Electrospray mass spectrometric investigation of the reactivity of the sulfide centers in [Pt$_2$(μ-S)$_2$(PPh$_3$)$_4$] towards organic dihalides and the catalytic potential of this complex in the syntheses of organosulfur materials

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Dedicated to Professor Renato Ugo on the occasion of his 65th birthday

Abstract

Activity of [Pt$_2$(μ-S)$_2$(PPh$_3$)$_4$] (**1**) towards 1,4-dichlorobutane, 1,2-dichloroethane, α-α′-dichloro-*o*-xylene and α-α′-dichloro-*m*-xylene and the catalytic role of **1** in the syntheses of organosulfur materials was studied by in situ electrospray mass spectroscopy (ESMS). An intermediate, [Pt$_2$(μ-SC$_2$H$_4$S)(PPh$_3$)$_4$][PF$_6$]$_2$ (**6**) was isolated and characterized by single-crystal X-ray crystallographic diffractometry. In all reactions studied, the {Pt$_2$S$_2$} core is preserved, except for those involving excess NaBH$_4$. Treatment of **6** with excess NaBH$_4$ leads to the formation of mononuclear complex [Pt(η-S$_2$C$_4$H$_8$)(PPh$_3$)].
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*Keywords:* Electrospray mass spectrometric; Sulfide; Organic dihalides; Catalytic; Organosulfur

1. Introduction

Ugo et al. [1] and Chatt and Mingos [2] independently developed [Pt$_2$(μ-S)$_2$(PR$_3$)$_4$], which has turned out to be one of the best known building blocks of homo-, hetero- and intermetallic sulfide aggregates today [3]. The PPh$_3$ derivative, [Pt$_2$(μ-S)$_2$(PPh$_3$)$_4$] (**1**) has been much better studied, despite its ready decomposition in chlorinated solvents [4]. Under controlled conditions, such disintegration can be harnessed and the sulfide becomes a key in the functionalization process [5,6]. We intend to develop this concept by ap-

plying **1** in a metal-mediated process for the synthesis of organosulfur materials (Scheme 1).

The sulfide centers in **1** can be functionalized with organic dihalides to give **2**. We have recently reported that the selenium analogue of **1**, viz. [Pt$_2$(μ-Se)$_2$-(PPh$_3$)$_4$] reacts with excess 1,4-dibromobutane to give 1,6-diselenacyclodecane **3** as a white powder, albeit in poor yields [7]. It would be valuable to develop a similar process for **1** since many organosulfur compounds are pharmacologically active. The catalytic value of **1** could be realized if we can recognize a mechanism to return **2** to **1** by releasing a useful organosulfur substrate and the platinum moiety. Details of the formation of **2** from **1**, and the intermediates and forces involved in regenerating **1** from **2** are key questions that need to be addressed. In this paper, we use electrospray

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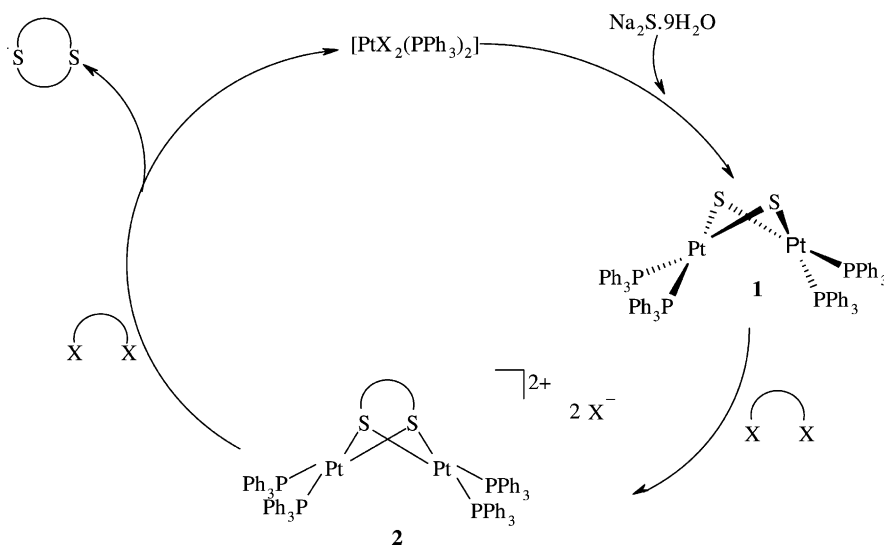
Scheme 1. A metal-mediated catalytic-like and stoichiometric synthesis of organosulfur materials.

mass spectrometry (ESMS) to study the feasibility of these conversions and to determine the active intermediates involved. The development of ESMS as a rapid and convenient tool to probe the chemistry of **1** with metal substrates has been discussed [5] and many successful ESMS-aided syntheses have been realized [8,9].

2. Experimental

2.1. Instrumentation

Solutions obtained from the reaction flask for ESMS analysis were diluted 10 times in 100% MeOH solution. Any suspension was filtered prior to dilution. Electrospray mass spectra were obtained with a Finnigan/MAT LCQ mass spectrometer coupled with TSP4000 HPLC system and the crystal 310 CE system. The mobile phase is 100% MeOH pumped at a flowrate of 0.4 ml/min. Samples were injected via a Rheodyne valve fitted with a 5 μl sample loop. The capillary temperature was 200 °C and the capillary voltage was 11 V. The capillary potential tip was 4500 V, with nitrogen used both as a sheath (4134 Torr) and an auxiliary gas (1034 Torr). Peaks were assigned from the *m/z* values and from the iso-

tope distributed patterns. The *m/z* values given are for the most intense peak in the envelopment in each case. 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.

2.2. Materials

All dihalide substrates were obtained directly from Aldrich. Solvents used were of analytical grade and used as received. All reactions were performed under pure dry nitrogen unless otherwise stated. Complex **1** was synthesized via metathesis of *cis*-[PtCl$_2$(PPh$_3$)$_2$] with Na$_2$S·9H$_2$O in benzene [2,10]. ESMS (100% MeOH): $m/z = 1503$ [M + H]$^+$.

2.2.1. Reaction of **1** with 1,4-dichlorobutane
Compound **1** (40.0 mg, 0.0266 mmol) was introduced into degassed methanol (20 ml), followed by 1,4-dichlorobutane (0.40 ml, 465.4 mg, 3.593 mmol, 100-fold excess). The mixture changed to a yellow solution after 24 h stirring under N$_2$. A sample of the clear solution was analyzed by ESMS. Excess NH$_4$PF$_6$ (20.0 mg, 0.1227 mmol) was added and the solution was stirred for 1 h. Deionized water (50 ml) was added to give precipitation of a yellow oil, which was extracted with C$_6$H$_6$ followed by

concentration in vacuo to give light-yellow powder (Yield: 14.77 mg).

2.2.2. Reaction of 1 with 1,2-dichloroethane

By using a similar procedure as in Section 2.2.1, excess 1,2-dichloroethane (0.30 ml, 375.9 mg, 3.799 mmol, 100-fold excess) and 40.0 mg (0.0266 mmol) of compound 1 gave a yellow suspension. A sample of it was filtered and analyzed by ESMS.

2.2.3. Synthesis of [Pt₂(μ-S₂C₂H₄)(PPh₃)₄][PF₆]₂ (6)

Compound 1 (40.0 mg, 0.0266 mmol) was introduced into degassed methanol (10 ml), followed by addition of 1,2-dichloroethane (0.30 ml, 100-fold excess). The mixture readily changed from a light orange to yellow suspension. The suspension was then refluxed overnight under N_2 at $60\,^{\circ}C$ to give a clear light-yellow solution. Excess NH_4PF_6 (30.0 mg, 0.184 mmol) was added, readily turning the solution into a white suspension. After stirring for another 2 h, 50 ml of deionized water was added to induce the precipitation. The solid was obtained using vacuum suction filtration and washed with 200 ml of deionized water and 100 ml of diethyl ether to yield a light-yellow powder (Yield: 43.14 mg). The solid was dissolved in chloroform and layered with hexane, and white crystals suitable for X-ray analysis were obtained.

2.2.4. Reaction of 1 with α-α′-dichloro-o-xylene

By using a similar procedure as in Section 2.2.1, excess α-α′-dichloro-o-xylene (468.6 mg, 2.676 mmol, 100-fold excess) and 40.0 mg (0.0266 mmol) of compound 1 gave a yellow solution after 10 min. After stirring for 3 h, a sample was analyzed by ESMS. Excess NH_4PF_6 (20.0 mg, 0.122 mmol) was added and the solution was stirred for 1 h. Deionized water of 50 ml was added to induce the precipitation. The white precipitate (26.76 mg) obtained using vacuum suction filtration was washed with 100 ml of deionized water and 30 ml of diethyl ether.

2.2.5. Reaction of 1 with α-α′-dichloro-m-xylene

By using a similar procedure as in Section 2.2.1, excess α-α′-dichloro-m-xylene (465.8 mg, 2.661 mmol, 100-fold excess) and 40.0 mg (0.0266 mmol) of compound 1 gave a yellow solution after 10 min. After

stirring for 3 h, a sample of the solution was analyzed by ESMS.

2.3. Crystal structure determinations

The data collection was performed on a Bruker AXS APEX diffractometer, equipped with a CCD area-detector using Mo Kα radiation ($\lambda = 0.71073$ Å). The software SMART [11] was used for collecting frames of data, indexing reflections, and the determination of lattice parameters, SAINT [11] for integration of intensity of reflections and scaling, SADABS [12] for empirical absorption correction, and SHELXTL [13] for space group and structure determination, refinements, graphics, and structure reporting. Hydrogen atoms were not located. The structure was refined by full-matrix least squares on F^2 with anisotropic thermal parameters for non-hydrogen atoms. A summary of parameters for the data collections and refinements is given in Table 1. One of the PF_6^- ions and the solvate ($CHCl_3$) are disordered. The quality of the data does not merit a detailed

Table 1
Selected crystallographic data for $[Pt_2(\mu\text{-}S_2C_2H_4)(PPh_3)_4]^{2+}$-$[PF_6]_2 \cdot 6CHCl_3 \cdot H_2O$

	6·6CHCl₃·H₂O
Formula	$C_{80}H_{72}Cl_{18}F_{12}P_6Pt_2S_2O$
f_w	2555.92
Crystal size (mm³)	$0.20 \times 0.18 \times 0.04$
Crystal system	Monoclinic
Space group	$P2(1)/c$
a (Å)	18.544(3)
b (Å)	18.300(3)
c (Å)	28.376(4)
α (°)	90
β (°)	99.964(4)
γ (°)	90
V (Å³)	9484(2)
Z	4
μ (mm⁻¹)	3.667
T (K)	223(2)
θ range (°)	1.65–22.50
Index ranges	$-19 < h < 19$
	$-19 < k < 19$
	$-26 < l < 30$
No. of reflections collected	42490
No. of unique reflections	12380
$R1$ ($I > 2\sigma(I)$)	0.1094
$wR2$ (all data)	0.2939

discussion of the bond data. However, there is little doubt on the identity of the molecular structure.

3. Results and discussion

3.1. General conditions in the use of ESMS in screening reactions between [Pt₂(μ-S)₂(PPh₃)₄] 1 and organic dihalides

$[Pt_2(\mu-Se)_2(PPh_3)_4]$ reacts with organic dihalides such as 1,2-dichloroethane, 1,4-dichlorobutane and α-α'-dichloro-o-xylene to yield stable di-cationic selenolato products [8,9]. These bifunctional substrates are expected to activate the sulfide centers of 1 en route to organosulfur precursors. Positive-mode ESMS was employed to monitor the progress of reactions. To maintain consistency, the same detection conditions are applied to all systems under study. Analysis takes place as soon as the reaction mixture

turns to a clear solution. The observed ion isotope distribution is compared with simulated isotope patterns of the identified species. The presence of peaks due to 1 would be interpreted as a non- or incomplete reaction. All systems in general give mono- and di-cationic sulfur-derivatized complexes due to nucleophilic attack at one or both of the two C–Cl sites. The dinuclear $\{Pt_2S_2\}$ core is preserved in all cases. Addition of a strong reducing agent, $NaBH_4$ to the di-cationic sulfur-derivatized complexes however, cleaves the Pt–S bonds and leads to disintegration of the core.

3.1.1. Reactivity of 1 with aliphatic dihalides

Reaction between excess 1,4-dichlorobutane and 1 in MeOH at RT gives rise to a clear yellow solution, which indicates facile formation of ionic products. The ES mass spectrum of this solution, after 24-h, is shown in Fig. 1. It consists of peaks at $m/z = 1594$ (major) and 780 (minor)
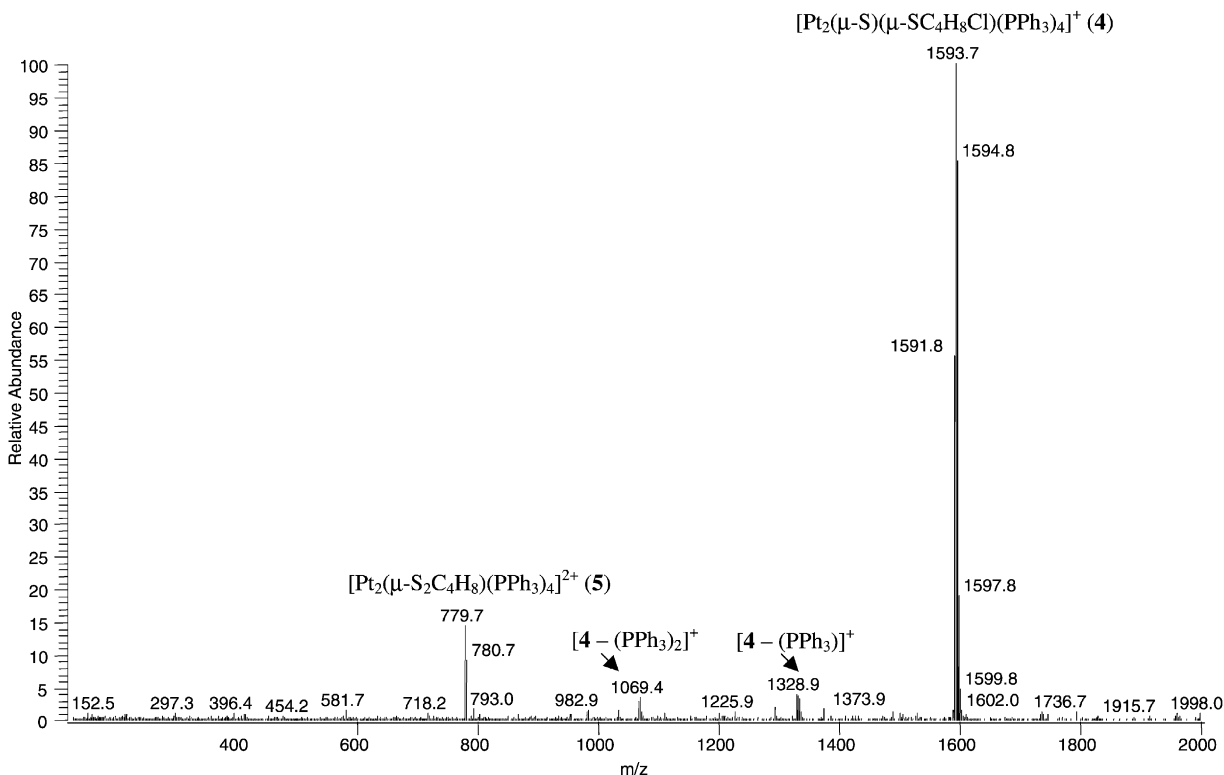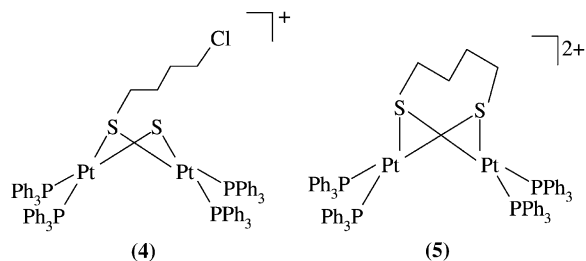

Fig. 1. Positive ion electrospray mass spectrum of a solution of $[Pt_2(\mu-S)_2(PPh_3)_4]$ (1) with 1,4-dichlorobutane in MeOH after 24 h of reaction.

corresponding to $[Pt_2(\mu\text{-}S)(\mu\text{-}SC_4H_8Cl)(PPh_3)_4]^+$ (**4**) and $[Pt_2(\mu\text{-}S_2C_4H_8)(PPh_3)_4]^{2+}$ (**5**), respectively. This demonstrates a clear step-wise alkylation and that both sulfur sites are susceptible to attack. Fragmentation of PPh$_3$ ligands from **4** is minimal.

(**4**)　　　　　　　　　　(**5**)

A yellow oil could be obtained from the solution upon metathesis with NH$_4$PF$_6$. In MeOH, this oil gave a spectrum that is predominantly **5** (Fig. 2). Its ^{31}P NMR spectrum is consistent with the formation of **5** (a singlet at 2612 Hz with the associated satellite

($^1J_{Pt-P} = 2907$ Hz)) and **4** (multiplets at 2989 Hz ($^1J_{Pt-P(1)} = 3218$ Hz and $^1J_{Pt-P(2)} = 2608$ Hz). The phosphines *trans* to the electron-withdrawing $\mu\text{-}S$-C$_4$H$_8$Cl ligand should give rise to the higher $^1J_{Pt-P(1)}$ value (3218 Hz).

Using a similar dihalide but with a shorter alkyl chain length, viz. 1,2-dichloroethane under similar conditions gave a yellow suspension, whose mass spectrum (Fig. 3) shows strong signals pertaining to the starting material **1** ($m/z = 1503$ for $[\mathit{1} + H]^+$; 1241 for $[\mathit{1} + H - (PPh_3)]^+$; and 979 for $[\mathit{1} + H - (PPh_3)_2]^+$), which are absent in Figs. 1 and 2. The di-cationic species $[Pt_2(\mu\text{-}S_2C_2H_4)(PPh_3)_4]^{2+}$ (**6**) can be detected as a weaker signal at $m/z = 766$. After 24 h, the ES mass spectrum of the reaction mixture shows the signal at $m/z = 766$ (**6**) is more intense but the starting materials are still prominent. After 72 h, the di-cation **6** became the dominant species. This prolonged reaction time also led to a new peak at $m/z = 1304$ (Fig. 4), attributed to
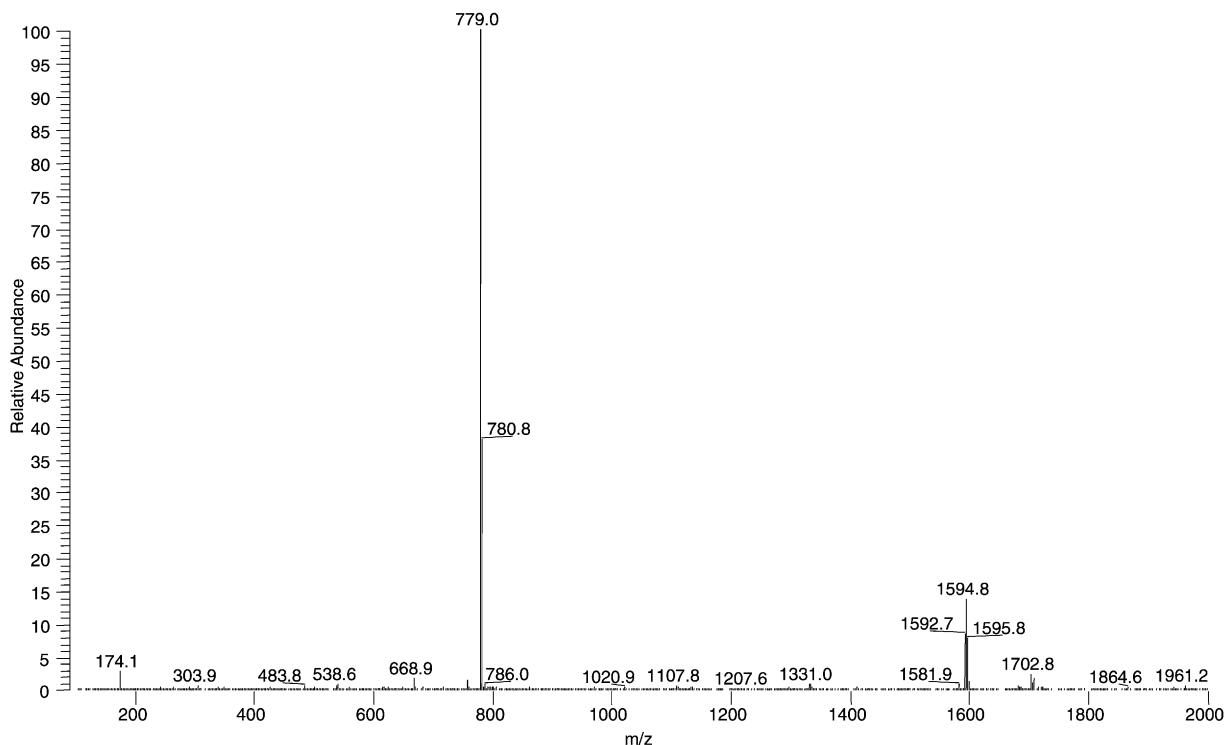

Fig. 2. Positive ion electrospray mass spectrum of the yellow oil obtained after solution of **1** with 1,4-dichlorobutane in MeOH had been metathesized.
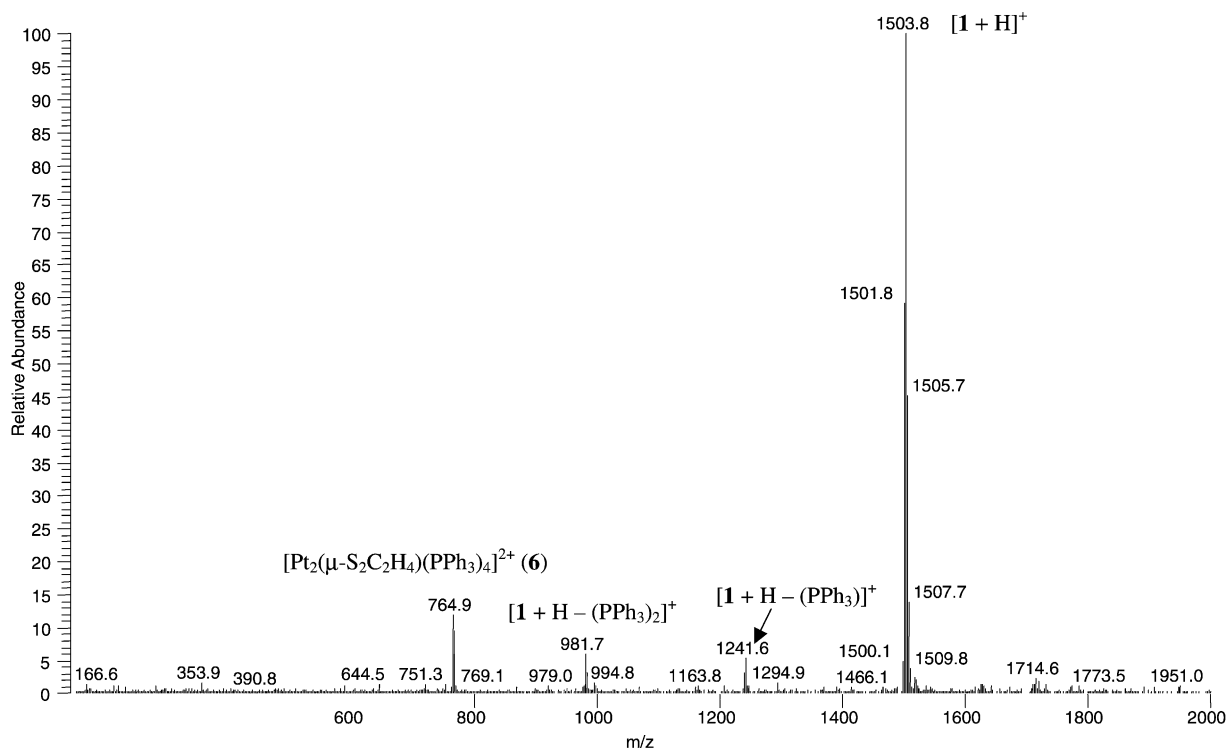
Fig. 3. Positive ion electrospray mass spectrum of a mixture of **1** with 1,2-dichloroethane in MeOH. Time taken for reaction: 24 h (RT).

$[Pt_2(\mu\text{-}S_2C_2H_4)(PPh_3)_3Cl]^+$ (**7**), whose formation suggests that phosphine dissociation and entry of chloride into the molecular core would represent a possible side reaction in the proposed catalytic methodology. At higher temperatures, the reaction proceeds faster, as supported by the absence of **1** in the spectrum of the clear yellow solution obtained after heating the reaction mixture under reflux for 24 h. A light-yellow powder was obtained after metathesis with NH_4PF_6. ^{31}P NMR analysis, with a singlet at 1883 Hz ($^1J_{Pt-P} = 3098$ Hz), suggested it to be $[Pt_2(\mu\text{-}S_2C_2H_4)(PPh_3)_4]^{2+}$ (**6**). Single-crystal crystallographic diffraction analysis confirmed a diplatinum core bridged by an ethanedithiolato ($-SCH_2CH_2S-$) group (Fig. 5; Tables 1 and 2). This marks the first step in the catalytic-like cycle (Scheme 1) in which sulfide is functionalized to give a dithiolato moiety. The stability and activity of this moiety is a subject of our on-going investigations.

(**6**)   (**7**)
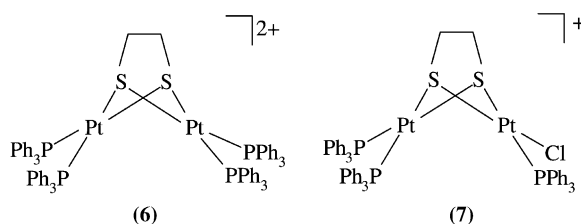
3.1.2. Reactivity of 1 with xylene dihalides

Reactions using aromatic and/or bulkier dihalides such as α-α′-dichloro-*o*-xylene and α-α′-dichloro-*m*-xylene proceed much more rapidly; they tend to give clear solutions at RT within 30 min. After treatment of α-α′-dichloro-*o*-xylene with **1** for 3 h at RT, the resulting solution in the ES mass spectrum gave an intense peak at $m/z = 1379$ (Fig. 6), inferring the formation of $[Pt_2(\mu\text{-}S_2CH_2C_6H_4CH_2)(PPh_3)_3Cl]^+$ (**8**), which is analogous to **7**. The expected di-cation $[Pt_2(\mu\text{-}S_2CH_2C_6H_4CH_2)(PPh_3)_4]^{2+}$ (**9**) ($m/z = 804$)
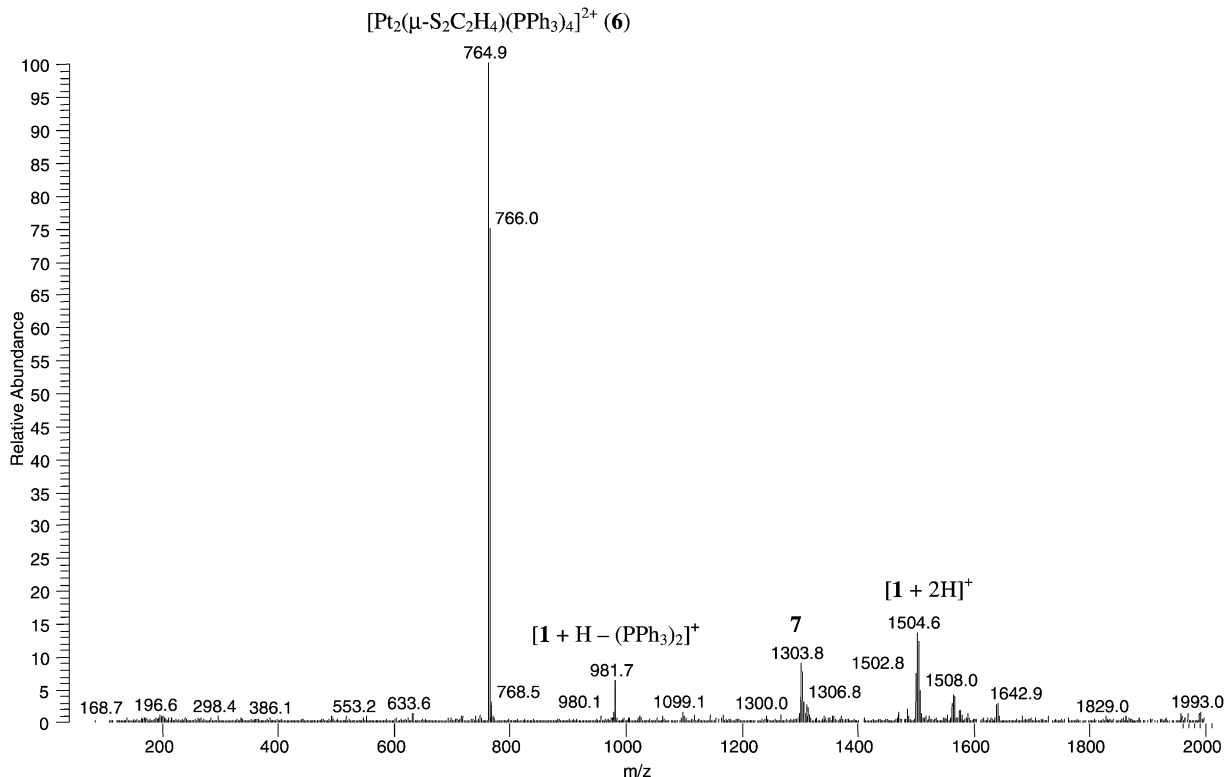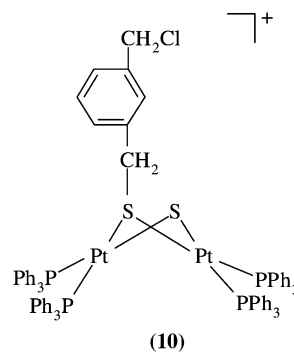
Fig. 4. Positive ion electrospray mass spectrum of a mixture of **1** with 1,2-dichloroethane in MeOH after 72 h reaction at RT.

is also prominent, and this species can be isolated as a white precipitate by metathesis with NH_4PF_6. However, unlike **6**, there are two sets of phosphines (from ^{31}P NMR analysis), which arise from unsymmetrical disposition of the xylene moiety. Similar behavior has been discussed in the selenium analogue [9].
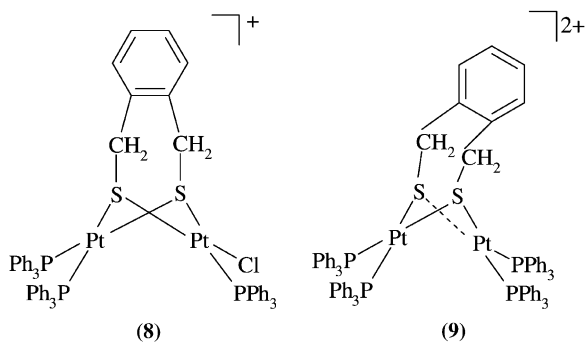
A substrate that is not suitable to serve as an overhead bridge between the sulfur centers, is α-α′-

dichloro-*m*-xylene and, as expected, gives predominantly the monocation $[Pt_2(\mu\text{-}S)(\mu\text{-}SCH_2C_6H_4\text{-}CH_2Cl)(PPh_3)_4]^+$ (**10**) ($m/z = 1642$), and some fragmentations (Fig. 7). Such substrates would be more suitable for organo(mono)sulfur syntheses whereas the dithiolato complexes could be more suitable for (di)sulfur macrocycles. These latter compounds are the target of our current study.
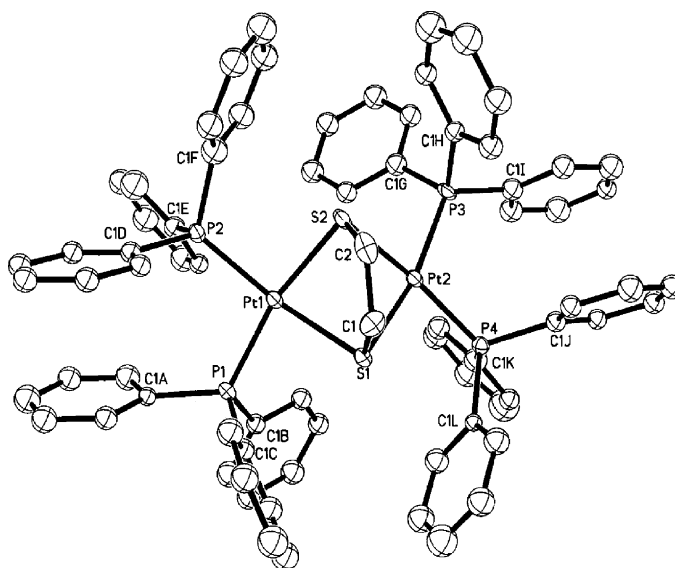
Fig. 5. ORTEP plot of the cation of the molecular structure of $[Pt_2(\mu-S_2C_2H_4)(PPh_3)_4][PF_6]_2 \cdot 6CHCl_3 \cdot H_2O$ with 50% probability thermal ellipsoid (anions and solvate are removed for clarity).
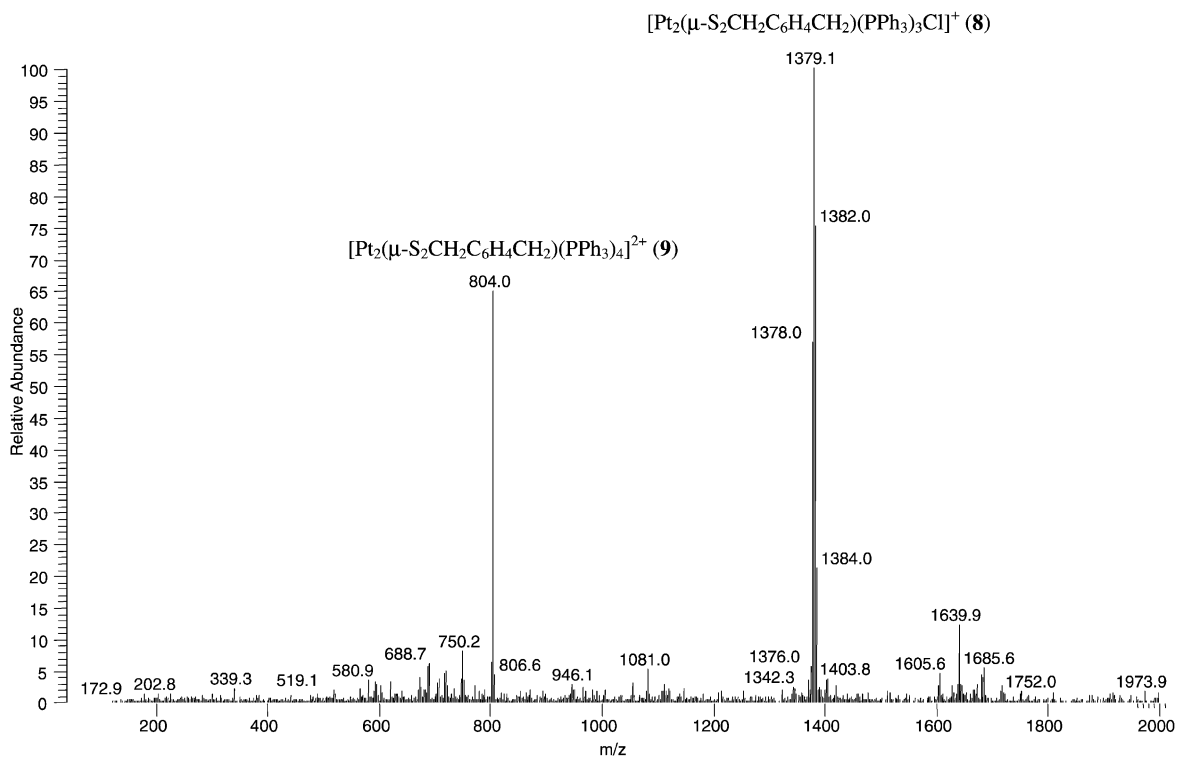

Fig. 6. Positive ion electrospray mass spectrum of a mixture of **1** with α-α′-dichloro-o-xylene in MeOH upon 3 h reaction.
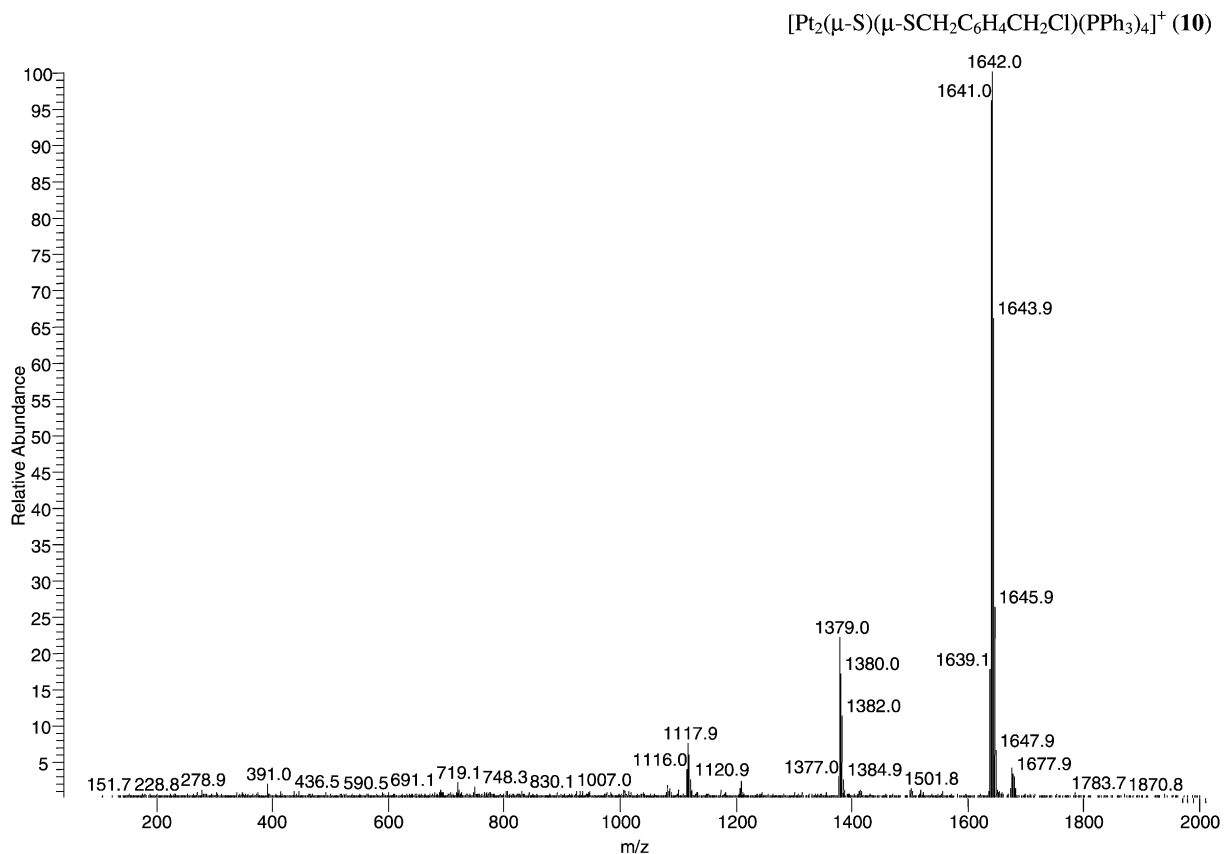
$[Pt_2(\mu\text{-}S)(\mu\text{-}SCH_2C_6H_4CH_2Cl)(PPh_3)_4]^+$ (**10**)
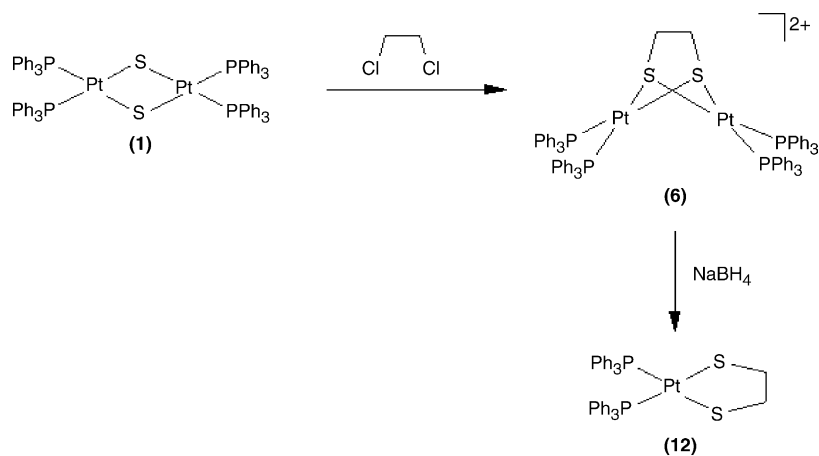

Fig. 7. Positive ion electrospray mass spectrum of a mixture of **1** with α-α′-dichloro-*m*-xylene in MeOH upon 3 h reaction.

Scheme 2. Disintegration of the $\{Pt_2S_2\}$ core in $[Pt_2(\mu\text{-}S_2C_2H_4)(PPh_3)_4]^{2+}$ (**6**) under excess $NaBH_4$.

3.1.3. Organosulfur materials

We have yet to detect free organosulfur macrocycles in the reaction mixtures. As this is an objective of our approach, we should investigate the strength of the Pt–S bonds in di-cationic **2**. In the presence of excess $NaBH_4$, $[Pt_2(\mu\text{-}S_2C_4H_8)(PPh_3)_4]^{2+}$ (**5**) (RT, 4 h) disintegrates to $[Pt(PPh_3)(PPh_2C_6H_4)]^+$ (**11**) ($m/z = 718$) (major) and $[4\text{–}(PPh_3)\text{–}S]^+$ ($m/z = 1297$) (minor) (Scheme 2). However, when $[Pt_2(\mu\text{-}S_2C_2H_4)(PPh_3)_4]^{2+}$ (**6**) is treated with excess $NaBH_4$ (RT, 24 h), Pt–S cleavage and formation of $[Pt(\eta\text{-}S_2C_4H_8)(PPh_3)]$ (**12**) ($m/z = 812$) is evident (Fig. 8). Its formation is encouraging as it could provide a pathway for the $[Pt(PPh_3)_2]$ moiety to be re-cycled (Scheme 1) and in doing so, generate a new dithiolato complex that can be used for the synthesis of organo(di)sulfur substrates.

Table 2
Selected bond lengths (Å) and angles (°) for $[Pt_2(\mu\text{-}S_2C_2H_4)(PPh_3)_4]^{2+}[PF_6]_2\cdot6CHCl_3\cdot H_2O$

	6·6CHCl$_3$·H$_2$O
Bond lengths	
Pt(1)–P(1)	2.294(6)
Pt(1)–P(2)	2.274(6)
Pt(1)–S(1)	2.373(6)
Pt(1)–S(2)	2.352(6)
Pt(2)–S(1)	2.359(6)
Pt(2)–S(2)	2.375(6)
S(1)–C(1)	1.83(2)
S(2)–C(2)	1.88(2)
Bond angles	
Pt(1)–S(2)–Pt(2)	87.4(2)
Pt(2)–S(1)–Pt(1)	87.3(2)
S(1)–Pt(2)–S(2)	76.9(2)
P(2)–Pt(1)–P(1)	99.1(2)
P(1)–Pt(1)–S(1)	89.5(2)
P(1)–Pt(1)–S(2)	166.6(2)
P(2)–Pt(1)–S(1)	169.8(2)
P(2)–Pt(1)–S(2)	94.1(2)
C(1)–S(1)–Pt(1)	94.5(8)
C(1)–S(1)–Pt(2)	96.7(9)
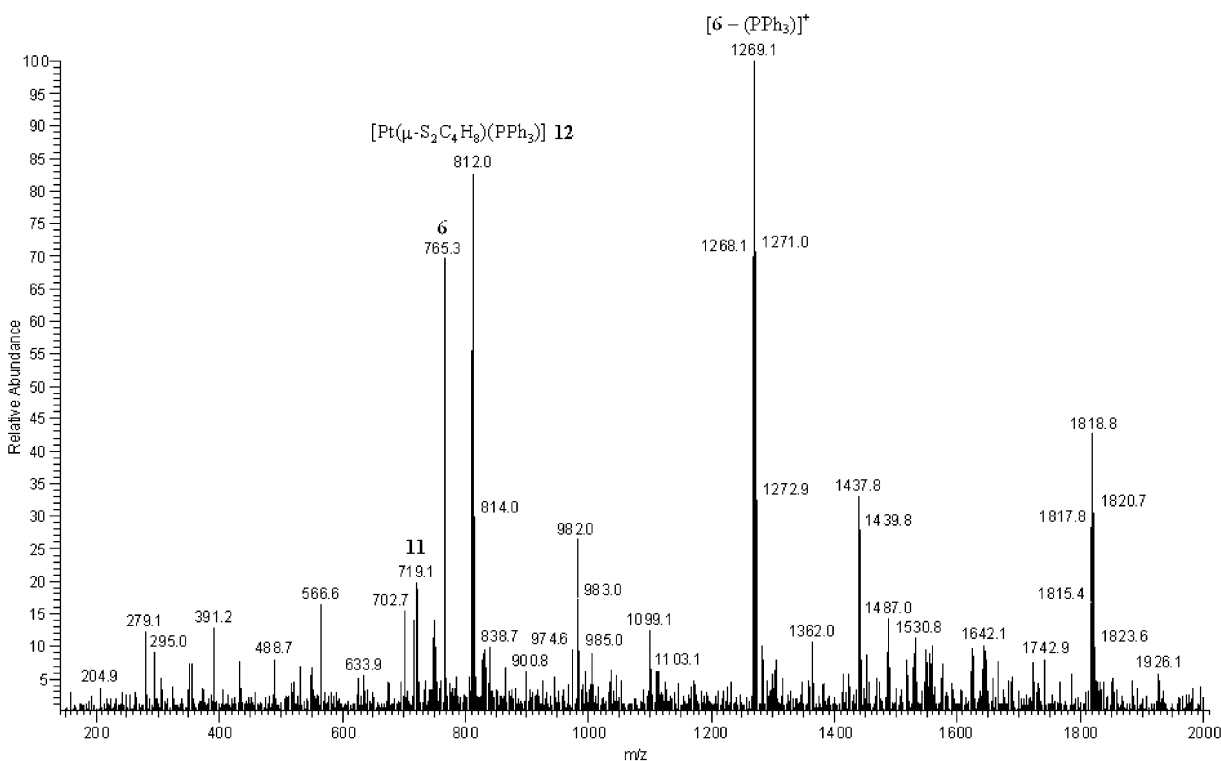
Fig. 8. Positive ion electrospray mass spectrum of a mixture of $[Pt_2(\mu\text{-}S_2C_2H_4)(PPh_3)_4]^{2+}$ (**6**) with $NaBH_4$ in MeOH after 24 h reactions.

4. Conclusion

The catalytic cycle proposed earlier is deceptively simple. Recent results suggested that for $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ (**1**) to have a significant catalytic impact, we need to promote its subsequent alkylation, and balance it with controlled Pt–S cleavage. We are encouraged by the variation in terms of single alkylation (versus double alkylation), monocation (versus di-cation) formation, and the preservation (versus disintegration) of the $\{Pt_2S_2\}$ core. The use of ESMS allowed us to observe these parallel and sometimes conflicting processes in solution. With an assortment of organic dihalides at hand, we are now able to study the subtle effects that the organic overhead can impart to these processes. In doing so, we are one step closer to exploiting this metal-mediated methodology in the design and synthesis of organosulfur substrates.

Acknowledgements

References

[1] R. Ugo, G. La Monica, S. Cenini, A. Segre, F. Conti, J. Chem. Soc. A (1971) 522.

[2] J. Chatt, D.M.P. Mingos, J. Chem. Soc. A (1970) 1243.

[3] S.W.A. Fong, T.S.A. Hor, J. Chem. Soc., Dalton Trans. (1999) 639.

[4] C.E. Briant, C.J. Gardner, T.S.A. Hor, N.D. Howells, D.M.P. Mingos, J. Chem. Soc., Dalton Trans. (1984) 2645.

[5] S.W.A. Fong, W.T. Yap, J.J. Vittal, T.S.A. Hor, W. Henderson, A.G. Oliver, C.E.F. Rickard, J. Chem. Soc., Dalton Trans. (2001) 1986.

[6] M. Capdevila, Y. Carrasco, W. Clegg, R.A. Coxall, P. Gonzalez-Duarte, A. Liedos, J.A. Ramirez, J. Chem. Soc., Dalton Trans. (1999) 3103.

[7] J.S.L. Yeo, J.J. Vittal, W. Henderson, T.S.A. Hor, Eur. J. Inorg. Chem. (2003) 277.

[8] J.S.L Yeo, J.J. Vittal, W. Henderson, T.S.A. Hor, J. Chem. Soc., Dalton Trans. (2001) 315.

[9] J.S.L. Yeo, J.J. Vittal, W. Henderson, T.S.A. Hor, Organometallics 21 (2002) 2944.

[10] T.S.A. Hor, D. Phil. Thesis, University of Oxford, 1983.

[11] SMART & SAINT Software Reference Manuals, Version 4.0, Siemens Energy & Automation Inc., Analytical Instrumentation, Madison, WI, 1996.

[12] G.M. Sheldrick, SADABS, a software for empirical adsorption correction, University of Gottingen, 1993.

[13] G.M. Sheldrick, SHELXTL, Version 5.03, Siemens Energy & Automation Inc., Analytical Instrumentation, Madison, WI, 1996.