Available online at www.sciencedirect.com
ScienceDirect
Inorganica Chimica Acta 361 (2008) 2123–2130
Inorganica Chimica Acta
www.elsevier.com/locate/ica

Serendipitous syntheses of $Rh(H)_2Cl(PRPh_2)_3$ complexes, and their crystal structures, where R = Me, Cy (cyclohexyl)

Fabio Lorenzini, Brian O. Patrick, Brian R. James *

Department of Chemistry, The University of British Columbia, Vancouver, British Columbia, Canada V6T 1Z1

Received 17 September 2007; received in revised form 27 October 2007; accepted 28 October 2007
Available online 6 November 2007

Abstract

Reactions of RhCl(cod)(THP) (cod = 1,5-cyclooctadiene; THP = $P(CH_2OH)_3$) with $PMePh_2$ or $PCyPh_2$ (Cy = cyclohexyl) in acetone/MeOH solution under H_2 surprisingly form the complexes *cis,mer*-$Rh(H)_2Cl(PRPh_2)_3$ (R = Me or Cy); both complexes are characterized by crystallography (the first structures in which the hydride ligands of such dihydrido-chloro-trisphosphine complexes have been located), and by detailed ^1H and ^{31}P NMR spectroscopy. The key role of the THP in the observed chemistry is discussed.

Keywords: Rhodium; Hydride complexes; Phosphine complexes; Crystallography; NMR spectroscopy

1. Introduction

The activation of molecular hydrogen by transition metal complexes after seven decades of study remains an extremely active research area, particularly in aspects of catalytic asymmetric hydrogenation. Key advances in terms of application in organic syntheses developed from studies in the 1960s when the groups of Halpern [1] and Wilkinson [2] reported, respectively, on the use of Ru and Rh species in solution for catalytic hydrogenation of olefins. Of historical note, the first success for olefin hydrogenation catalysts was with chlororuthenate(II) species within an aqueous system reported in 1961 [1], but the more well-known and more widely applicable system was that of (chloro)tris(triphenylphosphine)rhodium(I) in non-aqueous media reported in 1965 [2]. The $RhCl(PPh_3)_3$ complex is invariably and correctly called the "Wilkinson catalyst", although its activity for the olefin hydrogenation was independently discovered simultaneously by Coffey [3]. The complex was also made independently (again reported in 1965) by three other groups [4]. The historical aspects of homogeneous hydrogenation can be traced through a 1973 text [5], while reviews of the latest findings are available in three recent volumes [6].

There are now thousands of publications dealing with Rh–phosphine complexes (including recent ones) that still discuss mechanistic details of olefin hydrogenations catalyzed in solution by $RhCl(PPh_3)_3$ or other chloro-tertiary phosphine analogues [7]. The essentials of the mechanism seem clear, although the proposed species directly responsible for the hydrogenation are not detected: these are usually $RhClP_2S$, $Rh(H)_2ClP_2S$, $Rh(H)_2Cl(olefin)P_2$, and $RhH(alkyl)ClP_2$, where P = PPh_3 and S = solvent or coordination vacancy, whereas the precursor $RhClP_3$ and $Rh(H)_2ClP_3$ species are isolable [8]. During our recent studies on the isolation of water-soluble Rh^I–THP complexes and investigation of their chemistry (THP = tris(hydroxymethyl)phosphine, $P(CH_2OH)_3$) [9], we accidentally prepared the complexes *cis,mer*-$Rh(H)_2Cl(PRPh_2)_3$, where R = Me (complex **1**) or Cy (**2**). We were surprised to find that there was only one other crystallographically characterized Rh^{III}-dihydride of this type, the PPh_3 analogue, in which the hydride ligands were not located [10], and that there were limitations in the characterization of other isolated $Rh(H)_2Cl(PR_3)_3$ complexes, where R_3 = $EtPh_2$ [11], ^{t}BuMePh [12], and $(DBH)_3$ (DBH = 5-phenyl-5H-dibenzophosphole) [13]. A quite recent paper has reported ^1H

* Corresponding author.
E-mail address: brj@chem.ubc.ca (B.R. James).

0020-1693/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.ica.2007.10.044

NMR data (using *para*-hydrogen-induced polarization – the PHIP technique) for the hydride ligand of $Rh(H)_2Cl(PR_3)_3$ species formed in situ, where $R_3 = Me_3$, Me_2Ph, $MePh_2$, Et_3, Et_2Ph, $EtPh_2$ and $^nBu_3$ [14]. Our paper here describes the serendipitously synthesized complexes **1** and **2**, and their characterization, including X-ray structures with located hydrides, and detailed, conventional ^1H, and $^{31}P\{^1H\}$ NMR data.

2. Experimental

2.1. General considerations

The precursor complex RhCl(cod)(THP) (cod = 1,5-cyclooctadiene) was synthesized by our recently reported method [9]; the phosphines were used as received from Strem Chemicals, and the reactions with the Rh precursor were carried out under Ar or H_2, using standard SCHLENK techniques, or in a J-Young NMR-tube. MeOH was dried over Mg–I_2 and distilled under N_2, and acetone was dried over K_2CO_3 and distilled under N_2. $^{31}P\{^1H\}$, $^{13}C\{^1H\}$, ^1H, $^1H\{^{31}P\}$ and 2D NMR spectra were measured in 1:1 CD_3OD/acetone-d_6 or CD_2Cl_2 solutions at room temperature (~300 K), on a Bruker AV400 spectrometer; the deuterated solvents were used as received from Cambridge Isotope Laboratory. A residual deuterated solvent proton (relative to external $SiMe_4$) and external 85% aq H_3PO_4 were used as references (s = singlet, d = doublet, t = triplet m = multiplet; *J* values given in Hz). When necessary, atom assignments were made by means of ^{31}P–^1H (HMQC) NMR correlation spectroscopy. Elemental analyses were performed on a Carlo Erba 1108 analyzer.

2.2. Synthesis of *cis,mer*-$Rh(H)_2Cl(PMePh_2)_3$ (**1**)

Addition of $PMePh_2$ (11 μL, 57.9 mmol) in acetone-d_6 (0.4 mL) to a yellow CD_3OD solution (0.4 mL) of RhCl(cod)(THP) (10 mg, 27.0 mmol) at room temperature under Ar in a J-Young NMR-tube results in immediate formation of a brown solution. The Ar is then removed by evacuation, and the tube filled with H_2 and shaken, this resulting in a yellow-brown solution. Over 12 h, X-ray quality, yellow crystals of **1** deposit from the solution; these were filtered off, washed with 3 × 2 mL of Et_2O and then dried under vacuum overnight (10.9 mg; yield 76 % on $PMePh_2$). A satisfactory elemental analysis for a crystal of **1** could not be obtained. MS for $C_{39}H_{41}ClP_3Rh$: 703 ($[M-Cl-2H]^+$), 503 ($[M-Cl-2H-PMePh_2]^+$). ^1H NMR (CD_2Cl_2, see Fig. 1 for labeling): δ −17.94 (m, 1H, RhH_2 *cis* to P atoms, $J(H_2Rh) = 22.3$, $J(H_2H_1) = 2.0$, $J(H_2P_a) = 13.7$, $J(H_2P_b) = 9.2$), −9.55 (dddt, 1H, RhH_1 *trans* to P_b, $J(H_1Rh) = 12.0$, $J(H_1H_2) = 2.0$, $J(H_1P_a) = 12.0$, $J(H_1P_b) = 163.4$), 1.35 (br s, 3H, CH_3P_b), 1.78 (dd, 6H, $J(HP_a) \cong J(HRh) = 2.9$, C$H_3P_a$), 7.17 (m, 10H, $C_6H_5P_b$), 7.35 (m, 10H, $C_6H_5P_a$), 7.67 (m, 10H, $C_6H_5P_a$). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 6.01 (dt, 1P_b, $J(P_bRh) = 89.4$, $J(P_bP_a) = 22.7$), 24.94 (dd, 2P_a, $J(P_aRh) = 110.9$, $J(P_aP_b) = 22.7$). $^{13}C\{^1H\}$ NMR for a mixture of **1** and **3** – see below (CD_2Cl_2): δ 16.14 (CH_3), 128.03–133.77 (C_6H_5). Spectral integrations for **1** and **3** are 'normalized', assuming the absence of a mixture.

2.2.1. $RhCl(PMePh_2)_3$ (**3**)

^1H NMR (CD_2Cl_2, see Fig. 1 for labeling): δ 1.36 (br s, 3H, CH_3P_c), 1.68 (dd, 6H, $J(HP_d) \cong J(HRh) = 2.4$, C$H_3P_d$), 7.51 (m, 30H, C_6H_5). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 18.35 (dd, 2P_d, $J(P_dRh) = 139.6$, $J(P_dP_c) = 42.6$ Hz), 33.72 (dt, 1P_c, $J(P_cRh) = 186.1$, $J(P_cP_d) = 42.6$).

2.3. Synthesis of *cis,mer*-$Rh(H)_2Cl(PCyPh_2)_3$ (**2**)

The synthesis was exactly as described for complex **1**, but using $PCyPh_2$ (10.4 mg, 38.0 mmol) and 6.6 mg, 17.8 mmol of RhCl(cod)(THP), and again yellow, X-ray quality crystals of **2** · MeOH were deposited from the solution over a 12 h period; these were collected, washed with Et_2O and dried as for **1** (9.5 mg; yield 79% on $PCyPh_2$). *Anal.* Calc. for $C_{55}H_{69}OClP_3Rh$: C, 67.59; H, 7.12. Found: C, 67.93; H, 6.91%. MS: 908 ($[M-Cl-2H]^+$), 675 ($[M-2H-PCyPh_2]^+$). ^1H NMR (CD_2Cl_2; labeling corresponds to that in Fig. 1): δ −17.81 (m, 1H, RhH_2 *cis* to P atoms, $J(H_2Rh) = 22.3$, $J(H_2H_1) = 3.5$, $J(H_2P_a) = 13.8$, $J(H_2P_b) = 9.0$), −9.03 (dddt, 1H, RhH_1 *trans* to P_b, $J(H_1Rh) = 12.3$, $J(H_1H_2) = 3.5$, $J(H_1P_a) \cong 12.3$, $J(H_1P_b) = 154.7$), 0.22–2.64 (m, 33H, C_6H_{11}), 6.45–7.78 (m, 30H, C_6H_5). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 32.43 (m, 1P_b), 46.80 (br d, 2P_a, $J(P_aRh) \cong 110.9$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 26.71–29.86 (C_6H_{10}), 127.11–135.38 (C_6H_5).

2.4. Crystallographic analyses of **1** and **2**

X-ray data for the $Rh(H)_2Cl(PRPh_2)_3$ complexes (R = Me, **1**; R = Cy, **2**) were collected at 173 (±0.1) K on a Bruker X8 APEX diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) to maximum 2θ values of 56.3° (for **1**) and 56.0° (for **2**), in a series of φ and ω scans in 0.50° oscillations with 4.0 and 10.0 s exposures, respectively; the crystal-to-detector distance was 36.00 mm for both complexes. Of 29,629 and 27,487 reflections collected for **1** and **2**, respectively, 8,297 and 5,982 were unique (with corresponding R_{int} values of 0.032 and 0.045), equivalent reflections being merged. Data were collected and integrated using the Bruker SAINT software package [15], and were corrected for absorption effects using the multi-scan technique SADABS [16], with respective minimum and maximum transmission coefficients of 0.740 and 0.895 (for **1**), and 0.835 and 0.973 (for **2**). Data were corrected for Lorentz and polarization effects, and the structures were solved by direct methods [17]. Selected crystallographic data for **1** and **2** are shown in Table 1, and more details are provided in the Supporting Information. For complex **1**, all non-hydrogen atoms were refined anisotropically, while all H-atoms were placed in calculated positions, except H1 and H2, the metal hydrides (see Figs. 1 and 2),

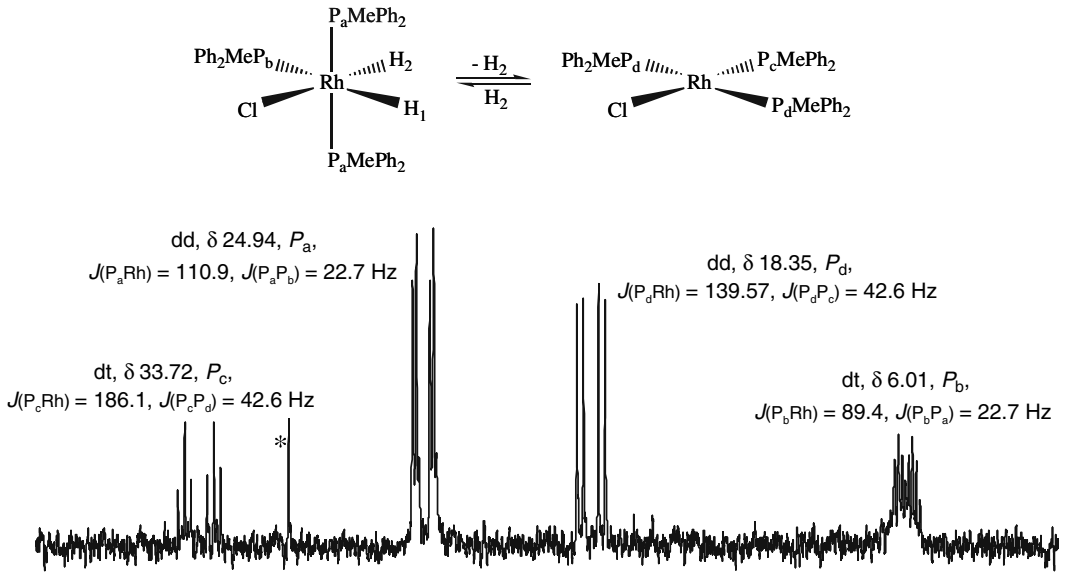


Fig. 1. $^{31}P\{^1H\}$ NMR spectrum of a CD_2Cl_2 solution of *cis,mer*-$Rh(H)_2Cl(PMePh_2)_3$ (**1**), showing the resulting mixture of **1** and $RhCl(PMePh_2)_3$ (**3**). *Impurity, probably $OPMePh_2$.

Table 1
Crystal data and structure refinements for *cis,mer*-$Rh(H)_2Cl(PMePh_2)_3$ (**1**) and *cis,mer*-$Rh(H)_2Cl(PCyPh_2)_3$ (**2**)

Compound	**1**	**2** · CH_3OH
Empirical formula	$C_{39}H_{41}P_3RhCl$	$C_{55}H_{69}OClP_3Rh$
Formula weight	740.99	945.37
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$ (#2)	$P2_1/m$ (#13)
Crystal size (mm^3)	$0.15 \times 0.35 \times 0.35$	$0.05 \times 0.15 \times 0.30$
a (Å)	9.9056(5)	10.0140(14)
b (Å)	11.8266(6)	22.598(3)
c (Å)	16.5794(9)	11.2538(16)
α (°)	103.006(2)	90.0
β (°)	91.063(3)	108.474(7)
γ (°)	112.870(2)	90.0
V ($Å^3$)	1731.47(16)	2415.5(6)
Z value	2	2
D_{calc} ($g\,cm^{-3}$)	1.421	1.342
μ (cm^{-1})	7.36	5.47
No. of reflections measured	29629	27487
Unique [R_{int}]	8297 [0.032]	5982 [0.045]
No. parameters	408	266
R_1[a], wR_2[b]	0.036, 0.067	0.058, 0.102
Goodness-of-fit indicator	1.05	1.03
Max. diffraction peak/hole (e $Å^{-3}$)	0.51/−0.40	0.90/−1.38

[a] $R_1 = \Sigma|(F_o) - (F_c)|/\Sigma(F_o)$.
[b] $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

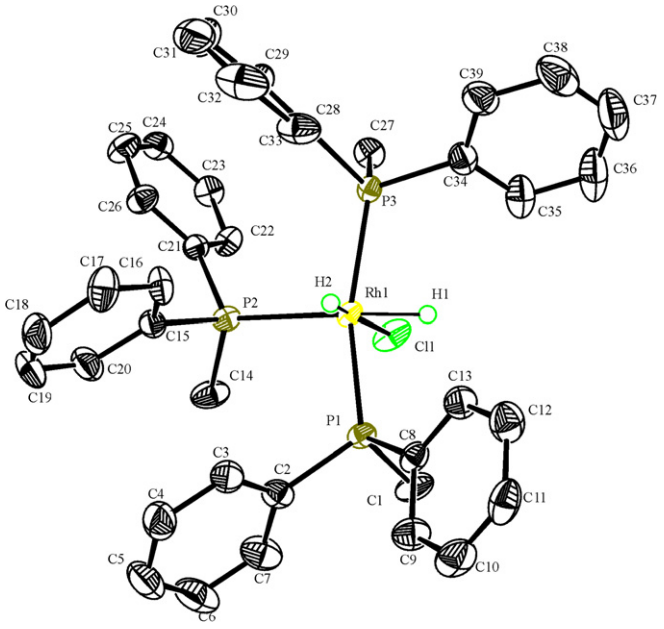


Fig. 2. Structure of *cis,mer*-$Rh(H)_2Cl(PMePh_2)_3$ (**1**), with 50% probability ellipsoids. Selected distances (Å) and angles (°): Rh(1)–P(1), 2.2850(5); Rh(1)–P(2), 2.3861(5); Rh(1)–P(3), 2.3101(5); Rh(1)–Cl(1), 2.5022(5); Rh(1)–H(1), 1.48(2); Rh(1)–H(2), 1.45(2); P(1)–Rh(1)–P(2), 98.246(19); P(1)–Rh(1)–P(3), 160.456(19); P(1)–Rh(1)–Cl(1), 95.156(18); P(1)–Rh(1)–H(1), 79.5(9); P(1)–Rh(1)–H(2), 81.9(8); P(2)–Rh(1)–P(3), 99.507(18); P(2)–Rh(1)–Cl(1), 91.124(19); P(2)–Rh(1)–H(1), 177.4(9); P(2)–Rh(1)–H(2), 95.5(8); P(3)–Rh(1)–Cl(1), 92.609(19); P(3)–Rh(1)–H(1), 82.9(9); P(3)–Rh(1)–H(2), 88.3(8); Cl(1)–Rh(1)–H(1), 87.8(9); Cl(1)–Rh(1)–H(2), 173.0(8); H(1)–Rh(1)–H(2), 85.4(12).

which were found in a difference map and refined isotropically. Complex **2** crystallizes with one half-molecule residing on a mirror plane perpendicular to the *b*-axis. All the substituents on P2 (see Fig. 5, below) are disordered, with two of the three positions sharing both a phenyl and cyclohexyl ring, while the third position has disordered phenyls across the mirror plane; all C-atoms of the disordered fragments were refined isotropically, while all other non-hydrogen atoms were refined anisotropically. The metal hydrides H1m and H2m (corresponding to H1 and H2 of complex **1**, respectively) were located in difference maps and refined isotropically; other H-atoms were placed in calculated positions. Finally, the MeOH molecule that crystallizes in the asymmetric unit of **2** is also disordered about the mirror plane.

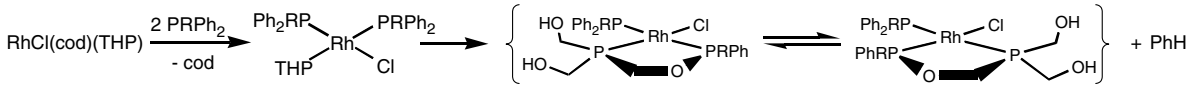
3. Results and discussion

3.1. The $PMePh_2$ system

We have reported recently [9a] on slow reactions of RhCl(cod)(THP) with 2 mol equivalents of $PMePh_2$ or $PCyPh_2$ in alcohol or acetone solution under Ar at room temperature. After a 12 h period, the final product is a mixture of isomers formed according to Scheme 1; the reactions involve a THP-promoted P–C_6H_5 bond cleavage of a $PRPh_2$ ligand with co-production of benzene, the required proton deriving from a THP-hydroxy group. In this current work, an atmosphere of H_2 was added to the mixture in the same media essentially immediately after mixing the reagents, and now the isolated products are *cis*,-*mer*-$Rh(H)_2Cl(PRPh_2)_3$, where R = Me (complex **1**), or Cy (**2**). The complexes **1** and **2** could be formed by oxidative addition of H_2 to $RhCl(PRPh_2)_3$, which is a well established reaction and typically a reversible process within other reported $RhClP_3$ systems, where P is a general, monodentate tertiary phosphine [11,14,18]. However, NMR evidence (see below) shows the presence of *cis*-$Rh(H)_2Cl(PRPh_2)_2$(THP) species that would be formed by oxidative addition of H_2 to $RhCl(PRPh_2)_2$(THP) (see Scheme 1) and, more plausibly, **1** and **2** could be formed by displacement of the THP of *cis*-$Rh(H)_2Cl(PRPh_2)_2$-(THP) by $PRPh_2$; in essence, the THP promotes the oxidative addition step.

Immediately after the phosphine and RhCl(cod)(THP) are mixed in the acetone–MeOH solvent under Ar, the in situ $^{31}P\{^1H\}$ NMR spectrum of the brown solution shows no signal for the Rh-cod precursor (δ_P 17.7, d, J(RhP) = 145 Hz), a small amount of free $PMePh_2$ (δ_P −28.0, s) corresponding to the slight excess for a 2:1 phosphine:Rh reaction, and a complex mixture of products with signals between δ_P −0.28 and 18.57; of note, no free THP (δ_P −25.0, s) is seen. If the solution is not exposed to H_2, this spectrum changes slowly with time to generate a roughly 1:1 mixture of the *cis*- and *trans*-isomer products shown in Scheme 1 [9a]; the $^{31}P\{^1H\}$ spectrum of this final mixture shows the signals for the three inequivalent P-atoms of each isomer, each P-atom giving a doublet of doublets of doublets, and all the resonances have been assigned [9a]. With the immediate H_2 treatment, however, the color instantly becomes lighter and the in situ ^1H and $^{31}P\{^1H\}$ NMR spectra show the major product to be *cis*,-*mer*-$Rh(H)_2Cl(PMePh_2)_3$ (**1**). Overnight, crystals of **1** are deposited and X-ray analysis corresponds to this structure (Fig. 2). The NMR data of isolated **1** in CD_2Cl_2 under Ar show the partial loss of H_2 to give some $RhCl(PMePh_2)_3$ (**3**), with a **1**:**3** equilibrium ratio of ~1.7 within the NMR tube; addition of H_2 at 1 atm completely regenerates **1**. The assignments of the key $^{31}P\{^1H\}$ and high-field hydride ^1H resonances (for **1**) are given in Section 2 and are reasonably straightforward. The P_a-atom gives a doublet of doublets due to coupling to P_b and Rh, and P_b gives rise to a doublet of triplets due to coupling to two P_a atoms and Rh (Fig. 1). The H_1-hydride gives a doublet of doublets of doublets of triplets due to coupling to Rh, the H_2-hydride, and the two P_a and P_b atoms; and the H_2-hydride generates a multiplet for a second-order spectrum that is well simulated using the illustrated J values for coupling to Rh, H_1, P_a and P_b (Fig. 3). The assignments of the H_1 and H_2 resonances of **1**, and the respective Me resonances to **1** and **3**, were obtained via use of a 2D HMQC $^{31}P\{^1H\}/^1H$ NMR spectrum (Fig. 4). An $^1H\{^{31}P\}$ NMR spectrum confirms assignment of all the ^1H NMR resonances, including the Me proton resonances which appear as a doublet of doublets for P_a–Me protons (coupled to P_a and Rh) and a broad singlet presumably due to a rapidly exchanging P_b ligand [19] (Fig. 4). To the best of our knowledge, this is the first comprehensive NMR characterization of a dihydride of general formula $Rh(H)_2Cl(PR_3)_3$ (R substituents are the same or different) by *conventional* NMR methods, and the high-field hydride data determined for **1** are in excellent agreement with literature data obtained in acetone-d_6 using the PHIP technique [14]. For $RhCl(PMePh_2)_3$ (**3**), the $^{31}P\{^1H\}$ NMR spectrum (Fig. 1) shows the expected doublet of triplets (for P_c) and a doublet of doublets for the P_d atoms; the protons of the Me groups are also assigned (Fig. 4). The various coupling constants for *cis* and *trans*-disposed P-atoms at Rh, and *cis*-hydrides (*cis* and *trans* to P-atoms at Rh) are consistent with those reported for analogous *cis*,*mer*-$Rh(H)_2Cl(PR_3)_3$ complexes, where the R substituents may be the same or different [7,14,18–20].

Many groups have studied such catalytically important Rh^{III}-dihydrides formed usually by reversible oxidative addition of H_2 to a Rh^I precursor. However, because of their short lifetimes and low concentrations in solutions [7,11–14,18–20], including decomposition in chlorinated solvents to chloro species [21], NMR data have not generally been definitive until the utilization of the much more sensitive PHIP technique (for ^{31}P, ^1H, and ^{103}Rh NMR), which has been applied for the in situ formed R_3 = Ph_3, Me_3, Me_2Ph, $MePh_2$, Et_3, Et_2Ph, $EtPh_2$ and $^nBu_3$ species [14,20]. Of note, complex **1** in the solid state does not lose H_2, even under the vacuum conditions used for drying the isolated crystals, but does so in solution under Ar but not under H_2.



Scheme 1. Synthesis of *trans*- and *cis*-$RhCl(PRPh_2)[P,P\text{-}Ph(R)POCH_2P(CH_2OH)_2]$ (R = Me, Cy); *trans* and *cis* refer to the disposition of the P-atoms with Ph substitutents.

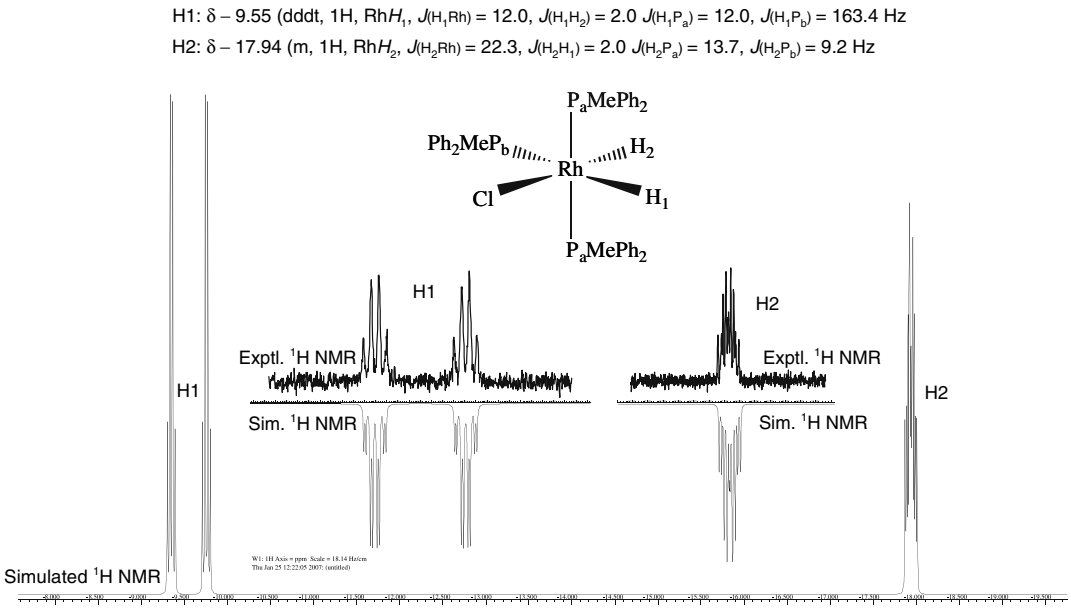


Fig. 3. Experimental and simulated ^{1}H NMR spectrum, in the hydride region, of a CD_2Cl_2 solution of *cis*,*mer*-Rh(H)$_2$Cl(PMePh$_2$)$_3$ (**1**).

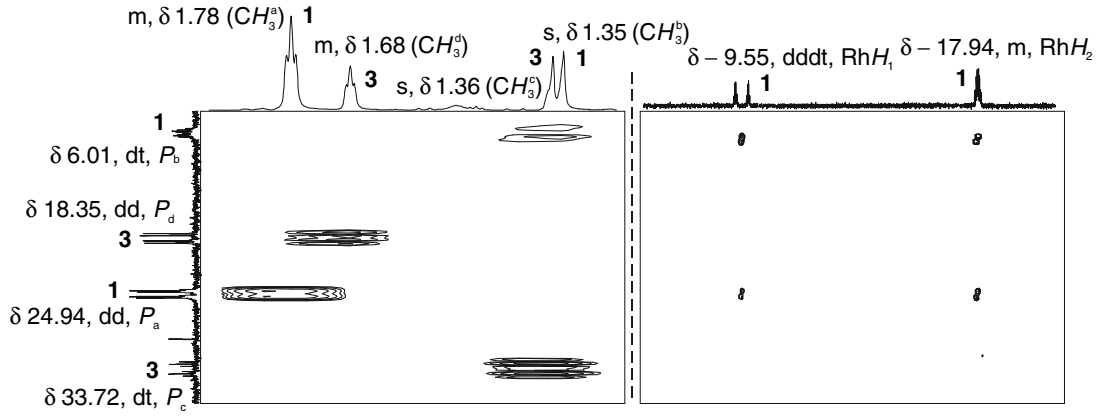


Fig. 4. HMQC ^{31}P{^{1}H}–^{1}H NMR spectrum of a CD_2Cl_2 solution of *cis*,*mer*-Rh(H)$_2$Cl(PMePh$_2$)$_3$ (**1**); enlargement of the methyl and hydride regions, allowing for assignment of the CH_3 resonances, and confirming assignment of the ^{31}P NMR resonances, of **1** and RhCl(PMePh$_2$)$_3$ (**3**).

Except for the crystallographically characterized *cis*,*mer*-Rh(H)$_2$Cl(PPh$_3$)$_3$ (the crystals being formed serendipitously as one of seven products formed from reaction of RhCl(PPh$_3$)$_3$ with catecholborane) [10], the only other isolated analogues are (as mentioned in Section 1) the R_3 = EtPh$_2$ [11], ^{t}BuMePh [12], and (DBH)$_3$ complexes [13]; however, the EtPh$_2$ species was characterized only by elemental analysis and IR data, only a tentative interpretation of the ^{1}H and ^{31}P NMR data was given for the ^{t}BuMePh species, and the high-field resonances for the DBH species were not detected because of loss of H_2 from the complex in solution.

The solid state structure of **1** (Fig. 2) shows the typical distorted octahedral coordination geometry for Rh^{III}. The two hydrides, the chloride and the P2 atom form an almost perfect plane, while the P1–Rh–P3 angle of ~160° reveals the octahedral distortion that results from the bulky phosphines and small hydride ligands. The Rh–P bond lengths for P1 and P3 are ~0.1 Å shorter than the Rh–P length for P2 *trans* to a hydride, and the Rh-hydride bond *trans* to P2 is 0.03 Å longer than that for the hydride *trans* to the chloride. Similar general features were found in the X-ray structure of *cis*,*mer*-Rh(H)$_2$Cl(PPh$_3$)$_3$, although hydride ligands were not located for this complex [10].

It should be noted that an aqueous solution of RhCl(TPPTS)$_3$ (TPPTS = P(*m*-C$_6$H$_4$SO$_3$Na)$_3$) reacts with H_2 to form not only *cis*,*mer*-Rh(H)$_2$Cl(TPPTS)$_3$, but also a species with a *cis*, *fac* arrangement of hydrogen and phosphine ligands; however, this species may be cationic in which the chloride has been replaced by an aquo ligand [18c]. In organic solvents, the *cis*,*mer*-isomer is considered

to be the thermodynamically stable species, although the phosphine *trans* to the hydride has been shown to reversibly dissociate rapidly [19]. Relevant to this, the in situ reaction of the Rh-cod precursor with $PMePh_2$ under H_2 described above does generate initially another dihydride species as a trace by-product (<5%); however, this is again a *cis*,*mer*-isomer as evidenced by the high-field ^1H NMR spectrum, which shows an almost identical pattern to that of complex **1**, but shifted upfield by ~1 ppm. Using the same P-atom labeling of Fig. 1, there is: a doublet of doublets of doublets of triplets at δ −10.39 (RhH_3 *trans* to P_b, $J(H_3Rh) = 13.6$, $J(H_3H_4) \cong 2.0$, $J(H_3P_a) = 13.6$, $J(H_3P_b) = 161.3$ Hz), and a second-order multiplet resonance at δ −19.02 (RhH_4 *cis* to P_a atoms, $J(H_4Rh) = 24.0$, $J(H_4H_3) \cong 2.0$, $J(H_4P_a) = 13.8$, $J(H_4P_b) = 8.0$ Hz). The species could be the THP-containing species *cis*-$Rh(H)_2Cl(PMePh_2)_2$-(THP), which is supported by some 2D NMR evidence where correlations are observed between ^1H resonances in the range (δ 4.45–3.86), typical of methylene protons of THP coordinated at Rh [9], and a weak broad $^{31}P\{^1H\}$ resonance centered at $\delta \sim 20.6$, a signal that was undetectable in the 1D $^{31}P\{^1H\}$ spectrum, but might refer to a coordinated THP-phosphorus atom [9]. Some data from the corresponding $PCyPh_2$ system (see below) also support such a formulation. Another possibility is that the chloride (*trans* to H_4) is displaced by solvent to form *cis*,*mer*-$[Rh(H)_2(solv)(PMePh_2)_3]Cl$ (solv = CD_3OD or acetone-d_6), but this is considered less likely since as noted above the phosphine *trans* to a hydride is typically more labile.

Reactions of RhCl(cod)(THP) with the more obvious three mole equivalents of $PMePh_2$ (or $PCyPh_2$, see below) under H_2 to generate the title $Rh(H)_2Cl(phosphine)_3$ complexes were attempted, but a much more complicated mixture of products was formed.

3.2. The $PCyPh_2$ system

The room temperature solution reaction of $PCyPh_2$ with RhCl(cod)(THP) (~2:1) under Ar was very similar to that of the $PMePh_2$ reaction: again immediately a slight excess of free $PCyPh_2$ was seen (δ_P−3.03 s) and there was no free THP, while the complicated mixture of products gave rise to δ_P resonances in the range δ 20.23 to 66.67 (corresponding $PCyPh_2$-containing products of those shown in Scheme 1 are again slowly formed) [9a]. Under H_2, the in situ NMR data correspond to formation of *cis*,*mer*-$Rh(H)_2Cl(PCyPh_2)_3$ (**2**) as the major product. Cleaner spectra are seen for isolated **2** dissolved in CD_2Cl_2. The $^{31}P\{^1H\}$ signal for P_a (Fig. S1, see Fig. 1 for comparison) is seen as a broad doublet at δ_P 45.39 ($J(P_aRh) \cong 110.9$ Hz), coupling to P_b not being resolved, and likewise the P_b signal is a broad symmetric multiplet at δ_P 31.12; both signals are unchanged as the temperature was varied between 323 and 213 K, and $J(P_aP_b)$ and $J(P_bRh)$ could not be resolved. The broadness of the resonances probably results from some exchange of the P_b phosphine *trans* to a hydride [19]. The H_1 hydride NMR resonance at δ_H −9.03 is again a doublet of doublets of doublets of triplets with J values similar to those seen in the $PMePh_2$ complex, and the multiplet for H_2 at δ_H − 17.81 was completely resolved by $^1H\{^{31}P\}$, $^1H\{^{31}P_a\}$ and $^1H\{^{31}P_b\}$ NMR spectra of CD_2Cl_2 solutions of the isolated, pure complex **2** (the shifts and J values are similar to those seen for **1** – see Section 2). The decoupled spectra also confirmed the assigned coupling constants for the H_1 resonance.

As in the $PMePh_2$ system, the in situ ^1H NMR spectrum shows a minor dihydride product (initially ~20%, but this decreases as crystals of **2** are formed); this dihydride species (a likely intermediate in formation of **2**) is characterized by two doublets of doublets of doublets of triplets in the hydride region at δ_H −9.95 (RhH_3 *trans* to P_b, $J(H_3Rh) = 12.7$, $J(H_3H_4) = 4.0$, $J(H_3P_c) = 12.7$, $J(H_3P_d) = 147.0$ Hz), and at δ − 19.76 (RhH_4 *cis* to P_a atoms, $J(H_4Rh) = 35.9$, $J(H_4H_3) = 4.0$, $J(H_4P_c) = 14.3$, $J(H_4P_d) = 9.26$ Hz). Unlike for the $PMePh_2$ system, the $^{31}P\{^1H\}$ NMR resonances for the minor product were now detected: a doublet of doublets at δ_P 45.92 (2 equiv. *trans* *P*-atoms), $J(P_{trans}Rh) = 110.1$, $J(P_{trans}P_{cis}) = 19.3$ Hz, and a doublet of triplets at δ_P 35.38 (P_{cis}), $J(P_{cis}Rh) = 98.2$, $J(P_{cis}P_{trans}) = 19.3$ Hz, where P_{cis} implies *cis* to two *trans*-phosphines. These data perhaps refer to *cis*-$Rh(H)_2Cl(PCyPh_2)_2$(THP), with THP being *cis* to two *trans* $PCyPh_2$ ligands; the NMR data for the *cis*-phosphines are very similar to those reported for *fac*-$RhCl_3(THP)_3$ (in CD_3OD, $\delta_P = 35.5$, $J(PRh) = 107$ Hz [22]; in D_2O, $\delta_P = 31.39$, $J(PRh) = 107$ Hz [23]).

The X-ray structure for complex **2** is shown in Fig. 5, and crystal and refinement data are given in Table 1. The distorted octahedral structure is analogous to that of complex **1** with again the two hydrides, the chloride, and the P-atom of one phosphine being planar, and the distortion coming from the *trans*-phosphines, where the P1–Rh–P1* angle is ~152°; however, in contrast to the structure of **1**, these two phosphines are structurally equivalent, and the overall structure is now a monoclinic, $P2_1/m$ system, versus the triclinic $P\bar{1}$ system of **1**. As for **1**, the two *trans*-$PCyPh_2$ ligands are 0.08 Å closer to the metal than the $PCyPh_2$ *trans* to the hydride, and the Rh–H bond length for the hydride *trans* to the phosphine is 0.08 Å longer than the Rh–H bond for the hydride *trans* to the chloride.

Surprisingly, and in contrast to **1**, complex **2** does not undergo reductive elimination of H_2 when dissolved in CH_2Cl_2 under Ar, as evidenced by NMR data. The difference in basicity between $PCyPh_2$ and $PMePh_2$ should be small, while steric effects should be insignificant for binding of the small H_2 molecule. A more quantitative study of the respective equilibria is needed to evaluate the factor(s) involved. (The steric effects are reflected in the P1–Rh–P3 and P1–Rh–P1* angles for **1** and **2**, respectively; the 8° smaller angle in **2** results from interactions of the cyclohexyl substituent of the *trans*-phosphines with that of the mutually *cis*-phosphines.)

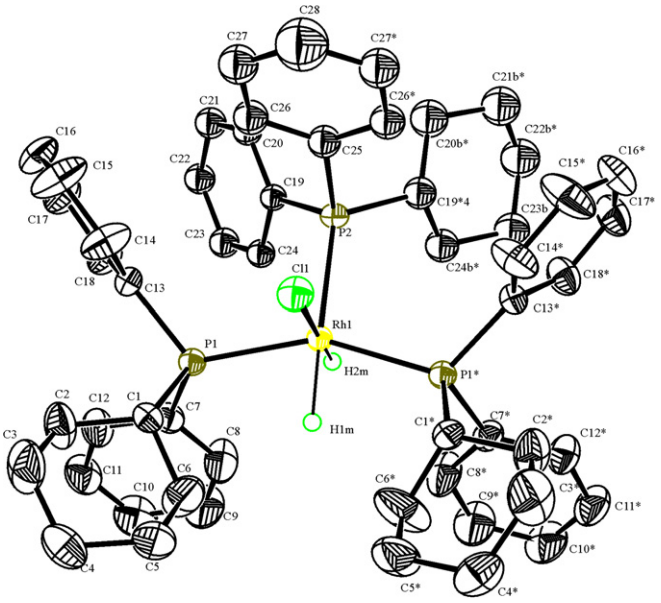


Fig. 5. Structure of *cis,mer*-$Rh(H)_2Cl(PCyPh_2)_3$ (**2**), with 50% probability ellipsoids. Selected distances (Å) and angles (°): Rh(1)–P(1) = Rh(1)–P(1)*, 2.3186(8); Rh(1)–P(2), 2.4021(10); Rh(1)–Cl(1), 2.4938(10); Rh(1)–H(1), 1.49(4); Rh(1)–H(2), 1.41(4); P(1)–Rh(1)–P(2) = P(1)*–Rh(1)–P(2), 103.971(18); P(1)–Rh(1)–P(1)*, 152.03(4); P(1)–Rh(1)–Cl(1) = P(1)*–Rh(1)–Cl(1), 89.475(19); P(1)–Rh(1)–H(1) = P(1)*–Rh(1)–H(1), 76.16(6); P(1)–Rh(1)–H(2) = P(1)*–Rh(1)–H(2), 90.9(4); P(2)–Rh(1)–Cl(1), 94.92(4); P(2)–Rh(1)–H(1), 169.1(15); P(2)–Rh(1)–H(2), 83.4(16); Cl(1)–Rh(1)–H(1), 96.0(15); Cl(1)–Rh(1)–H(2), 178.3(16); H(1)–Rh(1)–H(2), 86(2). The well defined Cy rings are the ones labeled C1,C2.. and C1*, C2*...

3.3. Other tertiary phosphine systems

The reactivity of RhCl(cod)(THP) with $PEtPh_2$, P(*p*-tol)$_3$, P(*p*-F-C_6H_4)$_3$ and P^nPr_3 in the presence of H_2 was also investigated using experimental conditions identical to those described above for the $PMePh_2$ and $PCyPh_2$ systems. However, in situ ^1H and $^{31}P\{^1H\}$ NMR spectra both revealed a complicated mixture of products, and no pure complexes could be isolated. Why the fortuitous, close to 80% yield syntheses of **1** and **2** were successful remains a mystery. The Rh-precursor and the phosphines are both soluble in acetone and in MeOH, and the use of the 1:1 solvent mixture just happened to deposit crystals of the dihydrides! Worth noting is the unusual observation of what appears to be the presence of a two-phase solvent system where the crystals of **1** and **2** begin to form; the presence of the water-soluble THP (a white solid in the free state) almost certainly plays a role, since the use of a more standard $[RhCl(diene)]_2$ under identical conditions does not precipitate the solid hydride complexes. Indeed, NMR evidence supports formation of **1** and **2** via the *cis*-$Rh(H)_2Cl(PRPh_2)_2$(THP) intermediate. A perhaps related phenomenon is the reproducible and remarkable observation of the immediate precipitation of crystals of RhCl(P–N)(THP) from an acetone solution of the complex (P–N is the *P*, *N*-chelated ligand *o*-$PPh_2(C_6H_4NMe_2)$, and THP is *trans* to the N-donor), when the solution is subjected to *an atmosphere of* H_2, even though there is no evidence for formation of any hydrido species! [24]. An important unanswered question in the syntheses is the fate of the THP, which does not finish up as free THP; this is a reactive phosphine and, as well the hydroxy-promoted cleavage reaction shown in Scheme 1, THP is a strong reducing agent (including the reduction of water to H_2), [9b] can readily form phosphonium salts [9a], and can decompose with loss of formaldehyde to generate $HP(CH_2OH)_2$ [9]. Structures of metal-THP complexes typically reveal extensive hydrogen-bonding networks involving oxygen and hydrogen atoms of the hydroxy substituent, and the hydrogens of the methylene groups [9]; it is not obvious how this may be a possible factor, but theoretical studies have revealed interactions of the hydrido ligands of *cis, mer*-$Rh(H)_2Cl(PMe_3)_3$ with protons [7c].

Appendix A. Supplementary material

CCDC 661134 and 661135 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2007.10.044.

References

[1] J. Halpern, J.F. Harrod, B.R. James, J. Am. Chem. Soc. 83 (1961) 753.
[2] (a) F.H. Jardine, J.A. Osborn, G. Wilkinson, J.F. Young, Chem. Ind. (Lond.) (1965) 560;
(b) J.F. Young, J.A. Osborn, F.H. Jardine, G. Wilkinson, Chem. Commun. (1965) 131.
[3] R.S. Coffey, ICI, Brit. Pat. 1,121,642 (filed 1965).
[4] (a) M.A. Bennett, P.A. Longstaff, Chem. Ind. (Lond.) (1965) 846;
(b) L. Vaska, R.E. Rhodes, J. Am. Chem. Soc. 87 (1965) 4970;
(c) K.C. Dewhirst, unpublished results quoted in W. Keim, J. Organomet. Chem. 14 (1968) 179.
[5] B.R. James, Homogeneous Hydrogenation, Wiley, New York, USA, 1973.
[6] J.G. de Vries, C.J. Elsevier (Eds.), Handbook of Homogeneous Hydrogenation, vol. 1–3, Wiley-VCH, Weinheim, Germany, 2007.
[7] For example (a) L.A. Bengtsson, B.T. Heaton, J.A. Iggo, C. Jacob, G.L. Monks, J. Ratnam, A.K. Smith, J. Chem. Soc., Dalton Trans. (1994) 1857;
(b) S.B. Duckett, C.L. Newell, R. Eisenberg, J. Am. Chem. Soc. 116 (1994) 10548;
(c) G. Kovács, G. Schubert, F. Joó, I. Pápai, Organometallics 24 (2005) 3059.
[8] L.A. Oro, D. Carmona, in: J.G. de Vries, C.J. Elsevier (Eds.), Handbook of Homogeneous Hydrogenation, vol. 1, Wiley-VCH, Weinheim, Germany, 2007 (Chapter 1), and refs. therein.
[9] (a) F. Lorenzini, B.O. Patrick, B.R. James, Inorg. Chem. 46 (2007) 8998;
(b) F. Lorenzini, B.O. Patrick, B.R. James, Dalton Trans. (2007) 3224.
[10] (a) K. Burgess, W.A. van der Donk, S.A. Westcott, T.B. Marder, R.T. Baker, J.C. Calabrese, J. Am. Chem. Soc. 114 (1992) 9350;
(b) W. Clegg, M.R.J. Elsegood, N.C. Norman, N.L. Pickett, Acta Crystallogr., Sect. E 58 (2002) m406.
[11] A. Sacco, R. Ugo, A. Moles, J. Chem. Soc. A (1966) 1670.

[12] C. Masters, B.L. Shaw, J. Chem. Soc. A (1971) 3679.
[13] D.G. Holah, A.N. Hughes, B.C. Hui, Can. J. Chem. 53 (1975) 3669.
[14] A. Koch, J. Bargon, Inorg. Chem. 40 (2001) 533.
[15] SAINT. Version 7.03A. Bruker AXS Inc., Madison, Wisconsin, USA, 1997–2003.
[16] SADABS. Bruker Nonius Area Detector Scaling and Absorption Correction – V2.10, Bruker AXS Inc., Madison, WI, USA, 2003.
[17] A. Altomare, M.C. Burla, M. Camalli, G.L. Cascarano, C. Giacovazzo, A. Guagliardi, A.G.G. Moliterni, G. Polidori, R. Spagna, J. Appl. Crystallogr. 32 (1999) 115.
[18] For example (a) C.A. Tolman, P.Z. Meakin, D.L. Lindner, J.P. Jesson, J. Am. Chem. Soc. 96 (1974) 2762;
(b) R.S. Drago, J.G. Miller, M.A. Hoselton, R.D. Farris, M.J. Desmond, J. Am. Chem. Soc. 105 (1983) 444;
(c) C. Larpent, H. Patin, J. Organomet. Chem. 335 (1987) C13;
(d) G.K. Anderson, R. Kumar, Inorg. Chim. Acta 146 (1988) 89;
(e) D. Rutherford, J.J.J. Juliette, C. Rocaboy, I.T. Horváth, J.A. Gladysz, Catal. Today 42 (1998) 381;
(f) B. Richter, A.L. Spek, G. van Koten, B.-J. Deelman, J. Am. Chem. Soc. 122 (2000) 3945;
(g) F. Joó, J. Kovács, A.Cs. Bényei, L. Nádasdi, G. Laurenczy, Chem. Eur. J. 7 (2001) 193.
[19] J.M. Brown, A.R. Lucy, J. Chem. Soc., Chem. Commun. (1984) 914, and refs. therein.
[20] For example (a) S.B. Duckett, G.K. Barlow, M.G. Partridge, R.J. Mawby, B.A. Messerie, Bull. Magn. Res. 18 (1996) 114, and refs. therein;
(b) B.A. Messerle, C.J. Sleigh, M.G. Partridge, S.B. Duckett, J. Chem. Soc., Dalton Trans. (1999) 1429.
[21] For example (a) M.L.H. Green, D.J. Jones, Adv. Inorg. Chem. Radiochem. 7 (1965) 115;
(b) J.P. Rourke, G. Stringer, P. Chow, R.J. Deeth, D.S. Yulfit, J.A.K. Howard, T.B. Marder, Organometallics 21 (2002) 429;
(c) M.A. Garralda, R. Hernández, L. Ibarlucea, E. Pinilla, M.R. Torres, M. Zarandona, Organometallics 26 (2007) 1031.
[22] F. Lorenzini, B.R. James, unpublished data.
[23] K. Raghuraman, N. Pillarsetty, W.A. Volkert, C. Barnes, S. Jurisson, K.V. Katti, J. Am. Chem. Soc. 124 (2002) 7276.
[24] F. Lorenzini, B.O. Patrick, B.R. James, Inorg. Chim. Acta, in press, doi:10.1016/j.ica.2007.11.017.