Reaction of the Tetrachalcogenides [ME$_4$(dppe)] (M = Pd, E = S; M = Pt, E = S, Se) with Activated Alkynes to Form Dithiolenes and Diselenolenes

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The tetrachalcogenides [ME$_4$(dppe)] (M = Pd, E = S; M = Pt, E = S, Se) react with the activated alkynes RO$_2$CC≡CCO$_2$R (R = Me, Et) to form the dithiolenes and diselenolenes [M{E$_2$C$_2$(CO$_2$R)$_2$}(dppe)]; the structures of the compounds with E = S, R = Et have been determined by X-ray crystallography; [PdS$_4$(dppe)] also reacts with the carbene complex [W(CO)$_5${C(OEt)C≡CPh}] to yield the bimetallic dithiolene [Pd{S$_2$C$_2$[C(OEt)W(CO)$_5$]Ph}(dppe)].

Introduction

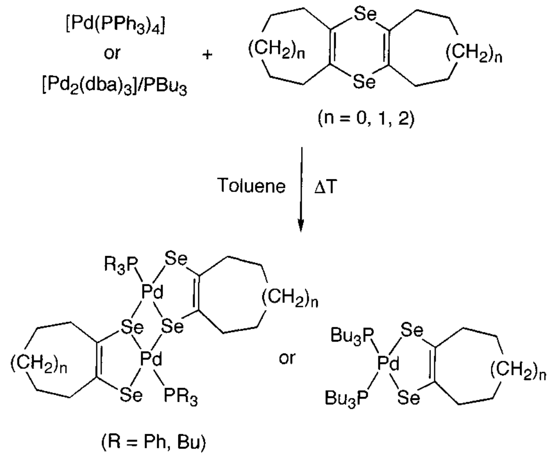
For many years, the potentially useful electrochemical and optical properties of transition metal dithiolenes have attracted the attention of chemists, physicists, and materials scientists.[1] Possible areas of application include molecular electronics, infrared dyes, liquid crystals, and catalysis.[2–4] By contrast, the selenium analogues of dithiolenes (diselenolenes) have been little studied,[5–10] largely because of the lack of generally applicable preparative methods. These complexes are, however, attractive synthetic targets since the incorporation of selenium should lead to a smaller HOMO–LUMO gap and an increase in the strength of intermolecular interactions in the solid state.

We are interested in the potential reactivity of metal polychalcogenides towards activated alkynes to yield dithiolenes and diselenolenes. Treatment of [PtS$_4$(PPh$_3$)$_2$][11] with dimethyl acetylenedicarboxylate (DMAD) has already been shown to lead to the dithiolene [Pt{S$_2$C$_2$(CO$_2$Me)$_2$}(PPh$_3$)$_2$] (Scheme 1).[12]

$$[\mathrm{PtS_4(PPh_3)_2}] + \mathrm{MeO_2CC{\equiv}CCO_2Me} \xrightarrow[\Delta T]{\mathrm{CH_2Cl_2}} [\mathrm{Pt\{S_2C_2(CO_2Me)_2\}(PPh_3)_2}]$$

Scheme 1

In a parallel study, we have recently prepared palladium diselenolenes bearing hydrocarbon substituents from Pd^0 complexes and 1,4-diselenines (Scheme 2).[13,14]



Scheme 2

We now report the preparation of a number of dithiolenes and diselenolenes starting from the tetrachalcogenides [PdS$_4$(dppe)], [PtS$_4$(dppe)], and [PtSe$_4$(dppe)][15] [dppe = 1,2-bis(diphenylphosphanyl)ethane].

Results and Discussion

The polychalcogenides [PdS$_4$(dppe)], [PtS$_4$(dppe)], and [PtSe$_4$(dppe)] are readily prepared from appropriate M^0 precursors and the elemental chalcogen. In an extension of the work of Dudis et al.[12] stirring [MS$_4$(dppe)] (M = Pd, Pt) with an activated alkyne (dimethyl or diethyl acetylenedicarboxylate) in dichloromethane at reflux leads to formation of the dithiolenes **1a**,**b** (M = Pd) and **2a**,**b** (M = Pt) (Scheme 3).

$$[\mathrm{MS_4(dppe)}] + \mathrm{RO_2CC{\equiv}CCO_2R} \xrightarrow[\Delta T]{\mathrm{CH_2Cl_2}} [\mathrm{M\{S_2C_2(CO_2R)_2\}(dppe)}]$$

	M	R
1a	Pd	Me
1b	Pd	Et
2a	Pt	Me
2b	Pt	Et

Scheme 3

The tetraselenide [PtSe$_4$(dppe)] reacts in an analogous fashion to yield the diselenolenes **3a**,**b** (Scheme 4). A similar reaction of the MSe$_4$ fragment has previously been observed for the anionic tungsten complex [WSe(Se$_4$)$_2$]$^{2-}$.[16]

$$[\mathrm{PtSe_4(dppe)}] + \mathrm{RO_2CC{\equiv}CCO_2R} \xrightarrow[\Delta T]{\mathrm{CH_2Cl_2}} [\mathrm{Pt\{Se_2C_2(CO_2R)_2\}(dppe)}]$$

	R
3a	Me
3b	Et

Scheme 4

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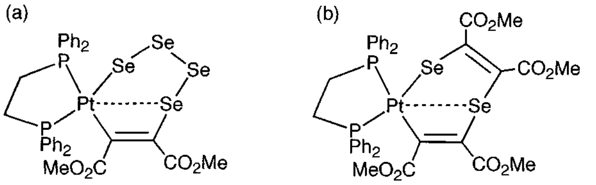
The reactivity within this system of the three tetrachalcogenides is noticeably different, with [PdS_4(dppe)] being the most reactive, followed by [$PtSe_4$(dppe)] and then [PtS_4(dppe)].

The reaction of [$PtSe_4$(dppe)] with a large excess of DMAD was monitored by ^{31}P-NMR spectroscopy. An intermediate is formed in the early stages of the reaction that has inequivalent phosphorus nuclei [**4a**: P_A, $\delta = 49.5$, $J(^{195}\text{Pt-}^{31}\text{P}) = 1906$ Hz; P_B, $\delta = 48.5$, $J(^{195}\text{Pt-}^{31}\text{P}) = 3166$ Hz; $J(^{31}P_A\text{-}^{31}P_B) = 10.8$ Hz]. This intermediate is not present once the starting material has been consumed. The final phosphorus-containing product is predominantly the diselenolene **3a**, but there is also a second species present in low concentration [**5a**: P_A, $\delta = 45.6$, $J(^{195}\text{Pt-}^{31}\text{P}) = 3223$ Hz; P_B, $\delta = 43.9$, $J(^{195}\text{Pt-}^{31}\text{P}) = 2054$ Hz; $J(^{31}P_A\text{-}^{31}P_B) = 7.4$ Hz]. The coupling constants in the ^{31}P-NMR spectra of **4a** and **5a** are comparable with those in the selenaketocarbene complex [$Pt(SeC_8H_{12})(PPh_3)_2$],[17] which has one phosphorus atom *trans* to selenium and one *trans* to carbon.

The reaction of [$Ti(\eta^5\text{-}C_5H_5)_2Se_5$] with DMAD to yield [$Ti(\eta^5\text{-}C_5H_5)_2\{Se_2C_2(CO_2Me)_2\}$] has been studied by Bollinger and Rauchfuss.[8] They showed that the mechanism involves binding of the alkyne to the chalcogenide chelate ring in the rate-determining step. The structure of an adduct between DMAD and the dithiolene [$Rh(\eta^5\text{-}C_5H_5)\{S_2C_2(CO_2Me)_2\}$] has been reported.[18] In this compound a new metal–carbon bond has been generated by insertion of the alkyne into the metal–chalcogen bond. We therefore tentatively assign the structures shown in Figure 1 to **4a** and **5a**.



4a **5a**

Figure 1. Proposed structures of **4a** and **5a**

Compounds **1a**, **2a**, and **3a** could not be obtained in a pure state due to the formation of polymeric material derived from DMAD, although the NMR-spectroscopic and mass-spectrometric data confirm their formulation as [$M\{E_2C_2(CO_2Me)_2\}$(dppe)] (**1a**: M = Pd, E = S; **2a**: M = Pt, E = S; **3a**: M = Pt, E = Se). No such problems were, however, encountered with the ethyl derivatives **1b**, **2b**, and **3b**, which were characterised by standard analytical and spectroscopic methods. It seems likely that the greater size of the ethyl substituents in DEAD inhibits the formation of a species analogous to **5a**, which might function as an intermediate in the polymerisation process.

The crystal structures of the isomorphous compounds **1b** and **2b** were determined by X-ray diffraction (Figure 2, Table 1). There are only very small differences between them, with the bonding in the dithiolene unit being slightly asymmetric in each case: One M–S bond is ca. 0.02 Å longer than the other, and one P–M–S angle is significantly expanded [**1b**: 96.51(5)° vs. 89.83(4)°; **2b**: 96.16(5)° vs. 90.26(5)°]. This feature does not appear to have been observed before in the structures of palladium and platinum dithiolenes, and is probably to be attributed to packing effects.

The structures of relatively few palladium mono-dithiolenes have been reported. The Pd–S distances in **1b** (2.284, 2.310 Å) are in the range of those previously observed (2.274–2.324 Å),[19] and are comparable with those in [$Pd\{S_2C_2(CH_2CH_2\text{-}N\text{-}2\text{-pyridinium})\}$(dppe)][$BPh_4$] (2.297, 2.303 Å).[20] Platinum mono-dithiolenes are more numerous, in part because of interest in their luminescent properties. The Pt–P distances in **2b** (2.268, 2.265 Å) may be compared with those in [$Pt\{S_2C_2S_2CS\}$(dppe)] (2.258, 2.250 Å)[21] and [$Pt\{S_2C_2(CN)_2\}$(dppe)] (2.262, 2.252 Å).[22] Comparable Pt–S distances to those in **2b** (2.297, 2.318 Å) are found in [$Pt\{S_2C_2(CO_2Me)_2\}\{P(OMe)_3\}_2$] (2.300, 2.302 Å)[23] and [$Pt\{S_2C_2(CO_2Me)_2\}(PPh_3)_2$] (2.304 Å).[12]

Crystals of **3b** suitable for study by X-ray diffraction could not be obtained. The spectroscopic data are, however, entirely in accord with a structure for **3b** analogous to those of **1b** and **2b**. The NMR data for all three compounds are strikingly similar. There are small, but significant differences between the palladium and platinum derivatives [particularly in the value of $\delta(^{31}P)$], which we have observed in other dppe complexes of these metals. Replacement of the sulfur in **2b** by selenium (**3b**) leads to a slight upfield shift in $\delta(^{13}C)$ for the dichalcogenolene carbons. This is accompanied by a slight downfield shift in $\delta(^{31}P)$ and an increase in the platinum-phosphorus coupling constant [$J(^{31}\text{P-}^{195}\text{Pt})$]. These changes may imply that the diselenolene ring in **3b** has a marginally greater electron density than the dithiolene ring in **2b**. A similar increase in $J(^{31}\text{P-}^{195}\text{Pt})$ was observed by Rauchfuss et al. for the analogous triphenylphosphane derivatives [$Pt\{E_2C_2(CO_2Me)_2\}(PPh_3)_2$] (E = S, Se).[8]

The ^{77}Se-NMR spectrum of **3b** is shown in Figure 3, together with the satellite structure of the ^{31}P resonance. Analysis of the data allows evaluation of the three coupling constants in this system: $J(^{31}P_{trans}\text{-}^{77}\text{Se}) = 64.3$ Hz; $J(^{31}P_{cis}\text{-}^{77}\text{Se}) = 31.8$ Hz; $J(^{31}\text{P-}^{31}\text{P}) = 13.9$ Hz. The values of $J(^{31}\text{P-}^{77}\text{Se})$ are significantly higher than those previously determined in platinum selenolate complexes,[24] but are comparable with that reported for the diselenolene [$Pt\{Se_2C_2(CO_2Me)_2\}(PPh_3)_2$] (52 Hz, presumably an average value).[8]

In the IR spectra of **1b**, **2b**, and **3b** four bands corresponding to C=O stretching are observed and these are at lower frequencies (by ca. 10–100 cm^{-1}) than $\nu_{C=O}$ in DEAD (1724 cm^{-1}). There is an accompanying small decrease (by ca. 20 cm^{-1}) of the C–O stretching frequency from its value in DEAD, which is 1255 cm^{-1}. These changes are reflected in a substantial increase (by ca. 16 ppm) in the ^{13}C-NMR chemical shift of the carbonyl carbon atoms [in DEAD $\delta(CO) = 151.7$]. All the compounds give intense molecular ions in their FAB mass spectra. Ions corresponding to the expected fragmentation patterns are also observed, of which

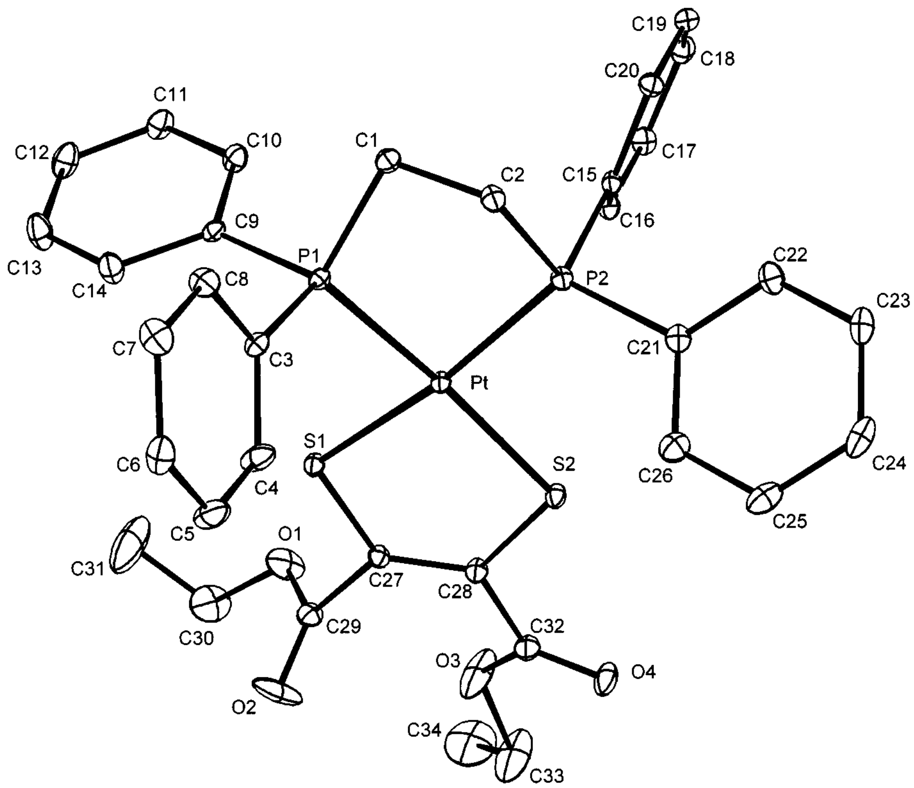


Figure 2. Molecular stuctures of [M$\{S_2C_2(CO_2R)_2\}$(dppe)] [M = Pd, **1b**; M = Pt, **2b** (shown)]

Table 1. Selected bond lengths [Å] and angles [°] for [M$\{S_2C_2(CO_2R)_2\}$(dppe)] (M = Pd, **1b**; M = Pt, **2b**)

	1b (M = Pd)	**2b** (M = Pt)
M–P(1)	2.2775(13)	2.268(2)
M–P(2)	2.2766(14)	2.265(2)
M–S(1)	2.2837(14)	2.297(2)
M–S(2)	2.3096(14)	2.318(2)
S(1)–C(27)	1.726(5)	1.730(6)
S(2)–C(28)	1.760(5)	1.767(6)
C(27)–C(28)	1.354(7)	1.341(8)
P(1)–M–P(2)	84.72(4)	85.05(5)
P(2)–M–S(2)	96.51(5)	96.16(5)
S(2)–M–S(1)	89.41(4)	89.02(5)
S(1)–M–P(1)	89.83(4)	90.26(5)
S(1)–C(27)–C(28)	123.3(4)	123.8(5)
C(27)–C(28)–S(2)	121.8(4)	121.8(4)
M–S(1)–C(27)	103.2(2)	103.1(2)
M–S(2)–C(28)	102.2(2)	102.3(2)

those arising from loss of DEAD {i.e. [ME_2(dppe)]$^+$} are particularly prominent.

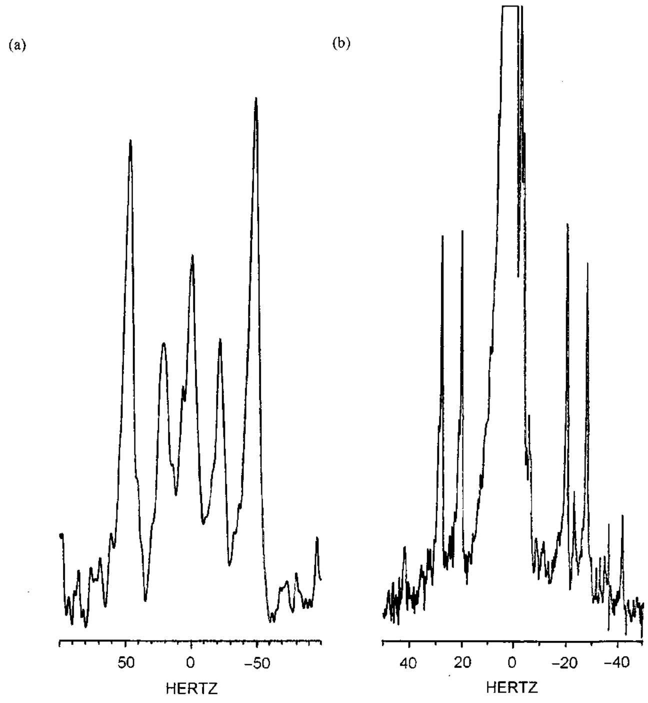
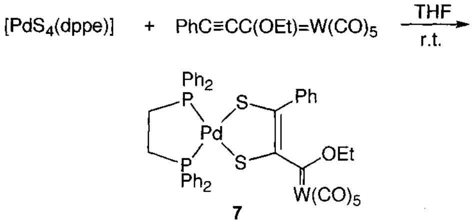


Figure 3. NMR spectra of **3b**: (a) structure of ^{77}Se resonance, (b) satellite structure of ^{31}P resonance; analysis of the data gives $J(^{31}P\text{-}^{77}Se)$ = 64.3 Hz, 31.8 Hz; $J(^{31}P\text{-}^{31}P)$ = 13.9 Hz

No products could be isolated from the reactions of [ME_4(dppe)] (M = Pd, E = S; M = Pt, E = S, Se) with less activated alkynes, such as PhC≡CH, PhC≡CPh, HC≡CCO_2Et, or PhC≡CCO_2Et. In the case of the most reactive of the tetrachalcogenides ([PdS_4(dppe)]), treatment with PhC≡CCO_2Et did lead to the observation of a new AB pattern in the ^{31}P-NMR spectrum, analysis of which yielded δ = 50.5, 50.2, J = 41.0 Hz. This is presumed to arise from the unsymmetrical dithiolene [Pd$\{S_2C_2(CO_2Et)Ph\}$(dppe)] (**6**), as the molecular ion for this species was observed in the mass spectrum of the reaction mixture. The NMR data are also strikingly similar to those for

$[Pd\{S_2C_2[C(OEt)W(CO)_5]Ph\}(dppe)]$ (**7**) (vide infra). The extent of conversion into product was, however, very low, and separation of compound **6** was not achieved.

The carbene complex $[W(CO)_5\{C(OEt)C{\equiv}CPh\}]$[25] is an alkyne bearing a highly electron-withdrawing substituent. It reacts with $[PdS_4(dppe)]$ {but not with the platinum tetrachalcogenides $[PtE_4(dppe)]$ (E = S, Se)} at room temperature in tetrahydrofuran solution to yield the unsymmetrical dithiolene $[Pd\{S_2C_2[C(OEt)W(CO)_5]Ph\}(dppe)]$ (**7**) in moderate yield (Scheme 5). The reaction could not be performed in dichloromethane, as decomposition occurs in this solvent. Some starting material remains unchanged and must be separated from the product by column chromatography. There are also a number of unidentified by-products. Compound **7** could not be obtained as a crystalline solid, but its composition is assured on the basis of NMR, UV/Vis, and IR spectroscopy and mass spectrometry.



7

Scheme 5

The ^{31}P-NMR spectrum of **7** contains the expected AB pattern for the inequivalent phosphorus atoms. Analysis of the data gives $\delta(^{31}P) = 50.0, 49.1$; $^2J(^{31}P\text{-}^{31}P) = 40.9$ Hz. The chemical shifts are similar to those observed for the symmetrical palladium dithiolenes **1a,b**. The coupling constant is comparable with that for the palladium diselenolene $[Pd\{Se_2C_7H_{10}\}(PBu_3)_2]$ (44 Hz),[14] and is significantly greater than that for the platinum analogue **3b** (13.9 Hz).

The ^{13}C-NMR spectrum of **7** has many similarities to that of **1b**. Each of the carbon atoms in the phenyl rings and the CH_2 group of dppe forms the X part of an AA′X system, and should therefore give rise to five lines in the spectrum. The outermost lines are often weak and were not observed in **1b**. In **7** the phenyl rings bound to the two inequivalent phosphorus atoms are themselves inequivalent, so we expect to see a doubling of the number of lines. This is essentially what is observed, although overlapping occurs in some cases. The greatest discrimination occurs for the carbon atoms in the dithiolene. These have chemical shifts of $\delta = 145.0$ and $\delta = 138.5$ in **7**. Although the equivalent single resonance was too weak to be observed in **1b**, in **2b** and **3b** it is at $\delta = 139.5$ and 137.3, respectively. We assign the resonance at $\delta = 145.0$ to the carbon bearing the highly electron-withdrawing carbene substituent.

Bands corresponding to C≡O stretching are not observed in the IR spectrum of **7**. This is surprising, given their prominence in the spectrum of the carbene starting material. Convincing evidence for the presence of the carbonyl ligands is, however, provided by the FAB mass spectrum. In addition to an intense molecular ion centred on $m/z = 1051$, there are clusters of peaks around $m/z = 967$ ($M^+ - 3$ CO) and $m/z = 911$ ($M^+ - 5$ CO), as well as several other fragments resulting from carbonyl loss.

Overall, it can be seen that the reactions of palladium and platinum tetrachalcogenides with activated alkynes provide an effective route to dithiolenes and diselenolenes bearing highly electron-withdrawing groups. This preparative method is thus complementary to the use of 1,2,3-selenadiazoles or 1,4-diselenines, which enables the synthesis of hydrocarbyl-substituted derivatives. We are now proceeding to examine in more detail the photophysical and electrochemical properties of this class of compound.

Experimental Section

General: All reactions were performed using standard Schlenk techniques and pre-dried solvents under dinitrogen. – ^1H- and ^{13}C-NMR spectra: Bruker AC400; tetramethylsilane as internal standard. ^{31}P-, ^{77}Se-, and ^{195}Pt-NMR spectra: Bruker WM250; 85% phosphoric acid, dimethyl selenide, or sodium hexachloroplatinate as external standard. – IR spectra: Perkin–Elmer 1725X. – UV/Vis spectra: Perkin–Elmer Lambda 9. – Mass spectra were recorded by the EPSRC Mass Spectrometry Centre, using Fast Atom Bombardment (FAB). Values of *m*/*z* quoted are for isotopomers containing ^{80}Se, ^{106}Pd, or ^{195}Pt as appropriate; expected isotope distribution patterns were observed. – Elemental analyses were performed by the analytical service of the University of Wales, Cardiff.

Bis(diphenylphosphanyl)ethane(tetrasulfido-*S*,*S*)palladium and -platinum,[12] bis(diphenylphosphanyl)ethane(tetraselenido-*Se*,*Se*)-platinum[14], and pentacarbonyl[phenylethynyl(ethoxy)carbene]-tungsten[25] were prepared by literature procedures.

Palladium Dithiolenes (1a,b), Platinum Dithiolenes (2a,b) and Platinum Diselenolenes (3a,b): The same general procedure was used for all three types of compound. A mixture of $[ME_4(dppe)]$ [0.063 g (M = Pd, E = S), 0.072 g (M = Pt, E = S) or 0.091 g (M = Pt, E = Se), 0.1 mmol] and dimethyl or diethyl acetylenedicarboxylate (0.43 g or 0.48 g, 3.0 mmol) in dichloromethane (50 mL) was heated under reflux for a prolonged period (**1a**,**b**: 18 h; **2a**,**b**: 6 d; **3a**,**b**: 4 d). After this time, a brown or red solid had precipitated. The mixture was filtered, and the solvent removed from the filtrate by evaporation under reduced pressure to leave an oily yellow to orange solid. This was purified by recrystallisation from a mixture of dichloromethane and petroleum ether (b.p. 30–40 °C). The products of the reaction with DMAD (**1a**, **2a**, **3a**) could not be obtained free of a polymeric impurity. Compounds **1b**, **2b**, **3b** are air-stable crystalline solids (**1b**, pale orange; **2b**, cream; **3b**, yellow) that are soluble in a wide range of organic solvents.

1a: ^{31}P NMR: $\delta = 52.0$. – MS; *m*/*z*: 710 [M^+].

1b: Yield: 0.052 g, 70%. – M.p. 248 °C (dec.). – $C_{34}H_{34}O_4P_2PdS_2$: calcd. C 55.3, H 4.63; found C 55.3, H 4.76. – ^1H NMR: $\delta = 7.82$ (m, 8 H), 7.48 (m, 12 H), 4.18 (q, $J = 7$ Hz, 4 H), 2.49 (m, 4 H), 1.25 (t, $J = 7$ Hz, 6 H). – ^{13}C NMR: ($C{=}O$, $C{=}C$ not observed), $\delta = 133.5$ [average $J(^{13}C\text{-}^{31}P) = 6$ Hz], 131.6, 129.5 [PC_{Ar}, average $J(^{13}C\text{-}^{31}P) = 19$ Hz], 129.0 [average $J(^{13}C\text{-}^{31}P) = 5$ Hz], 61.0 [OCH_2], 27.9 [PCH_2, average $J(^{13}C\text{-}^{31}P) = 24$ Hz], 14.1 [CH_3]. – ^{31}P NMR: $\delta = 52.0$. – IR (KBr disk): $\tilde{\nu} = 3053$ m, 2962 s, 2918 s, 2850 m, 1713 m, 1693 m, 1638 m, 1619 m, 1527 m, 1436 s, 1234 vs, 1102 vs, 1030 s, 804 m, 748 m, 716 m, 705 m, 692 s, 530 s, 484 w cm^{-1}. – UV/Vis (CH_2Cl_2), λ_{max} (ε [$dm^3\ cm^{-1}\ mol^{-1}$]) = 230

Table 2. Crystallographic data for $[M\{S_2C_2(CO_2R)_2\}(dppe)]$ (M = Pd, **1b**; M = Pt, **2b**)

Compound	**1b**	**2b**
Formula	$C_{34}H_{34}O_4P_2PdS_2$	$C_{34}H_{34}O_4P_2PtS_2$
M_r	739.07	827.76
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)
a [Å]	14.229(4)	14.279(2)
b [Å]	16.124(4)	16.165(3)
c [Å]	14.881(3)	14.907(2)
β [°]	90.14(2)	90.11(1)
V [Å^3]	3414(2)	3441(1)
Z	4	4
D_c [Mg m^{-3}]	1.438	1.598
Crystal size [mm]	0.15 × 0.50 × 0.50	0.15 × 0.25 × 0.55
μ [mm^{-1}]	0.795	9.927
Radiation	Mo-K_α (λ = 0.71069 Å)	Cu-K_α (λ = 1.54184 Å)
Data collected	$\pm h, +k, +l$	2.6 redundancy
Scan type	ω-2θ	CCD ω scans
2θ range for data [°]	5–50	6–115
Reflections collected	6295	11425
Unique reflections	5999 (R_{int} = 0.020)	4332 (R_{int} = 0.042)
Unique observed reflections with $I > 2\sigma(I)$	4446	3556
No. of parameters	390	390
$R1$ (observed reflections)	0.043	0.033
$R1$ (all unique reflections)	0.071	0.039
$wR2$	0.113	0.079
Goodness of fit	1.018	0.952
Largest features (max., min.) in final ΔF map [e Å^{-3}]	0.73, –0.58	0.93, –1.06

(30000), 280 (31000), 490 (150), 570 (1200) nm. – MS; *m/z*: 738 [M$^+$].

2a: ^{31}P NMR, δ = 44.9 [$J(^{195}$Pt-^{31}P) 2769 Hz]. – MS; *m/z*: 799 [M$^+$].

2b: Yield: 0.050 g, 60%. – M.p. 145 °C (dec.). – $C_{34}H_{34}O_4P_2PtS_2$: calcd. C 49.3, H 4.14; found C 46.9, H 4.33. – ^{1}H NMR: δ = 7.79 (m, 8 H), 7.45 (m, 12 H), 4.20 (q, J = 7 Hz, 4 H), 2.47 (m, 4 H), 1.25 (t, J = 7 Hz, 6 H). – ^{13}C NMR: δ = 167.1 [*C*=O], 139.5 [*C*=*C*, $J(^{13}$C-^{31}P) not resolved], 133.6 [average $J(^{13}$C-^{31}P) = 6 Hz], 131.6, 129.6 [P*C*$_{Ar}$, average $J(^{13}$C-^{31}P) = 30 Hz], 128.8 [average $J(^{13}$C-^{31}P) = 5 Hz], 61.1 [O*C*H$_2$], 28.6 [P*C*H$_2$, $J(^{13}$C-^{31}P) not resolved], 14.1 [*C*H$_3$]. – ^{31}P NMR: δ = 44.9 [$J(^{195}$Pt-^{31}P) = 2767 Hz]. – IR (KBr): ṽ = 3001 m, 2963 s, 2925 vs, 2858 m, 1717 s, 1695 s, 1638 vs, 1619 vs, 1526 s, 1436 m, 1385 m, 1236 s, 1103 s, 1040 m, 750 w, 717 m, 692 m, 617 s, 533 vs, 485 vs cm^{-1}. – UV/Vis (CH$_2$Cl$_2$), λ_{max} (ε [dm^3 cm^{-1} mol^{-1}]) = 230 (45000), 260 (35000), 320 (5800), 370 (770) nm. – MS; *m/z*: 827 [M$^+$].

3a: ^{31}P NMR: δ = 45.8 [$J(^{195}$Pt-^{31}P) = 2794 Hz]. – MS; *m/z*: 895 [M$^+$].

3b: Yield: 0.060 g, 65%. – M.p. 195 °C (dec.). – $C_{34}H_{34}O_4P_2PtSe_2$: calcd. C 44.3, H 3.72; found C 42.9, H 3.66. – ^{1}H NMR: δ = 7.75 (m, 8 H), 7.47 (m, 12 H), 4.18 (q, J = 7 Hz, 4 H), 2.43 (m, 4 H), 1.24 (t, J = 7 Hz, 6 H). – ^{13}C NMR: δ = 168.2 [*C*=O], 137.3 [*C*=*C*, average $J(^{13}$C-^{31}P) = 7 Hz], 133.5 [average $J(^{13}$C-^{31}P) = 5 Hz], 131.6, 129.5 [P*C*$_{Ar}$, average $J(^{13}$C-^{31}P) = 29 Hz], 128.8 [average $J(^{13}$C-^{31}P) = 5 Hz], 61.2 [O*C*H$_2$], 28.8 [P*C*H$_2$, average $J(^{13}$C-^{31}P) = 25 Hz], 14.1 [*C*H$_3$]. – ^{31}P NMR: δ = 45.8 [$J(^{195}$Pt-^{31}P) = 2790 Hz]. – ^{77}Se NMR: δ = 483 [$J(^{77}$Se-^{31}P) = 64.3, 31.8 Hz; $J(^{31}$P-^{31}P) = 13.9 Hz]. – ^{195}Pt NMR: δ = –2921 [$J(^{195}$Pt-^{31}P) = 2790 Hz]. – IR (KBr): ṽ = 2919 s, 2850 m, 1720 m, 1688 m, 1639 m, 1619 m, 1532 m, 1437 m, 1385 w, 1230 vs, 1105 m, 1034 m, 999 m, 751 w, 717 m, 704 m, 692 m, 618 w, 535 s, 487 m cm^{-1}. – UV/Vis (CH$_2$Cl$_2$), λ_{max} (ε [dm^3 cm^{-1} mol^{-1}]) = 230 (12000), 290 (9500), 310 (3700), 320 (3500), 330 (2600), 350 (1900), 370 (580) nm. – MS; *m/z*: 923 [M$^+$].

Palladium Complex 7: A mixture of [PdS$_4$(dppe)] (0.063 g, 0.1 mmol) and [W(CO)$_5$$\{$=C(OEt)C≡CPh$\}$] (0.048 g, 0.1 mmol) in THF (100 mL) was stirred at room temperature for 4 h. During this time the solution became cloudy and some of the [PdS$_4$(dppe)] remained undissolved. The solvent was removed from the mixture by evaporation under reduced pressure to give a dark red oily solid, which was chromatographed on a short column of silica, using toluene as eluent. A band was collected that was yellow on the column. On changing the eluent to dichloromethane, four bands were collected that were light brown, yellow, orange and pink in order of elution. The third of these contained the product, which was isolated as a dark red-brown oily solid after removal of the solvent. The others yielded dppe disulfide, [PdS$_4$(dppe)], and small amounts of unidentified compounds.

7: Yield: 0.036 g, 34%. – ^{1}H NMR: δ = 7.80 (m, 7 H), 7.42 (m, 15 H), 7.16 (m, 3 H), 4.18 (q, J = 7 Hz, 2 H), 2.48 (m, 4 H), 0.66 (t, J = 7 Hz, 3 H). – ^{13}C NMR: (*C*=O, *C*=W not observed), δ = 145.0 [*C*=C, $J(^{13}$C-^{31}P) not resolved], 138.5 [C=*C*, $J(^{13}$C-^{31}P) not resolved], 133.5 [four peaks], 131.4, 129.9 [P*C*$_{Ar}$, average $J(^{13}$C-^{31}P) = 22 Hz], 129.0 [four peaks], 128.4, 127.3, 126.2, C*C*$_{Ar}$ not observed, 67.4 [O*C*H$_2$], 27.9 [*C*H$_2$P, seven peaks], 12.7 [*C*H$_3$]. – ^{31}P NMR: δ = 50.0, 49.1 [AB: $J(^{31}$P-^{31}P) = 40.9 Hz]. – IR (KBr): ṽ = 2920 vs, 2850 s, 1635 m, 1465 w, 1435 m, 1384 w, 1234 m, 1102 s, 801 w, 745 w, 692 m, 529 m, 480 w cm^{-1}. – UV/Vis (CH$_2$Cl$_2$), λ_{max} (ε [dm^3 cm^{-1} mol^{-1}]) = 230 (90000), 270 (73000), 420 (16000), 480 (7300) nm. – MS; *m/z*: 1051 [M$^+$].

X-ray Crystallography: Details of the crystal structure determinations are given in Table 2. Measurements were carried out at room temperature with an Enraf–Nonius CAD4 diffractometer for **1b**, using graphite-monochromated Mo-K_α radiation, and with a Bruker-AXS CCD platform mounted on a rotating anode generator equipped with Göbel mirrors for **2b**, using Cu-K_α radiation. No crystal decay was observed during data collections, although **2b** was found to decompose if Mo-K_α radiation was used. Empirical corrections for absorption were applied, based on ψ scans (**1b**) or SADABS[26] (**2b**) [min., max. transmission factors: 0.93, 0.98 (**1b**);

0.412, 1.000 (**2b**)]. Structure solution was by direct methods, with SIR97,[27] and Fourier cycles with SHELXL-93,[28] which was also used for structure refinements. The final refinement cycles were performed against F^2 with all nonhydrogen atoms anisotropic and hydrogen atoms in calculated positions. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications CCDC-136286 (**1b**) and -136287 (**2b**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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