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Phosphine Control of the Oxidative Addition Chemistry of Tetrathiocins to Palladium(0): Characterization of Mono-, Di-, and Hexanuclear Palladium(II) Dithiolate Complexes

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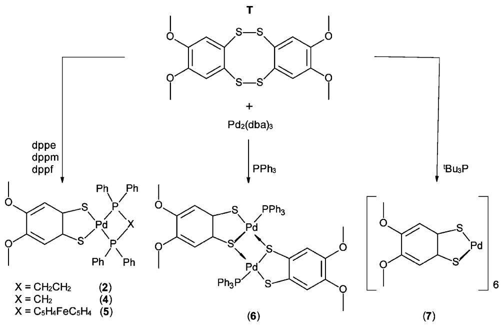
Supporting Information

ABSTRACT: The outcome of the oxidative addition reactions of bis(4′,5′-dimethoxybenzo)-1,2,5,6-tetrathiocin to Pd_2dba_3 under microwave conditions is sensitive to the nature of the phosphine coreagent; the bidentate phosphines dppm, dppe, and dppf afford the mononuclear dithiolates (dmobdt)Pd(dppm) (**4**), (dmobdt)Pd(dppe) (**2**), and (dmobdt)Pd(dppf) (**5**), whereas more labile monodentate phosphines lead to aggregation; Ph_3P afforded the dinuclear dithiolate $(dmobdt)_2Pd_2(PPh_3)_2$ (**6**), whereas $^tBu_3P$ generated the phosphine-free hexanuclear edge-capped octahedral complex $Pd_6(dmobdt)_6$ (**7**) [dmobdt = 4,5-dimethoxybenzenedithiolate, $(MeO)_2C_6H_2S_2^{2-}$].

Complexes of the redox-active dithiolene ligand system have continued to attract interest since initial investigations into their chemistry in the early 1960s.[1] In particular, the potential to tailor the electronic properties of the dithiolene ligand through modification of the substituents is central to future applications in areas such as nonlinear optics,[2] dyes,[3] catalysis,[4] and conducting[5] as well as magnetic materials.[6] Despite this, nearly 70% of the structures of bidentate benzodithiolate complexes reported in the CSD are restricted to just two derivatives: the benzenedithiolato and toluenedithiolato ligands.[7] We recently reported that the series of group 10 complexes (dmobdt)M(dppe) [M = Ni (**1**), Pd (**2**), Pt (**3**)] containing the $dmobdt^{2-}$ ligand ($dmobdt^{2-}$ = 4,5-dimethoxybenzenedithiolate) could be prepared in high yield in a one-pot microwave reaction from the oxidative addition of the corresponding bis(dimethoxybenzo)-tetrathiocin (**T**) to zerovalent group 10 metal complexes in the presence of the chelating phosphine dppe.[8] Notably microwave conditions offered cleaner reactions and shorter reaction times over conventional synthetic methods. In the current paper, we investigate the effect of the phosphine on the outcome of this reaction and find that the reaction outcome appears sensitive to the nature of the phosphine employed. Reaction of Pd_2dba_3 with **T** in the presence of Ph_3P afforded the binuclear complex (**6**) and the hexanuclear complex (**7**) in the presence of $^tBu_3P$ (Scheme 1).

Scheme 1. One-Step Synthesis of Palladium Dithiolates



Treatment of $Pd_2(dba)_3$ with tetrathiocin **T** in the presence of the chelate phosphine dppm, dppe, or dppf under microwave irradiation (20 min) led to a color change from dark amber to yellow/brown and the formation of a dark precipitate of **4**, **2**, and **5**, respectively. Conversely, the same reaction with dppe under conventional heating for 48 h did not afford any complex **2** but $dppeS_2$ among other products (see the Supporting Information), consistent with our previous observation that microwave heating appears to be more selective.[8] Recrystallization of the resultant air-stable precipitates afforded crystals of **2**, **4**, and **5** suitable for X-ray diffraction. They were additionally characterized by multinuclear NMR spectroscopy, mass spectrometry, IR spectroscopy, and elemental analysis. We previously reported the structure of the dppe complex (**2**).[8] The dppm derivative (**4**) crystallizes in the monoclinic space group $P2_1/c$ with two molecules per asymmetric unit, whereas the dppf derivative (**5**) crystallizes in the triclinic space group $P\overline{1}$ with three molecules in the asymmetric unit. A representative molecule from the structure of **5** is shown in Figure 1.

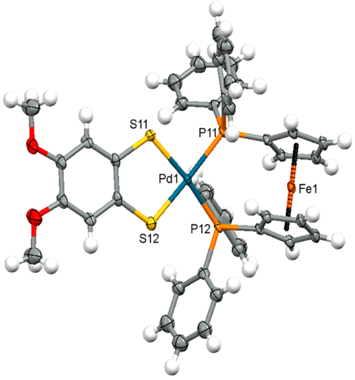


Figure 1. Crystal structure of **5** with thermal ellipsoids drawn at the 50% probability level.

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The Pd–S bond lengths in **4** and **5** are similar to those of the previously reported dppe derivative [**2**; 2.2977(6) Å], spanning the range 2.276(3)–2.304(4) Å, and the chelate S–Pd–S angles are correspondingly similar [85.5(1)–89.74(5)°]. While the palladium dithiolate component remains somewhat invariant, more pronounced changes are evident as the "bite" of the phosphine is adjusted. Although the Pd–P distances in **4** [2.270(2)–2.284(2) Å] are similar to those in **2** [2.2740(6) Å], the smaller bite of the dppm moiety leads to some strain, with a smaller P–Pd–P chelate angle [73.29(4)–73.50(4)°] compared to that of **2** [84.98(3)°]. Conversely, the large bite of the dppf ligand in **5** is accommodated by larger Pd–P distances [2.280(3)–2.321(3) Å] and larger P–Pd–P angles [96.7(1)–97.4(1)°]. Nevertheless, all coordination geometries are very close to planar with the sums of the internal angles at Pd in the range of 357.3–360.0°. Given the variation of the Pd–P bond length and angle with the chelate nature of the phosphine, we pursued bulkier monodentate phosphines (Ph_3P and $^tBu_3P$ have Tolman cone angles[9] of 145° and 182°, respectively).

Treatment of Pd_2dba_3 with tetrathiocin **T** in the presence of Ph_3P, under otherwise identical microwave conditions, led to the formation of a dark-green solution from which dark-green crystals of the dimeric complex $Pd_2(dmobdt)_2(PPh_3)_2$ (**6**) were grown from CH_2Cl_2/Et_2O. Similar reactivity has been observed for the oxidative addition of diselenides R_2Se_2 to $Pt(PPh_3)_4$ and $Pd(PPh_3)_4$, although ditellurides exhibit more complex reactivity with C–Te as well as Te–Te bond cleavage.[10] Unlike **2**, **4**, and **5**, which reveal just one singlet in the alkyl region of the ^1H NMR spectrum, the ^1H NMR spectrum of **6** revealed two distinct ^1H resonances in the alkyl region (at 2.9 and 3.6 ppm), consistent with retention of the dimeric structure in solution. This was further supported by mass spectrometry, which revealed the appropriate isotope distribution pattern around *m*/*z* 1138 corresponding to the M^+ ion, as well as further peaks at *m*/*z* 876 corresponding to $M^+ - PPh_3$. Crystallographic studies revealed a dimeric species in which one of the two dithiolate S atoms adopts a μ_2-bridging mode, with the molecule located about a crystallographic 2-fold axis (Figure 2).

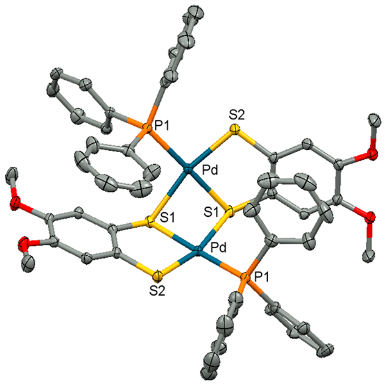

Figure 2. Crystal structure of **6** with thermal ellipsoids drawn at the 75% probability level. H atoms are omitted for clarity.

The Pd–S2 bond [2.2795(5) Å] is at the shorter end of those seen in other Pd(dmobdt) complexes [2.276(3)–2.304(4) Å], but the Pd–S1 distance [2.3246(5) Å] increases, consistent with its μ_2-bridging coordination mode. The sum of the internal angles at Pd (359.74°) is consistent with a planar geometry. While the S1–Pd–S2 angle of 89.31(2)° is similar to those observed in **2**, **4**, and **5** [85.5(1)–89.74(5)°]. The bridging S1–Pd–S1 angle [79.57(2)°] is rather acute and the P–Pd–S1 angle [99.70(2)°] is somewhat larger, leading to a *trans*-S1–Pd–S2 angle of 166.09(2)° to accommodate the bulk of the Ph_3P group. A search of the Cambridge Structural Database (2014) reveals just two previous dinuclear palladium dithiolate complexes of this type: $[Pd(S_2C_2H_2)(PPh_3)]_2$ and $[Pd(S_2C_2H_4)(PPh_3)]_2$.[11]

To further investigate the effect of the phosphine ligand on reactivity, we increased the steric demand of the phosphine by replacing Ph_3P with $^tBu_3P$. Treatment of Pd_2dba_3 with tetrathiocin **T** in the presence of $^tBu_3P$ under microwave irradiation led to the formation of a dark-brown solution, from which brown crystals of the hexanuclear homoleptic complex $[Pd(dmobdt)]_6$ (**7**) could be grown (Figure 3).

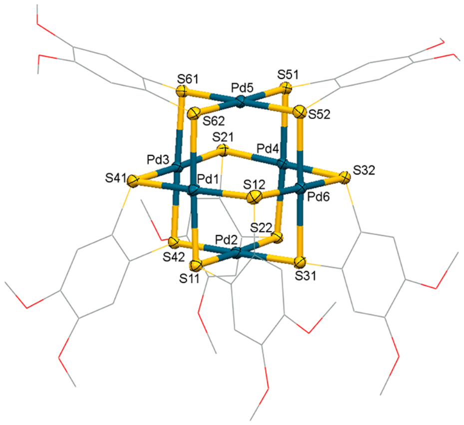

Figure 3. Crystal structure of complex **7** highlighting the edge-capped octahedral core. H atoms and solvate molecules are removed for clarity. Thermal ellipsoids for the Pd and S atoms are drawn at 50% probability.

The crystal structure of **7** comprises an octahedron of Pd ions, with each S atom of a dithiolate anion adopting a μ_2-bridging mode. Four $dmobdt^{2-}$ ions bridge from the "basal" Pd2 center to the four "equatorial" Pd centers (Pd1, Pd3, Pd4, and Pd6), whereas two $dmobdt^{2-}$ anions bridge from the apical Pd5 to the four "equatorial" Pd ions. The Pd–S distances fall in the range 2.294(2)–2.361(2) Å. It is noteworthy (in the context of the ^1H NMR) that there is a noncrystallographic 2-fold rotation axis passing through Pd2 and Pd5 such that the $dmobdt^{2-}$ ligands containing S51/S52 and S61/S62 are chemically equivalent. Similarly, the two $dmobdt^{2-}$ ligands containing S31/S32 and S41/S42, as well as those containing S11/S12 and S21/S22, are chemically equivalent.

Although a range of homoleptic palladium dithiolates of formula $[Pd(SR)_2]_6$ are known,[12] these are almost invariably based upon cyclic structures, whereas the current example adopts a cage motif. Just one previous example of a hexanuclear dithiolate cage complex of this type has been reported previously;[13] $[PdS_2C_2(COOMe)_2]_6$ was prepared from ligand exchange from the reaction of $(tmeda)ZnS_2C_2(COOMe)_2$ with $(MeCN)_2PdCl_2$. Notably these two hexameric clusters differ in the nature of the bridging mode of the dithiolate ligands around the Pd_6 core. In **7**, the structure contains a noncrystallographic 2-fold axis, whereas $[Pd(S_2C_2(COOMe)_2]_6$ exhibits a noncrystallographic S_6 axis.[13] The Pd_6S_{12} core of **7** is isolobal with Pd_6Cl_{12}.[14] Previous density functional theory (DFT) studies on the related Pt_6Cl_{12} indicated[15] the absence of M–M bonding within these structures, and while the intramolecular Pd···Pd contacts [3.2284(8)–3.3833(8) Å] are a little shorter than those reported for structures containing the Pd_6Cl_{12} unit (3.29–3.34

Å), they are consistent with a nonbonding metal···metal interaction.

The ^{1}H NMR spectrum of **7** afforded six singlets in the methoxy region and six corresponding peaks in the aryl C−H region consistent with retention of the hexanuclear structure in solution in which the noncrystallographic 2-fold axis affords three chemically distinct dmobdt^{2-} ligand environments. Retention of the molecular structure beyond the solid state is also reflected in the observation of a molecular ion in the FAB$^+$ mass spectrum.

Previous electrochemical studies on the hexanuclear complex $[PdS_2C_2(COOMe)_2]_6$ revealed a series of four reversible one-electron reductions in the range −0.186 to −1.524 V (with respect to a saturated calomel electrode).[13] Electrochemical studies on **7** reveal two reversible reduction processes with $E_{1/2}$ = −0.91 and −1.34 V and one clear reversible one-electron oxidation ($E_{1/2}$ = +1.25 V) coupled with a second oxidation at ca.1.52 V, close to the boundary of the electrochemical window (Figure 4). DFT studies reveal that these redox processes are associated with the Pd_6S_{12} core of **7** (see the Supporting Information).

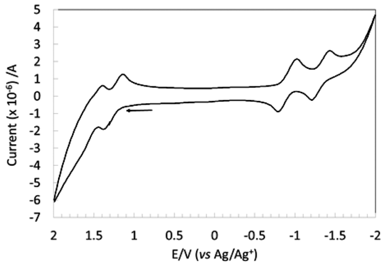

Figure 4. Cyclic voltammogram of **7** using a 0.1 M $[^nBu_4N][PF_6]$ supporting electrolyte in CH_2Cl_2 (scan rate 100 mV/s).

A search of the CSD has revealed several other group 10 metal phosphinedithiolate clusters of the formula $M_xL_xP_y$ (L = 1,2-dithiolate; P = phosphine) including $M_3L_3P_2$ and $M_2L_2P_2$.[16,17] These would indicate that an appropriate choice of monodentate phosphine and metal may lead to other polymetallic frameworks.

In conclusion, the outcome of the oxidative addition of tetrathiocins to low-valent transition-metal centers appears to be extremely sensitive to the steric, and potentially electronic, effects of the coligand. Further studies are now underway to extend this reactivity to other accessible dialkoxytetrathiocins[18] as well as the perhaloarene derivatives $(C_6X_4S_2)_2$ (X = F, Cl).[19]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.5b01555.

Crystallographic data for **4** in CIF format (CIF)
Crystallographic data for **5** in CIF format (CIF)
Crystallographic data for **6** in CIF format (CIF)
Crystallographic data for **7** in CIF format (CIF)
Experimental details for the synthesis of **4**−**7** (PDF)

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Notes

The authors declare no competing financial interest.

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