

# Synthesis and structure of dimeric Rh-bis(tertiary phosphine) complexes, exceptionally useful synthetic precursors

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**This paper is dedicated to the memory of John Osborn, a close friend and colleague of one of us (BRJ) for over 25 years; John was a person who enjoyed life and made life more enjoyable for others.**

**Abstract** – Removal of the MeOH and hydrogen from the known *cis,trans,cis*-Rh<sup>III</sup>-dihydrido complexes [Rh(H)<sub>2</sub>(PR<sub>3</sub>)<sub>2</sub>(MeOH)<sub>2</sub>](PF<sub>6</sub>) (R = Ph, *p*-tolyl) results in formation of the dimeric species [Rh<sub>2</sub>(PR<sub>3</sub>)<sub>4</sub>](PF<sub>6</sub>)<sub>2</sub>; X-ray analysis shows the complexes to be [(Ph<sub>3</sub>P)Rh(μ-PhPPh<sub>2</sub>)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub> (and the *p*-tolyl analogue) containing bridged η<sup>6</sup>-arene moieties, while <sup>1</sup>H and <sup>13</sup>C NMR data in CD<sub>2</sub>Cl<sub>2</sub> provide evidence for η<sup>4</sup>-coordination of the arene within the dimer. In more strongly coordinating solvents, formation of *cis*-[Rh(PR<sub>3</sub>)<sub>2</sub>(solvent)<sub>2</sub>](PF<sub>6</sub>) is observed, while formation of [(PR<sub>3</sub>)<sub>2</sub>Rh(η<sup>6</sup>-toluene)]PF<sub>6</sub> is evident in toluene solution, and this exists in equilibrium with the bis(solvent) species in the presence, for example, of acetone or MeOH. At ambient conditions, none of the arene-containing complexes effected catalytic H<sub>2</sub>-hydrogenation of toluene. **To cite this article:** P. Marcazzan et al., C. R. Chimie 5 (2002) 373–378 © 2002 Académie des sciences / Éditions scientifiques et médicales Elsevier SAS

phosphine complexes / Rh complexes / arene complexes / X-ray structures

**Résumé** – L'élimination du méthanol et de l'hydrogène des complexes connus *cis, trans, cis*-dihydrides du rhodium(III) [Rh(H)<sub>2</sub>(PR<sub>3</sub>)<sub>2</sub>(MeOH)<sub>2</sub>](PF<sub>6</sub>) (R = Ph, *p*-tolyl) résulte de la formation d'une espèce dimère [Rh<sub>2</sub>(PR<sub>3</sub>)<sub>4</sub>](PF<sub>6</sub>)<sub>2</sub>; l'analyse par diffraction des rayons X montre qu'il s'agit des complexes [(Ph<sub>3</sub>P)Rh(μ-PhPPh<sub>2</sub>)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub> (et de l'analogue *p*-tolyl), contenant des entités η<sup>6</sup>-arènes pontées, tandis que les données par RMN <sup>1</sup>H et <sup>13</sup>C dans CD<sub>2</sub>Cl<sub>2</sub> démontrent la coordination η<sup>4</sup> de l'arène dans le dimère. Dans les solvants plus fortement coordonnants, la formation de *cis*-[Rh(PR<sub>3</sub>)<sub>2</sub>(solvant)<sub>2</sub>](PF<sub>6</sub>) est observée, alors que celle de [(PR<sub>3</sub>)<sub>2</sub>Rh(η<sup>6</sup>-toluène)]PF<sub>6</sub> est manifeste en solution dans le toluène, en équilibre avec l'espèce bis(solvant), en présence, par exemple, d'acétone ou de méthanol. Dans des conditions ambiantes, aucun complexe contenant l'entité arène ne permet l'hydrogénation catalytique du toluène par H<sub>2</sub>. **Pour citer cet article:** P. Marcazzan et al., C. R. Chimie 5 (2002) 373–378 © 2002 Académie des sciences / Éditions scientifiques et médicales Elsevier SAS

complexes phosphine / complexes du rhodium / complexes arène / structures par rayons X

## 1. Introduction

Osborn's work with Schrock on cationic complexes of the type [Rh(diene)(PR<sub>3</sub>)<sub>2</sub>](PF<sub>6</sub>) (diene = 1,5-cyclooctadiene or norbornadiene; R = *p*-tolyl (**1a**), Ph (**1b**)) has become classic, and there has been a plethora of researchers who have used such complexes as precursors for various studies in homogeneous

catalysis. The syntheses of these complexes have been well documented [1–4], and their ability for catalyzing homogeneous H<sub>2</sub>-hydrogenation of C=C [4–7], C=O [1] and C=N [8,9] functionalities under relatively mild conditions has been long known. When treated with molecular H<sub>2</sub> at ambient conditions, these diene precursors react in the appropriate solvent medium usually, depending on the phosphine [10],

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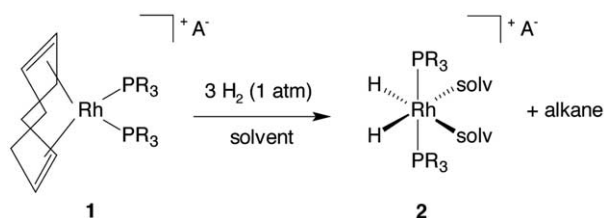


Fig. 1. Reaction of  $\text{Rh}(\text{COD})(\text{PR}_3)_2^+ \text{A}^-$  with  $\text{H}_2$  in MeOH or acetone;  $\text{A}^-$  = a monoanion, such as  $\text{PF}_6^-$ , solv = MeOH or acetone.

according to the stoichiometry exemplified in Fig. 1 (solvent = MeOH, acetone). In the absence of reducible substrate, the resting state of the active catalyst precursor, formed in solution after the diene has been “hydrogenated off”, is the well-known, six-coordinate dihydrido species  $[\text{Rh}(\text{H})_2(\text{PR}_3)_2(\text{solv})_2]\text{PF}_6$ ,  $\text{R} = p$ -tolyl (**2a**), Ph (**2b**), again first characterized by Osborn’s group [11]; the two phosphine ligands have rearranged from a mutually cis, in **1**, to a trans geometry in **2**.

Our recent interest in such chemistry stems from the ability of these cationic Rh systems to catalyze  $\text{H}_2$ -hydrogenation of aldimines and ketimines at ambient conditions [8,9], and this has allowed us to pursue mechanistic features of these generally poorly understood reactions [12,13]. The studies have led to the isolation of a new class of complexes of empirical formula  $[\text{Rh}_2(\text{PR}_3)_4][\text{PF}_6]_2$  (**3**), which are extremely versatile precursors for desired derivatives of the type  $\text{Rh}(\text{PR}_3)_2(\text{L})_2^+$ , where L is the ligand of choice; for our imine studies, L has been imine, imine derivatives such as oxime ethers or semicarbazones, or an amine, the corresponding hydrogenated product; our imine hydrogenation work [14,15] will be described in future publications. This current paper presents work describing synthesis and characterization, including X-ray analysis, of complexes **3a** ( $\text{R} = p$ -tolyl) and **3b** ( $\text{R} = \text{Ph}$ ), which have bridging arene moieties; for example, **3b** is more correctly written as  $[(\text{Ph}_3\text{P})\text{Rh}(\mu\text{-PhPPh}_2)]_2[\text{PF}_6]_2$ . After ~35 years of investigations on so-called ‘Osborn, cationic rhodium-phosphine complexes/catalysts’, there are still hidden mysteries to unfold. All the chemistry and spectroscopic measurements described were carried out at room temperature (r.t. ~ 20 °C).

## 2. Results and discussion

In vacuo removal of  $\text{H}_2$  (a reductive elimination reaction) and solvent from acetone or MeOH solutions of the dihydrido complexes **2** affords red-brown residues of the dinuclear Rh species  $[\text{Rh}_2(\text{PR}_3)_4][\text{PF}_6]_2$  (**3**) in quantitative yield and high purity; the syntheses are exemplified in Fig. 2. X-ray quality crystals of **3a**

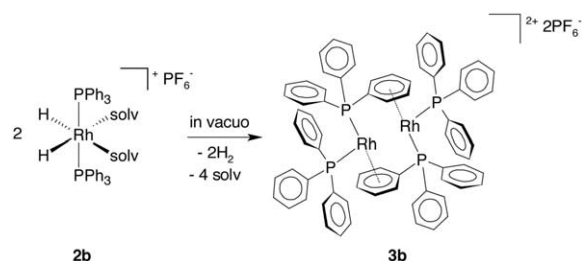


Fig. 2. Formation of the dimer **3b** from **2b**.

and **3b** were obtained by slow evaporation of  $\text{CHCl}_3$ /hexanes and  $\text{CH}_2\text{Cl}_2$  solutions of the residues; the complexes are reasonably air-stable in the solid state, and can be handled in air for brief periods, but they are extremely air-sensitive in solution. Of note, quantitative, in situ formation of these dimeric complexes is also observed (by NMR – see below) on treatment of the diene precursors **1** with 1 atm  $\text{H}_2$  in the weakly coordinating  $\text{CH}_2\text{Cl}_2$ , and this provides a further convenient route to **3**.

**3a** and **3b** have been fully characterized in the solid state by X-ray crystallography and elemental analysis, and in solution by  $^{31}\text{P}\{^1\text{H}\}$  and  $^1\text{H}$  NMR spectroscopy. Fig. 3 shows the molecular structure for **3a**, the  $p$ -tolyl complex, and that for **3b** is essentially the same (Fig. 4). In these dimeric structures, each Rh is bonded to two P-atoms and to a  $\eta^6$ -arene moiety present on one phosphine ligand of the other Rh atom. Both molecules are centrosymmetric and crystallize in the  $P\bar{1}$  space group; **3a** crystallized with a disordered but unidentified solvent molecule, and **3b** with three molecules of  $\text{CH}_2\text{Cl}_2$  per asymmetric unit. Selected crystallographic data are given in Table 1, while selected bond lengths and angles are summarized in Tables 2 and 3, respectively; the atom-numbering scheme for **3b** is not given in Fig. 4, but corresponds to that shown for **3a**. The geometry at Rh is seen to be pyramidal to the extent that the P(1)-

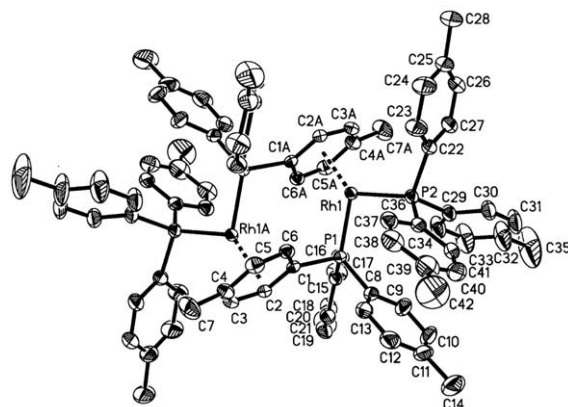
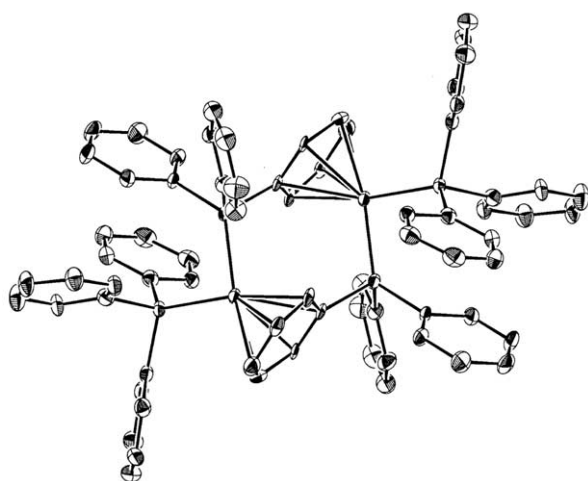


Fig. 3. Molecular structure of **3a** (50% ellipsoids shown).

Fig. 4. Molecular structure of **3b** (50% ellipsoids shown).Table 1. Selected crystal data for **3a** and **3b**.

	<b>3a</b>	<b>3b</b>
Formula	C <sub>45</sub> H <sub>48</sub> F <sub>6</sub> P <sub>3</sub> Rh	C <sub>78</sub> H <sub>72</sub> F <sub>12</sub> P <sub>6</sub> Rh <sub>2</sub> Cl <sub>12</sub>
FW	898.65	2054.50
Crystal system	triclinic	triclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> (Å)	13.2434(1)	13.367(1)
<i>b</i> (Å)	14.0911(2)	13.5822(8)
<i>c</i> (Å)	14.2864(2)	14.750(1)
$\alpha$ (°)	109.796(1)	96.524(3)
$\beta$ (°)	111.974(1)	115.708(2)
$\gamma$ (°)	101.268(1)	112.719(4)
<i>V</i> (Å <sup>3</sup> )	2161.93(5)	2094.4(3)
<i>Z</i>	2	1
<i>D</i> <sub>calc</sub> (g cm <sup>-3</sup> )	1.380	1.629
$\mu$ (Mo K $\alpha$ ) (mm <sup>-1</sup> )	0.562	0.960
<i>T</i> (K)	173(2)	173(1)
Total data collected	13 273	15 864
Independent reflections	7420	6574
<i>R</i> <sub>1</sub> (on <i>F</i> <sup>2</sup> , all data)	0.0333	0.090
<i>wR</i> <sub>2</sub> (on <i>F</i> <sup>2</sup> , all data)	0.0740	0.128

Rh(1)–C<sub>c</sub>, P(2)–Rh(1)–C<sub>c</sub>, and P(1)–Rh(1)–P(2) angles in **3a** (where C<sub>c</sub> is the center of the η<sup>6</sup>-arene moiety), are 132.7°, 132.0°, and 95°, respectively; the corresponding angles in **3b** are 133.6°, 132.7° and 94°. The only similar compound reported in the literature is [Rh<sub>2</sub>(diphos)<sub>2</sub>][BF<sub>4</sub>]<sub>2</sub>, which has the chelating diphos (1,2-diphenylphosphino(ethane)) in place of the two monophosphines of **3**. The diphos complex, shown schematically in Fig. 5a, was crystallized as a CF<sub>3</sub>CH<sub>2</sub>OH solvate [16]. The distances between the two metal centers in **3a** (4.483 Å) and **3b** (4.520 Å) show there is no significant Rh–Rh interaction [17,18]; in [Rh<sub>2</sub>(diphos)<sub>2</sub>]<sup>2+</sup>, the shorter Rh–Rh distance of 4.275 Å [16] likely arises from the presence of the chelating phosphine with its bite angle (P1–Rh–P2 = 84°) compared with 95° and 94° for the two PR<sub>3</sub> ligands in **3a** and **3b**, respectively.

Table 2. Selected bond lengths (Å) for **3a** and **3b**.

Bond	<b>3a</b>	<b>3b</b>
Rh(1)··Rh(1A)	4.483	4.520
Rh(1)–P(1)	2.2673(6)	2.259(1)
Rh(1)–P(2)	2.2688(6)	2.264(1)
Rh(1)–C(1A)	2.379(2)	2.403(4)
Rh(1)–C(2A)	2.338(2)	2.372(4)
Rh(1)–C(3A)	2.278(2)	2.281(5)
Rh(1)–C(4A)	2.404(2)	2.355(5)
Rh(1)–C(5A)	2.381(2)	2.343(5)
Rh(1)–C(6A)	2.276(2)	2.270(4)
P(1)–C(1)	1.851(2)	1.843(5)
P(1)–C(15)	1.832(2)	1.844(5)
C(1A)–C(2A)	1.411(3)	1.411(7)
C(2A)–C(3A)	1.418(3)	1.422(7)
C(3A)–C(4A)	1.418(4)	1.427(8)
C(4A)–C(5A)	1.407(4)	1.397(8)
C(5A)–C(6A)	1.411(3)	1.419(7)
C(6A)–C(1A)	1.420(3)	1.417(7)

Table 3. Selected bond angles (°) for **3a** and **3b**.

Bond	<b>3a</b>	<b>3b</b>
Rh(1)–P(1)–C(1)	109.17(7)	107.1(1)
P(1)–Rh(1)–P(2)	95.23(2)	93.67(4)
P(1)–Rh(1)–C(1A)	107.67(5)	107.1(1)
P(1)–Rh(1)–C(2A)	137.93(5)	135.8(1)
P(1)–Rh(1)–C(3A)	169.89(6)	170.1(1)
P(1)–Rh(1)–C(4A)	140.92(7)	144.1(1)
P(1)–Rh(1)–C(5A)	110.35(6)	112.6(1)
P(1)–Rh(1)–C(6A)	95.50(6)	96.2(1)
P(2)–Rh(1)–C(1A)	142.21(6)	143.7(1)
P(2)–Rh(1)–C(2A)	110.36(6)	112.0(1)
P(2)–Rh(1)–C(3A)	94.84(6)	95.2(1)
P(2)–Rh(1)–C(4A)	106.29(6)	106.0(1)
P(2)–Rh(1)–C(5A)	135.98(6)	135.3(1)
P(2)–Rh(1)–C(6A)	168.68(6)	169.4(1)
C(2A)–Rh(1)–C(4A)	63.29(8)	63.2(4)

The distances Rh(1)–(C1A–C6A) between the metal and the ring C-atoms in **3a** and **3b** (average Rh(1)–C<sub>arene</sub> = 2.343 and 2.337 Å, respectively) fall within the range reported for η<sup>6</sup>-arene bonding [17–19], but the differences between each of the Rh–C distances clearly show that the η<sup>6</sup>-arene ring is slightly distorted. Thus, the Rh(1)–C(*n*A) distances in **3a** decrease in the order *n* = 4 > 5 > 1 > 2 > 3 > 6, with the result that Rh(1)–C(3A) and Rh(1)–C(6A) are ca 0.1 Å shorter than the average of the four remaining ones, consistent with a deviation from planarity toward a distorted boat conformation of the phenyl ring (Fig. 5b). Such distortions are not unusual and have been observed previously [18,20–24] or inferred in Rh<sup>I</sup>-arene complexes [25]. The differences within the ring C–C bond lengths (Table 2) are not significant (averages of 1.414 and 1.416 Å for **3a** and **3b**, respectively). The angles defined by a ring

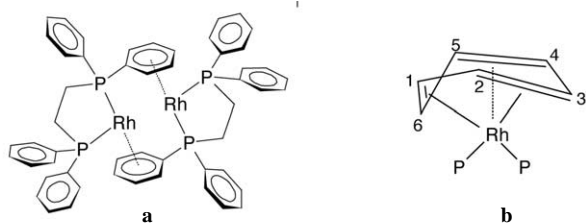


Fig. 5. **a.** Representation of the  $[\text{Rh}_2(\text{diphos})_2]^+$  structure. **b.** Deviation from planarity of an  $\eta^6$ -arene; P represents the donor P-atoms (not to scale).

C-atom, the Rh and each P-atom (Table 3) have very similar corresponding values for P(1)–Rh(1)–C<sub>arene</sub> and P(2)–Rh(1)–C<sub>arene</sub> in **3a** and **3b**. The Rh–P distances and P(1)–Rh(1)–P(2) angles in **3a** and **3b** are similar to those of other arene-bridged Rh(I) complexes containing monodentate tertiary phosphines (see below) [22,26].

The solution behavior of **3a** and **3b** is critically dependent on the solvent. The dimeric assembly is only retained in non- or weakly-coordinating media such as  $\text{CDCl}_3$  and  $\text{CD}_2\text{Cl}_2$ , where the expected AMX, two doublets of doublet pattern is seen in the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum; that for **3a** is shown in Fig. 6 ( $\delta$  39.63 dd,  $J_{\text{RhP}} = 212.6$ ,  $^2J_{\text{PP}} = 39$ ; 43.09 dd,  $J_{\text{RhP}} = 202.2$ ,  $^2J_{\text{PP}} = 38$ ). These  $\delta$  and  $J$  values are similar to those for reported monomeric Rh(I) units containing monodentate phosphines, one of which is involved in  $\eta^6$ -bonding; examples include  $[(\eta^6\text{-}\eta^1\text{-Ph}(\text{CH}_2)_2\text{P}^i\text{Pr}_2)\text{Rh}(\text{C}_8\text{H}_{14})]^+$  [23] and  $[(\eta^6\text{-}\eta^1\text{-PhO}(\text{CH}_2)_2\text{PPh}_2)\text{Rh}(\text{PPh}_2(\text{CH}_2)_2\text{OPh})]^+$  [26].  $^{31}\text{P}$ - $^1\text{H}$  HETCOR NMR experiments on **3a** show that the upfield resonance is due to the ‘bridging’ phosphine, and the lower field shift to the monodentate one. For **3b**, the doublets of doublets overlap somewhat, perhaps implying less efficient bridging capacity for a Ph vs *p*-tolyl group. The HETCOR data now show that the more downfield resonance ( $\delta$  47.47 dd,  $J_{\text{RhP}} = 210.9$ ,  $^2J_{\text{PP}} = 37$ ) is assigned to the ‘bridging’ phosphine, and the upfield one ( $\delta$  45.46 dd,  $J_{\text{RhP}} = 198.8$ ,  $^2J_{\text{PP}} = 38$ ) to the monodentate phosphine; in addition, each peak of the  $\delta$  47.47 resonance is split into a further doublet because of a small P–H coupling ( $J = 6.3$ ), as well as a strong correlation in the HETCOR NMR with  $^1\text{H}$  resonances in the more downfield aromatic region assigned to *o*-protons on the two non-coordinated Ph groups of the bridging phosphine; the small  $J_{\text{PH}}$  coupling possibly results

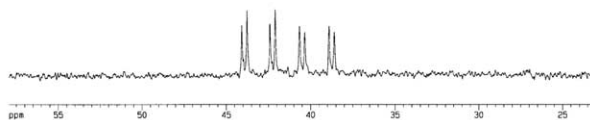


Fig. 6.  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **3a** in  $\text{CD}_2\text{Cl}_2$ .

from coupling to one H-atom of a bridging aryl that is non-symmetrically bonded (see below).

The  $^1\text{H}$  NMR data in  $\text{CD}_2\text{Cl}_2$  reveal a non-symmetric coordination of the bridging aryl groups in **3a** and in **3b**, which might be  $\eta^4$ -coordinated as exemplified in Fig. 7a. Thus **3a** shows upfield-shifted resonances for the protons on the  $\mu$ -aryl rings, at values comparable to those in other  $\eta^6$ -arene systems [18,19,22,26]. A doublet at  $\delta$  5.99 ( $^3J_{\text{HH}} = 6$ ) is assigned to  $\eta^4$ -aryl *m*-protons, each of which is coupled to the *o*-proton. An apparent triplet at  $\delta$  6.60 ( $^3J_{\text{HH}} = 6.6$ ) is attributed to  $\eta^4$ -aryl *o*-protons; this signal with P-decoupling collapses to a doublet without change in  $\delta$  or  $^3J_{\text{HH}}$ , implying that these protons are also coupled to  $^{31}\text{P}$  but with such a small  $^3J_{\text{HP}}$  value that the expected doublet of doublets in the coupled  $^1\text{H}$  NMR spectrum appears as a pseudo-triplet. Each of the  $\delta$  5.99 and 6.60 peaks integrates for three protons, supporting  $\eta^4$ -arene, or some other non-symmetric coordination; integration on the non-shifted aromatics in fact accounts for the remaining 42 protons. In addition, the room-temperature  $^{13}\text{C}$  NMR spectrum of **3a** in  $\text{CD}_2\text{Cl}_2$  confirms a non-symmetric bridging mode for the aryls, in that four different resonances for the *p*- $\text{CH}_3$  and for the *ipso* C-atoms are detected, each set in an approximate 6:4:1:1 ratio, instead of three in a 6:4:2 ratio expected for a symmetric  $\eta^6$ -coordination. The data indicate that these C-atoms on the bridging aryls experience different chemical environments, supporting a localized bonding with each Rh; in principle, a  $\eta^6$ -mode for one of the rings is not excluded. The  $^{13}\text{C}$  NMR evidence unmistakably shows that the two-bridged aryls are bonded differently. Characteristic upfield-shifted resonances for the *o*- and *m*-C-atoms of the bridging aryls [22] are also detected ( $\delta$  102.65, 103.32, 2 bs), but the equivocal hapticities of these aryls preclude a clear assignment for these resonances. The  $^1\text{H}$  resonances of the *p*- $\text{CH}_3$  groups appear as two resonances in a 1:5 ratio, corresponding to the ‘bridging’ and monodentate phosphines, respectively. Similarly, **3b** in  $\text{CD}_2\text{Cl}_2$  reveals upfield shifted  $^1\text{H}$  resonances. The poorly resolved triplet at  $\delta$  4.90 ( $^3J_{\text{HH}} \sim 6$ ) is attributed to ring-current effects on the *p*-H of the  $\mu$ -Ph group [26], and the sharp triplet at  $\delta$  6.89 ( $^3J_{\text{HH}} = 6.0$ ) integrating as 2:1 with the  $\delta$  4.90 resonance is assigned to the *m*-protons. The five protons of a coordinated Ph group would be expected to give rise to a set of three distinctive upfield-shifted resonances, but only two are seen, the third set presumably being hidden in the  $\delta$  7.0–7.8 region, again consistent with the protons being attached to a C=C moiety not bonded to Rh. This observation and integrations of the entire spectrum again provide evidence for  $\eta^4$ -arene coordination in solution. That molecular cations may

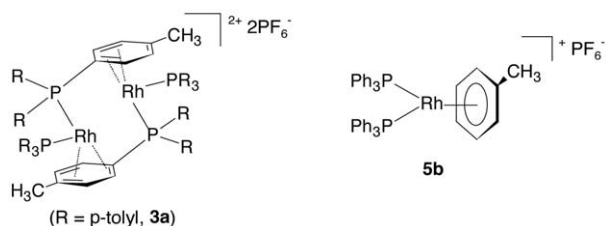
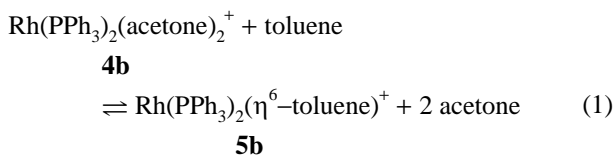


Fig. 7. **a.** Suggested  $\eta^4$ -arene coordination in solution structure of **3a** (and **3b**). **b.** Suggested structure of **5b**.

adopt either a 16- or 18-electron configuration, depending on the hapticity of an arene ring ( $\eta^4$  vs  $\eta^6$ ) has long been suggested for  $\text{Rh}^I$  centers [27].

In coordinating media ( $\text{CD}_3\text{OD}$ , acetone- $d_6$ ), the dimeric structure of species **3** is converted to the well known, solvated  $\text{cis-}[\text{Rh}(\text{PR}_3)_2(\text{solv})_2]\text{PF}_6$  species ( $\text{R} = p\text{-tolyl}$  (**4a**),  $\text{Ph}$  (**4b**)), in which the two now equivalent P-atoms give rise to a doublet in the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum [10]. The red solutions of species **4** readily react with 1 atm  $\text{H}_2$  to afford the pale yellow solutions of the previously mentioned dihydrido species **2** (cf. Fig. 1).

Addition of four equivalents of toluene to a solution of **3b** in  $\text{CD}_2\text{Cl}_2$  (toluene:  $\text{Rh} = 2$ ) affords quantitative in situ formation of the monomeric  $\eta^6$ -toluene complex **5b** (Fig. 7b), as evidenced by the characteristically upfield-shifted  $^1\text{H}$  resonances [22] for the coordinated toluene ( $\delta$  2.20, 3H,  $\text{CH}_3$ ; d,  $\delta$  5.33 d,  $^3J_{\text{HH}} = 6.0$ , 2H,  $o\text{-C}_6\text{H}_5$ ; 5.68 t,  $^3J_{\text{HH}} = 6.0$ , 2H,  $m\text{-C}_6\text{H}_5$ ; 6.80 t,  $^3J_{\text{HH}} = 6.0$ , 1H,  $p\text{-C}_6\text{H}_5$ ), while the  $^{31}\text{P}\{^1\text{H}\}$  signal appears as a doublet at  $\delta$  45.06 d,  $J_{\text{RHP}} = 207.0$ ); the excess toluene is the only other species seen in the solution. Upon addition of toluene (toluene:  $\text{Rh} = 2$ ) to an acetone- $d_6$  solution of **3b**, now present as  $\text{Rh}(\text{PPh}_3)_2(\text{acetone})_2^+$  (**4b**), an approximately 2:1 equilibrium is established between **4b** and **5b** (equation (1)):



as most easily detected by  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\delta$  54.20 d,  $J_{\text{RHP}} = 202.0$ , **4b**; 45.15 d,  $J_{\text{RHP}} = 207.7$ , **5b**); the  $^1\text{H}$  resonances for the  $\eta^6$ -toluene are very similar to those measured in  $\text{CD}_2\text{Cl}_2$ , but are at lower fields by  $\sim 0.1\text{--}0.3$  ppm. The reactivity of the  $p$ -tolyl dimer **3a** toward toluene is similar to that of **3b**, but the  $^1\text{H}$  NMR is more complicated because of the presence of Me groups in the phosphine and toluene. The toluene adducts in  $\text{CD}_2\text{Cl}_2$  do not react with 1 atm  $\text{H}_2$ , showing that in the absence of a sufficiently coordinating solvent, dihydrido species such as **2** ( $\text{Rh}(\text{H})_2(\text{PR}_3)_2(\text{solvent})_2^+$ ) are not formed (see

above), and the coordinated toluene is not displaced; in acetone- $d_6$ , the presence of the equilibrium between the toluene and bis(acetone) adducts allows for reactivity with  $\text{H}_2$ , resulting in complete formation of **2** and de-coordination of toluene and quantitative formation of **2a**. No hydrogenation of the toluene moiety is observed in either solvent at ambient conditions. The analogous diphos complex in MeOH, which exists as  $\text{Rh}(\text{diphos})(\text{MeOH})_2^+$  [16,28] (cf. Fig. 5a), catalyzes at 1 atm  $\text{H}_2$  and  $\sim 50^\circ\text{C}$  hydrogenation of activated aromatics such as anthracene, but not toluene itself [28]; further studies are needed to test our dimers for such activity. There are major effects of solvent in homogeneous hydrogenation of imines catalyzed by Rh-phosphine complexes, where, for example, MeOH is often a required solvent for effective hydrogenation [12–15]. The findings illustrated in this paper, especially the required presence of coordinating solvents for generation of hydrido species, will contribute to the understanding of such catalysis.

### 3. Experimental section

All reagents and products were manipulated in an Ar-filled glove box or using standard Schlenk techniques. Microanalyses were performed by Mr P. Borda of this Department. NMR spectra were recorded on Varian XL300, Bruker AV300 or AV400 spectrometers;  $^{31}\text{P}\{^1\text{H}\}$  NMR data are reported relative to 85% aq.  $\text{H}_3\text{PO}_4$ , and all  $J$  values are reported in Hz.  $\text{H}_2$  was purified by passing through an Englehard 'Deoxo' catalyst. Phosphines were purchased from Strem Chemicals. The  $[\text{Rh}(\text{COD})(\text{PR}_3)_2]\text{PF}_6$  complexes were prepared by literature procedures [3,4].

#### 3.1. Preparation of $[\text{Rh}_2(\text{PR}_3)_4][\text{PF}_6]_2$ (**3**) ( $\text{R} = p\text{-tolyl}$ , **3a**; $\text{Ph}$ , **3b**)

A suspension of  $[\text{Rh}(\text{COD})(\text{PR}_3)_2]\text{PF}_6$  (0.09 g,  $\sim 0.10$  mmol) in MeOH (10 ml) was stirred under 1 atm  $\text{H}_2$  for 1.5 h. The resultant pale yellow solution was then evaporated to dryness in vacuo to afford (**3**) as a dark red-brown residue that was dried in vacuo for 24 h; yields, 0.06 g,  $\sim 70\%$ .

(**3a**). Anal. calcd for  $\text{C}_{84}\text{H}_{84}\text{F}_{12}\text{P}_6\text{Rh}_2$ : C 58.89, H 4.94. Found: C 58.26, H 4.97.  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  39.63 (dd,  $J_{\text{RHP}} = 212.6$ ,  $^2J_{\text{PP}} = 39$ ), 43.09 (dd,  $J_{\text{RHP}} = 202.2$ ,  $^2J_{\text{PP}} = 38$ ).  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  2.20 (s, 6H,  $\eta^4\text{-}p\text{-C}_6\text{H}_4\text{CH}_3$ ), 2.38 (s, 30H,  $p\text{-C}_6\text{H}_4\text{CH}_3$ ), 5.99 (d, 3H,  $\eta^4\text{-}m\text{-C}_6\text{H}_4\text{CH}_3$ ,  $^3J_{\text{HH}} = 6.6$ ), 6.60 (t, 3H,  $\eta^4\text{-}o\text{-C}_6\text{H}_4\text{CH}_3$ ,  $^3J_{\text{HH}} = 6.6$ ) 6.80–7.30 (m, 42H,  $p\text{-C}_6\text{H}_4\text{CH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  18.95 (s, 1C,  $\eta^4\text{-}p\text{-C}_6\text{H}_4\text{CH}_3$ ), 20.96 (s, 6C,  $p\text{-C}_6\text{H}_4\text{CH}_3$ ), 21.06 (s, 4C,  $p\text{-C}_6\text{H}_4\text{CH}_3$ ), 21.37 (s, 1C,  $\eta^4\text{-}p\text{-C}_6\text{H}_4\text{CH}_3$ ), 102.65, 103.32 (2 bs,  $\eta^4\text{-}o,m\text{-C}_6\text{H}_4\text{CH}_3$ ), 122.70–133.92 (m, 'free'- and  $\eta^4\text{-}o,m\text{-C}_6\text{H}_4\text{CH}_3$ ),

140.91 (s, 1C, *ipso*- $\eta^4$ -C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>), 141.77 (s, 6C, *ipso*-C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>), 142.07 (s, 4C, *ipso*-C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>), 144.40 (s, 1C, *ipso*- $\eta^4$ -C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>3</sub>OD, species exists as **4a**):  $\delta$  55.15 (d,  $J_{\text{RHP}} = 207.7$ ). <sup>1</sup>H NMR (CD<sub>3</sub>OD, **4a**):  $\delta$  2.33 (s, 18H, *p*-C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>), 7.24 (s, 24H, *p*-C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>).

**(3b)**. Anal. Calcd for C<sub>72</sub>H<sub>60</sub>F<sub>12</sub>P<sub>6</sub>Rh<sub>2</sub>: C 55.98, H 3.91. Found: C 55.87, H 3.88. <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  45.46 (dd,  $J_{\text{RHP}} = 198.8$ ,  $^2J_{\text{PP}} = 38$ ), 47.47 (dd,  $J_{\text{RHP}} = 210.9$ ,  $^2J_{\text{PP}} = 36$ ). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  4.90 (pt, 2H,  $\eta^4$ -*p*-C<sub>6</sub>H<sub>5</sub>,  $^3J_{\text{HH}} = 6.0$ ), 6.89 (t, 4H,  $\eta^4$ -*m*-C<sub>6</sub>H<sub>5</sub>,  $^3J_{\text{HH}} = 6.0$ ), 7.05–7.70 (m, 54H, C<sub>6</sub>H<sub>5</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>3</sub>OD, **4b**):  $\delta$  57.02 (d,  $J_{\text{RHP}} = 206.8$ ). <sup>1</sup>H NMR (CD<sub>3</sub>OD, **4b**):  $\delta$  7.11–7.81 (m, 30H, C<sub>6</sub>H<sub>5</sub>).

### 3.2. X-ray crystallographic analyses of **3a** and **3b**

The crystals of the compound were mounted on glass fibers, and measurements were made at 173 K

with graphite monochromated Mo K $\alpha$  radiation on a Siemens SMART Platform CCD (for **3a**) or a Rigaku/ADSC CCD area detector (for **3b**). Data for **3a** were collected and processed using the SHELXTL-Plus V5.0 program [29], and corrected for absorption effects (SADABS); for **3b**, the d\*TREK program [30] was used, the data corrected for Lorentz, polarization and absorption effects, and calculations were performed using the teXsan [31] crystallographic software package of Molecular Structure Corporation. Neutral atom scattering factors were taken from Cromer and Waber [32]. Both structures were solved by direct methods, expanded using Fourier techniques, and refined by full-matrix least-squares cycles on  $F^2$  [33,34]. All non-hydrogen atoms were refined anisotropically, while H-atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters.

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