

$[\text{Me}_8\text{Pt}_4\text{ReS}_4]^-$ and related PtMe_2 -containing clusters derived from tetrathiorhenate [☆]

Haijun Yao, Thomas B. Rauchfuss ^{*}, Scott R. Wilson

Department of Chemistry, University of Illinois at Urbana-Champaign, 601 s. Goodwin, Urbana, IL 61801, USA

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Abstract

The reactions of $\text{Pt}_2\text{Me}_4(\mu\text{-SMe}_2)_2$ and $[\text{ReS}_4]^-$ in MeCN solution have been investigated. The resulting polyalkylated clusters: $\text{Et}_4\text{N}[\text{ReS}_4\text{PtMe}_2]$ ($\text{Et}_4\text{N}[\mathbf{1}]$), $\text{Et}_4\text{N}[\text{ReS}_4(\text{PtMe}_2)_2]$ ($\text{Et}_4\text{N}[\mathbf{2}]$), and $\text{Et}_4\text{N}[\text{ReS}_4(\text{PtMe}_2)_4]$ ($\text{Et}_4\text{N}[\mathbf{4}]$), were characterized by ^1H , ^{13}C , ^{195}Pt NMR spectroscopy and ESI mass spectrometry. The structure of $\text{Et}_4\text{N}[\mathbf{1}]$ was confirmed by single crystal X-ray diffraction, which demonstrated the expected square planar and tetrahedral coordination spheres bridged by a pair of sulfur atoms.
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1. Introduction

The ability of the tetrathiomallates to serve as ligands has been amply demonstrated [1]. Thousands of complexes have been prepared and characterized capitalizing on the strong chelating tendency of these thioanions as well as the stabilizing influence of the resulting metal–metal interactions. Noteworthy applications include the $\text{Cu}^{\text{I}}\text{-MoS}_4^{2-}$ derivatives related to Mo-antagonism of copper deficiency in ruminants [2], the $\text{Fe}^{\text{I/II}}\text{MoS}_4^{2-}$ models for the FeMo cofactor in nitrogenase [3], and diverse models for HDS catalysis [4].

Although thiomallate derivatives of organometallic centers are well developed [5], this otherwise substantial literature lacks examples of simple alkylmetal derivatives attached to thiomallates. Thiomallates bearing alkyl groups could in principle give rise to new types of polymerization catalysts and the reactivity of the metal–alkyl bond provides a useful handle for functionaliza-

tion. A more fundamental question is the compatibility of normally nucleophilic M–alkyl bonds and $\text{M}=\text{S}$ functionality. The absence of $\text{MS}_4\text{-M}'\text{-alkyls}$ can be attributed to the lack of suitable sources of metal alkyls bearing suitable substituents. The versatile reactivity [6,7] of $\text{PtMe}_2(\text{SMe}_2)_2$ and $\text{Pt}_2\text{Me}_4(\mu\text{-SMe}_2)_2$ presents the opportunity to explore the basic chemistry of the $\text{MS}_4\text{-PtMe}_2$ species. Treatment of $[\text{PtMe}_2]_x(\text{SMe}_2)_2$ reagents with donor ligands L is a reliable route to species of the type PtMe_2L_2 . This paper summarizes our study on the interaction of $\text{Pt}_2\text{Me}_4(\mu\text{-SMe}_2)_2$ and $[\text{ReS}_4]^-$ and $[\text{WS}_4]^{2-}$.

2. Results and discussion

2.1. Pt–W–S species

With the intention of generating PtMe_2 derivatives of the metal sulfides, we examined the reaction of $\text{Pt}_2\text{Me}_4(\mu\text{-SMe}_2)_2$ (Pt_2) with organic salts of two representative thiomallates, $[\text{WS}_4]^{2-}$ and $[\text{ReS}_4]^-$. The reaction of Pt_2 and $(\text{Et}_4\text{N})_2[\text{WS}_4]$ in MeCN solution at the ratio of 1:2 produces an unstable orange solid, which exhibited no

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^{*} Corresponding author. Tel.: +21 73335070; fax: +21 73332685.
E-mail address: rauchfuz@uiuc.edu (T.B. Rauchfuss).

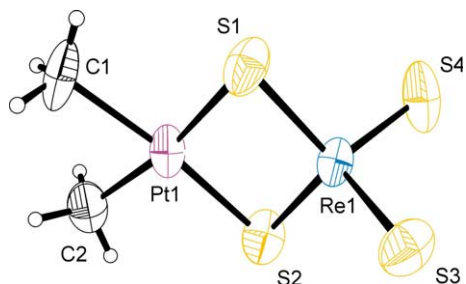


Fig. 1. View of the structure of the anion in $\text{Et}_4\text{N}[\text{ReS}_4\text{PtMe}_2]$ with 50% probability thermal ellipsoids. Hydrogen atoms were located crystallographically.

PtMe signal in its ^1H NMR spectrum. A weak signal for $[\text{WS}_4\text{PtMe}_2]^{2-}$ ($m/z = 535.8$) was observed by ESI-MS of the reaction mixture, and the M–Me and M–2Me were more intense. The reaction of two equiv Pt_2 and $(\text{Et}_4\text{N})_2[\text{WS}_4]$ in MeCN solution at 0°C afforded an orange solid that was insoluble in normal organic solvents.

2.2. $[\text{ReS}_4\text{PtMe}_2]^-$

Studies on $[\text{ReS}_4]^-$ derivatives of PtMe_2 were more fruitful than those involving $[\text{WS}_4]^{2-}$. Treatment of $\text{Et}_4\text{N}[\text{ReS}_4]$ with 0.5 equiv of Pt_2 in MeCN solution afforded a deep green 1:1 adduct upon mixing at -20°C . Work-up at room temperature gave analytically pure, air-sensitive crystals of $\text{Et}_4\text{N}[\text{ReS}_4\text{PtMe}_2]$ (**1**). ^1H NMR spectroscopy established the 2:4 ratio for the

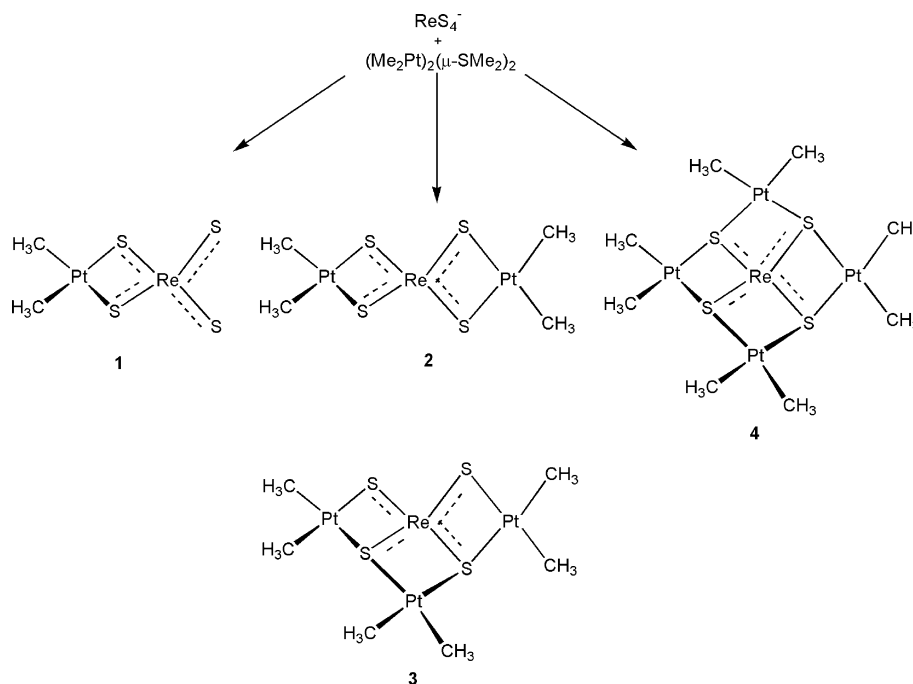
Me:Et groups and the expected equivalency of the Pt–Me groups.

Compound **1** was further characterized by single crystal X-ray diffraction, which demonstrated the expected combination of square planar and tetrahedral coordination spheres bridged by a pair of sulfur atoms (Fig. 1). At 2.12 \AA , the terminal $\text{Re}=\text{S}$ bonds are shorter than the $\text{Re}-\mu\text{-S}$ bonds (2.19 \AA) but match those in $\text{Bu}_4\text{N}[\text{ReS}_4]$ [8]. The Pt–Re distance of 2.72 \AA is clearly within bonding distance, consistent with Pt \rightarrow Re bonding. The S–Re–S angles are only slightly distorted compared to those in $\text{Bu}_4\text{N}[\text{ReS}_4]$ ($107.4\text{--}112.8$) [8]. The IR spectrum of **1** consists of a pair of intense bands near 500 cm^{-1} assigned as $\nu_{\text{Re}=\text{S}}$ ($510, 498\text{ cm}^{-1}$); another band at 458 assigned to $\nu_{\text{Re}-\mu\text{-S}}$. In contrast, $\nu_{\text{Re}-\text{S}}$ for $\text{Bu}_4\text{N}[\text{ReS}_4]$ is 484 cm^{-1} [8].

2.3. $[\text{ReS}_4(\text{PtMe}_2)_n]^-$ ($n = 2, 3, 4$)

Compound **1** is the first of a series of complexes of the general formula $[\text{ReS}_4(\text{PtMe}_2)_n]^-$ ($n = 1\text{--}4$). We investigated the preparation of the other members of this series using the appropriate stoichiometric reactions (see Scheme 1).

The green RePt (**1**) and red RePt₄ (**4**) compounds were isolated as analytically pure microcrystalline Et_4N^+ salts. As shown in Fig. 2, ^1H NMR spectra of **1**, **2** and **4** each consist of one methyl signal flanked by ^{195}Pt satellites with $J_{\text{Pt-H}}$ at $\sim 85\text{ Hz}$. The presence of single methyl signals indicates that each species is



Scheme 1.

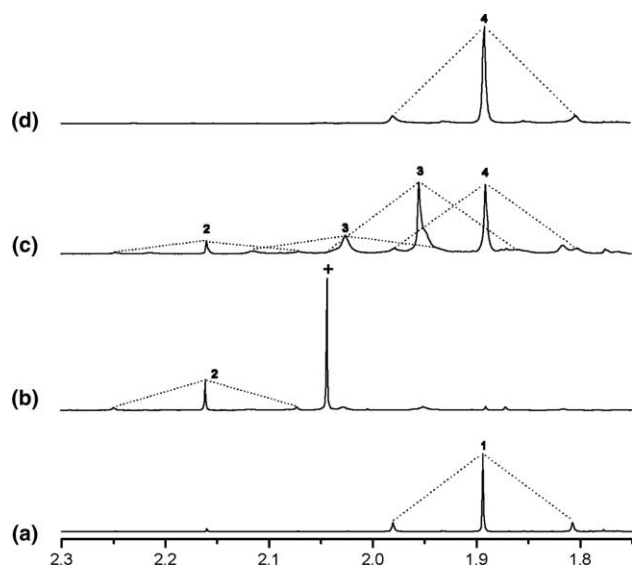


Fig. 2. ^1H NMR spectra (500 MHz) of $\text{Et}_4\text{N}[\text{ReS}_4(\text{PtMe}_2)_n]$ (d_8 -THF) in the Me_2Pt region: $n = 1$ (a), $n = 2$ (b) generated in situ and thus containing free Me_2S at (+), a mixture of $n = 2, 3$ and 4 (c), and 4 (d).

symmetrical. The ^{195}Pt NMR spectra of **1**, **2** and **4** consisted of one signal each. Compound **4** proved unreactive toward further equiv of Pt_2 . Thus, the apparent requirement for complexation is that no sulfur atom can bridge to more than three metals. Analogous to **3** and **4** are the clusters $[\text{Cp}^*\text{Ru}(\text{CO})_2\text{WS}_4[\text{PtMe}_2]_n]$ ($n = 1, 2$) prepared by the reaction of $\text{PtMe}_2(\text{cod})$ with $[\text{Cp}^*\text{Ru}(\text{CO})_2\text{WS}_4]$ [9].

The IR spectrum of **4** exhibits a weak band at 466 cm^{-1} in the $\nu_{\text{Re-S}}$ region.

We were unable to synthesize pure samples of $\text{Et}_4\text{N}[\text{ReS}_4(\text{PtMe}_2)_3]$ (**3**). This species is a particularly interesting member of the series **1–4** because its symmetry should be only C_2 and the PtMe_2 groups would be non-equivalent. Although we could not isolate **3** as a pure salt, a mixture containing this species could be generated by the addition of 1.5 equiv of Pt_2 to $\text{Et}_4\text{N}[\text{ReS}_4]$. The ^1H NMR spectrum of the resulting brown solution showed signals that could be assigned to **2** and **4** with additional signals in the approximate ratio of 1:2 assigned to **3** (Fig. 2). The two signals assigned to **3** also displayed ^{195}Pt satellites with J values similar to **1**, **2** and **4**. The ^{195}Pt NMR spectrum of the mixture showed four signals; signals at $-\delta$ 3597 and 3541 are assigned to **2** and **4**, while the other two signals at $-\delta$ 3862 and $-\delta$ 3610 with the intensity of 2:1 are assigned to **3**.

In an effort to generate **3** and to gain some understanding of the lability of these species, we tested the redistribution reactions. The fact that **2** could be isolated in pure form, however, indicated that the individual adducts do not readily interconvert. Furthermore, a THF- d_8 solution of **1** and **4** showed no tendency to form **2** or **3**. Solutions of **1** and **4** were also unreactive toward C_2H_4 , H_2 , and CO (1 atm).

3. Conclusions

The first examples of thiometallate derivatives of metal alkyls arise from the interaction of PtMe_2 sources and $[\text{ReS}_4]^-$. We succeeded in the synthesis of the series $[\text{ReS}_4(\text{PtMe}_2)_n]^-$ for n up to four. Sécheresse and coworkers [10] has reported the hexametallation of a thiometallate in the form of MoS_4Cu_6 clusters derived from $[\text{MoS}_4]^{2-}$ and cuprous chloride. Several Pt_3Re species have been characterized previously by Puddephatt. These workers employed $\text{Pt}_3(\text{PR}_3)_6$ platform to which was attached $\text{Re}(\text{CO})_3^+$ [11,12]. Pt–Re–S species are compositionally related to catalysts widely used in petroleum reforming [13].

4. Experimental

4.1. General

Standard Schlenk techniques were employed in all syntheses. $\text{Pt}_2\text{Me}_4(\mu\text{-SMe}_2)_2$ and $[\text{Et}_4\text{N}]\text{ReS}_4$ were prepared according to the literature methods [14,15]. Elemental analyses were conducted by the School of Chemical Sciences Microanalytical Laboratory. ^1H (500 MHz) ^{13}C (125.7 MHz) and ^{195}Pt NMR (128.5 MHz, referenced to 1.2 M Na_2PtCl_6 in D_2O) spectra were acquired on Varian Unity 400, 500 and Varian Unity Inova 600 MHz NMR spectrometers, respectively. Electrospray ionization-mass spectra (ESI-MS) and MS–MS measurements were acquired using a Micromass Quattro QHQ quadrupole–hexapole–quadrupole instrument. Infrared spectra were obtained on a Mattson Galaxy Series FT-IR 3000 on pressed KBr pellets.

4.2. $\text{Et}_4\text{N}[\text{ReS}_4(\text{PtMe}_2)]$ ($\text{Et}_4\text{N}[\mathbf{1}]$)

To a mixture of 114 mg (0.2 mmol) of $\text{Pt}_2\text{Me}_4(\mu\text{-SMe}_2)_2$ and 180 mg (0.4 mmol) of $\text{Et}_4\text{N}[\text{ReS}_4]$ at -20°C was added 10 mL of MeCN. The reaction mixture was allowed to warm to room temperature over 10 min, during which time the color turned from brown to green. After a further 10 min, solvents were removed under vacuum, and the residue was extracted with 10 mL of THF. Removal of THF afforded a green powder. Yield: 220 mg (82%). ^1H NMR (500 MHz, THF- d_8): δ 3.14 (q, 8H, NCH_2CH_3), 1.89 (t, 6H, PtCH_3 , $J_{\text{Pt-H}} = 87\text{ Hz}$), 1.19 (m, 12H, NCH_2CH_3). ^{13}C NMR (CD_3CN): δ 53.1 (s, NCH_2CH_3), 7.7 (s, NCH_2CH_3), -16.9 (s, PtCH_3). ^{195}Pt NMR (THF- d_8): $-\delta$ 3825. ESI-MS: M 539.0, M^+ 130.0 m/z . Anal. Calc. for $\text{C}_{10}\text{H}_{26}\text{NPtReS}_4$: C, 17.93; H, 3.91; N, 2.09. Found: C, 18.52; H, 4.07; N 2.22%. IR (KBr) 510 ($\nu_{\text{Re=S}}$), 498 ($\nu_{\text{Re-S}}$), 458 ($\nu_{\text{Re-S}}$). Deep green crystals of **1** were grown

by vapor diffusion of Et₂O into a solution of **1** in THF at –20 °C.

4.3. Et₄N[ReS₄(PtMe₂)₂] (Et₄N[**2**])

This salt was prepared analogously to Et₄N[**1**] using 29 mg (0.05 mmol) of Pt₂Me₄(μ-SMe₂)₂ and 23 mg (0.05 mmol) of Et₄N[ReS₄] and isolated as a green powder. Yield: 28 mg (74%). ¹H NMR (THF-d₈): δ 3.15 (q, 8H, NCH₂CH₃), 2.16 (t, 12H, PtCH₃, J_{Pt-H} = 88 Hz), 1.21 (m, 12H, NCH₂CH₃). ¹³C NMR (CD₃CN): δ 53.3 (s, NCH₂CH₃), 7.9 (s, NCH₂CH₃), –15.5 (s, PtCH₃). ¹⁹⁵Pt NMR (THF-d₈): –δ 3597. ESI-MS: M[–] 765.1 *m/z*, M⁺ 130.0 *m/z*.

4.4. Et₄N[ReS₄(PtMe₂)₄] (Et₄N[**4**])

This salt was prepared analogously to Et₄N[**1**] from 34 mg (0.06 mmol) of Pt₂Me₄(μ-SMe₂)₂ and 13 mg (0.03 mmol) of Et₄N[ReS₄] and isolated as a brown powder. Yield: 29 mg (80%). ¹H NMR (THF-d₈): δ 3.20 (q, 8H, NCH₂CH₃), 1.89 (t, 6H, PtCH₃, J_{Pt-H} = 89 Hz), 1.26 (t, 12H, NCH₂CH₃). ¹³C NMR (CD₃COCD₃): δ 53.0 (s, NCH₂CH₃), 7.8 (s, NCH₂CH₃), –15.5 (t, PtCH₃, J_{Pt-C} = 708 Hz). ¹⁹⁵Pt NMR (THF-xd₈): –δ 3541. ESI-MS: M[–] 1215.1, M⁺ 130.0 *m/z*. IR (KBr) 466 (ν_{Re-S}). Anal. Calc. for C₁₆H₄₄NPt₄ReS₄: C, 14.29; H, 3.30; N, 1.04. Found: C, 14.73; H, 3.43; N, 1.09%.

5. Crystallography

The crystal of Et₄N[**1**] was mounted to a 0.3 mm cryo-loop (Hampton Research) before being transferred to a Siemens Platform/CCD automated diffractometer for data collection. Data processing was performed with SAINT PLUS version 6.22 (Bruker AXS, Inc., Madison, WI USA, 2001). The structure was solved using direct methods and refined using full-matrix least-square on *F*² using the SHELXTL software package (Sheldrick, G.M. University of Göttingen, 1997). Details of the data collection and structure refinements are given in Table 1 in Supplementary data. Crystallographic data has been deposited with the Cambridge Crystallographic Data

Centre, CCDC 238513. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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Appendix A. Supporting information available

Supplementary data associated with this article can be found, in the online version at [doi:10.1016/j.jorganchem.2004.09.010](https://doi.org/10.1016/j.jorganchem.2004.09.010).

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