Journal of Organometallic Chemistry 693 (2008) 3011–3014

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Reactivity of thiophosphinous acid bound to ruthenium

Massimo Di Vaira [a], Maurizio Peruzzini [b], Stefano Seniori Costantini [a], Piero Stoppioni [a,*]

[a] Dipartimento di Chimica, Università di Firenze, via della Lastruccia 3, 50019 Sesto Fiorentino, Firenze, Italy
[b] ICCOM CNR, Via Madonna del Piano 10, 50019 Sesto Fiorentino, Firenze, Italy

ARTICLE INFO

Article history:
Received 5 May 2008
Received in revised form 17 June 2008
Accepted 17 June 2008
Available online 25 June 2008

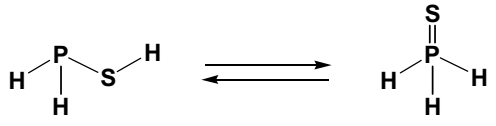
Keywords:
Ruthenium
Thiophosphinous acid
Reactivity
Cyclopentadienyl complexes
X-ray structure

ABSTRACT

The thiophosphinous acid coordinated to ruthenium through the phosphorus atom in $[CpRu(PPh_3)_2(PH_2SH)]CF_3SO_3$ (**1**) is deprotonated in the presence of proton sponge to yield the neutral compound $[CpRu(PPh_3)_2(PH_2S)]$ (**2**), where the thiophosphinite, PH_2S^-, anion remains bound to the metal through the phosphorus atom. The parent complex **1** is easily restored in the presence of a weak acid. The sulfur of the coordinated anion may be alkylated with CF_3SO_3Me to yield $[CpRu(PPh_3)_2(PH_2SCH_3)]CF_3SO_3$ (**3**), the methyl thioester of the acid being bound to ruthenium through the phosphorus. The new compounds have been characterized by elemental analyses, IR and multinuclear NMR spectroscopy. The crystal structure of **2** · **CH_3CN** has been determined by X-ray diffraction methods.

1. Introduction

A large number of aromatic and aliphatic mono- and poly-phophane sulfides have been synthesized and have been frequently used to assist organic transformations [1]. However, the simple ternary P, S and H derivatives, which are the parent compounds of substituted phosphine sulfides, are quite elusive due to their instability. As a result, the properties of the simplest compounds of this class, the thiophosphinous acid, PH_2SH (**I**), and its sulfide tautomer, $S{=}PH_3$ (**II**), are practically unknown in the free state. The former compound has been obtained in very poor yield at very low temperature and under harsh reaction conditions [2] or has been trapped in solid argon matrices [3]. At the same time, many theoretical studies have been undertaken to address the structures of the simplest phosphorus thiohydrides, the pathways for hydrogen migration accounting for the different thiohydride tautomers and eventually the energetics of these transformations [4–8].



I II

We have recently found that the plain hydrolysis of tetraphosphorus trisulfide, P_4S_3, $\eta^{1:1}$ doubly metallated to two $CpRu(PPh_3)_2$ ruthenium fragments through the apical and one of the basal phosphorus atoms, yields different products including PH_2SH, which is stabilized through coordination, via the phosphorus atom, to the $CpRu(PPh_3)_2$ unit [9]. $[CpRu(PPh_3)_2(PH_2SH)]CF_3SO_3$ (**1**), which was authenticated by X-ray methods, is quite stable both in the solid state and in dichloromethane solution. As it may be prepared in quite good amount, it appears to be a useful synthon for gaining some insight on the reactivity of the metal-coordinated PH_2SH molecule. In this article we report that, once coordinated to ruthenium, PH_2SH may be easily deprotonated in the presence of non nucleophilic bases, such as proton sponge, to yield the neutral compound $[CpRu(PPh_3)_2(PH_2S)]$ (**2**); reversibly, the parent complex **1** may be quantitatively restored by reacting **2** with a weak acid. The thiolate sulfur atom in **2** undergoes plain alkylation with methyl triflate to afford $[CpRu(PPh_3)_2(PH_2SCH_3)]CF_3SO_3$ (**3**), which is a rare example of coordinated methyl ester of the parent thiophosphinous acid. Compounds **2** and **3** have been characterized by elemental analyses and NMR measurements. The crystal structure of **2** · **CH_3CN** has been determined by X-ray diffraction methods.

2. Results and discussion

The tetraphosphorus trisulfide cage molecule, P_4S_3, coordinated to two ruthenium fragments through its apical and one of the basal phosphorus atoms in $[\{CpRu(PPh_3)_2\}_2(\mu,\eta^{1:1}\text{–}P_{apical}\text{–}P_{basal}\text{–}P_4S_3)](CF_3SO_3)_2$ (**4**), Fig. 1, undergoes selective hydrolysis to yield several

* Corresponding author. Tel.: +39 055 4573281.
E-mail address: piero.stoppioni@unifi.it (P. Stoppioni).

0022-328X/$ - see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2008.06.019

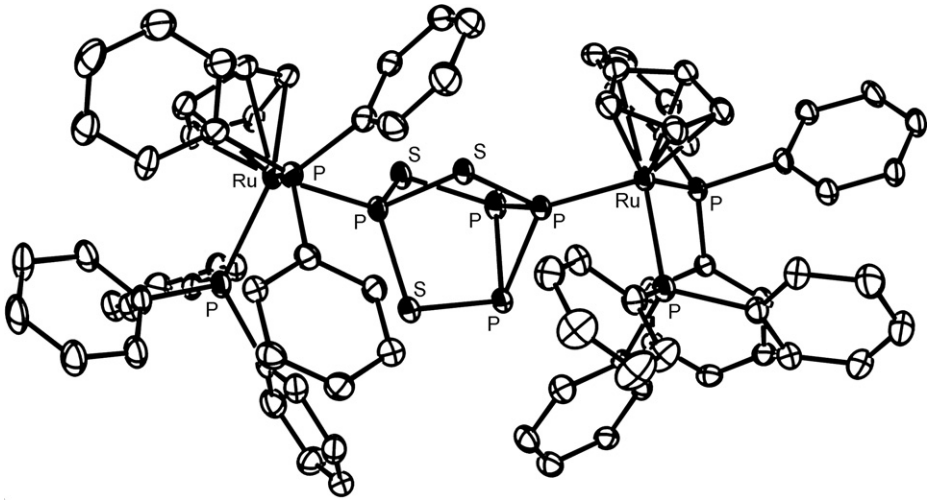


Fig. 1. The dimetal cation in the strucutre of (**4**) [9].

products among which the thiophosphinous acid, PH_2SH, is quantitatively obtained [9]. This molecule, highly reactive and practically unknown as a free species [3], is likely produced via metal-mediated tautomerization of the phosphane sulfide (**II**) generated from the hydrolysis of **4** and is stabilized by coordination to the ruthenium center via the phosphorus atom, yielding the compound $[CpRu(PPh_3)_2(PH_2SH)]CF_3SO_3$ (**1**) [10].

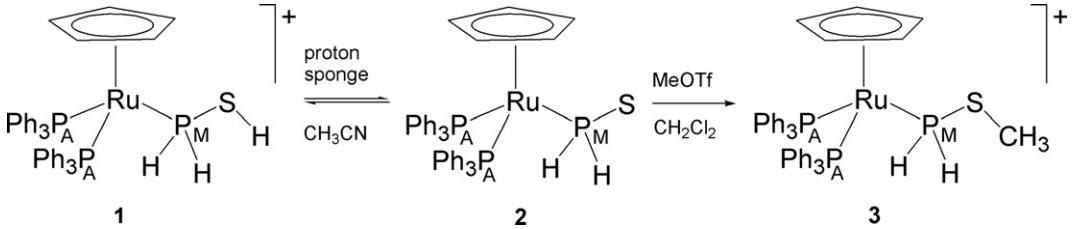
The coordinated thiophosphinous acid readily undergoes deprotonation by treatment of **1,** dissolved in CH_3CN, with the stoichiometric amount of the non nucleophilic base 1,8-bis-(dimethylamino)-naphthalene, i.e. proton sponge, giving the neutral complex $[CpRu(PPh_3)_2(PH_2S)]$, (**2**) (Scheme 1). Complex **2** was isolated as a yellow microcrystalline solid, stable under an inert atmosphere and soluble in common organic solvents such as acetone and dichloromethane.

Crystals of the CH_3CN solvate of **2** suitable for a crystallographic study were grown by slow evaporation of an acetonitrile solution of **1** containing the proton sponge. A view of complex **2** is shown in Fig. 2. The metal atom in **2** is in a pseudo-octahedral coordination environment formed by the atoms of the Cp ring, by the two triphenylphosphane P atoms and by the phosphorus atom of the PH_2S^- thiophosphinite anion. Both the coordination geometry and the overall molecular conformation are closely similar to those found for the parent complex cation containing the PH_2SH ligand [9].

However, the Ru–P distance involving the PH_2S^- ligand in compound **2** (Table 1) is 0.047 Å longer than that formed by PH_2SH in **1** [9]. This significant metrical change, which occurs on going from **1** to **2**, is clearly related to differences in P–S bonding, the P–S bond length in **2** being 0.098 Å shorter than that in **1**. The lengthening of the $Ru—P_{(PH_2S)}$ distance with respect to the $Ru—P_{(PH_2SH)}$ one, is accompanied by a small shortening of the triphenylphosphane Ru–P distances, by 0.04 Å in the mean. The sulfur atom in **2** is engaged in a weak hydrogen bond interaction with a C–H moiety of a phenyl group (Table 1 and Fig. 2), with an H···S separation of 2.781(2) Å. Since a symmetrical, minimum energy conformation may be attained by interaction of the thiophosphinite sulfur atom with a phenyl group of the other triphenylphosphane, the existence of these two alternative settings may rationalise some features of the ^1H NMR signals due to the PH_2 group, which are discussed below.

The $^{31}P\{^1H\}$ NMR spectrum of **2** in $CDCl_3$ exhibits the expected A_2M spin system, in which A and M are the phosphorus atoms of the triphenylphosphane molecules and of the PH_2S^- anion, respectively. Both resonances are downfield shifted with respect to those observed in the parent compound **1** [9]; such shift is particularly enhanced for the resonances ascribed to the phosphorus of the anion. In keeping with the $^{31}P\{^1H\}$ NMR pattern, the ^1H spectrum in the PH_2 region is consistent with an AA'MXX' spin system (where A, A' and M are the phosphorus atoms of the triphenylphosphanes and the PH_2S^- anion, respectively, and X, X' are the hydrogen atoms of the PH_2 group). This pattern can be successfully simulated only assuming an exchange process between P_A and $P_{A'}$ (k_{exch} = 46.7 s^{-1}). The nature of the dynamic process, however, is not clear although it is likely due to the presence of the formal negative charge on the sulfur atom and the consequent interaction highlighted in Fig. 2. This conclusion follows from the absence of any detectable dynamic process in the NMR spectrum of the compound $[CpRu(PPh_3)_2(PH_2SCH_3)]CF_3SO_3$ **3**, see below. $[CpRu(PPh_3)_2(PH_2SH)]CF_3SO_3$ is readily restored by adding the stoichiometric amount of triphenylphosphonium triflate, $[PPh_3H]CF_3SO_3$, to a $CHCl_3$ solution of **2**. Such result, according to the weak acidity of the phosphonium salt (pk_a = 11.2), highlights a pronounced basic character of the sulfur of the PH_2S^- thiophosphinite anion.

The addition of methyl trifluoromethansulfonate to a solution of **2** in CH_2Cl_2 yields $[CpRu(PPh_3)_2(PH_2SCH_3)]CF_3SO_3$ (**3**), see Scheme



Scheme 1.

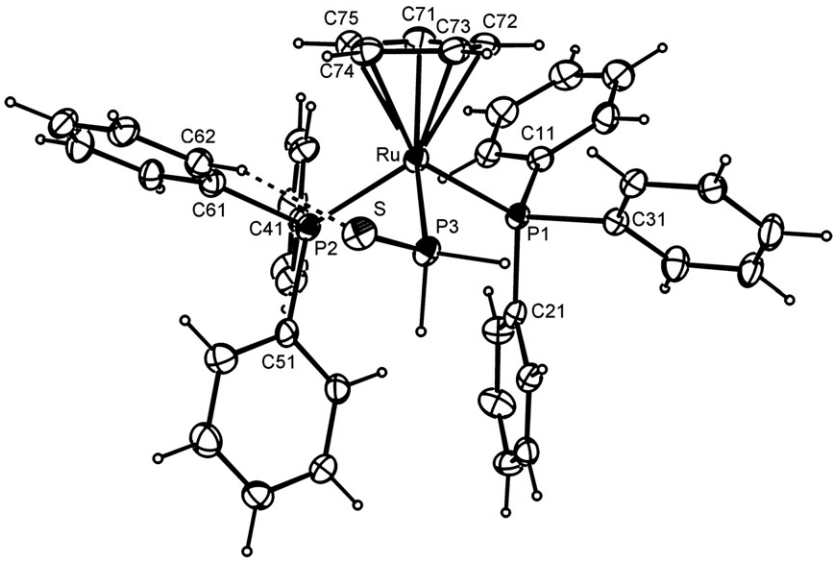


Fig. 2. A view of the complex molecule in the structure of $[CpRu(PPh_3)_2(PH_2S)] \cdot CH_3CN$ (**2**). Thermal ellipsoids are shown at the 30% probability level. Only the *ipso* carbon atoms of phenyl groups and the one involved in the weak C–H···S interaction discussed in the text are labelled.

Table 1
Selected bond lengths (Å) and angles (°) for $[CpRu(PPh_3)_2(PH_2S)] \cdot CH_3CN$ (**2**)

Ru–P(1)	2.304(2)	Ru–C(Cp)	2.231–2.250
Ru–P(2)	2.333(2)	P(3)–S	2.011(2)
Ru–P(3)	2.297(2)	S···H(62)	2.781(2)
P(1)–Ru–P(2)	102.48(6)	Ru–P(3)–S	119.24(9)
P(1)–Ru–P(3)	92.33(6)	C(62)–H(62)···S	166.0(4)
P(2)–Ru–P(3)	90.21(6)		

1. Compound **3** is stable under nitrogen in both the solid state and solution. The ^{31}P NMR spectrum yields an A_2M spin system, in which A are the phosphorus atoms of the triphenylphosphane and M the phosphorus of PH_2SCH_3. The NMR parameters are similar to those observed both for **1** and **2**. Such data show that the methylthioester, PH_2SCH_3, retains its coordination to the metal through the phosphorus atom. The presence of the methylated sulfur atom is confirmed by the occurrence of a three-proton resonance at 2.31 ppm doubled by a 10.3 Hz coupling with the neighbouring thiophosphinite P atom. Remarkably, the PH_2 portion of the spectrum does not show any fluxional behaviour and appears as a first order doublet of triplets. This behaviour corroborates the hypothesis that the scrambling process in **2** may be traced back to the engagement of a high-energy lone pair of the deprotonated sulfur atom, which should not be available in the case of **3**.

The chemistry here presented shows that the coordinated thiophosphinous acid, PH_2SH, stabilised by coordination to suitable organometallic platforms, may undergo simple chemical transformations resulting in the formation of new and unprecedented coordinated species like the PH_2S^- anion and the methylthioester PH_2SCH_3. Also, the present results show that the tautomerization processes via fast and low-energy mobility pathways, causing instability of PH2SH as a free molecule [4], are blocked by coordination of the phosphorus atom to the metal.

3. Experimental

All reactions and manipulations were performed under an atmosphere of dry oxygen-free argon. The solvents were purified according to standard procedures [11]. The ^1H, ^{19}F and $^{31}P\{^1H\}$ NMR spectra were run at room temperature on a Bruker Avance 400 DRX spectrometer. ^{19}F and ^{31}P chemical shifts are relative to external $CFCl_3$ and to 85% H_3PO_4, respectively. ^1H chemical shifts are relative to tetramethylsilane as external reference and were calibrated against the residual solvent resonance. Coupling constants of **2** were obtained from 1D $^{31}P\{^1H\}$, ^1H and $^1H\{^{31}P\}$ NMR spectra with the aid of computer simulation using the gNMR program [12]. Chemical shifts are relative to tetramethylsilane (^1H), $CFCl_3$ (^{19}F) and H_3PO_4 85% (^{31}P) as external standards at 0.00 ppm, with downfield values taken as positive; coupling constants are in Hertz. IR spectra were recorded on a Perkin–Elmer Spectrum BX FT-IR system spectrometer in nujol mull between sodium chloride plates. Analytical data for carbon, hydrogen and phosphorus were obtained from the Microanalytical Laboratory of the Department of Chemistry of the University of Firenze. The complex $[CpRu(PPh_3)_2(PH_2SH)]CF_3SO_3$ (**1**) was synthesized according to literature method [9]. Trifluoromethansulfonic acid, methyl trifluoromethansulfonate and 1,8-bis-(dimethylamino)-naphthalene, proton sponge, were purchased from Aldrich and used as received apart for proton sponge which was purified by sublimation prior the use.

3.1. $[PPh_3H]CF_3SO_3$

One equivalent of trifluromethansulfonic acid was added to triphenylphosphane (520 mg, 2.0 mmol) dissolved in toluene (8 ml); the salt was precipitated by cooling the resulting suspension with an ice bath. Yield: 670 mg, 81%. Anal. Calc. for $C_{19}H_{16}F_3O_3PS$: C, 55.3; H, 3.9; P, 7.5%; M, 412.3. Found: C, 55.1; H 4.0; P, 7.2%.

3.2. $[CpRu(PPh_3)_2(PH_2S)]$ (**2**)

Proton sponge (43 mg, 0.2 mmol) dissolved in CH_3CN (5 ml) was added to a solution of $[CpRu(PPh_3)_2(PH_2SH)]CF_3SO_3$ (**1**) (181 mg, 0.2 mmol) in CH_3CN (10 ml). A yellow microcrystalline material was obtained by stirring the resulting solution for 1 h. The solid was separated from the solution, washed with cold CH_3CN (2 ml) and dried under vacuum. Yield: 118 mg, 78%. Anal. Calc. for $C_{41}H_{37}P_3RuS$: C, 65.1; H, 4.9; P, 12.3%; M, 755.8. Found: C, 65.1; H 5.0; P, 12.2%. IR (ν_{max}/cm^{-1}): (PH) 2305 s. ^1H NMR ($CDCl_3$, 298 K): δ_H 7.40–7.10 (30H, m, Ph), 6.19 (2H, AA'MXX' spin

Table 2
Crystal data and structure refinement parameters for $[CpRu(PPh_3)_2(PH_2S)] \cdot CH_3CN$ (**2**)

Formula	$C_{43}H_{40}NP_3RuS$
Formula weight	796.80
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å)	12.0041(3)
b (Å)	13.1006(4)
c (Å)	24.7880(10)
α (°)	90
β (°)	100.768(3)
γ (°)	90
V (Å^3)	3829.5(2)
Z	4
Crystal size (mm)	0.18 × 0.20 × 0.60
μ (Mo Kα, mm^{-1})	0.621
T (K)	170(2)
Reflections collected	26228
Independent reflections	7085
Reflections with $I > 2\sigma(I)$ [R_{int}]	4673 [0.0856]
No. of parameters [restraints]	445 [1]
R_1; wR_2 [$I > 2\sigma(I)$]	0.0608; 0.1547
R_1; wR_2 [all data]	0.0915; 0.1651
Goodness-of-fit	1.090

system, $^1J_{XM} = {}^1J_{X'M} = 350.1$, $^2J_{XX'} = 18.2$, $^3J_{XA} = {}^3J_{X'A'} = 1.8$, $^3J_{X'A} = {}^3J_{XA'} = 10.8$, PH_2), 4.48 (5H, s, C_5H_5); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 298 K): δ_P 48.1 (2P, d, $^2J_{PP}$ = 46.1, PPh_3), −17.4 (1P, t, PH_2S).

Crystals suitable for X-ray analysis were obtained on leaving a CH_3CN solution of **1** and proton sponge overnight.

3.3. *[CpRu(PPh$_3$)$_2$(PH$_2$SCH$_3$}]CF$_3$SO$_3$ (**3**)*

One equivalent of neat $CF_3SO_3CH_3$ was added to a solution of **2** (113 mg, 0.15 mmol) in CH_2Cl_2 (10 ml). The resulting solution was stirred at room temperature for 15 min; after than the solvent was removed under reduced pressure leaving a yellow residue. The yellow solid was washed with diethylether and dried under vacuum. Yield 117 mg, 85%. Anal. Calc. for $C_{43}H_{40}F_3O_3P_3RuS_2$: C, 56.1; H, 4.4; P, 10.1%; M, 919.8. Found: C, 56.0; H 4.5; P, 9.5%. IR (ν_{max}/cm^{-1}): (PH) 2290 s. ^{1}H NMR ($CDCl_3$, 298 K): δ_H 7.40–6.80 (30H, m, Ph), 5.49 (2H, dt, $^1J_{HP}$ 370.3, $^3J_{HP}$ 6.0, PH_2), 4.58 (5H, s, C_5H_5), 2.31 (3H, d, $^3J_{HP}$ 10.3, CH_3); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 298 K): δ_P, 43.1 (2P, d, $^2J_{PP}$ 47.4, PPh_3), 3.2 (1P, t, PH_2SCH_3); ^{19}F NMR ($CDCl_3$, 298 K): δ_F, −75.5 (s, $CF_3SO_3^-$).

3.4. *X-ray crystallography of [CpRu(PPh$_3$)$_2$(PH$_2$S)]·CH$_3$CN (**2**)*

X-ray diffraction data for **2**, as the acetonitrile solvate, were collected at 170(2) K on an Oxford Diffraction Xcalibur 3 CCD diffractometer, using Mo Kα radiation (λ = 0.71073 Å). Crystal data and the main data collection and structure refinement parameters are given in Table 2. Lattice constants were obtained from the setting angles of 15460 reflections in the θ range 3.7–28.0°. Intensity data were corrected for absorption by a multi-scan procedure [13]. The structure was solved by direct methods, with SIR-97 [14], and was refined by full-matrix least-squares on F^2 values [15]. All non-hydrogen atoms were refined anisotropically. All hydrogens bound to carbons were placed in idealized positions, each riding on the respective carrier atom, with its temperature factor linked to the overall U of the latter. The positions of the PH_2S hydrogens were allowed to refine, with a geometrical restraint on P–H distances. Programs used for crystallographic calculations included PARST [16] and ORTEP was used for drawings [17].

4. Supplementary material

CCDC 686518 contains the supplementary crystallographic data for **2**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgement

We acknowledge financial support by the Ministero dell'Università e della Ricerca Scientifica e Tecnologica (Rome).

References

[1] (a) See for example: B.A. Trofimov, S.F. Malysheva, N.K. Gusarova, N.A. Belogorlova, S.F. Vasilevsky, V.B. Kobychev, B.G. Sukhov, I.A. Ushakov, Mendeleev Commun. 17 (2007) 181;
(b) P. Yan, Y. Hashimoto, Tetrahedron Lett. 47 (2006) 3467;
(c) R.E. Medsker, A. Sebenik, H.J. Harwood, Polym. Bull. 48 (2002) 17;
(d) R. Romeo, L.A. Wozniak, C. Chatgilialoglu, Tetrahedron Lett. 41 (2000) 9899;
(e) W.I. Cross, S.M. Godfrey, S.L. Jackson, C.A. McAuliffe, R.G. Pritchard, J. Chem. Soc., Dalton Trans. (1999) 2225;
(f) A.M. Caminade, J.P. Majoral, R. Mathieu, Chem. Rev. 91 (1991) 575.
[2] P.W. Schenk, B. Leutner, Angew. Chem. 78 (1966) 942;
P.W. Schenk, B. Leutner, Angew. Chem., Int. Ed. 5 (1966) 898.
[3] Z. Mielke, L. Andrews, J. Phys. Chem. 97 (1993) 4313.
[4] W. Na Wang, W. Liang Wang, Q. Luo, Q. Shu Li, Chem. Phys. Lett. 415 (2005) 370.
[5] W. Schneider, W. Thiel, A. Komornicki, J. Phys. Chem. 92 (1988) 5611.
[6] J.S. Kwiatkowski, J. Leszczynski, J. Phys. Chem. 96 (1992) 6636.
[7] M.W. Schmidt, M.S. Gordon, J. Am. Chem. Soc. 107 (1985) 1922.
[8] T. Wong, J.K. Terlouw, H. Keck, W. Kucken, P. Tommes, J. Am. Chem. Soc. 114 (1992) 8208.
[9] P. Barbaro, M. Di Vaira, S. Seniori Costantini, M. Peruzzini, P. Stoppioni, Chem. Eur. J. 13 (2007) 6682.
[10] D. Akbayeva, M. Di Vaira, S. Seniori Costantini, M. Peruzzini, P. Stoppioni, The ruthenium fragment $CpRu(PPh_3)_2$ promotes the tautomerization of hypophosphorous and phosphorous acids into the corresponding $PH(OH)_2$ and $P(OH)_3$ hydroxyphosphine tautomers, that remain coordinated to the metal, Dalton Trans. (2006) 389.
[11] D.D. Perrin, W.L.F. Armarego, Purification of Laboratory Chemicals, third ed., Pergamon, New York, 1988.
[12] P.H.M. Budzeaar, gNMR V4.0, Published by Cherwell Scientific Publishing, Copyright Ivory Soft 1995–1997.
[13] G.M. Sheldrick, SADABS, Program for Empirical Absorption Corrections, University of Göttingen, Göttingen, Germany, 1986.
[14] A. Altomare, M.C. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, A. Guagliardi, A.G. Moliterni, G. Polidori, R. Spagna, J. Appl. Crystallogr. 32 (1999) 115.
[15] G.M. Sheldrick, SHELXL97, Program for Crystal Structure Refinement, University of Göttingen, Göttingen, Germany, 1997.
[16] M. Nardelli, J. Appl. Crystallogr. 28 (1995) 659.
[17] L.J. Farrugia, J. Appl. Crystallogr. 32 (1999) 837.