Structure Solution Package; University of Göttingen: Göttingen, Germany, 1986.

(43) Sheldrick, G. M. *SHELX-76*, Program for Crystal Structure Determination; Cambridge University Press: Cambridge, U.K., 1976.

Final residuals are given in Table 5.

**$ZrCl(\mu\text{-}C_5Me_4PMe_2)_2(\mu\text{-}Cl)(\mu\text{-}H)RuH(PPh_3)$ (1).** (a) To avoid formation of any $RuHCl(PPh_3)_3$, which is often found when solutions of **1** stand at room temperature for more than 2 days, we have used a modified procedure from that previously described[5e] to prepare **1**: $(C_5Me_4PMe_2)_2ZrCl_2$ (0.170 g, 0.32 mmol) was stirred with 1 equiv (0.289 g, 0.32 mmol) of $H_2(H_2)Ru(PPh_3)_3$ in diethyl ether (50 mL) at room temperature for 6 h. After filtration, the orange filtrate was concentrated to ca. 10 mL, pentane (20 mL) was added, and immediately a yellow orange powder precipitated. This crude material was collected, washed with 5 mL of cold pentane, and dried under vacuum during 1 h. The same operation was done with the mother liquor to give finally 153 mg of **1** (yield: 52.8%) which was pure according to the NMR data. IR (Nujol mull $cm^{-1}$): $\nu_{Ru-H}$ 2079 (w), 1970 (str). (**b**) A 5 mg (9.5 $\mu$mol) sample of $(C_5Me_4PMe_2)_2ZrCl_2$ was weighed into an NMR tube closed with a "YOUNG" stopcock. Then, 0.4 mL of $C_6D_6$ and 1 equiv of a toluene solution ($C$ = 1 M) of $NaHBEt_3$ (5.5 $\mu$L, 5.5 $\mu$mol) were added. The yellow solution turned to colorless within 1 min, and the $^{31}P$ and $^1H$ NMR analyses showed the total consumption of the zirconium precursor. After addition of 8.8 mg (9.5 $\mu$mol) of $HClRu(PPh_3)_3$, the mixture, analyzed by NMR, showed the presence of bimetallic **1** (yield $\approx$ 30%).

**Reactivity of $(C_5Me_4PMe_2)_2ZrCl_2$ towards $HClRu(PPh_3)_3$.** An equimolar mixture of $(C_5Me_4PMe_2)_2ZrCl_2$ and $HClRu(PPh_3)_3$ was allowed to stand for several hours at room temperature: no reaction occurred. After 3 h at 60 °C, the NMR spectra showed the disappearance of 80% of the starting material and the formation of unidentified products.

**$ZrCl(\mu\text{-}C_5Me_4PMe_2)_2(\mu\text{-}H)_2RuCl(PPh_3)$ (2).** A solution of **1** (0.050 g, 0.056 mmol) in benzene (20 mL) was stirred with 1 equiv of either $HNEt_3BPh_4$ (0.024 g, 0.057 mmol) or $DNEt_3BPh_4$ (0.024 g, 0.057 mmol) at 60 °C (2 h) and then at room temperature (4 h). After evaporation, diethyl ether (20 mL) was added and the brown reddish solution was filtered to remove the acid. Slow concentration (ca. 8 mL), followed by addition of pentane (10 mL) led to small orange-red crystals within 6 h. The crystals were washed with cold pentane (3 mL) and dried (yield: 0.033 g, 66.2%). IR (Nujol mull, $cm^{-1}$): $\nu_{Ru-H}$ 1919 (w), 1784 (str). Anal. Calcd for $C_{40}H_{53}P_3Cl_2RuZr$: C, 53.98; H, 6.00; Cl, 7.97. Found: C, 55.03; H, 6.01; Cl, 8.45.

**Reactivity of 1 and 2 towards $N_2$, $H_2$, or 3,3-Dimethylbut-1-ene.** In a typical experiment, 5 mg (5.6 $\mu$mol) of **1** (or **2**) was weighed in an NMR tube closed with a YOUNG stopcock. Then 0.4 mL of $C_6D_6$ was added, the tube was freeze−pump−thaw degassed, and pressurized with either $N_2$, $H_2$, or 3,3-dimethyl-but-1-ene. NMR analysis did not show any reaction, even after several days at room temperature.

**Reactivity of 1 toward an Excess of $HNEt_3BPh_4$.** In a typical experiment, 4 mg (4.5 $\mu$mol) of **1** (contaminated with 1 equiv of $PPh_3$) was weighed into an NMR tube closed with a YOUNG stopcock. Then 0.4 mL of THF-$d_8$ and an excess of $HNEt_3BPh_4$ (9.4 mg, 22.5 $\mu$mol) were added. The well-known complexes $RuHCl(PPh_3)_3$ and $Ru(H_2)H_2(PPh_3)_3$ were characterized immediately in the NMR spectra. In addition, the $T_1$ value of 16 ms (200 MHz, 243 K) determined for the H ligands of $Ru(H_2)H_2(PPh_3)_3$ corresponds well to the magnitude reported earlier for this complex.[31]

**Reactivity of 1 toward $H^-$.** In a typical experiment, 5 mg (5.6 $\mu$mol) of **1** was weighed into an NMR tube closed with a YOUNG stopcock. Then 0.4 mL of $C_6D_6$ and 1 equiv of a toluene solution ($C$ = 1 M) of $NaHBEt_3$ (5.5 $\mu$L, 5.5 $\mu$mol) were added. The color of the solution turned pale yellow within 1 min, and the reaction mixture was analyzed by $^{31}P$ and $^1H$ NMR. The only detected products were the two isomers **3** and **4** (80% and 20%, respectively). A period of 2 days later, the NMR spectra showed equal quantity of the two isomers, and after 1 week the transformation of **3** into **4** was complete.

**Reactivity of 2 toward $H^-$.** In a typical experiment, 5 mg (5.6 $\mu$mol) of **2** was weighed into an NMR tube closed with a YOUNG stopcock. Then 0.4 mL of $C_6D_6$ and 1 equiv of a toluene solution ($C$ = 1 M) of $NaHBEt_3$ (5.5 $\mu$L, 5.5 $\mu$mol) were added. The color of the solution turned pale yellow within 1 min. The $^{31}P$ and $^1H$ NMR spectra showed the quantitative formation of trihydride **4**. The solution was stable at room temperature during several weeks.

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**Supporting Information Available:** Tables of anisotropic temperature factors, least-squares planes, full bond lengths and angles, and hydrogen and non-hydrogen atom coordinates (7 pages). Ordering information is given on any current masthead page.

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