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Combinative use of high-pressure, metal-templating and sulfur-nucleophilicity towards dithiacyclophane synthesis and its complex intermediates

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Abstract

Combined use of elevated pressure in the liquid phase (15 kbar), a metal template and the sulfur nucleophilicity of $[Pt_2(\mu\text{-}S)_2(P\text{–}P)_2]$ (P–P = diphosphine or 2 · monophosphine) facilitates the one-pot synthesis of 3,8-dibenzo-1,6-dithiacyclodecane. Under r.t.p., nucleophilic addition of $[Pt_2(\mu\text{-}S)_2(P\text{–}P)_2]$ [P–P = 2 · PPh_3; $Ph_2P(CH_2)_nPPh_2$, $n = 2$, 1,2-bis(diphenylphosphino)ethane (dppe), 3, 1, 3-bis(diphenylphosphino)propane (dppp)] with α-α′-dichloro-*o*-xylene would terminate as a dithiolato bridged cation viz. $[Pt_2(\mu\text{-}SCH_2C_6H_4CH_2S)(P\text{–}P)_2]^{2+}$. Under high pressure (15 kbar) at r.t., these stoichiometric reactions progress via a "catalytic-like" pathway to yield 3,8-dibenzo-1,6-dithiacyclodecane (up to 35%), and a series of mechanistically relevant intermediates and byproducts. The dithiolated intermediates $[Pt_2(\mu\text{-}SCH_2C_6H_4CH_2S)(P\text{–}P)_2]^{2+}$ for PPh_3 and dppp have been isolated as PF_6^- complexes and their crystal structure determined. The formation of 3,8-dibenzo-1,6-dithiacyclodecane demonstrates a convenient synthetic strategy over the multi-step synthesis of this macrocyclic dithioether.

Keywords: High-pressure; Platinum; Sulfide; Template; Nucleophilicity; Dithiacyclophane

1. Introduction

High-pressure in the liquid phase promotes organic reactions such as cycloadditions, carbonyl condensations and ionogenic reactions [1]. Its application in organometallic chemistry, and particularly catalytic processes, is much less developed [2] despite the synthetic utility of these reactions [3] and the potential for this technique to promote bond formation, overcome steric hindrance and inhibit decomposition at ambient temperatures. We herein report an example of a novel reaction of this type that does not proceed under conventional conditions.

The coordinating ability of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ (**1a**) towards metals [4] and non-metallic electrophiles [5] under ambient conditions have been demonstrated. Recently, we have advocated the concept for its use as a templating reagent for pharmacologically active macrocyclic sulfur [6], and proved that, at least in the selenide analogue, it is an achievable target [7]. For the methodology to be synthetically significant, we need to harness the functionalization of the μ_2-bridging sulfide, and, even more importantly, to activate the stable alkylated mono- or dication [5] towards further alkylation. This is a challenging problem because μ_3 to μ_4 transformation (or strictly, μ_2 thiolate to μ_2 thioether) in this type of cationic complex is kinetically inhibitive and thermodynamically unfavorable. There are also competing facile pathways that could supersede the desired reactions, such as phosphine dissociation, ligand replacement and monomerization through Pt–S bridge cleavage. The challenge is compounded by a stereogeometric problem in which the remaining sulfide lone pairs are

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not oriented towards further electrophilic attack from an organodihalide. As a methodological development, we also need to transform the synthesis from stoichiometric to catalytic for this to be synthetically applicable.

By using $[Pt_2(\mu\text{-}S)_2(P\text{–}P)_2]$ [P–P = $2PPh_3$ (**1a**), dppp (**1b**) and dppe (**1c**)] (dppp = 1,3-bis(diphenylphosphino)-propane; dppe = 1,2-bis(diphenylphosphino)ethane) as a mediator, we herein describe the successful use of pressure to facilitate and overcome the robust dithiolato intermediate and force the liberation of a dithiacyclophane. In doing so, we also trapped and characterized some key intermediates and byproducts that are mechanistically significant. These experiments highlight the value of high-pressure techniques in the use of organometalloid reagents towards difficult organic syntheses in pressure-sensitive reaction pathways.

2. Experimental

2.1. Materials and equipments

The high pressure equipment is a PSIKA Pressure Systems Limited Piston Cylinder High Pressure Reactor. α-α′-dichloro-*o*-xylene was obtained directly from Aldrich. Solvents used were generally analytical grade (J.T. Baker), dried and deoxygenated before use. Complex **1a** was synthesized via metathesis of *cis*-$[PtCl_2(PPh_3)_2]$ with $Na_2S \cdot 9H_2O$ in benzene. ESI–MS (80% MeOH, 20% H_2O): $m/z = 1503$ $[M + H]^+$. Complexes **1b** and **1c** were synthesized according to published methods [8,9]. ESI–MS (80% MeOH, 20% H_2O): $m/z = 1279.2$ $[M + H]^+$ for **1b**; $m/z = 1251.2$ $[M + H]^+$ and 1283.3 $[M + MeOH + H]^+$ for **1c**.

Elemental analyses were performed on a Perkin–Elmer PE 2400 CHNS Elemental Analyzer. The ^{31}P NMR spectra were recorded at 25 °C on a Bruker ACF 300 spectrometer at 121.50 MHz with 85% H_3PO_4 as external reference. $CDCl_3$ was used as the solvent. Electrospray mass spectra were obtained in positive-ion mode with a Finnigan/MAT LCQ mass spectrometer coupled with TSP4000 HPLC system and the crystal 310 CE system. The mobile phase was 80% methanol/20% H_2O pumped at a flow-rate of 0.4 ml/min. The capillary temperature was 150 °C. Peaks were assigned from the *m*/*z* values and from the isotope distribution patterns.

2.2. Method

Approximately 10 mol excess of α-α′-dichloro-*o*-xylene were dissolved in methanolic suspension of **1a**–**c**. Upon solubilization, the reaction mixture were transferred and placed inside a Teflon reaction vessel, which was then filled with a mixture of castor oil/methanol (80%:20%). The reaction vessel was placed in a PSIKA Pressure Systems Limited Piston Cylinder High Pressure Reactor and the reaction were carried out at 15 kbar, 25°; 15 kbar, 60 °C and 10 kbar, 25° for a specific duration as stated in the discussion. Purification by chromatography (90% CH_2Cl_2/10% methanol) yielded complexes as reported above.

2.3. Isolation of intermediates

2.3.1. $[Pt_2(\mu\text{-}SCH_2C_6H_4CH_2S)(PPh_3)_4][PF_6]_2$ (**2a**)

Compound **2a** was prepared by adding excess NH_4PF_6 (20.0 mg, 0.122 mmol) to the second chromatographic fraction (eluent for column chromatography: dichloromethane/methanol = 9:1) of the crude mixture in the reaction of **1a** (31.6 mg, 0.0210 mmol) with 10-fold excess α-α′-dichloro-*o*-xylene (69.8 mg, 0.3988 mmol) in 20.0 ml methanol under 15 kbar and 25 °C. The solution was stirred for 1 h, after which deionized water was added to induce precipitation. The pale yellow precipitate (19.5 mg, 58%) obtained using vacuum suction filtration was washed with 100 ml of deionized water and 100 ml of Et_2O. Anal. Calc. for $C_{80}H_{68}F_{12}S_2P_6Pt_2$: C, 47.1; H, 3.5; S, 3.4. Found: C, 47.4; H, 3.4; S, 2.8%. $^{31}P\{^1H\}$ NMR ($CDCl_3$): triplet of doublets, δ_P 19.8 ($^1J_{Pt\text{–}P(1)} = 2960$ Hz) and δ_P 17.7 ($^1J_{Pt\text{–}P(2)} = 3058$ Hz). Two sets of phosphine signals due to the unsymmetrical disposition of the xylene moiety. ESI–MS (MeOH–H_2O): *m*/*z* 804.0 $[M]^{2+}$. Pale yellow crystals of $[Pt_2(\mu\text{-}SCH_2C_6H_4CH_2S)(PPh_3)_4][PF_6]_2$ suitable for X-ray analysis were obtained from a mixture of CH_2Cl_2/acetone/hexane.

2.3.2. $[Pt_2(\mu\text{-}SCH_2C_6H_4CH_2S)(DPPP)_2][PF_6]_2$ (**2b**)

Compound **2b** was prepared similarly as **2a**, in the reaction of **1b** (80.9 mg, 0.0633 mmol) with excess α-α′-dichloro-*o*-xylene (14.7 mg, 0.0840 mmol) in 15.0 ml methanol under 15 kbar and 25 °C. Excess NH_4PF_6 (20.0 mg, 0.122 mmol) was added to the third chromatographic fraction (eluent for column chromatography: CH_2Cl_2/methanol = 9:1). The pale yellow precipitate (50.1 mg, 57%) obtained using vacuum suction filtration was washed with 100 ml of deionized water and 100 ml of Et_2O. Anal. Calc. for $C_{62}H_{60}F_{12}S_2P_6Pt_2$: C, 44.5; H, 3.6; S, 3.6. Found: C, 45.6; H, 3.6; S, 3.6%. $^{31}P\{^1H\}$ NMR ($CDCl_3$): triplet of doublets, δ_P −1.4 ($^1J_{Pt\text{–}P(1)} = 2747$ Hz) and δ_P −2.1 ($^1J_{Pt\text{–}P(2)} = 2766$ Hz)] ESI–MS (MeOH–H_2O): *m*/*z* 691.9 $[M]^{2+}$. Pale yellow crystals of $[Pt_2(\mu\text{-}SCH_2C_6H_4CH_2S)(PPh_3)_4][PF_6]_2$ suitable for X-ray analysis were obtained from a mixture of CH_2Cl_2/ethanol.

2.4. X-ray crystallographic characterization

All measurements are made at 223 K on a Bruker AXS SMART APEX diffractometer, equipped with a CCD area-detector using Mo Kα radiation ($\lambda = 0.71073$ Å). The software SMART [10] was used for collecting frames of data, indexing reflections, and the determination of lattice parameters, SAINT [10] for integration of intensity of reflections and scaling, SADABS [11] for empirical absorption correction, and SHELXTL [12] 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.

2.4.1. $2a \cdot CH_3C(O)CH_3 \cdot CH_2Cl_2 \cdot C_6H_{14}$

$C_{90}H_{90}Cl_2F_{12}OP_6Pt_2S_2$, $M = 2126.64$, triclinic, space group $P\bar{1}$, $a = 13.7291(13)$ Å, $b = 13.9315(19)$ Å, $c = 23.386(3)$ Å, $\alpha = 95.006(3)°$, $\beta = 91.790(3)°$, $\gamma = 98.969(3)°$, $V = 4396.9(10)$ Å^3, $T = 223(2)$ K, $Z = 2$, $\rho_{calc} = 1.606$ Mg cm^{-3}, λ(Mo Kα) = 0.71073 Å, 47,173 reflections measured, 15,490 unique ($R_{int} = 0.0339$) which were used in all calculations. The data were collected on a Bruker AXS SMART diffractometer and solved by direct methods in conjunction with standard difference Fourier techniques. Non-hydrogen atoms were refined anisotropically. Refinement converged to $R_F = 0.0405$, $wR(F^2) = 0.1173$ (all data).

2.4.2. $2b \cdot 4CH_2Cl_2$

$C_{66}H_{68}Cl_8F_{12}P_6Pt_2S_2$, $M = 2012.92$, triclinic, space group $P\bar{1}$, $a = 12.7963(5)$ Å, $b = 14.0826(6)$ Å, $c = 23.6753(10)$ Å, $\alpha = 75.3490(10)°$, $\beta = 76.4430(10)°$, $\gamma = 67.7630(10)°$, $V = 3774.6(3)$ Å^3, $T = 223(2)$ K, $Z = 2$, $\rho_{calc} = 1.771$ Mg cm^{-3}, λ(Mo Kα) = 0.71073 Å, 47,234 reflections measured, 13,283 unique ($R_{int} = 0.0609$) which were used in all calculations. Non-hydrogen atoms were refined anisotropically. Refinement converged to $R_F = 0.0551$, $wR(F^2) = 0.1385$ (all data).

3. Results and discussion

Application of pressure (15 kbar or $1.5 \cdot 10^9$ Pa) on the reaction of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ (**1a**) with excess α-α′-dichloro-*o*-xylene for a period of 5 days in MeOH resulted in a product mixture, whose identity was established by electrospray ionization (ESI) mass spectrometry. It comprises $[Pt_2(\mu\text{-}SCH_2C_6H_4CH_2S)(PPh_3)_4]^{2+}$ (**2a**) (*m*/*z* 804.5, major), $[Pt_2(\mu\text{-}SCH_2C_6H_4CH_2S)(PPh_3)_3Cl]^{+}$ (**3a**) (*m*/*z* 1379.7) and 3,8-dibenzo-1,6-dithiacyclodecane (**4**) (fragmentation peaks of **4**: *m*/*z* 189.1 and 104.9 for the 2-mercaptomethyl-phenyl-methanethiol and the *o*-xylene fractions, respectively). Compound **4** was extracted and purified by column chromatography as white solids in low yield (7%). Its ESI spectrum gave the solvated parent ion with expected protonation and Na^+ association (*m*/*z* 335.4 for $[\mathbf{4} + 2MeOH + H]^+$; 313.4 for $[\mathbf{4} + H_2O + Na]^+$; 295.4 for $[\mathbf{4} + Na]^+$) and peaks assignable to secondary fragmentation peaks. Its ^{1}H NMR spectrum is satisfactory (a singlet at 3.5 ppm for the methyl protons and two sets of multiplets at 7.2 and 7.5 ppm for the aromatic protons) and is in agreement with the literature value reported for the same compound synthesized using boric acid as a mediator [13]. Complex **2a**, which eluted together with **3a**, could be subsequently purified and isolated as PF_6^- salt, after metathesis with NH_4PF_6, as white powder (58%). Its X-ray crystal structure confirmed that alkylation has taken place at both sulfides, thus yielding a xylyl dithiolato bridging complex (see Table 1). The xylyl ring is disordered across the S···S axis (3.055 Å), which is the hinge of a folded structure with a dihedral angle of 139.7° between two $Pt^{II}S_2$ planes (Fig. 1). $^{31}P\{^1H\}$ NMR analysis of **2a** shows two discrete resonances [triplet of doublets, δ_P 19.8 ($J_{Pt-P(1)}$ 2960 Hz) and δ_P 17.7 ($J_{Pt-P(2)}$ 3058 Hz)] corresponding to the inequivalent sets of phosphines. Its selenato derivative has been isolated [14].

Change of monophosphine to a stable chelating diphosphine analogue viz. $[Pt_2(\mu\text{-}S)_2(dppp)_2]$ (**1b**) resulted in shorter duration (from 5 to 3 days) with a significantly improved yield of **4** (35%) under the same pressure (15 kbar). The higher nucleophilicity of sulfide when *trans* to diphosphine with a stronger donicity (especially dppp) [8] and the suppressed phosphine dissociation due to the chelate effect are possible factors that contributed to the positive outcome. The *ortho*-xylyl-bridged dithiolated intermediate, $[Pt_2(\mu\text{-}SCH_2C_6H_4CH_2S)(dppp)_2]^{2+}$ (**2b**) was isolated as PF_6^- salt at a moderate yield of 57%. Its presence accounts

Table 1
Selected bond lengths (Å) and angles (°) for compounds **2a** and **2b**

	2a	2b
Pt(1)–P(1)	2.288(16)	2.260(2)
Pt(1)–P(2)	2.299(15)	2.266(2)
Pt(1)–S(1)	2.367(14)	2.381(2)
Pt(1)–S(2)	2.366(15)	2.379(2)
Pt(2)–S(1)	2.362(15)	2.366(2)
S(2)–C(1)	1.863(7)	1.862(9)
Pt(1)–S(1)–Pt(2)	91.37(5)	86.60(7)
S(1)–Pt(1)–S(2)	80.40(5)	82.38(7)
P(1)–Pt(1)–P(2)	99.13(6)	95.54(9)
P(1)–Pt(1)–S(1)	92.72(5)	172.63(8)
P(1)–Pt(1)–S(2)	173.12(5)	90.43(8)
P(2)–Pt(1)–S(1)	166.28(5)	91.58(8)
P(2)–Pt(1)–S(2)	87.69(5)	173.66(8)
C(1)–S(2)–Pt(1)	104.9(2)	101.6(3)
C(1)–S(2)–Pt(2)	104.5(2)	110.7(3)

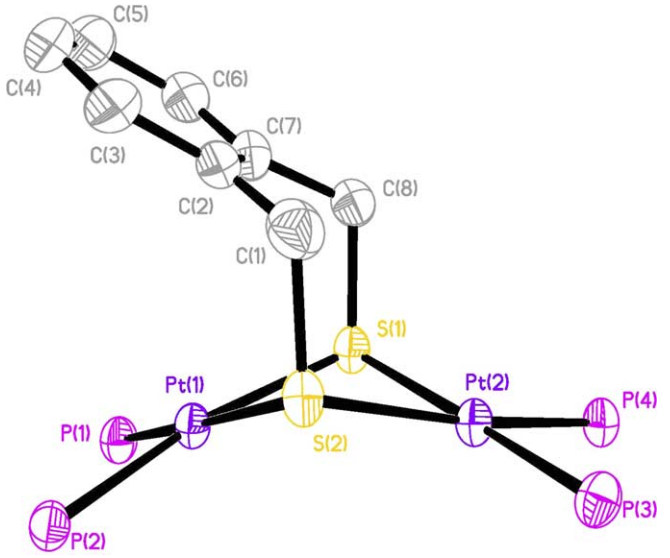


Fig. 1. Molecular structure of the cation of $[Pt_2(\mu\text{-}SCH_2C_6H_4CH_2S)_2(PPh_3)_4][PF_6]_2$ (**2a**). The phenyl rings of the terminal phosphines and protons are omitted for clarity.

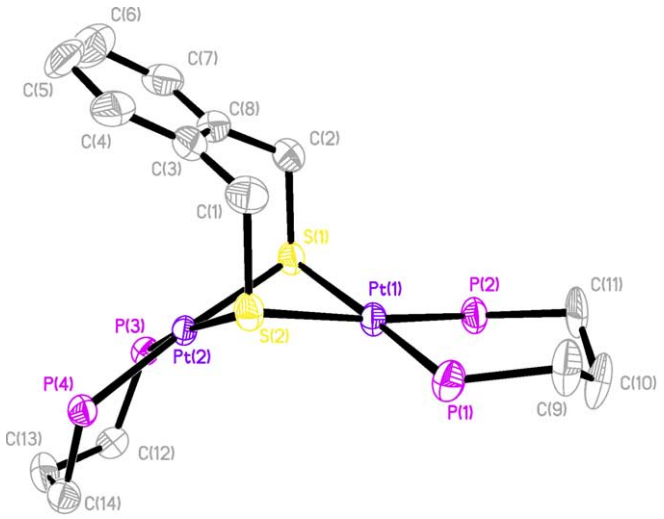
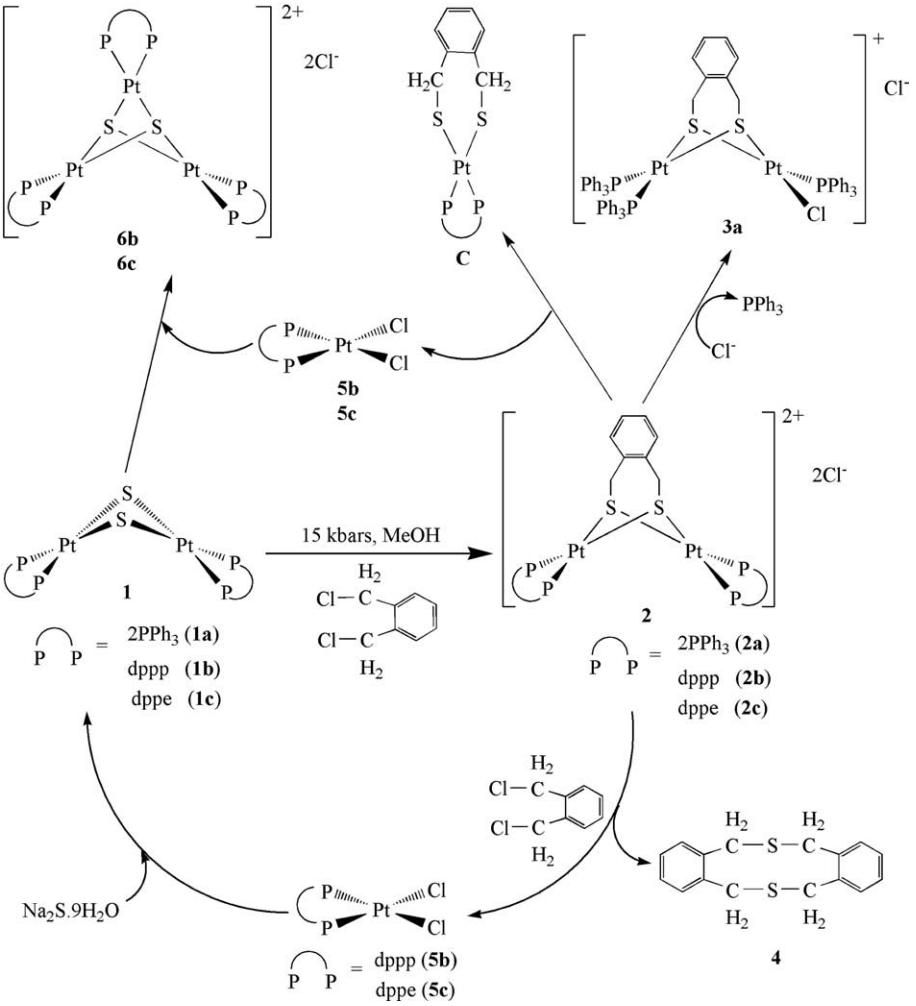


Fig. 2. Molecular structure of the cation of $[Pt_2(\mu\text{-}SCH_2C_6H_4CH_2S)_2(dppp)_2][PF_6]_2$ (**2b**). The phenyl rings of diphosphines and protons are omitted for clarity.

for the incomplete conversion to **4**. The X-ray crystal structure of **2b** (Fig. 2) is similar to that of **2a**, suggesting that the phosphine does not play an active chemical or structural role in the alkylation. The smaller hinge (132.4°), however, could point to more space available for the second alkylation to occur. The unsymmetric disposition of the xylyl also leads to two discrete phosphine signals [$^{31}P\{^1H\}$ NMR ($CDCl_3$): triplet of doublets, δ_P −1.4 ($J_{Pt-P(1)}$ 2747 Hz) and δ_P −2.1 ($J_{Pt-P(2)}$ 2766 Hz)]. Similar experiments on $[Pt_2(\mu\text{-}S)_2(dppe)_2]$ (**1c**) also gave rise to **4** (ESI–MS evidence), which was not purified or isolated, and the recovery of white crystalline solids of $[PtCl_2(dppe)]$ (**5c**) [$^{31}P\{^1H\}$ NMR ($CDCl_3$): δ_P 41.2 (s, J_{Pt-P} 3620 Hz)]. The latter reacts with excess $Na_2S \cdot 9H_2O$ to give **1c**, thereby turning a stoichiometric into a catalytic-like preparation of dithiacyclophane (Scheme 1).

Formation of **4** and its intermediates and byproducts, albeit in different yields, is consistent among the phosphines used. These products demonstrated the expected

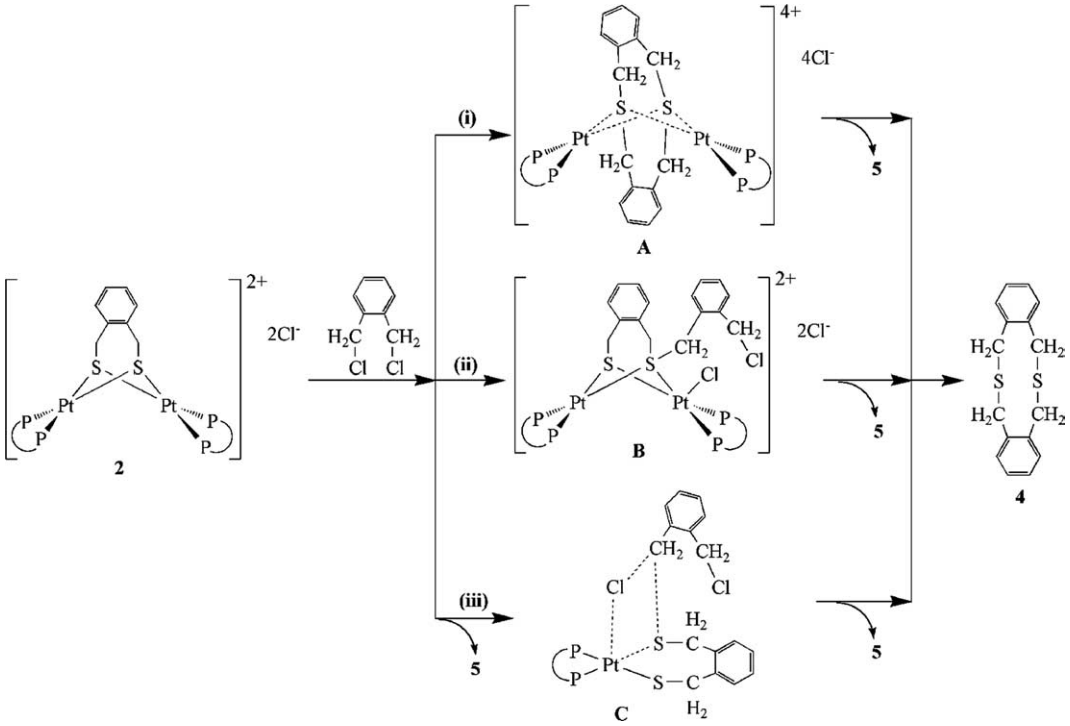


Scheme 1. Reaction mechanism showing the metal-mediated preparation of 3,8-dibenzo-1,6-dithiacyclodecane (**4**) and the proposed formation of the trinuclear $[Pt_3(\mu_3\text{-}S)_2(dppp)_3]Cl_2$ (**6b**) and $[Pt_3(\mu_3\text{-}S)_2(dppe)_3]Cl_2$ (**6c**).

concomitant alkylation of both sulfide centres in **1** to afford the over-head-bridged intermediate **2**, and the desirable formation of **4**. Formation of **3a** highlights a side reaction of ligand displacement of PPh_3 by chloride (Scheme 1). This poses a threat to the synthesis since this could pave a pathway for premature bridge cleavage upon further attack from a second chloride, thus leading to **5a**. Use of a diphosphine as in **1b** and **1c** has alleviated this problem. Preparation of **4** has been reported in a multi-step synthesis with a yield of 67% from the starting point [13]. Apart from its pharmacological value, it could be of use in molecular sensors and conductive polymers [15]. If we could raise the yield to a significant level and make the reaction catalytic rather than stoichiometric, this methodology could offer an attractive one-step alternative to the literature method. Even more importantly, the method described here could be extended to other alkyl and aryl dihalides, thus potentially reaching out to a series of dithiamacrocycles.

Noteworthy in the pressure reactions of **1b** and **1c** was the formation of the known trinuclear species $[Pt_3(\mu_3\text{-}S)_2(dppp)_3]^{2+}$ (**6b**) (*m*/*z* 958.6) and $[Pt_3(\mu_3\text{-}S)_2(dppe)_3]^{2+}$ (**6c**) (*m*/*z* 921.5) [16]. These are stable entities easily derived from **6b** or **6c** with **1b** or **1c**, respectively (Scheme 1). Formation of **2** suggested that the synthesis is initiated by the nucleophilicity of sulfur, not the metal. Its prominence points to its reluctance to undergo further alkylation, thus posing a stumbling block in this approach. Nevertheless, its isolation, recovery and recyclability allowed us to minimize mass loss. Although the formation of **4** requires the second alkylation of **2** at sulfur, the mode of attack is presently unclear. We are working towards three possible mechanistic routes that are consistent with the observations, especially the liberation of **5**, followed by **4** (Scheme 2). Complex **2** could capture the second α-α′-dichloro-*o*-xylene through the remaining sulfur lone pairs or an oxidative-addition-type mechanism across the weakened Pt–S bond, giving $[Pt_2(\mu\text{-}S(CH_2C_6H_4CH_2)_2S)(PP)_2]^{4+}$ (PP = 2 · PPh_3, dppe, dppp) (**A**) and $[Pt_2Cl(\mu\text{-}S(CH_2C_6H_4CH_2)(ClCH_2C_6H_4\text{-}CH_2)S)(PP)_2]^{2+}$, **B**, respectively. Both would readily lead to **4**, releasing **5**. Alternatively, **2** could split to **5** and **C**. The latter could react with the organic substrate to yield **4** and liberate **5**, or return to **2** by capturing the adventitious **5**.

The use of high pressure (15 kbar) to promote the formation of **4** is evident (see Table 2). For example, reactions using **1a** under ambient conditions would only give **2a** and **3a**. At a moderate pressure such as 10 kbar, the products are similar to those observed under ambient conditions. Similar ambient reactions of **1b** and **1c** resulted only in **2b** and **2c**. All our syntheses were conducted at room temperature (~25 °C). Reactions of **1b** and **1c** at 15 kbar at higher temperature (up to 60 °C) did not improve the yield of **4**. All the observations are consistent with the expectation that the second alkylation on both sulfide is the key step in these syntheses. It involves an associative attack from the second α-α′-dichloro-*o*-xylene and formation of a highly charged species, both of which are known features that could benefit from the use of pressure. The alkylated intermediates (**2**) is subject to bridge cleavage to give



Scheme 2. Three possible mechanistic pathways illustrating the formation of 3,8-dibenzo-1,6-dithiacyclodecane (**4**) in the pressurized reactions of $[Pt(\mu\text{-}S)_2(dppp)_2]$ (**1b**) and $[Pt(\mu\text{-}S)_2(dppe)_2]$ (**1c**).

Table 2
Comparison of different reaction conditions using electrospray mass spectrometry

$[Pt_2(\mu\text{-}S)_2(P\text{–}P)_2]$	Conditions	Principal ions (m/z, %)
1a	15 kbar, 25 °C, 5 days	$[Pt_2(\mu\text{-}SCH_2C_6H_4CH_2S)(PPh_3)_4]^{2+}$ (**2a**) (804.5, 100) $[Pt_2(\mu\text{-}SCH_2C_6H_4CH_2S)(PPh_3)_3Cl]^{+}$ (**3a**) (1379.7, 10) Fragmentation peaks of **4** (104.9, 16), (189.1, 12)
1a	15 kbar, 25 °C, 4 days	$[Pt_2(\mu\text{-}SCH_2C_6H_4CH_2S)(PPh_3)_4]^{2+}$ (**2a**) (804.0, 100)
1a	1 bar, 25 °C, 5 days	$[Pt_2(\mu\text{-}SCH_2C_6H_4CH_2S)(PPh_3)_4]^{2+}$ (**2a**) (803.5, 100)
1b	15 kbar, 25 °C, 3 days	$[C_6H_4(CH_2)_2S_2(CH_2)_2C_6H_4]$ **4**+Na^+ (295.0, 32) **4** + 2MeOH + H^+ (334.8, 24) $[Pt_2(\mu\text{-}SCH_2C_6H_4CH_2S)(dppp)_2]^{2+}$ (**2b**) (690.3, 100) $[Pt_3(\mu_3\text{-}S)_2(DPPP)_3]^{2+}$ (**6b**) (959.0, 15)
1b	15 kbar, 25 °C, 2 days	$[Pt_2(\mu\text{-}SCH_2C_6H_4CH_2S)(DPPP)_2]^{2+}$ (**2b**) (691.6, 100) $[Pt_2(\mu\text{-}SCH_2C_6H_4CH_2S)(DPPP)_2][Cl]^{+}$ (1418.8, 18) $[Pt_3(\mu_3\text{-}S)_2(DPPP)_3]^{2+}$ (**6b**) (959.2, 12)
1b	10 kbar, 25 °C, 3 days	$[Pt_2(\mu\text{-}SCH_2C_6H_4CH_2S)(DPPP)_2]^{2+}$ (**2b**) (691.7, 100) $[Pt_2(\mu\text{-}SCH_2C_6H_4CH_2S)(DPPP)_2][Cl]^{+}$ (1418.0, 40) $[DPPP + MeOH + H]^{+}$ (445.3, 61)
1b	15 kbar, 60 °C, 3 days	$[Pt_2(\mu\text{-}SCH_2C_6H_4CH_2S)(DPPP)_2]^{2+}$ (**2b**) (691.7, 100) $[Pt_2(\mu\text{-}SCH_2C_6H_4CH_2S)(DPPP)_2][Cl]^{+}$ (1418.0, 22) Fragmentation peaks of **4** (166.9, 26)
1b	1 bar, 25 °C, 5 days	$[Pt_2(\mu\text{-}SCH_2C_6H_4CH_2S)(DPPP)_2]^{2+}$ (**2b**) (692.0, 100)
1c	15 kbar, 25 °C, 3 days	Fragmentation peaks of **4** (135.0, 5), (166.8, 32) $[C_6H_4(CH_2)_2S_2(CH_2)_2C_6H_4]$ **4** + Na^+ (295.1, 5) $[Pt_2(\mu\text{-}SCH_2C_6H_4CH_2S)(DPPE)_2]^{2+}$ (**2c**) (677.2, 100) $[Pt_3(\mu_3\text{-}S)_2(DPPE)_3]^{2+}$ (**6c**) (921.5, 30)
1c	15 kbar, 60 °C, 3 days	$[C_6H_4(CH_2)_2S_2(CH_2)_2C_6H_4]$ **4** + Na^+ + $2H_2O$ (392.9, 100) $[C_6H_4(CH_2)_2S_2(CH_2)_2C_6H_4]$ **4** + Na^+ + H_2O (312.8, 19) $[C_6H_4(CH_2)_2S_2(CH_2)_2C_6H_4]$ **4** + Na^+ (295.1, 10) $[Pt_2(\mu\text{-}SCH_2C_6H_4CH_2S)(DPPE)_2]^{2+}$ (**2c**) (677.8, 33) $[Pt_3(\mu_3\text{-}S)_2(DPPE)_3]^{2+}$ (**6c**) (922.2, 22)
1c	1 bar, 25 °C, 5 days	$[Pt_2(\mu\text{-}SCH_2C_6H_4CH_2S)(DPPE)_2]^{2+}$ (**2c**) (677.5, 100)

mononuclear thiolato species (**C**, Scheme. 1), which are established [17], and phosphine dissociation (**3a**). The use of pressure to inhibit such dissociative disintegration is helpful. Our strategy lies in a combinative use of pressure, nucleophilicity and metal-template to achieve the dual-benefit in overcoming a kinetic barrier, and inhibiting a facile competing process. It highlights the rich potential of pressure in realizing many otherwise unachievable organometallic syntheses and reactions.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2005.08.055.

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