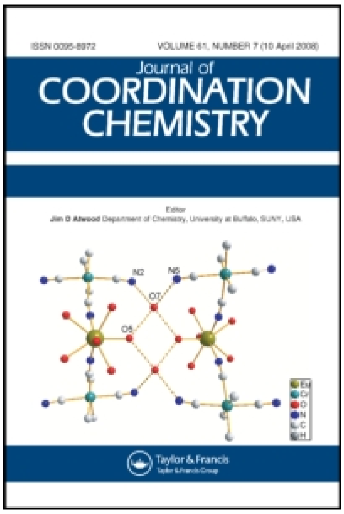

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Synthesis of a Re-Pt_2 Complex with Bridging Sulfido Ligands

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SYNTHESIS OF A Re–Pt_2 COMPLEX WITH BRIDGING SULFIDO LIGANDS

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The reaction of $Cp'ReCl_2S_3$ (where $Cp' = C_5EtMe_4$) with $Pt(PPh_3)_3$ in toluene in air results in the formation of the heteronuclear product $[Cp'ReO(\mu_3\text{-}S)_2Pt_2(PPh_3)_3Cl]ReO_4$, **1**. The product has been characterized by spectroscopic methods, cyclic voltammetry and by an X-ray diffraction study. The cation contains an unusual triangular array of one rhenium and two platinum ions with one Pt–Re bond. Under the same reaction conditions, the reaction of the known platinum dimer $(PPh_3)_4Pt_2(\mu\text{-}S)_2$ with $Cp'ReOCl_2$ was unsuccessful as a route to the cation of **1**.

Keywords: Trimetallic; Rhenium; Platinum; μ-sulfido; Oxo

INTRODUCTION

Several metal clusters and dinuclear derivatives containing both rhenium and platinum have been reported [1–8], and interesting examples of cooperative reactivity have been observed [4,7]. Heterogeneous Pt–Re surfaces are used commercially as naptha reforming catalysts [8–11], and the homogeneous Re–Pt complexes provide the opportunity to probe fundamental questions regarding electronic interactions and structural effects for these mixed metal species [8]. Sulfidation of the commercial catalysts to form Pt–Re–S composites has been found to significantly extend the lifetime and stability of the active catalysts [12–14], but little is known about the structural features or electronic effects within these composites. In view of the redox active nature of rhenium sulfide complexes [15] and the highly reactive character of sulfur ligands in many metal clusters, the investigation of Pt–Re clusters with sulfur ligands is likely to be a rich area of study. However, very few compounds that combine Re, Pt and sulfido or other sulfur ligands have been reported [1,3c,d].

We have recently synthesized new organometallic rhenium complexes with sulfido, disulfido, or polysulfido ligands [16], and these compounds may have potential in the syntheses of discrete organometallic Re–Pt-sulfido derivatives. We report here our initial attempts to prepare a rather simple Re–Pt dimer with bridging sulfido ligands. We reasoned that such a derivative may result from the reaction of $Cp'ReCl_2S_3$

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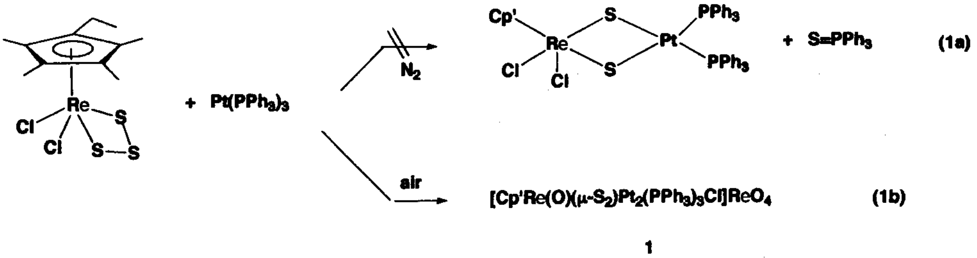
(where $Cp' = C_5Me_4Et$) with $Pt(PPh_3)_3$ as shown in Eq. (1a). However, a more complex transformation was observed, and the resulting product is described here.



1

RESULTS AND DISCUSSION

When reaction **1** was carried out under nitrogen, Cp′-containing products were observed only in very low yields in the NMR spectrum. In some cases broad signals were observed that suggested the presence of paramagnetic products; these could arise *via* redox reaction between the Re(V) and the Pt(0) reagents. However, we were unsuccessful in obtaining single crystals of a product from this reaction. When reaction **1** was carried out in the presence of air in toluene at 45°C, the solution changed from red to brown with a green precipitate, and a new Cp′-containing product was observed in the NMR spectra of both solution and precipitate. This product was isolated by column chromatography and single crystals were obtained by slow crystallization from CH_2Cl_2–ether.

The crystal structure established that the isolated product was a salt with the formulation $[Cp'ReO(\mu\text{-}S)_2Pt_2(PPh_3)_3Cl]ReO_4$, **1**. The formation of the perrhenate anion under oxidative conditions has been observed in other reactions of Cp*–Re derivatives [17]. A perspective drawing of the cation is shown in Fig. 1 and selected bond distances and angles are given in Table I. The cation contains a triangular array of one rhenium and two platinum ions bridged by two μ^3-sulfido ligands. To our knowledge, the structure is the first characterized example of a triangular complex with the Pt_2Re composition. The rhenium is additionally coordinated by a terminal oxo and a η^5–Cp′ ligand, and it undergoes a bonding interaction with one of the platinum centers, Re–Pt(2) = 2.9557(4) Å. The distance is similar to those of weak Re–Pt bonds bridged by sulfido ligands (ave = 2.974 Å) in the cluster $[Pt_3\{Re(CO)_3\}(\mu_3\text{-}S)_2(dppm)_3]^+$, **2** [3d]. The other Re–Pt distance of 3.54 Å precludes a bonding interaction. The Pt(1)–Pt(2) distance in **1** is 3.0961(4) Å. Although a bond between the two Pt(II) ions is unlikely, the distance represents a relatively short contact and is significantly shorter than the non-bonding distance between Pt(II) ions in $(PPhMe_2)_2Pt(\mu\text{-}S)_2Pt(PPhMe_2)_2$ and related derivatives (3.17–3.20 Å) [18]. The observed triangular array of metals with one M–M bond is consistent with the 48 valence electron count of **1**, where one 18 e^- and two 16 e^- metals are involved [19].

The two platinum ions in the structure show significantly different metal–ligand distances that reflect the different coordination numbers of the two platinum centers. For example the Pt(1)–S(1) distance *trans* to a phosphine of 2.351(1) Å is significantly shorter than the analogous Pt(2)–S distances of 2.391(1) and 2.383(1) Å. Similarly, the

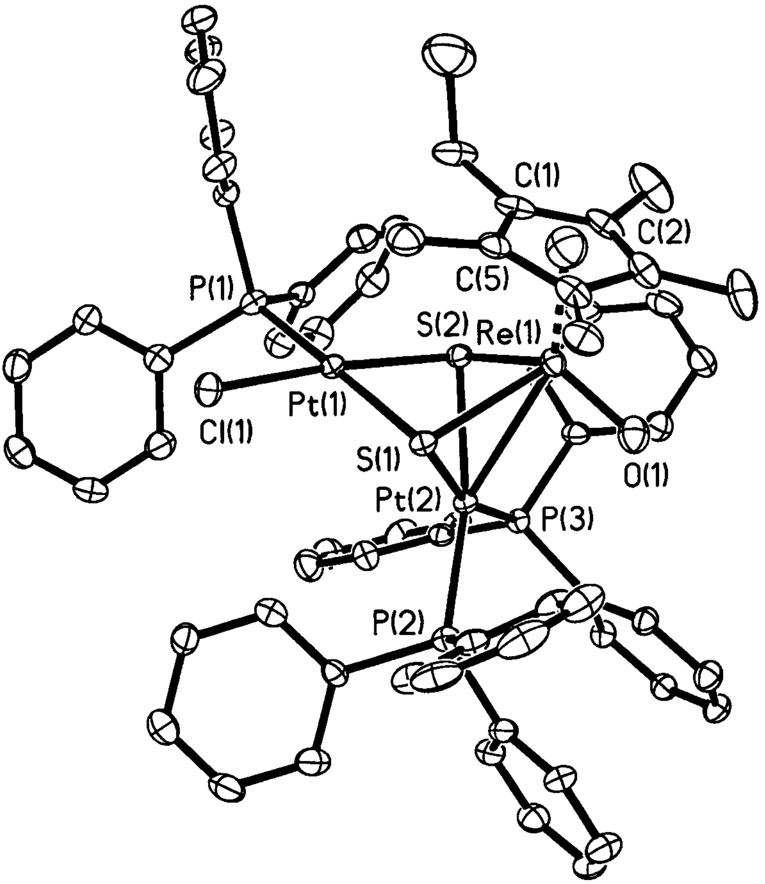


FIGURE 1 ORTEP drawing and numbering scheme for the cation of $[Cp'ReO(\mu^3\text{-}S)_2Pt_2(PPh_3)_3Cl]ReO_4$, **1**. Thermal ellipsoids are shown at the 50% probability level.

TABLE I Selected bond distances (Å) and angles (deg) for **1**

Distances			
Re(1)–O(1)	1.707(4)	Pt(1)–S(1)	2.3509(13)
Re(1)–S(1)	2.4062(13)	Pt(1)–S(2)	2.2951(12)
Re(1)–S(2)	2.4211(13)	Pt(1)–Cl(1)	2.3512(13)
Re(1)–Pt(2)	2.9557(4)	Pt(2)–P(2)	2.2992(13)
Pt(1)–P(1)	2.2556(14)	Pt(2)–P(3)	2.2879(12)
Pt(2)–S(1)	2.3911(12)	Pt(2)–S(2)	2.3833(12)
Pt(1)···Pt(2)	3.0961(4)		
Angles (deg)			
Pt(1)–S(1)–Re(1)	96.13(4)	Pt(1)–S(1)–Pt(2)	81.52(4)
Pt(2)–S(1)–Re(1)	76.07(4)	Pt(1)–S(2)–Pt(2)	82.85(4)
Pt(1)–S(2)–Re(1)	97.21(4)	Cl(1)–Pt(1)–S(2)	170.30(5)
Pt(2)–S(2)–Re(1)	75.93(4)	P(1)–Pt(1)–S(1)	176.18(4)
P(2)–Pt(2)–S(2)	163.81(4)	P(3)–Pt(2)–S(1)	164.58(4)
P(2)–Pt(2)–P(3)	104.97(5)	P(1)–Pt(1)–Cl(1)	90.26(5)
S(1)–Pt(1)–S(2)	78.15(4)	S(1)–Pt(2)–S(2)	75.68(4)

TABLE II Crystallographic data for [Cp′ReO(μ-S)$_2$Pt$_2$(PPh$_3$)$_3$Cl]ReO$_4$, **1**

Formula	$C_{65}H_{62}ClO_5P_3Pt_2Re_2S_2$
Fw	1878.21
Cryst syst	Triclinic
Space group	$P\bar{1}$
a, b, c (Å)	11.6237(10), 15.1997(10), 18.3859(16)
α, β, γ (°)	89.560(9), 76.261(8), 80.839(8)
V (Å^3)	3113.6(5)
Z	2
D (g/cm^3)	2.003
Total reflns	41735
Indep reflns	18495
μ (mm^{-1})	8.589
Radiation (λ, Å)	Mo Kα (0.71073)
T (K)	143(2)
$R1$, $wR2^{a}$	0.0413, 0.1015

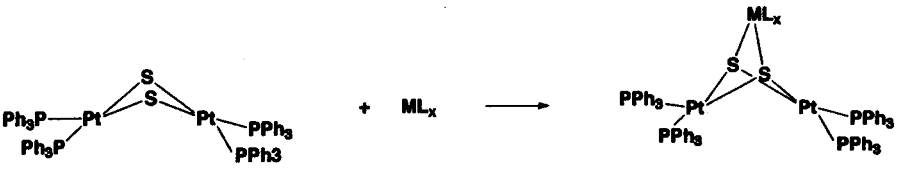
$^{a}R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w\,(F_o^2)^2]\}^{1/2}$.

Pt(1)–P(1) distance of 2.256(1) Å is shorter than the Pt(2)–P distances which average 2.294(1) Å.

The spectroscopic data for **1** are consistent with the structure discussed above. The MALDI and electrospray mass spectra show an envelope at $m/z = 1627$ that corresponds to the parent cation. Envelopes that can be attributed to the loss of triphenylphosphine and chloride ligands are also observed. The ^{31}P NMR spectrum of **1** confirms the presence of three inequivalent phosphine ligands with resonances at 16.82, 13.25 and 11.72 ppm with $J_{\mathrm{P-Pt}}$ of 3585, 3635, and 3465 Hz, respectively. On the basis of $J_{\mathrm{P-P}}$ values, the resonance at 13.2 ppm is assigned to P1, (see Fig. 1 for numbering scheme). The resonance at 11.7 ppm, (P2 or P3) shows coupling to both P1 with $J_{\mathrm{P3-P1}} = 6.0$ Hz and to the adjacent *cis* phosphorus, $J_{\mathrm{P3-P2}} = 16.5$ Hz. No coupling is resolved between P1 and the second phosphine on Pt2.

The cyclic voltammogram of **1**, recorded in acetonitrile, shows a reversible reduction wave at −1.49 V and a reversible oxidation at 0.62 V *vs* Fc. These electron transfer processes are associated with the rhenium center since redox activity is generally not observed for the Pt$_2$(μ-S)$_2$L$_4$ moiety [20]. The complex Cp′ReO(SC$_2$H$_4$S) which has a similar coordination environment around rhenium undergoes a reversible reduction at −2.13 V *vs* Fc and an irreversible oxidation at 0.68 V [21]. Comparisons of the potentials for **1** and the mononuclear derivative suggest that electron density is withdrawn from the rhenium ion in **1** by coordination to the platinum and sulfide ligands.

The structure of **1** is related to heteronuclear aggregates formed in the reactions of Pt$_2$(μ-S)$_2$(PPh$_3$)$_4$ with electrophilic metal centers [18b]. Several different structures have been characterized in these reactions, but reactions of late transition metals (Pd, Pt, Ag, Au, Cu, Co, Ru), with the platinum dimer generally lead to the formation of trinuclear products that do not undergo metal–metal bonding interactions, Eq. (2).



(2)

Reactions of the platinum dimer with early transition metal fragments appear to be less investigated. $Pt_2(\mu\text{-}S)_2(PPh_3)_4$ was reacted with $Cp'ReOCl_2$ in order to determine whether this is an alternate route to the cation of **1**. Reactions were carried out under nitrogen in THF at room temperature, and in toluene at 50–60°C. Both reaction conditions produced a mixture of complexes (see Experimental), but the ^1H and ^{31}P NMR spectra on the crude products established that $[\mathbf{1}]^+$ was not a significant product formed under either set of conditions. Further work is in progress to determine whether other Cp′Re–Pt products can be successfully prepared from reactions of Cp′Re reagents with $Pt_2(PPh_3)_4(\mu\text{-}S)_2$.

In summary, this work establishes that $Cp'ReCl_2S_3$ is a viable reagent for the construction of mixed metal sulfido assemblies. Reaction of the trisulfide complex with $Pt(PPh_3)_3$ leads to the formation of a stable trinuclear cation $[Cp'ReO(\mu^3\text{-}S)_2\text{-}Pt_2(PPh_3)_3Cl]^+$ which contains an unusual triangular array of one rhenium and two platinum ions.

EXPERIMENTAL

Material and Instrumentation $Cp'ReS_3Cl_2$ [16b], $Pt(PPh_3)_3$ [22], $Cp'ReOCl_2$ [23], and $Pt_2(\mu\text{-}S)_2(PPh_3)_4$ [24] were prepared according to literature procedures. ^1H and ^{31}P NMR spectra were recorded on a Varian Inova 500 MHz instrument, and chemical shifts are reported in ppm relative to tetramethylsilane (^1H) or an external standard of phosphoric acid (^{31}P). Mass spectra were obtained on a VG Autospec with EI/CI sources and liquid ion secondary ion MA capabilities, or a Hewlett-Packard 5989A electrospray ionization LC mass spectrometer, or on a Finnigan MATR LCQ ion trap mass spectrometer. Infrared spectra were obtained on KBr pellets using a Perkin-Elmer Model 1600 FTIR spectrometer. Cyclic voltammetry experiments were carried out on acetonitrile solutions containing 0.1 M Bu_4NBF_4 with a Cypress Systems electrolysis system. Ferrocene was used as an internal standard. Elemental analyses were performed by Desert Analytical Laboratory, Tucson, AZ.

Synthesis of **1** $Pt(PPh_3)_3$ (0.724 g, 0.738 mmol) was dissolved in toluene and $Cp'ReCl_2S_3$ (0.185 g, 0.369 mmol) was added. The solution was stirred in air and heated to 45°C for two hours. The resulting brown solution was filtered, removing a small amount of tan ppt. The brown filtrate was stirred for 18 h at RT. This produced a brown solution and an olive green ppt. The solution was filtered and the ppt was purified by chromatography on silica gel, eluting with 1 : 1 dichloromethane–acetonitrile. The green fraction was collected from the column. Yield: 30%. The product was further recrystallized from dichloromethane–ether in order to remove a by-product identified as $Pt(PPh_3)_2Cl_2$. ^1H NMR data for **1** ($CDCl_3$): 2.13 (s, 6H CpMe); 2.05, 2.02 (2s, 6H, CpMe); 1.04 (t, 3H, $CpCH_2CH_3$); 2.23 (m, 2H, $CpCH_2$); 7.0–7.5 (m, 45H, Ph). ^{31}P NMR ($CDCl_3$); 13.25 (d, P1, $J_{P\text{–}Pt} = 3635$ Hz, $J_{P1\text{–}P2\text{ or }3} = 6.0$ Hz); 11.72 (dd, P2 or 3, $J_{P\text{–}Pt} = 3465$ Hz, $J_{P2\text{–}P3} = 16.5$ Hz); 16.82 (d, P3 or 2, $J_{P\text{–}Pt} = 3585$ Hz). IR (KBr): 904 cm^{-1}, $\nu_{Re=O}$. ES MS: *m*/*z* 1627 (P of cation); 1330 (P–PPh_3, Cl); 1068 (P–$2PPh_3$, Cl); 719 ($Pt(PPh_3)_2$). Analysis calcd. for $C_{65}H_{62}ClO_5P_3Pt_2Re_2S_2$(%): C, 41.56; H, 3.33. Found: C, 41.99; H, 3.35.

X-ray Diffraction Study of **1** Green parallelpiped crystals were grown from diffusion of diethyl ether into a concentrated dichloromethane solution. The specimen crystal was mounted with a small quantity of silicone vacuum grease to the tip of a small glass fiber affixed to a tapered copper mounting-pin and transferred to the 143 K cold stream of a Siemens SMART CCD diffractometer equipped with a locally-modified LT-2A low temperature apparatus.

Cell parameters were determined using reflections harvested from three orthogonal sets of 20 0.3°ω scans. Final cell parameters were refined using 8192 reflections with $I > 10\sigma(I)$ chosen from 41,735 in the entire data set. An arbitrary hemisphere of data was collected to 0.68 Å using 0.3°ω scan measured for 30 s in 2 correlated 30 s. exposures. All data were corrected for Lorentz, polarization, and absorption effects.

Structure solution *via* direct methods in the centrosymmetric space group $P\bar{1}$ revealed the non-hydrogen structure. All non-hydrogen atoms were refined with parameters for anisotropic thermal motion. Hydrogen atoms were placed at calculated geometries and allowed to ride on the position of the parent atom. Hydrogen thermal parameters were set to 1.2 times the equivalent isotropic thermal parameter of the parent atom. No significant features were present in the final difference electron density map. Details of the structure determination are given in Table II.

Reaction of $Cp'ReOCl_2$ *with* $Pt_2(\mu\text{-}S)_2(PPh_3)_4$ The platinum dimer (0.042 g, 0.028 mmol) was dissolved in toluene, the solution was purged with N_2, and the rhenium complex (0.012 g, 0.028 mmol) was added. The solution was stirred at 50–60°C for 3–4 h. The color of the solution changed to gold. The solvent was removed in *vacuo* and the remaining solid was extracted with $CHCl_3$. The chloroform solution was filtered and dried. The ^{1}H NMR of the crude product showed several pairs of methyl resonances indicating new Cp′-containing products: 2.06, 1.99; 2.19, 2.12; 2.13, 2.04. In the ^{31}P NMR spectrum only a trace amount of **1** was detected. Major resonances were observed at 44 ppm ($Pt_2(\mu\text{-}S)_2(PPh_3)_4$) and 15 ppm ($PtCl_2(PPh_3)_2$).

A similar reaction was carried out in THF at room temperature. No evidence for **1** was observed in the ^{1}H and ^{31}P NMR spectra of the crude product.

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Supporting Information Available

Tables giving crystal data, positional and thermal parameters, bond distances, and bond angles for **1**. This materials is available free of charge *via* the Internet at http://www.pubs.acs.org

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