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Open Platinum Aggregate Frameworks with Overhead Dithiolate Bridges

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A convenient method has been developed to bring together two discrete moieties of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ to give an open Pt_4 aggregate of $Pt_2\cdots(\text{spacer})\cdots Pt_2$, as exemplified in the isolation of $[(PPh_3)_4Pt_2(\mu\text{-}S)(\mu\text{-}SRS)(\mu\text{-}S)Pt_2(PPh_3)_4](PF_6)_2$ [R = *m*-$CH_2C_6H_4CH_2$, *p*-$CH_2C_6H_4CH_2$, $CH_2C_{10}H_6CH_2$, and $CH_2(C_6H_4)_2CH_2$]. The spacer is a dithiolate with an extended skeletal backbone formed from the alkylation of sulfide with a suitable dibromo-organic compound. This synthetic methodology can tolerate a range of conformationally contrasting thiolate substituents with different chemical functionalities. Shorter or stereochemically more restrictive spacers could opt to be an intramolecular bridge over the Pt_2 core, as given in $[Pt_2(\mu\text{-}S\text{-}o\text{-}CH_2C_6H_4\text{-}C_6H_4CH_2S)(PPh_3)_4](PF_6)_2$. A few representative complexes have been characterized by single-crystal X-ray diffraction analysis.

Introduction

Owing to the rich nucleophilicity of the $\{Pt_2(\mu\text{-}S)_2\}$ core, the $[Pt_2(\mu\text{-}S)_2(P\text{-}P)_2]$ (P-P = diphosphane or $2\times PR_3$) (**1**) complexes have evolved to be a versatile metalloligand[1] and an efficacious thio-template for organic reactions.[2] The well-developed metallation chemistry of **1** has resulted in a large number of homo-, hetero-, and intermetallic polynuclear structures, which are best described as metal aggregates, not clusters, as they generally do not have active and direct M–M bonds. One of the objectives for this type of supramolecular assembly is to construct a mega-aggregate framework using sub-aggregates as building blocks. Parallel to this development is the use of organic moieties, instead of metal species, to connect the aggregate and build up the nuclearity. Conceptually, this can be viewed as an application of the growing alkylation chemistry of $[Pt_2(\mu\text{-}S)_2(P\text{-}P)_2]$.[1c,3–4] The nuclearity growth is controlled by the electronic and geometric features of the spacer. Adjusting the nucleophilicity of both sulfide centers could help to control the mono- or dialkylation selectivity, as evidenced from our recent study of the alkylation and arylation chemistry of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ (**1a**) using Electrospray Ionization Mass Spectrometry (ESI-MS).[3a] While simple monohalides predominantly give monoalkylated products of the type, $[Pt_2(\mu\text{-}SR)(\mu\text{-}S)(PPh_3)_4]^+$ (**2**), reactive halides, dimethyl sulfate, and α,ω-dialkylating agents result in dialkylated products, such as $[Pt_2(\mu\text{-}SR)_2(PPh_3)_4]^{2+}$ (**3**) and $[Pt_2(\mu\text{-}S_2R)(PPh_3)_4]^{2+}$ (**4**). Of particular interest here is the use of α,ω-dialkylating agents, with more rigid spacers; the spacer length between the alkylating groups [typically halides (X), e.g. XRX] determines the extent of functionalization in **1a**. For example, with a spacer containing up to four carbons, the end product of the reaction is the bridged complex (**4**), but with a longer separation, monoalkylation tends to dominate, resulting in complexes of the type $[Pt_2(\mu\text{-}SRX)(\mu\text{-}S)(PPh_3)_4]^+$ (**5**). In the case where the dihalides have a hydrocarbon chain which is too long to fit into the overhead S···S bridge, they can opt to intermolecularly bridge two sulfides, thus resulting in Pt_4 dications.[3a]

We herein present a synthetic application of our earlier ESI-MS study by preparing, isolating, and characterizing the tetranuclear platinum (Pt_4) sulfide aggregates $[(PPh_3)_4Pt_2(\mu\text{-}S)(\mu\text{-}SRS)(\mu\text{-}S)Pt_2(PPh_3)_4]^{2+}$ (**6**), which up to now have only been observed spectroscopically.[3a] This type of high-nuclearity platinum complex, in which the metal centers interact through ligand bridges, has attracted attention for their structural diversity,[5] luminescent[6] and redox[7] properties, electronics,[8] catalysis,[7] and as molecular precursors for inorganic materials under mild conditions,[9] as possible models in redox-active metalloproteins,[10] and as anti-cancer agents.[11]

Results and Discussion

Constructing Linkages to Build Platinum Sulfide Aggregates

The use of dihalides (XRX) of an appropriate spacer length to cross both sulfur atoms in $[Pt_2(\mu\text{-}S)_2(P\text{-}P)_2]$ (**1**) has provided the first solution to stable dialkylated derivatives of **1**.[2,3b] Early alkylation studies of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ (**1a**) demonstrate that while monoalkylation is facile, dialky-

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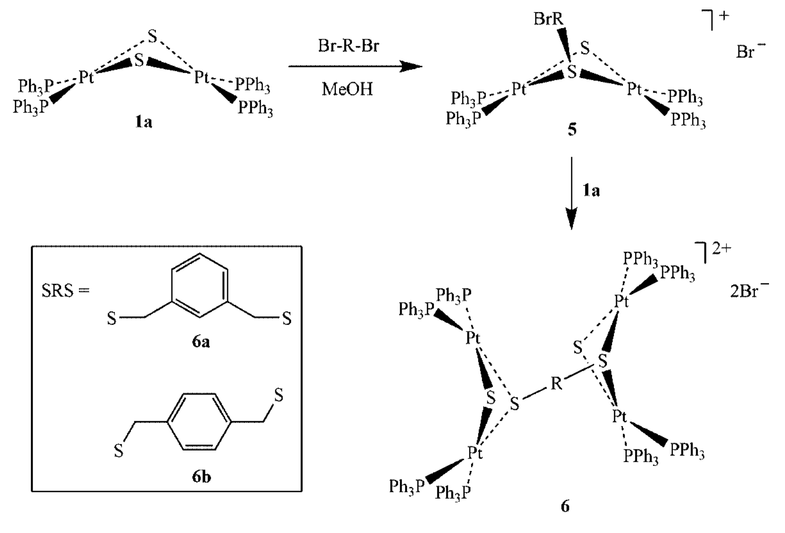


Scheme 1. Formation of a Pt_4 aggregate (**6**) through the linkage of two moieties of **1a**.

lation is elusive since the second sulfide is deactivated upon alkylation of the first in the initially formed monocation, $[Pt_2(\mu\text{-}SR)(\mu\text{-}S)(PPh_3)_4]^+$ (**2**)[3a–3b] or disintegration of the $\{Pt_2(\mu\text{-}S)_2\}$ core that follows dialkylation with CH_2Cl_2[4a–4c] and protic acids.[12] This method of sulfide functionalization in **1** leads to the isolation of stable overhead-bridged dialkylated products, such as $[Pt_2(\mu\text{-}SC_nH_{2n}S)(PPh_3)_4](PF_6)_2$ (n = 2 and 4)[3b] and $[Pt_2(\mu\text{-}S\text{-}o\text{-}CH_2C_6H_4CH_2S)(P\text{-}P)_2](PF_6)_2$ [P-P = 2 × PPh_3 and $Ph_2PC_3H_6PPh_2$ (dppp)].[2a] The latter complex has been shown to be a useful precursor in the catalytic-like preparation of dithiacyclophanes.

As mentioned previously, dihalides with a hydrocarbon chain which is too long or insufficiently flexible to fit into the overhead S···S bridge will lead to monoalkylation, giving $[Pt_2(\mu\text{-}SRX)(\mu\text{-}S)(PPh_3)_4]^+$ (**5**).[3a–3b] By taking advantage of the dehalogenation capability of $\{Pt_2(\mu\text{-}S)_2\}$[3d] to displace the halide in **5**, Pt_4 dications of the type, $[(PPh_3)_4Pt_2(\mu\text{-}S)(\mu\text{-}SRS)(\mu\text{-}S)Pt_2(PPh_3)_4]^{2+}$ (**6**) can be readily obtained (Scheme 1). Initial alkylation of **1a** with one equivalent of α,α′-dibromo-*m*-xylene gives the stable monoalkylated $[Pt_2(\mu\text{-}S\text{-}m\text{-}CH_2C_6H_4CH_2Br)(\mu\text{-}S)(PPh_3)_4]^+$ (**5a**) (*m*/*z* 1687, 100%), followed by the formation of $[(PPh_3)_4Pt_2(\mu\text{-}S)(\mu\text{-}S\text{-}m\text{-}CH_2C_6H_4CH_2S)(\mu\text{-}S)Pt_2(PPh_3)_4](PF_6)_2$ (**6a**) upon addition of another equivalent of **1a**, and metathesis with NH_4PF_6. Single-crystal X-ray diffraction analysis of **6a** (Figure 1) reveals two $\{Pt_2(\mu\text{-}S)_2\}$ butterflies joined together by $\text{-}CH_2C_6H_4CH_2\text{-}$ at each of their sulfides, resulting in a "coat hanger-like" structure. Similarly, in the case of the *para* isomer (α,α′-dibromo-*p*-xylene), the two $\{Pt_2(\mu\text{-}S)_2\}$ butterflies are connected at both ends of the xylyl bridge (Figure 2) to give the intermolecularly bridged complex, $[(PPh_3)_4Pt_2(\mu\text{-}S)(\mu\text{-}S\text{-}p\text{-}CH_2C_6H_4CH_2S)(\mu\text{-}S)Pt_2(PPh_3)_4](PF_6)_2$ (**6b**). It is expected that the dihedral angles in each of the $\{Pt_2(\mu\text{-}S)_2\}$ moieties would be the same within the same molecule, and that is observed in the case of complex

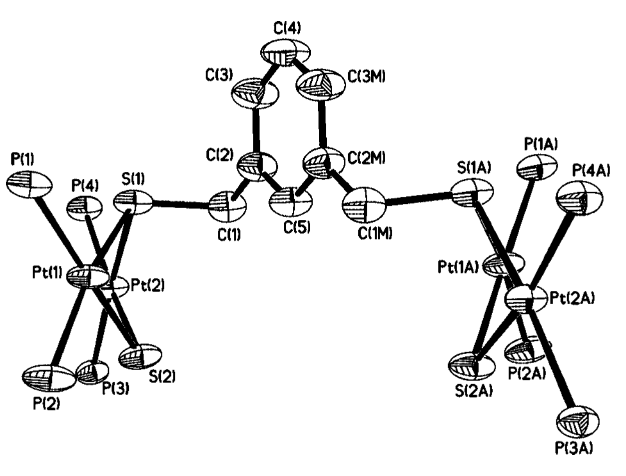


Figure 1. A 50% thermal ellipsoid representation of the cation of $[(PPh_3)_4Pt_2(\mu\text{-}S)(\mu\text{-}S\text{-}m\text{-}CH_2C_6H_4CH_2S)(\mu\text{-}S)Pt_2(PPh_3)_4](PF_6)_2$ (**6a**). The phenyl rings of PPh_3 and hydrogen atoms are omitted for clarity.

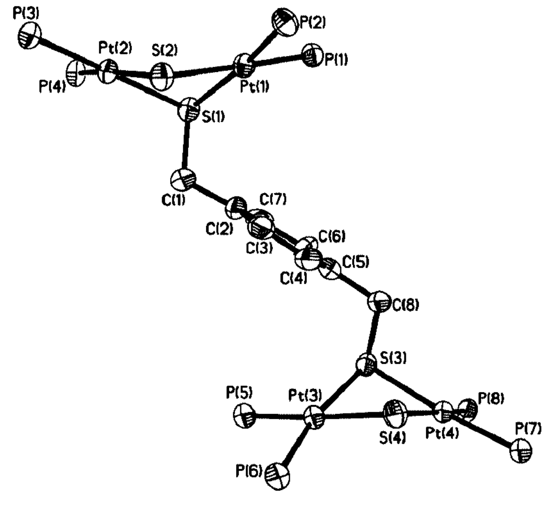
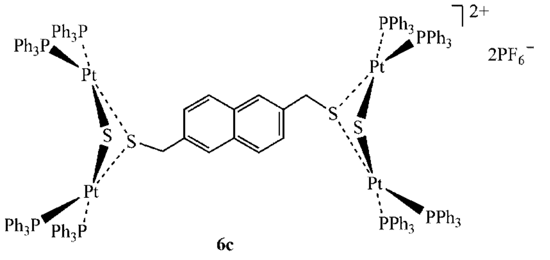


Figure 2. A 50% thermal ellipsoid representation of the cation of $[(PPh_3)_4Pt_2(\mu\text{-}S)(\mu\text{-}S\text{-}p\text{-}CH_2C_6H_4CH_2S)(\mu\text{-}S)Pt_2(PPh_3)_4](PF_6)_2$ (**6b**). The phenyl rings of PPh_3 and hydrogen atoms are omitted for clarity.

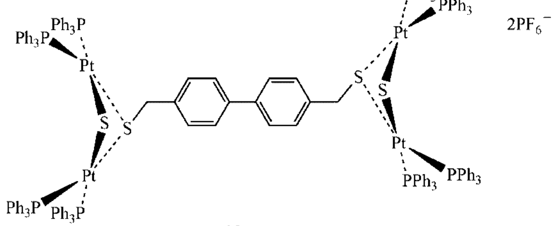
6a where both $\{Pt_2(\mu\text{-}S)_2\}$ rings are hinged with the dihedral angle of 132°. Interestingly, each of the $\{Pt_2(\mu\text{-}S)_2\}$ rings in complex **6b** are hinged to a slightly different extent – the moiety with the Pt(1)–S(1)–S(2)–Pt(2) core has a dihedral angle of 133° while the one with the Pt(3)–S(3)–S(4)–Pt(4) core has a dihedral angle of 138°. The slight difference in the dihedral angles is a result of having two noncrystallographically related $\{Pt_2(\mu\text{-}S)_2\}$ rings in **6b**. In contrast, the asymmetric unit for complex **6a** is half a molecule, so the two $\{Pt_2(\mu\text{-}S)_2\}$groups are symmetry-related and must therefore have exactly the same dihedral angle.

The $^{31}P\{^1H\}$ NMR characteristics of the two complexes are similar. The two sets of phosphanes have very similar chemical shifts and are differentiated by the different Pt-P couplings; a multiplet due to the overlap of the two phosphane signals at δ_P 23.2–23.8 ppm ($^1J_{Pt,P(1)}$ = 3292, $^1J_{Pt,P(2)}$ = 2627 Hz) and δ_P 23.3–23.6 ppm ($^1J_{Pt,P(1)}$ = 3293, $^1J_{Pt,P(2)}$ = 2591 Hz) for **6a** and **6b**, respectively. The thiolate ligand, $SCH_2C_6H_4CH_2S$ has a lower *trans* influence than a sulfido ligand, so the Pt–P bond *trans* to thiolate is shorter and has a larger $J_{Pt,P}$ coupling.

Isolation of complexes **6a** and **6b** suggested that we could conveniently control the directionality of the aggregate alignment by adjusting the geometry effect of the spacer. This synthetic methodology opens up the opportunity for the preparation of platinum sulfide aggregates that can be linked by a variety of organic alkyl or aryl chains. Application of this technique to two other dihalides: 2,6-bis(bromomethyl)naphthalene and 4,4′-bis(chloromethyl)-1,1′-biphenyl results in similar Pt_4 aggregates; $[(PPh_3)_4Pt_2(\mu\text{-}S)(\mu\text{-}SCH_2C_{10}H_6CH_2S)(\mu\text{-}S)Pt_2(PPh_3)_4](PF_6)_2$ (**6c**) and $[(PPh_3)_4Pt_2(\mu\text{-}S)(\mu\text{-}SCH_2(C_6H_4)_2CH_2S)(\mu\text{-}S)Pt_2(PPh_3)_4](PF_6)_2$ (**6d**). $^{31}P\{^1H\}$ NMR confirms successful syntheses and displays a multiplet from the overlap of the two phosphane signals at δ_P 23.5–24.2 ppm ($^1J_{Pt,P(1)}$ = 3289, $^1J_{Pt,P(2)}$ = 2630 Hz) and δ_P 23.7–24.4 ppm ($^1J_{Pt,P(1)}$ = 3282, $^1J_{Pt,P(2)}$ = 2628 Hz) for **6c** and **6d**, respectively.



6c



6d

From Linker to a Bridge

An unexpected overhead-bridged dialkylated complex, $[Pt_2(\mu\text{-}S\text{-}o\text{-}CH_2C_6H_4\text{-}C_6H_4CH_2S)(PPh_3)_4](PF_6)_2$ (**7**) with a long (C_6) spacer between the alkylating groups has been successfully isolated using 2,2′-bis(bromomethyl)-1,1′-biphenyl as the difunctional alkylating agent. Prior to this, dihalides with a spacer more than four C–C bonds long impeded dialkylation significantly and resulted predominantly in monoalkylation (**6**).[2] Despite the long C_6 distance that would normally result in monoalkylation of **1a**, dialkylation occurs rapidly and is completed within 2 h. Any signal corresponding to monoalkylation is absent in the ESI mass spectrum of the reaction monitored in MeOH. The bridging nature of the dithiolate ($\mu\text{-}S\text{-}o\text{-}CH_2C_6H_4\text{-}C_6H_4CH_2S$) ligand as opposed to the expected monothiolate ($\mu\text{-}SCH_2C_6H_4\text{-}C_6H_4CH_2Br$) ligand is confirmed by the single-crystal X-ray diffraction analyses of

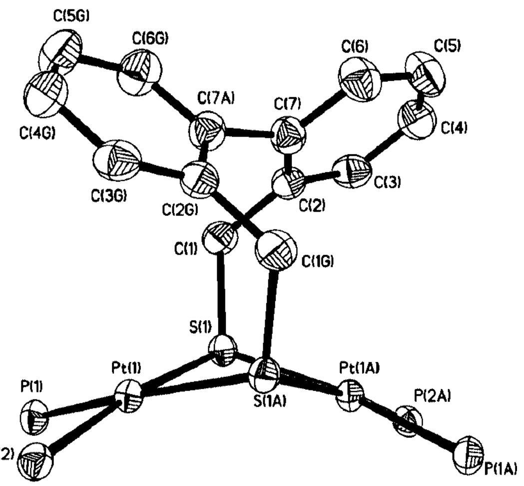


Figure 3. A 50% thermal ellipsoid representation of the cation of $[Pt_2(\mu\text{-}S\text{-}o\text{-}CH_2C_6H_4\text{-}C_6H_4CH_2S)(PPh_3)_4](PF_6)_2$ (**7**). The phenyl rings of PPh_3 and hydrogen atoms are omitted for clarity.

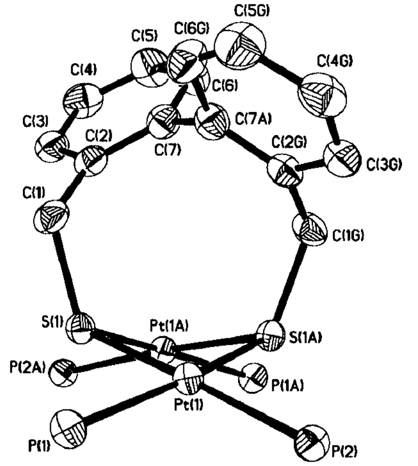


Figure 4. View along the Pt(1)–Pt(1A) axis. A 50% thermal ellipsoid representation of the cation of $[Pt_2(\mu\text{-}S\text{-}o\text{-}CH_2C_6H_4\text{-}C_6H_4CH_2S)(PPh_3)_4](PF_6)_2$ (**7**). The phenyl rings of PPh_3 and hydrogen atoms are omitted for clarity.

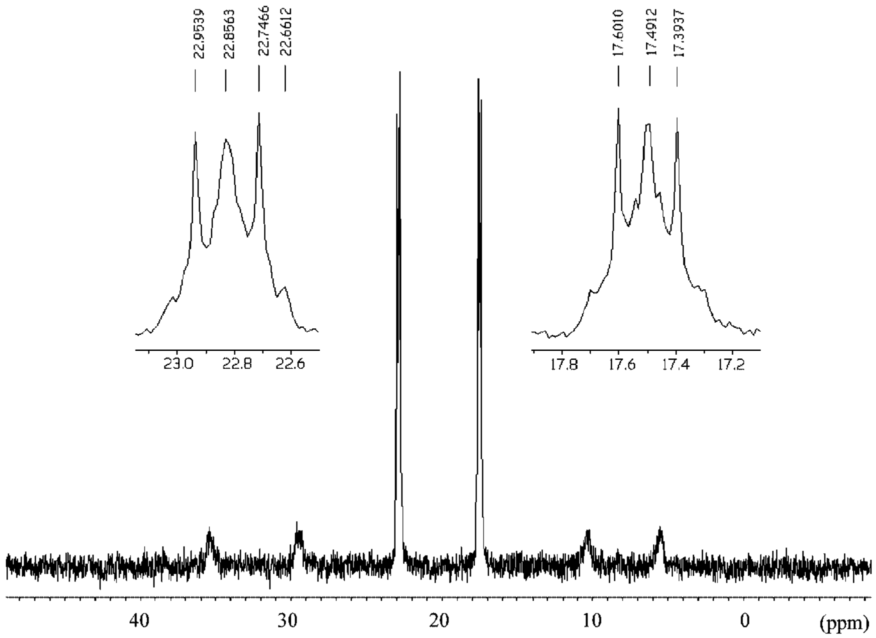


Figure 5. $^{31}P\{^1H\}$ NMR spectrum of $[Pt_2(\mu\text{-}S\text{-}o\text{-}CH_2C_6H_4\text{-}C_6H_4CH_2S)(PPh_3)_4](PF_6)_2$ (**7**) in $[D_6]$DMSO.

complex **7** in Figures 3 and 4. When viewed along the S(1A)–S(1) axis (Figure 3), the two phenyl groups which are joined at the C(7A)–C(7) bond are pointing away from one another as they are bent about the $\{S_2C_2\}$ plane. The conformationally flexible C(7A)–C(7) bond appears almost perpendicular to the S(1)–C(1) and S(1A)–C(1G) bonds, which are in a *syn-exo* conformation, pointing away from the sterically bulky triphenylphosphanes. These conformational features allow the flexible C_6 chain to fit into the S···S bridge. When viewed along the Pt(1)–Pt(1A) axis (Figure 4), complex **7** shows a unique and unusual bicyclic nine-membered metallosulfur-carbon ring. Its structure has a bent $\{Pt_2(\mu\text{-}S)_2\}$ ring and a dihedral angle of 147°. The dissymmetry created by the bridge generated two sets of inequivalent phosphanes that give two discrete resonances at $\delta_P = 17.5$ (m, $^1J_{Pt,P} = 2923$, $^2J_{P,P} = 13$ Hz) and 22.9 ppm (m, $^1J_{Pt,P} = 3043$, $^2J_{P,P} = 13$ Hz) in its $^{31}P\{^1H\}$ NMR spectrum (Figure 5). Such NMR characteristics have been observed in the xylyl dithiolato-bridged complex, $[Pt_2(\mu\text{-}S\text{-}o\text{-}CH_2C_6H_4CH_2S)(PPh_3)_4](PF_6)_2$.[2a]

Conclusions

The isolation of tetranuclear platinum sulfide aggregates that can be linked by a variety of organic chains marks an extension to the scope of alkylation chemistry in the $\{Pt_2(\mu\text{-}S)_2\}$ systems. The choice of appropriate alkylating agents coupled with the excellent dehalogenation capability of the sulfide centers in $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ (**1a**) makes the preparation possible. In principle, all dibromo-organic compounds with an extended skeleton can function as an overhead bridge across the sulfide centers. If it is stereochemically too restrictive to serve as an intramolecular bridge within the Pt_2 core, it could be switched to the intermolecular mode and interlink two Pt_2 cores, giving $[(PPh_3)_4Pt_2(\mu\text{-}S)(\mu\text{-}SRS)(\mu\text{-}S)Pt_2(PPh_3)_4](PF_6)_2$ (**6**). Our next synthetic target is to activate the unsubstituted sulfide atoms of the aggregate. The strategies used could be adapted from the method we recently developed for the alkylation of the $[Pt_2(S)(SR)]^+$ core to $[Pt_2(SR)_2]^{2+}$.[13] The success of such a synthesis would pave the way to stepwise alignment of Pt aggregates $\cdots Pt_2 \cdots Pt_2 \cdots Pt_2 \cdots$ with sole dithiolate spacers.

Experimental Section

Materials and Methods

All manipulations were carried out at room temperature under an atmosphere of dinitrogen. Solvents used were generally of analytical grade (Tedia) and were dried and deoxygenated before being used. The complex $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ (**1a**) was synthesized by metathesis of *cis*-$[PtCl_2(PPh_3)_2]$ with $Na_2S{\cdot}9H_2O$ (Riedel-de Haën) in benzene. Complex **1a** was obtained in 86% yield {ESI-MS (80% MeOH/20% H_2O): *m*/*z* 1504 (100%) $[M + H]^+$}. The following chemicals were used as supplied from Aldrich: α,α′-dibromo-*m*/*p*-xylenes, 2,2′-bis(bromomethyl)-1,1′-biphenyl, 2,6-bis(bromomethyl)naphthalene, 4,4′-bis(chloromethyl)-1,1′-biphenyl, and ammonium hexafluorophosphate (NH_4PF_6).

Electrospray mass spectra were obtained in the positive-ion mode with a Finnigan/MAT LCQ mass spectrometer coupled with a TSP4000 HPLC system and the crystal 310 CE system. The mobile phase was 80% methanol/20% H_2O (flow rate: 0.4 mL min^{-1}). The capillary temperature was 150 °C. Peaks were assigned from the *m*/*z* values and from the isotope-distribution patterns. The charge(s) on the species could be confirmed by comparing the experimental and calculated isotope-distribution patterns. Elemental analyses were performed with a Perkin–Elmer PE 2400 CHNS elemental analyzer. ^1H NMR spectra were recorded at 25 °C with a Bruker ACF 300 spectrometer (at 300 and 75.47 MHz, respectively) with Me_4Si

as internal standard. The ^{31}P NMR spectra were recorded at 25 °C and 121.50 MHz with 85% H_3PO_4 as external reference. The ^{31}P NMR spectra of **6a**–**d** and **7** obtained are generally higher-order spectra which were treated with first-order approximations. Detailed analysis of similar six-spin systems ($4 \times {}^{31}P + 2 \times {}^{195}Pt$) has been reported.[4d]

Syntheses

$[(PPh_3)_4Pt_2(\mu\text{-}S)(\mu\text{-}S\text{-}m\text{-}CH_2C_6H_4CH_2S)(\mu\text{-}S)Pt_2(PPh_3)_4](PF_6)_2$ (6a): Compound **1a** (29.6 mg, 0.020 mmol) and a stoichiometric amount of α,α′-dibromo-*m*-xylene (5.0 mg, 0.019 mmol) in methanol (15 mL) was stirred for 2 h, followed by the addition of a slight excess of **1a** (36.2 mg, 0.024 mmol, 1.2 equiv.). The yellow suspension was stirred for a further 2.5 h and filtered to remove any unreacted **1a**. Excess NH_4PF_6 (20.0 mg, 0.123 mmol) was added to give a yellow suspension. Deionized water (40 mL) was then used to complete the precipitation. A yellow powder of **6a** (56.2 mg, 76%) was obtained by washing with deionized water (100 mL) and diethyl ether (100 mL) using vacuum suction filtration. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): $\delta_P = 23.6$ ppm (m, $^1J_{Pt,P(1)} = 3292$, $^1J_{Pt,P(2)} = 2627$ Hz). ^1H NMR (CD_2Cl_2): $\delta_H = 3.84$ (br. s, 4 H, 2 SCH_2), 5.82–5.85 (d, $J = 8.0$ Hz, 2 H, $CH_2C_6H_4CH_2$), 6.49 (b t, $J = 7.7$ Hz, 1 H, $CH_2C_6H_4CH_2$), 6.76 (s, 1 H, $CH_2C_6H_4CH_2$), 7.03–7.43 ppm (m, 120 H, 24 C_6H_5). ESI-MS ($MeOH/H_2O$): *m/z* (%) = 1555 (100) $[M]^{2+}$. $C_{152}H_{128}F_{12}P_{10}Pt_4S_4$ (3400.94): calcd. C 53.68, H 3.79, S 3.77; found C 53.65, H 3.76, S 3.98. Yellow crystals of $[(PPh_3)_4Pt_2(\mu\text{-}S)(\mu\text{-}S\text{-}m\text{-}CH_2C_6H_4CH_2S)(\mu\text{-}S)Pt_2(PPh_3)_4](PF_6)_2$ suitable for X-ray crystallographic analysis were obtained from dichloromethane/benzene (1:1).

$[(PPh_3)_4Pt_2(\mu\text{-}S)(\mu\text{-}S\text{-}p\text{-}CH_2C_6H_4CH_2S)(\mu\text{-}S)Pt_2(PPh_3)_4](PF_6)_2$ (6b): A procedure similar to that used above was employed. A stoichiometric amount of α,α′-dibromo-*p*-xylene (6.8 mg, 0.026 mmol) was introduced into an orange suspension of compound **1a** (40.0 mg, 0.027 mmol) in methanol (20 mL). The mixture changed from an orange suspension to a yellow solution in 2 h. Another 40.5 mg (0.027 mmol) of **1a** was added, resulting in a yellow suspension. The mixture was stirred for a further 2 h, and the resultant suspension was filtered, followed by the addition of excess NH_4PF_6 (20.0 mg, 0.123 mmol). Deionized water (50 mL) was used to complete the precipitation. A yellow powder of **6b** (64.2 mg, 71%) was obtained by washing with deionized water (100 mL) and diethyl ether (100 mL) using vacuum suction filtration. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): $\delta_P = 23.5$ ppm (br. s, $^1J_{Pt,P(1)} = 3293$, $^1J_{Pt,P(2)} = 2591$, $^2J_{P(1)-P(2)} = 18$ Hz). ^1H NMR (CD_2Cl_2): $\delta_H = 3.39$ (br. s, 4 H, 2 SCH_2), 6.12 (s, 4 H, $CH_2C_6H_4CH_2$), 6.99–7.43 ppm (m, 120 H, 24 C_6H_5). ESI-MS ($MeOH/H_2O$): *m/z* (%) = 1555 (100) $[M]^{2+}$. $C_{152}H_{128}F_{12}P_{10}Pt_4S_4$ (3400.94): calcd. C 53.68, H 3.79, S 3.77; found C 53.43, H 3.75, S 3.47. Yellow crystals of $[(PPh_3)_4Pt_2(\mu\text{-}S)(\mu\text{-}S\text{-}p\text{-}CH_2C_6H_4CH_2S)(\mu\text{-}S)Pt_2(PPh_3)_4](PF_6)_2$ suitable for X-ray crystallographic analysis were obtained from dichloromethane/ethanol (1:1).

$[(PPh_3)_4Pt_2(\mu\text{-}S)(\mu\text{-}SCH_2C_{10}H_6CH_2S)(\mu\text{-}S)Pt_2(PPh_3)_4](PF_6)_2$ (6c): Stoichiometric amount of 2,6-bis(bromomethyl)naphthalene (8.0 mg, 0.026 mmol) was introduced into an orange suspension of compound **1a** (39.1 mg, 0.026 mmol) in methanol (22 mL). The mixture changed from an orange suspension to a yellow solution in 2 h. Another 40.4 mg (0.027 mmol) of **1a** was added, resulting in a yellow solution in 2 h, and the mixture was left to stir overnight. The resultant yellow solution which was slightly cloudy was filtered, followed by the addition of excess NH_4PF_6 (20.0 mg, 0.123 mmol). Deionized water (50 mL) was used to complete the precipitation. A yellow powder of **6c** (48.5 mg, 53%) was obtained by washing with deionized water (100 mL) and diethyl ether (100 mL) using vacuum suction filtration. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): $\delta_P = 23.5$–24.2 ppm (m, $^1J_{Pt,P(1)} = 3289$, $^1J_{Pt,P(2)} = 2630$ Hz). ^1H NMR (CD_2Cl_2): $\delta_H = 3.82$ (br. s, 4 H, 2 SCH_2), 6.83–7.45 (m, 6 H, $C_{10}H_6$), 6.83–7.45 ppm (m, 120 H, 24 C_6H_5). ESI-MS ($MeOH/H_2O$): *m/z* (%) = 1580 (100) $[M]^{2+}$. $C_{156}H_{130}F_{12}P_{10}Pt_4S_4$ (3451.0): calcd. C 54.29, H 3.80, S 3.72; found C 54.44, H 3.72, S 3.54.

$[(PPh_3)_4Pt_2(\mu\text{-}S)(\mu\text{-}SCH_2(C_6H_4)_2CH_2S)(\mu\text{-}S)Pt_2(PPh_3)_4](PF_6)_2$ (6d): A stoichiometric amount of 4,4′-bis(chloromethyl)-1,1′-biphenyl (4.8 mg, 0.019 mmol) was introduced into an orange sus-

Table 1. Selected bond lengths [Å] and angles [°] for complexes **6a**, **6b**, and **7**.

$[(PPh_3)_4Pt_2(\mu\text{-}S)(\mu\text{-}S\text{-}m\text{-}CH_2C_6H_4CH_2S)(\mu\text{-}S)Pt_2(PPh_3)_4](PF_6)_2$ (**6a**)			
Pt(1)–P(1)	2.289(15)	Pt(2)–S(2)	2.322(13)
Pt(1)–P(2)	2.293(15)	Pt(2A)–S(1A)	2.373(13)
Pt(2A)–P(4A)	2.308(14)	Pt(2A)–S(2A)	2.322(13)
Pt(2A)–P(3A)	2.273(14)	Pt(1A)–S(1A)	2.345(14)
Pt(1)–S(1)	2.345(14)	Pt(1A)–S(2A)	2.334(15)
Pt(1)–S(2)	2.334(15)	S(1)–C(1)	1.842(6)
Pt(2)–S(1)	2.373(13)		
Pt(1)–S(1)–Pt(2)	87.30(5)	P(2)–Pt(1)–S(1)	166.66(6)
Pt(1)–S(2)–Pt(2)	88.77(5)	P(2)–Pt(1)–S(2)	174.19(5)
Pt(2A)–S(1A)–Pt(1A)	87.30(5)	P(4A)–Pt(2A)–S(1A)	87.49(5)
Pt(2A)–S(2A)–Pt(1A)	88.77(5)	P(4A)–Pt(2A)–S(2A)	168.06(5)
S(1)–Pt(1)–S(2)	81.06(5)	P(3A)–Pt(2A)–S(1A)	172.31(5)
S(1A)–Pt(2A)–S(2A)	80.70(5)	P(3A)–Pt(2A)–S(2A)	91.65(5)
P(1)–Pt(1)–P(2)	99.04(6)	C(1)–S(1)–Pt(1)	105.54(18)
P(4A)–Pt(2A)–P(3A)	100.13(5)	C(1)–S(1)–Pt(2)	102.50(18)
P(1)–Pt(1)–S(1)	94.16(5)	θ[a]	132
P(1)–Pt(1)–S(2)	174.19(5)		
$[(PPh_3)_4Pt_2(\mu\text{-}S)(\mu\text{-}S\text{-}p\text{-}CH_2C_6H_4CH_2S)(\mu\text{-}S)Pt_2(PPh_3)_4](PF_6)_2$ (**6b**)			
Pt(1)–P(1)	2.296(3)	Pt(2)–S(2)	2.327(2)
Pt(1)–P(2)	2.287(3)	Pt(3)–S(3)	2.355(2)
Pt(3)–P(5)	2.296(3)	Pt(3)–S(4)	2.337(2)
Pt(3)–P(6)	2.291(3)	Pt(4)–S(3)	2.370(2)
Pt(1)–S(1)	2.341(2)	Pt(4)–S(4)	2.329(2)
Pt(1)–S(2)	2.340(2)	S(1)–C(1)	1.850(10)
Pt(2)–S(1)	2.377(2)	S(3)–C(8)	1.845(9)
Pt(1)–S(1)–Pt(2)	90.04(8)	P(2)–Pt(1)–S(2)	84.57(9)
Pt(1)–S(2)–Pt(2)	91.32(8)	P(5)–Pt(3)–S(3)	94.17(9)
Pt(3)–S(3)–Pt(4)	87.93(8)	P(5)–Pt(3)–S(4)	175.12(9)
Pt(3)–S(4)–Pt(4)	89.35(8)	P(6)–Pt(3)–S(3)	166.68(9)
S(1)–Pt(1)–S(2)	81.19(8)	P(6)–Pt(3)–S(4)	85.89(9)
S(3)–Pt(3)–S(4)	80.95(9)	C(1)–S(1)–Pt(1)	104.8(4)
P(1)–Pt(1)–P(2)	100.05(9)	C(1)–S(1)–Pt(2)	99.8(3)
P(5)–Pt(3)–P(6)	98.99(9)	C(8)–S(3)–Pt(3)	106.3(3)
P(1)–Pt(1)–S(1)	94.25(9)	C(8)–S(3)–Pt(4)	98.1(3)
P(1)–Pt(1)–S(2)	174.63(9)	θ [Pt(1)–S(1)–S(2)–Pt(2)]	133
P(2)–Pt(1)–S(1)	165.66(9)	θ [Pt(3)–S(3)–S(4)–Pt(4)]	138
$[Pt_2(\mu\text{-}S\text{-}o\text{-}CH_2C_6H_4\text{-}C_6H_4CH_2S)(PPh_3)_4](PF_6)_2$ (**7**)			
Pt(1)–P(1)	2.304(8)	Pt(1)–S(1A)	2.357(7)
Pt(1)–P(2)	2.306(8)	Pt(1A)–S(1)	2.357(7)
Pt(1)–S(1)	2.377(7)	S(1)–C(1)	1.856(3)
Pt(1)–S(1)–Pt(1A)	92.67(3)	P(2)–Pt(1)–S(1)	173.22(3)
S(1)–Pt(1)–S(1A)	81.92(3)	P(2)–Pt(1)–S(1A)	93.71(3)
P(1)–Pt(1)–P(2)	97.86(3)	C(1)–S(1)–Pt(1)	113.90(12)
P(1)–Pt(1)–S(1)	85.97(3)	C(1)–S(1)–Pt(1A)	113.44(11)
P(1)–Pt(1)–S(1A)	166.77(3)	θ[a]	147

[a] θ = Dihedral angle between the two PtS_2 planes.

pension of compound **1a** (30.5 mg, 0.020 mmol) in methanol (15 mL). The mixture was stirred for 3.5 h followed by the addition of another 30.6 mg (0.020 mmol) of **1a**. The resultant yellow suspension was left to stir overnight. The suspension was then filtered, followed by the addition of excess NH_4PF_6 (20.0 mg, 0.123 mmol). Deionized water (30 mL) was used to complete the precipitation. A yellow powder of **6d** (45.8 mg, 66%) was obtained by washing with deionized water (100 mL) and diethyl ether (100 mL) using vacuum suction filtration. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ_P = 23.7–24.4 ppm (m, $^1J_{Pt,P(1)}$ = 3282, $^1J_{Pt,P(2)}$ = 2628 Hz). ^1H NMR (CD_2Cl_2): δ_H = 3.73 (br. s, 4 H, 2 SCH_2), 6.65–7.45 (m, 8 H, 2 C_6H_4), 6.65–7.45 ppm (m, 120 H, 24 C_6H_5). ESI-MS (MeOH/H_2O): *m*/*z* (%) = 1592 (100) $[M]^{2+}$. $C_{158}H_{132}F_{12}P_{10}Pt_4S_4$ (3477.03): calcd. C 54.58, H 3.83, S 3.69; found C 54.57, H 3.36, S 3.40.

$[Pt_2(\mu\text{-}S\text{-}o\text{-}CH_2C_6H_4\text{-}C_6H_4CH_2S)(PPh_3)_4](PF_6)_2$ (7): 2,2′-Bis(bromomethyl)-1,1′-biphenyl (32.3 mg, 0.095 mmol, 3 equiv.) and compound **1a** (48.7 mg, 0.032 mmol) in methanol (20 mL) gave a pale yellow solution in 15 min and was left to stir for 2 h. Excess NH_4PF_6 (20.0 mg, 0.123 mmol) was then added, resulting in an off-white suspension. Deionized water (40 mL) was used to complete the precipitation. A cream-colored powder of **7** (58.7 mg, 92%) was obtained by washing with deionized water (100 mL) and diethyl ether (100 mL) using vacuum suction filtration. $^{31}P\{^1H\}$ NMR ($[D_6]$DMSO): δ_P = 17.5 (m, $^1J_{Pt,P}$ = 2923, $^2J_{P,P}$ = 13 Hz), 22.9 ppm (m, $^1J_{Pt,P}$ = 3043, $^2J_{P,P}$ = 13 Hz). ^1H NMR ($[D_6]$DMSO): δ_H = 3.32 (s, 4 H, 2 SCH_2), 6.85–6.88 (d, *J* = 7.6 Hz, 2 H, C_6H_4-C_6H_4), 6.76–6.78 (d, *J* = 7.4 Hz, 2 H, C_6H_4-C_6H_4), 7.86 (t, *J* = 7.4 Hz, 2 H, C_6H_4-C_6H_4), 7.56 (t, *J* = 6.8 Hz, 2 H, C_6H_4-C_6H_4), 6.99 (br. s, 12 H, 12 C_6H_5), 7.15 (br. s, 24 H, 12 C_6H_5), 7.43 ppm (br. s, 24 H, 12 C_6H_5). ESI-MS (MeOH/H_2O): *m*/*z* (%) = 842 (100) $[M]^{2+}$, 1827 (10) $[[M]^{2+}[PF_6]^-]$. $C_{86}H_{74}F_{12}OP_6Pt_2S_2$ (1991.62): calcd. C 51.86, H 3.74, S 3.22; found C 51.85, H 3.49, S 3.59. Pale yellow crystals of $[Pt_2(\mu\text{-}S\text{-}o\text{-}CH_2C_6H_4\text{-}C_6H_4CH_2S)(PPh_3)_4](PF_6)_2$ suitable for X-ray crystallographic analysis were obtained from dichloromethane/ethanol (1:1).

X-ray Crystal Structure Determination and Refinement

Selected bond lengths and angles for complexes **6a**, **6b**, and **7** are given in Table 1. All measurements were made with a Bruker AXS SMART APEX diffractometer equipped with a CCD area detector by using Mo-K_α radiation (λ = 0.71073 Å). The software SMART[14] was used for the collection of data frames, for indexing reflections, and to determine lattice parameters; SAINT[14] was used for the integration of the intensity of the reflections and for scaling; SADABS[15] was used for empirical absorption correction; and SHELXTL[16] was used for space group and structure determination, refinements, graphics, and structure reporting. The structure was refined by full-matrix least-squares on F^2 with anisotropic thermal parameters for non-hydrogen atoms. A summary of crystallographic parameters for the data collections and refinements is given in Table 2.

For **6a**, the asymmetrical unit contains half a titled cation, two halves of the PF_6^- counteranion, one benzene, and one and a half dichloromethane molecules. The whole of the molecule can be generated by a twofold symmetry. One of the half PF_6^- counteranions is at a special position and the other is disordered. The disordered PF_6^- counteranion is refined only with isotropic thermal parameters. The half dichloromethane molecule is also disordered. For **6b**, the asymmetric unit contains one titled cation, two counter PF_6^- counteranions, seven dichloromethane solvent molecules, and one disordered water molecule. One of the dichloromethane molecules is slightly disordered. The phenyl rings are refined as fixed hexagon rings with anisotropic thermal parameters. For **7**, the asymmetrical unit contains one half of the titled cation, two halves of PF_6^-, and two disordered dichloromethane molecules.

CCDC-646073 (for **6a**), -646074 (for **6b**), and -646075 (for **7**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 2. Crystallographic data for complexes **6a**, **6b**, and **7**.

Complex	**6a**·$3CH_2Cl_2\cdot 2C_6H_6$	**6b**·$7CH_2Cl_2\cdot H_2O$	**7**·$4CH_2Cl_2$
Formula	$C_{167}H_{146}Cl_6F_{12}P_{10}Pt_4S_4$	$C_{159}H_{144}Cl_{14}F_{12}O\ P_{10}Pt_4S_4$	$C_{90}H_{80}Cl_8F_{12}\ P_6Pt_2S_2$
M	3811.84	4011.33	2313.26
Crystal system	monoclinic	triclinic	monoclinic
Space group	*P*2/*n*	$P\bar{1}$	*C*2/*c*
a [Å]	18.932(6)	19.279(5)	14.525(7)
b [Å]	18.241(6)	19.532(5)	24.413(12)
c [Å]	23.469(7)	22.936(6)	26.261(13)
α [°]	90	98.30(6)	90
β [°]	105.210(10)	93.838(7)	94.972(10)
γ [°]	90	103.42(6)	90
V [Å^3]	7820.7(4)	8267(4)	9277(8)
Z	2	2	4
$\rho_{calcd.}$ [g cm^{-3}]	1.619	1.611	1.656
μ [mm^{-1}]	3.890	3.810	3.460
Temperature [K]	223(2)	223(2)	223(2)
Reflections measured	54806	90694	32398
Independent reflections	17962	29107	10646
R_{int}	0.0583	0.0988	0.0356
Parameters	927	1416	567
R (*F*, $F^2 > 2\sigma$)	0.0466	0.0576	0.0290
R_w (F^2, all data)	0.1149	0.1479	0.0725
Goodness of fit F^2	0.993	1.009	1.033
Max., min. electron density [e Å^{-3}]	1.817, –1.345	1.518, –1.047	1.237, –1.028

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