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FULL PAPER

$P(CH_2CH_2PPh_2)_3$ Bridged Group 10 dimetal centres

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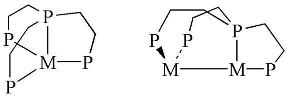
The complexes $[M(\eta^4\text{-}PP_3)Cl]Cl$ (M = Ni, Pd or Pt, $PP_3 = P(CH_2CH_2PPh_2)_3$) were treated with the metal based nucleophiles $[Pt(PPh_3)_2(C_2H_4)]$, $[Pt(\eta^2\text{-bicyclo(2.2.1)hept-2-ene})_3]$ or $[Pd_2(dba)_3]$ (dba = dibenzylideneacetone) to produce PP_3 bridged metal–metal bonded homo- and heterodinuclear complexes in which the central and one terminal phosphorus of the PP_3 ligand are chelated to one metal whilst the other two terminal phosphorus atoms bridge to the second metal centre. The products are characterised by ^{31}P and ^{195}Pt NMR spectroscopy; X-ray crystal structures were determined for $[Pt_2(PP_3)(PPh_3)Cl]Cl$ and $[Pd_2(PP_3)Cl_2]$.

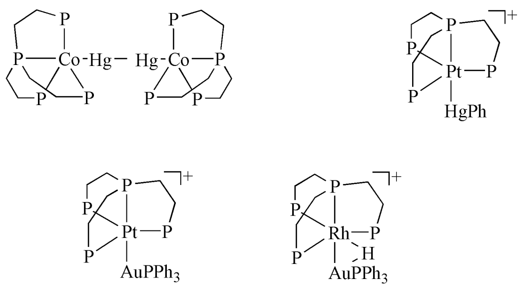
Introduction

The ability of diphosphines $Ph_2P(CH_2)_nPPh_2$ to adopt a chelating or bridging bonding mode depends on the length of the alkylene chain. It is well known that dppe is an excellent chelate ligand whilst dppm has a great tendency to act as bridging ligand and readily locks two metals in close proximity as is exemplified by a rich chemistry based on metal–metal bonded complexes of the type $M_2(\mu\text{-dppm})_2$.[1]

The tetradentate ligand PP_3 is a relative of dppe ($n = 2$) and forms a multitude of complexes in which a $\eta^4\text{-}PP_3$ ligand coordinates to a metal centre adopting an octahedral or trigonal bipyramidal geometry as shown in Scheme 1. All complexes of PP_3 involving metal–metal bonds reported so far (Scheme 2) involve this bonding mode.[2–5]



Scheme 1

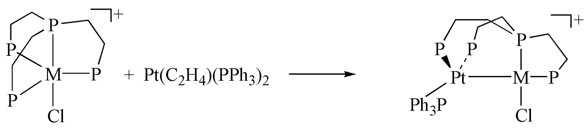


Scheme 2

We report here on the facile formation of dinuclear metal–metal bonded $M_2(\mu\text{-}PP_3\text{-}P,P' : P'',P''')$ fragments depicted in Scheme 1.

Results and discussion

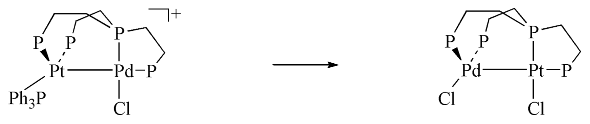
As indicated in Scheme 3, the treatment of the divalent platinum complex $[Pt(\eta^4\text{-}PP_3)Cl]Cl$ with the zerovalent species $[Pt(PPh_3)_2(C_2H_4)]$ produces the dinuclear complex **1**. The reaction proceeds within minutes in almost quantitative yield. There is no analogous reaction of $[Pt(\eta^4\text{-}PP_3)H]^+$, $[Pt(\eta^4\text{-}PP_3)(AuPPh_3)]^+$ or $[Pt(\eta^4\text{-}PP_3)(PPh_3)]^+$ with $[Pt(PPh_3)_2(C_2H_4)]$. Treatment of $[Pd(\eta^4\text{-}PP_3)Cl]Cl$ or $[Ni(\eta^4\text{-}PP_3)Cl]Cl$ with $[Pt(PPh_3)_2(C_2H_4)]$ produces the heterodinuclear complexes **2** and **3** according to Scheme 3.



M = Pt: **1**
Pd: **2**
Ni: **3**

Scheme 3

The triphenylphosphine ligand of **2** is readily oxidised upon exposure to air to give Ph_3PO and **4**, in which Pt and Pd changed place relative to the PP_3 ligand according to Scheme 4. This complex is also formed directly upon treatment of $[Pt(\eta^4\text{-}PP_3)Cl]Cl$ with $[Pd_2(dba)_3]$.



2 **4**

Scheme 4

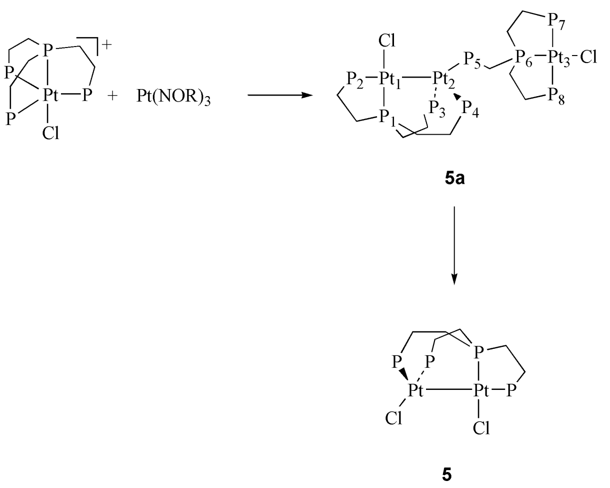
Upon treatment of $[Pt(\eta^4\text{-}PP_3)Cl]Cl$ with $[Pt(\eta^2\text{-bicyclo(2.2.1)hept-2-ene})_3]$ the homodinuclear complex **5** is formed. The reaction takes four days and involves two intermediates, one of which was identified by ^{31}P NMR spectroscopy as **5a** (Scheme 5, NOR = bicyclo(2.2.1)hept-2-ene). The corresponding palladium complex **6** is formed within minutes from $[Pd(\eta^4\text{-}PP_3)Cl]Cl$ and $[Pd_2(dba)_3]$.

Crystal structures

The molecular structure of **1** is established by single crystal X-ray diffraction. Selected bond distances and angles are summarised in Table 1. As shown in Fig. 1, a diplatinum core is doubly bridged by a PP_3 ligand. This bonding mode is, as far as we know, unprecedented for a metal–metal bonded species.[6]

Table 1 Selected distances [Å] and angles [°] in **1** and **6**

1			
Pt1–P1	2.183(4)	Pt2–P4	2.293(4)
Pt1–P2	2.266(4)	Pt2–P3	2.315(4)
Pt1–Cl1	2.395(4)	Pt2–P5	2.345(4)
Pt1–Pt2	2.616(2)		
P1–Pt1–Cl1	170.6(2)	P4–Pt2–P3	144.40(15)
P1–Pt1–Cl1	170.6(2)	P4–Pt2–P5	104.91(15)
P2–Pt1–Cl1	100.4(2)	P3–Pt2–P5	102.44(14)
P1–Pt1–Pt2	88.86(12)	P4–Pt2–Pt1	81.05(11)
P2–Pt1–Pt2	176.63(12)	P3–Pt2–Pt1	84.02(10)
Cl1–Pt1–Pt2	82.93(11)	P5–Pt2–Pt1	154.50(11)
6			
Pd1–P1	2.2014(11)	Pd2–P4	2.2980(11)
Pd1–P2	2.2925(11)	Pd2–P3	2.3072(12)
Pd1–Cl1	2.3976(11)	Pd2–Cl2	2.4848(11)
Pd1–Pd2	2.5593(6)		
P1–Pd1–P2	86.92(4)	P4–Pd2–P3	144.78(4)
P1–Pd1–Cl1	169.13(4)	P4–Pd2–Cl2	97.60(4)
P2–Pd1–Cl1	101.84(4)	P3–Pd2–Cl2	107.96(4)
P1–Pd1–Pd2	86.97(3)	P4–Pd2–Pd1	84.31(3)
P2–Pd1–Pd2	173.81(3)	P3–Pd2–Pd1	82.85(3)
Cl1–Pd1–Pd2	84.34(3)	Cl2–Pd2–Pd1	154.35(3)



Scheme 5

The Pt1 atom is co-ordinated by the central and one terminal phosphorus atom of the tetradentate PP$_3$ and by one chloride ligand, Pt2 is co-ordinated by the other two terminal phosphorus atoms of the PP$_3$ ligand and one triphenylphosphine ligand. Including the Pt–Pt bond both platinum atoms have a co-ordination number of four. The PP$_3$ ligand forms one five-membered η^2 and two six-membered μ rings, one in a twist-like, the other in a boat conformation. The pseudoaxial positions of the Pt$_2$ system are occupied by triphenylphosphine and one terminal phosphorus atom of the PP$_3$ ligand: the PP$_3$ phosphorus atom is almost colinear with the Pt–Pt vector (P2Pt1Pt2 177°), the corresponding angle for the PPh$_3$ ligand amounts to 154°. Whereas the co-ordination geometry around Pt1 is almost square planar, there are substantial distortions around Pt2 which are thought to be due to the steric requirements of the PP$_3$ ligand. The mean co-ordination planes around the two platinum atoms form an angle of 83° compared with 43° observed for [Pt$_2$Cl(PPh$_3$)(μ-dppm)$_2$]$^+$.[7]

The Pt–P distances vary within a range of 2.18–2.34 Å. The Pt–Pt distance is 2.616(2) Å and lies within the common range of Pt–Pt bond lengths found for diplatinum(I) complexes.[8]

A different co-ordination mode of the related ligand NP$_3$ (NP$_3$ = N(CH$_2$CH$_2$PPh$_2$)$_3$) was observed in the dinuclear complex [Pt$_2$(NP$_3$)(μ-PEt$_2$)(PPh$_3$)]$^+$ which was obtained by treatment of the terminal phosphido complex [Pt(η^4-NP$_3$)(η^1-PEt$_2$)]$^+$ with [Pt(PPh$_3$)$_2$(C$_2$H$_4$)]: the nitrogen atom and two phosphorus donors of the NP$_3$ ligand co-ordinate to one Pt centre, the third phosphorus bridges to the other Pt atom.[9] In view of the different co-ordination numbers of the platinum centres the Pt–Pt interaction was described as a polar bond between a d^{10} Pt(0) and a d^8 Pt(II) centre.

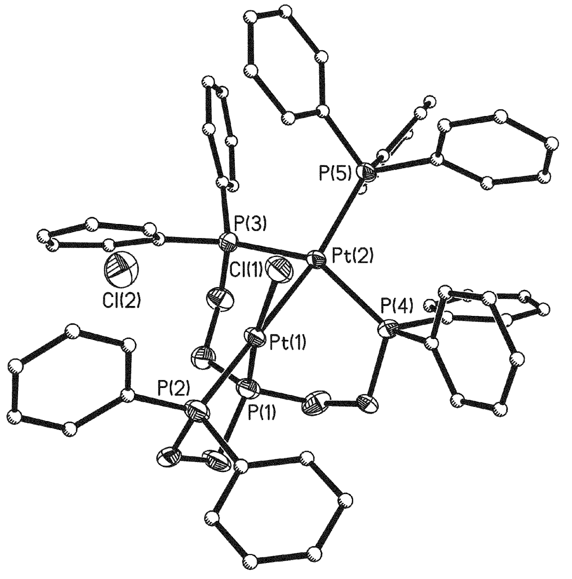


Fig. 1 Molecular structure of **1**.

The X-ray structure of the dipalladium complex **6** is shown in Fig. 2, selected bond distances and angles are included in Table 1. The complex involves the same bonding mode of the PP$_3$ ligand and a geometry closely related to **1**.

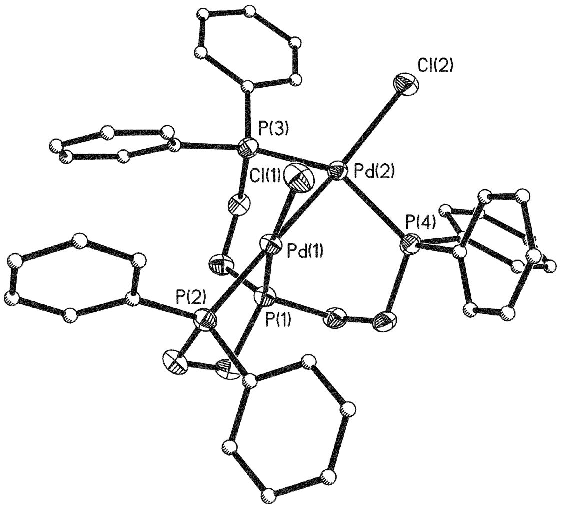


Fig. 2 Molecular structure of **6**.

NMR spectroscopy

The ^{31}P and ^{195}Pt NMR data of the new compounds are summarised in Table 2. The solid state structure of **1** is retained in solution: The ^{195}Pt NMR spectrum of **1** is depicted in Fig 3. The platinum centres are co-ordinated by two and three phosphorus donor atoms, the assignment to Pt1 and Pt2 is confirmed by the coupling pattern of the two equivalent terminal P atoms of the PP$_3$ ligand.

The ^{31}P NMR spectrum shows four different shifts. The individual phosphorus atoms of **1** are readily identified according to the values of the one bond Pt–P coupling constants extracted from the ^{195}Pt NMR pattern of the isotopomer containing one ^{195}Pt atom.

The phosphorus atoms 1 and 2 (labelling according to Fig. 1) are at relatively high chemical shifts in keeping with the ring

Table 2 ^{31}P and ^{195}Pt data of **1**–**6** (numbering scheme as in Fig. 1)

	1	**2**	**3**	**4**	**5**	**6**
$\delta(P_1)$	79.1	98.4	89.8	78.8	68.1	91.0
$\delta(P_2)$	54.5	47.9	50.6	41.2	44.9	31.7
$\delta(P_{3,4})$	23.0	30.4	23.2	25.0	31.5	27.4
$\delta(P_5)$	42.0	31.7	17.4	—	—	—
$\delta(Pt_1)$	−4451	—	—	—	−4569	—
$\delta(Pt_2)$	−4525	−4637	−4686		−4374	
$^2J(P_1–P_2)$	6.1	9.8	8.5	8.5	7.3	3.7
$^3J(P_1–P_{3,4})$	13.8	9.7	12.2	8.5	12.1	4.3
$^3J(P_1–P_5)$	13.6	9.8	62	—	—	—
$^3J(P_2–P_{3,4})$	23.0	24	19.5	53.7	6.1	63.5
$^3J(P_2–P_5)$	167	206	155	—	—	—
$^2J(P_{3,4}–P_5)$	10	13.4	18.5	—	—	—
$^1J(Pt_1–P_1)$	3544	—	—	3663	3734	
$^1J(Pt_1–P_2)$	3003	—	—	3077	2937	
$^2J(Pt_1–P_{3,4})$	103	—	—	93	113	
$^2J(Pt_1–P_5)$	287	—	—	—	—	
$^1J(Pt_2–P_{3,4})$	3454	3389	3662	—	3519	—
$^1J(Pt_2–P_5)$	2740	2803	2429	—	—	—
$^2J(Pt_2–P_1)$	42	15	198	—	166	—
$^2J(Pt_2–P_2)$	225	439	291	—	834	—
$^1J(Pt_1–Pt_2)$	555	—	—	—	1565	—

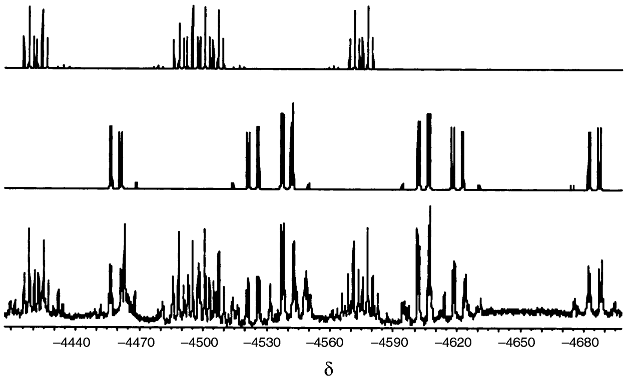


Fig. 3 ^{195}Pt{^{1}H} NMR spectra of **1**: simulated for the isotopomers containing one ^{195}Pt nucleus in site 1 (upper trace) and 2 (middle) respectively (labelling as in Fig. 1) and experimental (bottom).

contribution of five-membered chelate rings.[10] The ^{31}P shift of PPh_3 is relatively high for a monodentate phosphine and this seems to be characteristic for a linear $Ph_3P–Pt–Pt$ arrangement. The relative orientation of P2 and P5 is confirmed by a P–Pt–Pt–P coupling of 167 Hz which is characteristic for phosphorus atoms in the pseudoaxial positions of diplatinum(I) systems. The assignment of all phosphorus atoms is confirmed by their individual coupling multiplicities.

The NMR spectra of **2**–**6** are interpreted similarly and are included in Table 2.

The ^{31}P NMR spectrum of **5a** shows six different P sites, the intensity and multiplicity of the signals exhibit that two sites represent two equivalent P atoms respectively. The resulting eight P atoms are attributed to two PP_3 ligands: The patterns of the phosphorus atoms labelled 1–5 in Scheme 5 are closely related to that of **1**, the pattern of the phosphorus atoms 6–8 resembles that of $[Pt(\eta^3\text{-}PhP(CH_2PPh_2)_2)Cl]Cl$.[11] The link between these substructures is a 41.5 Hz coupling between the phosphorus atoms 5 and 6 indicating that the P atom 5 is the third terminal P atom of a η^3-PP_3 ligand and is co-ordinated to the diplatinum(2+) fragment. A similar coupling seems to be present in a previously reported $[Pt(\eta^3\text{-}PP_3)]$ system.[12]

Experimental

NMR spectra were recorded using a Bruker 300 DPX spectrometer. ^{31}P/^{195}Pt chemical shifts are reported relative to 85% H_3PO_4/1 M Na_2PtCl_6, used as an external reference. Coupling constants are reported in Hertz. Mass spectra were obtained by use of a Finnigan MAT 95 instrument, elemental analyses were provided by Institut für Physikalische Chemie der Universität Wien. Unless otherwise noted, reagents were from commercial suppliers. The compounds $[M(\eta^4\text{-}PP_3)Cl]Cl$, M = Ni, Pd and Pt and $[Pt(\eta^2\text{-bicyclo(2.2.1)hept-2-ene})_3]$ were prepared according to literature procedures.[13,14] The solvents were dried using standard procedures. All operations were carried out under standard Schlenck conditions.

Synthesis and data

Complex 1. 0.1 mmol (74.8 mg) of $[Pt(PPh_3)_2(C_2H_4)]$ and 0.1 mmol (93.7 mg) of $[Pt(\eta^4\text{-}PP_3)Cl]Cl$ were dissolved in CH_2Cl_2 (0.5 ml). As monitored by ^{31}P NMR spectroscopy, **1** was formed quantitatively within 5 min. In order to remove the PPh_3, the solvent was evaporated *in vacuo* and the residue was washed with toluene–CH_2Cl_2 (20/1, 3 × 1 ml) leaving the product in 30% yield (44 mg, not optimised). Found: C, 49.92; H, 3.62. Calc. for $C_{60}H_{57}Cl_2P_5Pt_2\cdot CH_2Cl_2$: C, 49.54; H, 4.02%.

Complex 2. 0.05 mmol (37.4 mg) of $[Pt(PPh_3)_2(C_2H_4)]$ and 0.05 mmol (42.4 mg) of $[Pd(\eta^4\text{-}PP_3)Cl]Cl$ were dissolved in CH_2Cl_2 (1.0 ml). As monitored by ^{31}P NMR spectroscopy, **2** was formed quantitatively within 5 min. The solvent was evaporated *in vacuo* and the residue was washed with toluene–CH_2Cl_2 (20/1, 3 × 1 ml). Recrystallisation from CH_2Cl_2-MeOH gave the product in 61% yield (82 mg). Found: C, 54.68; H, 4.50. Calc. for $C_{60}H_{57}Cl_2P_5PdPt\cdot CH_3OH$: C, 54.78; H, 4.60%.

Complex 3. 0.1 mmol (80.0 mg) of $[Ni(\eta^4\text{-}PP_3)Cl]Cl$ and 0.12 mmol (89.7 mg) of $[Pt(PPh_3)_2(C_2H_4)]$ were dissolved in CH_2Cl_2 (0.7 ml) and MeOH (0.2 ml). After 1 h 80% of the product was formed according to ^{31}P NMR. The solvent was evaporated *in vacuo* and the residue was washed with toluene–CH_2Cl_2 (20/1, 3 × 1 ml). Recrystallisation from CH_2Cl_2-MeOH gave the product in 24% yield (36 mg, not optimised.). Found: C, 50.69; H, 4.20. Calc. for $C_{60}H_{57}Cl_2P_5NiPt\cdot 3CH_2Cl_2$: C, 50.03; H, 4.20%.

Complex 4. 0.025 mmol (25.9 mg) of $[Pd_2(dba)_3]\cdot CHCl_3$ and 0.05 mmol (46.8 mg) of $[Pt(\eta^4\text{-}PP_3)Cl]Cl$ were dissolved in CH_2Cl_2 (1.0 ml). As monitored by ^{31}P NMR spectroscopy, **4** was formed quantitatively within 5 min. The product precipitated after addition of 10 ml of ethyl acetate. Yield 80% (87 mg) Found: C, 47.12; H, 4.08. Calc. for $C_{42}H_{42}Cl_2P_4PdPt\cdot 0.5\,CH_2Cl_2$: C, 47.02; H, 3.99%.

Complex 5. 0.1 mmol (47.8 mg) of $[Pt(\eta^2\text{-bicyclo(2.2.1)hept-2-ene})]$ and 0.1 mmol (93.7 mg) of $[Pt(\eta^4\text{-}PP_3)Cl]Cl$ were dissolved in CH_2Cl_2 (1.0 ml). After 4 d the solvent and bicyclo(2.2.1)hept-2-ene were removed *in vacuo*. Yield 90% (102 mg). Found: C, 44.65; H, 3.90. Calc. for $C_{42}H_{42}Cl_2P_4Pt_2$: C, 44.57; H, 3.74%.

^{31}P NMR data of **5a** (labelling according to Scheme 5): $\delta(P_1)$ 78.7; $^2J(P_1–P_2)$ 5; $^3J(P_1–P_{3,4})$ 12.2; $^3J(P_1–P_5)$ 12.5; $^1J(Pt_1–P_1)$ 3544; $\delta(P_2)$ 55.3; $^3J(P_2–P_{3,4})$ 24.5; $^3J(P_2–P_5)$ 169.7; $^1J(Pt_1–P_2)$ 2996; $^2J(Pt_2–P_2)$ 260; $\delta(P_{3,4})$ 22.4; $^2J(Pt_1–P_{3,4})$ 85; $^1J(Pt_2–P_{3,4})$ 3432; $\delta(P_5)$ 37.1; $^2J(P_{3,4}–P_5)$ 8.2; $^3J(P_5–P_6)$ 41.5; $^2J(Pt_1–P_5)$ 232; $^1J(Pt_2–P_5)$ 2696; $\delta(P_6)$ 90.0; $^1J(Pt_3–P_6)$ 2948; $\delta(P_{7,8})$ 44.0; $^1J(Pt_3–P_{7,8})$ 2499.

Complex 6. 0.018 mmol (19.0 mg) of $[Pd_2(dba)_3]\cdot CHCl_3$ and 0.35 mmol (29.7 mg) of $[Pd(\eta^4\text{-}PP_3)Cl]Cl$ were stirred in CH_2Cl_2 (0.5 ml) for 5 min to give a clear solution. The product crystallised upon standing for 2 d in 60% yield (60 mg). MS (FAB; *m*/*z*) 919.0 ((M + H$^+$)-HCl). Found: C, 50.81; H, 4.38. Calc. for $C_{42}H_{42}Cl_2P_4Pd_2\cdot 0.5CH_2Cl_2$: C, 51.21; H, 4.35.

Crystallography

Crystals were mounted on a glass fibre, X-ray data were collected on a Siemens P4 diffractometer (MoKα radiation,

Table 3 Crystal data for **1** and **6**

	1	**6**
Formula	$C_{60}H_{57}Cl_2P_5Pt_2\cdot 4MeOH\cdot CH_2Cl_2\cdot H_2O$	$C_{42}H_{42}Cl_2P_4Pd_2\cdot 3CH_2Cl_2$
M	1625.10	1209.11
a/Å	13.933(8)	12.450(2)
b/Å	32.568(7)	23.723(5)
c/Å	15.599(13)	17.271(2)
β/°	111.84(3)	102.40(1)
V/Å^3	6570.3(68)	4982.0(14)
Z	4	4
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$ (no. 14)	$P2_1/c$ (no. 14)
T/K	213(2)	218(2)
Reflections collected	6703	6703
Unique reflections $[I > 2\sigma(I)]$	4898	5704
R $[I > 2\sigma(I)]$	$R1 = 0.0518$, $wR2 = 0.1182$	$R1 = 0.0312$, $wR2 = 0.0663$
R (all data)	$R1 = 0.0946$, $wR2 = 0.2365$	$R1 = 0.0426$, $wR2 = 0.0791$

monochromator: highly oriented graphite crystal, ω-scan). Data were corrected for Lorentz-polarisation and absorption effects (ψ-scans). The structures were solved by direct methods and subsequent difference Fourier techniques (SHELXS-86).[15] Refinement on F^2 with all measured reflections was carried out by full-matrix least-squares technique (SHELXL-93).[16] Crystal data for **1** and **6** are given Table 3.

CCDC reference numbers 179758 and 179759.

See http://www.rsc.org/suppdata/dt/b2/b201709a/ for crystallographic data in CIF or other electronic format.

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