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Synthesis of neutral iridium(III) and rhodium(III) complexes with the proligands Pr₂ⁱP(C₆H₄–SH-2) [*pr*ⁱPSH]¹; PhP(C₆H₄–SH-2)₂ [*ph*PS₂H₂]² and PhP(C₂H₄SH)₂ [*e*PS₂H₂]³. The X-ray crystal structures of [Ir(*pr*ⁱPS)₃] and [Rh(H)(*ph*PS₂)(CO)(PPh₃)]

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Abstract

The reactivity of the hybrid phosphorus–sulfur proligands $pr^{i}PSH$, $phPS_{2}H_{2}$ and $ePS_{2}H_{2}$ with iridium and rhodium precursors has been explored. By reacting IrCl₃ with $pr^{i}PSH$ in the presence of NEt₃ as base, the octahedral Ir(III) specie [Ir($pr^{i}PS$)₃] was obtained and its crystal structure determined. Reactions of the potentially tridentated proligands $phPS_{2}H_{2}$ and $ePS_{2}H_{2}$ with *trans*-[MF(CO)(PPh₃)₂] (M = Rh and Ir) were also investigated. Complexes of general formula [M(H)($phPS_{2}$)(CO)(PPh₃)] were obtained with $phPS_{2}H_{2}$. A single crystal X-ray structure determination for [Rh(H)($phPS_{2}$)(CO)(PPh₃)] showed the complex to be octahedral. Reactions with the aliphatic proligand $ePS_{2}H_{2}$ afforded analogous species to those with $phPS_{2}H_{2}$. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Phosphorus-sulfur proligands; Rhodium complexes; Iridium complexes; Hydrides; Crystal structures

1. Introduction

The chemistry of metal complexes of both simple and bulky thiolate ligands has been well documented [1]. Recently, attention has increasingly been paid to the coordination chemistry of polydentate ligands incorporating both thiolate and tertiary phosphine donor ligands, as their combination is likely to confer unusual structures and reactivities on their metal complexes [2]. Some of these complexes have been used as models of biologically active centres in metalloproteins such as ferredoxins, nitrogenase, blue copper proteins and metallothioneins [3] or as models for the design of complexes with potential application as radiopharma-

¹ (phenyl-2-thiol)diisopropylphosphine.

ceuticals [4]. These complexes have shown an intriguing variety of structures [5] or unusual oxidation states and enhanced solubility [6], making these species excellent candidates for further studies in reactivity. In the specific case of compounds with elements of the Groups 8-10 these may be suitable species for catalytic screening. Moreover, the presence of these ligands in the coordination sphere of transition metal-complexes may render interesting behaviours in solution as these ligands can be capable of full or partial de-ligation (hemilability) [7] being able to provide important extra coordination sites for incoming substrates during a catalytic process [8]. To date, most studies have focused on bidentate ligands such as R₂PCH₂CH₂SH [9] and $R_2P(C_6H_4-SH-2)$ [10], while the potentially tridentate proligands $RP(CH_2CH_2SH)_2$ and $RP(C_6H_4-SH-2)_2$ have received much less attention [11]. We report here on the coordination chemistry of rhodium and iridium with the mixed phosphine-thiol proligands $Pr_2^iP(C_6H_4-$ SH-2) $[pr^{i}PSH]$; PhP(C₆H₄-SH-2)₂ $[phPS_2H_2]$ and $PhP(C_2H_4SH)_2 [ePS_2H_2].$

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² bis(phenyl-2-thiol)phenylphosphine.

³ bis(ethyl-2-thiol)phenylphosphine.

2. Experimental

2.1. Materials and methods

Unless stated otherwise, all reactions were carried out under an atmosphere of dinitrogen using conventional Schlenk glassware, solvents were dried using established procedures and distilled under dinitrogen immediately prior to use. The IR spectra were recorded on a Perkin-Elmer Paragon FT IR spectrometer as nujol mulls. The ¹H NMR spectra were recorded on a JEOL EX270 spectrometer. Chemical shifts are reported in ppm down field of TMS using the solvent (CDCl₃, $\delta = 7.27$) as internal standard. ³¹P NMR spectra were recorded with complete proton decoupling and are reported in ppm using 85% H₃PO₄ as external standard. Elemental analyses were determined on a Perkin-Elmer 240 at the University of Essex, UK. Positive-ion FAB mass spectra were recorded on a JEOL SX102 mass spectrometer operated at an accelerating voltage of 10 kV. Samples were desorbed from a nitrobenzyl alcohol (NOBA) matrix using 3 keV xenon atoms. Mass measurements in FAB are performed at a resolution of 3000 using magnetic field scans and the matrix ions as the reference material or, alternatively, by electric field scans with the sample peak bracketed by two (polyethylene glycol or cesium iodide) reference ions. The IrCl₃ was obtained from Aldrich Chemical Co. and used without further purification. The proligand prⁱPSH was synthesised in analogous manner to that of the known phosphino-thiol phPSH [12]. The proligands phPS₂H₂ [12] and ePS₂H₂ [11b] and the starting materials trans- $[MF(CO)(PPh_3)_2]$ (M = Rh and Ir) [13] were prepared according to published procedures.

2.2. $[Ir(pr^{i}PS)_{3}]$ (1)

A methanol solution consisting of IrCl₃ (100 mg, 12 mmol) and the phosphino-thiol $pr^{i}PSH$ (3 equiv.), in the presence of NEt₃ as base, were heated under reflux for 2 h, after this time the yellow precipitate formed was filtered and washed with cold ether. Yield 218 mg (75%). ¹H NMR (CDCl₃, 200 MHz): $\delta = 7.6-6.7$ (m, 12H, arom.), 3.35–3.15 (m, br, 2H, CH), 3.1–2.85 (m, br, 2H, CH), 2.7–2.3 (m, br, 2H, CH). ³¹P NMR (CDCl₃, 81.0 MHz): $\delta = 15.88$ (s, br), 9.80 (s, br), 7.94 (s, br). Elem. Anal. C₃₆H₅₄P₃S₃Ir (868.15): calcd. C 49.8, H 6.2. Found C 49.8, H 6.3%. Mol. mass 868 (M⁺).

2.3. $[Rh(H)(phPS_2)(CO)(PPh_3)]$ (2)

To a solution of *trans*-[RhF(CO)(PPh₃)₂] (100 mg, 0.15 mmol) in toluene (25 cm³) 1 equiv. of the phosphino-dithiol $phPS_2H_2$ was added. The solution was stirred for 45 min. The volume was then reduced in

vacuum and the reddish-brown residue recrystallised from a double layer solvent system of CH₂Cl₂/MeOH. Yield 90 mg (85%). IR (nujol): v = 2049 cm⁻¹ [v(Rh-H)], 1979 cm⁻¹ [v(C=O)]. ¹H NMR (CDCl₃, 200 MHz): $\delta = 8.6-6.6$ (m, 28H, arom.). ³¹P NMR (CDCl₃, 81.0 MHz): Not observed. Elem. Anal. C₃₇H₂₉OP₂S₂Rh (718.61): calcd. C 61.8, H 4.1. Found C 61.8, H 4.0%. Mol. mass 689 (M⁺-H-CO).

2.4. $[Rh(H)(ePS_2)(CO)(PPh_3)]$ (3)

To a solution of *trans*-[RhF(CO)(PPh₃)₂] (100 mg, 0.15 mmol) in methanol (25 cm³) precooled to -78 °C (dry-ice/acetone bath) was added 1 equiv. of the phosphino-dithiol *e*PS₂H₂. The solution was stirred for 10 min at this temperature and then the heating bath was removed to allow the solution to reach room temperature (r.t.). The volume was then reduced in vacuum and the residue redisolved in the minimum volume of CH₂Cl₂ and precipitated with *n*-pentane. Yield 74 mg (80%). IR (nujol): v = 2057 cm⁻¹ [v(Rh–H)], 1965 cm⁻¹ [v(C≡O)]. ¹H NMR (CDCl₃, 200 MHz): $\delta = 8.0-7.0$ (m, 20H, arom.), 3.0–0.9 (m, 8H, CH₂). ³¹P NMR (CDCl₃, 81.0 MHz): Not observed. Elem. Anal. C₂₉H₂₉OP₂S₂Rh (622.52): calcd. C 56.0, H 4.7. Found C 56.3, H 4.6%. Mol. mass 593 (M⁺–H–CO).

2.5. $[Ir(H)(phPS_2)(CO)(PPh_3)]$ (4)

The title complex was synthesised in a similar manner to that of complex (2). By reacting *trans*-[Ir-F(CO)(PPh₃)₂] (100 mg, 0.13 mmol) with the phosphino-dithiol *ph*PS₂H₂ in equivalent amounts. The product was recrystallised from a double layer solvent system of CH₂Cl₂/MeOH. Yield 95 mg (90%). IR (nujol): $v = 2100 \text{ cm}^{-1} [v(\text{Rh}-\text{H})]$, 2026 cm⁻¹ [v(C=O)]. ¹H NMR (CDCl₃, 200 MHz): $\delta = 7.7-6.7$ (m, 28H, arom.), -11.36 (t, 1H, *Ir*-H, ²*J*_{H-P} = 11.74 Hz). ³¹P NMR (CDCl₃, 81.0 MHz): $\delta = 58.09$ (d, ²*J*_{P-P} = 297.1 Hz), 4.36 (d, ²*J*_{P-P} = 297.1 Hz). Elem. Anal. C₃₇H₂₉OP₂S₂Ir (807.92): calcd. C 55.0, H 3.6. Found C 55.0, H 3.7%. Mol. mass 779 (M⁺-H-CO).

2.6. $[Ir(H)(ePS_2)(CO)(PPh_3)]$ (5)

Complex (5) was synthesised in an analogous manner to that of complex (2). By reacting *trans*-[Ir-F(CO)(PPh₃)₂] (100 mg, 0.13 mmol) and the phosphinodithiol ePS_2H_2 in equivalent amounts. The product was redisolved in the minimum volume of CH₂Cl₂ and precipitated with *n*-pentane. Yield 70 mg (75%). ¹H NMR (CDCl₃, 200 MHz): $\delta = 8.0-6.9$ (m, 20H, arom.), 3.0-0.8 (m, 8H, CH₂). ³¹P NMR (CDCl₃, 81.0 MHz): $\delta = 48.50$ (d, ²J_{P-P} = 169.8 Hz), 43.15 (d, ²J_{P-P} = 169.8 Hz). Elem. Anal. C₂₉H₂₉OP₂S₂Ir (711.84): calcd. C 48.9, H 4.1. Found C 48.7, H 4.3%. Mol. mass 711 (M⁺-H).

2.7. Data Collection and refinement for $[Ir(pr^iPS)_3]$ (1) and $[Rh(H)(phPS_2)(CO)(PPh_3)]$ (2).

Intensity data were collected (graphite-monochromated Mo K α radiation, $\lambda = 0.71069$ Å) on an Enraf-Nonius CAD4 diffractometer [14] for complex (1) and at EPSRC service, Cardiff, UK on a Delft-Instruments FAST-TV Area detector diffractometer for (2). In both cases the data were corrected for Lorentz and polarisation factors and absorption correction was applied using ψ -scans of nine reflections. The structures were solved via direct methods [15] and refined by F_o^2 by full-matrix least squares [16]. All non-hydrogen atoms were anisotropic and the hydride atom was not considered in the refinement (complex 2). The hydrogen atoms (except hydride atom in complex 2) were included in idealised positions with Uiso free to refine. Sources of scattering factors were as in reference [16]. The details of the structure determination are given in Table 1 and selected bond lengths (Å) and angles (°) in Table 2 (complex 1). The numbering of the atoms are

Table 1

Summary of crystal structure data for complexes ${\bf 1}$ and ${\bf 2}$

	1	2
Empirical formula	C ₃₆ H ₅₄ IrP ₃ S ₃	C37H28OP2RhS2
Formula weight	868.08	717.56
Temperature (K)	293(2)	293(2)
Crystal system	monoclinic	monoclinic
Space group	$P2_{1}/c$	$P2_{1}/c$
a (Å)	17.775(1)	13.258(7)
b (Å)	11.886(1)	13.614(4)
<i>c</i> (Å)	19.060(2)	18.383(4)
α (°)	90	90
β (°)	115.84(1)	101.430(2)
γ (°)	90	90
V (Å ³)	3624.2(5)	3252(2)
Z	4	4
θ Range (lattice) (°)	$8.29 < \theta < 12.8$	$1.87 < \theta < 25.07$
D_{calc} (g cm ⁻³)	1.591	1.460
$\mu ({\rm mm}^{-1})$	4.014	0.781
F(000)	1760	1460
Crystal colour	Yellow	Red
Crystal description	Prism	Prism
Crystal size (mm)	$0.35 \times 0.30 \times 0.14$	$0.14 \times 0.14 \times 0.14$
Reflections measured	7161	12 289
Independent reflections	6954	4805
Observed reflections	5869	1504
$[I > 2\sigma(I)]$		
h, k, l Ranges	-21-19, 0-14,	-15-9, -15-15,
	0–21	-21-21
Data/restraints/parameters	5869/0/400	4805/0/388
R_1	0.0205	0.0445
wR_2^{a}	0.0340	0.0837
Largest difference peak	0.478 and	0.604 and
and hole (e \dot{A}^{-3})	-0.445	-0.335

Details in common: θ_{max} 25°, weighting schemes $w = 1/[\sigma^2(F_o^2) + (0.0179P)^2 + 0.0000P]$ where $P = (F_o^2 + 2F_o^2)/3$. ^a $R_1 = |F_o - F_c|/|F_o|$, $wR_2 = [w((F_o)^2 - (F_o)^2)^2/w(F_o)^2]^{1/2}$.

Table 2 Selected bond lengths (Å) and angles (°) for $[Ir(pr^{i}PS)_{3}]$ (1)

Bond lengths (Å)	
Ir–P(1)	2.3484(8)
Ir-S(1)	2.3523(7)
Ir-P(2)	2.3619(7)
Ir-S(2)	2.3805(7)
Ir-P(3)	2.3908(7)
Ir–S(3)	2.4157(7)
Bond angles (°)	
P(1)-Ir- $S(1)$	87.63(3)
P(1)–Ir–P(2)	96.22(3)
S(1)–Ir–P(2)	93.85(3)
P(1)–Ir–S(2)	93.59(3)
S(1)–Ir–S(2)	176.80(2)
P(2)–Ir–S(2)	83.07(3)
P(1)–Ir–P(3)	94.98(3)
S(1)–Ir–P(3)	86.32(3)
P(2)-Ir-P(3)	168.80(3)
S(2)–Ir–P(3)	96.52(3)
P(1)–Ir–S(3)	170.38(3)
S(1)–Ir–S(3)	83.02(3)
P(2)–Ir–S(3)	86.64(3)
S(2)–Ir–S(3)	95.88(3)
P(3)-Ir-S(3)	82.26(2)



Fig. 1. An ORTEP representation of the structure of $[Ir(pr^iPS)_3]$ (1) at 50% of probability showing the atom labelling scheme.

shown in Fig. 1 (complex 1) and Fig. 2 (complex 2) (ORTEP) [17].

3. Results and discussion

3.1. Synthesis and characterisation of $[Ir(pr^iPS)_3]$ (1)

The reaction between $IrCl_3$ and pr^iPSH in refluxing methanol in a 1:3 molar ratio yields complex $[Ir(pr^iPS)_3]$ (1) as a bright yellow powder in good yield. Complex (1) is stable both in solution and in the solid state. The infrared and multinuclear NMR experiments performed confirm the proposed formulation. FAB

Mass Spectrometry (FAB MS) and elemental analysis results were also consistent with the proposed formulation. Complex (1) is soluble in most of the common solvents but insoluble in methanol, pentane and diethylether. The infrared spectrum of (1) shows a group of absorptions at 2872-3093 and 1416-1470 cm⁻¹ assigned, respectively, to the stretching and deformation vibration modes of the isopropyl groups in the molecule. Additional bands at 701-738 and 1548-1574 cm^{-1} are due to the stretching vibrations of the aromatic rings. The ¹H NMR exhibits a group of signals in the usual area for the aromatic protons, additional signals at 2.3–3.2 (CH) and 0.8–1.9 ppm (CH₃) are assigned to the protons in the isopropyl groups. The signals observed between 0.8 and 1.9 ppm can be separated in two groups, one consisting of signals at 0.8-1.1 and 1.7-1.9 ppm and the other of multiplets at 1.2–1.4 and 1.4–1.65 ppm. The ratio between these two groups of signals is 1:2, which is in agreement with a mer configuration. In terms of symmetry it is evident that there is no plane of symmetry since four different types of methyl groups are observed. However, according to the complexity of the signals there is some free rotation about the P-C bond. The ³¹P NMR only shows three groups of broad signals at 15.88, 9.80 and 7.94 ppm. Still, these signals can be assigned to three non-equivalent phosphorus nuclei, as expected for the structure suggested. Assignment of these broad signals can be done analogously with that of the previously reported compound $[Ir(phPS)_3]$ [18], where the two signals at higher field are assigned to the *trans*-P atoms and the one at lower field to the phosphorus trans to sulfur. The FAB MS shows the molecular ion $[M]^+$ at



Fig. 2. An ORTEP representation of the structure of $[Rh(H)(phPS_2)-(CO)(PPh_3)]$ (2) at 50% of probability showing the atom labelling scheme.

868 m/z, another peak at 643 m/z, due to the loss of one $pr^{i}PS^{-}$ ligand and the most intense peak at 225 m/z corresponding to the molecular weight for one molecule of ligand $[pr^{i}PS]^{+}$.

3.2. X-ray crystal structure of $[Ir(pr^iPS)_3]$ (1)

Crystals of complex (1) were obtained from a double layer solvent system of CH₂Cl₂/MeOH as bright yellow prisms. The X-ray crystal structure (Fig. 1) shows the Ir to be in a slightly distorted octahedral arrangement. The three P and S atoms occupy meridional sites. The central Ir-P(1) bond is shorter and the central Ir-S(3)bond [*trans* to Ir-P(1)] is longer than others of the same type, suggesting an enhanced trans influence of the central Ir-P(1) bonds on the central Ir-S(3) bonds. The same is not true for the d^4 complexes of $[Tc(phPS)_3]$ and $[\text{Re}(phPS)_3]$ [19]. In other respects the bond distances are normal and the angles in the coordination octahedron are all close to 90 or 180°. The chelation of the PS ring systems varies slightly and this can be attributed to the fact that the Ir atom lies out of the least-square planes of the P-C-C-S units by different amounts. This is similar, but not as marked as, the differences found in the structures of $[Tc(phPS)_3]$ and $[Re(phPS)_3]$ analogues. The chelated rings are distinguishable, and may be classified as (c, e), (e, c) and (e, e) according to whether the P and the S atoms are central (c) or end-positioned (e) in the mer configuration. The (e, c) chelate ring shows both the smallest bite angle at Ir and the longest Ir-P(3) and Ir-S(3) distances within one chelate ring, and the greatest displacement of the chelate ring of Ir. As is the case in $[Ir(phPS)_3]$ it has to be assumed that the ligands (c, e) and (e, e) are affected either by steric or by very sensitive electronic factors. In the $[Tc(phPS)_3]$ and $[Re(phPS)_3]$ complexes the (c, e) ligands show the longest M-P and M-S distances and the smallest bite angles. This suggests strongly that the electron configuration of the metal (d^4 for Tc and Re, d^6 for Ir) plays a significant role in the details of the geometry. In the case of (1), as there was no variation of the geometry after changing phenyls by isopropyl on the phosphorus it has to be concluded that electronic rather than steric effects govern the details of the geometry.

3.3. Synthesis and characterisation of $[Rh(H)(phPS_2)(CO)(PPh_3)]$ (2) and $[Rh(H)(ePS_2)(CO)(PPh_3)]$ (3)

Reaction of equivalent amounts of *trans*- $[RhF(CO)(PPh_3)_2]$ and the proligand $(phPS_2H_2)$ in toluene, yield complex **2** as a brown–reddish powder, in good yield. Similar reaction with the proligand ePS_2H_2 at low temperature (-78 °C) affords complex **3** as a yellow powder. For both complexes elemental analysis,



Scheme 1. Proposed interconversion mechanism in solution for the complex $[Rh(H)(phPS_2)(CO)(PPh_3)]$ (2).



Scheme 2. Proposed mechanism for the formation of complex $[Rh(H)(phPS_2)(CO)(PPh_3)]$ (2).

IR and NMR spectroscopic and FAB MS experiments were performed to confirm the proposed formulations. Complexes 2 and 3 are stable in the solid state in air, but decompose in solution under aerobic conditions. The IR spectra show absorptions at 2049 cm⁻¹ for 2 and 2057 cm⁻¹ for **3**, which are assigned to the hydride vibrations Rh-H. Absorptions corresponding the C=O stretching vibrations are observed at 1979 and 1965 cm^{-1} for complexes 2 and 3, respectively. Other absorptions at 690-740 and 1570 cm⁻¹ are due to the aromatic rings. For both complexes ¹H NMR exhibits multiplets at 6.6–8.6 ppm due to the aromatic protons, and for complex 3 an additional group of broad signals at 0.9 and 3.0 ppm assigned to the methylene groups is observed. In both cases, no signals due to hydride were detected. This may be due to a fast decomposition process or to a fluxional behaviour where one of the S groups originally bonded to the metal centre is converted to free (or bond) SH by a hydride shift, with or without loss of phosphine 11b (Scheme 1). NMR experiments carried out at temperatures as low as -60 °C, still show broad signals in both the ¹H and the ³¹P spectra, suggesting that if there is any fluxional behaviour it should be very fast. However, in view of the

observation of peaks at 30.7 and -4.0 ppm (OPPh₃ and PPh₃) in the ³¹P NMR the simplest explanation is that there is substantial decomposition to Rh(III) or paramagnetic Rh(II) species. Same behaviour is observed for complex **3** with broad signals at 37.0–50.0 ppm in the ³¹P NMR spectrum. An additional signal at -4.1 ppm corresponding to free PPh₃ complement the theory of a decomposition process in solution. The FAB MS shows a strong peak at 689 m/z which corresponds to the fragment [M – (H + CO)]⁺. Another peak due to the loss of a PPh₃ molecule is observed at 427 m/z, in agreement with the proposed formulations. The proposed mechanism of formation and proposed structure for complex **2** is shown in Scheme 2.

3.4. X-ray crystal structure of [Rh(H)(phPS₂)(CO)(PPh₃)] (2)

Crystals for X-ray crystal structure experiments were obtained from a double layer solvent system of $CH_2Cl_2/$ MeOH as red prisms. The crystals were of relatively poor quality, and although, the coordination about the metal was established unequivocally, it is not appropriate to discuss bond lengths or angles. The structure of **2** (Fig. 2) can be described as a distorted square pyramid where the vacant site is presumed occupied by the hydride ligand. The coordination sphere is completed by CO, PPh₃, and the tridentate ligand *ph*PS₂.

3.5. Synthesis and characterisation of $[Ir(H)(phPS_2)(CO)(PPh_3)]$ (4) and $[Ir(H)(ePS_2)(CO)(PPh_3)]$ (5)

In analogous procedure to that used to prepare complex 2, compounds 4 and 5 were obtained. The IR and ¹H, ³¹P NMR spectroscopic studies as well as elemental analysis and FAB MS were performed to confirm the proposed formulations. Both complexes are stable in the solid state and in solution. The IR spectra of complexes 4 and 5 show weak absorptions due to the presence of hydride ligands at 2100 and 2119 cm⁻¹, respectively. Other strong absorptions observed at 2026 or at 2016 cm⁻¹ correspond to the C=O stretching vibrations. Additional signals due to the aromatic rings are observed at 668-813 and 1572 cm⁻¹. The ¹H NMR of 4 shows signals for the aromatic rings between 6.7 and 7.7 ppm and a triplet at high field due to the hydride, with a P-H coupling constant value consistent with a cis arrangement of the hydride relative to the P donors $({}^{2}J_{H-P} = 11.74 \text{ Hz})$. For complex 5, the ${}^{1}\text{H}$ NMR spectrum exhibits a multiplet at 6.9-8.0 ppm for the aromatic protons, additional series of broad signals at 0.8-3.0 ppm assigned to the CH₂ groups. In this case no signal for a hydride was observed. The ³¹P NMR of complex 4 shows two doublets at 58.09 and 4.36 ppm, both with a coupling constant ${}^{2}J_{P-P} = 297.1$ Hz. The ${}^{31}P$ NMR spectrum of **5** shows the same pattern as that of **4**, with two doublets being located at 48.50 and 43.15 ppm having equivalent coupling constants of ${}^{2}J_{P-P} =$ 169.8 Hz. In both cases this pattern is in accordance with a complex with two non-equivalent mutually *trans* phosphorus nuclei. The FAB MS of complex **4** shows the molecular ion at 778.8 m/z [M^+ –(CO + H)]. Another peak due to the further loss of PPh₃ is observed at 516.8 m/z. For complex **5** the FAB MS shows peaks at 711 and 420 m/z assigned respectively to [M–H]⁺ and [M–(CO + H + PPh₃)]⁺.

4. Supplementary material

Supplementary data for complexes 1 and 2 have been deposited at the Cambridge Crystallographic Data Centre. Copies of this information are available free of charge on request from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk) quoting the deposition numbers CCDC 150 082 and 150 083, respectively.

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