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P–C and C–H bond cleavages of dppm in the thermal reaction of [Ru3(CO)10(μ-dppm)] with benzothiophene: X-ray structures of [Ru6(μ-CO)(CO)13{μ4-PhP(C6H4)PPh}(μ6-C)] and [Ru4(CO)9(μ3-η2-PhPCH2PPh2)(μ4-η6:η1:η1-C6H4)(μ-H)]

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Abstract

The thermal reaction of $[Ru_3(CO)_{10}(\mu\text{-dppm})]$ (**1**) with benzothiophene in refluxing toluene gives a complex mixture of products. These include the known compounds $[Ru_2(CO)_6\{\mu\text{-}CH_2PPh(C_6H_4)PPh\}]$ (**2**), $[Ru_2(CO)_6\{\mu\text{-}C_6H_4PPh(CH_2)PPh\}]$ (**3**), $[Ru_3(CO)_9\{\mu_3\text{-}\eta^3\text{-}(Ph)PCH_2P(Ph)C_6H_4\}]$ (**4**) and $[Ru_3(CO)_{10}\{\mu\text{-}\eta^2\text{-}PPh(CH_2)(C_6H_4)PPh\}]$ (**6**), as well as the new clusters $[Ru_6(\mu\text{-CO})(CO)_{13}\{\mu_3\text{-}\eta^2\text{-}PhP(C_6H_4)PPh\}(\mu_6\text{-C})]$ (**5**) and $[Ru_4(CO)_9(\mu_3\text{-}\eta^2\text{-}PhPCH_2PPh_2)(\mu_4\text{-}\eta^6:\eta^1:\eta^1\text{-}C_6H_4)(\mu\text{-H})]$ (**7**). The solid-state molecular structures of **5** and **7** were confirmed by single crystal X-ray analyses. Compound **5** consists of interesting example of a hexaruthenium interstitial carbido cluster having a tetradentate diphosphine ligand derived from the activation of P–C and C–H bonds of the dppm ligand in **1**. The tetranuclear compound **7** consists of a unique example of a non-planar spiked triangular metal fragment of ruthenium [Ru(1), Ru(2) and Ru(3)] unit with Ru(4) being bonded to Ru(1). The $\mu_4\text{-}\eta^1:\eta^6:\eta^1$-benzyne ligand in this compound represents a previously uncharacterized bonding mode for benzyne. Compounds **5** and **7** do not contain any benzothiophene-derived ligand. The reaction of **4** with benzothiophene gives **2**, **3**, **5** and **6**. Thermolysis of **1** in refluxing toluene gives **2**, **3** and **4**; none of **5** and **7** is detected in reaction mixture.

Graphical abstract

The thermal reaction of $[Ru_3(CO)_{10}(\mu\text{-dppm})]$ (**1**) with benzothiophene in toluene gave a mixture of products. Four previously reported compounds $[Ru_2(CO)_6\{\mu\text{-}CH_2PPh(C_6H_4)PPh\}]$ (**2**), $[Ru_2(CO)_6\{\mu\text{-}C_6H_4PPh(CH_2)PPh\}]$ (**3**), $[Ru_3(CO)_9\text{-}\{\mu_3\text{-}\eta^3\text{-}(Ph)PCH_2P(Ph)C_6H_4\}]$ (**4**) and $[Ru_3(CO)_{10}\{\mu\text{-}\eta^2\text{-}PPh(CH_2)(C_6H_4)PPh\}]$ (**6**) and two new clusters $[Ru_6(\mu\text{-CO})(CO)_{13}\{\mu_3\text{-}\eta^2\text{-}PhP(C_6H_4)PPh\}(\mu_6\text{-C})]$ (**5**) and $[Ru_4(CO)_9(\mu_3\text{-}\eta^2\text{-}PhPCH_2PPh_2)(\mu_4\text{-}\eta^6:\eta^6:\eta^6\text{-}C_6H_4)(\mu\text{-H})]$ (**7**) were obtained from the reaction of $[Ru_3(CO)_{10}(\mu\text{-dppm})]$ (**1**) with benzothiophene at 110 °C.

Keywords

1. Introduction
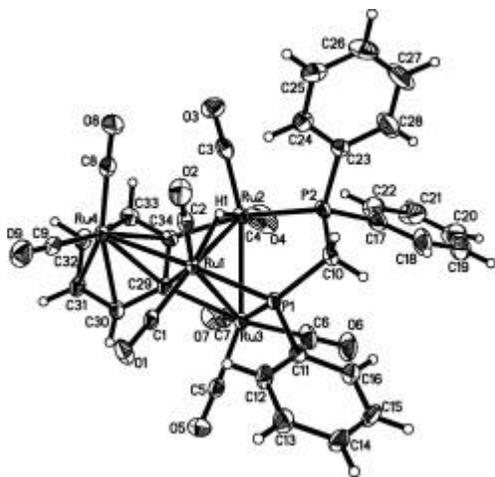
During the past decade, considerable attention has been devoted to the synthesis and reactivity of osmium and ruthenium carbonyl clusters bearing sulfur-containing ligands such as thiophene, benzothiophene and dibenzothiophene which are common sulfur containing contaminants in petroleum feedstocks.[1, 2, 3, 4, 5, 6, 7] Of these sulfur-containing molecules, benzothiophene is of particular interest because its alkylated derivatives are more difficult to desulfurize than thiophene itself. Arce and co-workers reported that $[Ru_3(CO)_{12}]$ reacts with benzothiophene in refluxing THF to produce two di- and one trinuclear complexes, $[Ru_3(CO)_8(\mu\text{-}C_8H_6)]$, $[Ru_2(CO)_6(\mu\text{-}C_8H_6S)]$ and $[Ru_2(CO)_6(\mu\text{-}C_8H_6)]$, all of which contain ring-opened or desulfurized benzothiophene ligands.[1] Recently, García et al. demonstrated that $[Ru_3(CO)_{12}]$ reacts with dibenzothiophene at 98 °C to give the dinuclear complex $[Ru_2(C_{12}H_8)(CO)_5(\mu\text{-}CO)]$, by a double C–S bond activation–desulfurization process.[6] The lightly stabilized osmium cluster $[Os_3(CO)_{10}(MeCN)_2]$ reacts with thiophene and benzothiophene to give a series of Os-thiophene complexes in which the thiophene has undergone bond cleavage to give C–S and C–H bond activated products. For example, $[Os_3(CO)_{10}(MeCN)_2]$ reacts with benzothiophene at ambient temperature to give $[Os_3(CO)_{10}(\mu\text{-}C_8H_5S)(\mu\text{-}H)]$ and $[Os_3(CO)_9(\mu_3\text{-}C_8H_4S)(\mu\text{-}H)_2]$; whereas, at elevated temperature (80 °C) an additional ring-cleaved complex, $[Os_3(CO)_{10}(\mu\text{-}C_8H_6S)]$, is also obtained.[2,5] Arce et al. have reported that $[Os_3(CO)_{10}(MeCN)_2]$ reacts with dibenzothiophene in refluxing cyclohexane to affords only one product, the nonacarbonyl species $[Os_3(CO)_9(\mu_3\text{-}C_{12}H_6S)(\mu\text{-}H)_2]$.[3] Recently, we have demonstrated that the unsaturated triosmium cluster $[(\mu\text{-}H)Os_3(CO)_8\{\mu_3\text{-}\eta^2\text{-}Ph_2PCH_2P(Ph)C_6H_4\}]$ reacts with benzothiophene at 139 °C to give three triosmium compounds, $[Os_3(CO)_7(\mu\text{-}PPh_2)(\mu\text{-}PMePh)(\mu_3\text{-}\eta^2\text{-}C_6H_4)]$, $[Os_3(CO)_8(\mu\text{-}CO)(\mu_3\text{-}\eta^2\text{-}PPh(C_6H_4)CH_2PPh)]$ and $[Os_3(CO)_7(\mu_3\text{-}\eta^2\text{-}PPh(C_6H_4)CH_2PPh)(\mu_3\text{-}\eta^3\text{-}C_8H_5S)(\mu\text{-}H)]$[7]; the first two of which are derived from the activation of P–C and C–H bonds of the diphosphine ligand and do not contain any benzothiophene-derived ligand; whereas, the last compound contains an unusual $\mu_3\text{-}\eta^2$-benzothienyl ligand (Scheme 1). It is well documented that in addition to their ability to maintain the metal cluster framework intact during chemical reactions the dppm ligand in $[Ru_3(CO)_{10}(\mu\text{-}dppm)]$ (**1**) can also undergo C–H and P–C bond cleavage and M–H and M–C bond forming reactions to give many interesting reactions.[8, 9, 10, 11] Adams et al. reported the thermal transformation of the coordinated PMe_2Ph ligands in $[Ru_6(CO)_{15}(PMe_2Ph)(\mu_6\text{-}C)]$ to give a series of interesting hexaruthenium carbide complexes $[Ru_6(CO)_{13}(PMe_2)(\mu_3\text{-}\eta^3\text{-}Me_2PC_6H_4)(\mu_6\text{-}C)]$, $[Ru_6(CO)_{14}(PMe_2Ph)(\mu\text{-}\eta^2\text{-}MePhPCH_2)(\mu_6\text{-}C)(\mu\text{-}H)]$, $[Ru_6(CO)_{14}(\mu\text{-}PMe_2)(\mu\text{-}\eta^2\text{-}MePhPCH_2)(\mu_6\text{-}C)]$, and $[Ru_6(CO)_{12}(\mu\text{-}PMe_2)_2(\mu_3\text{-}\eta^2\text{-}C_6H_4)(\mu_6\text{-}C)]$ via C–H and P–H bond cleavages.[12]
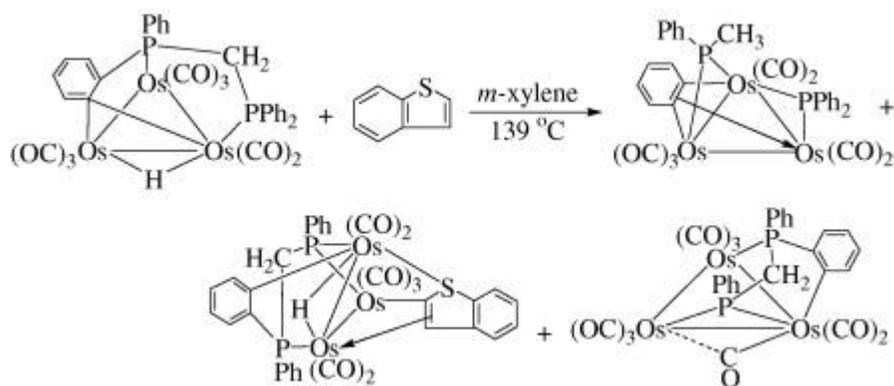
Scheme 1.

As part of our on going studies on reactions of thiophenic ligands with metal carbonyl clusters we set out to investigate the reactivity of **1** with benzothiophene. Unfortunately, the reaction does not appear to give any benzothiophene derived product, instead oxidative addition of P–C and C–H bonds of the dppm ligand occurs together with aggregation of the cluster producing the carbido cluster [$Ru_6(\mu$-CO)(CO)$_{13}\{\mu_3$-η^2-PhP(C$_6$H$_4$)PPh$\}(\mu_6$-C)] (**5**) and tetraruthenium cluster [$Ru_4(CO)_9(\mu_3$-η^2-PhPCH$_2$PPh$_2$)(μ_4-η^1:η^6:η^1-C$_6$H$_4$)(μ-H)] (**7**) containing μ_4-η^6:η^1:η^1-benzyne ligand.

2. Experimental

All the reactions were performed under a nitrogen atmosphere, using standard Schlenk techniques. Solvents were dried and distilled prior to use by standard methods. Benzothiophene was purchased from Aldrich and used as received. The starting cluster [$Ru_3(CO)_{10}(\mu$-dppm)] (**1**) was prepared according to the literature procedure.[13] Infrared spectra were recorded on a Shimadzu FTIR 8101 spectrophotometer. ^{1}H and ^{31}P{H} NMR spectra were recorded on Varian Unity Plus 500 spectrometer. Chemical shifts for the ^{31}P{H} NMR spectra are relative to 85% H$_3$PO$_4$. Fast atom bombardment mass spectra were obtained on a JEOL SX-102 spectrometer using 3-nitrobenzyl alcohol as matrix and CsI as calibrant.

2.1. Reaction of [Ru$_3$(CO)$_{10}$(μ-dppm)] (1) with benzothiophene

A mixture of **1** (200 mg, 0.21 mmol) and benzothiophene (60 mg, 0.45 mmol) in toluene (30 mL) was heated to reflux under nitrogen for 40 min. The solvent was removed under reduced pressure and the residue chromatographed by TLC on silica gel. Elution with cyclohexane/CH$_2$Cl$_2$ (9:1, v/v) developed six bands. The first, second and the third bands gave the known compounds [$Ru_2(CO)_6\{\mu$-CH$_2$PPh(C$_6$H$_4$)PPh$\}$] (**2**) (20 mg, 9%), [$Ru_2(CO)_6\{\mu$-C$_6$H$_4$PPh(CH$_2$)PPh$\}$] (**3**) (21 mg, 10%) and [$Ru_3(CO)_9\{\mu_3$-η^3-(Ph)PCH$_2$P(Ph)C$_6$H$_4\}$] (**4**) (32 mg, 18%), respectively. The fourth band gave the new compound [$Ru_6(\mu$-CO)(CO)$_{13}\{\mu_3$-η^2-PhP(C$_6$H$_4$)PPh$\}(\mu_6$-C)] (**5**) (19 mg, 14%) as red crystals after recrystallization from hexane/CH$_2$Cl$_2$ at −4 °C. Anal. Calc. for C$_{33}$H$_{14}$O$_{14}$P$_2$Ru$_6$: C, 30.42; H, 1.08. Found: C, 30.61, H, 1.22%. IR (v(CO), KBr): 2070 s, 2019 vs, 2001 s, 1956 w, 1886 w, cm^{-1}; ^{1}H NMR (CDCl$_3$): δ 7.61–7.71 (m, 2H), 7.51

(m, 10H), 7.26–7.38 (m, 2H). $^{31}P\{^1H\}$ NMR (CD$_2$Cl$_2$): δ 165.5 (s). MS (FAB): m/z 1304 (M$^+$). The fifth band gave the known compound [Ru$_3$(CO)$_{10}$\{μ-η^2-PPh(CH$_2$)(C$_6$H$_4$)PPh\}] (**6**) (6 mg, 3%), while the slowest moving band afforded the new compound [Ru$_4$(CO)$_9$(μ_3-η^2-PhPCH$_2$PPh$_2$)(μ_4-η^6:η^1:η^1-C$_6$H$_4$)(μ-H)] (**7**) (24 mg, 15%) as yellow crystals after recrystallization from hexane/CH$_2$Cl$_2$ at −4 °C. Anal. Calc. for C$_{34}$H$_{21}$O$_9$P$_2$Ru$_4$: C, 39.28; H, 2.04. Found: C, 39.45, H, 2.12%. IR (ν(CO), CH$_2$Cl$_2$): 2055 s, 2027 vs, 2007 vs, 1986 s, 1963 w, 1946 w, 1932 w cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$): δ 7.21–7.71 (m, 15H), 6.62(m, 1H), 6.55 (m, 1H), 5.40 (m, 1H), 5.24 (m, 1H), 4.20 (m, 1H), 4.05 (m, 1H), −18.18 (dd, 1H, J = 10.4, 4.4 Hz). $^{31}P\{^1H\}$ NMR (CD$_2$Cl$_2$): δ 19.5 (d, J = 103.9 Hz), 115.5 (d, J = 103.9 Hz). MS (FAB): m/z 1042 (M$^+$).

2.2. Reaction of 4 with benzothiophene

A toluene solution (30 mL) of **4** (100 mg, 0.12 mmol) and benzothiophene (32 mg, 0.24 mmol) was refluxed for 30 min. The solvent was removed under reduced pressure and the residue chromatographed by TLC on silica gel. Elution with hexane/CH$_2$Cl$_2$ (9:1, v/v) developed four bands, which afforded **2** (0.018 g, 9%), **3** (0.016 g, 8%), **4** (0.022 g, 11%) and **5** (0.012 g, 6%).

2.3. Thermolysis of 1

A toluene solution (30 mL) of **1** (200 mg, 0.21 mmol) was heated to reflux under nitrogen for 40 min. A similar workup and chromatographic separation as above afforded **2** (30 mg, 21%), **3** (23 mg, 7%) and **4** (82 mg, 46%), respectively.

2.4. Thermolysis of 4

A similar thermolysis to that above of **4** (100 mg, 0.12 mmol) in toluene (30 mL) followed by similar chromatographic separation gave **2** (13 mg, 16%), **3** (10 mg, 13%) and unconsumed **4** (25 mg), respectively.

2.5. X-ray crystallography

Single crystals of compounds **5**, **6** and **7** were mounted on a Nylon fiber with mineral oil, and diffraction data were collected at 100(2) K on a Bruker AXS SMART diffractometer equipped with an APEXII CCD detector using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Integration of intensities and data reduction were performed using SAINTprogram.[15] Multi-scan absorption correction was applied for compounds **6** and **7** using SADABS procedure;[16] whereas, numerical absorption correction was applied for compound **5** based on the real shape of the crystal.[17a]

The structures were solved by direct methods[17b] and refined by full-matrix least-squares on F^2.[17c] All non-hydrogen atoms were refined anisotropically. Positions of hydrogen atoms were calculated geometrically and were included into refinement with B(iso) = 1.2B(iso/eq) of an adjacent carbon atom

using a riding model. The bridging hydride atom was localized in a difference Fourier map and was positionally refined in isotropic approximation.

All crystal data along with experimental conditions and refinement details are summarized in Table 1.

Table 1. Crystallographic data and structure refinement[a] for **5**, **6** and **7**

Compound	5	6	7
Empirical formula	$C_{33}H_{14}O_{14}P_2Ru_6$	$C_{29}H_{16}O_{10}P_2Ru_3 \cdot CH_2Cl_2$	$C_{34}H_{22}O_9P_2Ru_4 \cdot (CH_2Cl_2)_{0.08}$
Formula weight	1302.80	974.49	1047.70
Crystal system	Tetragonal	Triclinic	Monoclinic
Space group	$P4/n$	$P\bar{1}$	$P2_1/c$
a (Å)	26.402(1)	12.906(3)	34.254(4)
b (Å)	26.402(1)	17.049(4)	9.055(1)
c (Å)	10.943(1)	18.410(4)	37.856(4)
α (°)	90	62.921(3)	90
β (°)	90	81.674(3)	115.167(2)
γ (°)	90	70.302(3)	90
Volume (Å³)	7628.0(10)	3395.6(1)	1062.7(2)
Z	8	4	12
D_{calc} (Mg/m³)	2.269	1.906	1.964
μ (Mo Kα) (mm⁻¹)	2.465	1.623	1.828
$F(000)$	4944	1896	6089
Crystal size (mm)	0.25 × 0.06 × 0.05	0.40 × 0.10 × 0.06	0.55 × 0.08 × 0.05
ϑ Range (°)	2.01–31.92	1.41–31.94	1.31–32.06
Index ranges	$-27 \leqslant h \leqslant 27, 0 \leqslant k \leqslant 38, 0 \leqslant l \leqslant 16$	$-18 \leqslant h \leqslant 18, -21 \leqslant k \leqslant 25, 0 \leqslant l \leqslant 27$	$-50 \leqslant h \leqslant 45, 0 \leqslant k \leqslant 13, 0 \leqslant l \leqslant 56$
Reflections collected	125 706	55 288	174 339
Independent reflections (R_{int})	12 798 (0.0538)	21 560 (0.0282)	34 988 (0.0522)
Maximum and minimum transmission	0.8867 and 0.5777	0.9089 and 0.5629	0.9141 and 0.4330
Data/restraints/parameters	12798/0/502	21560/22/886	34988/0/1364
Goodness-of-fit on F^2	0.979	1.027	1.175
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0308$, $wR_2 = 0.0532$	$R_1 = 0.0284$, $wR_2 = 0.0629$	$R_1 = 0.0570$, $wR_2 = 0.1009$
R indices (all data)	$R_1 = 0.0496$, $wR_2 = 0.0567$	$R_1 = 0.0385$, $wR_2 = 0.0667$	$R_1 = 0.0738$, $wR_2 = 0.1059$

Compound	5	6	7
Largest difference in peak and hole (e Å⁻³)	1.068 and −0.887	0.982 and −0.744	1.716 and −1.260

[a]Details in common: X-radiation, Mo Kα (λ = 0.71073 Å), temperature (K) 100(2), refinement method: full-matrix least-squares on F^2. The molecular formula for **7** in the cif file has a 3:1 ratio of compound:solvent. The PLATON program, which is used to check cif files immediately detects that the solvent has only 24% population (because 76% of its stoichiometric amount was gone over time) and insists on 12:1 ratio compound:solvent as a result.

3. Results and discussion

The reaction of [$Ru_3(CO)_{10}(\mu$-dppm)] (**1**) with benzothiophene in refluxing toluene, followed by chromatographic separation, gave the previously reported compounds [$Ru_2(CO)_6\{\mu$-$CH_2PPh(C_6H_4)PPh\}$] (**2**), [$Ru_2(CO)_6\{\mu$-$C_6H_4PPh(CH_2)PPh\}$] (**3**), [$Ru_3(CO)_9\{\mu_3$-η^3-$(Ph)PCH_2P(Ph)C_6H_4\}$] (**4**), [$Ru_3(CO)_{10}\{\mu$-η^2-$PPh(CH_2)(C_6H_4)PPh\}$] (**6**) together with the new hexanuclear compound [$Ru_6(\mu$-$CO)(CO)_{13}\{\mu_4$-$PhP(C_6H_4)PPh\}(\mu_6$-$C)$] (**5**) and the tetranuclear compound [$Ru_4(CO)_9(\mu_3$-η^2-$PhPCH_2PPh_2)(\mu_4$-η^1:η^6:η^1-$C_6H_4)(\mu$-$H)$] (**7**) in 9, 10, 18, 3, 14 and 15% yields, respectively (Scheme 2).
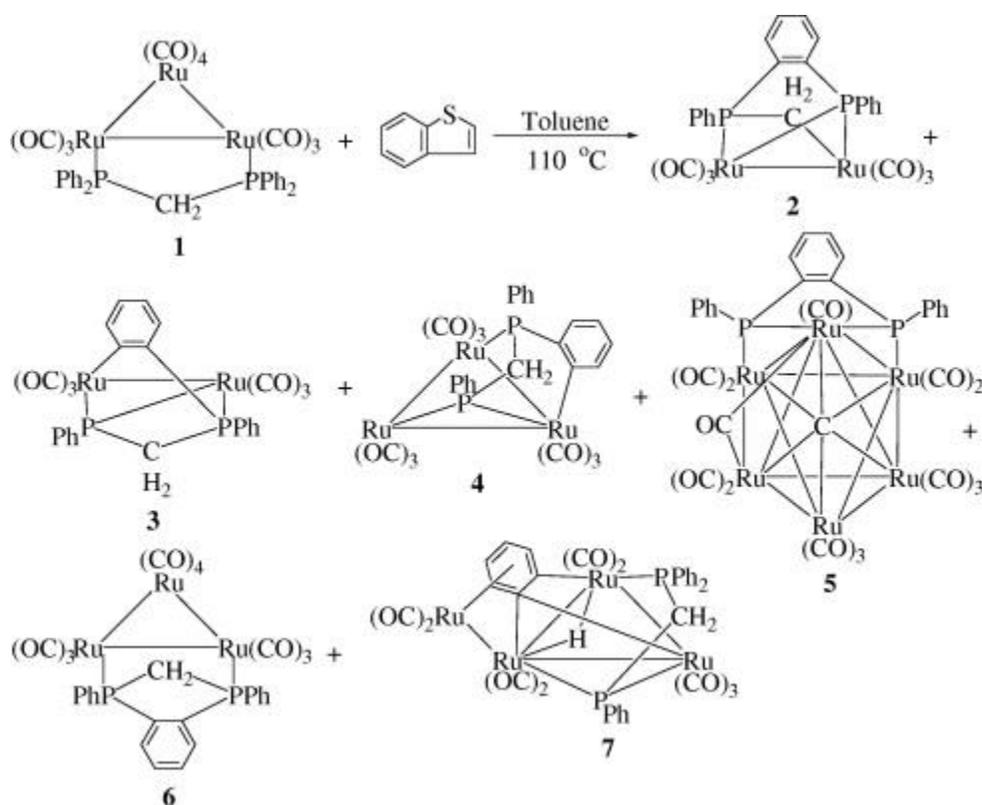
Scheme 2.

Compounds **2**, **3**, **4** and **6** were previously characterized by spectroscopic data and single crystal X-ray diffraction studies.[8a, 11, 14] We have characterized the known compounds by comparing the

spectroscopic data with those reported[8a, 11] and the new compounds **5** and **7** by a combination of spectroscopic data and X-ray diffraction studies.

The solid-state molecular structure of **5** is depicted in Fig. 1, crystal data are given in Table 1 and selected bond distances and angles are listed in Table 2. The metal framework consists of an octahedral arrangement of six ruthenium atoms with an interstitial carbon atom occupying the central cavity. The carbonyl polyhedron of **5** is made up 13 terminal carbonyl ligands, together with a semi-bridging CO predominantly bound to Ru(4) with a secondary interaction to Ru(1). The Ru–Ru bond distances lie in the range 2.8134(3)–2.9990(4) Å {average 2.8984(3) Å}, the relatively shorter Ru–Ru bonds corresponds to the phosphido bridging edges {Ru(1)–Ru(3) = 2.8134(3), Ru(1)–Ru(2) = 2.8137(3) Å} in fairly good agreement with those reported for the hexanuclear cluster [(μ_6-C)Ru$_6$(CO)$_{13}$(μ-η^5:η^3-C$_5$H$_4$C{CH$_2$})] and [Ru$_6$(CO)$_{14}$(μ-η^5:η^3-C$_5$H$_4$CH$_2$)(μ_6-C)].[18] The Ru–C(carbido) distances average 2.050(2) Å, these values being typical to those found in [Ru$_6$(CO)$_{17}$(μ_6-C)].[19] The carbido ligand does not lie in the exact center of the Ru$_6$ octahedron but is shifted closer to the Ru(6) atom {Ru(6)–C(0) = 2.013 (2) Å}.
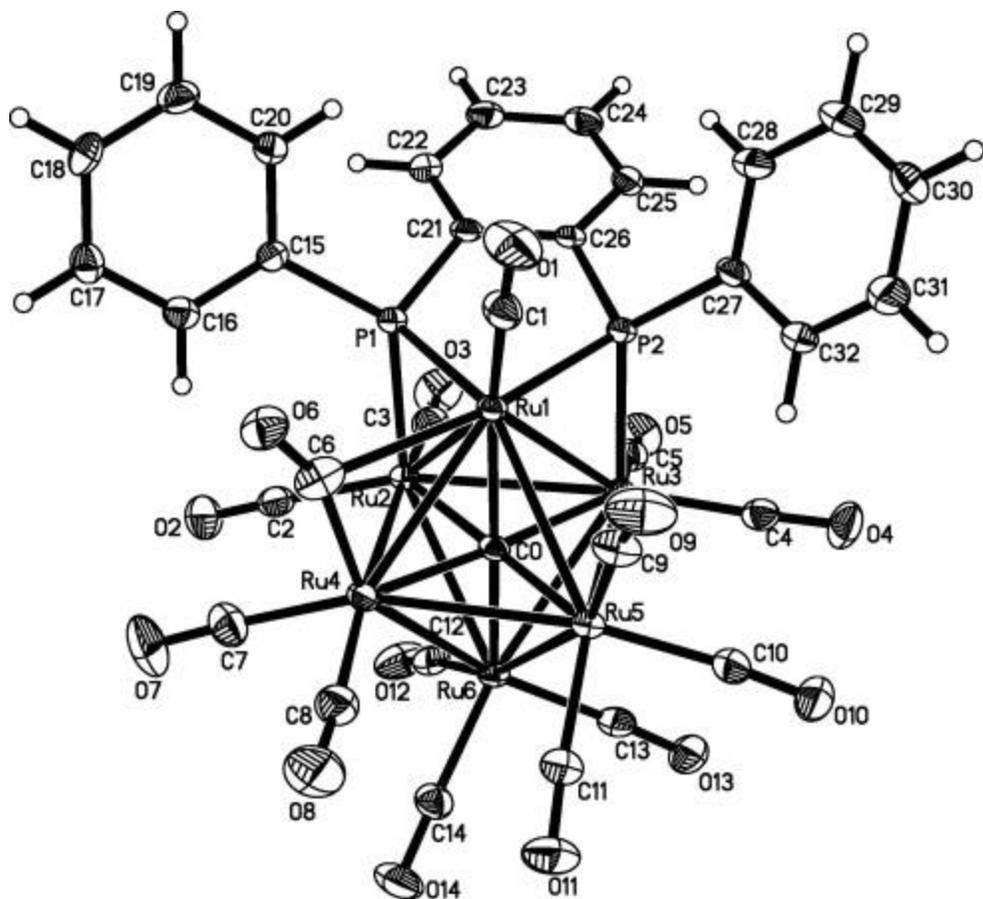

Fig. 1. The solid-state molecular structure of [Ru$_6$(μ-CO)(CO)$_{13}${μ_4-PhP(C$_6$H$_4$)PPh}(μ_6-C)] **(5)**.

Table 2. Selected bond lengths (Å) and angles (°) for $[(\mu_6\text{-C})Ru_6(\mu\text{-CO})(CO)_{13}\{\mu_4\text{-PhP}(C_6H_4)PPh\}]$ (**5**)

Ru(1)–C(0)	2.061(2)	Ru(3)–C(0)	2.066(3)
Ru(1)–P(1)	2.2311(7)	Ru(3)–P(2)	2.2906(7)
Ru(1)–P(2)	2.2394(7)	Ru(3)–Ru(5)	2.9255(3)
Ru(1)–C(6)	2.582(3)	Ru(3)–Ru(6)	2.9681(4)
Ru(1)–Ru(3)	2.8134(3)	Ru(4)–C(6)	1.945(3)
Ru(1)–Ru(2)	2.8137(3)	Ru(4)–C(0)	2.049(3)
Ru(1)–Ru(4)	2.8885(4)	Ru(4)–Ru(5)	2.8712(4)
Ru(1)–Ru(5)	2.9990(4)	Ru(4)–Ru(6)	2.9076(3)
Ru(2)–C(0)	2.060(3)	Ru(5)–C(0)	2.050(3)
Ru(2)–P(1)	2.3091(7)	Ru(5)–Ru(6)	2.8426(3)
Ru(2)–Ru(4)	2.9057(3)	Ru(6)–C(0)	2.013(2)
Ru(2)–Ru(6)	2.9159(4)	Ru(2)–Ru(3)	2.9292(3)
P(1)–Ru(1)–P(2)	84.90(3)	Ru(6)–Ru(2)–Ru(3)	61.032(8)
P(1)–Ru(1)–C(6)	89.04(7)	Ru(5)–Ru(6)–Ru(4)	59.898(8)
C(6)–Ru(1)–Ru(4)	41.17(7)	Ru(5)–Ru(4)–Ru(2)	90.702(8)

The most interesting feature of the structure is the mode of coordination of the diphosphine ligand, PhP(C₆H₄)PPh, formed by cleavage of P–C and C–H bonds of the dppm ligand, along the Ru(1)–Ru(2) and Ru(1)–Ru(3) edges. This ligand, sits on top of the hexametallic framework so that the P_1 atom asymmetrically bridges the Ru(1)–Ru(2) edge {Ru(1)–P(1) = 2.2311(7) and Ru(2)–P(1) = 2.3091(7) Å} while the P_2 atom asymmetrically bridges the Ru(1)–Ru(3) edge {Ru(1)–P(2) = 2.2394(7) and Ru(3)–P(2) = 2.2906(7) Å}. The transformations of the dppm ligand to $\mu\text{-}\eta^3\text{-CH}_2PPh(C_6H_4)PPh$,[12] $\mu\text{-}\eta^3\text{-C}_6H_4PPh(CH_2)PPh$,[14] $\mu_3\text{-}\eta^3\text{-(Ph)PCH}_2P(Ph)C_6H_4$[8] and $\mu_3\text{-}\eta^3\text{-CH}_2PPh$[11] from the pyrolysis of **1** have been described but the formation of PhP(C₆H₄)PPh provides a new example of a tetradentate ligand at a triruthenium center.

The spectroscopic data of **5** are consistent with the solid-state structure. The mass spectrum shows the molecular ion peak at *m/z* 1305. The infrared spectrum in KBr in the carbonyl stretching region shows absorption bonds at 2070 s, 2019 vs, 2001 s, 1986w, 1956 w, 1886 w cm⁻¹. The ¹H NMR spectrum of **5** shows multiplets at δ 7.31–7.81 for the phenyl protons of the diphosphine ligand. The ³¹P{¹H} NMR spectrum of **5** displays a singlet resonance at δ165.5 supporting that the ³¹P nuclei are equivalent, and as expected, the ³¹P chemical shifts of μ-P atoms are well downfield of 85% H₃PO₄, the large deshielding effect being typical for a phosphorus atom integrated in a five-membered metallacycle.[20, 21, 22]

We have determined the structure of **6** by single crystal X-ray diffraction studies at low temperature (100 K). A determination of the unit cell parameters indicated that the molecule had packed in a different unit cell than that reported by Lugan et al.[8] The solid-state molecular structure of **6** is depicted in Fig. 2, crystal data are given in Table 1 and selected bond distances and angles are listed in the caption. The structure consists of a trinuclear cluster of ruthenium atoms, where the Ru–Ru bond distances {Ru(1)–Ru(3) = 2.8455(6), Ru(1)–Ru(2) = 2.8670(6) and Ru(2)–Ru(3) = 2.8432(6) Å} and the Ru–P bond distances {Ru(1)–P(1) = 2.3130(7), Ru(2)–P(2) = 2.3231(7) Å} are in fairly good agreement with those reported previously.[8]
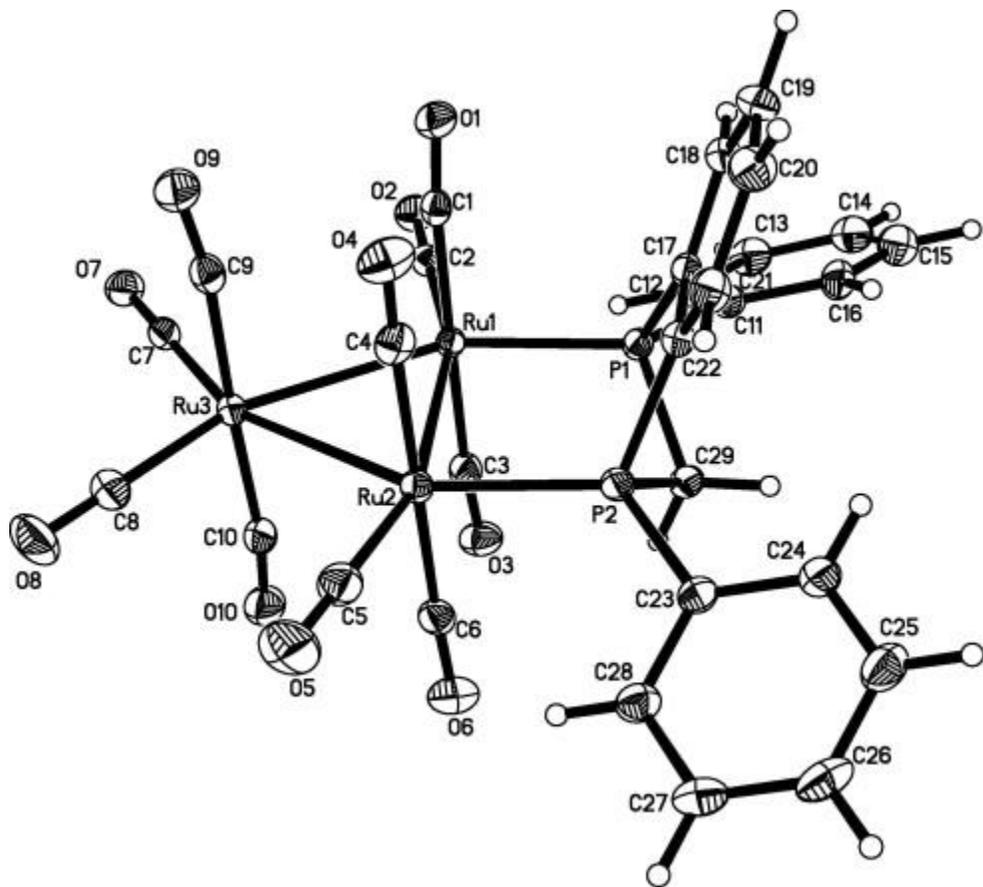

Fig. 2. The solid-state molecular structure of $[Ru_3(CO)_{10}\{\mu\text{-}\eta^2\text{-}PPh(CH_2)(C_6H_4)PPh\}]$ (**6**). Selected bond distances (Å) and angles (°). Ru(1)–P(1) 2.3130(7), Ru(2)–P(2) 2.3231(7), Ru(1)–Ru(3) 2.8455(6), Ru(1)–Ru(2) 2.8670(6), Ru(2)–Ru(3) 2.8432(6), P(1)–Ru(1)–Ru(3) 148.45(2), P(1)–Ru(1)–Ru(2) 88.76(2), P(2)–Ru(2)–Ru(3) 149.11 (2), P(2)–Ru(2)–Ru(1) 89.36(2), P(1)–C(29)–P(2) 98.01(1).

The unusual structure of **7** is confirmed by single crystal X-ray analysis. The molecular structure of one of the two independent molecules from the asymmetric unit of **7** is depicted in Fig. 3, crystal data are given in Table 1 and selected bond distances and angles are listed in Table 3. Due to close similarity of the two molecules, only one will be discussed. The tetranuclear cluster consists of a triangulotriruthenium {Ru(1), Ru(2) and Ru(3)} unit with Ru(4) being bonded to Ru(1). The structural

features of **7** are of interest from several points of view. According to the skeletal electron pair (SEP) theory,[23] eight electrons (4-SEP) are available for intermetallic bonding in **7**. Formal distribution of these electrons {4e-Ru(1); 2e-Ru(2); 2e-Ru(3)} implies that the formation of the Ru(1)–Ru(4) bond involves an interaction between a 'filled donor orbital' on Ru(4) and a 'vacant acceptor orbital' on Ru(1). The Ru_3core can be described as an isosceles triangle, the three metal–metal bonds being Ru(1)–Ru(2) = 2.9694(6), Ru(2)–Ru(3) = 2.8494(5) and Ru(1)–Ru(3) = 2.8476(5) Å. The organic ligands in **7** consists of nine terminal carbonyl ligands, two bonded to each of Ru(1), Ru(2), Ru(4) and three to Ru(3), a three-way bridging benzyne, a hydride and a bridging PPh_2CH_2PPh ligand. The bridging hydride ligand was directly located along the long Ru(1)–Ru(2) edge which is also supported by the carbonyl ligands distribution, in particular the large C(4)–Ru(2)–Ru(1) angle of 148.43(16)° and C(1)–Ru(1)–Ru(2) angle of 156.68(13)°, as expected. Another intriguing structural feature of **7** is the three-way bridging benzyne ligand, a bonding mode, which had not been observed hitherto. The bonding of the benzyne ligand involves an η^6-interaction with Ru(4) {Ru(4)–C(44) = 2.248(5), Ru(4)–C(43) = 2.274(4), Ru(4)–C(45) = 2.287(5), Ru(4)–C(42) = 2.288(4), Ru(4)–C(46) = 2.320(4), Ru(4)–C(41) = 2.322(4) Å}, a μ-η^1 interaction with Ru(1) and Ru(3) {Ru(3)–C(41) = 2.253(4), Ru(1)–C(41) = 2.270(4) Å} and an η^1 interaction with Ru(2) {Ru(4)–C(46) = 2.076(4) Å}. The tetradentate phosphine ligand, PPh_2CH_2PPh sits on the top of the $(\mu\text{-H})Ru_3(CO)_7$ fragment so that P(2) atom is bonded to Ru(2) while the P(1) atom bridges Ru(1) and Ru(3) atoms, thus capping one face of the triangular metal framework forming two five-membered Ru(1)–P(1)–C(10)–P(2)–Ru(2) and Ru(1)–P(1)–C(10)–P(2)–Ru(2) metallacycles. A similar bonding mode of the PPh_2CH_2PPh ligand was observed in $[Ru_3(CO)_9\{\mu\text{-}\eta^2\text{-}PPh_2CH_2PPh\}(\mu\text{-H})]$, obtained from the thermolysis of **6** in the presence of H_2[8] and in $[Ru_3(CO)_6(\mu\text{-}\eta^2\text{-}PPh_2CH_2PPh)(\mu\text{-}PPh_2)(\mu\text{-H})]$, obtained from the reaction of **1** with PPh_2H.[24] The Ru–P bond distances involving the diphosphine ligand in **7** {Ru(2)–P(2) = 2.3806(12), Ru(1)–P(1) = 2.2574(11), Ru(3)–P(1) = 2.3578(12)} are comparable to the corresponding distances in $[Ru_3(CO)_9(\mu\text{-}\eta^2\text{-}PPh_2CH_2PPh)(\mu\text{-H})]$[8] and $[Ru_3(CO)_6(\mu\text{-}\eta^2\text{-}PPh_2CH_2PPh)(\mu\text{-}PPh_2)(\mu\text{-H})]$.[24]
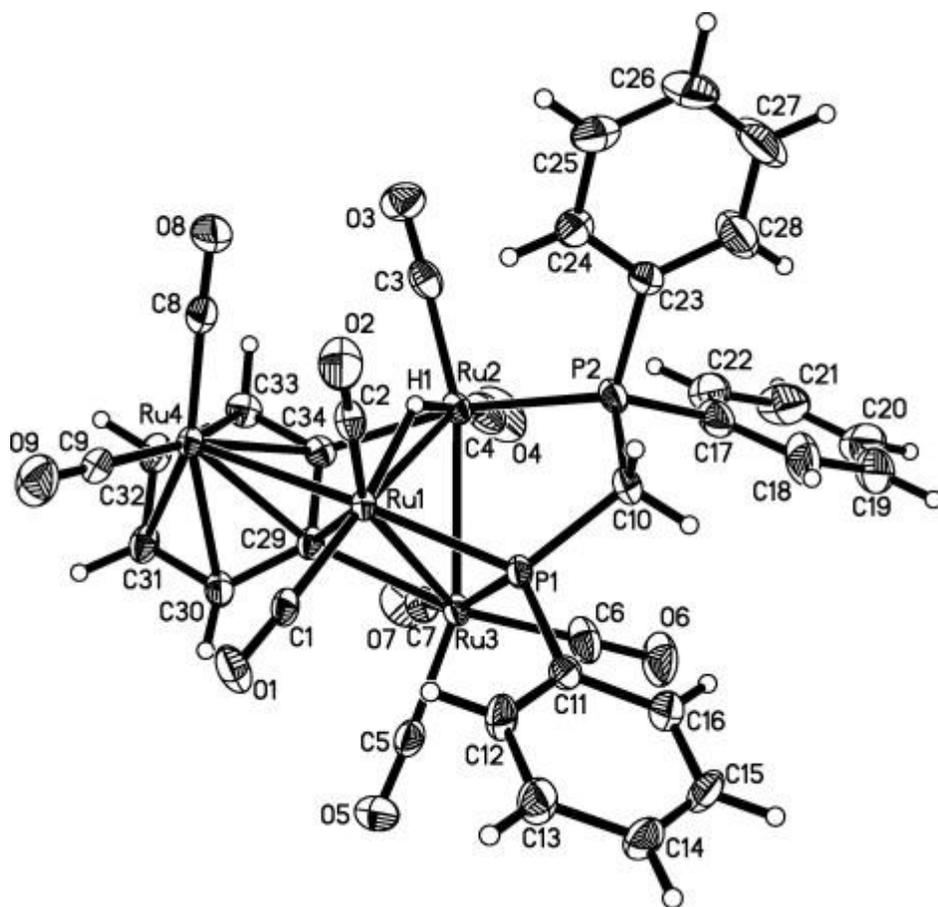
Fig. 3. The solid-state molecular structure of [Ru$_4$(CO)$_9$(μ_3-η^2-PhPCH$_2$PPh$_2$)(μ_4-η^6:η^1:η^1-C$_6$H$_4$)(μ-H)] (**7**).

Table 3. Selected bond lengths (Å) and angles (°) for **7**

Ru(1)–P(1)	2.258(1)	Ru(3)–P(1)	2.358(1)
Ru(1)–C(41)	2.270(4)	Ru(4)–C(44)	2.248(5)
Ru(1)–Ru(4)	2.7866(5)	Ru(4)–C(43)	2.274(4)
Ru(1)–Ru(3)	2.8476(5)	Ru(4)–C(45)	2.287(5)
Ru(1)–Ru(2)	2.9694(6)	Ru(4)–C(42)	2.288(4)
Ru(2)–C(46)	2.076(4)	Ru(4)–C(46)	2.320(4)
Ru(2)–P(2)	2.381(1)	Ru(4)–C(41)	2.322(4)
Ru(2)–Ru(3)	2.8494(5)	P(1)–C(10)	1.842(4)
Ru(3)–C(41)	2.253(4)	P(2)–C(10)	1.845(5)
P(1)–Ru(3)–Ru(1)	50.33(3)	C(46)–Ru(2)–Ru(3)	73.7(1)
C(41)–Ru(3)–Ru(2)	65.6(1)	P(2)–Ru(2)–Ru(3)	91.49(3)
P(1)–Ru(3)–Ru(2)	79.75(3)	C(46)–Ru(2)–Ru(1)	66.82(12)
P(1)–Ru(1)–Ru(4)	156.98(3)	C(45)–Ru(4)–Ru(1)	103.0(1)

C(41)–Ru(1)–Ru(4)	53.5(1)	C(42)–Ru(4)–Ru(1)	77.2(1)
P(1)–Ru(1)–Ru(3)	53.51(3)	C(46)–Ru(4)–Ru(1)	67.9(1)
C(41)–Ru(1)–Ru(3)	50.7(1)	C(41)–Ru(4)–Ru(1)	51.8(1)
P(1)–Ru(1)–Ru(2)	78.71(3)	P(1)–C(10)–P(2)	111.6(2)
C(41)–Ru(1)–Ru(2)	63.2(1)		

The spectroscopic data of **7** in solution are in agreement with the structure observed in the solid-state. The infrared spectrum indicates that all the carbonyl groups are terminal. The mass spectrum shows the molecular ion peak at *m/z* 1042. In addition to usual phenyl proton resonances at δ 7.21–7.71, the ^{1}H NMR spectrum shows four multiplets at δ 6.62, 6.55, 5.40 and 5.24, each integrating for one hydrogen, assigned to protons of the benzyl ligand and two multiplets at δ 4.05 and 4.20 are due to the diastereotopic methylene protons of the diphosphine ligand. The hydride region of the spectrum contains a doublet of doublets at δ−18.18 due to coupling to two nonequivalent ^{31}P nuclei. The ^{31}P{^{1}H} NMR exhibits two equal intensity doublets at δ 19.5 and 115.5. The deshielded doublet at δ 115.5 is attributed to the μ-P atom while the doublet at δ 19.5 is assigned to the η^1-P atom of the PPh$_2$CH$_2$PPh ligand.

All attempts to synthesize triruthenium clusters containing bridging dppm and benzothiophene derived ligand as well as to know the role of benzothiophene ligand in the formation of **5** and **7** are, however, unsuccessful. We studied the thermolysis of **I** and its orthometallated derivative **4** under various conditions and obtained only compounds **2**, **3** and **4**, which agrees with the earlier findings of Bruce et al. Despite the results obtained, where benzothiophene plays an important role in formation of **5** and **7** from its reaction with **1** the function of the ligand is still unknown. Efforts to understand the role of the benzothiaphene in the formation of compounds **5** and **7** are still under investigations in our laboratory and will be reported elsewhere.

4. Supplementary material

CCDC 298955, 634411 and 298956 contain the supplementary crystallographic data for **5**, **6**, and **7**. 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.

Acknowledgements

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