

Half-sandwich trihydrido ruthenium complexes

Alexandr L. Osipov^a, Dmitry V. Gutsulyak^{a,b}, Lyudmila G. Kuzmina^c,
Judith A.K. Howard^d, Dmitry A. Lemenovskii^a, Georg Süss-Fink^e, Georgii I. Nikonov^{a,b,*}

^a Chemistry Department, Moscow State University, Vorob'evy Gory, 119992 Moscow, Russia

^b Chemistry Department, Brock University, 500 Glenridge Ave., St. Catharines, ON, Canada L2S 3A1

^c Institute of General and Inorganic Chemistry, RAS, Leninskii Prosp. 31, 119991 Moscow, Russia

^d Chemistry Department, University of Durham, South Road, Durham DH1 3LE, UK

^e Institut de Chimie, Université de Neuchâtel, Case Postale 158, CH-2009 Neuchâtel, Switzerland, UK

Abstract

This paper reports facile preparation of half-sandwich trihydrido complexes of ruthenium based on the reactions of the readily available precursors $[\text{Cp}(\text{R}_3\text{P})\text{Ru}(\text{NCCH}_3)_2][\text{PF}_6]$ with LiAlH_4 . The target complexes were characterized by spectroscopic methods and X-ray structure analysis of $\text{Cp}(\text{PhPr}'_2\text{P})\text{RuH}_3$.

Keywords: Ruthenium; Hydride

1. Introduction

Half-sandwich complexes of ruthenium find multiple applications in chemistry as effective catalysts [1] and as platforms to support unusual metal–ligand and ligand–ligand bonding [2–5]. Our interest in this field stems from the observation that the CpLRu fragment (where L is a two-electron donor) is formally isolobal with the Cp_2M ($\text{M} = \text{Nb}, \text{Ta}, \text{Ti}$), $\text{Cp}(\text{RN})\text{M}$ ($\text{M} = \text{V}, \text{Nb}, \text{Ta}$) and $(\text{RN})_2\text{M}$ ($\text{M} = \text{Mo}, \text{W}$) moieties [6] which were found to support a variety of $\text{H}\cdots\text{SiX}$ and $\text{H}\cdots\text{GeCl}$ interligand interactions [7–10]. Given the fact that Group 5 trihydrides Cp_2MH_3 ($\text{M} = \text{Nb}, \text{Ta}$) are readily available [11] and are very useful starting points in the chemistry of Group 5 metallocenes [12], we expected that ruthenium trihydrides $\text{Cp}(\text{R}_3\text{P})\text{RuH}_3$ would exhibit an analogously rich chemis-

try. Apart from their potential synthetic utility, ruthenium trihydrides are also of interest because of their propensity to manifest quantum-mechanical exchange coupling [13].

Previously, only one trihydride complex with unsubstituted Cp ring, $\text{Cp}(\text{Ph}_3\text{P})\text{RuH}_3$ (**1a**), has been reported [14]. By contrast, a family of permethyl substituted complexes $\text{Cp}^*(\text{R}_3\text{P})\text{RuH}_3$ ($\text{Cp}^* = \text{C}_5\text{Me}_5$) is well described [15], including the X-ray structure of $\text{Cp}^*(\text{Ph}_3\text{P})\text{RuH}_3$ [16]. Complex **1a** is a classical trihydride [16], whereas the isolobal tris(pyrazolyl)borate complex $\text{Tp}(\text{Ph}_3\text{P})\text{RuH}(\eta^2\text{-H}_2)$ exist in a hydride(dihydrogen) form [17], underpinning the strong effect of the ring on the extent of Ru–H interaction. Here, we report facile general access to a series of complexes $\text{Cp}(\text{R}_3\text{P})\text{RuH}_3$ ($\text{R}_3\text{P} = \text{Ph}_3\text{P}$ (**a**), $\text{Ph}_2\text{Pr}'\text{P}$ (**b**), $\text{PhPr}'_2\text{P}$ (**c**) and $\text{Pr}'_3\text{P}$ (**d**)) and the crystal structure of complex $\text{Cp}(\text{Ph}_2\text{Pr}'\text{P})\text{RuH}_3$.

2. Results and discussion

Davis et al. previously reported that reaction of $\text{Cp}(\text{Ph}_3\text{P})_2\text{RuCl}$ with LiAlH_4 in THF affords a 4:1 mixture

* Corresponding author. Address: Chemistry Department, Brock University, 500 Glenridge Ave., St. Catharines, ON, Canada L2S 3A1.
Tel.: +1 905 6885550x3350; fax: +1 905 9328846.
E-mail address: gnikonov@brocku.ca (G.I. Nikonov).

of $\text{Cp}(\text{Ph}_3\text{P})\text{RuH}_3$ and $\text{Cp}(\text{Ph}_3\text{P})_2\text{RuH}$, from which the former complex can be isolated by recrystallization from ether [14]. In our hands, however, difficult-to-separate mixtures of variable ratios of $\text{Cp}(\text{Ph}_3\text{P})\text{RuH}_3$ and $\text{Cp}(\text{Ph}_3\text{P})_2\text{RuH}$ were produced. Attempts to extend this approach to the preparation of other complexes $\text{Cp}(\text{R}_3\text{P})\text{RuH}_3$ by reacting the mixed phosphine precursors $\text{Cp}(\text{R}_3\text{P})(\text{Ph}_3\text{P})\text{RuCl}$ [18] with LiAlH_4 lead to mixtures containing predominantly the monohydrides $\text{Cp}(\text{R}_3\text{P})(\text{Ph}_3\text{P})\text{RuH}$.

The related permethyl substituted complexes $\text{Cp}^*(\text{R}_3\text{P})\text{RuH}_3$ (Cp^* – pentamethylcyclopentadiene) have been previously prepared by the reaction of $\text{Cp}^*(\text{R}_3\text{P})\text{RuCl}_2$ with NaBH_4 in ethanol [15a], with LiBHET_3 in THF [15b] and by dihydrogen addition to the 16e compound $\text{Cp}^*(\text{R}_3\text{P})\text{RuOR}$ [15c]. None of these precursor chloride or alkoxide compounds are available for the fragment $\text{Cp}(\text{R}_3\text{P})\text{Ru}$ yet. We designed an alternative strategy to the half-sandwich Ru trihydrides based on the reaction of cationic complexes $[\text{Cp}(\text{R}_3\text{P})\text{Ru}(\text{NCCH}_3)_2][\text{PF}_6]$ (**2a–d**) (Scheme 1) with LiAlH_4 . The key starting material, the compound $[\text{CpRu}(\text{NCCH}_3)_3][\text{PF}_6]$ (**3**), has recently become available through the contribution of Kündig et al. [19], which opens a new facile route to the vast chemistry of the cation $[\text{CpRu}(\text{NCCH}_3)_3]^+$ [1a,20]. Reactions of **3** with an equivalent of phosphine R_3P allow for easy preparation of the corresponding exchange products $[\text{Cp}(\text{R}_3\text{P})\text{Ru}(\text{NCCH}_3)_2][\text{PF}_6]$ (**2a–d**) characterized by NMR and IR spectroscopy (Scheme 1) [21]. In particular, the $\text{N}\equiv\text{C}$ triple bond gives rise to a band in the IR spectrum at 2276 cm^{-1} , whose position does not depend on the type of phosphine ligand being present. Treatment of these precursors with LiAlH_4 in THF followed by quenching the reaction mixture with degassed water affords, after work-up, the trihydrides $\text{Cp}(\text{R}_3\text{P})\text{RuH}_3$ (**1a–d**) in good yields.

The new trihydrides **1b–d** and the previously reported complex $\text{Cp}(\text{Ph}_3\text{P})\text{RuH}_3$ (**1a**) were characterized by NMR and IR spectroscopy, and by X-ray structure of the compound **1b**. Like in their Cp^* analogues, at room temperature the hydrides in **1a–d** give rise to one, averaged hydride signal in the region between -10.3 and -11.3 ppm coupled with the phosphine. The IR spectra show corresponding Ru–H bands in the region $2010\text{--}2001\text{ cm}^{-1}$.

The molecular structure of complex **1b** is shown in Fig. 1. Spectroscopic data for the related compound $\text{Cp}(\text{Ph}_3\text{P})\text{RuH}_3$ (**1a**) have been previously rationalized in terms of a classical C_{3v} structure, with the bulky phosphine occupying a position trans to the Cp ring and the three

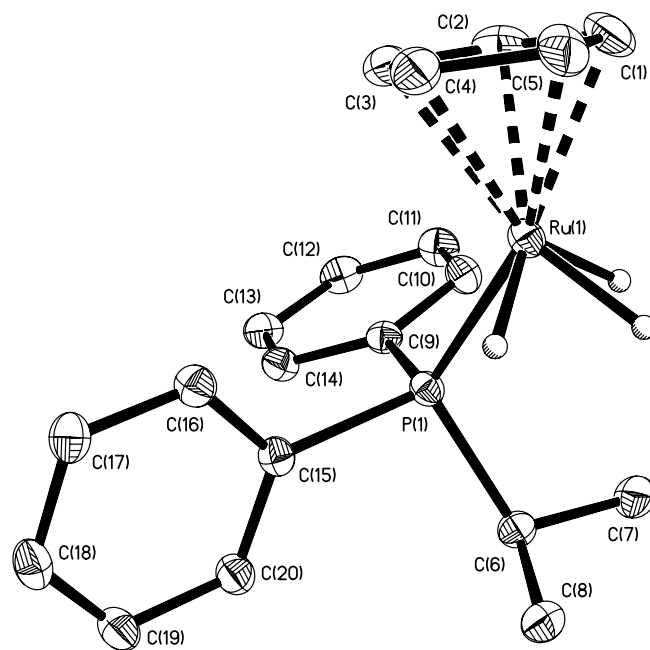
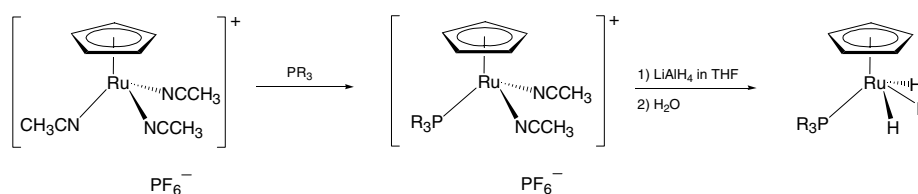


Fig. 1. Molecular structure of complex **1b**. Selected molecular parameters (bonds in Å, angles in °): Ru(1)–P(1) 2.2465(4), Ru(1)–H(1) 1.50(3), Ru(1)–H(2) 1.54(3), Ru(1)–H(3) 1.55(3), P(1)–C(15) 1.8410(15), P(1)–C(9) 1.8426(16), P(1)–C(6) 1.8659(16), and P(1)–Ru(1)–H(1) 74.7(10), P(1)–Ru(1)–H(2) 96.5(10), P(1)–Ru(1)–H(3) 77.6(10), H(1)–Ru(1)–H(2) 64.4(14), H(1)–Ru(1)–H(3) 114.7(16), H(2)–Ru(1)–H(3) 61.7(14).

hydrides forming an equatorial plane in a pseudo-TBP structure [14]. In fact, the experimental geometry of **1b** is similar to that one of the analogous complex $\text{Cp}^*(\text{Ph}_3\text{P})\text{RuH}_3$, which can be better described as a four-leg piano-stool [15a]. The CNT–Ru and Ru–P vectors, where CNT is the centroid of the Cp-ring, form an angle of 125.7° . Surprisingly enough, although less steric interaction of phosphine with the ring could have been anticipated, the Ru–CNT distance of 1.927 Å in **1b** is slightly longer than the corresponding parameter in the more crowded complex $\text{Cp}^*(\text{Ph}_3\text{P})\text{RuH}_3$ (1.91 Å) [22]. By way of contrast, the Ru–P bond lengths of $2.2465(4)\text{ Å}$ in **1b** is shorter than the Ru–P distance in $\text{Cp}^*(\text{Ph}_3\text{P})\text{RuH}_3$ ($2.252(1)\text{ Å}$), probably due to a combination of a better donating phosphine and a less bulky Cp ring. These observations can be explained in terms of interplay of bonding capabilities of a more donating phosphine and a less donating cyclopentadienyl ring in **1b** in comparison with $\text{Cp}^*(\text{Ph}_3\text{P})\text{RuH}_3$. The Ru–H hydride bond lengths, although subject to the well known uncertainty of finding



Scheme 1. Preparation of $[\text{Cp}(\text{R}_3\text{P})\text{Ru}(\text{NCCH}_3)_2][\text{PF}_6]$ and $\text{Cp}(\text{R}_3\text{P})\text{RuH}_3$.

hydride ligands by X-ray diffraction, fall in a narrow range of 1.503–1.548 Å, which is typical for Ru–H bonds.

In summary, we describe a convenient general approach to the trihydride complexes $\text{Cp}(\text{R}_3\text{P})\text{RuH}_3$ and the X-ray structure of the complex $\text{Cp}(\text{Ph}_2\text{Pr}^i\text{P})\text{RuH}_3$. We are currently exploring application of these compounds to the synthesis of silylhydride derivatives of ruthenium.

3. Experimental

All manipulations were carried out using conventional high-vacuum or argon-line Schlenk techniques. Solvents were dried over sodium or sodium benzophenone ketyl and either kept under argon or distilled into the reaction vessel by high vacuum gas phase transfer. NMR spectra were recorded on a Bruker (^1H , 300 MHz; ^{13}C , 75.4 MHz) and Varian (^1H , 400 MHz; ^{13}C , 100.6 MHz; ^{31}P , 161.9 MHz) spectrometers. IR spectra were obtained as Nujol mulls with an ATI Mattson FTIR spectrometer spectrometer. $\text{RuCl}_3\cdot\text{aq}$ was purchased from Precious-Metals-on-Line, other reagents were from Sigma-Aldrich. Complexes $[\text{CpRu}(\text{NCCH}_3)_3][\text{X}]$ ($\text{X} = \text{PF}_6, \text{BF}_4$) [19] and phosphines were prepared according to the literature methods.

3.1. General procedure for the preparation of $[\text{Cp}(\text{R}_3\text{P})\text{Ru}(\text{NCCH}_3)_2][\text{BF}_4]$: example of $[\text{Cp}(\text{Pr}^i_3\text{P})\text{Ru}(\text{NCCH}_3)_2][\text{BF}_4]$ [23]

Solution of PPr^i_3 (0.161 g, 1.01 mmol) in CH_3CN (20 mL) was added dropwise to a solution of $[\text{CpRu}(\text{NCCH}_3)_3][\text{BF}_4]$ (0.380 g, 1.01 mmol) in CH_3CN (20 mL). The mixture was stirred for 3 h at ambient temperature. Concentration of the resulting yellow solution to 5 mL in vacuum and addition of 40 mL of diethyl ether precipitated the product in the form of yellow crystals. Yield: 0.470 g (94%). The corresponding PF_6 salt was prepared with a similar yield. IR (Nujol): $\nu(\text{CN}) = 2276 \text{ cm}^{-1}$. ^1H NMR (CDCl_3): δ 4.50 (s, 5, C_5H_5), 2.39 (s, 6, CH_3CN), 2.29 (d sept, $J(\text{H}-\text{H}) = 7.2 \text{ Hz}$, $J(\text{P}-\text{H}) = 8.5 \text{ Hz}$, 2, $\text{P}(\text{CH}(\text{CH}_3)_2)_2$), 1.18 (dd, $J(\text{H}-\text{H}) = 7.2 \text{ Hz}$, $J(\text{P}-\text{H}) = 13.2 \text{ Hz}$, 6, $\text{P}(\text{CH}(\text{CH}_3)_2)$). ^{31}P NMR (CDCl_3): δ 56.0. ^{13}C NMR (CDCl_3): δ 128.1 (CH_3CN), 74.9 (Cp), 26.6 (d, $J(\text{P}-\text{C}) = 18.7 \text{ Hz}$, $\text{P}(\text{CH}(\text{CH}_3)_2)_2$), 19.7 (s, $\text{P}(\text{CH}(\text{CH}_3)_2)$), 4.0 (s, CH_3CN). Elemental analysis for $[\text{Cp}(\text{Pr}^i_3\text{P})\text{Ru}(\text{NCCH}_3)_2][\text{PF}_6]$, $\text{C}_{18}\text{H}_{32}\text{F}_6\text{N}_2\text{P}_2\text{Ru}$ (553.468). Anal. Calc.: C, 39.06; N, 5.06; H, 5.83. Found: C, 38.84; N, 5.08; H, 5.79%.

3.2. $[\text{Cp}(\text{Pr}^i_2\text{PhP})\text{Ru}(\text{NCCH}_3)_2][\text{BF}_4]$

This compound was prepared analogously to $[\text{Cp}(\text{Pr}^i_3\text{P})\text{Ru}(\text{NCCH}_3)_2][\text{BF}_4]$, using PPr^i_2Ph (0.232 g, 1.19 mmol) and $[\text{CpRu}(\text{NCCH}_3)_3][\text{BF}_4]$ (0.450 g, 1.19 mmol). Yield: 0.600 g (95%). The corresponding PF_6 salt was prepared with a similar yield. IR (Nujol): $\nu(\text{CN}) = 2276 \text{ cm}^{-1}$. ^1H NMR (CDCl_3): δ 7.55 (m, 2, *o*-Ph), 7.42 (m, 3, *m*-Ph and *p*-Ph),

4.47 (s, 5, C_5H_5), 2.56 (m, 2, $\text{P}(\text{CH}(\text{CH}_3)_2)_2$), 2.41 (s, 6, CH_3CN), 1.08 (dd, $J(\text{H}-\text{H}) = 7.1 \text{ Hz}$, $J(\text{P}-\text{H}) = 14.0 \text{ Hz}$, 6, $\text{P}(\text{CH}(\text{CH}_3)(\text{CH}_3)_2)$), 1.05 (dd, $J(\text{H}-\text{H}) = 7.1 \text{ Hz}$, $J(\text{P}-\text{H}) = 15.1 \text{ Hz}$, 6, $\text{P}(\text{CH}(\text{CH}_3)(\text{CH}_3)_2)$). ^{31}P NMR (CDCl_3): δ 54.0. ^{13}C NMR (CDCl_3): δ 133.2 (d, $J(\text{P}-\text{C}) = 9.1 \text{ Hz}$, $\text{Ph}^{2,6}$), 132.5 (d, $J(\text{P}-\text{C}) = 33.2 \text{ Hz}$, Ph^1), 128.5 (CN), 128.2 (d, $J(\text{P}-\text{C}) = 8.8 \text{ Hz}$, $\text{Ph}^{3,5}$), 75.4 (Cp), 27.5 (d, $J(\text{P}-\text{C}) = 22.0 \text{ Hz}$, $\text{P}(\text{CH}(\text{CH}_3)_2)_2$), 18.9 (s, 2C, $\text{P}(\text{CH}(\text{C}^a\text{H}_3)_2)_2$), 18.6 (s, $\text{P}(\text{CH}(\text{C}^b\text{H}_3)_2)_2$), 4.3 (s, CH_3CN). Elemental analysis for $[\text{Cp}(\text{Pr}^i_2\text{PhP})\text{Ru}(\text{NCCH}_3)_2][\text{PF}_6]$, $\text{C}_{21}\text{H}_{30}\text{F}_6\text{N}_2\text{P}_2\text{Ru}$ (587.484). Anal. Calc.: C, 42.93; N, 4.77; H, 5.15. Found: C, 42.87; N, 4.53; H, 5.36%.

3.3. $[\text{Cp}(\text{Pr}^i\text{Ph}_2\text{P})\text{Ru}(\text{NCCH}_3)_2][\text{BF}_4]$

Prepared analogously to $[\text{Cp}(\text{Pr}^i_3\text{P})\text{Ru}(\text{NCCH}_3)_2][\text{BF}_4]$, using PPr^iPh_2 (0.290 g, 1.27 mmol) and $[\text{CpRu}(\text{NCCH}_3)_3][\text{BF}_4]$ (0.480 g, 1.27 mmol). Yield: 0.670 g (93%). The corresponding PF_6 salt was prepared with a similar yield. IR (Nujol): $\nu(\text{CN}) = 2276 \text{ cm}^{-1}$. ^1H NMR (CDCl_3): δ 7.47–7.37(m, 10, Ph), 4.27 (s, 5, C_5H_5), 2.76 (m, 1, $\text{P}(\text{CH}(\text{CH}_3)_2)$), 2.34 (s, 6, CH_3CN) 1.10 (dd, $J(\text{H}-\text{H}) = 7.1 \text{ Hz}$, $J(\text{P}-\text{H}) = 15.5 \text{ Hz}$, 6, $\text{P}(\text{CH}(\text{CH}_3)_2)$). ^{31}P NMR (CDCl_3): δ 51.3. ^{13}C NMR (CDCl_3): δ 133.9 (d, $J(\text{P}-\text{C}) = 38.4 \text{ Hz}$, *i*-Ph), 133.0 (d, $J(\text{P}-\text{C}) = 9.9 \text{ Hz}$, *o*-Ph), 129.9 (d, $J(\text{P}-\text{C}) = 2.2 \text{ Hz}$, *p*-Ph), 128.3 (d, $J(\text{P}-\text{C}) = 9.0 \text{ Hz}$, *m*-Ph), 128.1 (CH_3CN), 76.2 (s, Cp), 29.1 (d, $J(\text{P}-\text{C}) = 24.2 \text{ Hz}$, $\text{P}(\text{CH}(\text{CH}_3)_2)$), 18.8 (s, $\text{P}(\text{CH}(\text{CH}_3)_2)$), 4.2 (s, CH_3CN). Elemental analysis for $[\text{Cp}(\text{Pr}^i\text{Ph}_2\text{P})\text{Ru}(\text{NCCH}_3)_2][\text{PF}_6]$, $\text{C}_{24}\text{H}_{28}\text{F}_6\text{N}_2\text{P}_2\text{Ru}$ (621.501). Anal. Calc.: C, 46.83; N, 4.51; H, 4.54. Found: C, 46.77; N, 4.87; H, 4.74%.

3.4. $[\text{Cp}(\text{Ph}_3\text{P})\text{Ru}(\text{NCCH}_3)_2][\text{BF}_4]$ [21]

This complex was prepared analogously to $[\text{Cp}(\text{Pr}^i_3\text{P})\text{Ru}(\text{NCCH}_3)_2][\text{BF}_4]$, using PPh_3 (0.348 g, 1.35 mmol) and $[\text{CpRu}(\text{NCCH}_3)_3][\text{BF}_4]$ (0.500 g, 1.33 mmol). Yield: 0.750 g (94%). Characterization data agree with those reported in the literature.

3.5. $[\text{Cp}(\text{Pr}^i_3\text{P})\text{RuH}_3]$

LiAlH_4 (0.090 mg, 2.4 mmol), recrystallized from diethyl ether, was added to a solution of $[\text{Cp}(\text{Pr}^i_3\text{P})\text{Ru}(\text{NCCH}_3)_2][\text{BF}_4]$ (0.470 g, 0.95 mmol) in 40 ml of THF. The resulting solution was stirred overnight at ambient temperature and then slowly hydrolyzed with degassed water. After evaporation of the solvent, the brown residue was extracted with hexane ($3 \times 10 \text{ ml}$). Removal of volatiles and recrystallization at $-30 \text{ }^\circ\text{C}$ from ether/ethanol (2:1) afforded 0.200 g of $\text{Cp}(\text{Pr}^i_3\text{P})\text{RuH}_3$ in the form of grey crystals, which deliquesce when brought to room temperature. Yield: 63%. IR (Nujol): $\nu(\text{Ru}-\text{H}) = 2010 \text{ cm}^{-1}$. ^1H NMR (toluene- d_8): δ 4.94 (s, 5, C_5H_5), 1.42 (d sept, $J(\text{H}-\text{H}) = 7.0$, $J(\text{P}-\text{H}) = 9.2 \text{ Hz}$, 3, $\text{P}(\text{CH}(\text{CH}_3)_2)_3$), 0.95 (dd, $J(\text{H}-\text{H}) = 7.0 \text{ Hz}$, $J(\text{P}-\text{H}) = 13.6 \text{ Hz}$, 9, $\text{P}(\text{CH}(\text{CH}_3)_2)$), -11.26 (d, $J(\text{P}-\text{H}) = 20.5 \text{ Hz}$, 3, RuH_3). ^{31}P (toluene- d_8):

δ 103.0. ^{13}C (toluene- d_8): δ 81.5 (s, C_5H_5), 30.1 (d, $7J(\text{P}-\text{C}) = 30.2$ Hz, $\text{PCH}(\text{CH}_3)_2$), 28.9 (d, $J(\text{P}-\text{C}) = 25.6$ Hz, $\text{PCH}(\text{CH}_3)_2$). Elemental analysis for $\text{C}_{14}\text{H}_{29}\text{RuP}$ (329.42). Anal. Calc.: C, 51.04; H, 8.87. Found: C, 51.10; H, 8.95%.

3.6. $[\text{Cp}(\text{Pr}^i\text{PhP})\text{RuH}_3]$

This complex was prepared analogously to $\text{Cp}(\text{Pr}^i\text{P})\text{RuH}_3$ with LiAlH_4 (0.100 g, 2.6 mmol) and $[\text{Cp}(\text{Pr}^i\text{PhP})\text{Ru}(\text{NCCH}_3)_2][\text{BF}_4]$ (0.550 g, 1.03 mmol). Yield: 0.320 g (85%). IR (Nujol): 2009 cm^{-1} . ^1H NMR (CD_2Cl_2): 7.79 (m, 2, *o*-Ph), 7.36 (m, 3, *m*-Ph and *p*-Ph), 5.08 (s, 5, Cp), 2.13 (dsept, $J(\text{H}-\text{H}) = 6.8$ Hz, $J(\text{P}-\text{H}) = 9.5$ Hz, 2 $\text{P}(\text{CH}(\text{CH}_3)_2)_2$), 1.00 (dd, $J(\text{P}-\text{H}) = 15.9$ Hz, $J(\text{H}-\text{H}) = 6.6$ Hz, 6, $\text{P}(\text{CH}(\text{C}^a\text{H}_3)_2)_2$), 0.76 (dd, $J(\text{P}-\text{H}) = 15.0$ Hz, $J(\text{H}-\text{H}) = 6.9$ Hz, 6, $\text{P}(\text{CH}(\text{C}^b\text{H}_3)_2)_2$), -11.33 (d, $J(\text{P}-\text{H}) = 20.1$ Hz, 3, RuH_3). ^{31}P NMR (CD_2Cl_2): 97.6 (s). ^{13}C NMR (CD_2Cl_2): 134.1 (d, $J(\text{P}-\text{C}) = 9.6$ Hz, *o*-Ph), 129.5 (d, $J(\text{P}-\text{C}) = 2.3$ Hz, *p*-Ph), 127.6 (d, $J(\text{P}-\text{C}) = 8.4$ Hz, *m*-Ph), 82.0 (d, $J(\text{P}-\text{C}) = 1.7$ Hz, Cp), 26.5 (d, $J(\text{P}-\text{C}) = 31.7$ Hz, $\text{P}(\text{CH}(\text{CH}_3)_2)_2$), 19.5 (d, $J(\text{P}-\text{C}) = 3.5$ Hz, $\text{P}(\text{CH}(\text{C}^a\text{H}_3)_2)_2$), 18.8 (s, $\text{P}(\text{CH}(\text{C}^b\text{H}_3)_2)_2$). Elemental analysis for $\text{C}_{17}\text{H}_{27}\text{RuP}$ (363.440). Anal. Calc.: C, 56.18; H, 7.49. Found: C, 56.47; H, 7.88%.

3.7. $[\text{Cp}(\text{Pr}^i\text{Ph}_2\text{P})\text{RuH}_3]$

This complex was prepared analogously to $\text{Cp}(\text{Pr}^i\text{P})\text{RuH}_3$ with LiAlH_4 (0.101 mg, 2.7 mmol) and $[\text{Cp}(\text{Pr}^i\text{Ph}_2\text{P})\text{Ru}(\text{NCCH}_3)_2][\text{BF}_4]$ (0.600 g, 1.06 mmol). Yield: 0.350 g (83%). IR (Nujol): 2001 cm^{-1} . ^1H NMR (C_6D_6): 7.65 (dt, $J(\text{H}-\text{H}) = 6.9$ Hz, 4, *o*-Ph), 7.03 (m, 6, *m*-Ph + *p*-Ph), 4.88 (s, 5, Cp), 2.25 (m, 1, CH), 0.92 (dd, $J(\text{H}-\text{H}) = 6.6$ Hz, $J(\text{P}-\text{H}) = 16.8$ Hz, 6, Me), -10.30 (d, $J(\text{P}-\text{H}) = 20.1$ Hz, 3 H). ^{31}P NMR (C_6D_6): 87.0 (s). ^{13}C NMR (C_6D_6): δ 133.0 (d, $^2J = 10.5$ Hz, *o*-Ph), 128.1–127.5 (m, *p,m*-Ph), 82.7 (s, C_5H_5), 29.1 (d, $^1J = 33.2$ Hz, $\text{P}(\text{CH}(\text{CH}_3)_2)_2$), 18.8 ($\text{P}(\text{CH}(\text{CH}_3)_2)_2$). Elemental analysis for $\text{C}_{20}\text{H}_{25}\text{RuP}$ (397.456). Anal. Calc.: C, 60.44; H, 6.34. Found: C, 61.34; H, 6.94%.

3.8. $[\text{Cp}(\text{Ph}_3\text{P})\text{RuH}_3]$

This known complex [14] was prepared analogously to $\text{Cp}(\text{Pr}^i\text{P})\text{RuH}_3$, using LiAlH_4 (0.088 g, 2.3 mmol) and $[\text{Cp}(\text{Ph}_3\text{P})\text{Ru}(\text{NCCH}_3)_2]\text{BF}_4$ (0.550 g, 0.92 mmol). Yield: 0.246 g (62%).

3.9. Crystal structure determinations of **1b**

Colourless crystals of **1b** were grown from hexane by cooling the solutions to -25 to -30 °C. Single crystal of **1b** was coated by polyperfluoro oil and mounted directly to the Bruker Smart three-circle diffractometer with CCD area detector at 123(2) K. The crystallographic data and characteristics of structure solution and refinement are

Table 1
Crystal data and structure refinement for **1b**

Empirical formula	$\text{C}_{20}\text{H}_{25}\text{PRu}$
Formula weight	397.44
Temperature	123(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2(1)/c
<i>Unit cell dimensions</i>	
<i>a</i> (Å)	11.7325(2)
<i>b</i> (Å)	7.4373(2)
<i>c</i> (Å)	20.1921(4)
α (°)	90
β (°)	97.3950(10)
γ (°)	90
Volume (Å ³)	1747.27(7)
<i>Z</i>	4
D_{calc} (Mg/m ³)	1.511
Absorption coefficient (mm ⁻¹)	0.983
$F(000)$	816
Crystal size (mm ³)	$0.32 \times 0.23 \times 0.12$
θ Range for data collection (°)	1.75–30.01
Index ranges	$-15 \leq h \leq 16$, $-9 \leq k \leq 10$, $-21 \leq l \leq 28$
Reflections collected	11968
Independent reflections [R_{int}]	5040 [0.0170]
Completeness to $\theta = 30.01^\circ$	98.5%
Maximum and minimum transmission	0.8911 and 0.7437
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	5040/0/299
Goodness-of-fit on F^2	1.065
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0236$, $wR_2 = 0.0587$
R indices (all data)	$R_1 = 0.0278$, $wR_2 = 0.0612$
Largest difference in peak and hole (e Å ⁻³)	0.788 and -0.597

given in Table 1. The structure factor amplitudes for all independent reflections were obtained after the Lorentz and polarization corrections. A multi-scan absorption correction was applied. The structures were solved by heavy-atom methods [24] and refined by full-matrix least squares procedures, using $\omega(|F_o^2| - |F_c^2|)^2$ as the refined function. All hydrogen atoms were found from the difference map. In the final cycles of refinement, all the non-hydrogen atoms were refined with anisotropic temperature parameters. The hydride ligands were refined isotropically, other hydrogen atoms were refined using the riding scheme. The largest residuals in the final difference Fourier maps were small (0.788 and $-0.597 \text{ e \AA}^{-3}$), location and magnitude of the residual electron density was of no chemical significance.

Acknowledgements

GIN thanks NSERC for financial support and CFI for a generous equipment grant. L.G.K. and J.A.K.H. thank the Royal Society (London) for a Joint Research Grant. L.G.K. also thanks the Royal Society of Chemistry (London) for the RSC Journal Award for International Authors.

Appendix A. Supplementary material

CCDC 647983 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorgchem.2007.07.024.

References

- [1] (a) B.M. Trost, M.U. Frederiksen, M.T. Rudd, *Angew. Chem., Int. Ed.* 44 (2005) 6630;
(b) C. Bruneau, P.H. Dixneuf, *Angew. Chem., Int. Ed.* 45 (2006) 2176.
- [2] (a) B.K. Campion, R.H. Heyn, T.D. Tilley, A.L. Rheingold, *J. Am. Chem. Soc.* 115 (1993) 5527;
(b) D.A. Straus, C. Zhang, G.E. Quimbata, S.K. Grumbine, R.H. Heyn, T.D. Tilley, A.L. Rheingold, S.J. Geib, *J. Am. Chem. Soc.* 112 (1990) 2673;
(c) S.K. Grumbine, D.A. Straus, T.D. Tilley, A.L. Rheingold, S.J. Geib, *Polyhedron* 112 (1995) 127;
(d) S.K. Grumbine, G.P. Mitchell, D.A. Straus, T.D. Tilley, A.L. Rheingold, S.J. Geib, *Organometallics* 17 (1998) 5607;
(e) G.P. Mitchell, T.D. Tilley, *J. Am. Chem. Soc.* 119 (1997) 11236.
- [3] (a) H. Suzuki, T. Takao, M. Tanaka, Y. Moro-oka, *Chem. Commun.* (1992) 476;
(b) T. Takao, M. Amako, H. Suzuki, *Organometallics* 22 (2003) 3855, and references therein;
(c) B.K. Campion, R.H. Heyn, T.D. Tilley, *Organometallics* 11 (1992) 3918.
- [4] (a) H. Tobita, H. Wada, K. Ueno, H. Ogino, *Organometallics* 13 (1994) 2545;
(b) H. Wada, H. Tobita, H. Ogino, *Organometallics* 16 (1997) 2200;
(c) H. Tobita, H. Kurita, H. Ogino, *Organometallics* 17 (1998) 2844;
(d) H. Tobita, H. Kurita, H. Ogino, *Organometallics* 17 (1998) 2850;
(e) H. Wada, H. Tobita, H. Ogino, *Chem. Lett.* (1998) 993;
(f) T.N. Choo, W.-H. Kwock, C.E.F. Rickard, W.R. Roper, L.J. Wright, *J. Organomet. Chem.* 645 (2002) 235.
- [5] (a) J. Yin, J. Klosin, K.A. Abboud, W.M. Jones, *J. Am. Chem. Soc.* 117 (1995) 3298;
(b) F.R. Lemke, *J. Am. Chem. Soc.* 116 (1994) 11183.
- [6] (a) A.L. Osipov, S.F. Vyboishchikov, K.Y. Dorogov, L.G. Kuzmina, J.A.K. Howard, D.A. Lemenovskii, G.I. Nikonov, *Chem. Commun.* (2005) 3349;
(b) G.I. Nikonov, S.F. Vyboishchikov, L.G. Kuzmina, J.A.K. Howard, *Chem. Commun.* (2002) 568.
- [7] (a) S.K. Ignatov, N.H. Rees, B.R. Tyrrell, S.R. Dubberley, A.G. Razuvaev, P. Mountford, G.I. Nikonov, *Chem.-Eur. J.* 10 (2004) 4991;
(b) K.Y. Dorogov, E. Dumont, N.-N. Ho, A.V. Churakov, L.G. Kuzmina, J.-M. Poblet, A.J. Schultz, J.A.K. Howard, R. Bau, A. Lledós, G.I. Nikonov, *Organometallics* 23 (2004) 2845;
(c) G.I. Nikonov, L.G. Kuzmina, J.A.K. Howard, *J. Chem. Soc., Dalton Trans.* (2002) 3037;
(d) V.I. Bakhmutov, J.A.K. Howard, D.A. Keen, L.G. Kuzmina, M.A. Leech, G.I. Nikonov, E.V. Vorontsov, C.C. Wilson, *J. Chem. Soc., Dalton Trans.* (2000) 1631;
- (e) G.I. Nikonov, L.G. Kuzmina, S.F. Vyboishchikov, D.A. Lemenovskii, J.A.K. Howard, *Chem.-Eur. J.* 5 (1999) 2497.
- [8] (a) S.R. Dubberley, S.K. Ignatov, N.H. Rees, A.G. Razuvaev, P. Mountford, G.I. Nikonov, *J. Am. Chem. Soc.* 125 (2003) 644;
(b) G.I. Nikonov, P. Mountford, S.K. Ignatov, J.C. Green, P.A. Cooke, M.A. Leech, L.G. Kuzmina, A.G. Razuvaev, N.H. Rees, A.J. Blake, J.A.K. Howard, D.A. Lemenovskii, *Dalton Trans.* (2001) 2903.
- [9] S.K. Ignatov, N.H. Rees, S.R. Dubberley, A.G. Razuvaev, P. Mountford, G.I. Nikonov, *Chem. Commun.* (2004) 952.
- [10] G.I. Nikonov, A.V. Churakov, M.Y. Antipin, *Organometallics* 22 (2003) 2178.
- [11] F.N.J. Tebbe, *Am. Chem. Soc.* 95 (1973) 5412.
- [12] J.A. Labinger, in: R.W. Able, G. Wilkinson, FGA. Stone (Eds.), *Comprehensive Organometallic Chemistry*, vol. 3, Pergamon, Elmsford, NY, 1983.
- [13] (a) B. Chaudret, S. Sabo-Etienne, *Chem. Rev.* 98 (1998) 2077;
(b) D.M. Heinekey, N.G. Payne, C.D. Sofield, *Organometallics* 9 (1990) 2643.
- [14] (a) S.G. Davies, S.D. Moon, S.J. Simpson, *Chem. Commun.* (1983) 1278;
(b) G.J. Baired, S.G. Davies, S.D. Moon, S.J. Simpson, R.H. Jones, *J. Chem. Soc., Dalton Trans.* (1985) 1479.
- [15] (a) H. Suzuki, D. Lee, N. Oshima, Y. Moro-oka, *Organometallics* 6 (1987) 1569;
(b) T. Arligie, C. Border, B. Chaudret, J. Devillers, R. Poiblan, *Organometallics* 8 (1989) 1308;
(c) T. Johnson, P.S. Coan, K.G. Caulton, *Inorg. Chem.* 32 (1993) 4594;
(d) S. Grundemann, H.-H. Limbach, V. Rodriguez, B. Donnadiou, S. Sabo-Etienne, B. Chaudret, *Ber. Chem.* 102 (1998) 344;
(e) V. Rodriguez, B. Donnadiou, S. Sabo-Etienne, B. Chaudret, *Organometallics* 17 (1998) 3809.
- [16] D.M. Heinekey, W.J. Oldman Jr., *J. Am. Chem. Soc.* 116 (1994) 3137.
- [17] Y.-Z. Chen, W.C. Chan, C.P. Lau, H.S. Chu, H.L. Lee, G. Jia, *Organometallics* 16 (1997) 1241.
- [18] A.L. Osipov, D.V. Gutsulyak, G.I. Nikonov, in preparation.
- [19] P.E. Künding, F.R. Monnier, *Adv. Synth. Catal.* 346 (2004) 901.
- [20] (a) The previously reported preparation of $[\text{CpRu}(\text{NCCH}_3)_3]^+$ included using of a thallium compound (TlCp) or photochemical activation. T.P. Gill, K.R. Mann, *Organometallics* 1 (1982) 485;
(b) B.M. Trost, C.M. Older, *Organometallics* 21 (2002) 2544.
- [21] (a) Complex $[\text{Cp}(\text{Ph}_3\text{P})\text{Ru}(\text{NCCH}_3)_2]^+$ (**2a**) and some similar compounds were prepared by an analogous reaction by other workers: E. Rüba, W. Simanko, K. Mauthner, C. Slugovc, K. Mereiter, R. Schmid, K. Kirchner, *Organometallics* 18 (1999) 3843;
(b) S. Pavlik, K. Mereiter, R. Schmid, K. Kirchner, *Organometallics* 22 (2003) 1771.
- [22] The esd for the Ru-CNT distance can be estimated as an average esd for the Ru-C bonds. The corresponding values for the Cp and Cp* derivatives are 0.002 and 0.003, respectively. The esd for the difference in Ru-CNT distances can be estimated then as $(0.002^2 + 0.003^2)^{1/2} = 0.0036$. The observed difference in Ru-CNT distances is, therefore, statistically meaningful.
- [23] The related compound $[\text{Cp}(\text{Pr}_i^f\text{P})\text{Ru}(\text{NCCH}_3)_2][\text{PF}_6]$ has been previously reported, but NMR data were missing: C.M. Standfest-Hauser, K. Mereiter, R. Schmid, K. Kirchner, *Eur. J. Inorg. Chem.* (2003) 1883.
- [24] G.M. Sheldrick, *SHELXTL 5.04/VMS. An Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data*, Siemens Analytical X-ray Instrument Inc., Madison, WI, 1995.