

A new access to palladium–phosphine chemistry. Formation of polynuclear palladium compounds *via* the oxidation of ligands in simple palladium(II) complexes

Weiping Su, Rong Cao,* Maochun Hong,* Daxu Wu and Jiaxi Lu

State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, P. R. China.
E-mail: hmc@ms.fjirsm.ac.cn

Received 4th November 1999, Accepted 2nd March 2000

Published on the Web 10th April 2000

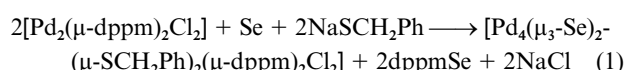
The reactions of [Pd(dppp)(edt)] **1** or [Pd(dppp)(pdt)] **2** (edt^{2−} = ethane-1,2-dithiolate, pdt^{2−} = propane-1,3-dithiolate, dppp = 1,3-bis(diphenylphosphino)propane) with oxygen or elemental Se under different reaction conditions gave rise to a series of polynuclear palladium complexes. The oxidation of **1** by oxygen in alkaline DMF solution yielded a dinuclear complex with sulfinato ligand, [Pd₂(O₂SCH₂CH₂SO₂)(edt)(dppp)] **3**, while that of **2** afforded a hexanuclear complex, [Pd₆(pdt)₆] **4**. The molecular structure of **3** consists of two fragments [Pd(O₂SCH₂CH₂SO₂)] and [Pd(dppp)]²⁺, which are linked by an edt^{2−} bridging ligand. The structure of **4** is made up of [Pd(pdt)] units forming a cyclic neutral complex, of which the Pd₆S₁₂ core possesses pseudo *D*_{6d} symmetry and six Pd atoms form a nearly regular six-membered ring with Pd···Pd distances ranging from 3.050 to 3.090 Å. The treatment of **2** with elemental Se in the ratios 2:1 and 1:1 generated [Pd₂(dppp)₂(pdt)]Cl₂ **5** and [Pd₃(dppp)₂(pdt)₂]Cl₂ **6**, respectively. The molecular structure of **5** and **6** can be considered as two fragments [Pd(dppp)]²⁺ linked by pdt^{2−} and [Pd(pdt)]^{2−}, respectively. The reaction of **1** with 0.5 equivalent Se led to formation of [Pd₂(dppp)₂(edt)]Cl₂ **7**. The molecular structure of **7** is quite similar to that of **5**. All palladium atoms in the complexes are four-co-ordinated with distorted square-planar geometry. The complexes **1**, **3–7** have been characterized by NMR, IR and electronic spectra.

Introduction

Palladium complexes containing phosphine ligands attract considerable attention owing to their numerous applications in organic synthesis and catalysis^{1–5} and their rich co-ordination chemistry.^{5–11} Owing to the high affinity of palladium for sulfur, the palladium complexes with phosphine ligands readily react with organosulfur compounds^{3,5,8,9} to give very stable sulfide and thiolate complexes, which are probably responsible for the poisoning of palladium catalysts by organosulfur impurities in feedstocks.^{8c} Thus, the studies on the palladium complexes with both phosphine ligands and thiolate ligands are significant in understanding the reaction mechanisms of the poisoning of palladium catalysts by organosulfur impurities and recovering catalytic activity of poisoned palladium catalysts. However, the studies on palladium–phosphine complexes, especially those with diphosphine ligands, have mainly been focused on the complexes of palladium in lower oxidation state of 0 and +1,^{5–7,9} such as [Pd₂(dppm)₂]²⁺, [Pd₂(dppm)₃],^{7f} [Pd₃(dppm)₃(μ₃-S)H]PF₆,^{7g,h} [Pd₄(dppm)₄(H)₂]X₂,^{7e} and {[Pd(μ-SC₆F₅)(μ-dppm)Pd(μ-SC₆F₅)]₄}^{6c} (dppm = bis(diphenylphosphino)methane). The palladium(II) complexes blending both phosphine and thiolate ligands have received attention only in recent years.¹⁰

Reactions¹¹ performed in our laboratory revealed that the oxidation of [Ni(edt)(PR₃)₂] (edt = ethane-1,2-dithiolate) by oxygen results in the cleavage of the C–S bond of edt^{2−} and the condensation of two edt^{2−} groups into tpdt (tpdt = 3-thiapentane-1,5-dithiolate), or the condensation of mononuclear complexes into dinuclear complexes *via* oxidation of PR₃. As a part of the systematic investigation of the chemical properties and stereochemistry of transition metal complexes with mixed thiolate and phosphine ligands, more recently we reported a tetranuclear complex [Pd₄(μ₃-Se)₂(μ-SCH₂Ph)₂(μ-dppm)₂Cl₂]

formed *via* the reaction of [Pd₂(μ-dppm)₂Cl₂] with selenium powder in the presence of NaSCH₂Ph in DMF,^{12a} eqn. (1). The



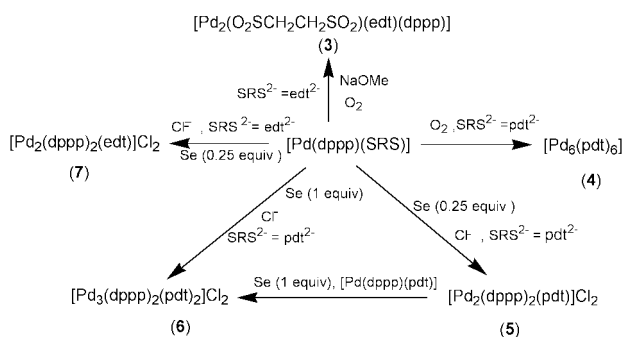
features of this complex are its novel structure arising from the asymmetrically co-ordination by phosphorus, selenium, sulfur and chlorine atoms and its formation involving considerable rearrangement of the initial components. The notable structure as well as the interesting synthetic reaction prompted us to employ other diphosphine ligands such as dppp for studying this kind of reaction.

In this paper we report the condensation reactions of mononuclear palladium(II) complexes with mixed diphosphine and thiolate ligands, [Pd(dppp)(SRS)] (SRS^{2−} = edt^{2−} **1** or propane-1,3-dithiolate **2**, through oxidation of the ligands with oxygen or elemental Se, and the crystal structures of a series of polynuclear palladium complexes isolated from the condensation reactions along with their spectroscopic properties.

Results and discussion

Synthesis

The reactions of [Pd(dppp)(SRS)] (SRS = pdt^{2−} or edt^{2−}) with oxygen or elemental Se have been carried out under different conditions. As shown in Scheme 1, these reactions depended on the conditions and yielded a series of di-, tri- and hexa-nuclear palladium complexes. The oxidation of [Pd(dppp)(edt)] **1** by O₂ in alkaline solution gave rise to a binuclear complex containing sulfinato ligand, [Pd₂(O₂SCH₂CH₂SO₂)(edt)(dppp)] **3**. The oxidation of [Pd(dppp)(pdt)] **2** by O₂ in neutral solution led to the formation of a hexanuclear complex [Pd₆(pdt)₆] **4**. These results

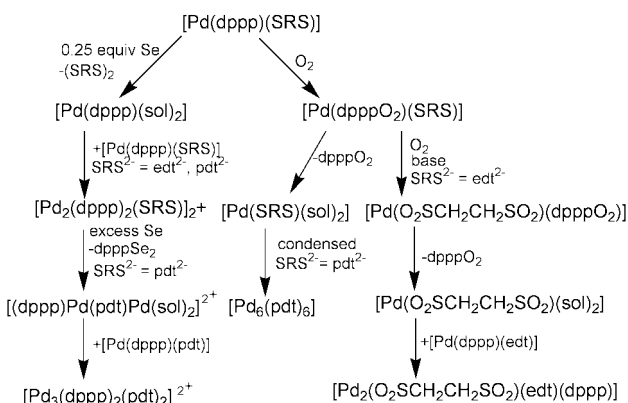


Scheme 1

indicate that the products of the reactions $[\text{Pd}(\text{dppp})(\text{SRS})]/\text{O}_2$ depend on the basicity of the media, although we failed to characterize the reactions of $[\text{Pd}(\text{dppp})(\text{edt})]$ with O_2 in neutral solution and $[\text{Pd}(\text{dppp})(\text{pdt})]$ with O_2 in alkaline solution due to the poor quality of the crystals obtained. Our results agree well with those for nickel thiolate complexes in the literature, for example the reaction of $[\text{Ni}(\text{S}_2\text{C}_2\text{Ph}_2)_2]^{2-}$ with oxygen in neutral solution gave a complex $[\text{Ni}(\text{S}_2\text{C}_2\text{Ph}_2)_2]$, however in alkaline solution, the system generated an irreversible oxidation product $[\text{Ni}(\text{O}_2\text{S}_2\text{C}_2\text{Ph}_2)_2]^{2-}$.^{13,14}

The reaction of $[\text{Pd}(\text{dppp})(\text{pdt})]$ **2** and $[\text{Pd}(\text{dppp})(\text{edt})]$ **1** with 0.25 equivalent of elemental Se in the presence of Me_4NCl afforded two analogous products, $[\text{Pd}_2(\text{dppp})_2(\text{pdt})]\text{Cl}_2$ (**5**) and $[\text{Pd}_2(\text{dppp})_2(\text{edt})]\text{Cl}_2$ (**7**), respectively. However, the reaction of **2** with 1 equivalent elemental Se gave a trinuclear complex $[\text{Pd}_3(\text{dppp})_2(\text{pdt})_2]\text{Cl}_2$ **6**. Complex **6** can also be obtained from the stoichiometric reaction of **5** and Se followed by the addition of 1 equivalent of **2** in DMF. Thus, the amount of selenium powder used controlled the formation of products in reactions with $[\text{Pd}(\text{dppp})(\text{SRS})]$. The results are somewhat similar to those of the oxidation reactions of simple metal thiolate complexes by elemental S or Se,^{15–17} which give polynuclear complexes through the oxidation and release of thiolate ligands.

The studies on the formation mechanisms of polynuclear nickel complexes with chelating thiolate ligands^{17–19} suggest that solvated nickel thiolate fragments are basic intermediates. Accordingly, as illustrated in Scheme 2, possible routes to our



Scheme 2

palladium complexes have been deduced to understand their formation. For the formation of **3**, first **1** is oxidized by O_2 in alkaline DMF solution to give solvated $[\text{Pd}(\text{O}_2\text{SCH}_2\text{CH}_2\text{SO}_2)]$ species and phosphate. Then, the condensation of solvated $[\text{Pd}(\text{O}_2\text{SCH}_2\text{CH}_2\text{SO}_2)]$ species and a $[\text{Pd}(\text{dppp})(\text{edt})]$ molecule generates **3**. The formation of $[\text{Pd}_6(\text{pdt})_6]$ probably proceeds through a complicated multistep mechanism, in which the oxidation of $[\text{Pd}(\text{dppp})(\text{pdt})]$ by O_2 produces solvated $[\text{Pd}(\text{pdt})]$ species and phosphate in the initial reaction step. In the subsequent steps these species combine to yield $[\text{Pd}_6(\text{pdt})_6]$.

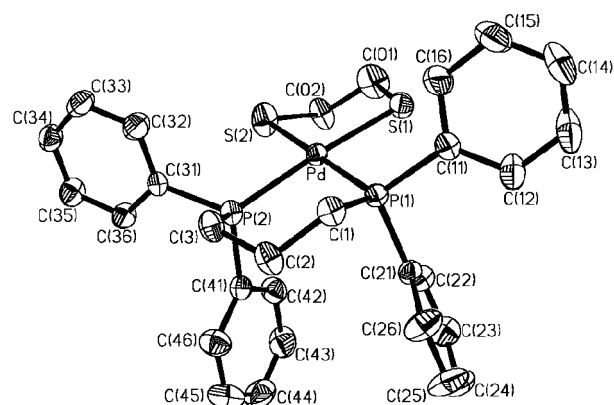


Fig. 1 Structure of complex **1**.

The reaction of $[\text{Pd}(\text{dppp})(\text{pdt})]$ or $[\text{Pd}(\text{dppp})(\text{edt})]$ with elemental Se may first lead to detachment of ligands from complexes due to oxidation to form fragments such as solvated $[\text{Pd}(\text{dppp})]^{2+}$ species. These species undergo further displacement of ligated solvent and are linked by bridging ligands (edt^{2-} or pdt^{2-}) in other species to form the resultant products. As shown in Scheme 2, the reaction of $[\text{Pd}(\text{SRS})(\text{dppp})]$ ($\text{SRS}^{2-} = \text{edt}^{2-}$ or pdt^{2-}) with 0.25 equivalent elemental Se may primarily produce the solvated $[\text{Pd}(\text{dppp})(\text{sol})_2]^{2+}$ species and $(\text{SRS})_2$, then the solvated species combines with initial $[\text{Pd}(\text{SRS})(\text{dppp})]$ to give $[\text{Pd}_2(\text{SRS})(\text{dppp})_2]^{2+}$. When the amount of Se is raised to 1 equivalent, dppp may be further oxidized and $[\text{Pd}_2(\text{SRS})(\text{dppp})_2]^{2+}$ is converted into $[(\text{dppp})\text{Pd}(\text{SRS})\text{Pd}(\text{sol})_2]^{2+}$ (sol = solvent) species and dpppSe_2 ; the combination of $[(\text{dppp})\text{Pd}(\text{SRS})\text{Pd}(\text{sol})_2]^{2+}$ with $[\text{Pd}(\text{dppp})(\text{SRS})]$ results in $[\text{Pd}_3(\text{dppp})_2(\text{SRS})_2]^{2+}$.

It should be mentioned that some side products isolated from the reaction systems, such as dpppSe , $\text{dppp}(\text{O})_2$, and $\text{dppp}(\text{Se})_2$ have also been characterized structurally and support to some extent our speculation in Scheme 2.

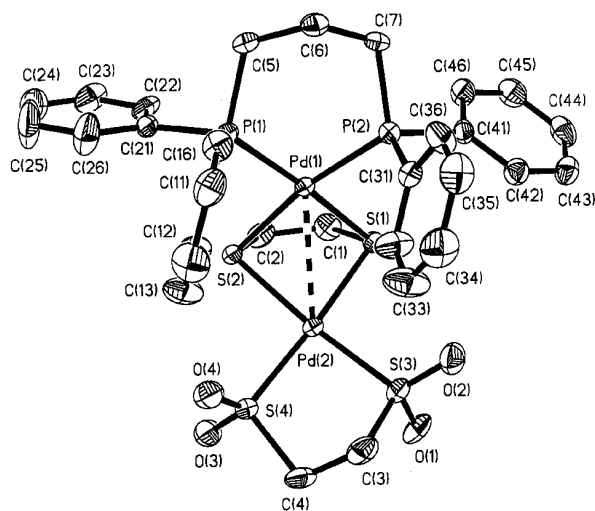
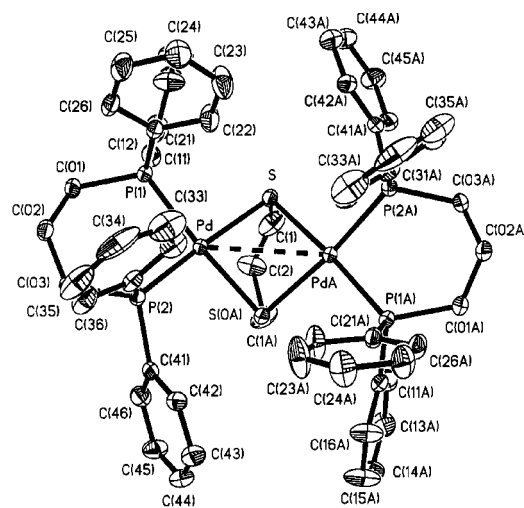
Description of the structures

The structure of complex **1**, as shown in Fig. 1, is a mononuclear neutral molecule. The palladium atom is co-ordinated by two phosphorus atoms from dppp ligand and two sulfur atoms from edt^{2-} ligand in a slightly distorted square-planar geometry. The Pd atom is 0.06 Å above the least squares plane $\text{S}(1)\text{S}(2)\text{P}(1)\text{P}(2)$. The dppp ligand chelates to Pd forming a six-membered ring $[\text{P}(1)\text{C}(1)\text{C}(2)\text{C}(3)\text{P}(2)\text{Pd}]$ in a chair form, while ligand edt^{2-} chelates to Pd to give a five-membered ring $[\text{S}(1)\text{C}(01)\text{C}(02)\text{S}(2)\text{Pd}]$ in a twist conformation. Two bite angles $\text{P}(1)\text{--Pd--P}(2)$ and $\text{S}(1)\text{--Pd--S}(2)$ are 91.60 and 89.22°, respectively (Table 1). The latter is 5° smaller than that of $[\text{Pd}(\text{dppp})(\text{pdt})]$.^{12c} The Pd–P and Pd–S bond lengths are 2.280(1) and 2.315(1) Å, respectively, which are comparable to those of palladium thiolate complexes with phosphine ligands reported previously.^{20,21}

The molecular structure of complex **3** is shown in Fig. 2. The structure consists of two fragments $[\text{Pd}(\text{O}_2\text{SCH}_2\text{CH}_2\text{SO}_2)]$ and $[\text{Pd}(\text{dppp})]^{2+}$, which are bridged by an edt^{2-} ligand. The structure may be also viewed as two square-planar co-ordination units PdP_2S_2 and PdS_4 sharing a common edge. Thus, two kinds of environment of palladium atoms are present: Pd(1) is co-ordinated by four sulfur atoms from edt^{2-} and sulfinato ligands, being 0.11 Å above the least squares plane $\text{S}(1)\text{S}(2)\text{S}(3)\text{S}(4)$, while Pd(2) is surrounded by two phosphorus and two sulfur atoms in a distorted square-planar arrangement being 0.10 Å out of the least squares plane. The molecule is folded along the $\text{S} \cdots \text{S}$ vector of the two bridging-sulfur atoms with the dihedral angle between the mean planes $\text{S}(1)\text{S}(2)\text{S}(3)\text{S}(4)$ and $\text{S}(1)\text{S}(2)\text{P}(1)\text{P}(2)$ being 108.5°. The $\text{S}_\text{b}\text{--Pd--S}_\text{b}$ angles with an average value of 79.4° are smaller than $\text{S}_\text{t}\text{--Pd--S}_\text{t}$ angles (average

Table 1 Bond lengths (Å) and angles (°) for complexes **1** and **3–6**

Compound				
1	Pd–P(2)	2.2797(9)	P(2)–Pd–P(1)	91.60(3)
	Pd–P(1)	2.2810(10)	P(2)–Pd–S(2)	88.84(4)
	Pd–S(2)	2.3096(11)	P(1)–Pd–S(2)	178.12(4)
	Pd–S(1)	2.3184(11)	P(2)–Pd–S(1)	173.48(4)
			P(1)–Pd–S(1)	90.14(4)
3			S(2)–Pd–S(1)	89.22(4)
	Pd(1)–P(2)	2.285(2)	P(2)–Pd(1)–P(1)	89.89(7)
	Pd(1)–P(1)	2.285(2)	P(2)–Pd(1)–S(1)	93.93(7)
	Pd(1)–S(1)	2.374(2)	P(1)–Pd(1)–S(2)	96.92(7)
	Pd(1)–S(2)	2.381(2)	S(1)–Pd(1)–S(2)	79.21(7)
	Pd(1)···Pd(2)	3.0297(9)	S(4)–Pd(2)–S(3)	87.57(7)
	Pd(2)–S(4)	2.266(2)	S(3)–Pd(2)–S(1)	96.35(7)
	Pd(2)–S(3)	2.274(2)	S(4)–Pd(2)–S(2)	96.41(7)
	Pd(2)–S(1)	2.361(2)	S(1)–Pd(2)–S(2)	79.63(6)
	Pd(2)–S(2)	2.373(2)	Pd(2)–S(1)–Pd(1)	79.56(6)
	S(3)–O(2)	1.451(6)	Pd(2)–S(2)–Pd(1)	79.18(6)
	S(3)–O(1)	1.445(6)	O(2)–S(3)–O(1)	114.3(4)
	S(4)–O(4)	1.458(6)	O(2)–S(3)–C(3)	105.3(4)
	S(4)–O(3)	1.464(6)	O(1)–S(3)–C(3)	105.1(4)
	S(4)–C(4)	1.826(8)	O(4)–S(4)–O(3)	114.7(4)
			O(4)–S(4)–C(4)	104.9(4)
			O(3)–S(4)–C(4)	105.0(4)
4	Pd(1)–S(1)	2.332(4)	Pd(3)–Pd(1)–Pd(2)	119.42(4)
	Pd(1)–S(6)	2.332(4)	Pd(3)–Pd(2)–Pd(1)	123.33(4)
	Pd(1)–S(2)	2.331(4)	Pd(1)–Pd(3)–Pd(2)	117.25(4)
	Pd(1)–S(3)	2.340(4)	S(1)–Pd(1)–S(2)	81.98(13)
	Pd(1)···Pd(3A)	3.052(2)	S(6)–Pd(1)–S(2)	98.73(13)
	Pd(1)···Pd(2)	3.152(2)	S(1)–Pd(1)–S(3)	99.33(13)
	Pd(2)–S(1)	2.327(3)	S(6)–Pd(1)–S(3)	79.83(13)
	Pd(2)–S(5)	2.327(4)	S(1)–Pd(2)–S(5)	98.18(13)
	Pd(2)–S(2)	2.329(4)	S(1)–Pd(2)–S(2)	82.11(12)
	Pd(2)–S(4)	2.338(3)	S(5)–Pd(2)–S(4)	79.99(13)
	Pd(2)···Pd(3)	3.0902(14)	S(2)–Pd(2)–S(4)	99.73(13)
	Pd(3)–S(4)	2.307(4)	S(4)–Pd(3)–S(5)	79.99(13)
	Pd(3)–S(3A)	2.311(3)	Pd(2)–S(1)–Pd(1)	85.14(11)
	Pd(3)–S(6A)	2.315(4)	Pd(2)–S(2)–Pd(1)	85.00(12)
	Pd(3)–S(5)	2.316(3)	Pd(3)–S(4)–Pd(2)	83.40(12)
	Pd(3)···Pd(1A)	3.0520(20)	Pd(3)–S(5)–Pd(2)	83.45(12)
5	Pd–P(2)	2.2889(11)	P(2)–Pd–P(1)	90.47(4)
	Pd–P(1)	2.2897(12)	P(2)–Pd–S	170.60(4)
	Pd–S	2.3741(12)	P(1)–Pd–S	92.61(4)
			S–Pd–S	81.87(4)
6			Pd–S–Pd	86.23(4)
	Pd(1)–P(2)	2.277(3)	P(2)–Pd(1)–P(1)	91.98(11)
	Pd(1)–P(1)	2.288(3)	P(2)–Pd(1)–S(1)	92.13(10)
	Pd(1)–S(1)	2.361(3)	P(1)–Pd(1)–S(1)	171.13(10)
	Pd(1)–S(2)	2.370(3)	P(2)–Pd(1)–S(2)	172.85(10)
	Pd(1)···Pd(2)	3.0932(8)	P(1)–Pd(1)–S(2)	92.15(10)
	Pd(2)–S(1)	2.326(2)	S(1)–Pd(1)–S(2)	83.00(10)
	Pd(2)–S(2)	2.320(2)	Pd(2)–S(1)–Pd(1)	82.59(8)
			Pd(2)–S(2)–Pd(1)	82.31(8)

**Fig. 2** Structure of complex **3**.**Fig. 3** Structure of complex **5**.

87.6°). Grouping the Pd–S bonds, *i.e.* Pd–S_t and Pd–S_b, gives the average bond lengths 2.373(2) and 2.270(2) Å, respectively. The Pd–S_t bond length of 2.272(2) Å is shorter than those in most of the palladium(II) thiolate complexes reported previously^{10c,22} and those in **1** and **2**; this may be illustrated by the π -back bond, in which the electron density is shifted from the higher density d orbitals of the palladium atom to the empty π -acceptor orbitals of the sulfur atoms in sulfinato ligands due to the increased Lewis acidity of the sulfur atoms caused by the electronegative oxygen atoms, resulting in the strengthened Pd–S_t bond. The fact that the Pd–S_b bond length is 0.05 Å longer than those in complexes **1** and **2** results from *trans* influences exerted by the terminal thiolate and phosphine ligands.^{10a} The average S–O bond length of the sulfinato ligands is 1.456(6) Å and corresponds to that in free S=O (1.48 Å),²² suggesting that the S–O bonds in **3** adopt typical S=O double bond characters, consistent with the IR result ($\nu_{\text{S=O}}$) 1035.6, 1139.7 cm^{−1}).

The cation structure of complex **5** is depicted in Fig. 3. The [Pd₂(dppp)₂(pdt)]²⁺ cations occupy a crystallographic twofold axis. The complex may be viewed as two [Pd(dppp)]²⁺ fragments sharing a common pdt^{2−} ligand. It may also be considered as a [Pd(dppp)(pdt)] unit to which the [Pd(dppp)]²⁺ is bonded in a *cis* fashion. As a result, each of the two sulfur atoms of pdt^{2−} bridges two Pd atoms, and the Pd₂S₂ moiety is folded along its S···S vector, different from those reported in related complexes [(dppe)M(μ-SC₅H₉NMe)₂M(dppe)]^{10c} (M = Pd or Pt) in which the central M₂S₂ ring is exactly planar. The Pd–P bond lengths of **5** (2.289 Å) are similar to those of other Pd–dppp complexes in this paper. The average Pd–S bond length (2.35 Å) is approximately 0.04 Å longer than those in **1** and **2** owing to the existence of steric hindrance.

The cation [Pd₃(dppp)₂(pdt)₂]²⁺ complex **6** is depicted in Fig. 4. The structure possesses a crystallographic inversion center. As a consequence, the three metal atoms are strictly linear and the structure may be viewed as two [Pd(dppp)]²⁺ sharing a [Pd(pdt)₂]^{2−} subunit. Alternatively, it may be viewed as a central palladium chelated by two identical [Pd(dppp)(pdt)] fragments. The average Pd–S bond length within these fragments is 2.367 Å, and is 0.04 Å longer than that of the central Pd (2.326 Å), which may be explained by *trans* influences exerted by the phosphine ligands, as in other complexes in this paper. The planarity of the central PdS₄ unit is required by symmetry and only a small distortion from planarity is observed for the two PdP₂S₂ entities. The two PdP₂S₂ and one PdS₄ units are condensed through opposite edges in a *trans* fashion to form the Pd₃P₄S₄ core of **6**. The Pd···Pd distance is 3.0935(8) Å, indicating no direct metal–metal interaction.

The molecular structure of complex **4** is shown in Fig. 5. The molecule possesses a crystallographic twofold axis. The Pd₆

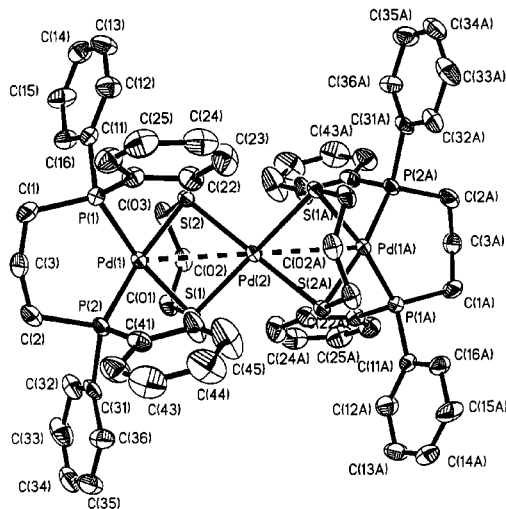


Fig. 4 Cation structure of complex 6.

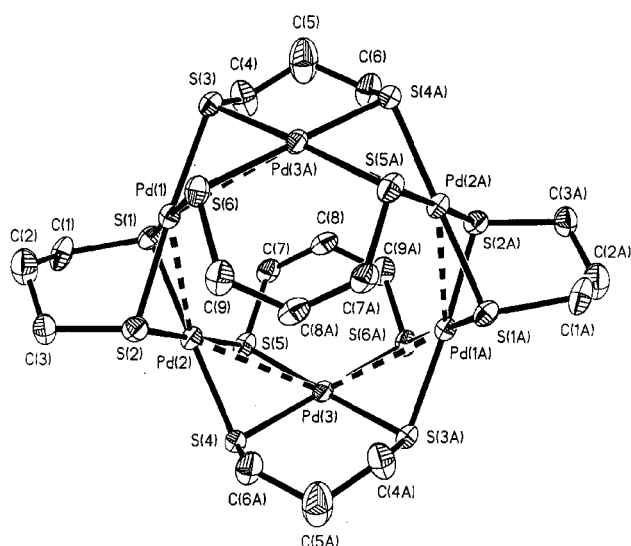


Fig. 5 Structure of complex 4.

core is similar to that of a cyclic complex with twelve monothiolate ligands, $[\text{Pd}_6(\text{SCH}_2\text{CH}_2\text{CH}_3)_{12}]^{2-}$.²³ The molecular structure may be derived from a hypothetical $[\text{Pd}(\text{pdt})_2]^{2-}$ anion, to which palladium(II) and $[\text{Pd}(\text{pdt})]$ fragments are linked in a *cis* fashion, giving a $[\text{Pd}_3(\text{pdt})_3]$ subunit. Two $[\text{Pd}_3(\text{pdt})_3]$ subunits connect head to tail in a *cis* fashion by sharing two common pdt^{2-} ligands to form a cyclic hexanuclear structure $[\text{Pd}_6(\text{pdt})_6]$. Each of the palladium atoms is surrounded by four sulfur atoms in a slightly distorted square-planar arrangement, and lies 0.11 Å above the corresponding S_4 least squares planes. The dihedral angles between PdS_2 planes fall in the range 159.42–165.03°. Of six pdt^{2-} ligands, four act as both chelating and bridging ligands bound to three Pd atoms and the other two as bridges between two Pd atoms. There are three six-membered rings in the Pd_6S_{12} core unit, *i.e.* two sulfur rings and one palladium ring, which form a sandwich in an antiprismatic configuration. The $\text{Pd}\cdots\text{Pd}$ and $\text{Pd}-\text{S}_6$ distances vary in the ranges 3.050–3.090 and 2.300–2.343 Å, respectively.

Electronic spectra

Electronic spectral data of complexes 3, 5, 6, and 7 in CH_2Cl_2 are provided in Table 2. All spectra are dominated by strong charge-transfer bands between 200 and 400 nm trailing out into regions of higher wavelengths. The bands in the regions $\lambda < 300$ nm are due to the diphosphine ligands and will not be discussed

Table 2 UV-Vis Spectral data and ^{31}P NMR chemical shifts (CDCl_3) of complexes 1, 3, 5–7

Complex	Absorption peak ($\lambda_{\text{max}}/\text{nm}$)	Chemical shifts δ
1 $[\text{Pd}(\text{dppp})(\text{edt})]$	235, 275	3.08
3 $[\text{Pd}(\text{O}_2\text{SCH}_2\text{CH}_2\text{SO}_2)(\text{edt})(\text{dppp})]$	235, 275, 320, 400	5.84
5 $[\text{Pd}_2(\text{dppp})_2(\text{pdt})]\text{Cl}_2$	255, 280, 340	7.15
6 $[\text{Pd}_3(\text{dppp})_2(\text{pdt})_2]\text{Cl}_2$	255, 285, 310, 380	6.91
7 $[\text{Pd}_2(\text{dppp})_2(\text{edt})]\text{Cl}_2$ dppp ²⁵	240, 285, 325	–16.7

here. In the case of the complexes with edt^{2-} ligands, the spectrum of 7 shows a strong band at λ_{max} 325 nm, while that of 3 exhibits a strong band at 320 nm and a shoulder at 400 nm. An obvious difference was observed when one ligand changed from dppp to sulfinate. In the case of the complexes with pdt^{2-} ligands, the electronic spectrum of 5 reveals an absorption peak at 340 nm. The spectrum of 6 is characterized by two bands at 310 and 380 nm. The spectrum of 1 shows two peaks at 275 and 235 nm which appear in the electronic spectra of 3 and are comparable to peaks at 240 and 285 nm for 7, but no peaks in the region $\lambda > 300$ nm. Since the difference between the co-ordination environment of palladium of 1 and those of 7 and 3 mainly comes from the coordination mode of the edt^{2-} ligand, it is likely that the absorptions at 325 nm for 7, 320 nm for 3, 340 nm for 5, 310 and 380 nm for 6 arise from sulfur-to-palladium LMCT transition. For complex 6 the two bands at 380 and 310 nm may belong to the absorption of 6 and another complex from dissociation of 6 in CH_2Cl_2 . The shoulder at 400 nm in the electronic spectrum of 3 should originate from sulfur-to-palladium LMCT transition in the PdS_4 moiety.

^{31}P NMR spectra

Table 2 includes the ^{31}P NMR data of all the complexes described in this paper and the related free diphosphine except for 7 whose spectrum could not be determined due to poor solubility. The spectra of 1–3, 5 and 6 show a single resonance peak in the range δ 7.15–3.08, indicating that their configurations in solution are consistent with their solid-state structures. The chemical shifts of these compounds increase as the ratio of $\text{Pd}^{2+}:\text{edt}^{2-}$ or pdt^{2-} increases, suggesting that their entire core structures influence the electron density around the P nucleus.

Conclusion

We have systematically investigated the condensation reactions of mononuclear palladium(II) complexes $[\text{Pd}(\text{dppp})(\text{edt})]$ and $[\text{Pd}(\text{dppp})(\text{pdt})]$ through the oxidation of the ligands by oxygen and elemental Se under different reaction conditions. The results obtained illustrate that the reactions depend on the media or the molar ratio of the reactants. It is suggested that the oxidation of ligands in simple complexes leads to detachment of ligands to form solvated active fragments, and the combination of the latter through the displacement of ligated solvent molecules gives rise to di- and poly-nuclear complexes. Braunstein *et al.*^{6a} have reported that the reaction of $[\text{Pd}_2(\text{dppm})_2\text{Cl}_2]$ with copper(I) ions gives a Pd_4 cluster, which is ascribed to dimerization of Pd_2 active fragments resulting from abstraction of Cl^- from $[\text{Pd}_2(\text{dppm})_2\text{Cl}_2]$ by Cu^+ . In spite of the difference in synthetic method, the condensation reactions presented by us correspond with Braunstein's reaction in terms of the assembly of active fragments. Therefore, in a sense, the chemistry described here has presented insight into the formation of polynuclear complexes in general. Our synthetic method used has opened a new way to palladium–phosphine chemistry.

Table 3 Crystallographic data for complexes **1**, **3**–**6**

	1	3	4	5	6
Formula	C ₂₉ H ₃₀ P ₂ PdS ₂	C ₃₁ H ₃₅ O _{4.5} P ₂ Pd ₂ S ₄	C ₁₈ H ₃₆ OPd ₆ S ₁₂	C ₅₇ H ₅₈ Cl ₂ P ₄ Pd ₂ S ₂	C ₆₃ H ₇₅ Cl ₂ NO ₃ P ₄ Pd ₃ S ₄
<i>M</i>	611.0	882.57	1293.7	1214.73	1536.46
Crystal system	Monoclinic	Orthorhombic	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P2₁/n</i>	<i>Aba2</i>	<i>P2₁/c</i>	<i>C2/c</i>	<i>C2/c</i>
<i>a</i> /Å	10.354(2)	15.905(3)	10.506(2)	22.5683(7)	27.118(5)
<i>b</i> /Å	25.041(5)	22.848(5)	16.789(3)	11.6585(4)	14.987(3)
<i>c</i> /Å	11.332(2)	18.904(4)	10.837(2)	20.5798(5)	20.477(4)
β /°	107.87(3)		99.83(3)		
<i>V</i> /Å ³	2796.3(9)	6870(3)	1883.4(6)	5363.3(3)	6677
<i>Z</i>	4	8	2	4	4
μ /mm ^{−1}	0.944	1.420	3.484	1.005	1.149
<i>T</i> /K	298	298	298	298	298
Reflections measured	5285	13643	8794	10133	11457
Unique reflections	5010	5790	3269	4613	5962
<i>R</i> _{int}	0.022	0.054	0.054	0.045	0.086
<i>R</i>	0.036	0.047	0.064	0.054	0.071
<i>R</i> _w	0.100	0.080	0.151	0.070	0.149

Experimental

Syntheses

All syntheses and manipulations were performed under a purified dinitrogen atmosphere using standard Schlenk techniques except as noted otherwise. The solvents were degassed prior to use. All common chemicals were of reagent grade. The solvents, PdCl₂ and elemental Se (amorphous red selenium) were purchased from Shanghai Chemical Reagents Factory, the other reagents from Aldrich chemical Co. The salts Na₂edt and Na₂pdt were prepared from the reaction of dithiol and sodium metal in absolute ethanol and precipitated by addition of diethyl ether in small portions to the solution. The products were collected by filtration, washed thoroughly with ether and dried in vacuum. The complex [Pd(dppp)(pdt)]^{12c} **2** was prepared by the literature method. All elemental analyses were carried out by the Elemental Analysis Laboratory in this Institute.

[Pd(dppp)(edt)] 1. A mixture of PdCl₂ (0.90 g, 5 mmol) and dppp (2.10 g, 5 mmol) in MeCN (20 ml) was stirred for 1 h at room temperature to yield a white precipitate. Upon addition of Na₂edt (0.70 g, 5 mmol) in EtOH (30 ml) the white precipitate immediately dissolved and the reaction solution turned orange-red. After stirring for 2 h, the solution was filtered and the filtrate kept at 4 °C for 2 days to yield orange crystals, which were collected by filtration, washed with water, ethanol and finally diethyl ether, and dried in vacuum, affording 1.89 g (62%). Calc. for C₂₉H₃₀P₂PdS₂: C, 57.0; H, 4.95. Found: C, 59.5; H, 4.96%. IR (KBr): 3048w, 2883w, 1434s, 1099m, 744m, 700s, 692s, 659m, 511s, 491m and 428w cm^{−1}. ¹H NMR (CDCl₃): δ 7.5–7.2 (20H, PC₆H₅), 2.93 (m, 4H, SCH₂), 2.51 (m, 4H, PCH₂) and 1.63 (s, 2H, PCCH₂).

[Pd₂(O₂SCH₂CH₂SO₂)(edt)(dppp)] 3. To a solution of complex **1** (1.20 g, 2 mmol) in DMF (15 ml) was added solid MeONa (0.04 g, 1 mmol) under vigorous stirring. Oxygen was bubbled into the reaction mixture at ambient temperature and then the temperature was raised to 90 °C when maintaining a slow stream of O₂. After 8 h the mixture was cooled to room temperature, then 20 ml MeOH were added. The solution was filtered and kept at 4 °C for one week to give yellow block crystals of **3**·0.5H₂O, yield 0.35 g (30%). Calc. for C₃₁H₃₅O_{4.5}P₂Pd₂S₄: C, 42.16; H, 4.00. Found: C, 43.77; N, 3.88%. IR (KBr): 3052w, 2915w, 1627m, 1434s, 1193s, 1064m, 1035s, 997m, 970m, 916m, 833w, 690s, 524w and 513s cm^{−1}. ¹H NMR (CDCl₃): δ 7.6–7.2 (20H, PC₆H₅), 3.59 (m, 4H, O₂SCH₂), 3.01, 2.96 (m, 4H, SCH₂), 2.57, 2.56, 2.55 (s, 4H, PCH₂) and 1.57 (m, 2H, PCCH₂).

[Pd₆(pdt)₆] 4. Solid complex **2** (1.25 g, 2 mmol) was dissolved in DMF (15 ml). Oxygen was bubbled into the solution at ambient temperature and then the temperature was raised to 90 °C whilst maintaining a slow stream of O₂. After 10 h the mixture was cooled to room temperature. During this period reaction solution gradually turned dark red from orange. It was filtered. After cooling the filtrate was mixed with MeOH (20 ml), and then kept at 4 °C for ten days to give dark red cubic crystals of **4**·H₂O, yield 0.11 g (26%). Calc. for C₁₈H₃₆OPd₆S₁₂: C, 16.7; H, 2.96. Found: C, 16.3; H, 3.07%. IR (KBr): 2900w, 1670s, 1261m, 1085w, 993w, 661w, 509w and 487w cm^{−1}. ¹H NMR (CDCl₃): δ 3.37 (m, 4H, SCH₂) and 1.83 (m, 2H, SCCH₂).

[Pd₂(dppp)₂(pdt)]Cl₂ 5. To a solution of complex **2** (0.63 g, 1 mmol) and Me₄NCl (0.11 g, 1 mmol) in CH₃CN (20 ml) was added elemental Se (0.02 g, 0.25 mmol). After stirring for 3 h the yellow precipitate formed was collected by filtration and washed with distilled water and ethanol, giving 0.11 g crystals of **5** (20%) on recrystallization from CH₂Cl₂. Calc. for C₅₇H₅₈Cl₂P₄Pd₂S₂: C, 56.3; H, 4.81. Found: C, 55.4, H, 4.81%. IR (KBr) 3068w, 3014w 2925w, 1434s, 1272w, 1103m, 977m, 756m, 709m, 692s, 513s and 493m cm^{−1}. ¹H NMR (CDCl₃): δ 7.78–7.19 (40H, PC₆H₅), 3.54, 3.32 (m, 4H, SCH₂), 2.80, 2.35 (m, 8H, PCH₂), 1.94 (m, 2H, SCCH₂) and 1.73 (m, 4H, PCCH₂).

[Pd₃(dppp)₂(pdt)₂]Cl₂ 6. To a solution of complex **2** (0.62 g, 1 mmol) in DMF (15 ml) were added elemental Se (0.08 g, 1 mmol) and Me₄NCl (0.11 g, 1 mmol). After stirring for 2 h at room temperature the solution was filtered. The final dark red solution was mixed with 2-propanol (15 ml), and kept at 4 °C for one week to give yellow crystals of **7**·DMF·2H₂O, yield 0.24 g (50%). Calc. for C₆₃H₇₅Cl₂NO₃P₄Pd₃S₄: C, 49.24; H, 4.92. Found: C, 51.4; H, 5.03%. IR (KBr): 3047w, 2900w, 1664s, 1434s, 1157w, 1101m, 703m, 511s and 487m cm^{−1}. ¹H NMR (CDCl₃): δ 8.02–7.13 (40H, PC₆H₅), 3.66, 3.47 (m, 8H, SCH₂), 2.962, 2.889 (s, 6H, (CH₃)₂NCHO), 2.68, 2.66, 2.46, 2.40, 2.32 (s, 8H, OCH₂), 1.87 (m, 4H, SCCH₂) and 1.75 (m, 4H, PCCH₂). Complex **6** can also be prepared from the stoichiometric reaction of **5** and Se followed by the addition of 1 equivalent of **2** in DMF.

[Pd₂(dppp)₂(edt)]Cl₂ 7. The preparation was similar to that of complex **5** described above except for the use of **1** as starting material. Recrystallization from DMF/MeOH afforded 0.08 g crystals of **7** (14%). Calc. for C₂₈H₂₈ClP₃PdS: C, 56.0; H, 4.70. Found: C, 57.5; H, 4.55%. IR (KBr): 3047w, 2987w, 1664w, 1434s, 1315w, 1151m, 1101s, 948w, 744m, 793s, 671m, 514s and 497m cm^{−1}.

Physical measurements

Infrared spectra in the range 4000–400 cm⁻¹ were recorded on a Magna 750 IR spectrometer with the use of pressed KBr pellets, electronic absorption spectra in CH₂Cl₂ solution on a Shimadzu UV-3000 spectrophotometer and ¹H NMR spectra for all compounds on a Varian Unity-500 spectrometer. Chemical shifts are quoted in ppm relative to the signal of TMS. All spectra were acquired at room temperature.

Crystallographic studies

For compounds **1**, **3–7**, cell dimension measurements and data collections were performed on a Siemens smart CCD diffractometer with graphite-monochromated Mo-K α radiation ($\lambda = 0.71073$ Å) at $23 \pm 1^\circ$. For the structure analyses, all calculations were performed on an HP/586 computer with the SHELXL PC program.²⁴ Crystallographic data are listed in Table 3. In the case of **1**, **3** and **4** all non-hydrogen atoms were refined anisotropically. The C02 atom of edt²⁻ for **1**, β -carbon atom of pdt²⁻ ligand for **5**, and the atoms in two DMF solvent molecules for **6**·DMF were treated for disorder in two positions by refining the site occupancies. Owing to the poor structural data, the *R* value of structure **7** is rather high. Crystal dimensions $0.12 \times 0.20 \times 0.30$ mm, C₅₆H₅₆Pd₂Cl₂P₂S₂, *M* = 1200.8, monoclinic, space group *C2/c* (no. 15), *a* = 22.300(7), *b* = 11.649(4), *c* = 20.307(6) Å, $\beta = 96.99(2)^\circ$, *V* = 3890(1) Å³, *Z* = 4, isotropic refinement of all non-hydrogen atoms on *F*_o for 2366 observations ($F \geq 2.0\sigma(F)$) and 173 variables, $R(R_w) = 0.166(0.217)$. Considering its structure is similar to that of **5**, the detailed structure is not discussed in this paper.

CCDC reference number 186/1882.

See <http://www.rsc.org/suppdata/dt/a9/a908788e/> for crystallographic files in .cif format.

Acknowledgements

This work was supported by grants from the National Science Foundation of China, the Natural Science Foundation of Fujian Province and the Youth Fund of Chinese Academy of Sciences.

References

- 1 R. F. Heck, *Palladium Reagents in Organic Synthesis*, Academic Press, San Diego, CA, 1985; J. Tsuji, *Palladium Reagents and Catalysts*, Wiley, New York, 1995.
- 2 V. V. Grushin, *Chem. Rev.*, 1996, **96**, 2011.
- 3 A. L. Balch, in *Homogeneous Catalysis with Metal Phosphine Complexes*, ed. L. Pignolet, Plenum Publishing, New York, 1983, ch. 5.
- 4 B. L. Edelbach, R. J. Lachicotte and W. D. Jones, *J. Am. Chem. Soc.*, 1998, **120**, 2843; D. Ferraris, B. Young, T. Dudding and T. Lectka, *J. Am. Chem. Soc.*, 1998, **120**, 4585.
- 5 R. J. Puddephatt, *Chem. Soc. Rev.*, 1983, **12**, 99; B. Chaudret, B. Delavaux and R. Poilblanc, *Coord. Chem. Rev.*, 1988, **86**, 191.
- 6 (a) P. Braunstein, M. A. Luke, A. Tiripicchio and M. T. Camellini, *Angew. Chem., Int. Ed. Engl.*, 1987, **26**, 768; (b) R. Usón, J. Forníés, L. R. Falvello, M. A. Usón, I. Usón and S. Herrero, *Inorg. Chem.*, 1993, **32**, 1066; (c) R. Usón, J. Forníés, J. F. Sanz, M. A. Usón, I. Usón and S. Herrero, *Inorg. Chem.*, 1997, **36**, 1912.
- 7 (a) S. Kannan, A. T. James and P. R. Sharp, *J. Am. Chem. Soc.*, 1998, **120**, 215; (b) T. Murahashi, T. Otani, E. Mochizuki, Y. Kai and H. Kurosawa, *J. Am. Chem. Soc.*, 1998, **120**, 4536; (c) J. Dupont, M. Pfeffer, M. A. Rotteveel, A. De Cian and J. Fischer, *Organometallics*, 1989, **8**, 1116; (d) A. L. Balch, J. R. Boehm, H. Hope and M. M. Olmstead, *J. Am. Chem. Soc.*, 1976, **98**, 7431; (e) I. Gautheron, J. Gagnon, T. Zhang, D. Rivard, D. Lucas, Y. Mugnier and P. D. Harvey, *Inorg. Chem.*, 1998, **37**, 1112; (f) R. V. Kireess and R. Eisenberg, *Inorg. Chem.*, 1989, **28**, 3372; (g) M. C. Jennings, N. C. Payne and R. J. Puddephatt, *J. Chem. Soc., Chem. Commun.*, 1986, 1809; (h) M. C. Jennings, N. C. Payne and R. J. Puddephatt, *Inorg. Chem.*, 1987, **26**, 3776; (i) M. T. Reetz, E. Bohres, R. Goddard, M. C. Holthausen and W. Thiel, *Chem. Eur. J.*, 1999, **5**, 2101.
- 8 (a) A. L. Balch, L. S. Benner and M. M. Olmstead, *Inorg. Chem.*, 1979, **18**, 2996; (b) C. T. Hunt and A. L. Balch, *Inorg. Chem.*, 1981, **20**, 2267; (c) A. L. Balch, C. T. Hunt, C. L. Lee, M. M. Olmstead and T. P. Farr, *J. Am. Chem. Soc.*, 1981, **103**, 3764; (d) M. Ebner, H. Otto and H. Werner, *Angew. Chem., Int. Ed. Engl.*, 1985, **24**, 518; (e) G. Ferguson, B. R. Lloyd, L. Manojlović-Muir, K. W. Muir and R. J. Puddephatt, *Inorg. Chem.*, 1986, **25**, 4190; (f) S. Okeya, H. Kameda, H. Kawashima, H. Shimomura, T. Nishioka and K. Isobe, *Chem. Lett.*, 1995, 501.
- 9 M. J. H. Russel and C. F. J. Barnard, in *Comprehensive Coordination Chemistry*, eds. G. Wilkinson, R. D. Gillard and J. A. McCleverty, Pergamon Press Ltd., Oxford, 1987, vol. 5, p. 1103.
- 10 (a) D. L. Reger and J. E. Collins, *Inorg. Chem.*, 1995, **34**, 2473; (b) S. P. Kaiwar, J. K. Hsu, L. M. Liable-Sands, A. L. Rheingold and R. S. Pilato, *Inorg. Chem.*, 1997, **36**, 4234; (c) M. Capdevila, W. Clegg, P. Gonzalez-Duarte, B. Harris, L. Mira, J. Sola and I. C. Taylor, *J. Chem. Soc., Chem. Commun.*, 1992, 2817; (d) K. A. Van Houten, D. C. Heath, C. A. Barringer, A. L. Rheingold and R. S. Pilato, *Inorg. Chem.*, 1998, **37**, 4647.
- 11 R. Cao, M. Hong, F. Jiang, X. Xie and H. Liu, *J. Chem. Soc., Dalton Trans.*, 1994, 3459.
- 12 (a) R. Cao, W. Su, M. Hong, W. Zhang, W. T. Wong and J. X. Lu, *Chem. Commun.*, 1998, 2083; (b) R. Cao, M. Hong, F. Jiang, X. Xie and H. Liu, *Polyhedron*, 1996, **15**, 2661; (c) W. Su, R. Cao, M. Hong, Z. Zhou, F. Xie, H. Liu and T. Mak, *Acta Crystallogr., Sect. C*, 1996, **52**, 2691; (d) W. Su, R. Cao, M. Hong, Z. Zhou, F. Xie, H. Liu and T. Mak, *Polyhedron*, 1997, **16**, 2531.
- 13 G. N. Schrauzer, C. Zhang and R. Chadha, *Inorg. Chem.*, 1990, **29**, 4104.
- 14 T. Nicholson and J. Zubieta, *Inorg. Chem.*, 1987, **26**, 2094.
- 15 G. Christou and C. D. Garner, *J. Chem. Soc., Dalton Trans.*, 1979, 1093; G. Christou, B. Ridge and H. N. Rydon, *J. Chem. Soc., Dalton Trans.*, 1978, 1423; K. S. Hagen, J. G. Reynolds and R. H. Holm, *J. Am. Chem. Soc.*, 1981, **103**, 4054.
- 16 I. G. Dance, A. Choy and M. L. Scudder, *J. Am. Chem. Soc.*, 1984, **106**, 6285.
- 17 R. J. Mereinik, *Rev. Inorg. Chem.*, 1979, **1**, 11.
- 18 B. S. Snyder, C. P. Rao and R. H. Holm, *Aust. J. Chem.*, 1986, **39**, 963.
- 19 W. Tremel, M. Kriege, B. Krebs and G. Henkel, *Inorg. Chem.*, 1988, **27**, 3886.
- 20 W. L. Steffen and G. J. Palenik, *Inorg. Chem.*, 1976, **15**, 2432.
- 21 K. Osakada, Y. Ozawa and A. Yamamoto, *Bull. Chem. Soc. Jpn.*, 1991, **64**, 2002; R. H. Fenn and G. R. Segrott, *J. Chem. Soc., Dalton Trans.*, 1972, 330; I. Hakanishi, S. Tanaka, K. Matsamoto and S. Ooi, *Acta Crystallogr., Sect. C*, 1994, **50**, 58.
- 22 F. X. Power and D. R. Lide, *J. Chem. Phys.*, 1964, **41**, 1413; L. Markó, B. M. Monostory, T. Madach and H. Vahrenkamp, *Angew. Chem., Int. Ed. Engl.*, 1980, **19**, 226; P. Lorenz, J. Messlhäuser, W. Hiller and K. Haug, *Angew. Chem., Int. Ed. Engl.*, 1985, **24**, 228; G. Besenyi, C. Lee, J. Gaulinski, S. J. Rettig, B. R. James, D. A. Nelson and M. A. Lilga, *Inorg. Chem.*, 1987, **26**, 3622.
- 23 N. R. Kunchur, *Acta Crystallogr., Sect. B*, 1968, **24**, 1623.
- 24 G. M. Sheldrick, SHELXL 93, Program for Crystal Structure Refinement, Universität Göttingen, 1993.
- 25 D. G. Gorenstein and D. O. Stah, *³¹P NMR Principles and Application*, Academic Press, New York, 1984.