

Available online at www.sciencedirect.com



Inorganica Chimica Acta 347 (2003) 181-188

www.elsevier.com/locate/ica

Inorganic

### $\eta^5$ -Indenylruthenium(II) hydride complexes: synthesis and protonation reactions

M. Pilar Gamasa<sup>a</sup>, J. Gimeno<sup>a,\*</sup>, Covadonga González-Bernardo<sup>a</sup>, B.M. Martín-Vaca<sup>a,1</sup>, Javier Borge<sup>b</sup>, Santiago García-Granda<sup>b</sup>

<sup>a</sup> Departamento de Química Orgánica e Inorgánica, Facultad de Química, Instituto de Química Organometálica 'Enrique Moles' (Unidad Asociada al CSIC), Universidad de Oviedo, 33071 Oviedo, Spain

<sup>b</sup> Departamento de Química Física y Analítica, Facultad de Química, Universidad de Oviedo, 33071 Oviedo, Spain

Received 4 July 2002; accepted 25 September 2002

Dedicated to Professor Rafael Usón with great admiration for his outstanding contribution to modern Inorganic Chemistry

#### Abstract

Hydride complexes [RuH( $\eta^{5}$ -1,2,3-C<sub>9</sub>R<sub>3</sub>R<sub>4</sub>)LL'] (R = R' = H, LL' = dppm (1), dppe (2); L = L' = PMe<sub>2</sub>Ph (3); L = PPh<sub>3</sub>, L' = PMe<sub>3</sub> (4), PMe<sub>2</sub> Ph (5), PMePh<sub>2</sub> (6); L = CO, L' = P<sup>i</sup>Pr<sub>3</sub> (7); R = Me, R' = H, LL' = dppm (8); L = CO, L' = PPh<sub>3</sub> (9), P<sup>i</sup>Pr<sub>3</sub> (10); R = R' = Me, L = CO, L' = P<sup>i</sup>Pr<sub>3</sub> (11)) have been prepared by the reaction of complexes [RuX( $\eta^{5}$ -1,2,3-C<sub>9</sub>R<sub>3</sub>R<sub>4</sub>)LL'] (X = Cl, Br) with an excess of NaOMe in methanol (reflux or room temperature). Protonation of the hydride complex [RuH( $\eta^{5}$ -C<sub>9</sub>H<sub>7</sub>)(PPh<sub>3</sub>)L] (L = PPh<sub>3</sub> (12), PMe<sub>3</sub> (4)) with HBF<sub>4</sub>·OEt<sub>2</sub> in Et<sub>2</sub>O yields the dihydride complexes [RuH<sub>2</sub>( $\eta^{5}$ -C<sub>9</sub>H<sub>7</sub>)(PPh<sub>3</sub>)L][BF<sub>4</sub>] (L = PPh<sub>3</sub> (13), PMe<sub>3</sub> (14)). Crystal structures of [RuH( $\eta^{5}$ -C<sub>9</sub>H<sub>7</sub>)(PPh<sub>3</sub>)<sub>2</sub>] (12) and [RuH<sub>2</sub>( $\eta^{5}$ -C<sub>9</sub>H<sub>7</sub>)(PPh<sub>3</sub>)<sub>2</sub>][BF<sub>4</sub>]·CH<sub>2</sub>Cl<sub>2</sub> (13) have been determined by X-ray crystallography.

© 2002 Elsevier Science B.V. All rights reserved.

Keywords: Hydride complexes; Dihydride complexes; Indenyl; Ruthenium

#### 1. Introduction

Hydride transition metal complexes are among the most important precursors in organometallic chemistry. Group 8 derivatives, in particular ruthenium hydride complexes, have been widely used both in stoicheiometric and catalytic processes [1].

Special relevance are the hydride complexes which are prone to undergo insertion reactions into the Ru-H

bond of unsaturated hydrocarbon molecules, since the insertion of alkenes and alkynes constitutes one of the key fundamental steps in many catalytic transformations [2]. The study of this type of process has become a classic goal in the chemistry of hydride ruthenium derivatives. We have recently reported regio and stereoselective insertion reactions of alkynes into the Ru–H bond of indenylruthenium(II) hydride complexes [3,4]<sup>2</sup> and we have found that such a reactivity is strongly dependent on the ancillary ligands.

<sup>\*</sup> Corresponding author. Tel.: +34-985-103-461; fax: +34-985-103-446.

E-mail address: jgh@sauron.quimica.uniovi.es (J. Gimeno).

<sup>&</sup>lt;sup>1</sup> Present address: Laboratoire d'Hétérochimie Fondamentale et Appliqueé (UPRES-A CNRS 5069), 118 Route de Narbonne, Université Paul Sabatier (Bât 2R1), F-31062 Toulouse Cedex 04, France.

<sup>&</sup>lt;sup>2</sup> The hydride complex [RuH( $\eta^5$ -C<sub>9</sub>H<sub>7</sub>)(dppm)] as well as the vinyl derivative [Ru{(*E*)-CH=(H)Ph}( $\eta^5$ -C<sub>9</sub>H<sub>7</sub>)(dppm)] are active species in the catalytic dimerization of phenylacetylene to give (*E*) and (*Z*) 1,4-diphenylbut-1-en-3-yne.

When this work was initiated, only the indenyl hydride complex  $[RuH(\eta^5-C_9H_7)(PPh_3)_2]$  was known [5]. The limited availability of hydride ruthenium(II) precursors required for the development of the above mentioned insertion reaction studies led us to the preparation of novel derivatives. Here, we report the synthesis of indenyl-hydride complexes of the type  $[RuH(\eta^5-C_9H_7)LL']$  (LL' = dppm (1), dppe (2); L = L' = PMe\_2Ph (3); L = PPh\_3, L' = PMe\_3 (4), PMe\_2Ph (5), PMePh\_2 (6); L = CO, L' = P<sup>i</sup>Pr\_3 (7)),  $[RuH(\eta^5-1,2,3-C_9H_4Me_3)LL']$  (LL' = dppm (8), L = CO, L' = PPh\_3 (9), P<sup>i</sup>Pr\_3 (10)) and  $[RuH(\eta^5-C_9Me_7)(CO)(P<sup>i</sup>Pr_3)]$  (11).

On the other hand, it is now well established that hydride ruthenium derivatives can be used as appropriate precursors of dihydride or dihydrogen complexes through protonation reactions. For a number of cases the equilibrium of dihydride/dihydrogen tautomers are favored [6]. In this paper, we also describe the synthesis and characterization of the dihydride complexes  $[RuH_2(\eta^5-C_9H_7)(PPh_3)L][BF_4]$  (L = PPh<sub>3</sub> (13), PMe<sub>3</sub> (14)) obtained by reaction of HBF<sub>4</sub>·OEt<sub>2</sub> with the hydride complexes  $[RuH(\eta^5-C_9H_7)(PPh_3)L]$ .

#### 2. Experimental

The reactions were carried out under dry nitrogen using standard Schlenk techniques. Solvents were dried by standard methods and distilled under nitrogen before use. The complexes [RuX( $\eta^{5}$ -1,2,3-C<sub>9</sub>R<sub>3</sub>R<sub>4</sub>)LL'] (R = R' = H, X = Cl; R = Me, R' = H, Me, X = Br) and [RuH( $\eta^{5}$ -C<sub>9</sub>H<sub>7</sub>)(PPh<sub>3</sub>)<sub>2</sub>] (**12**) were prepared by literature methods [5,7].<sup>3</sup>

Infrared spectra were recorded on a Perkin–Elmer Paragon 1000 spectrometer. The conductivities were measured at room temperature, in ca.  $10^{-3}$  mol dm<sup>-3</sup> acetone solutions, with a Jenway PCM3 conductimeter. The C, H and N analyses were carried out with a Perkin–Elmer 240-B microanalyzer. NMR spectra were recorded on a Bruker AC300 instrument at 300 MHz (<sup>1</sup>H), 121.5 MHz (<sup>31</sup>P) or 75.4 MHz (<sup>13</sup>C) or a Bruker AC200 instrument at 200 MHz (<sup>1</sup>H), 81.01 MHz (<sup>31</sup>P) or 50.32 MHz (<sup>13</sup>C), using SiMe<sub>4</sub> or 85% H<sub>3</sub>PO<sub>4</sub> as standards. <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopic data for the hydride complexes (1–11) are collected in Table 1. The instability of complexes 8 and 11 prevented us from obtaining any satisfactory analyses. 2.1. Synthesis and characterization of hydride complexes  $[RuH(\eta^{5}-C_{9}H_{7})LL']$  (LL' = dppm (1), dppe (2); L = L' = PMe\_{2}Ph (3); L = PPh\_{3}, L' = PMe\_{3} (4), PMe\_{2}Ph (5), PMePh<sub>2</sub> (6); L = CO, L' = P<sup>i</sup>Pr<sub>3</sub> (7)), [RuH(\eta^{5}-1,2,3-C\_{9}H\_{4}Me\_{3})LL'] (LL' = dppm (8); L = CO, L' = PPh<sub>3</sub> (9), P<sup>i</sup>Pr<sub>3</sub> (10)) and [RuH(\eta^{5}-C\_{9}Me\_{7})(CO)(P<sup>i</sup>Pr\_{3})] (11)

Excess of NaOMe (ca. 5:1), prepared in situ by reaction of NaOH and MeOH, was added to a suspension of  $[RuX(\eta^{5}-1,2,3-C_{9}R_{3}R_{4})LL']$  (R = R' = H, X = Cl; R = Me, R' = H, Me, X = Br) (1 mmol) in MeOH (100 ml). The mixture was stirred at room temperature (r.t.) (3-6) or heated under reflux (1-2, 7-11). When the reaction was completed, the solvent was evaporated and the residue was recrystallized from diethyl ether. Reaction times, colour, yield (%), IR (KBr, v(Ru-H), cm<sup>-1</sup>), (MeOH,  $\nu$ (CO), cm<sup>-1</sup>), analytical and <sup>13</sup>C{<sup>1</sup>H} NMR spectroscopic data are as follows: For 1, 3 h, yellow solid; 80; 1994 w; Anal. Calc. for C34H30P2Ru: C, 67.88; H, 4.98. Found: C, 66.80; H, 4.80%. For 2, 3 h, yellow solid; 70; 1981 w; Anal. Calc. for C<sub>35</sub>H<sub>32</sub>P<sub>2</sub>Ru: C, 66.70; H, 5.13. Found: C, 67.30; H, 5.10%. For 3, 1.5 h, yellow oil; 75; 1962 w; Anal. Calc. for C<sub>25</sub>H<sub>30</sub>P<sub>2</sub>Ru: C, 60.84; H, 6.13. Found: C, 60.56; H, 6.05%. For 4, 2 h, yellow solid; 85; 1974 w; Anal. Calc. for C<sub>30</sub>H<sub>32</sub>P<sub>2</sub>Ru: C, 64.80; H, 5.76. Found: C, 63.95; H, 5.90%. For 5, 2 h, yellow solid; 80; 2043 w; Anal. Calc. for C<sub>35</sub>H<sub>34</sub>P<sub>2</sub>Ru: C, 68.06; H, 5.55. Found: C, 67.49; H, 5.65%. For 6, 2 h, yellow solid; 85; 2008 w; Anal. Calc. for C<sub>40</sub>H<sub>36</sub>P<sub>2</sub>Ru: C, 70.61; H, 5.29. Found C, 69.80; H, 5.14%. For 7, 11 h; orange solid; 70; 1994 w, 1916 vs; Anal. Calc. for C19H29OPRu: C, 56.28; H, 7.21. Found: C, 55.51; H, 7.32%. For 8, 3.5 h; orange solid; 95; 1965 vw;  ${}^{13}C{}^{1}H{}$ (C<sub>6</sub>D<sub>6</sub>)  $\delta$  12.87 (s, Me-1,3), 14.01 (s, Me-2), 57.23 (t,  $J_{\rm CP} = 21.5$  Hz, PCH<sub>2</sub>P), 79.55 (d,  ${}^{2}J_{\rm CP} = 4.7$  Hz, C-1,3), 103.99 (s, C-3a,-7a), 104.15 (s, C-2), 121.39 and 122.98 (s, C-4,7 or C-5,6), 123.97-142.86 (m, Ph, C-4,7 or C-5,6), 210.26 (d,  ${}^{2}J_{CP} = 17.1$  Hz, CO). For 9, 8 h; yellow solid; 85; 1967 w, 1920 vs; Anal. Calc. for C<sub>31</sub>H<sub>29</sub>OPRu: C, 67.75; H, 5.32. Found: C, 67.78; H, 5.56; <sup>13</sup>C{<sup>1</sup>H} (C<sub>6</sub>D<sub>6</sub>) δ 9.59 (s, Me), 11.69 (s, Me), 12.28 (s, Me), 81.90 (s) and 86.01 (d,  ${}^{2}J_{CP} = 8.3$  Hz) (C-1 and C-3), 106.47 (s), 108.98 (d,  ${}^{2}J_{CP} = 2.8$  Hz) and 111.56 (s) (C-2, C-3a and C-7a), 119.77 (s), 122.62 (s), 123.17 (s) and 124.94 (s) (C-4,5,6,7), 129.95–138.48 (m, Ph), 209.25 (d,  ${}^{2}J_{CP} =$ 15.7 Hz, CO). For 10, 2.5 h; yellow solid; 98; 2046 w, 1908 vs; Anal. Calc. for C22H35OPRu: C, 59.04; H, 7.88. Found: C, 60.01; H, 8.14%;  ${}^{13}C{}^{1}H{}$  (C<sub>6</sub>D<sub>6</sub>)  $\delta$  11. 49 (s, Me), 11.63 (s, Me), 13.85 (s, Me), 19.83, 20.45 (s, 26.12 (d,  $J_{\rm CP} = 22.0$  $P(CH(CH_3)_2)_3),$ Hz,  $P(CH(CH_3)_2)_3)$ , 80.34 (s) and 84.53 (d,  ${}^2J_{CP} = 7.3$  Hz) (C-1 and C-3), 107.03 (s), 107.84 (d,  ${}^{2}J_{CP} = 2.5$  Hz) and 112.09 (s) (C-2, C-3a and C-7a), 120.11 (s), 121.50 (s), 122.76 (s) and 123.44 (s) (C-4,5,6,7), 210.26 (d,  ${}^{2}J_{CP} =$ 17.1 Hz, CO). For 11, 1.5 h; orange oil; 98; 2061 w, 1899

<sup>&</sup>lt;sup>3</sup> The halide complexes [RuBr( $\eta^{5}$ -1,2,3-C<sub>9</sub>R<sub>3</sub>R<sub>4</sub>)LL'] (R = Me, R' = H, L = CO, L' = PPh<sub>3</sub>, P<sup>i</sup>Pr<sub>3</sub>; LL' = dppm; R = R' = Me, L = CO, L' = P<sup>i</sup>Pr<sub>3</sub>) are easily prepared in high yields from [RuBr( $\eta^{5}$ -1,2,3-C<sub>9</sub>R<sub>3</sub>R<sub>4</sub>)(CO)<sub>2</sub>] by substitution of one or two carbonyl groups with the appropriate phosphine.

Compound	$^{31}P\{^{1}H\}$	<sup>1</sup> H						
	$\overline{\eta^5}$ -ring <sup>i</sup>					Ru–H	$^{2}J_{\mathrm{HP}}$	Others
		H-1,3	H-2	Me-1,2,3,4,5,6,7	H-4,7, H-5,6	-		
$[RuH(\eta^{5}-C_{9}H_{7})(dppm)]$ (1)	19.14 s	5.34 d (2.7)	5.23 t (2.7)		6.65 (m, 2H) <sup>b</sup>	-14.12 td <sup>c</sup>	31.2	3.62 (dt, 1H, $J_{HH} = 14.2$ , ${}^{2}J_{HP} = 10.9$ , PCH <sub>2</sub> P), 4.50 (ddt, 1H, $J_{HH} = 14.2$ , ${}^{2}J_{HP} = 9.5$ , $J_{HH} = 4.0$ , PCH <sub>2</sub> P), 7.10– 7.50 (m, 22H, H-4.7 or H-5.6, PPh <sub>2</sub> )
$[RuH(\eta^{5}-C_{9}H_{7})(dppe)]$ (2)	89.33 s	5.06 d	5.41 t		6.54 (m, 2H), 6.74 (m, 2H)	−17.07 t	33.8	$1.80 \text{ (m, 4H, P(CH_2)_2P), 7.24-7.67 (m, 20H, PPh_2)}$
$[RuH(\eta^5-C_9H_7)(PMe_2Ph)_2]$ (3)	26.19 s	(2.4) 4.74 d (2.4)	5.64 t (2.4)		b	-16.90 t	34.2	1.30 (vt, 12H, $ J_{HP}+J_{HP'}  = 8.4$ , PMe <sub>2</sub> ), 7.02–7.76 (m, 14H, H-4,5,6,7, PPh)
$[RuH(\eta^{5}-C_{9}H_{7})(PMe_{3})(PPh_{3})]$ (4)	8.00 d (PMe <sub>3</sub> ) <sup>d</sup> , 69.80 d (PPh <sub>3</sub> ) <sup>d</sup>	3.90 br s, 4.90 br s	5.57 m		6.15 (m, 1H), 6.80 (m, 1H), 6.96 (m, 1H) 7.46 (m, 1H)	-16.12 dd	30.3, 35.4	$0.90$ (d, 9H, ${}^{2}J_{\text{HP}} = 18.4$ , PMe <sub>3</sub> ), 7.01– 7.32 (m, 15H, PPh <sub>3</sub> )
$[RuH(\eta^{5}-C_{9}H_{7})(PMe_{2}Ph)(PPh_{3})]$ (5)	22.80 d (PMe <sub>2</sub> Ph) $^{\rm e}$ , 68.99 d (PPh <sub>2</sub> ) $^{\rm e}$	f	f		6.04 (m, 1H) <sup>b</sup>	-15.86 t	32.2	1.04 (m, 6H, PMe <sub>2</sub> ), 6.77–8.22 (m, 23H, H-4 5.6 or 7, PPh, PPh <sub>2</sub> )
$[RuH(\eta^5-C_9H_7)(PMePh_2)(PPh_3)]$ (6)	$\begin{array}{l} 43.12 \text{ d} (\text{PMePh}_2)^{\text{g}}, \\ 68.59 \text{ d} (\text{PPh}_3)^{\text{g}} \end{array}$	h	h		6.07 (m, 1H) <sup>b</sup>	-15.44 dd	33.6, 29.9	1.17 (d, 3H, ${}^{2}J_{HP} = 7.6$ , PMe), 6.91– 7.92 (m, 28H, H-4,5,6 or 7, PPh <sub>2</sub> , PPh <sub>3</sub> )
$[RuH(\eta^{5}-C_{9}H_{7})(CO)(P^{i}Pr_{3})] (7)$	86.24 s	i	i		6.84 (m, 2H), 7.00 (m, 1H), 7.30 (m, 1H)	-14.88 d	30.5	$0.84 \text{ (m, 18H, P(CH(Me)_2)_3), 1.58 (m, 3H, P(CH(Me)_2)_3)}$
$[RuH(\eta^{5}-1,2,3-C_{9}H_{4}Me_{3})(dppm)] (8)$	19.98 s			2.42 (s, 3H, Me-2), 2.56 (s, 6H, Me-1,3)	b	-12.85 t	30.2	3.66 and 4.45 (m, 1H each one, PCH <sub>2</sub> P), 7.13–7.89 (m, 24H, H- 4.5.6.7, PPh <sub>2</sub> )
$[RuH(\eta^{5}-1,2,3-C_{9}H_{4}Me_{3})(CO)(PPh_{3})] (9)$	63.47s			1.53 (s, 3H), 2.33 (s, 3H), 2.60 (s, 3H)	b	-12.99 d	33.6	6.76–8.08 (m, 19H, H-4,5,6,7, PPh <sub>3</sub> )
$RuH(\eta^{5}\text{-}1,2,3\text{-}C_{9}H_{4}Me_{3})(CO)(P^{i}Pr_{3})] \text{ (10)}$	83.48 s			2.25 (s, 3H), 2.36 (s, 3H), 2.59 (d, 3H, ${}^{4}J_{HP} = 2.3$ )	7.14 (m, 2H), 7.26 (m, 1H), 7.62 (m, 1H)	-14.23 d	32.1	1.04 (dd, 9H, $J_{HH} = 6.9$ , ${}^{3}J_{HP} = 13.7$ , P(CH(Me) <sub>2</sub> ) <sub>3</sub> ), 1.14 (dd, 9H, $J_{HH} = 6.9$ , ${}^{3}J_{HP} = 13.7$ , P(CH(Me) <sub>2</sub> ) <sub>3</sub> ), 1.85 (m, 3H, P(CH(Me) <sub>2</sub> ) <sub>3</sub> )
$[RuH(\eta^5-C_9Me_7)(CO)(P^iPr_3)]$ (11)	82.02 s			$\begin{array}{l} 2.07 \; ({\rm s}, {\rm 3H}), 2.13 \; ({\rm s}, {\rm 3H}),\\ 2.14 \; ({\rm d}, {\rm 3H}, {}^4J_{\rm HP}{=} 1.5), 2.26 \\ ({\rm s}, {\rm 3H}), 2.36 \; ({\rm s}, {\rm 3H}), 2.54 \; ({\rm d}, {\rm 3H}, {}^4J_{\rm HP}{=} 2.0), 2.64 \; ({\rm s}, {\rm 3H}) \end{array}$		—14.18 d	33.0	0.76 (dd, 9H, $J_{HH} = 6.9$ , ${}^{3}J_{HP} = 12.8$ , P(CH(Me) <sub>2</sub> ) <sub>3</sub> ), 0.96 (dd, 9H, $J_{HH} =$ 7.1, ${}^{3}J_{HP} = 13.5$ , P(CH(Me) <sub>2</sub> ) <sub>3</sub> ), 1.72 (m, 3H, P(CH(Me) <sub>2</sub> ) <sub>3</sub> )

Table 1  $^{31}P{^{1}H}$  and  $^{1}H$  NMR data for the monohydride complexes <sup>a</sup>

<sup>a</sup> Spectra recorded in CD<sub>2</sub>Cl<sub>2</sub> (1-2), (CD<sub>3</sub>)<sub>2</sub>CO (3-6) or C<sub>6</sub>D<sub>6</sub> (7-11).  $\delta$  in ppm and J in Hz. Abbreviations: s, singlet; d, doublet; t, triplet; m, multiplet; vt, virtual triplet; br, broad. J<sub>HH</sub> in parenthesis.

<sup>b</sup> Overlapped by aromatic signals.

<sup>c</sup> <sup>4</sup> $J_{HH} = 4.0.$ <sup>c</sup> <sup>4</sup> $J_{HH} = 4.0.$ <sup>d</sup> <sup>2</sup> $J_{PP} = 31.7.$ <sup>e</sup> <sup>2</sup> $J_{PP} = 30.0.$ <sup>f</sup> 4.02, 4.46 and 5.59 (br s, 1H each one, H-1,2,3). <sup>g</sup> <sup>2</sup> $J_{PP} = 28.7.$ 

<sup>h</sup> 4.22, 4.56 and 5.90 (br s, 1H each one, H-1,2,3). <sup>i</sup> 4.94, 5.38, 5.56 (br s, 1H each one, H-1,2,3). <sup>j</sup> Legend for atoms:

vs;  ${}^{13}C{}^{1}H{}(C_6D_6) \delta{}$  14.75 (s, Me), 15.31 (s, Me), 15.81 (s, Me), 17.10 (s, Me), 17.37 (s, Me), 17.91 (s, Me), 18.00 (s, Me),), 19.50, 21.08 (s, P(CH(CH\_3)\_2)\_3), 28.82 (d,  $J_{CP} = 21.9$  Hz, P(CH(CH\_3)\_2)\_3, 80.60 (s) and 85.43 (d,  ${}^{2}J_{CP} = 7.0$  Hz) (C-1 and C-3), 104.58 (s), 108.03(d,  ${}^{2}J_{CP} = 3.1$  Hz) and 113.06 (s) (C-2, C-3a and C-7a), 124.97-132.04 (m, C-4,5,6,7), 210.98 (d,  ${}^{2}J_{CP} = 16.4$  Hz, CO).

## 2.2. Synthesis and characterization of the dihydride complexes $[RuH_2(\eta^5-C_9H_7)(PPh_3)L][BF_4]$ ( $L = PPh_3$ (13), $PMe_3$ (14))

A stirred solution of the hydride complexes [RuH( $\eta^{5}$ - $C_9H_7$ )(PPh<sub>3</sub>)L] (L = PPh<sub>3</sub> (12), PMe<sub>3</sub> (4)) (1 mmol) in diethyl ether (100 ml), at r.t., was treated dropwise with a dilute solution of HBF<sub>4</sub>·Et<sub>2</sub>O (1:1 molar ratio) in diethyl ether. Immediately, an insoluble yellow-brown solid precipitated. After stirring for 15 min, the solution was decanted and the solid washed with diethyl ether  $(3 \times 20 \text{ ml})$  and vacuum-dried. Yield (%), IR (KBr,  $v(\text{RuH}), v(\text{BF}), \text{ cm}^{-1})$ , conductivity (acetone, 20 °C,  $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>), analytical and NMR spectroscopic data are as follows: For 13, 80; 1974, 1059; 120; Anal. Calc. for C<sub>45</sub>H<sub>39</sub>BF<sub>4</sub>P<sub>2</sub>Ru: C, 65.15; H, 4.74. Found: C, 65.84; H, 4.69%; <sup>1</sup>H (CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  -8.29 (t, 2H, <sup>2</sup>J<sub>HP</sub> = 26.3 Hz, RuH<sub>2</sub>), 4.62 (t, 1H,  $J_{HH} = 2.4$  Hz, H-2), 5.19 (d, 2H, J<sub>HH</sub> = 2.4 Hz, H-1,3), 6.69 (m, 2H, H-4,7 or H-5,6), 7.20–7.47 (m, 32H, H-4,7 or H-5,6, PPh<sub>3</sub>);  ${}^{31}P{}^{1}H{}$ (CD<sub>2</sub>Cl<sub>2</sub>) δ 59.38 (s). For 14: 75; 2005, 1057; 112; Anal. Calc. for C<sub>30</sub>H<sub>33</sub>BF<sub>4</sub>P<sub>2</sub>Ru: C, 56.00; H, 5.17. Found: C, 55.18; H, 4.86%; <sup>1</sup>H (CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  -9.72 (dd, 2H, <sup>2</sup>J<sub>HP</sub> =  $^{28.0, 2}J_{HP'} = 30.0 \text{ Hz}, \text{RuH}_2$ ), 1.16 (d,  $^{2}J_{HP} = 11.32 \text{ Hz},$ 9H, PMe<sub>3</sub>), 5.05 (t, 1H,  $J_{HH} = 2.4$  Hz, H-2), 5.54 (d, 2H,  $J_{\rm HH} = 2.4$  Hz, H-1,3), 6.69, 7.10 (m, 2H each one, H-4,7 and H-5,6), 7.28–7.42 (m, 15H, PPh<sub>3</sub>);  ${}^{31}P{}^{1}H{}$  $(CD_2Cl_2) \delta$  46.53 (d, <sup>2</sup>J<sub>PP'</sub> = 20.0 Hz, PMe<sub>3</sub>), 62.47 (d,  $^{2}J_{\text{PP}'} = 20.0 \text{ Hz}, \text{ PPh}_{3}$ ).

#### 2.3. X-ray diffraction

Data collection, crystal, and refinement parameters are collected in Table 2. The unit cell parameters were obtained from the least-squares fit of 25 reflections (with  $\theta$  between 5 and 20° (12) and between 10 and 20° (13)). Data were collected on a Nonius CAD4 diffractometer with the  $\omega - 2\theta$  scan technique and a variable scan rate, with a maximum scan time of 60 s per reflection. The final drift correction factors were between 0.99 and 1.01 (12) and between 0.71 and 1.05 (13). On all reflections, profile analysis [8,9] were performed. Lorentz and polarization corrections were applied and the data were reduced to  $|F_0|$  values.

The structures were solved by DIRDIF [10] (Patterson methods and phase expansion). Isotropic least-squares refinement using SHELX-76 [11,12] converged to R =

Table 2 Crystallographic Data for Complexes 12 and 13·CH<sub>2</sub>Cl<sub>2</sub>

	12	$13 \cdot CH_2Cl_2$
Formula	C45H38P2Ru	C45H39BF4P2Ru·CH2Cl2
a (Å)	10.968(8)	11.41(1)
$b(\mathbf{A})$	19.994(8)	12.07(2)
c (Å)	16.676(6)	15.14(1)
α (°)	90	89.0(1)
β	103.7(2)	83.11(9)
γ (°)	90	67.6(1)
Molecular weight	741.76	829.58
V (Å <sup>3</sup> )	3553(3)	1913(4)
Z	4	2
$D_{\rm calc}$ (g cm <sup>-3</sup> )	1.387	1.441
F(000)	1528	848
Wavelength (Å)	0.71073	0.71073
T (K)	293	200
Radiation	Μο Κα	Μο Κα
Monochromator	graphite cryst	graphite cryst
Space group	$P 2_1/n$	$P\bar{1}$
Crystal system	monoclinic	triclinic
Crystal size (mm <sup>3</sup> )	$0.30 \times 0.26 \times$	$0.26 \times 0.20 \times 0.20$
	0.20	
$\mu  ({\rm mm}^{-1})$	0.563	0.545
Diffraction geom	$\omega - 2\theta$	$\omega - 2\theta$
$\theta$ Range (°)	1.62 - 25.00	1.36-25.00
Index ranges for data	0 < h < 13.	$0 \le h \le 13, -12 \le k \le 14,$
collected	$0 \le k \le 23.$	-17 < l < 17
	-19 < l < 19	
Reflections measured	6802	7101
Independent reflec-	$6232 [R_{int} =$	$6727 [R_{int} = 0.037]$
tions	0.019]	
Variables	438	479
Refinement method	full-matrix least-	full-matrix least-squares or
	squares on $F^2$	$F^2$
Goodness-of-fit	1.025	1.107
on $F^2$		
Final R factors	$R_1$ (4561 rflns)	$R_1$ (5834 rflns) = 0.0158.
$(I > 2\sigma(I))$	$= 0.0269, wR_2$	$wR_2$ (5834 rflns) = 0.0391
	(4561  rflns) =	2 ( )
	0.0693	
Final <i>R</i> factors	$R_1 = 0.0542$ .	$R_1 = 0.0191, wR_2 = 0.0394$
(all data) <sup>a</sup>	$wR_{2} = 0.0732$	
Largest difference	0.275  and  -0.411	0.266 and $-0.243$
peak and hole		
$(e Å^{-3})$		
( )		

0.060 for complex 12 and to R = 0.098 for complex 13. At this stage an empirical absorption corrections were applied using DIFABS [13].

Hydrogen atoms were geometrically placed, except H(1) in complex 12. During the final stages of the refinement, the positional parameters and the anisotropic thermal parameters of the non-H atoms were refined. The geometrically placed hydrogen atoms were isotropically refined with a common thermal parameter, riding on their parent atoms. H(1) in complex 12 was also isotropically refined with an independent thermal parameter. Hydride atoms could not be found in complex 13.



Finally, full-matrix least-squares refinements on  $F_o^2$  were made, for complexes 12 and 13, using SHELXL-93 [14].

- a) Complex 12: the function minimized was  $[\Sigma w(F_o^2 F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2}$ ,  $w = 1/[\sigma^2(F_o^2) + (0.0410P)^2]$ where  $P = (\max(F_o^2, 0) + 2F_c^2)/3$  with  $\sigma^2(F_o^2)$  from counting statistics. The maximum shift to e.s.d. ratio in the last full-matrix least-squares cycle was -0.082. The final difference Fourier map showed no peaks higher than 0.27 e Å<sup>-3</sup>, nor deeper than -0.41 e Å<sup>-3</sup>.
- b) Complex 13 · CH<sub>2</sub>Cl<sub>2</sub>: the function minimized was  $[\Sigma w(F_o^2 F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$ ,  $w = 1/[\sigma^2(F_o^2) + (0.0197P)^2]$  where  $P = (\max(F_o^2, 0) + 2F_c^2)/3$  with  $\sigma^2(F_o^2)$  from counting statistics. The maximum shift to e.s.d. ratio in the last full-matrix least-squares cycle was -0.005. The CH<sub>2</sub>Cl<sub>2</sub> solvent molecule was affected by strong structural disorder and could not be located. Therefore, it was omitted from the parameter set of the refined discrete-atom model. It was taken into account in the structure factor calculations by direct Fourier transformation of the electron density in the corresponding cavity, using BYPASS [15]. The final difference Fourier map showed no peaks higher than 0.27 e Å<sup>-3</sup>, nor deeper than -0.24 e Å<sup>-3</sup>.

Atomic scattering factors were taken from International Tables for X-ray Crystallography (1974) [16]. Geometrical calculations were made with PARST [17]. The crystallographic plots were made with EUCLID [18]. All calculations were made at the University of Oviedo on the X-ray group ALPHA-AXP computers.

#### 3. Results and discussion

#### 3.1. Synthesis of hydride ruthenium(II) complexes

The treatment of complexes [RuX( $\eta^5$ -1,2,3-C<sub>9</sub>R<sub>3</sub>R<sub>4</sub>)LL'] (R = R' = H, X = Cl; R = Me, R' = H,

Me, X = Br) with an excess of NaOMe (ca. 1:20) in refluxing methanol (or at room temperature for 3–6) affords the hydride complexes [RuH( $\eta^{5}$ -1,2,3-C<sub>9</sub>R<sub>3</sub>R<sub>4</sub>)LL'] (1–11) (Eq. (1)).

The progress of the reaction has been monitored, in the case of the carbonyl derivatives, by infrared spectroscopy in the carbonyl region. The reactions are discontinued when the IR spectra only show a new v(CO)absorption between 1920–1899 cm<sup>-1</sup>.

All the complexes are isolated (70-98% yield) as yellow or orange solids (except **3** and **11** which are oils), and are very air and moisture-sensitive in solution and in solid state. These complexes are soluble in polar and non-polar solvents as diethyl ether and hexane, but some of them react with chorinated solvents to give the corresponding chloro-ruthenium complexes. They have been characterized by elemental analyses, IR and NMR (<sup>1</sup>H, <sup>31</sup>P{<sup>1</sup>H} and <sup>13</sup>C{<sup>1</sup>H}) spectroscopy (details are given in Section 2 and in Table 1).

Significant spectroscopic features are: (i) A weak intensity v(Ru-H) absorption at ca. 2043–1967 cm<sup>-1</sup> in the IR spectra (KBr) (see Section 2). (ii) The resonance of the hydride group appears in the <sup>1</sup>H NMR spectra at very high field ( $\delta - 12.85$  to -17.07) in accordance with the data reported in the literature [19,20] for other analogous cyclopentadienyl hydride ruthenium complexes. The signal is observed as a doublet (7, 9–11), triplet (2, 3, 5, 8), doublet of doublets (4, 6) or triplet of doublets (1), the  ${}^{2}J_{\rm HP}$  coupling being ca. 30 Hz (see Table 1). It is worth noting that the hydride signal for complex 1 appears as a triplet of doublets ( ${}^{2}J_{HP} = 31.2$ ,  ${}^{4}J_{HH} = 4.0$  Hz) by coupling with two phosphorus atoms and one methylene proton of the dppm ligand [21]<sup>4</sup>. (iii) A single resonance in the  ${}^{31}P{}^{1}H$  NMR spectra consistent with the chemical equivalence of the phosphorus atoms (1-3, 8) or with the presence of a unique phosphorus atom (7, 9-11).

 $<sup>^4</sup>$  This type of coupling has been already reported in the complex  $[RuH(\eta^5\text{-}C_5Me_5)(dppm)].$ 

The spectra of complexes 4-6, which have two different phosphines, show two doblets.

The formation of these complexes can be easily explained on the basis of the classical route for the synthesis of transition metal hydride derivatives (see Scheme 1), which involves the  $\beta$ -hydrogen elimination from a methoxide intermediate complex to give the hydride complex and formaldehyde [19].

$$[Ru]-X \xrightarrow{\text{NaOMe}} [Ru]-O-C \xrightarrow{H}_{H} \xrightarrow{H}_{-H_2C=O} [Ru]-H$$
Scheme 1.

### 3.2. Synthesis of dihydride complexes $[RuH_2(\eta^5 - C_9H_7)L_2][BF_4]$ $(L = PPh_3$ (13), $PMe_3$ (14))

The treatment of a solution of complexes  $[RuH(\eta^{2} C_{9}H_{7}L_{2}$ [BF<sub>4</sub>] (L = PPh<sub>3</sub> (12), PMe<sub>3</sub> (4) in diethyl ether with a solution of  $HBF_4 \cdot OEt_2$  (1:1 molar ratio), at room temperature, affords the dihydride complexes 13 and 14 as insoluble yellow-brown solids (75-80% yield). These complexes are soluble in acetone and chlorinated solvents and insoluble in non-polar solvents as diethyl ether and hexane. They have been characterized by elemental analyses, IR and NMR (<sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H}) spectroscopy (details are given in Section 2). Significant spectroscopic features are: (i) A weak intensity v(Ru-H)absorption at ca. 1974 (13) and 2005 cm<sup>-1</sup> (14) in the IR spectra (KBr). (ii) The resonance of the hydride group appears in the <sup>1</sup>H NMR spectra at very high field as a triplet ( $\delta - 8.29$ ,  ${}^{2}J_{\text{HP}} = 26.3$  Hz) for **13** and a doublet of doublets for 14 ( $\delta$  -9.72,  ${}^{2}J_{HP}$  = 30.0,  ${}^{2}J_{HP'}$  = 28.0 Hz). (iii) The  ${}^{31}P{}^{1}H$  NMR spectra show a single resonance (13) and two doublets (14), in accordance with the chemical equivalence and inequivalence of the phosphorus atoms.

When the protonation of the complex 12 is carried out in  $Et_2O$ , at 203 K, the dihydride complex (13) is also exclusively formed as insoluble yellow-brown solid. It be that complex  $[RuH_2(n^5$ should noted  $C_9H_7$  (PPh<sub>3</sub>)<sub>2</sub> [BF<sub>4</sub>] (13) is also the only species observed in the <sup>1</sup>H NMR spectrum ( $CD_2Cl_2$ , room temperature), as well as after crystalization (CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O, room temperature). Jia and coworkers have recently reported the formation of the similar complex  $[RuH_2(\eta^5 C_9H_7$ )(PPh<sub>3</sub>)<sub>2</sub>][CF<sub>3</sub>SO<sub>3</sub>] which is generated and spectroscopically characterized in situ at low temperature. However, it is reported that the complex is unstable at room temperature in THF-d<sub>8</sub> giving the complex  $[RuH(\eta^6-C_9H_8)(PPh_3)_2][CF_3SO_3]$  via proton migration [6j].

It is known, from previous literature data [6c], that the stability of dihydride complexes relative to the

corresponding dihydrogen tautomers is dependent on the metals and auxiliary ligands. So, the use of monodentate phosphines favors the formation of the dihydride complexes while the stability of  $\eta^2$ -dihydrogen complexes is favored by bidentate diphosphines of small chelating ring sizes. We have tried the protonation of the complexes 1 and 2 with  $HBF_4 \cdot Et_2O$  in  $Et_2O$  or  $Me_2CO$  $d_6$  at 203 K yielding the dihydrogen complex [Ru( $\eta^2$ - $H_2$ )( $\eta^5$ -C<sub>9</sub> $H_7$ )(dppm)][BF<sub>4</sub>] and a mixture of dihydrogen  $[Ru(\eta^2 - H_2)(\eta^5 - C_9H_7)(dppe)][BF_4]$ and dihydride  $[RuH_2(\eta^5-C_9H_7)(dppe)][BF_4]$  complexes, respectively. When these Me<sub>2</sub>CO-d<sub>6</sub> solutions are allowed to warm to room temperature, the complexes [RuH( $\eta^6$ - $C_9H_8$ )(dppm)][BF<sub>4</sub>] and [RuH( $\eta^6$ - $C_9H_8$ )(dppe)][BF<sub>4</sub>] are generated. These variable temperature NMR studies are in accordance with those recently described by Jia [6] and do not merit further comments.

# 3.3. Molecular structure of complexes $[RuH(\eta^{5}-C_{9}H_{7})(PPh_{3})_{2}]$ (12) and $[RuH_{2}(\eta^{5}-C_{9}H_{7})(PPh_{3})_{2}]/BF_{4}] \cdot CH_{2}Cl_{2}$ (13 · CH<sub>2</sub>Cl<sub>2</sub>)

The structures of the complex 13 as well as of the hydride precursor 12 have been determined by singlecrystal X-ray analysis. ORTEP type views of the molecular structures of 12 and of the cation of 13 are shown in Figs. 1 and 2 and selected bond distances and angles are collected in Table 3. The complex 12 shows the typical pseudoctahedral three-legged piano stool geometry of indenyl ruthenium(II) complexes [22] in which the metal atom is bonded to the  $\eta^5$  indenyl group, to two phosphorus atoms and to the hydrogen atom. The geometry of the cation of 13 is best described in terms of 'four-legged piano stool' with the 'legs' comprising the phosphines and the hydride ligands. Although the hydride ligands could not be reliably located for 13. their positions can be inferred from the observed molecular geometry. Thus, the angle between the  $C_5H_5$ plane of indenyl ligand and the ML<sub>2</sub> plane is  $87.93(14)^{\circ}$ and the P-Ru-P angle is  $114.3(1)^{\circ}$ , in the ranges reported for Lemke and Brammer for other [MH<sub>2</sub>Cp'L<sub>2</sub>] (M (d<sup>4</sup>), Cp' =  $\eta^{5}$ -C<sub>5</sub>H<sub>5</sub>,  $\eta^{5}$ -C<sub>5</sub>Me<sub>5</sub>,  $\eta^{5}$ -C<sub>5</sub>H<sub>4</sub>Me) complexes [20a]<sup>5</sup>. These values confirm the *trans* dihydride structure of complex 13, with a four-legged piano stool geometry, even without locating the hydride ligands crystallographically. To our knowledge there is no experimental evidence to support the presence of a *cis*-

<sup>&</sup>lt;sup>5</sup> For leading references see Lemke and Brammer who have reported several general structural trends between related [MHCp'L<sub>2</sub>] (M (d<sup>6</sup>)) and [MH<sub>2</sub>Cp'L<sub>2</sub>] (M (d<sup>4</sup>)) (Cp' =  $\eta^5$ -C<sub>5</sub>H<sub>5</sub>,  $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>,  $\eta^5$ -C<sub>5</sub>H<sub>4</sub>Me) complexes: the mean angle between the Cp'plane and the ML<sub>2</sub> is 67.6(13) and 87.6(4)°, respectively and the mean angle L–M– L' is 93.0(19) and 107.2(10)°, respectively. On the other hand, the angle between the M–H vector and the normal to the ML<sub>2</sub> plane is generally less than 10° (mean 7.9(12)°) for d<sup>6</sup> [MHCp'L<sub>2</sub>] complexes.



Fig. 1. ORTEP type view of the molecular structure of the hydride complex  $[RuH(\eta^5-C_9H_7)(PPh_3)_2]$  (12) drawn at 30% probability level. For clarity, only the C *ipso* of the aryl groups of the triphenylphosphine ligands are drawn.

dihydride species in any of the  $[RuH_2Cp'L_2]^+$  systems studied to date [6c,20b,f].

The ruthenium-hydride ligand was located and refined in **12** to give a Ru-H1 bond distance of 1.57(3) Å, in the range found for analogous semisandwich hydride cyclopentadienyl complexes (range 1.427– 1.630 Å) [20] and comparable to that of the analogue [RuH( $\eta^{5}$ -C<sub>9</sub>H<sub>7</sub>)(dppm)] (1.59(2) Å) [6j]. The angle between the C<sub>5</sub>H<sub>5</sub> plane of indenyl ligand and the ML<sub>2</sub> plane is 78.32(10)°, the P-Ru-P angle is

Table 3
---------

Selected bond distances, slip parameter  $\Delta^{a}$  (Å), bond, dihedral, FA<sup>b</sup>, HA<sup>c</sup> and CA<sup>d</sup> angles (°) for complexes **12** and **13** · CH<sub>2</sub>Cl<sub>2</sub>

	12	13
Bond distances		
Ru–P1	2.271(1)	2.321(4)
Ru–P2	2.279(3)	2.276(4)
Ru-H1	1.57(3)	
Ru-C*	1.945(3)	1.928(2)
Δ	0.154(3)	0.102(3)
Bond angles		
C*-Ru-P1	127.4(1)	126.4(4)
C*-Ru-P2	129.0(1)	119.2(3)
C*-Ru-H1	118.69(95)	
P1-Ru-P2	99.13(7)	114.3(1)
P1-Ru-H1	83.9(9)	
P2-Ru-H1	81.6(9)	
FA	8.4(3)	8.6(2)
HA	5.1(3)	4.8(2)
CA	15.06(71)	.,

<sup>a</sup>  $\Delta = d(Ru-C74, C70) - d(Ru-C71, C73).$ 

<sup>b</sup> FA (fold angle) = angle between the planes defined by [C71, C72, C73] and [C70, C74, C75, C76, C77, C78].

<sup>c</sup> HA (hinge angle) = angle between the planes defined by [C71, C72, C73] and [C73, C74, C70, C71].

<sup>d</sup> CA (conformational angle) = angle between the planes defined by [C\*\*, C\*, Ru] and [C\*, Ru, H1]. C\* = centroid of C70, C71, C72, C73, C74. C\*\* = centroid of C70, C74, C75, C76, C77, C78.

99.13(7)° and the angle between the M–H vector and the normal to the ML<sub>2</sub> plane is  $11.32(85)^{\circ}$  [20a]. The orientation of the hydride ligand in complex **12** is almost trans (CA =  $15.06(71)^{\circ}$ ) relative to the benzo ring of the indenyl ligand, in accordance with the relative trans influence of the hydride and phosphine ligands [22,23].



Fig. 2. ORTEP type view of the molecular structure of the dihydride cation complex  $[RuH_2(\eta^5-C_9H_7)(PPh_3)_2]^+$  (13) drawn at 30% probability level. For clarity, only the C *ipso* of the aryl groups of the triphenylphosphine ligands are drawn.

The rest of the main structural parameters are rather similar to those found for analogous indenyl-phosphinoruthenium(II) complexes reported by us [22] and, therefore, do not deserve further analysis.

#### 4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 188860 and 188861 for compounds 12 and  $13 \cdot CH_2Cl_2$ , respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

#### Acknowledgements

This work was supported by the Ministerio de Ciencia y Tecnología (MCT, Project BQU 2000-0227). We thank the Fundación para la Investigación Científica y Técnica de Asturias (FICYT) for the fellowships granted to B.M. M.-V. and C.G.-B.

#### References

[1] (a) A. Dedieu (Ed.), Transition Metal Hydrides, VCH, New York, 1992;

(b) J.A. Martinho Simoes, J.L. Beauchamp, Chem. Rev. 90 (1990) 629;

(c) S. Otsuka, A. Nakamura, Adv. Organomet. Chem. 14 (1976) 245;

(d) P.A. Chaloner, M.A. Esteruelas, F. Joó, L.A. Oro, Homogeneous Hydrogenation, Kluwer, Dordrecht, 1994;
(e) M. Peruzzini, R. Poli, Recent Advances in Hydride Chemistry,

Elsevier, Amsterdam, 2001.

[2] (a) G.W. Parshall, S.D. Ittel, Homogeneous Catalysis, 2nd ed., Wiley, New York, 1992;

(b) R.H. Crabtree, The Organometallic Chemistry of the Transition Metals, 2nd ed., Wiley, New York, 1994;

(c) G.O. Spessard, G.L. Miessler, Organometallic Chemistry, Prentice Hall, Upper Saddle River, NJ, 1997;

(d) J.P. Collman, L.S. Hegedus, J.R. Norton, R.G. Finke, Principles and Applications of Organotransition Metal Chemistry, University Science Books, Mill Valley, CA, 1987.

[3] (a) M. Bassetti, P. Casellato, M.P. Gamasa, J. Gimeno, C. Gonzalez-Bernardo, B. Martín-Vaca, Organometallics 16 (1997) 5470;

(b) K. Bieger, J. Díez, M.P. Gamasa, J. Gimeno, M. Pavlišta, Y. Rodríguez-Álvarez, S. García-Granda, R. Santiago-García, Eur. J. Inorg. Chem. (2002) 1647.

[4] M. Bassetti, S. Marini, F. Tortorella, V. Cadierno, J. Díez, M.P. Gamasa, J. Gimeno, J. Organomet. Chem. 593–594 (2000) 292.

- [5] L.A. Oro, M.A. Ciriano, M. Campo, C. Foces-Foces, F.H. Cano, J. Organomet. Chem. 289 (1985) 117.
- [6] (a) G.J. Kubas, Metal Dihydrogen and σ-Bond Complexes: Structure, Theory and Reactivity, Kluwer, New York, 2001;
  (b) J.K. Law, H. Mellows, D.M. Heinekey, J. Am. Chem. Soc. 122 (2002) 1024:
  - (c) G. Jia, C-P. Lau, Coord. Chem. Rev. 190–192 (1999) 83 (and references therein);
  - (d) S. Sabo-Ettiene, B. Chaudret, Coord. Chem. Rev. 178-180 (1998) 381;
  - (e) D.M. Heinekey, W.J. Oldham, Jr, Chem. Rev. 93 (1993) 913;
    (f) P.G. Jessop, R.H. Morris, Coord. Chem. Rev. 121 (1992) 155;
    (g) R.H. Crabtree, Angew. Chem., Int. Engl. Ed. 32 (1993) 789;
  - (h) R.H. Crabtree, Acc. Chem. Rev. 23 (1990) 95;

(i) For an account of the catalytic activity of dihydrogen complexes see: M.A Esteruelas, L.A. Oro, Chem. Rev. 98 (1988) 577;

(j) M.Y. Hung, S.M. Ng, Z. Zhou, C.P. Lau, G. Jia, Organometallics 19 (2000) 3692.

- [7] (a) M.P. Gamasa, J. Gimeno, C. González-Bernardo, B. Martín-Vaca, D. Monti, M. Bassetti, Organometallics 15 (1996) 302;
  (b) M.P. Gamasa, J. Gimeno, C. González-Bernardo, Unpublished results.
- [8] D.F. Grant, E.J. Gabe, J. Appl. Crystallogr. 11 (1978) 114.
- [9] M.S. Lehman, F.K. Larsen, Acta Crystallogr., A 30 (1974) 580.
- [10] P.T. Beurskens, G. Admiraal, G. Beurskens, W.P. Bosman, S. García-Granda, R.O. Gould, J.M.M. Smits, C. Smykalla, The DIRDIF Program System, Technical Report, Crystallographic Laboratory, University of Nijmegen, Nijmegen, 1992.
- [11] G.M. Sheldrick, SHELX-76, Program for Crystal Structure Determination, University of Cambridge, Cambridge, 1976.
- [12] J.F. van der Maelen Uría, PhD thesis, University of Oviedo, Spain, 1991.
- [13] N. Walker, D. Stuart, Acta Crystallogr., Sect. A 39 (1983) 158.
- [14] G.M. Sheldrick, SHELXL-93, in: H.D. Flack, P. Parkanyi, K. Simon (Eds.), Crystallographic Computing 6, IUCr/Oxford University Press, Oxford, 1993.
- [15] P. Van der Sluis, A.L. Spek, Acta Crystallogr., A 46 (1990) 194.
- [16] International Tables for X-ray Crystallography, vol. IV, Kynoch Press, Birmingham, 1974.
- [17] M. Nardelli, Comput. Chem. 7 (1983) 95.
- [18] A.L. Spek, The EUCLID Package, D. Sayre (Ed.), Computational Crystallography, Clarendon Press, Oxford, 1982, p. 528.
- [19] M.I. Bruce, M.G. Humphrey, A.G. Swincer, R.C. Wallis, Aust. J. Chem. 37 (1984) 1747.
- [20] (a) F.R. Lemke, L. Brammer, Organometallics 14 (1995) 3980;
  (b) L. Brammer, W.T. Klooster, F.R. Lemke, Organometallics 15 (1996) 1721 (and references therein);
  (c) R.T. Hembre, J.S. McQueen, V.W. Day, J. Am. Chem. Soc. 118 (1996) 798;
  (d) A.C. Ontko, J.F. Houlis, R.C. Schnabel, D.M. Roddick, T.P. Fong, A.J. Lough, R.H. Morris, Organometallics 17 (1998) 5467 (and references therein);
  (e) C. Romming, K.T. Smith, M. Tilset, Inorg. Chim. Acta 259

(1997) 281;

- (f) G. Jia, C-P. Lau, J. Organomet. Chem. 565 (1998) 37.
- [21] G. Jia, R.H. Morris, J. Am. Chem. Soc. 113 (1991) 875.
- [22] V. Cadierno, J. Díez, M.P. Gamasa, J. Gimeno, E. Lastra, Coord. Chem. Rev. 193–195 (1999) 147.
- [23] J.W. Faller, R.H. Crabtree, A. Habib, Organometallics 4 (1985) 929.