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PAPER

Reactivity of the bridged-sulfide complex $Pd_2Cl_2(\mu\text{-}S)(\mu\text{-}dmpm)_2$ toward electrophiles†

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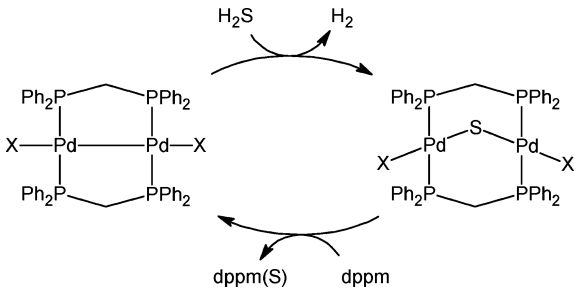
The dipalladium(I) complex $Pd_2Cl_2(dmpm)_2$ (**1a**) [dmpm = bis(dimethylphosphino)methane‡] is known to react with elemental sulfur (S_8) to give the bridged-sulfide complex $Pd_2Cl_2(\mu\text{-}S)(dmpm)_2$ (**2a**) but, in the presence of excess S_8, $PdCl_2[P,S\text{-}dmpm(S)]$ (**4a**) and $dmpm(S)_2$ are generated. Treatment of **1a** with elemental selenium (Se_8), however, gives only $Pd_2Cl_2(\mu\text{-}Se)(dmpm)_2$ (**3a**). Complex **4a** is best made by reaction of *trans*-$PdCl_2(PhCN)_2$ with dmpm(S). Complex **2a** reacts with MeI to yield initially $Pd_2I_2(\mu\text{-}S)(dmpm)_2$ and MeCl, and then $Pd_2I_2(\mu\text{-}I)_2(dmpm)_2$ and Me_2S, whereas alkylation of **2a** with MeOTf generates the cationic, bridged-methanethiolato complex $[Pd_2Cl_2(\mu\text{-}SMe)(dmpm)_2]OTf$ (**5**). Oxidation of **2a** with *m*-CPBA forms a mixture of $Pd_2Cl_2(\mu\text{-}SO)(dmpm)_2$ and $Pd_2Cl_2(\mu\text{-}SO_2)(dmpm)_2$, whereas $Pd_2Br_2(\mu\text{-}S)(dmpm)_2$ reacts selectively to give $Pd_2Br_2(\mu\text{-}SO)(dmpm)_2$ (**6b**). Treatment of the $Pd_2X_2(\mu\text{-}S)(dmpm)_2$ complexes with X_2 (X = halogen) removes the bridged-sulfide as S_8, with co-production of Pd^{II}(dmpm)-halide species. X-ray structures of **3a**, **5** and **6b** are presented. Reactions of dmpm with S_8 and Se_8 are clarified. Differences in the chemistry of the dmpm systems with that of the corresponding dppm systems [dppm = bis(diphenylphosphino)methane‡] are discussed.

Introduction

We published recently a paper describing reactions of the bis(dimethylphosphino)methane (dmpm) complexes $Pd_2X_2(dmpm)_2$ (X = halogen) with H_2S, S_8, COS, and CS_2.[1] The studies evolved from earlier findings from our laboratory on the stoichiometric reaction of the corresponding bis(diphenylphosphino)methane (dppm) species, $Pd_2X_2(dppm)_2$, with H_2S to generate $Pd_2X_2(\mu\text{-}S)(dppm)_2$ and H_2, as well as an associated catalytic conversion of H_2S and dppm to H_2 and the monosulfide dppm(S), see Scheme 1.[2] Related to this is a more recent report noting that PMe_3-stabilized Mo-sulfide species correspondingly catalyse conversion of H_2S to H_2 and $SPMe_3$.[3] Within Scheme 1, any reagent that can remove the bridging sulfur to regenerate the reactive Pd–Pd bond will clearly lead to a catalytic process utilising H_2S. Other strategies have involved, for example, oxidation of the bridged-sulfide with H_2O_2 or *m*-chloroperbenzoic acid (*m*-CPBA), which results in the formation of a bridged-sulfur dioxide complex that subsequently



Scheme 1 Pd-catalysed reaction between H_2S and dppm to form H_2 and dppm(S).

eliminates SO_2 and regenerates the reactive Pd(I) species;[4] thus a two-stage process effecting catalysis of the reaction shown in eqn (1) could certainly be realised.

$$H_2S + 2\ \text{“O”} \rightarrow H_2 + SO_2 \quad (1)$$

The findings of the enhanced reactivity of $Pd_2Cl_2(dmpm)_2$ (**1a**), compared to that of $Pd_2Cl_2(dppm)_2$, toward H_2S,[1] and SO_2,[5] and discovery of reactions of **1a** with COS and CS_2 while the dppm analogue is unreactive,[1] prompted us to investigate the reactivity of the bridged-sulfide derivative $Pd_2Cl_2(\mu\text{-}S)(dmpm)_2$ (**2a**). The solubility of Pd-dmpm species in water, in contrast to the non-solubility of the dppm analogues,[5] was also a key factor in motivating our studies. This paper mainly describes reactivity of **2a** toward some electrophilic reagents, where again some unusual behaviour (not seen in the dppm analogue) is observed. For example, reaction with elemental sulfur (S_8) leads

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† Electronic supplementary information (ESI) available: ORTEP of $dmpm(S)_2$, $^{31}P\{^1H\}$-NMR spectra of $dmpm(Se)_2$, dmpm(S)(Se) and complex **5**. CCDC reference numbers 849399–849401. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1dt11961c

‡ In all the dipalladium complexes mentioned in this paper, the dmpm and dppm ligands (unless stated otherwise) are bridging, but for convenience the μ-symbol is omitted.

§ Deceased October 27, 1998.

Table 1 Selected NMR data for the dmpm derivatives, and some new Pd-complexes[a]

Compound	δ_H (PCH_2P protons)	δ_P ($^{31}P\{^1H\}$)[b]
dmpm	1.33	−54.5[c]
dmpm(S)	2.01 (13.5)[c]	−48.1, 40.7 (53.4)[d]
dmpm$(S)_2$	2.67 (13.4)[e]	32.5
dmpm(S)(Se)	2.84 (13.3)[f]	12.6, 33.9 (16.4)[d,g]
dmpm$(Se)_2$	3.01 (13.4)[e]	12.9 (17.0)[h]
Pd_2Cl_2(μ-Se)(dmpm)$_2$ (**3a**)	2.15 (3.3, 13.4)[i]; 3.41 (5.7, 13.4)[i]	−13.6
$PdCl_2$[*P*,*S*-dmpm(S)] (**4a**)[j]	3.49 (12.3)[f]	33.6, 63.8 (22.5)[d]
PdI_2[*P*,*S*-dmpm(S)] (**4c**)[j]	3.37[k]	35.5, 69.6 (32.4)[d]
$PdCl_2$[*P*,*Se*-dmpm(Se)]	Unidentified	32.6, 36.1 (29.0)[d]
[Pd_2Cl_2(μ-SMe)(dmpm)$_2$]OTf (**5**)[l]	2.02 (14.7)[m]; 2.47 (15.4)[m]; 2.73 (15.4)[m]; 3.11 (14.7)[m]	−8.3, 0.2[n]
Pd_2Cl_2(μ-SO)(dmpm)$_2$ (**6a**)[o]	2.54 (10.0, 14.4)[p]; 3.13 (12.5, 12.7)[p]	−12.9, 4.8[n]
Pd_2Br_2(μ-SO)(dmpm)$_2$ (**6b**)	1.07 (7.3, 12.1, 14.3)[q]; 1.36 (6.6, 11.6, 13.2)[q]; 2.60 (10.1, 14.3)[p]; 3.18 (12.8, 13.3)[p]	−13.5, 4.5[n]

[a] δ_H = ^{1}H shift for PCH_2P protons; δ_P = $^{31}P\{^1H\}$ shift; J_{PH} and J_{HH} values in Hz given in parentheses. [b] Singlets in $CDCl_3$ at 20 °C, unless indicated otherwise. [c] Pseudodoublet ($^2J_{PH}$). [d] AB pattern ($^2J_{PP}$). [e] Triplet ($^2J_{PH}$). [f] Pseudotriplet ($^2J_{PH}$). [g] $^1J_{PSe}$ = −705 Hz. [h] $^2J_{PP}$ value determined from ^{77}Se satellites; $^1J_{PSe}$ = −707 Hz. [i] Doublet of quintets ($^2J_{PH}$, $^2J_{HH}$). [j] In DMSO-d_6. [k] Multiplet, overlap with H_2O signal (δ_H 3.32). [l] −60 °C in CD_2Cl_2. [m] Doublet of multiplets ($^2J_{PH}$ unresolved, $^2J_{HH}$ shown). [n] AA′BB′ pattern. [o] Two sets of CH_2 signals hidden in the CH_3-region. [p] Doublet of triplets for one CH_2-proton ($^2J_{PH}$, $^2J_{HH}$). [q] Doublet of triplets of triplets for one CH_2 proton ($^4J_{PH}$, $^2J_{PH}$, $^2J_{HH}$).

to decomposition of the Pd(II)-dmpm framework with oxidation of dmpm to the phosphine sulfides. Related studies with elemental selenium (Se_8) are described, as well as reactions with *m*-CPBA and halogens, and methylation reactions with MeOTf and MeI.

Results and discussion

Sulfur and selenium derivatives of dmpm

The reactions to be described reveal formation of sulfur and selenium derivatives of dmpm as co-products, and thus the characterisation of these compounds was investigated. The mono- and di-sulfides, dmpm(S) and dmpm$(S)_2$, were obtained pure from reaction of dmpm with elemental sulfur. The NMR data are given in Table 1 with those of some new Pd complexes discussed in this paper.

Reaction of dmpm with elemental sulfur

The *in situ* reaction of dmpm with elemental S_8 (2.2 mole equiv.) in $CDCl_3$ at room temperature (r.t., ~295 K) generates dmpm$(S)_2$ in quantitative yield as indicated by a single resonance at δ_P 32.5 in the $^{31}P\{^1H\}$ NMR spectrum, but a 1 : 1 reaction gave a colourless mixture of dmpm (δ_P −54.5), dmpm(S) (δ_P = −48.1, δ_{PS} = 40.7, $^2J_{PP}$ = 53.4 Hz) and dmpm$(S)_2$. The well-characterised disulfide has been isolated previously from a similar phosphine/S_8 method,[6] as well as a by-product from the reaction of S_8 with Ge[$(Me_2P)_2CH(SiMe_3)$]$_2$.[7] A 1 : 1 preparative scale reaction in benzene, after removal of the volatile components *in vacuo*, gave a solid mixture of dmpm(S) and dmpm$(S)_2$ that was isolated as described previously in a BP patent.[8] Attempts to separate the components by column chromatography were unsuccessful, but pure dmpm(S) was isolated from the mixture by vacuum sublimation as an air-stable, white solid in 46% yield. The air-stability contrasts with the pyrophoric nature of dmpm, the reactivity of the P(III) atom presumably being attenuated by the P(V) site. Dissolution of the non-volatile, white residue in CH_2Cl_2, followed by filtration, evaporation, and recrystallisation allowed for isolation of pure dmpm$(S)_2$ (in 18% yield). The dmpm sulfides were characterised by melting point, elemental analysis, and NMR spectroscopy.

The $^2J_{PP}$ value for dmpm(S) is in the 50–85 Hz range reported for several unsymmetrical bis(diphenylphosphino)methane compounds, including dppm(S) ($^2J_{PP}$ = 76 Hz).[9] The CH_2 protons of dmpm(S) appear as a pseudodoublet (δ_H 2.01, $^2J_{PH}$ = 13.5 Hz), the $^2J_{PH}$ coupling to one of the P-atoms not being resolved. A doublet signal has similarly been reported for $Ph_2PCH_2P(S)Me_2$ ($^2J_{PH}$ = 14.0 Hz).[6]

Slow evaporation of a solution of analytically pure dmpm(S) in EtOH, ^{i}PrOH, or H_2O surprisingly yielded colourless crystals of dmpm$(S)_2$ and, as a result, the molecular structure of this compound was accidentally redetermined. The ORTEP diagram and selected geometric parameters are shown in Figure S1†, and the data are essentially identical to those previously reported.[7] Both P-atoms are in distorted tetrahedral environments, and the P–S distances of 1.950 and 1.952 Å are in the standard range.[10] The P–C–P angle (118.75°) is larger than that of 114(3)° observed for gas-phase dmpm.[11] In contrast to behaviour in the polar protic solvents, a $CDCl_3$ solution of dmpm(S) was stable, even in air, for days. The disproportionation reaction, readily detected by the distinctive smell of dmpm and the associated δ_P −54.5 singlet (Table 1), was not light-induced.

The facile dispropoprtionation of dmpm(S) contrasts with the stability of dppm(S) under similar conditions,[2b] and indeed dppm(S) has been made by direct reaction of dppm and dppm$(S)_2$.[12] Whether the difference in reactivity between dmpm(S) and dppm(S) arises from steric or electronic effects is unclear. Enthalpy values show that protonation is much more favourable for the dmpm system,[13] but such protonated species were not observed in this work. Lack of steric protection in dmpm(S) might allow closer contact between the P-lone pair and the S-atom of an adjacent molecule, and facilitate S-atom transfer; in any case, the volatility and air-sensitivity of the dmpm will likely force the disproportionation to completion, especially when the reaction is carried out in air. Of note, a mixture of the dmpm sulfides has been used to promote the Rh-catalysed acetic acid synthesis from CO and MeOH, and dmpm(S) was patented for use as a co-catalyst, although its role was not identified.[8] The

carbonylation process takes place in neat MeOH under conditions where disproportionation would likely take place. Our finding that dmpm(S) readily decomposes to the volatile and pyrophoric dmpm makes dmpm(S) an unlikely candidate for large-scale catalytic processes.

Reaction of dmpm with elemental selenium

The addition of a $CDCl_3$ suspension of amorphous, red Se_8 to a $CDCl_3$ solution of dmpm (Se: dmpm = 2) generated quantitatively *in situ* a single product showing a $^{31}P\{^1H\}$ singlet resonance at δ_P 12.9 and characteristic, satellites doublets of ^{77}Se ($I = \frac{1}{2}$, 7.6% abundant), data that are consistent with the presence of dmpm(Se)$_2$ (Fig. S2-a†). This known compound, identified *in situ* as a by-product in the reaction of Ge[(Me$_2$P)$_2$CH(SiMe$_3$)]$_2$ with Se, has a δ_P value of 10.4 in C_6D_6, but the $^1J_{PSe}$ coupling was not given.[7] In addition, the $^2J_{PP}$ coupling constant (17.0 Hz) could also be determined from the ^{77}Se satellites in $CDCl_3$ even though the P-atoms are chemically equivalent.[9,14] The value is consistent with the dmpm(E)$_2$ formulation (E = O, S, Se), as monosubstituted diphosphines typically have larger $^2J_{PP}$ values, for example, 76.0 Hz for dppm(S)[8] and 53.4 Hz for dmpm(S) (see above). For dmpm(Se)$_2$, $^1J_{PSe}$ = −707 Hz, comparable to values of −684 and −752 Hz, respectively, for SePMe$_3$[15] and dppm(Se)$_2$;[9] such coupling constants are negative, as determined by a triple resonance NMR technique.[15,16]

An attempted, preparative scale synthesis from a 1 : 1 Se/dmpm reaction in C_6H_6 yielded a pink solid, which on vacuum sublimation gave a white solid, whose C/H analysis was between those calculated for dmpm(Se) and dmpm(Se)$_2$ but closer to that of the monoselenide. The ^1H and $^{31}P\{^1H\}$ NMR spectra ($CDCl_3$) of the sublimed material imply rapid disproportionation to dmpm(Se)$_2$ and dmpm, with no signals for dmpm(Se) being seen. Attempts to isolate dmpm(Se)$_2$ from a 2 : 1 Se/dmpm reaction in CH_2Cl_2 yielded initially a colourless material, but this rapidly turned pink at r.t., presumably due to elimination of elemental Se. The findings suggest that dmpm(Se) readily disproportionates in the solid state and in solution, and that dmpm(Se)$_2$ readily eliminates Se under ambient conditions. The dmpm(Se) and dmpm(Se)$_2$ compounds (like the corresponding sulfides) are less stable than the easily characterised dppm analogues;[9] like the S-analogues, dppm(Se)$_2$ and dppm readily react in EtOH to give quantitatively isolable dppm(Se).[17]

Reaction of dmpm(S) with elemental selenium

In order to characterise the mixed chalcogenide derivative, a $CDCl_3$ suspension of Se_8 was added to a $CDCl_3$ solution of dmpm(S) at r.t. [Se:dmpm(S) = 1]. The *in situ* $^{31}P\{^1H\}$ NMR data (Table 1) are consistent with formation of dmpm(S)(Se) (Fig. S2-b†), δ_{PSe} being at a higher field than δ_{PS} (*cf.* δ 12.9 for dmpm(Se)$_2$ and δ 32.5 for dmpm(S)$_2$); the $^1J_{PSe}$ and $^2J_{PP}$ values resemble those reported previously for dppm(S)(Se).[9,17] The dppm(S)(Se) compound has been similarly isolated from a Se/dppm(S) reaction,[9] or as a 1 : 1 mixture with dppm(Se) from the reaction of dppm(Se)$_2$ and dppm(S).[17] In contrast to the quantitative reactions of dmpm(S) or dppm(S) with selenium, the 1 : 1 reaction of dppm(Se) with elemental sulfur gives a mixture of dppm(Se)$_2$, dppm(S)(Se) and dppm(S)$_2$.[17]

Table 2 Selected bond lengths (Å) of Pd_2Cl_2(μ-Se)(dmpm)$_2$ (**3a**), [Pd_2Cl_2(μ-SMe)(dmpm)$_2$]OTf (**5**), and Pd_2Br_2(μ-SO)(dmpm)$_2$ (**6b**), with estimated standard deviations in parentheses

3a			
Pd(1)···Pd(2)	3.0961(3)	Pd(1)–P(1)	2.2944(9)
Pd(1)–Cl(1)	2.3730(9)	Pd(1)–Se(1)	2.4142(4)
Pd(2)–Cl(2)	2.3831(10)	Pd(2)–Se(1)	2.4182(5)
5			
Pd(1)···Pd(2)	3.1933(3)	Pd(1)–P(1)	2.3410(7)
Pd(1)–Cl(1)	2.3430(7)	Pd(1)–S(1)	2.2929(6)
Pd(2)–Cl(2)	2.3412(7)	Pd(2)–S(1)	2.2879(6)
S(1)–C(11)	1.809(3)		
6b			
Pd(1)···Pd(2)	3.2007(4)	Pd(1)–P(1)	2.3137(11)
Pd(1)–Br(1)	2.5202(5)	Pd(1)–S(1)	2.2729(10)
Pd(2)–Br(2)	2.5195(5)	Pd(2)–S(1)	2.2706(10)
S(1)–O(1)	1.502(3)		

Table 3 Selected bond angles (Å) of Pd_2Cl_2(μ-Se)(dmpm)$_2$ (**3a**), [Pd_2Cl_2(μ-SMe)(dmpm)$_2$]OTf (**5**), and Pd_2Br_2(μ-SO)(dmpm)$_2$ (**6b**), with estimated standard deviations in parentheses

3a			
Pd(1)–Se(1)–Pd(2)	79.687(14)	P(1)–Pd(1)–P(3)	173.35(3)
Cl(1)–Pd(1)–Se(1)	176.89(3)	Pd(1)–P(1)–C(1)	110.67(13)
Cl(1)–Pd(1)–P(1)	96.20(3)	Pd(1)–P(1)–C(3)	115.25(14)
Cl(1)–Pd(1)–P(3)	88.63(3)	P(1)–C(1)–P(2)	113.53(19)
Se(1)–Pd(1)–P(1)	82.58(3)	Se(1)–Pd(1)–P(3)	92.36(2)
5			
Pd(1)–S(1)–Pd(2)	88.39(2)	P(1)–Pd(1)–P(3)	173.38(2)
Cl(1)–Pd(1)–S(1)	175.81(2)	Pd(1)–P(1)–C(1)	122.00(8)
Cl(1)–Pd(1)–P(1)	86.93(2)	Pd(1)–P(1)–C(2)	108.32(11)
Cl(1)–Pd(1)–P(3)	92.67(2)	P(1)–C(1)–P(2)	114.59(13)
S(1)–Pd(1)–P(1)	97.00(2)	S(1)–Pd(1)–P(3)	83.26(2)
Pd(1)–S(1)–C(11)	111.91(10)	Pd(2)–S(1)–C(11)	117.26(10)
6b			
Pd(1)–S(1)–Pd(2)	89.57(3)	P(1)–Pd(1)–P(3)	165.08(4)
Br(1)–Pd(1)–S(1)	169.24(3)	Pd(1)–P(1)–C(1)	114.94(15)
Br(1)–Pd(1)–P(1)	91.48 (3)	Pd(1)–P(1)–C(2)	111.71(18)
Br(1)–Pd(1)–P(3)	88.04(3)	P(1)–C(1)–P(2)	116.0(2)
S(1)–Pd(1)–P(1)	92.87(5)	P(3)–C(6)–P(4)	113.1(2)
S(1)–Pd(1)–P(3)	90.26(4)	Pd(2)–S(1)–O(1)	113.82(15)
Pd(1)–S(1)–O(1)	115.32(15)		

Reactions of Pd_2Cl_2(μ-S)(dmpm)$_2$ (2a) and the selenide analogue (3a) with sulfur

When the bridged-sulfide complex **2a** was synthesised by reaction of Pd_2Cl_2(dmpm)$_2$ (**1a**) with sulfur,[1] an observation that use of excess S_8 initiated formation of an insoluble, reddish precipitate prompted an investigation of the reactivity of **2a** with S_8. The findings were unexpected since other Pd_2Cl_2(μ-S)(P–P)$_2$ complexes, where P–P = bis(diethylphosphino)methane (depm)[1] or dppm,[4b] were stable toward S_8. The enhanced reactivity led to studies on reactions of **2a** with other reagents, and a study of the reaction of the selenide analogue with S_8.

The brown Pd_2Cl_2(μ-Se)(dmpm)$_2$ complex (**3a**) was best made from the reaction of Pd_2Cl_2(dmpm)$_2$ with excess Se_8 (which does not react with **3a**) in CH_2Cl_2. Crystals were grown by diffusion of Et_2O into a CH_2Cl_2 solution of the complex, and the structure determined by X-ray analysis (Fig. 1, Tables 2–4). The structure resembles closely that of **2a**.[1] The Pd-atoms are in approximately square planar environments, but the two P–Pd–P axes are twisted so that the $Pd_2P_4C_2$ ring is distorted into an extended boat conformation; such distortions, which are not apparent in the

Table 4 Crystallographic data[a] for $Pd_2Cl_2(\mu\text{-Se})(dmpm)_2$ (**3a**), $[Pd_2Cl_2(\mu\text{-SMe})(dmpm)_2]OTf$ (**5**), and $Pd_2Br_2(\mu\text{-SO})(dmpm)_2$ (**6b**)

	3a	**5**	**6b**
Empirical formula	$C_{10}H_{28}Cl_2P_4Pd_2Se$	$C_{12}H_{31}Cl_2F_3O_3P_4Pd_2S_2$	$C_{10}H_{28}Br_2OP_4Pd_2S$
fw	634.86	752.07	692.88
Colour, habit	Brown, prism	Yellow, prism	Red, irregular
Cryst. size/mm	0.20 × 0.35 × 0.40	0.30 × 0.35 × 0.40	0.35 × 0.40 × 0.45
Cryst. system	Monoclinic	Orthorhombic	Orthorhombic
Space group	$P2_1$ (#4)	*Pbca* (#61)	$P2_12_12_1$ (#19)
a/Å	8.1062(1)	12.2968(2)	10.794(1)
b/Å	8.5205(3)	15.1722(1)	13.7756(3)
c/Å	15.3582(4)	27.7363(3)	14.8223(4)
β (°)	93.511(1)	90	90
V/Å^3	1058.8(2)	5174.8(1)	2204.0(2)
Z	2	8	4
D_c/g cm^{-3}	1.991	1.931	2.088
μ/cm^{-1}	39.59	20.39	56.5
Unique reflns	4623	7341	5409
R_{int}	0.021	0.030	0.027
No. with $I \geq 2\sigma(I)$	4366	6229	5121
No. of variables	180	262	190
$R(F)$ $(I \geq 2\sigma(I))$	0.021	0.034	0.026
$R_w(F^2)$ (all data)	0.053	0.089	0.066
GOF	1.05	1.16	1.03
residual density, *e*/Å^3	–1.36	–1.27	–0.84

[a] Function minimised $\Sigma w(F_o^2 - F_c^2)^2$, where $w = 1/\sigma^2(F_o^2)$; $R = \Sigma \| F_o^2 | - | F_c^2 \| / \Sigma | F_o^2 |$, $R_w = [\Sigma w(| F_o^2 | - | F_c^2 |)^2 / \Sigma w F_o^4]^{1/2}$.

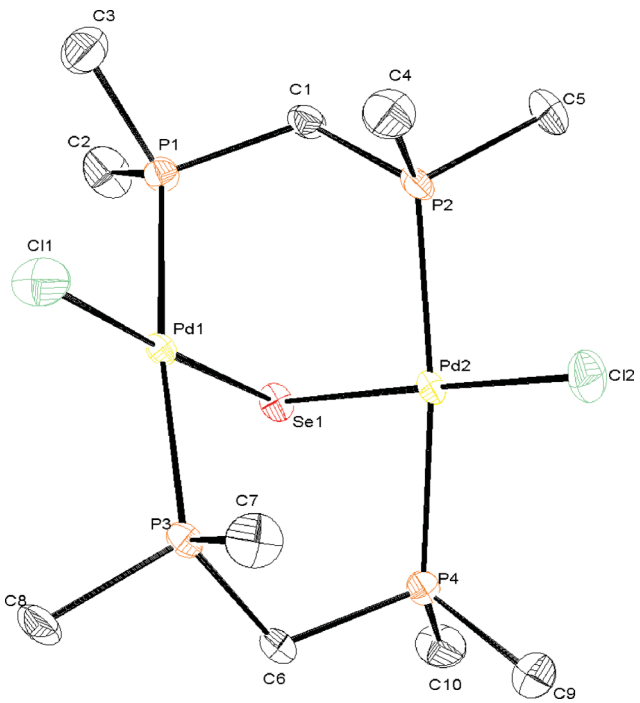
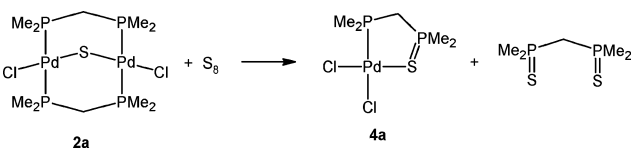


Fig. 1 ORTEP diagram of $Pd_2Cl_2(\mu\text{-Se})(dmpm)_2$ (**3a**) with 50% probability thermal ellipsoids.

structure of **2a**, relieve the $Pd_2P_4C_2$ ring strain, and allow for closer contact between the Pd-atoms (3.096 *vs.* 3.342 Å in **2a**). The Pd(1)–Cl(1) and Pd(2)–Cl(2) bond lengths of 2.373 and 2.383 Å suggest that the μ-Se ligand may have a somewhat stronger *trans* influence than the μ-S ligand in **2a**, where the corresponding distances are 2.365 and 2.361 Å. The NMR data for **3a** (Table 1) are very similar to those described for **2a**.[1] The $Pd_2Cl_2(\mu\text{-Se})(depm)_2$ complex has also been made.[18]

An NMR-scale, r.t. reaction of **2a** with S_8 (~8 mole equiv. S) in $CDCl_3$ gave a dark red precipitate and a colourless solution containing $dmpm(S)_2$ as the only ^{31}P-containing co-product. After collection of the solid, washing with hexanes and redissolving in DMSO-d_6, a new AB pattern was noted in the $^{31}P\{^1H\}$ spectrum (δ_P 33.6, δ_{PS} 63.8; $^2J_{PP}$ = 22.5 Hz), with an associated ^1H pseudotriplet signal for the CH_2 protons at δ_H 3.49 ($^2J_{PH}$ = 12.3 Hz) (Fig. 2); these data (aided by the $^1H\{^{31}P\}$ spectrum) are due to the *P*,*S*-chelate complex $PdCl_2[dmpm(S)]$ (**4a**) (Scheme 2). An *in situ* **2a**/S_8 reaction in DMSO-d_6 at 50 °C showed after 10 min formation of **4a**, $dmpm(S)_2$, and ~15% of an unidentified species characterised by a $^{31}P\{^1H\}$ AB pattern (δ_P 34.3, 38.5; $^2J_{PP}$ = 14.1). Analytically pure **4a** was obtained in 89% yield as a yellow solid by a 1 : 1 reaction of dmpm(S) with *trans*-$PdCl_2(PhCN)_2$ in CH_2Cl_2 in which **4a** is insoluble. The iodo analogue $PdI_2[dppm(S)]$ (**4c**) was similarly made from the nitrile precursor, but using added NaI for the halide exchange, and was characterised by NMR data, which were similar to those of **4a**. The analogous $PdX_2[dppm(S)]$ complexes (X = halogen) have also been made from this nitrile precursor.[19]



Scheme 2 Reaction of **2a** with S_8.

In an attempt to determine more precisely the fate of the bridged-chalcogenide ligand in the Scheme 2 reaction, an *in situ* reaction of $Pd_2Cl_2(\mu\text{-Se})(dmpm)_2$ (**3a**) with S_8 (7.7 mole equiv. S) was monitored in DMSO-d_6. The initial red-brown suspension was heated at 50 °C for 10 min, when NMR analysis showed the presence of a mixture of **4a**, $dmpm(S)_2$, and a species almost certainly $PdCl_2[dmpm(Se)]$, formed *via* net insertion of the μ-Se

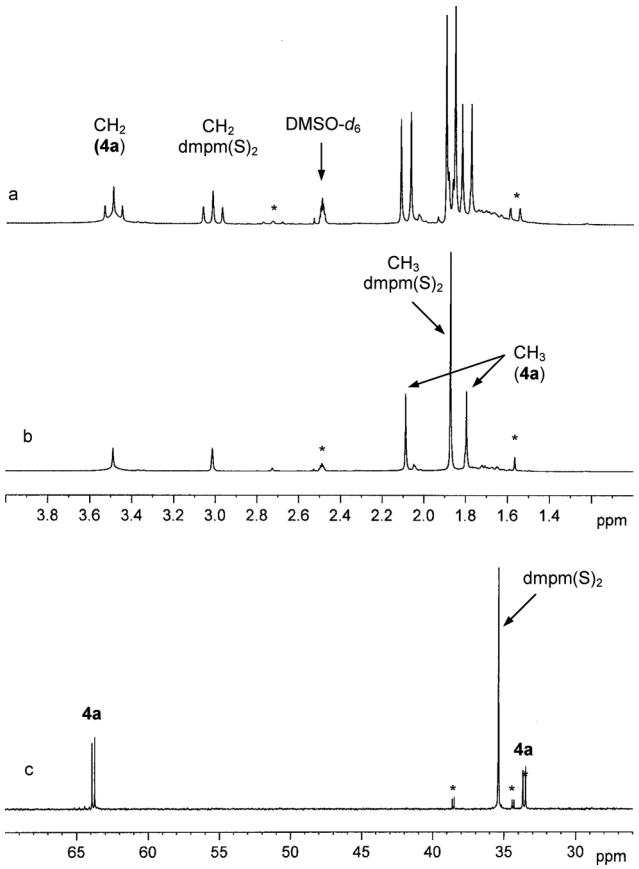


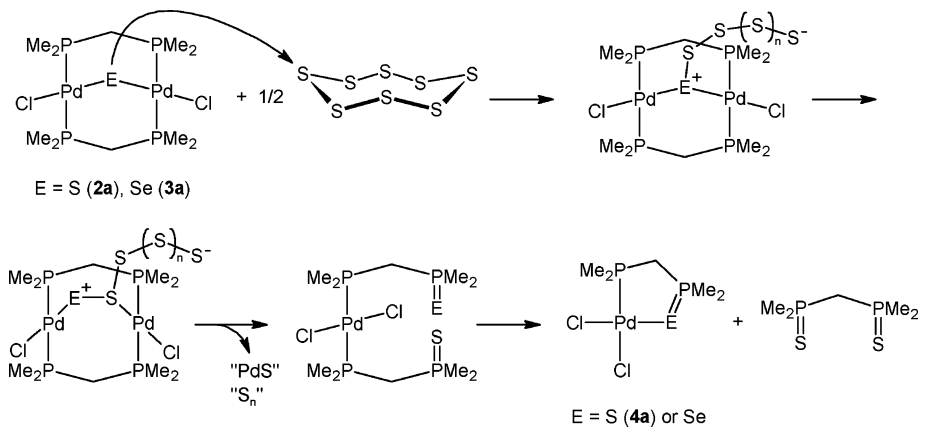
Fig. 2 ^{1}H, $^{1}H\{^{31}P\}$ (300.1 MHz, a and b) and $^{31}P\{^{1}H\}$ (121.5 MHz, c) NMR spectra (DMSO-d_6) of the products formed when $Pd_2Cl_2(\mu\text{-}S)(dmpm)_2$ (**2a**) is treated with excess S_8. The peaks labeled with an asterisk indicate a minor, unidentified species.

into a Pd–P bond. Unfortunately, its independent synthesis was not possible because of the instability of dmpm(Se) (see above). The *in situ* $^{31}P\{^{1}H\}$ spectrum shows an AB pattern (δ_P 32.6, δ_{PSe} 36.1; J_{PP} = 29.0), with the higher field resonance close to that seen in **4a**; the δ_{PSe} value (*vs.* δ_{PS} = 63.8 for **4a**) also follows the established trend ($\delta_{PO} < \delta_{PSe} < \delta_{PS}$).[9] The ^{77}Se satellites expected in the $^{31}P\{^{1}H\}$ spectrum of $PdCl_2$[dmpm(Se)] were not resolved because of the poor signal-to-noise ratio of the spectrum. Of note, dmpm(S)(Se), dmpm(Se), and dmpm$(Se)_2$, were not detected.

The reaction shown in Scheme 2 and the corresponding **3a**/S_8 reaction likely involves initial attack of the S_8 ring by the bridged-chalcogenide ligand, just as elemental sulfur reacts with nucleophilic phosphines.[20] Direct insertions of elemental sulfur into metal-carbon and -hydride bonds,[21–23] and insertion of a S-atom into a Ge–P bond,[7] have been reported, but the distribution of products obtained in the **3a**/S_8 reaction suggests possible reactivity *via* an undetected $Pd^{II}(\eta^1\text{-dmpm})$ species, with the "dangling" P-atom being oxidised by S_8. It is known also that S_8 can act as a multidentate ligand, for example, in structurally characterised polymeric Rh complexes containing 1,3- and 1,3,6-coordinated S_8 ligands.[24] A speculative mechanism for the reaction of S_8 with **2a** and **3a** is shown in Scheme 3. The reddish precipitates seen during the reactions are likely the eliminated PdS species of which many phases, typically red-brown, are known,[25] but this material was characterised only by a broad absorption band at ~360 nm in a UV-vis spectrum in DMSO.

Reactions of 2a–c with methyl iodide and methyl triflate

Tests for S-abstraction from the μ-S complexes were made using alkyl halides: MeI showed reactivity, while EtI was completely unreactive. The r.t. reaction of **2a** with MeI (10.0 equiv.) in $CDCl_3$, monitored by NMR spectroscopy, rapidly gave a mixture of $Pd_2Cl(I)(\mu\text{-}S)(dmpm)_2$ (**2a′**) and $Pd_2I_2(\mu\text{-}S)(dmpm)_2$ (**2c**) [1] *via* halide metathesis, concomitant with increasing amounts of the MeCl (δ_H 3.00); **2a′** (also formed exclusively in a 1 : 1 **2a**/NaI reaction) shows an expected $^{31}P\{^{1}H\}$ AA′BB′ pattern. Addition of further MeI (~135 equiv.) then converted both **2a′** and **2c** quantitatively to the known, purple species $Pd_2I_2(\mu\text{-}I)_2(dmpm)_2$,[26] with co-production of Me_2S. The reactions are outlined in Scheme 4. The $Pd_2Br_2(\mu\text{-}S)(dmpm)_2$ (**2b**)[1] reacts similarly, with corresponding generation of MeBr (δ_H 2.67). With $Pd_2I_2(\mu\text{-}S)(dmpm)_2$ (**2c**) as reactant, no mixed halide species can be seen, of course, and just Me_2S is formed along with the $(\mu\text{-}I)_2$ complex, which has been structurally characterised previously, following its synthesis *via* I_2-oxidation of $Pd_2I_2(dmpm)_2$.[26] The complexes $Pd_2Cl_2(dmpm)_2$ (**1a**) and $Pd_2I_2(dmpm)_2$ (**1c**) were unreactive toward Me_2S at r.t. in $CDCl_3$. Solutions of $Pd_2Cl_2(\mu\text{-}S)(dppm)_2$ react similarly with



Scheme 3 Speculative mechanism for the reaction of $Pd_2Cl_2(\mu\text{-}E)(dmpm)_2$ with S_8; E = S (**2a**), Se (**3a**).

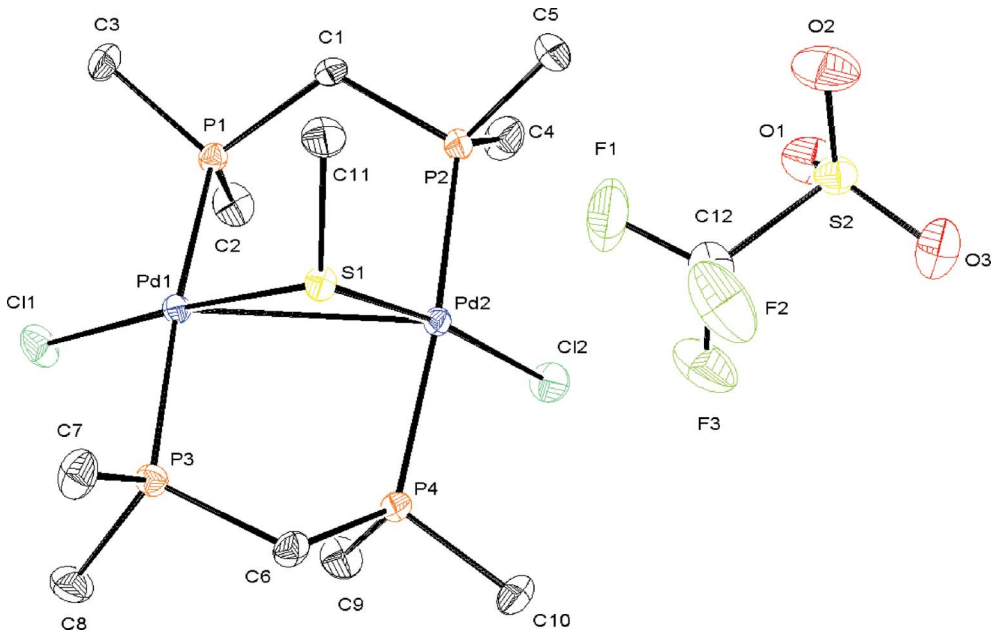
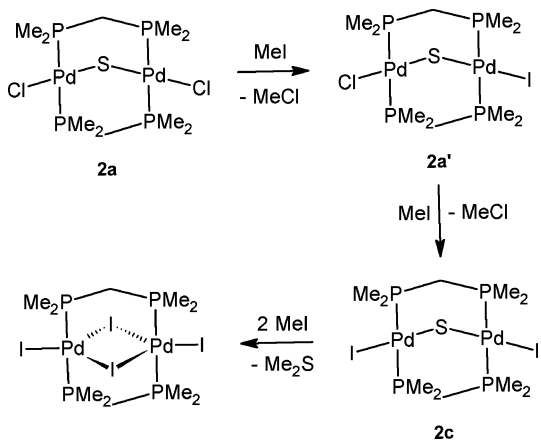


Fig. 3 ORTEP diagram of $[Pd_2Cl_2(\mu\text{-SMe})(dmpm)_2]OTf$ (**5**) with 50% probability thermal ellipsoids.



Scheme 4 Stepwise reaction of $Pd_2Cl_2(\mu\text{-S})(dmpm)_2$ (**2a**) with MeI.

excess MeI to yield MeCl and Me_2S, with the iodo product being $PdI_2(dppm)$.[27]

The r.t. reaction of **2a** with MeOTf in CH_2Cl_2 generates quantitatively $[Pd_2Cl_2(\mu\text{-SMe})(dmpm)_2]OTf$ (**5**) that was isolated as a yellow solid in 70% yield; crystals were obtained from a concentrated $CDCl_3$ solution of the complex. The structure of the cation (Fig. 3, Tables 2–4) confirms methylation of the bridged-sulfide. The Pd···Pd distance of 3.193 Å is ~0.15 Å shorter than that in **2a**[1] due to increased twisting about the Pd···Pd axis within a $Pd_2P_4C_2$ boat conformation. The average Pd–Cl distance (2.342 Å) is also marginally shorter than in **2a** (2.362 Å), but a comparison of the relative *trans* influence of the sulfide and thiolato ligands is likely tenuous when comparing neutral and cationic species. The S-atom is approximately pyramidal, and there are no significant interactions between the methyl C-atom and the O-atoms of the triflate counterion. The Pd···Pd and other bond lengths, and the Pd–S–Pd angle in **5**, are similar to those found in the neutral complex *cis*-$Pd_2Cl_2(\mu\text{-Cl})(\mu\text{-SMe})(PMe_3)_2$, formed *via* reaction of $[PdCl(PMe_3)]_2(\mu\text{-Cl})_2$ with MeSH,[28] and in the cationic cluster complex $[Pd_4(\mu\text{-Cl})_2(\mu\text{-SMe})_4(dmpm)_2][BF_4]_2$, made by protonation of $[PdCl]_2(\mu\text{-MeSC}{=}\text{CSMe})(dmpm)_2$ with HBF_4.[29] The C, H, and S elemental analyses for **5**, together with the solution NMR data (see below) and the conductivity in acetone,[30] are consistent with the solid state structure.

The r.t. NMR spectra of **5** show broad resonances due to fluxional behaviour, but at –60 °C the dynamic process is 'frozen out', and a $^{31}P\{^1H\}$-AA′BB′ pattern is resolved and readily simulated (Fig. 4); coalescence to a single broad resonance occurs at ~60 °C in CD_3NO_2 (Fig. S3†). The AA′BB′ spectrum and J_{PP} values are similar to those seen in r.t. spectra of other unsymmetrical Pd_2 A-frame complexes.[4a,31,32] The –60 °C, ^1H NMR spectrum reveals broad multiplets that appear to be comprised of two doublets of triplets and two doublets of triplets of triplets for the four diastereotopic dmpm-CH_2 protons; these signals are better resolved as doublets in the $^1H\{^{31}P\}$ spectrum. The SMe protons appear as a broad singlet at δ_H 2.28.

The fluxionality most likely occurs *via* intramolecular inversion of the pyramidal S-atom *via* a planar, trigonal transition state, as suggested for $[RhMn(CO)_4(\mu\text{-SMe})(dppm)_2]OTf$, where the coalescence temperature in the $^{31}P\{^1H\}$ spectra was about –30 °C; this complex was also made by methylation of the μ-S species with MeOTf.[33] The complex $[Pt_2(H)_2(\mu\text{-SMe})(dppm)_2]PF_6$, prepared from the corresponding μ-H precursor by reaction with MeSH with elimination of H_2, also shows similar dynamic behaviour.[34]

It is interesting that, although MeOTf is a mild and effective halide abstracting agent,[35] the terminal chlorides of $Pd_2Cl_2(\mu\text{-S})(dmpm)_2$ and $[Pd_2Cl_2(\mu\text{-SMe})(dmpm)_2]^+$ remain unaffected in the presence of excess MeOTf. In contrast, when $Pd_2Cl_2(\mu\text{-S})(dppm)_2$ or $Pd_2Cl_2(\mu\text{-S})(depm)_2$ are treated with MeOTf (1–15 equiv.) in CH_2Cl_2, the solutions rapidly become dark red and MeCl is evolved; several new $^{31}P\{^1H\}$ NMR singlet resonances

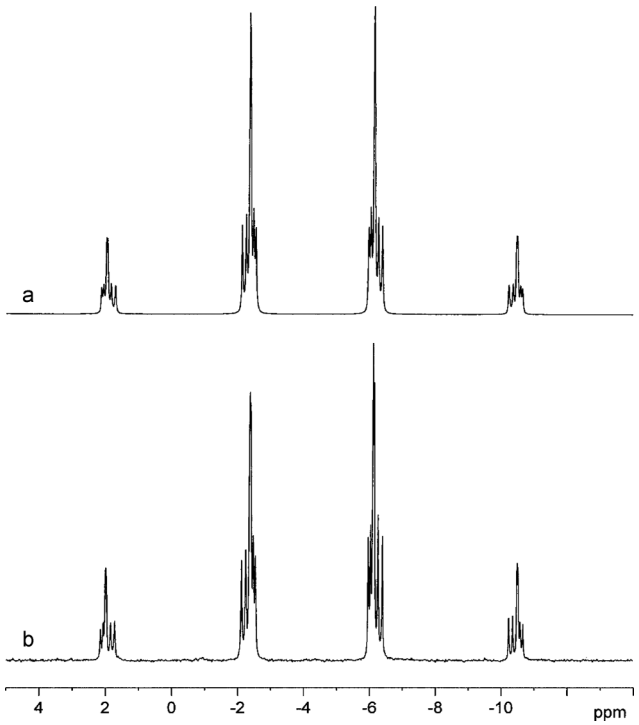


Fig. 4 Simulated and (b) actual $^{31}P\{^{1}H\}$ NMR spectra (121.5 MHz, CD_2Cl_2, –60 °C) of $[Pd_2Cl_2(\mu\text{-SMe})(dmpm)_2]OTf$ (**5**). Coupling constants were determined from the simulated spectrum: $J_{AA'} = 45.4$, $J_{AB} = J_{A'B'} = 522.8$, $J_{BB'} = 13.2$, $J_{AB'} = J_{A'B} = -0.4$ Hz.

at δ_P –41.0, –38.1 and 15.5, and multiplets in the δ_P 48.4–57.7 and 66.6–86.5 regions, are seen, but work-up methods provided only intractable dark red or black oils.

The $Pd_2Cl_2(dmpm)_2$ complex is also completely unreactive toward MeOTf, whereas $Pd_2Cl_2(dppm)_2$ reacts instantaneously with 2.0 equiv. of MeOTf to yield MeCl and $[Pd_4(\mu\text{-Cl})_2(dppm)_4][OTf]_2$ (Scheme 5), that was isolated as CH_2Cl_2 solvated crystals. Since the corresponding PF_6^-, ClO_4^- and BF_4^- salts of this cationic cluster were characterised previously, the first two by X-ray analysis,[36] no such analysis was carried out on the new triflate salt, which was characterised by $^{31}P\{^{1}H\}$ NMR spectroscopy and elemental analysis. The formation of MeCl was also seen in the reaction of $Pd_2Cl_2(depm)_2$ with MeOTf, but the NMR spectra were poorly resolved and no product isolation methods were attempted.

Reactions of 2a–c with *m*-chloroperbenzoic acid (*m*-CPBA)

From solutions of **2a** in CD_2Cl_2 or $CDCl_3$ treated with 1 equiv. *m*-CPBA at r.t. or at –30 °C, an isolated residue showed partial conversion to a mixture that included $Pd_2Cl_2(\mu\text{-SO})(dmpm)_2$ (**6a**) and the known $Pd_2Cl_2(\mu\text{-SO}_2)(dmpm)_2$ complex,[5] along with unidentified products (δ_P singlets at –20.4, –7.2 and 44.8). The μ-SO species was indentified by comparison with NMR data for isolated $Pd_2Br_2(\mu\text{-SO})(dmpm)_2$ (**6b**), which was formed exclusively in the corresponding reaction of $Pd_2Br_2(\mu\text{-S})(dmpm)_2$ with *m*-CPBA. The r.t. $^{31}P\{^{1}H\}$ and ^{1}H NMR spectra of **6b**, which was characterised crystallographically using red crystals grown from a CH_2Cl_2/Et_2O solution (Fig. 5, Tables 2–4), are consistent with reduced symmetry introduced by a pyramidal S-atom. The $^{31}P\{^{1}H\}$ spectrum is an AA′BB′ pattern centered at δ_P –13.5 and 4.5, similar to that observed for the μ-SMe complex (**5**) at low temperature. For **6a**, the AA′BB′ pattern is centered at δ_P –12.9 and 4.8. The ^{1}H NMR spectrum of **6b** like that for **5** reveals four inequivalent dmpm-CH_2 protons, two appearing as doublets of triplets, and two consisting of doublets of triplets of triplets; with **6a**, two of the CH_2 proton signals are obscured within the complicated methyl region (see Table 1).

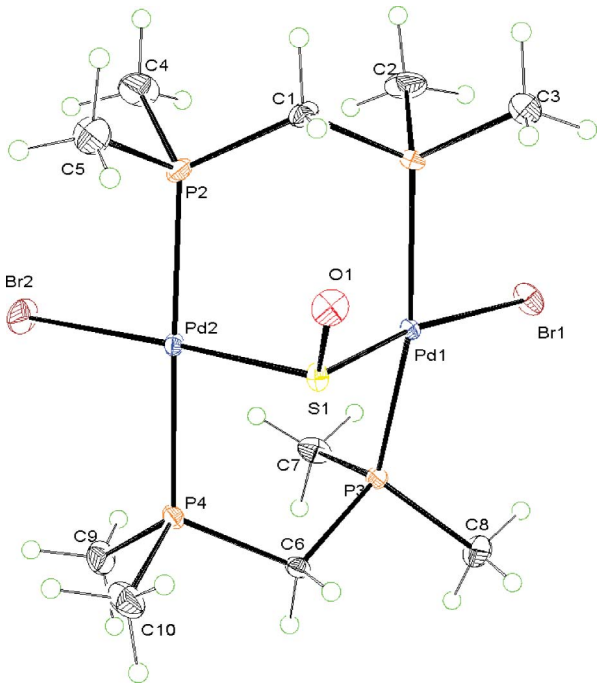
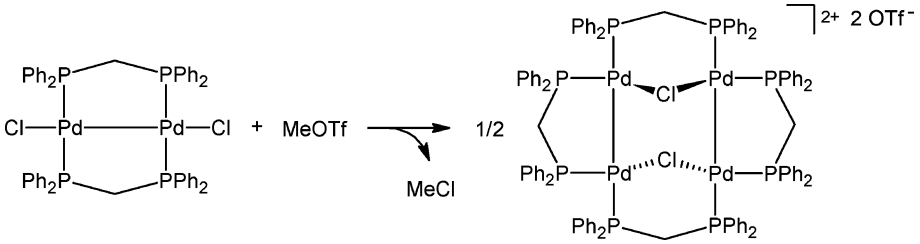


Fig. 5 ORTEP diagram of $Pd_2Br_2(\mu\text{-SO})(dmpm)_2$ (**6b**) with thermal ellipsoids shown at the 50% probability level.

Compared to structural data for $Pd_2Br_2(\mu\text{-S})(dmpm)_2$ (**2b**),[1] the Pd···Pd distance of 3.201 Å in **6b** is 0.13 Å longer, the Pd–S bond lengths of 2.271 and 2.273 Å are ~0.03 Å shorter, and the Pd–S–Pd



Scheme 5 Reaction of $Pd_2Cl_2(dppm)_2$ with MeOTf.

angle of 89.57° is 6° is more obtuse, showing that the S-atom of the μ-SO ligand is closer to the center of the Pd···Pd vector. The Pd–Br distances are of ~0.03 Å longer than those in **2b**, implying a slightly stronger *trans* influence for μ-SO *vs.* *μ*-S; data for the corresponding dppm analogues[4a] lead to the same conclusion. The structure of **6b** in general closely resembles that of the dppm analogue, $Pd_2Cl_2(\mu\text{-SO})(dppm)_2$,[4a] although in the dppm structure the O-atoms were disordered over two sites, with S–O bond lengths of 1.34(4) and 1.45(3) Å that are significantly shorter than the 1.502 Å length in **6b**. Remarkably, the 'same' value (1.504 Å) is reported for $[CpMn(CO)_2]_2(\mu\text{-SO})$, in which the S-atom has trigonal planar, sp^2-hybridized geometry and the μ-SO ligand acts as a 4-electron donor.[37] The pyramidal geometry in **6b** implies a 3 center, 2-electron donor, and the single IR band at 932 cm^{-1} supports this.[19] To the best of our knowledge, **6b** is only the fifth dimetallic μ-SO complex to be characterised crystallographically.[4a,38]

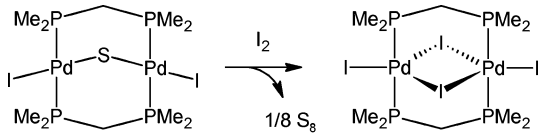
A brown solid, isolated from the reaction of $Pd_2I_2(\mu\text{-S})(dmpm)_2$ (**2c**) with *m*-CPBA, contained ~95% of an unidentified species (**Z**) that was associated with a singlet in CD_2Cl_2 at δ_P −18.1, a CH_2 quintet at δ_H 3.57 (J_{PH} = 4.3 Hz), and a CH_3 singlet resonance at δ_H 2.11, implying a symmetric species that is not $Pd_2I_2(\mu\text{-I})_2(dmpm)_2$.[26] This $(\mu\text{-I})_2$ complex is often formed as an impurity during reactions involving $Pd_2I_2(dmpm)_2$ (**1c**) or **2c** (*e.g.* in reactions with MeI, and with I_2 -see below). The brown solid contains small amounts of $Pd_2I_2(dmpm)_2$ (δ_P −38.4; δ_H 2.82 qn, J_{PH} = 3.6 Hz),[26] and a further unidentified species (δ_P −20.5; δ_H 1.75–1.89 m).

Reaction of 2a–c with halogens

Previous studies from this group[19] have demonstrated the chemistry of eqn (2) for the dppm systems, where the μ-S is oxidised to elemental sulfur (X = halogen). The "face-to-face" intermediates, *trans*-$[PdX_2(dppm)]_2$, were also detected in the reaction between $Pd_2X_2(dppm)_2$ and X_2;[39] in the corresponding dmpm systems, the analogous X = Cl and Br, yellow complexes were isolated, and the X = I species was isolated as the purple-coloured $Pd_2I_2(\mu\text{-I})_2(dmpm)_2$.[26]

$$\begin{aligned} &Pd_2X_2(\mu\text{-S})(dppm)_2 + X_2 \xrightarrow{-\frac{1}{8}S_8} \\ &trans\text{-}[PdX_2(dppm)]_2 \rightarrow 2\ PdX_2(dppm) \end{aligned} \quad (2)$$

The sulfide oxidation process was studied in this present work using the $Pd_2X_2(\mu\text{-S})(dmpm)_2$ complexes as reactants, and the findings establish the chemistry of eqn (2) for the dmpm analogues. The chloro and bromo species at r.t. in $CHCl_3/CDCl_3$ gave the *trans*-$[PdX_2(dppm)]_2$ products, and the iodo species formed $Pd_2I_2(\mu\text{-I})_2(dmpm)_2$ (Scheme 6). In the iodo system, the S_8 co-product was isolated as a residue from the filtrate following extraction of the $(\mu\text{-I})_2$ complex with CS_2 and passage through a short column of neutral alumina; EI mass spectral analysis showed the distinctive fragmentation pattern of the S_8, presumably formed *via* catenation of the liberated sulfur.



2c

Scheme 6 Reaction of $Pd_2I_2(\mu\text{-S})(dmpm)_2$ (**2c**) with I_2.

Conclusions

The studies clarify syntheses, characterisation, and properties of dmpm(E), $dmpm(E)_2$ (E = S, Se), and dmpm(S)(Se), the findings being complicated by facile disproportionation of the dmpm(E) compounds; such behaviour contrasts with that of the corresponding stable dppm compounds.

Further examples of the different reactivity of Pd-dmpm species compared to that of the dppm analogues are presented (these are in addition to those we reported recently on reactivity toward CS_2 and COS).[1] They include: (i) breakdown of the $Pd_2Cl_2(\mu\text{-E})(dmpm)_2$ framework by reaction with elemental sulfur to give $PdCl_2[P,S\text{-dmpm(E)}]$, whereas the dppm analogue is unreactive, (ii) the conversion of $Pd_2Cl_2(\mu\text{-S})(dmpm)_2$ to $[Pd_2Cl_2(\mu\text{-SMe})(dmpm)_2]OTf$ by reaction with MeOTf, whereas the dppm analogue does not undergo methylation, and (iii) $Pd_2Cl_2(dmpm)_2$ does not react with MeOTf, while the dppm analogue gives a Pd_4-cluster product.

Similarities between the dmpm and dppm systems are also presented: (i) $Pd_2Cl_2(\mu\text{-S})(dmpm)_2$ with MeI initially results in halide metathesis to give iodo-species with subsequent removal of the μ-S as Me_2S and generation of $Pd_2I_2(\mu\text{-I})_2(dmpm)_2$; the dppm species reacts similarly but the final Pd-product is $PdI_2(dppm)$, (ii) the $Pd_2X_2(\mu\text{-S})(dmpm)_2$ complexes (X = halogen) react with *m*-CPBA to give μ-SO and μ-SO_2 derivatives, analogous to the dppm species, (iii) the $Pd_2X_2(\mu\text{-S})(dmpm)_2$ complexes react with X_2, similarly to the dppm analogues, with oxidation of the μ-S to elemental sulfur and co-production of Pd-halide-dmpm species.

Experimental section

General

Unless otherwise noted, all synthetic procedures were carried out using standard Schlenk techniques under dry N_2. Reagent grade solvents were distilled under N_2 from the appropriate standard drying agent. Deuterated solvents were obtained from Cambridge Isotope Laboratories and were used as received. Gas-tight Sample-Lok™ syringes (Dynatech) were used for handling gaseous reagents.

The dmpm (Strem), S_8 (Fisher Scientific), Cl_2 (UHP), Br_2 (Acros), and I_2 (AnalaR) were used as received, as were the Aldrich products: dppm, MeI, MeOTf, and *m*-CPBA (available as 57–86%, impurities being *m*-chlorobenzoic acid and H_2O). Amorphous red Se (Se_8) was available in this laboratory, having been prepared by reaction of SeO_2 (Alfa) with aq. N_2H_4 (Alfa).[40] The complexes *trans*-$PdCl_2(PhCN)_2$,[41] $Pd_2X_2(dmpm)_2$ (X = halogen),[26] $Pd_2Cl_2(depm)_2$,[26] $Pd_2X_2(\mu\text{-S})(dmpm)_2$ and $Pd_2Cl_2(\mu\text{-S})(depm)_2$,[1] were prepared as reported in the given references.

NMR spectra were recorded on a Bruker AV300 spectrometer (300.13 MHz for ^1H, 121.49 MHz for ^{31}P). Residual deuterated solvent proton (relative to external $SiMe_4$) or external $P(OMe)_3$ (^{31}P, δ_P 141.0 relative to 85% H_3PO_4) were used as references (s = singlet, d = doublet, t = triplet, qn = quintet, m = multiplet, br = broad, ps = pseudo). *J* values are reported in Hz. UV-vis absorption spectra were recorded on a Hewlett Packard 8452A

diode-array spectrometer, data being presented as λ_{max} (nm) ($\varepsilon_{max} \times 10^{-3}$, M^{-1} cm^{-1}). Conductivity measurements were made at 298 K using a model RCM151B Serfass conductance bridge (A. H. Thomas Co. Ltd.) connected to a 3403 cell from the Yellow Springs Instrument Co. The cell was calibrated using a standard 0.01000 M aq. KCl solution (Λ_M = 141.3 Ω^{-1} cm^2 mol^{-1} at 298 K), the cell constant being 1.016 cm^{-1}. Low resolution electron impact mass spectra (EIMS) were obtained on a Kratos MS-50 double-focusing spectrometer. Elemental analyses were performed by Mr. P. Border of the UBC Microanalytical Service.

Preparation of dmpm(S) and dmpm(S)$_2$

A suspension of S_8 (139 mg, 4.33 mmol S) in C_6H_6 (10 mL) was added dropwise to a solution of dmpm (0.688 mL, 590 mg, 4.33 mmol) in C_6H_6 (20 mL), and the resulting colourless solution was stirred for 1 h. Evaporation of the solvent provided a white solid that was dried *in vacuo* at r.t. for 16 h in order to remove unreacted dmpm; $^{31}P\{^1H\}$ data for a $CDCl_3$ solution of the solid showed a composition of dmpm(S) (70%) and dmpm(S)$_2$ (30%). Vacuum sublimation at 50 °C at ~0.1 torr provided pure dmpm(S) as an air-stable, white solid. Yield: 336 mg (46% based on dmpm). Mp 58–60 °C. ^1H NMR ($CDCl_3$): δ 1.20 (m, 6H, PCH_3), 1.78 (m, 6H, P(S)CH_3), 2.01 (ps d, 2H, CH_2, $^2J_{PH}$ = 13.5). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ_P −48.1, δ_{PS} 40.7 (AB, $^2J_{PP}$ = 53.4). Anal. Calcd for $C_5H_{14}P_2S$: C, 35.71; H, 8.39; S, 19.06. Found: C, 35.83; H, 8.28; S, 19.11.

The white residue remaining after the sublimation was dissolved in CH_2Cl_2 (20 mL) and the solution eluted through a column of neutral Al_2O_3. The filtrate was evaporated and the resulting white solid was recrystallised from hot EtOH to yield colourless crystals of dmpm(S)$_2$. Yield: 158 mg (18% based on dmpm). Mp 163–165 °C. ^1H NMR ($CDCl_3$): δ 1.99 (d, 12H, CH_3, $^2J_{PH}$ = 12.3), 2.67 (t, 2H, CH_2, $^2J_{PH}$ = 13.4). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 32.5 (s); δ 31.1 in C_6D_6.[9] ^1H NMR (DMSO-d_6): δ 1.87 (d, 12H, CH_3, $^2J_{PH}$ = 12.6), 3.01 (t, 2H, CH_2, $^2J_{PH}$ = 13.7). $^1H\{^{31}P\}$ NMR (DMSO-d_6): δ 1.87 (s, 12H, CH_3), 3.01 (s, 2H, CH_2). $^{31}P\{^1H\}$ NMR (DMSO-d_6): δ 38.2 (s). Anal. Calcd for $C_5H_{14}P_2S_2$: C, 29.99; H, 7.05; S, 32.02. Found: C, 30.24; H, 6.91; S, 31.81.

Recrystallisation of dmpm(S) from H_2O or alcohols in air resulted in X-ray diffraction quality crystals of dmpm(S)$_2$.

Reaction of dmpm with elemental Se

An NMR scale, *in situ* reaction in $CDCl_3$ between dmpm and a suspension of Se_8 (Se:P = 2) generated dmpm(Se)$_2$ quantitatively. ^1H NMR ($CDCl_3$): δ 2.20 (d, 12H, CH_3, $^2J_{PH}$ + $^4J_{PH}$ = 12.4), 3.01 (t, 2H, CH_2, $^2J_{PH}$ = 13.4). $^1H\{^{31}P\}$ NMR ($CDCl_3$): δ 2.20 (s, 12H, CH_3), 3.01 (s, 2H, CH_2). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 12.9 (s, $^1J_{PSe}$ = −707, $^2J_{PP}$ = 17.0). Evaporation initially yielded a white solid, but this rapidly turned pink, presumably due to elimination of Se_8.

A suspension of Se_8 (75 mg, 0.95 mmol Se) in C_6H_6 (5 mL) was added dropwise to a solution of dmpm (0.150 mL, 129 mg, 0.95 mmol) in C_6H_6 (5 mL). The red solution became colourless on being stirred for 1 h. Evaporation provided 180 mg of a pink mixture (likely dmpm, dmpm(Se) and dmpm(Se)$_2$) that was dried *in vacuo* for 1 h at r.t. to remove the dmpm. Vacuum sublimation of the residue provided 21 mg of a waxy, white solid. The NMR data ($CDCl_3$) corresponded to those of dmpm(Se)$_2$. Anal. Calcd for $C_5H_{14}P_2Se$: C, 27.92; H, 6.56. Calcd for $C_5H_{14}P_2Se_2$: C, 20.42; H, 4.80. Found: C, 26.75; H, 6.54. The remaining off-white residue was dissolved in CH_2Cl_2 (10 mL) and the solution eluted through a short column of neutral alumina; evaporation of the eluent gave a white solid, whose NMR data again corresponded to those of dmpm(Se)$_2$.

Reaction of dmpm(S) with elemental Se

A solution of dmpm(S) (11 mg, 0.065 mmol) in C_6H_6 (2 mL) was treated with Se_8 (5.2 mg, 0.066 mmol Se). The mixture was stirred for 30 min and then filtered through Al_2O_3; evaporation of the eluent provided a pale pink residue still containing dmpm(S). However, a corresponding *in situ* reaction in $CDCl_3$ (~1 mL) showed quantitative formation of dmpm(S)(Se) after 5 min. ^1H NMR ($CDCl_3$): δ 1.98 (d, 6H, CH_3, $^2J_{PH}$ = 13.1, $^3J_{SeH}$ = 12.7), 2.19 (d, 6H, CH_3, $^2J_{PH}$ = 13.3), 2.84 (ps t, 2H, CH_2, $^2J_{PH}$ = 13.3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ_{PSe} 12.6, δ_{PS} 33.9 (AB, $^2J_{PP}$ = 16.4, $^1J_{PSe}$ = 705).

Preparation of PdX_2[dmpm(S)], X = (4a) and I (4c)

To a solution of dmpm(S) (62 mg, 0.369 mmol) in CH_2Cl_2 (10 mL) was added a solution of *trans*-$PdCl_2(PhCN)_2$ (141 mg, 0.368 mmol) in CH_2Cl_2 (10 mL). The yellow precipitate of **4a** was filtered off, washed with CH_2Cl_2 (2 × 5 mL) and hexanes (2 × 5 mL), and dried *in vacuo*. Yield: 113 mg (89%). ^1H NMR (DMSO-d_6): δ 1.80 (d, 6H, CH_3, $^2J_{PH}$ = 13.2), 2.09 (d, 6H, CH_3, $^2J_{PH}$ = 14.1), 3.49 (ps t, 2H, CH_2, $^2J_{PH}$ = 12.3). $^1H\{^{31}P\}$ NMR (DMSO-d_6): δ 1.80 (s, 6H, CH_3), 2.09 (s, 6H, CH_3), 3.49 (s, 2H, CH_2). $^{31}P\{^1H\}$ NMR (DMSO-d_6): δ_P 33.6, δ_{PS} 63.8 (dd, $^2J_{PP}$ = 22.5). Anal. Calcd for $C_5H_{14}Cl_2P_2PdS$: C, 17.38; H, 4.08. Found: C, 17.61; H, 4.10.

To a solution of $PdCl_2(PhCN)_2$ (30 mg, 0.079 mmol) and NaI (197 mg, 1.31 mmol) in MeOH (5 mL) was added a solution of dmpm(S) (16 mg, 0.094 mmol) in CH_2Cl_2 (5 mL). The brown suspension was refluxed at 50 °C for 2 h and then evaporated to dryness. The orange residue was washed with H_2O (5 × 5 mL), dried *in vacuo* overnight and extracted with DMSO-d_6. ^1H NMR (DMSO-d_6): δ 2.04 (d, 6H, CH_3, $^2J_{PH}$ = 12.3), 2.07 (d, 6H, CH_3, $^2J_{PH}$ = 14.1), 3.37 (m, 2H, partially obscured by an intense signal due to H_2O at δ 3.32). $^{31}P\{^1H\}$ NMR (DMSO-d_6): δ_P 35.5, δ_{PS} 69.6 (dd, $^2J_{PP}$ = 32.4). Successful elemental analysis of **4c** was thwarted by the presence of water.

In situ reaction of Pd_2Cl_2(μ-S)(dmpm)$_2$ (2a) with S_8

To a red solution of **2a** (8 mg, 0.014 mmol) in DMSO-d_6 (0.6 mL) was added S_8 (3.5 mg, 0.109 mmol S). The suspension was heated to ~50 °C for 10 min, and the NMR-tube was then shaken for 1 min prior to analysis. ^1H NMR (DMSO-d_6): δ 1.57 (d, CH_3, J_{PH} = 13.3, unidentified), 1.80 (d, CH_3, $^2J_{PH}$ = 13.2, **4a**), 1.87 (d, CH_3, $^2J_{PH}$ = 12.6, dmpm(S)$_2$), 2.09 (d, CH_3, $^2J_{PH}$ = 14.1, **4a**), 2.72 (t, CH_2, 14.0, unidentified), 3.01 (t, CH_2, $^2J_{PH}$ = 13.7, dmpm(S)$_2$), 3.49 (pseudotriplet, CH_2, $^2J_{PH}$ = 12.3, **4a**). $^1H\{^{31}P\}$ NMR (DMSO-d_6): δ 1.57 (s, CH_3, unidentified), 1.80 (s, CH_3, **4a**), 1.87 (s, CH_3, dmpm(S)$_2$), 2.09 (s, CH_3, **4a**), 2.72 (s, CH_2, unidentified), 3.01 (s, CH_2, dmpm(S)$_2$), 3.49 (s, CH_2, **4a**). $^{31}P\{^1H\}$ NMR (DMSO-d_6): δ_P 33.6, δ_{PS} 63.8 (dd, $^2J_{PP}$ = 22.5, **4a**), 34.3, 38.5 (dd, $^2J_{PP}$ = 14.1, unidentified), 35.4 (s, dmpm(S)$_2$).

Preparation of $Pd_2Cl_2(\mu\text{-Se})(dmpm)_2$ (3a)

To a solution of **1a** (247 mg, 0.445 mmol) in CH_2Cl_2 (20 mL) was added Se_8 (105 mg, 1.33 mmol Se). The resulting brown suspension was stirred for 2 h, and then filtered through Celite to remove excess Se_8. The filtrate was concentrated to ~5 mL and Et_2O (5 mL) was added to precipitate a brown solid that was collected, washed with Et_2O (2 × 5 mL) and dried *in vacuo* at 78 °C. Yield: 237 mg (84%). ^1H NMR (CD_2Cl_2): δ 1.65 (br s, 12H, CH_3), 1.69 (br s, 12H, CH_3), 2.15 (dqn, 2H, CH_2, $^2J_{PH}$ = 3.3, $^2J_{HH}$ = 13.4), 3.41 (dqn, 2H, CH_2, $^2J_{PH}$ = 5.7, $^2J_{HH}$ = 13.4). $^1H\{^{31}P\}$ NMR (CD_2Cl_2): δ 1.65 (s, 12H, CH_3), 1.69 (s, 12H, CH_3), 2.15 (d, 2H, CH_2, $^2J_{HH}$ = 13.4), 3.41 (d, 2H, CH_2, $^2J_{HH}$ = 13.4). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ −13.6 (s). UV-vis (CH_2Cl_2): 482 (0.70). Anal. Calcd for $C_{10}H_{28}Cl_2P_4Pd_2Se$: C, 18.92; H, 4.45. Found: C, 19.23; H, 4.45.

In situ reaction of $Pd_2Cl_2(\mu\text{-Se})(dmpm)_2$ (3a) with S_8

To a brown solution of **3a** (12 mg, 0.019 mmol) in DMSO-d_6 (0.6 mL) was added S_8 (4.7 mg, 0.147 mmol S). The resulting suspension was heated to ~50 °C for 10 min, and the NMR-tube was then shaken for 1 min. The $^{31}P\{^1H\}$ NMR spectra were of poor quality compared to those noted for the reaction of **2a** with S_8 (see above). $^{31}P\{^1H\}$ NMR: δ −3.0 to 18.7 (overlapping multiplets, unidentified), δ_P 32.6 and δ_{PSe} 36.1 (dd, $^2J_{PP}$ = 29.0, $PdCl_2$[dmpm(Se)]), δ_P 33.6 and δ_{PS} 63.8 (dd, $^2J_{PP}$ = 22.5, **4a**), 38.2 (s, dmpm$(S)_2$).

In situ reaction of $Pd_2Cl_2(\mu\text{-S})(dmpm)_2$ (2a) with MeI

A solution of **2a** (7 mg, 0.012 mmol) in $CDCl_3$ was treated with MeI (0.007 mL, 0.12 mmol), and the NMR spectra were recorded periodically. After ~15 min, the solution contained **2a**, $Pd_2Cl(I)(\mu\text{-S})(dmpm)_2$ (**2a′**), $Pd_2I_2(\mu\text{-S})(dmpm)_2$ (**2c**) and MeCl (δ_H 3.00). Addition of further MeI (0.100 mL, 1.61 mmol) led to complete conversion over 24 h of **2a**, **2a′**, and **2c** to $Pd_2I_2(\mu\text{-I})_2(dmpm)_2$ and generation of Me_2S (δ_H 2.05). $^{31}P\{^1H\}$ NMR of **2a′** ($CDCl_3$): δ −16.6, −12.2 (AA′BB′). NMR data for **2a**, **2c** and the $(\mu\text{-I})_2$ complex are given in our earlier publications.[1,26]

Preparation of $[Pd_2Cl_2(\mu\text{-SMe})(dmpm)_2]OTf$ (5)

To a solution of **2a** (41 mg, 0.069 mmol) in CH_2Cl_2 (5 mL) was added MeOTf (0.078 mL, 0.689 mmol). The resulting yellow solution was stirred for 1 h, filtered through Celite and evaporated to ~2 mL. Slow addition of cold hexanes (10 mL) at 0 °C precipitated a yellow solid that was collected, washed with hexanes (3 × 10 mL) and dried *in vacuo*. Yield: 36 mg (70%). ^1H NMR (CD_2Cl_2, −60 °C): δ 1.60 to 1.74 (m, 24H, CH_3), 2.02 (br m, 1H, CH_2), 2.28 (br s, 3H, SCH_3), 2.47 (br m, 1H, CH_2), 2.73 (br m, 1H, CH_2), 3.11 (br m, 1H, CH_2). $^1H\{^{31}P\}$ NMR (CD_2Cl_2, −60 °C): δ 1.63 (s, 6H, CH_3), 1.64 (s, 6H, CH_3), 1.69 (s, 6H, CH_3), 1.74 (s, 6H, CH_3), 2.02 (d, 1H, CH_2, $^2J_{HH}$ = 14.7), 2.28 (s, 3H, SCH_3), 2.47 (d, 1H, CH_2, $^2J_{HH}$ = 15.4), 2.73 (d, 1H, CH_2, $^2J_{HH}$ = 15.4), 3.11 (d, 1H, CH_2, $^2J_{HH}$ = 14.7). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −60 °C): δ −0.2, −8.3 (AA′BB′, $J_{AA'}$ = 45.4, J_{AB} = $J_{A'B'}$ = 522.8, $J_{BB'}$ = 13.2. $J_{AB'}$ = $J_{A'B}$ = −0.4). UV-vis (CH_2Cl_2): 236 (17.8); 264 (18.5); 312 (9.40). Λ_M (acetone): 98 Ω^{-1} mol^{-1} cm^2. Anal. Calcd for $C_{12}H_{31}Cl_2F_3O_3P_4Pd_2S_2$: C, 19.16; H, 4.15; S, 8.53. Found: C, 19.28; H, 4.16; S, 8.68.

Preparation of $[Pd_4(\mu\text{-Cl})_2(dppm)_4][OTf]_2 \cdot 2\,CH_2Cl_2$

To a solution of $Pd_2Cl_2(dppm)_2$ (73 mg, 0.069 mmol) in acetone (10 mL) was added MeOTf (0.039 mL, 57 mg, 0.346 mmol). The resulting orange solution darkened slightly, and was stirred at r.t. for 16 h, filtered through Celite and evaporated to ~5 mL, when $^{31}P\{^1H\}$ data in $CDCl_3$ revealed quantitative formation of the title complex (AA′BB′ pattern centred at δ −6.9, −15.5). Addition of hexanes (10 mL) generated a red oil from which 5.2 mg (~3% yield) of solid was obtained by dissolving the oil in CH_2Cl_2/Et_2O and leaving it to stand ~24 h. Red crystals, grown from concentrated CH_2Cl_2 solutions of the oil and dried at 78 °C *in vacuo*, gave good C/H analyses, and $^{31}P\{^1H\}$ data consistent with those reported for the PF_6^-, BF_4^- and ClO_4^- salts.[36] UV-vis (relative intensities, CH_2Cl_2): 264 (1.0); 346 (0.34); 430 (0.40); 510 (0.33). Anal. Calcd for $C_{104}H_{92}Cl_6F_6O_6P_8Pd_4S_2$: C, 49.92; H, 3.71. Found: C, 49.84; H, 3.63.

Reaction of $Pd_2Cl_2(\mu\text{-S})(dmpm)_2$ (2a) with *m*-CPBA

The purity of *m*-CPBA was assumed to be 57% to ensure the presence of at least 1.0 oxidising equiv.

To an orange solution of **2a** (76 mg, 0.11 mmol) in CH_2Cl_2 (10 mL) at −30 °C was slowly added a cold solution of *m*-CPBA (33 mg, ~1 equiv.) in CH_2Cl_2 (2 mL), when the solution darkened from yellow-orange to red. After 5 min, the addition of hexanes (10 mL) generated a red oil. The reaction vessel was pumped on overnight, and the residue analysed. $^{31}P\{^1H\}$ ($CDCl_3$): δ −20.4 (s, unidentified), −12.9, 4.8 (AA′BB′, $Pd_2Cl_2(\mu\text{-SO})(dmpm)_2$ (**6a**)), −11.6 (s, **2a**), −7.2 (s, unidentified), 8.8 (s, $Pd_2Cl_2(\mu\text{-SO}_2)(dmpm)_2$), 44.8 (br s, unidentified). ^1H NMR ($CDCl_3$): δ 1.55–2.25 (overlapping multiplets, CH_3), 2.54 (dt, 1H, CH_2, $^2J_{PH}$ = 10.0, $^2J_{HH}$ = 14.4), 3.13 (dt, 1H, CH_2, $^2J_{PH}$ = 12.5, $^2J_{HH}$ = 12.7), 7.40 to 7.80 (m, Ph, traces of *m*-CPBA or 3-chlorobenzoic acid), 9.44 (br s, OH, traces of *m*-CPBA or *m*-chlorobenzoic acid).

Preparation of $Pd_2Br_2(\mu\text{-SO})(dmpm)_2$ (6b)

To a red solution of **2b** (63 mg, 0.093 mmol) in CH_2Cl_2 (10 mL) at −30 °C was added a cold solution of *m*-CPBA (28 mg, ~1 equiv.) in CH_2Cl_2 (3 mL). The solution was stirred for 5 min, warmed slowly to r.t., stirred for 1 h, and then concentrated to ~5 mL. Slow addition of Et_2O (15 mL) yielded a reddish precipitate that was collected, washed with Et_2O (3 × 5 mL) and dried *in vacuo* at 78 °C. Yield: 32 mg (49%). The pale red filtrate was stored in the freezer when after 24 h more red crystals (25 mg) were isolated. Combined yield: 88%. ^1H NMR ($CDCl_3$): δ 1.07 (dtt, 1H, CH_2, $^4J_{PH}$ = 7.3, $^2J_{PH}$ = 12.1, $^2J_{HH}$ = 14.3), 1.36 (dtt, 1H, CH_2, $^4J_{PH}$ = 6.6, $^2J_{PH}$ = 11.6, $^2J_{HH}$ = 13.2), 1.53 (m, 6H, CH_3), 1.67 (m, 6H, CH_3), 1.71 (m, 6H, CH_3), 1.85 (m, 6H, CH_3), 2.60 (dt, 1H, CH_2, $^2J_{PH}$ = 10.1, $^2J_{HH}$ = 14.3), 3.18 (dt, 1H, CH_2, $^2J_{PH}$ = 12.8, $^2J_{HH}$ = 13.3). $^1H\{^{31}P\}$ NMR ($CDCl_3$): δ 1.06 (d, 1H, CH_2, $^2J_{HH}$ = 14.3), 1.34 (d, 1H, CH_2, $^2J_{HH}$ = 13.2), 1.53 (s, 6H, CH_3), 1.67 (s, 6H, CH_3), 1.71 (s, 6H, CH_3), 1.85 (s, 6H, CH_3), 2.59 (d, 1H, CH_2, $^2J_{HH}$ = 14.3), 3.19 (d, 1H, CH_2, $^2J_{HH}$ = 13.3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −13.5, 4.5 (AA′BB′, $J_{AA'}$ = 100, J_{AB} = $J_{A'B'}$ = 395, $J_{BB'}$ = 58.5, $J_{AB'}$ = $J_{A'B}$ = −3.2). UV-vis (CH_2Cl_2) = 300 (18.5), 380 (8.2), 424 (12.6). IR (KBr pellet): ν(SO) = 932 cm^{-1}. Anal. Calcd for $C_{10}H_{28}Br_2OP_4Pd_2S$: C, 17.33; H, 4.07; S, 4.63. Found: C, 17.57; H, 4.09; S, 4.88.

Reaction of $Pd_2I_2(\mu\text{-}S)(dmpm)_2$ (2c) with *m*-CPBA

To a brown solution of **2c** (58 mg, 0.075 mmol) in CH_2Cl_2 (10 mL) at −30 °C was added a cold solution of *m*-CPBA (23 mg, ~1.0 equiv.) in CH_2Cl_2 (1 mL). The solution became dark brown and was stirred for 30 min at r.t. *In situ* NMR analysis revealed small amounts of **2c** and $Pd_2I_2(dmpm)_2$ (**1c**), and a new, unidentified species (**Z**) as the major product. Addition of Et_2O (10 mL) and hexanes (10 mL) precipitated the Pd-containing species as a brown solid mixture that contained **Z** in ~95% purity (^{1}H NMR). The solid was collected, washed with hexanes (2 × 10 mL) and dried at 78 °C *in vacuo* for 24 h. ^{1}H NMR ($CDCl_3$): δ 1.75–1.89 (m, unidentified), 1.81 (s, CH_3, **1c**), 2.11 (s, 12H, CH_3, **Z**), 2.82 (qn, 4H, CH_2, J_{PH} = 3.6, **1c**), 3.57 (qn, 2H, CH_2, J_{PH} = 4.3, **Z**), 7.38, 7.41, 7.92 and 7.77 (m, traces of *m*-CPBA or *m*-chlorobenzoic acid), 9.44 (br s, OH, traces of *m*-CPBA or *m*-chlorobenzoic acid). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −38.4 (s, **1c**), −20.5 (s, unidentified), −18.1 (s, **Z**). Anal. Found: C, 20.44; H, 3.52. Anal. Calcd for $Pd_2I_2(\mu\text{-}SO)(dmpm)_2$ (**6c**), $C_{10}H_{28}I_2OP_4Pd_2S$: C, 15.26; H, 3.59. Anal. Calcd for $Pd_2I_2(\mu\text{-}SO_2)(dmpm)_2$ $C_{10}H_{28}I_2O_2P_4Pd_2S$: C, 14.96; H, 3.51.

Reaction of $Pd_2I_2(\mu\text{-}S)(dmpm)_2$ (2c) with I_2

Addition of I_2 (1 equiv.) to a solution of **2c** in $CDCl_3$ results in the instantaneous formation of $Pd_2I_2(\mu\text{-}I)_2(dmpm)_2$ and elemental sulfur. The purple solution was evaporated and the residue was extracted with CS_2, and this suspension was filtered through a short column of alumina to remove traces of the insoluble Pd complex. The filtrate was evaporated to provide a pale yellow residue, and the low-resolution EI mass spectrum of this material exhibited the characteristic fragmentation pattern of S_8.[42]

X-ray crystallographic analyses

Crystalline samples of **3a**, **5** and **6b** were prepared as described in the Results and discussion sections. X-ray analyses were carried out at 180 K on a Rigaku/ADSC CCD area detector with graphite monochromated Mo-Kα radiation (0.71069 Å). The structures are shown in Fig. 1, 3 and 5. Selected bond lengths and angles are given in Tables 2 and 3, and some associated crystallographic data are given in Table 4, with more details being provided in the Supporting Information.† The final unit-cell parameters were based on 9184 reflections with $2\theta_{max}$ = 60.1° for **3a**, 44930 reflections with $2\theta_{max}$ = 61.0° for **5**, and 16508 reflections with $2\theta_{max}$ = 60.1° for **6**, in a series of ϕ and ω scans in oscillations of 0.50° (for **3a** and **6b**) and 0.30° (for **5**), with respective exposures of 15, 5 and 30.0 s; the crystal-to-detector distance was ~39 mm. Data were processed using the d*TREK area detector program,[43] and the structures were solved by direct methods.[44] All refinements were performed using the SHELXL-97 program[45] *via* the WinGX interface.[46] All non-H-atoms in the three structures were refined anisotropically. All the H-atoms were fixed in idealised, calculated positions.

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