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Pressure-Assisted Hetero- and Homodialkylation of Sulfide in $[Pt_2(\mu\text{-}S)_2(dppp)_2]$: One-Pot Conversion of $\{Pt_2(\mu\text{-}S)_2\}$ into $\{Pt_2(SR)_2\}$ and $\{Pt_2(SR)(SR')\}$

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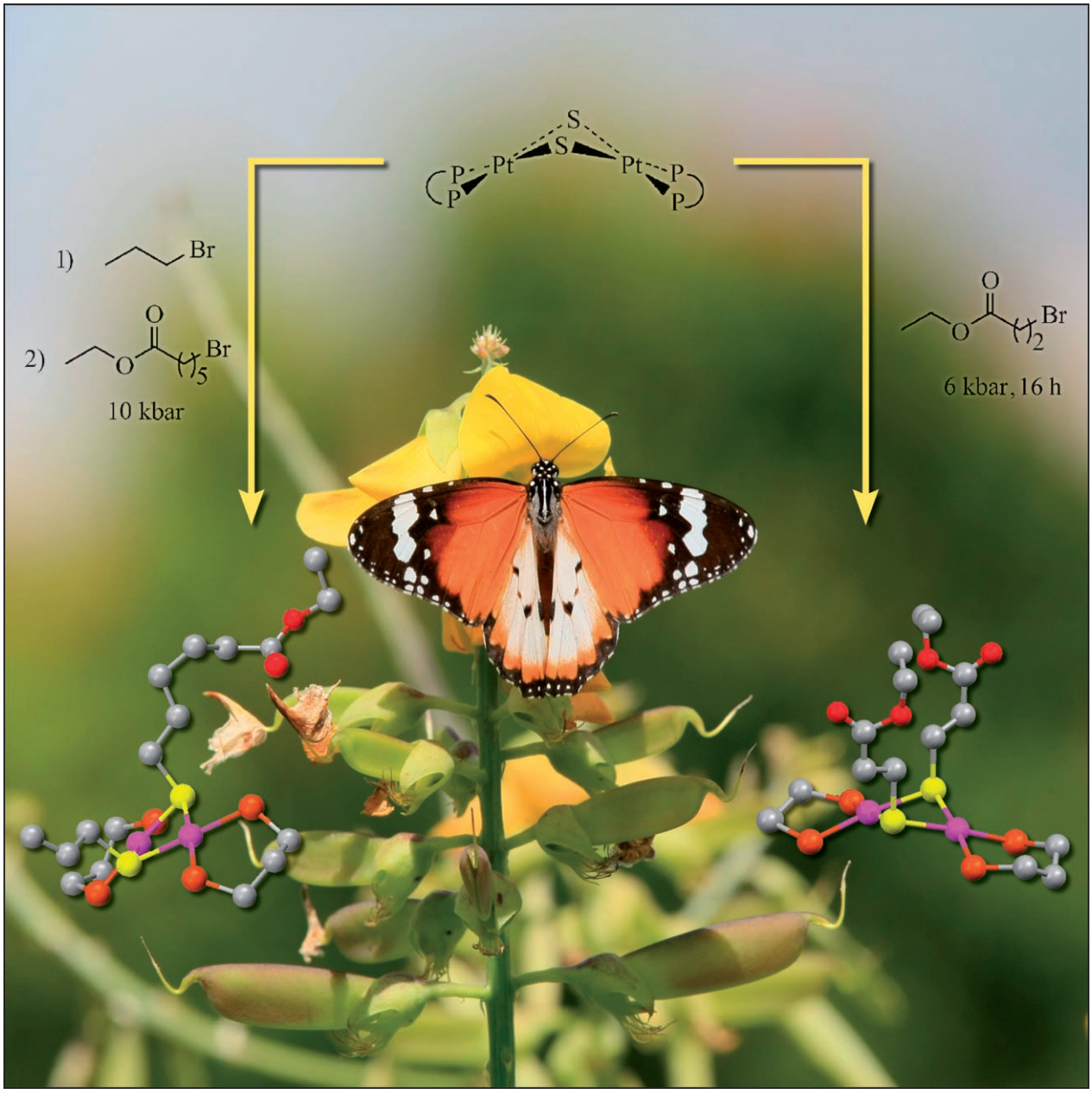

Abstract: Heterodialkylation of $[Pt_2(\mu\text{-}S)_2(dppp)_2]$ (dppp = $Ph_2P(CH_2)_3PPh_2$) was achieved under high pressure (10 kbar). This enabled the synthesis of rare diplatinum complexes with structurally diverse thiolate bridges, such as $[Pt_2(\mu\text{-}SC_5H_{10}CO_2CH_2CH_3)(\mu\text{-}SC_3H_7)(dppp)_2](PF_6)_2$, which was crystallographically identified. Complete homodialkylation was also achieved under similar conditions (6 kbar at room temperature), thus permitting the isolation of $[Pt_2(\mu\text{-}SC_2H_4CO_2CH_2CH_3)_2(dppp)_2](PF_6)_2$. The isolation of these complexes extends the applications of high-pressure chemistry to thiolato homo- and heterobridged complexes that are otherwise not accessible.

Keywords: alkylation · dithiolate complexes · high-pressure chemistry · platinum · sulfides

Introduction

The sulfide centers of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ (**1**) have a rich history in metalation chemistry.[1] Recent investigations have explored the functionalization of the nucleophilic sulfide with organic electrophiles as a simple way of constructing binuclear platinum complexes with novel thiolate bridges.[2] The functionalization of $[Pt_2(\mu\text{-}S)_2(P\text{-}P)_2]$ (P-P = 2 × monophosphine or diphosphine) complexes with organic electrophiles has seen a recent surge of interest.[2–3] It also prompted González-Duarte et al. to carry out a theoretical study on the reaction mechanism that underlies the reactivity of $[Pt_2(\mu\text{-}S)_2(P\text{-}P)_2]$ with organic dihalides.[4] The first successful isolation of binuclear platinum complexes that contain heterogeneous thiolate bridges,[5] $[Pt_2(\mu\text{-}SR)(\mu\text{-}SCH_3)(PPh_3)_4]^{2+}$ (**2**), marked a milestone in the alkylation chemistry of $[Pt_2(\mu\text{-}S)_2(P\text{-}P)_2]$ complexes since dialkylation, in particular, heterodialkylation, which has proved to be challenging. These complexes are rare, although a large number of d^8 doubly bridging thiolate complexes of the type $[M_2(\mu\text{-}SR)_2L_4]^{n+}$ are known.[6–7] Notably, heterodialkylation of $[Pt_2(\mu\text{-}SR)(\mu\text{-}S)(PPh_3)_4]^+$ (**3**) has been limited to methylation (to give SCH_3) at the unsubstituted sulfide by using a powerful alkylating agent (dimethyl sulfate) that is able to overcome the positive charge of the initially formed monocationic species **3**. The deactivation of the free sulfide in **3** imposed by the positive charge makes further alkylation difficult, even in a large excess of halide.[2]

The methylation of $[Pt_2(\mu\text{-}SR)(\mu\text{-}S)(PPh_3)_4]^+$ (**3**) represents the simplest heterodialkylation of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ (**1**). By adopting a sequential alkylation of **1** with monohalides, RX, followed by methylation with dimethyl sulfate, novel diplatinum complexes with two different thiolate bridges, $[Pt_2(\mu\text{-}SR)(\mu\text{-}SCH_3)(PPh_3)_4]^{2+}$ (**2**), are readily obtained.[5] Related analogues with two chemically identical SR thiolate bridges are much more commonly found for Pt,[6] Fe,[8] and so on. Very recently, Ni complexes with two different thiolate bridges were synthesized from two types of potassium salt of the thiols, S*i*Pr or S*t*Bu and methylthioethanethiolate (mtet).[9] The hexanuclear *cyclo*-[{Ni(μ-S*i*Pr)(μ-mtet)}$_6$] and the decanuclear *cyclo*-[{Ni(μ-S*t*Bu)(μ-mtet)}$_{10}$] clusters have a flexible core that could be used in molecular recognition and as magnetic materials.

High pressure in the liquid phase has been successfully applied to the alkylation of $[Pt_2(\mu\text{-}S)_2(P\text{-}P)_2]$ (P-P = 2 × PPh_3 or $Ph_2P(CH_2)_3PPh_2$ (1,3-bis(diphenylphosphanyl)propane or dppp)) in the synthesis of dithiacyclophanes.[10] We demonstrate herein that high pressure (15 kbar) can promote the second alkylation, thus allowing for functionalization of the unsubstituted sulfide in $[Pt_2(\mu\text{-}SR)(\mu\text{-}S)(PPh_3)_4]^+$ (**3**). This is consistent with the knowledge that bond-forming and/or ionogenic reactions are accompanied by a decrease in activation volume and are, hence, accelerated by pressure.[11] We investigated the heterodialkylation of $\{Pt_2(\mu\text{-}S)_2\}$ in an attempt to convert $\{Pt_2(\mu\text{-}S)_2\}$ into $\{Pt_2(SR)(SR')\}$ (in which $R \neq R' \neq CH_3$) entities in a one-pot manner by using pressure, and to establish that the dialkylation of $\{Pt_2(\mu\text{-}S)_2\}$ to $\{Pt_2(SR)_2\}$ is accelerated at elevated pressure.

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Results and Discussion

Pressure-Promoted Heterodialkylation of $\{Pt_2(\mu\text{-}S)_2\}$

Attempts to modify the substituent on the SCH_3 thiolate ligand of complex **2** failed to give complexes of the type $[Pt_2(\mu\text{-}SR)(\mu\text{-}SR')(PPh_3)_4]^{2+}$ (**4**; $R \neq R' \neq CH_3$). This is exemplified in the alkylation reaction of **1** with benzyl bromide followed by diethyl sulphate, which stopped at the first alkylation stage to give $[Pt_2(\mu\text{-}SCH_2C_6H_5)(\mu\text{-}S)(PPh_3)_4]^{+}$ (**3a**). An increase in carbon-chain length of just one C atom (i.e., from CH_3 to CH_2CH_3) impeded heterodialkylation significantly. A similar observation was made in the reaction of **1** with allyl bromide and diethyl sulphate studied by electrospray ionization mass spectrometry (ESI-MS), in which the predominant monoalkylated species, $[Pt_2(\mu\text{-}SCH_2CHCH_2)(\mu\text{-}S)(PPh_3)_4]^{+}$ (**3b**; $m/z = 1544$, 100%), was formed together with the diethylated $[Pt_2(\mu\text{-}SCH_2CH_3)_2(PPh_3)_4]^{2+}$ ($m/z = 780.5$, 58%) and diallylated $[Pt_2(\mu\text{-}SCH_2CHCH_2)_2(PPh_3)_4]^{2+}$ ($m/z = 792$, 35%) complexes, as well as $[Pt_2(\mu\text{-}SCH_2CHCH_2)_2(PPh_3)_4]^{2+}Br^{-}$ ($m/z = 1402$, 33%). Elevated pressure (up to 10 kbar) did not result in the formation of the expected mixed di-μ-thiolato complexes (e.g., $[Pt_2(\mu\text{-}SCH_2C_6H_5)(\mu\text{-}SC_2H_5)(PPh_3)_4]^{2+}$ (**4a**) and $[Pt_2(\mu\text{-}SCH_2CHCH_2)(\mu\text{-}SC_2H_5)(PPh_3)_4]^{2+}$ (**4b**)).

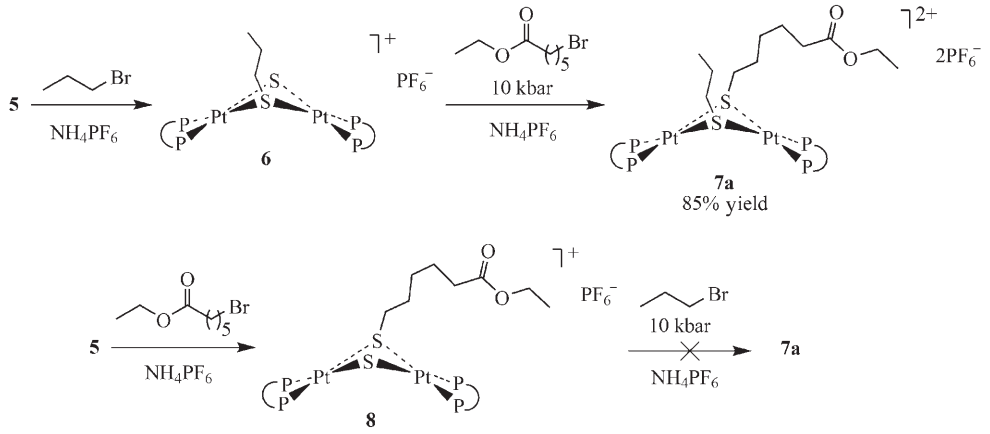
Therefore, a different method was required to achieve heterodialkylated $\{Pt_2(\mu\text{-}SR)(\mu\text{-}SR')\}$ complexes. The terminal phosphine ligand of **1** was replaced by dppp in $[Pt_2(\mu\text{-}S)_2(dppp)_2]$ (**5**) to increase the nucleophilicity of the sulfido ligands. It is also important to apply the correct alkylation sequence to **5**. For example, attachment of a substituent with a long and/or bulky alkyl chain hinders the approach of a second substituent. Reversal of the order, that is, introduction of the smaller substituent first, may solve the problem, but functionalization of both sulfide centers by the first halide is likely to occur. Thus, in our endeavor to prepare a diplatinum complex that contains both long-chain ester thiolate and propyl thiolate ligands, the propyl substituent was attached first by treating the starting complex **5** with 1-bromopropane to yield $[Pt_2(\mu\text{-}S)(\mu\text{-}SC_3H_7)(dppp)_2](PF_6)$ (**6**). The reaction was stopped within 10 min so that **6** was isolated as the only product. Successful heterodialkylation to give $[Pt_2(\mu\text{-}SC_5H_{10}CO_2CH_2CH_3)(\mu\text{-}SC_3H_7)(dppp)_2](PF_6)_2$ (**7a**) was then accomplished by pressurizing a suspension of **6** and ethyl 6-bromohexanoate overnight in MeOH at 10 kbar and 25 °C, followed by the addition of excess NH_4PF_6 (Scheme 1). Notably, this alkylation sequence is opposite to that used for the preparation of $[Pt_2(\mu\text{-}SR)(\mu\text{-}SCH_3)(PPh_3)_4]^{2+}$ complexes. When ethyl 6-bromohexanoate was introduced first to give $[Pt_2(\mu\text{-}SC_5H_{10}CO_2CH_2CH_3)(\mu\text{-}S)(dppp)_2](PF_6)_2$ (**8**), steric hindrance caused by the long ester chain blocked the approach of 1-bromopropane.

The structural characteristics of **7a** (Tables 1 and 2) are similar to those found in $[Pt_2(\mu\text{-}SR)(\mu\text{-}SCH_3)(PPh_3)_4]^{2+}$ complexes. The crystal structure of **7a** (Figure 1) confirms the presence of two different bridging thiolate ligands that are projected away from each other. Both ester thiolate and

Table 1. Selected bond lengths (Å) and angles (°) for complexes **7a** and **8**.

$[Pt_2(\mu\text{-}SC_5H_{10}CO_2CH_2CH_3)(\mu\text{-}SC_3H_7)(dppp)_2](PF_6)_2$ (**7a**)			
Pt(1)–P(1)	2.270(2)	Pt(2)–S(1)	2.375(2)
Pt(1)–P(1A)	2.270(2)	Pt(2)–S(1A)	2.375(2)
Pt(1)–S(1)	2.358(2)	S(1)–C(1)	1.854(10)
Pt(1)–S(1A)	2.358(2)		
Pt(1)–S(1)–Pt(2)	92.58(8)	P(1A)–Pt(1)–S(1)	173.88(8)
S(1)–Pt(1)–S(1A)	83.51(11)	P(1A)–Pt(1)–S(1A)	91.04(8)
P(1)–Pt(1)–P(1A)	94.26(12)	C(1)–S(1)–Pt(1)	105.0(3)
P(1)–Pt(1)–S(1)	91.04(8)	C(1)–S(1)–Pt(2)	107.7(3)
P(1)-Pt(1)-S(1 A)	173.88(8)	θ[a]	150
$[Pt_2(\mu\text{-}SC_2H_4CO_2CH_2CH_3)_2(dppp)_2](PF_6)_2$ (**8**)			
Pt(1)–P(1)	2.262(4)	Pt(1)–S(1A)	2.365(3)
Pt(1)–P(2)	2.287(4)	Pt(1A)–S(1)	2.365(3)
Pt(1)–S(1)	2.372(3)	S(1)–C(1)	1.94(2)
Pt(1)–S(1)–Pt(1A)	90.14(11)	P(1)–Pt(1)–S(1A)	174.04(13)
S(1)–Pt(1)–S(1A)	83.02(12)	C(1)–S(1)–Pt(1)	104.2(6)
P(1)–Pt(1)–P(1A)	91.71(14)	C(1)–S(1)–Pt(1A)	106.1(6)
P(1)–Pt(1)–S(1)	91.04(13)	θ[a]	142

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



Scheme 1. The sequence of alkylation in $[Pt_2(\mu\text{-}S)_2(dppp)_2]$ (**5**) is important for the selective formation of the heterodi-μ-thiolato binuclear platinum complex $Pt_2(\mu\text{-}SC_5H_{10}CO_2CH_2CH_3)(\mu\text{-}SC_3H_7)(dppp)_2](PF_6)_2$ (**7a**).

Table 2. Crystallographic data for complexes **7a** and **8**.

Complex	**7a**·$2CH_2Cl_2$·CH_3CH_2OH	**8**
Formula	$C_{69}H_{84}Cl_4F_{12}O_3P_6Pt_2S_2$	$C_{64}H_{70}F_{12}O_4P_6Pt_2S_2$
M_r	1971.28	1771.32
Crystal system	monoclinic	monoclinic
Space group	$P21m$	$C2/c$
a [Å]	13.0749(10)	19.8783(14)
b [Å]	14.9897(12)	19.2771(14)
c [Å]	20.3330(14)	17.3441(12)
α [°]	90	90
β [°]	105.842(2)	92.678(2)
γ [°]	90	90
V [Å^3]	3833.7(5)	6638.9(8)
Z	2	4
ρ_{calcd} [g cm^{-3}]	1.708	1.772
μ [mm^{-1}]	4.038	4.498
T [K]	233(2)	243(2)
Reflections measured	20685	27063
Independent reflections	6994	5321
R_{int}	0.0658	0.1368
Parameters	457	408
R (F, $F^2>2\sigma$)	0.0505	0.0677
R_w (F^2, all data)	0.1386	0.1617
Goodness of fit on F^2	0.957	0.963
Max., min. electron density [e Å^{-3}]	1.549, −1.359	2.443, −2.264

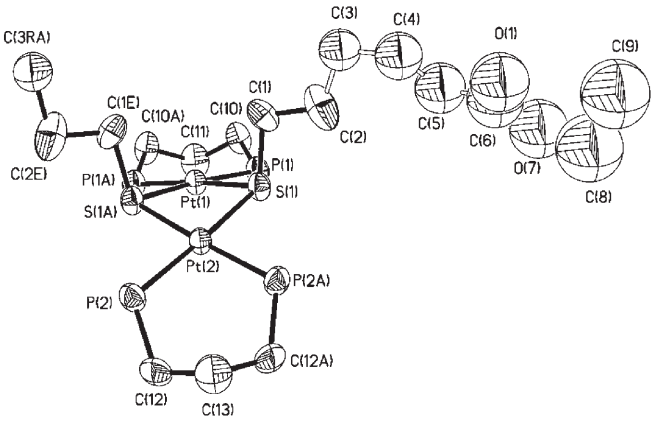


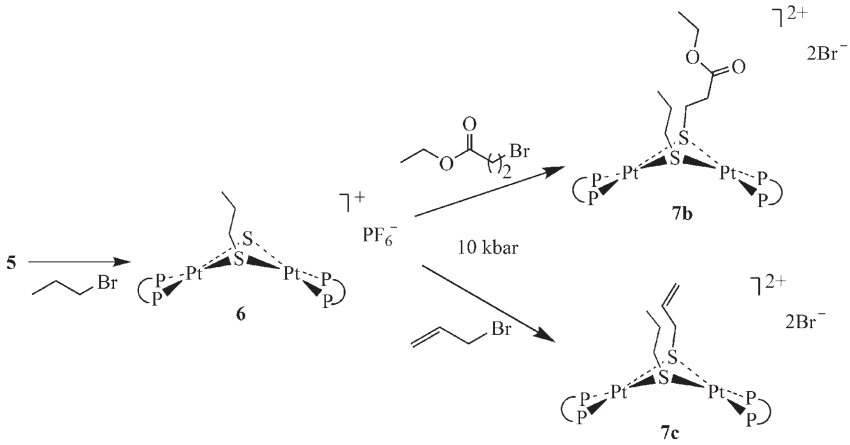
Figure 1. ORTEP diagram of the cation of $[Pt_2(\mu\text{-}SC_5H_{10}CO_2CH_2CH_3)(\mu\text{-}SC_3H_7)(dppp)_2](PF_6)_2$ (**7a**) with thermal ellipsoids at 50% probability. Phenyl rings of dppp and hydrogen atoms are omitted for clarity.

propyl thiolate ligands adopt a *syn-exo* conformation about the central $\{Pt_2(\mu\text{-}S)_2\}$ ring, which is inevitably folded with a dihedral angle of 150°. X-ray diffraction analysis also revealed the disorder of the two aliphatic chains (C_3H_7 and $C_5H_{10}CO_2CH_2CH_3$) of the SR groups, which switch positions (50:50) between the two sulfur atoms. The ^{31}P NMR chemical shifts of **7a** were indistinguishable ($\delta=0.7$ ppm), but the two sets of Pt–P couplings ($^1J_{Pt-P}=2714$, 2736 Hz) were evident. The phosphine ligand *trans* to the more strongly electron-withdrawing $\mu\text{-}SC_5H_{10}CO_2CH_2CH_3$ should have the slightly larger $^1J_{Pt-P}$ value. The introduction of a functional group with an extended tail structure (such as $C_5H_{10}CO_2CH_2CH_3$) to the unsubstituted sulfide in **6** was hindered by the crowding of the phenyl rings (of dppp) above the $\{Pt_2(\mu\text{-}S)_2\}$ core at lower and ambient pressures. This process was, however, achieved at elevated pressure (Scheme 1).

Heterodialkylation was also accomplished with a propyl residue in conjunction with either ethyl 3-bromopropionate, an ester with a shorter alkyl chain, or allyl bromide (Scheme 2). ESI-MS analysis of a mixture of $[Pt_2(\mu\text{-}S)(\mu\text{-}SC_3H_7)(dppp)_2](PF_6)$ (**6**) and either substrate in MeOH after the application of 10 kbar pressure for 16 h at 25 °C revealed the formation of $[Pt_2(\mu\text{-}SC_2H_4CO_2CH_2CH_3)(\mu\text{-}SC_3H_7)(dppp)_2]^{2+}$ (**7b**; $m/z=711$, 45% for $[M]^{2+}$ and 1503, 46% for $[M]^{2+}Br^-$) and $[Pt_2(\mu\text{-}SCH_2CHCH_2)(\mu\text{-}SC_3H_7)(dppp)_2]^{2+}$ (**7c**; $m/z=681$, 67% for $[M]^{2+}$ and 1442, 25% for $[M]^{2+}Br^-$), respectively. An assortment of different substituents can therefore potentially be appended to the bridging sulfides of **5** to construct a wide range of mixed dithiolato ligands. We are currently exploring the prospect of applying such heterofunctionalization to graft the $\{Pt_2(\mu\text{-}S)_2\}$ core onto solid surfaces.

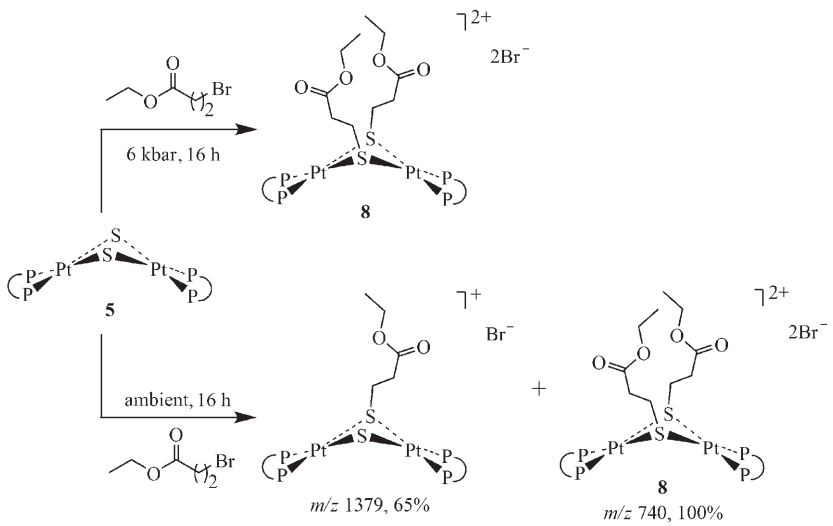
Accelerated Dialkylation of $\{Pt_2(\mu\text{-}S)_2\}$ to $\{Pt_2(\mu\text{-}SR)_2\}$ under Pressure

The dimethylated $[Pt_2(\mu\text{-}SCH_3)_2(PPh_3)_4](PF_6)_2$ is the only $[Pt_2(\mu\text{-}SR)_2(P\text{-}P)_2]^{2+}$ complex with two chemically identical μ-SR thiolato bridges that has been prepared by the alkylation of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ (**1**).[2] The intermediate $[Pt_2(\mu\text{-}SR)(\mu\text{-}S)(PPh_3)_4]^+$ (**3**) contains a deactivated sulfide, which resists substitution, and a monocationic charge, which disfavors electrophilic attack. There is also an increased likelihood of bridge cleavage when the dicationic $[Pt_2(\mu\text{-}SR)_2(P\text{-}$



Scheme 2. Formation of the heterodialkylation complexes $[Pt_2(\mu\text{-}SC_2H_4CO_2CH_2CH_3)(\mu\text{-}SC_3H_7)(dppp)_2]^{2+}$ (**7b**) and $[Pt_2(\mu\text{-}SCH_2CHCH_2)(\mu\text{-}SC_3H_7)(dppp)_2]^{2+}$ (**7c**).

$P)_2]^{2+}$ is formed. This is partially alleviated if the PPh_3 ligands are replaced by the chelating dppp. The strong electron-donating capacity of dppp in $[Pt_2(\mu\text{-}S)_2(dppp)_2]$ (**5**) also results in a more electron-rich sulfide and greater basicity.[12] We have already established[13] the identities of a number of dialkylated complexes of the type $[Pt_2(\mu\text{-}SR)_2(dppp)_2]^{2+}$ ($R = CH_2C_6H_5$, CH_2CHCH_2, CH_2CN, $C_2H_4CO_2CH_2CH_3$ and $C_5H_{10}CO_2CH_2CH_3$) by using ESI-MS. This method can be applied to most monohalides and gives rise to a greater variety of bridging dithiolate ligands. The rate of dialkylation of **5**, however, can be sluggish with some long-chain halides and/or those that contain additional functionalities.



Scheme 3. Application of pressure (6 kbar) accelerates dialkylation to form the complex $[Pt_2(\mu\text{-}SC_2H_4CO_2CH_2CH_3)_2(dppp)_2]^{2+}$ (**8**). The same reaction conducted at ambient pressure resulted in a mixture of mono- and dialkylated products.

The reaction of **5** with ethyl 3-bromopropionate at 6 kbar and 25 °C for 16 h resulted in complete dialkylation to form the doubly bridging ester thiolate complex $[Pt_2(\mu\text{-}SC_2H_4CO_2CH_2CH_3)_2(dppp)_2]^{2+}$ (**8**; $m/z = 740$, 100% for $[M]^{2+}$ and 1560, 35% for $[M]^{2+}Br^-$) (Scheme 3). The same reaction at ambient pressure resulted in incomplete dialkylation and required more than 4 days at room temperature or 2 days at 60 °C to reach completion. Complex **8** can be isolated as the PF_6 salt. The $^{31}P\{^1H\}$ NMR spectrum of **8** is typical of a symmetrical structure and displays a singlet at $\delta = 0.1$ ppm with associated satellites for Pt–P coupling ($^1J_{Pt-P} = 2741$ Hz) for the chemically equivalent phosphine groups. Confirmation of its identity was accomplished by X-ray diffraction (Figure 2 and Tables 1 and 2), which shows the two ester thiolate ligands in a *syn-exo* conformation, which is consistent with complex **7a**. The geometry of the central $\{Pt_2(\mu\text{-}S)_2\}$ ring is hinged with a dihedral angle of 142°.

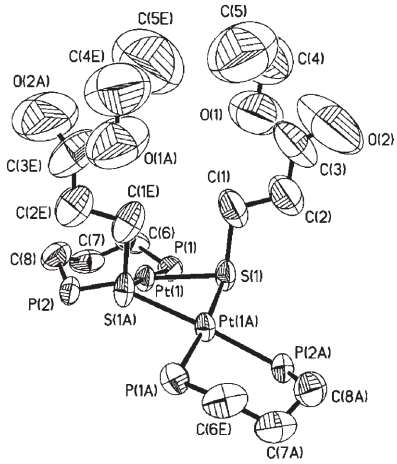


Figure 2. ORTEP diagram of the cation of $[Pt_2(\mu\text{-}SC_2H_4CO_2CH_2CH_3)_2(dppp)_2](PF_6)_2$ (**8**) with thermal ellipsoids at 50% probability. Phenyl rings of dppp and hydrogen atoms are omitted for clarity.

Conclusions

Elevated pressures in the liquid phase facilitates homo- and heterodialkylation of $[Pt_2(\mu\text{-}S)_2(dppp)_2]$ (**5**) to provide binuclear platinum bis(μ-thiolato) complexes, which are otherwise difficult to obtain. It also avoids the use of obnoxious thiols as substrates. The method is potentially applicable to a range of functional alkyls and aryls, thus permitting the design of different functionalities for specific uses such as in catalysis, optics, molecular electronics, or as therapeutic agents.[14]

Experimental Section

Methods and Materials

All manipulations were carried out at room temperature, unless otherwise stated, under an atmosphere of dinitrogen. Solvents were generally of analytical grade (Tedia) and were dried and deoxygenated before used. Complex **5** was synthesized according to published methods.[12] The following chemicals were used as supplied from Aldrich: benzyl bromide, allyl bromide, diethyl sulfate, and NH_4PF_6. Ethyl 6-bromohexanoate and ethyl 3-bromopropionate were obtained from TCI, and 1-bromopropane was obtained from Fluka.

Reactions were carried out in teflon vessels, which were placed in the chamber of a PSIKA dual-piston cylinder (20 kbar) ultrahigh-pressure reactor with castor oil/MeOH (85:15) as the pressure-transmitting medium and subjected to pressure. ESI 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 methanol (80%)/H_2O (20%) (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) of the species were confirmed by comparing the experimental and calculated isotope-distribution patterns. Elemental analysis was performed on a Perkin–Elmer PE 2400 CHNS elemental analyzer. ^{1}H and ^{13}C NMR spectra were recorded at 25°C on a Bruker ACF300 spectrometer (300 and 75.47 MHz, respectively) with Me_4Si as internal standard. ^{31}P NMR spectra were recorded at 25°C at 121.50 MHz with 85% H_3PO_4 as external reference.

Syntheses

6: 1-Bromopropane (0.01 mL, 13.5 mg, 0.110 mmol, 3 equiv) and **5** (50.1 mg, 0.039 mmol) were mixed in methanol (20 mL) and gave a yellow solution instantaneously. After the mixture was stirred for 10 min, excess NH_4PF_6 (15.0 mg, 0.092 mmol) was added. Deionized water (40 mL) was used to complete precipitation. The yellow precipitate was washed with deionized water (100 mL) and diethyl ether (100 mL) by using vacuum suction filtration to yield a yellow powder of **6** (41.9 mg, 73%). ^{1}H NMR (300 MHz, CD_2Cl_2): $\delta = 0.34$ (t, $J = 7.0$ Hz, 3H; CH_2CH_3), 0.42 (t, $J = 7.0$ Hz, 2H; SCH_2), 0.56–0.64 (m, 2H; SCH_2CH_2), 2.29–2.92 (br m, 12H; PC_3H_6P), 7.15–7.74 ppm (m, 40H; $8C_6H_5$); ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$): $\delta = 0.4$–1.6 ppm (m, $^1J_{Pt-P(1)} = 3012$ Hz, $^1J_{Pt-P(2)} = 2425$ Hz); MS (ESI, MeOH/H_2O): *m/z* (%) = 1321 (100) $[M]^+$.

7a: Ethyl 6-bromohexanoate (60.7 mg, 0.272 mmol, 10 equiv) was added to a yellow solution of **6** (39.9 mg, 0.027 mmol) in methanol (15 mL). The mixture was pressurized to 10 kbar at 30°C for 16 h. Excess NH_4PF_6 (20.0 mg, 0.123 mmol) was added to the resultant pale-yellow solution. Deionized water (40 mL) was used to complete precipitation. The off-white powder of **7a** (40.8 mg, 85%) was obtained by washing with deionized water (100 mL) and diethyl ether (100 mL). ^{1}H NMR (300 MHz, CD_2Cl_2): $\delta = 0.16$ (br s, 3H; $SCH_2CH_2CH_3$), 0.41 (t, $J = 7.0$ Hz, 3H; OCH_2CH_3), 0.79–0.84 (br m, 2H; CH_2CH_2CO), 1.11–1.29 (m, 4H; $SCH_2CH_2CH_2$), 1.83–2.09 (m, 8H; PC_3H_6P), 2.28–2.33 (m, 4H; PC_3H_6P), 2.91 (br s, 4H; SCH_2), 2.91 (br s, 2H; $SCH_2CH_2CH_3$), 2.91 (br s, 2H; CH_2CO), 3.39–3.46 (m, $J = 7.0$ Hz, 2H; OCH_2), 7.37–7.46 ppm (m, 60H; $12C_6H_5$); ^{31}P{^{1}H} NMR (121.5 MHz, CD_2Cl_2): $\delta = 0.7$ ppm (s, $^1J_{Pt-P(1)} = 2714$ Hz, $^1J_{Pt-P(2)} = 2736$ Hz); MS (ESI, MeOH/H_2O): *m/z* (%) = 733 (100) $[M]^+$, 1611 (26) $[M]^{2+}[PF_6]^-$; elemental analysis: calcd (%) for $Pt_2S_2C_{65}H_{74}P_6F_{12}O_2$ (1755.40): C 44.47, H 4.25, S 3.65; found: C 45.25, H 4.06, S 3.46. Pale-yellow crystals of **7a** suitable for X-ray crystallographic analysis were obtained from dichloromethane/ethanol (1:1).

8: Ethyl 3-bromopropionate (0.08 mL, 100.8 mg, 0.557 mmol, 10 equiv) was added to a bright-yellow solution of **5** (74.5 mg, 0.058 mmol) in methanol (20 mL). The mixture was pressurized to 6 kbar at 25°C for 16 h. Excess NH_4PF_6 (25.0 mg, 0.153 mmol) was then added to the resultant yellow solution. Deionized water (40 mL) was used to complete the precipitation. The pale-yellow powder of **8** (78.5 mg, 76%) was obtained by washing with deionized water (100 mL) and diethyl ether (100 mL) by using vacuum suction filtration. ^{1}H NMR (300 MHz, CD_2Cl_2): $\delta = 0.94$ (t, $J = 8.5$ Hz, 4H; $2CH_2CO$), 1.21 (t, $J = 7.1$ Hz, 6H; OCH_2CH_3), 1.98 (br s, 4H; SCH_2), 2.70 (br s, 4H; PC_3H_6P), 2.93 (br s, 8H; PC_3H_6P), 3.97–4.04 (q, $J = 7.1$ Hz, 4H; OCH_2), 7.24–7.48 ppm (m, 40H; $8C_6H_5$); ^{13}C NMR (75.47 MHz, CD_2Cl_2): $\delta = 14.2$, 18.2, 23.9, 29.7, 35.3, 61.1, 129.6, 132.6, 133.7, 170.1 ppm; ^{31}P{^{1}H} NMR (121.5 MHz, CD_2Cl_2): $\delta = 0.07$ ppm (s, $^1J_{Pt-P} = 2741$ Hz); MS (ESI, MeOH/H_2O): *m/z* (%) = 740 (100) $[M]^+$, 1625 (48) $[M]^{2+}[PF_6]^-$; elemental analysis: calcd (%) for $Pt_2S_2C_{64}H_{70}P_6F_{12}O_4$ (1771.35): C 43.40, H 3.98, S 3.62; found: C 45.05, H 4.04, S 3.74. Pale-yellow crystals of **8** 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 **7a** and **8** are given in Table 1. All measurements were made on a Bruker AXS SMART APEX diffractometer equipped with a CCD area detector by using $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). The software SMART[15] was used for the collection of data frames, for indexing reflections, and to determine the lattice parameters; SAINT[15] was used for the integration of the intensity of the reflections and for scaling; SADABS[16] was used for empirical absorption correction; and SHELXTL[17] 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 data collection and refinement is given in Table 2.

For complex **7a**, one half of the cation is in the asymmetric unit together with two halves of the PF_6^- anions as well as two halves of dichloromethane and half of ethanol solvent molecules. The two aliphatic chains (C_3H_7 and $C_5H_{10}CO_2CH_2CH_3$) of the SR groups are disordered and switch positions (50:50) between the two sulfur atoms. The whole cation can be obtained by the crystal symmetry. The $C_5H_{10}CO_2CH_2CH_3$ atoms were located from difference maps and were refined with restraints in bond lengths and fixed thermal parameters. For **8**, the asymmetric unit contains one half of the cation and two halves of the PF_6^- anions. The whole cation can be generated by the twofold symmetry. The aliphatic ester chain showed large thermal parameters, which explains the poor R_{int} value. Restraints in bond lengths and thermal parameters were therefore applied. CCDC-647873 (**7a**) and -647874 (**8**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: mail-to:deposit@ccdc.cam.ac.uk) or at www.ccdc.cam.ac.uk/conts/retrieving.html.

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