Journal of Organometallic Chemistry, 320 (1987) C51–C55
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Preliminary communication

SELECTIVE FORMATION OF BIS(DIPHENYLPHOSPHINO)-METHANIDO- OR -PHOSPHIDO-BRIDGED DIHYDRIDORUTHENIUM-RHODIUM COMPLEXES IN REACTIONS OF $RuRhH_2Cl(C_8H_{12})(Ph_2PCH_2PPh_2)_2$ WITH TRIALKYLBOROHYDRIDES AS A FUNCTION OF SOLVENT AND REAGENT BASICITY

HASSAN BENLAARAB, BRUNO CHAUDRET*, FRANÇOISE DAHAN, and RENÉ POILBLANC

Laboratoire de Chimie de Coordination du CNRS, Unité No. 8241 liée par convention à l'Université Paul Sabatier, 205 route de Narbonne, 31077 Toulouse Cedex (France)

(Received October 14th, 1986)

Summary

$RuRhH_2Cl(COD)(dppm)_2$ (**1**) (COD = 1,5-C_8H_{12}, dppm = $Ph_2PCH_2PPh_2$) does not react with $LiBHEt_3$ in THF, but in toluene $RuRhH_2(PhPCH_2PPh_2)(dppm)(COD)$ (**3**) is formed quantitatively. In contrast, the reaction of **1** with $KBH(sec\text{-}Bu)_3$ in THF selectively gives $RuRhH_2(CH(PPh_2)_2)(dppm)(COD)$ (**4**), whereas in toluene a mixture of **3** and **4** is obtained. Mechanisms are proposed for these reactions. The X-ray crystal structure of **4** · $PhCH_3$ reveals direct coordination of a methanido group to rhodium and a long metal–metal distance (3.3006(6) Å).

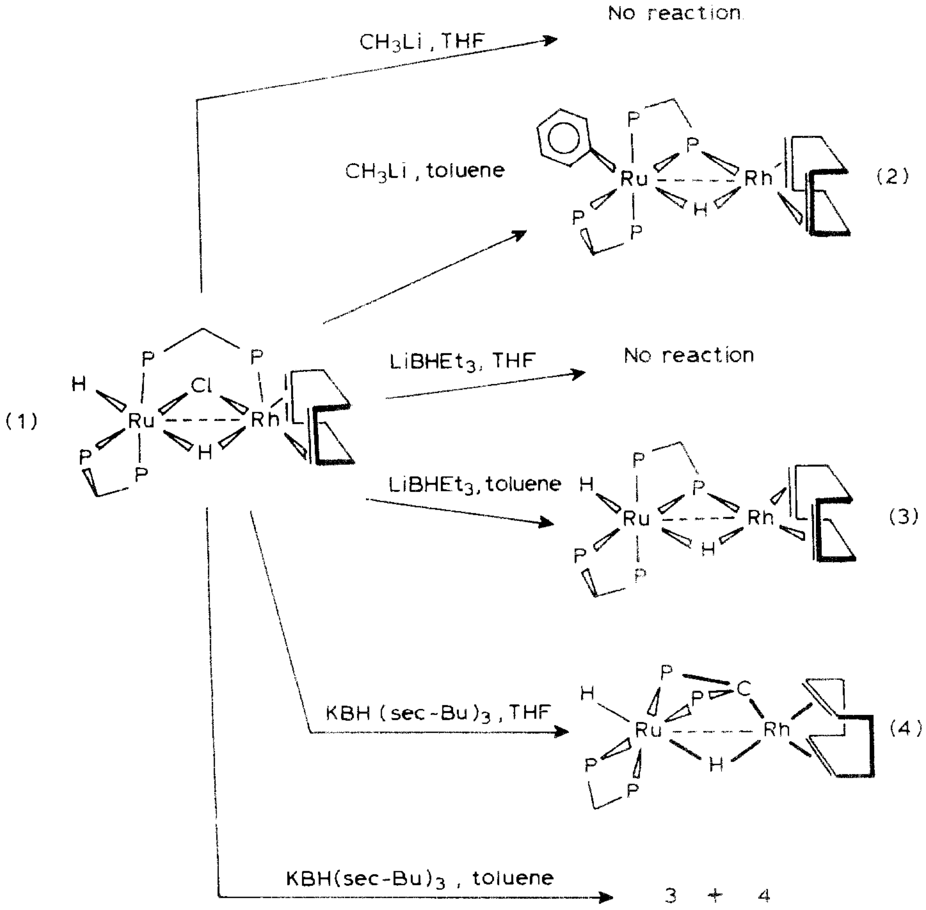
Reactions of halogeno derivatives with $NaBH_4$ or $LiAlH_4$ provide the most common route to transition metal hydrido complexes [1], but, the reactions are often heterogeneous and non-selective. Recently it has been shown that trialkyl borohydrides such as $LiBHEt_3$ or $KBH(sec\text{-}Bu)_3$ can also be used for the preparation of such hydrido derivatives. For example, dihydrido- and anionic trihydridoruthenium complexes were conveniently prepared by reaction of $RuCl_2(PPh_3)_3$ with $LiBHEt_3$ or $KBH(sec\text{-}Bu)_3$ [2]. It is well known that in the presence of a strong base, coordinated dppm can be deprotonated [3–7] to give a methanido ligand which may either coordinate to a metal center present in the molecule [4], be alkylated [6] or react with other metal salts [5,7].

In our search for reactive bimetallic polyhydride complexes, we have prepared $RuRhH_2Cl(COD)(dppm)_2$ [8] and studied some reduction reactions. With $NaBH_4$ the very unsaturated $RuRhH_3(dppm)_2$ [9] is formed in an heterogeneous reaction, whereas with CH_3Li in toluene the phosphido-bridged complex $RuRhH(Ph)(PhPCH_2PPh_2)(dppm)(COD)$ (**2**), is formed following initial attack of CH_3^- on rhodium. Studies on carbon–phosphorus bond cleavage are of interest because such reactions are involved in deactivation of phosphine catalysts [10,11].

0022-328X/87/$03.50

In order to try to prepare trihydride selectively at low temperature, we used LiBHEt$_3$ or KBH(sec-Bu)$_3$ in THF or toluene, and found that in both cases we could obtain wholly selective but different reactions depending on the site of attack of the reagent determined by the nature of the solvent and basicity of the reagent.

The complex RuRhH$_2$Cl(COD)(dppm)$_2$ (**1**) was found not to react with LiBHEt$_3$ in THF but in toluene at 0°C a deep yellow solution was obtained from which yellow crystals were isolated after addition of hexane. The IR spectrum shows a band at 1885 cm^{-1}, suggesting the presence of a terminal hydride, and this is confirmed by ^{1}H NMR spectroscopy. Thus, two complicated multiplets in 1/1 ratio are observed at δ −5.70 (H(1)) and −8.67 (H(2)) ppm. After noise decoupling, of the phosphorus, an ABX pattern is obtained with J(H(1)–H(2)) 11.8 Hz and J(H(2)–Rh) 18.0 Hz [12]. This is consistent with the presence of two *trans* hydride ligands one of which is bridging between ruthenium and rhodium. The ^{31}P{^{1}H} NMR spectrum is similar to that of RuRhH(Ph)(PhPCH$_2$PPh$_2$)(COD)(dppm) (**2**), and in particular shows a phosphido bridging group at δ 49.8 ppm [12].



SCHEME 1. Reactions of RuRhH$_2$Cl(COD)(dppm)$_2$ with strong bases.

TABLE 1

SELECTED BOND LENGTHS (Å) AND ANGLES (deg) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Ru–Rh3.0306(6)			
Rh–M(12) [a]	2.069(6)	Rh–H(1)	1.82(4)
Rh–M(56)	2.025(5)	Rh–C(9)	2.113(5)
Rh–C(1)	2.200(6)	Rh–C(5)	2.156(5)
Rh–C(2)	2.158(6)	Rh–C(6)	2.122(6)
Rh...P(1)	2.990(1)	Rh...P(2)	2.836(1)
M(12)–Rh–C(9)	178.9(3)	M(56)–Rh–H(1)	175(2)
		H(1)–Rh–C(9)	92(2)
Ru–H(1)	1.61(5)	Ru–H(2)	1.55(4)
Ru–P(1)	2.309(1)	Ru–P(3)	2.276(1)
Ru–P(2)	2.329(1)	Ru–P(4)	2.311(1)
H(1)–Ru–H(2)	169.(2)	P(1)–Ru–P(4)	176.47(6)
		P(2)–Ru–P(3)	173.97(5)
	Ru–H(1)–Rh	124.(3)	
P(1)–C(9)	1.781(5)	P(3)–C(10)	1.849(5)
P(2)–C(9)	1.809(5)	P(4)–C(10)	1.849(6)
P(1)–C(9)–P(2)	93.4(2)	P(3)–C(10)–P(4)	93.4(2)

[a] M(12) and M(56) are the midpoints of C(1)–C(2) and C(5)–C(6) bonds.

The ^{13}C NMR spectrum is also similar to that of **2**, and in particular shows signals for olefinic carbons *cis* and *trans* to the phosphido group. The complex may thus be formulated as $RuRhH_2(PhPCH_2PPh_2)(dppm)(COD)$ (**3**), with the same basic structure as **2** (Scheme 1). The mechanism of formation of **3** in toluene must be similar to that proposed for **2**, i.e. attack of the hydride reagent on rhodium to form a trihydride which can then lose benzene to give a phosphido bridge. This is a well known process for the formation of diphenylphosphido-bridged species from hydrido triphenylphosphine derivatives [10]. Again the reaction is completely selective, and occurs at low temperature, which is unusual for breaking of P–C bonds.

We found that the reaction of **1** with CH_3Li was also inhibited in THF, implying that, at least in a transient species, a coordinating solvent can interact with rhodium and block a coordination site, even though no evidence was found for direct coordination of THF.

Similar reactions were performed with KBH(sec-butyl)$_3$ in toluene, but in this case two compounds were formed in a roughly 20/80 ratio. The first was **3**, and the second isolated by recrystallisation from toluene/hexane, was **4** (yield ca. 60%). Complex **4** like **3**, shows a broad terminal M–H band at 1970 cm^{-1} in its infrared spectrum and two *trans* hydrides in its highfield ^{1}H NMR spectrum at δ −7.55 and −11.10 ppm (J(H(1)–H(2)) 13.5 Hz, J(H(2)–Rh) 20.9 Hz), one of which is coupled

---

* The atomic coordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW (Great Britain). Any request should be accompanied by a full literature citation for this communication.

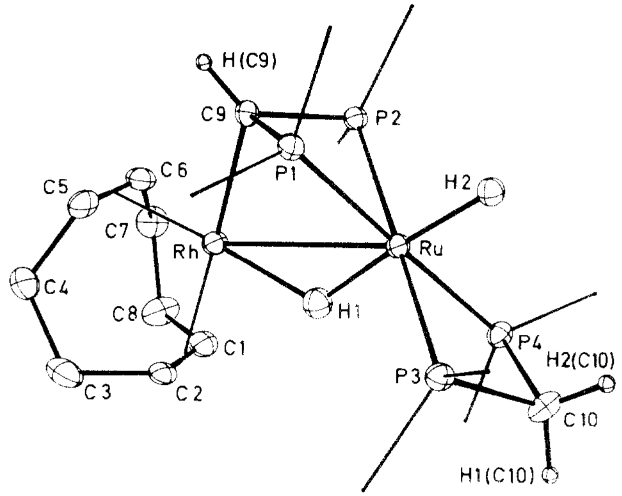


Fig. 1. Perspective view of $RuRhH_2(Ph_2PCHPPh_2)(dppm)(COD)$ (4) (The cyclooctadiene protons and phenyl groups have been omitted for the sake of clarity).

to rhodium. The $\{^1H\}$ ^{31}P NMR spectrum shows now an AA′BB′X pattern, but with a coupling constant J(PB–Rh) (7.5 Hz) which rules out any direct coordination of phosphorus to rhodium while J_{AB} is large (~ 240 Hz). As these results were not immediately understandable, an X-ray crystal structure determination was carried out (Table 1). The molecular structure is shown in Fig. 1 *. The ruthenium atom has a normal *trans* dihydride tetrakis(phosphine) environment, very similar for example to that of *trans*-$RuHCl(dppm)_2$ [8b], while the rhodium atom is in a square planar environment.

Evidently one proton of a methylene group of dppm has been abstracted and a rhodium–carbon bond formed (Rh–C 2.113(5) Å). No strong rhodium–phosphorus interaction is present (shortest Rh–P distance: 2.836(1) Å). The metal–metal distance is long (3.0306(6) Å). Although deprotonation of coordinated dppm followed by metallation is well known (see introduction) this is to our knowledge the first observation of such a rearrangement in a metal–metal bonded species.

If the same reaction is carried out in THF, **4** is the only product, probably again because THF blocks the reaction site on rhodium. The reaction clearly involves deprotonation of a dppm ligand, but it is not possible to decide whether this is the chelating or the bridging ligand of **1**. Furthermore, this reaction gives a basicity scale for the reagents used: $KBH(sec\text{-}Bu)_3$ is more basic than $LiBHEt_3$. It is also noteworthy that dppm is usually readily deprotonated by CH_3Li, and weaker bases, even when coordinated [3–7]. It seems then that coordination on ruthenium or in a bridging position between ruthenium and rhodium decreases the acidity of the methylene protons of dppm. The mechanisms of these reactions are being further investigated.

References and notes

1 D.S. Moore, and S.D. Robinson, Chem. Soc. Rev., 12 (1983) 415.
2 A.S.C. Chan, H.-S. Shieh, J. Chem. Soc., Chem. Commun., (1985) 1379.

3 M.P. Brown, A. Yavari, L. Manojlovic-Muir, and K.W. Muir, J. Organomet. Chem., 256 (1983) C19.

4 G.M. Dawkins, M. Green, J.C. Jeffery, C. Sambale, and F.G.A. Stone, J. Chem. Soc., Dalton Trans., (1983) 499.

5 (a) R. Uson, A. Laguna, M. Laguna, B.R. Manzano, P.G. Jones, and G.M. Sheldrick, J. Chem. Soc., Dalton Trans., (1984) 839; (b) R. Uson, A. Laguna, M. Laguna, M.C. Gimeno, P.G. Jones, C. Fittschen, and G.M. Sheldrick, J. Chem. Soc., Chem. Commun. (1986) 509 and ref. therein.

6 See: (a) S. Al Jibori, and B.L. Shaw, J. Chem. Soc., Chem. Commun. (1982) 286; (b) S. Al Jibori, and B.L. Shaw, Inorg. Chim. Acta, 74 (1983) 235; (c) G.R. Cooper, D.M. McEwan, and B.L. Shaw, Inorg. Chim. Acta, 76 (1983) L165; (d) G.R. Cooper, F. Hassan, B.L. Shaw, and M. Thornton-Pett, J. Chem. Soc., Chem. Commun., (1985) 614; (e) S. Al Jibori, M. Hall, A.T. Hutton and B.L. Shaw, J. Chem. Soc., Dalton Trans., (1984) 863.

7 A. Al Jibori, and B.L. Shaw, J. Organomet. Chem., 272 (1984) 213.

8 (a) B. Delavaux, B. Chaudret, F. Dahan, and R. Poilblanc, Organometallics 4 (1985) 935; (b) B. Delavaux, B. Chaudret, J. Devillers, F. Dahan, G. Commenges, and R. Poilblanc, J. Am. Chem. Soc., 108 (1986) 3703.

9 B. Delavaux, B. Chaudret, N.J. Taylor, S. Arabi, and R. Poilblanc, J. Chem. Soc., Chem. Commun., (1985) 805.

10 P.E. Garrou, Chem. Rev., 85 (1985) 171.

11 (a) N.M. Doherty, G. Hogarth, S.A.R. Knox, K.A. MacPherson, F. Melchior, and A.G. Orpen, J. Chem. Soc., Chem. Commun., (1986) 540; (b) G.R. Doel, N.D. Feasey, S.A.R. Knox, A.G. Orpen, and J. Webster, ibid., (1986) 342.

12 $RuRhH_2(PhPCH_2PPh_2)(Ph_2PCH_2PPh_2)(C_8H_{12})$: IR: ν(Ru–H) 1885 cm^{-1}, ^1H NMR, δ(H(1)) -5.70 ppm J(H(1)H(2)) 11.7 Hz, J(H((1)P(1) ~ 12 Hz, $J(H(1)P(2)) = J(H(1)P(3)) = J(H(1)P(4)) =$ 19.3 Hz; δ(H(2)) -8.67 ppm, J(H(2)Rh) 18.0 Hz, J(H(2)P(1)) 18.5 Hz; $\delta(CH_2COD)$ 1.5–2 ppm, δ 4.0, 6.3, 6.6 ppm (CHCOD), 4.5, 4.7 (CH_2dppm). ^{31}P NMR, δ(P(1)) 49.8 ppm, δ(P(2)), δ(P(3)) 8.5 ppm, δ(P(4)) 7 ppm, $J(P(1)P(4)) \cong -240$ Hz, J(P(1)P(2)) 40 Hz, J(P(1)P(3)) 30 Hz, J(P(1)P(4)) 34 Hz, J(P(3)P(4)) 47 Hz (approximative values), ^{13}C NMR: δ 30.68, 31.84, 32.92 (CH_2COD), 56.37, 59.18 (CH_2dppm), 68.76 (J(Rh–C) 12.3 Hz, CHCOD), 73.11 (J(Rh–C) 12.0 Hz, CH.COD) 91.43 ($J(C-P) \cong J(C-Rh) \cong 6$ Hz, CHCOD), 92.65 ($J(C-P) \cong J(C-Rh) \cong 8$ Hz; CHCOD).

13 $RuRhH_2(CH(PPh_2)_2)(Ph_2PCH_2PPh_2)(C_8H_{12})$: IR ν(Ru–H) 1970 cm^{-1}, ^1H NMR δ(H(1)) -7.48 ppm, J(H(1)H(2)) 13.4 Hz, δ(H(2)) -11.03 ppm, J(H(2)–Rh) 21.0 Hz, δ 1–2 ppm (CH_2COD), 4.8–4.2 CHCOD, CH_2 dppm. ^{13}C NMR, δ 30.55, 31.84 ppm (CH_2COD), 60.5 ppm ($J(C-P) \cong 15$ Hz, CH_2dppm), 81.0 ppm (CHCOD, J(P) 9.2 Hz), 81.7 ppm (CHCOD, J(CP) 11.3 Hz). ^{31}P NMR AA′BB′X $\delta_A \cong 9$ pp,; $\delta_B \cong 0$ ppm; $J_{AA'}$ 55.7 Hz, $J_{AB} = J_{A'B'} = 241.3$ Hz, $J_{AB'} = J_{A'B} = -32$ Hz, $J_{BB'}$ 33.6, $J(B-Rh) = J(B'-Rh) = 7.3$ Hz.

14 Crystal data: $C_{58}H_{58}P_4RhRu.\ C_6H_5CH_3$, a 24.772(3), b 12.160(2), c 37.642(5) Å, β 98.38(1)°, monoclinic, space group C^6_{2h}-$C2/c$, $Z = 8$. Intensity data were recorded in $\theta-2\theta$ scan mode on a CAD4 diffractometer using Mo-K_α radiation (λ 0.71073 Å). Full-matrix least-squares refinement with 3960 reflections having $I > 3\sigma(I)$ led to final $R = 0.033$.