

The preparation and structure of methanedithiolatobis(dimethylphenylphosphine)platinum(II), $(\text{PMe}_2\text{Ph})_2\text{Pt}(\text{S}_2\text{CH}_2)$

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Attempts to prepare the complexes $\text{cis-L}_2\text{Pt}(\text{SH})_2$, where $\text{L} = \text{PPh}_3$, PMePh_2 , and PMe_2Ph by treatment of the appropriate dichloro complexes with NaSH in the presence of CH_2Cl_2 have resulted in the isolation of the complexes $\text{L}_2\text{Pt}(\text{S}_2\text{CH}_2)$. The X-ray structure determination of the compound for which $\text{L} = \text{PMe}_2\text{Ph}$ confirms the presence of the $\text{CH}_2\text{S}_2^{2-}$ ligand.

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Des essais réalisés dans le but de préparer les complexes $\text{L}_2\text{Pt}(\text{SH})_2\text{-cis}$, dans lesquels $\text{L} = \text{PPh}_3$, PMePh_2 et PMe_2Ph , par la réaction des complexes dichlorés appropriés avec du NaSH en présence de CH_2Cl_2 n'ont conduit qu'à la formation de complexes $\text{L}_2\text{Pt}(\text{S}_2\text{CH}_2)$. Une détermination de la structure du composé dans lequel $\text{L} = \text{PMe}_2\text{Ph}$, en faisant appel à la diffraction des rayons-X, permet de confirmer la présence du ligand $\text{CH}_2\text{S}_2^{2-}$.

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Introduction

Compounds containing the SH^- ligand have been shown to be good precursors to complexes of catenated polysulfur ligands. Thus, $\text{CpW}(\text{CO})_3\text{SH}$ reacts with sulfur transfer reagents of the type $\text{R-S}_x\text{-Imidyl}$, where $x = 1, 2$ and $\text{Imidyl} = \text{pthalimide}$, to give $\text{CpW}(\text{CO})_3\text{S}_x\text{R}$ (1). The bithiolo complex $\text{Cp}_2\text{Ti}(\text{SH})_2$ reacts with the difunctional sulfur transfer reagents $\text{Imidyl-S}_x\text{-Imidyl}$, where $x = 1, 2$ to give Cp_2TiS_5 , containing the cyclic S_5 ligand (2) and with R-S-Imidyl to give $\text{Cp}_2\text{Ti}(\text{SSR})_2$, when $\text{R} = \text{alkyl}$ and $\text{Cp}_2\text{Ti}(\text{SR})(\text{SSSR})$ when $\text{R} = \text{aryl}$ (3). Thus, the reports (4-6) of the complex $\text{cis}-(\text{PPh}_3)_2\text{Pt}(\text{SH})_2$, **1**, were of particular interest to us. However, despite the fact that three different preparative routes to this complex have been reported, we found it to be somewhat elusive. In this paper, we report our attempts to prepare this complex during which we have observed a novel reaction between CH_2Cl_2 and the reactants $\text{cis-L}_2\text{PtCl}_2/\text{NaSH}$, where $\text{L} = \text{PPh}_3$, PMePh_2 , and PMe_2Ph , to give the complexes $\text{L}_2\text{Pt}(\text{S}_2\text{CH}_2)$, **2-4**. These contain the chelating ligand $\text{CH}_2\text{S}_2^{2-}$ as confirmed by the X-ray structure of complex **4**.

Experimental

The general techniques used to prepare and characterize the complexes were similar to those already described (7). All solvents were of spectrograde quality. Melting points were determined in air on a Thomas-Hoover Uni-melt apparatus and are uncorrected. Proton nmr spectra were obtained on a Varian T-60 spectrometer, using CDCl_3 (Merck, Sharpe and Dohme of Montreal) as solvent and TMS as internal standard. Phosphorus nmr spectra were recorded using a Bruker WH-90 instrument operating in the pulsed Fourier Transform mode. The ^{31}P chemical shifts of the samples in CDCl_3 solution are reported in ppm upfield (negative) from 85% H_3PO_4 as external standard, using D_2O as the lock signal. Elemental analyses were performed by Midwest MicroLab Ltd., Indianapolis, IN. Molecular weights were obtained in benzene or CHCl_3 by Spang Microanalytical

Laboratory, Eagle Harbor, MI. The reactions were conducted under N_2 atmosphere with workup of the products carried out in air. The starting materials $(\text{PPh}_3)_2\text{PtO}_2$ (**8**) and $\text{cis-bis}(\text{phosphine})\text{PtCl}_2$ (**9-11**) were prepared by literature methods. Technical grade ($\geq 98.5\%$) dihydrogen sulfide gas (Linde) was passed through a column of "Drierite" (Anachemia) before use. Sodium hydrogen sulfide was prepared by the standard procedure (12).

A. *cis-Bis(thiolo)bis(triphenylphosphine)platinum(II)*, $\text{cis}-(\text{PPh}_3)_2\text{Pt}(\text{SH})_2$, **1**

H_2S was bubbled through a THF suspension (40 mL) of $(\text{PPh}_3)_2\text{PtO}_2$ (0.52 g, 0.7 mmol) for 15 min. The white precipitate which formed was filtered, washed with THF and hexane, and pumped on (0.35 g, 64%).

Methanedithiolato complexes

The complexes $\text{L}_2\text{Pt}(\text{S}_2\text{CH}_2)$, where $\text{L} = \text{PPh}_3$, **2**; PMePh_2 , **3**; PMe_2Ph , **4**, could be prepared by a number of similar routes as outlined in the Results section. The preparation of **4** is given as a typical example.

B. *Methanedithiolatobis(dimethylphenylphosphine)platinum(II)*, $(\text{PMe}_2\text{Ph})_2\text{Pt}(\text{S}_2\text{CH}_2)$, **4**

The complex $\text{cis}-(\text{PMe}_2\text{Ph})_2\text{PtCl}_2$ (0.88 g, 1.6 mmol) and NaSH (0.25 g, 45 mmol) were refluxed under nitrogen in a mixture of toluene (10 mL) and ethanol (25 mL) for 5 h. The reaction mixture was filtered in air, the filtrate evaporated in *vacuo* to a yellow oil which was extracted with a minimum amount of CH_2Cl_2 , washed with 2×100 mL of H_2O , and dried over anhydrous MgSO_4 . Addition of ether to the CH_2Cl_2 solution and cooling at -12°C gave **4** as yellow crystals which were collected, washed with $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$, and Et_2O , dried in a stream of N_2 , and pumped on for 24 h (0.32 g, 37%).

X-ray structure determination

Crystal data:

$\text{C}_{17}\text{H}_{24}\text{P}_2\text{PtS}_2$ fw = 549.56
 Monoclinic, $P2_1/c$, $a = 9.555(6)$, $b = 16.478(9)$, $c = 13.485(8)$,
 $\beta = 112.67(5)^\circ$, $V = 1959.1 \text{ \AA}^3$, $Z = 4$, $\rho_o = 1.88(2)$, $\rho_c = 1.863$
 g cm^{-3} , ($\text{MoK}\alpha\lambda = 0.71069 \text{ \AA}$, 20°C , $\mu = 75.98 \text{ cm}^{-1}$).

The crystal used in the structure determination was grown from a mixture of methylene chloride and hexanes. It was a small irregularly shaped fragment with no dimension exceeding 0.1 mm. Preliminary photographic data unambiguously established the space group as monoclinic, $P2_1/c$. The unit cell was measured by accurately aligning

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TABLE I. Analytical and physical data

Compound	mp, °C	Analysis								
		% C		% H		% S		Mol. wt.		
		Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	
<i>cis</i> -(PPh ₃) ₂ Pt(SH) ₂	1	215–217	55.0	53.4	4.08	4.46	8.15	8.05		
(PPh ₃) ₂ Pt(S ₂ CH ₂)	2	227–230	55.7	55.1	4.02	4.14	8.02	7.03		
(PMePh ₂) ₂ Pt(S ₂ CH ₂)	3	191–193	48.1	48.1	4.16	4.14	9.51	9.17	673	612
(PMe ₂ Ph) ₂ Pt(S ₂ CH ₂)	4	175–177	37.1	35.8	4.37	4.34	11.7	11.9	549	520

TABLE 2. Nuclear magnetic resonance data of complexes 1–4 and selected literature nmr data for some other platinum(II)–thiolo complexes

Compound	τ	S-R ^a	
		J(Pt—H)	J(P—H)
<i>cis</i> -(PPh ₃) ₂ Pt(SH) ₂	10.36	50.3	8.5
	9.82 ^b	50	8.5
	8.11 ^c	^d	^d
	8.26 ^e	^d	^d
<i>trans</i> -(PEt ₃) ₂ Pt(SH) ₂	11.5 ^f	54	10
<i>trans</i> -(PPh ₃) ₂ Pt(SH)(H)	11.4 ^g	44	10
<i>trans</i> -(PBz ₃) ₂ Pt(SH)(H)	11.39 ^h		
<i>trans</i> -(PEt ₃) ₂ Pt(SH)(H)	10.12 ⁱ	44	8
	11.1 ^j	42	11
<i>trans</i> -(PEt ₃) ₂ Pt(SH)(I)	10.8 ^l	68	11
(PPh ₃) ₂ Pt(S ₂ CH ₂) ^j	4.33	43	1.8
(PMePh ₂) ₂ Pt(S ₂ CH ₂) ^k	4.17	39	1.7
(PMe ₂ Ph) ₂ Pt(S ₂ CH ₂) ^l	3.93	36	1.6

^aChemical shifts of SH or CH₂; phenyl resonances occur in the range 2–3 τ for complexes 1–4; solvent is CDCl₃ unless stated otherwise.

^bReference 5, CD₂Cl₂.

^cReferences 6 and 15.

^dNot reported.

^eReference 16.

^fReference 17, CH₂Cl₂.

^gReference 18.

^hReference 19, Bz = benzyl.

ⁱReference 20, toluene.

^jPhosphorus chemical shift (α) in ppm upfield (negative) from 85% H₃PO₄; α = -21.4, J(Pt—P) = 2979 Hz.

^kP—CH₃: τ 8.27, J(Pt—H) = 32 Hz, J(P—H) = 9 Hz; α = -0.74, J(Pt—P) = 2854 Hz.

^lP—CH₃: τ 8.53, J(Pt—H) = 32 Hz; J(P—H) = 10 Hz; α = 19.90, J(Pt—P) = 2815 Hz.

30 reflections on a Picker Nuclear FACS-1 fully automated diffractometer, and then performing a least-squares calculation. The data were collected using a θ–2θ scan and profile analysis (13). The scan speed was 2.0 deg min⁻¹. A unique quadrant of data was collected in the region ±h, +k, +l, with three standards re-measured every 50 measurement cycles. The intensity of these standards varied randomly by less than 1%. The data were corrected for Lorentz and polarization effects, but due to the small size and poorly definable shape of the crystal no absorption correction was attempted. After data processing of 2561 measured reflections, 1883 having I > σ(I) were retained for the structure solution. The following formulae were used for data reduction:

$$I = [N - B \cdot t_s / t_b]$$

$$\sigma(I) = [N + B(t_s/t_b)^2 + (0.02N)^2]^{1/2}$$

$$(Lp)^{-1} = \sin 2\theta_s (\cos^2 2\theta_n + 1) / (\cos^2 2\theta_m + \cos^2 2\theta_s)$$

where I is the net intensity derived from N, the measured count during the scan of duration t_s; B is the background count estimated from the peak profile analysis (13) during a time t_b; Lp is the Lorentz-polarization correction calculated using 2θ_m and 2θ_s, the diffraction

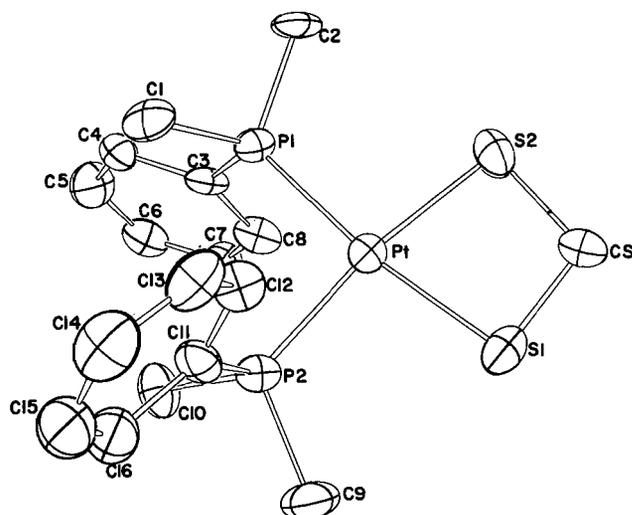


FIG. 1. The molecular configuration and numbering scheme for 4.

TABLE 3. Final positional parameters for 4^a

Atom	X	Y	Z
Pt	4797.0(6)	1094.5(3)	1589.6(4)
P1	6918(4)	1287.6(24)	1279(3)
P2	6041(5)	931.9(25)	3379(3)
S1	2426(5)	939(3)	1629(4)
S2	3171(5)	3770(3)	4814(4)
CS	1536(22)	1036(11)	178(14)
C1	8472(19)	583(9)	1886(14)
C2	6676(20)	3780(10)	4902(13)
C3	7698(17)	2295(8)	1711(10)
C4	9274(16)	2456(11)	2004(12)
C5	9791(19)	3242(12)	2379(16)
C6	8807(22)	3826(10)	2438(14)
C7	7332(18)	3666(10)	2140(13)
C8	6742(19)	2896(8)	1771(12)
C9	4851(23)	1036(12)	4148(16)
C10	7580(19)	1636(10)	4082(14)
C11	6823(17)	-77(9)	3759(11)
C12	3578(17)	4336(9)	2013(13)
C13	3087(19)	3517(10)	1684(16)
C14	2185(22)	3349(11)	692(18)
C15	1772(25)	1038(14)	4895(18)
C16	2241(20)	4753(12)	125(15)

^aThe estimated standard deviations in parentheses are right justified to the least significant digit of the preceding numbers, which have been multiplied by 10⁴.

angles at the monochromator and the sample crystals, respectively.

The structure was solved by conventional heavy atom methods and refined by block-diagonal least squares. All atoms were assigned anisotropic thermal parameters during the final cycles. No attempt was

TABLE 4. Bond lengths (Å) and angles (deg) for **4**

Bond	Length	Bond	Length	Bond	Length	Bond	Length
Pt—S1	2.301(5)	P1—C1	1.81(2)	C3—C4	1.43(2)	C11—C12	1.36(2)
Pt—S2	2.309(5)	P1—C2	1.78(2)	C4—C5	1.41(2)	C12—C13	1.44(2)
Pt—P1	2.244(4)	P1—C3	1.82(1)	C5—C6	1.37(3)	C13—C14	1.31(3)
Pt—P2	2.257(5)	P2—C9	1.82(2)	C6—C7	1.33(2)	C14—C15	1.41(3)
S1—CS	1.82(2)	P2—C10	1.82(2)	C7—C8	1.40(2)	C15—C16	1.37(3)
S2—CS	1.84(2)	P2—C11	1.81(2)	C8—C3	1.37(2)	C16—C12	1.45(2)

Bonds	Angle	Bonds	Angle	Bonds	Angle
S1—Pt—S2	76.1(2)	Pt—P1—C1	117.8(6)	Pt—P2—C9	114.3(7)
S1—Pt—P1	171.1(2)	Pt—P1—C2	114.9(6)	Pt—P2—C10	117.8(6)
S1—Pt—P2	94.6(2)	Pt—P1—C3	110.9(5)	Pt—P2—C11	113.6(5)
S2—Pt—P1	95.0(2)	C1—P1—C2	100.7(8)	C9—P2—C10	101.5(9)
S2—Pt—P2	170.7(2)	C1—P1—C3	106.1(7)	C9—P1—C11	101.9(8)
P1—Pt—P2	94.3(2)	C2—P1—C3	105.2(7)	C10—P2—C11	105.9(7)
Pt—S1—CS	91.3(7)	P1—C3—C4	121(1)	P2—C11—C12	118(1)
Pt—S2—CS	90.4(6)	P1—C3—C8	119(1)	P2—C11—C16	120(1)
S1—CS—S2	102.1(10)	C4—C3—C8	120(1)	C12—C11—C16	122(1)
		C3—C4—C5	117(1)	C11—C12—C13	118(1)
		C4—C5—C6	121(2)	C12—C13—C14	121(2)
		C5—C6—C7	121(2)	C13—C14—C15	120(2)
		C6—C7—C8	121(2)	C14—C15—C16	122(2)
		C7—C8—C3	119(1)	C15—C16—C11	116(2)

made to find or refine hydrogen atoms. Calculated parameters shifts were multiplied by 0.6 after each cycle and anisotropic refinement was terminated when the largest shift was less than 1/10th of the corresponding standard deviation. A final difference Fourier synthesis showed no features above 0.4 e/Å³. The final discrepancy indices were $R_f = 0.056$, $R_{wf} = 0.077$, and the "goodness-of-fit" = 1.30. The final atomic parameters are listed in Table 1.³ The function minimized in the least-squares refinement was: $[\sum w(|F_o| - |F_c|)^2]$, where $w = [(\sigma(F)^2 + 0.03 F^2)]^{-1}$. The conventional discrepancy indices are $R_f = \sum(|F_o| - |F_c|)/\sum|F_o|$, $R_{wf} = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$ and the "goodness-of-fit" is $[\sum w(|F_o| - |F_c|)^2/(m - n)]^{1/2}$.

The program to control the diffractometer and the programs used for the data processing, solution and refinement of the structure were parts of the N.R.C. Package of programs written for the PDP-8a mini-computer by Larson and Gabe (14).

Results

The analytical and physical data of complexes **1–4** are given in Table 1. The nmr data of these complexes and the data reported for some other platinum thiol complexes are given and compared in Table 2. The preparation of **1** was a modification of a literature method (5). The use of chlorinated solvents, recommended by other reports, was found to lead to decomposition. Complex **1** reacts with CH₂Cl₂ in the presence of K₂CO₃ but the product(s) could not be identified. The routes to *cis*-(PPh₃)₂Pt(SH)₂ described by Schmidt and Hoffmann (6, 15) did not work in our hands. Treatment of *cis*-(PPh₃)₂PtCl₂ with H₂S/K₂CO₃ or with NaSH in CH₂Cl₂ gave mostly starting material plus some **2**. While it might be tempting to assign complex **1** to be *cis*-(PPh₃)₂Pt(SH)₂, the elemental analysis of **1**, while close to that required, was not satisfactory. The chemical shift of the S—H protons compares well to that of several

other Pt—SH species but does not agree with any of the three different values reported for *cis*-(PPh₃)Pt(SH)₂ (5, 6, 15, 16). The values of the coupling constants between the S—H protons and the platinum and phosphorus atoms are in the range reported in the literature. However, it must be noted that **1** was quite insoluble and the nmr data may be of material extracted from the bulk and thus not representative. The infrared spectrum of **1** was not informative being similar to other platinum-sulfur systems (7, 9). Bands due to the S—H stretching vibration are often weak and difficult to detect. Reaction of **1** with sulfur transfer reagents led to intractable brown tars.

Treatment of L₂PtCl₂ with NaSH in the presence of CH₂Cl₂ led to the isolation of complexes **2–4**. The characterization of these complexes (Tables 1 and 2) is consistent with their formulation as compounds of the simple methanedithiolato ligand. The complexes were formed in varying yields from treatment of the dichloride with: NaSH in CH₂Cl₂, or H₂S and pulverized K₂CO₃ in CH₂Cl₂ or NaSH in toluene/ethanol followed by extraction of the dried residue with CH₂Cl₂. The latter method appears to work best. A large excess of NaSH was used since it has been found that this promotes the preparation of other MSH species. The methylene is strongly bonded to the sulfur atoms. No reaction occurred when **3** was refluxed under N₂ with lithium metal in THF for 2 h. However, benzyl chloride reacted with **3** to give the dichloride complex and presumably PhCH₂SCH₂SCH₂Ph; however, the latter was not isolated.

The structure of **4** consists of a square planar arrangement of two phosphine ligands and the chelating CH₂S₂²⁻ ligand (Fig. 1). The final positional parameters are listed in Table 3 and the listing of the bond lengths and angles appears in Table 4. The P₂PtS₂C grouping of atom is remarkably flat, deviations from planarity being less than 0.003 Å. The phenyl rings are disposed in an *anti* fashion. Comparison of the bond lengths and angles about the coordinated atoms of **4** with those of the complex (PPh₃)Pt(SCH₂CH₂S), **5** (21), which has a two carbon atom bridge between the two sulfur atoms, reveals the effect of

³ Table 6 (temperature factors for *cis*-(PMe₂Ph)₂Pt(S₂CH₂) and Table 7 (observed and calculated structure amplitudes *cis*-(PMe₂Ph)₂Pt(S₂CH₂)) may be purchased from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ont., Canada K1A 0S2.

TABLE 5. Comparison of selected average bond lengths and angles in $(\text{PMe}_2\text{PH})_2\text{Pt}(\text{S}_2\text{CH}_2)$ and $(\text{PPh}_3)_2\text{Pt}(\text{SCH}_2\text{CH}_2\text{S})$

Parameter	Value	
	S_2CH_2	$\text{SCH}_2\text{CH}_2\text{S}^a$
Pt—P	2.251	2.289
Pt—S	2.305	2.321
C—S	1.83	1.83
S—Pt—S	76.1	87.7
S—Pt—P	94.8	86.8
P—Pt—P	94.3	99.0
Pt—S—C	90.9	102.3

^aReference 21.

the $\text{CH}_2\text{S}_2^{2-}$ ligand (Table 5). As expected the S—Pt—S and Pt—S—C angles are reduced in **4**. Interestingly the average Pt—P and Pt—S bond distances are also slightly shorter in **4**. The S—C—S angle in **4** (102.1) is intermediate between those for $\text{Fe}(\text{CO})_6(\text{S}_2\text{CH}_2)$ (94.55 (22)) and $[\text{Os}_3\text{H}(\text{CO})_{10}]_2(\mu\text{-S}_2\text{CH}_2)$ (105.3 (23)). The $\text{CH}_2\text{S}_2^{2-}$ ligand in the Osmium complex is not chelating. The S—S distance in **4** is 2.841(5) Å, which is longer than that in $\text{Fe}_2(\text{CO})_6(\text{S}_2\text{CH}_2)$ (2.673(2)) and much longer than that in $\text{Fe}_2(\text{CO})_6\text{S}_2$ (2.007(5)) where a S—S bond exists (24).³

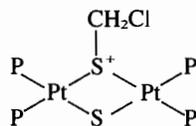
Discussion

Since CH_2Cl_2 can, under certain circumstances, couple two thiol molecules to give a dithioacetal (25), it is tempting to suggest that complexes **2–4** were formed by the reaction of



CH_2Cl_2 with the appropriate *cis*- $\text{L}_2\text{Pt}(\text{SH})_2$ complex. The latter, however, were not isolated except for $\text{L} = \text{PPh}_3$, **1**, and there remains some doubt about its characterization. Complex **1** reacts with CH_2Cl_2 but the products could not be identified. The odor of H_2S was detected during the preparations of **2–4** which is consistent with the reaction of the excess NaSH present with HCl produced by the reaction of CH_2Cl_2 .

An alternative possibility involves the recognition (26) of the strong nucleophilicity of the sulfur atoms in $[\text{Pt}(\mu\text{-S})(\text{PPh}_3)_2]_n$, **6**. This complex reacts with CH_2Cl_2 to give $[\text{Pt}_2(\mu\text{-S})(\mu\text{-SCH}_2\text{Cl})(\text{PPh}_3)_4] \cdot \text{Cl}$ a cation with a bridging $\text{CH}_2\text{S}^+\text{Cl}^-$ ligand, **7**. Complex **7** is reported to decompose in CH_2Cl_2 .



7

Complex **6** has been reported as the product upon treatment of **1** with NaOEt (15). It is possible that **1** could dimerize (7) to give **6** via elimination of H_2S . This type of reaction has been observed for $\text{Cp}_2\text{Zr}(\text{SH})_2$ leading to $[\text{Cp}_2\text{Zr}(\mu\text{-S})_2]$ (2). Conversion of **7** to **2** can be envisioned via internal alkylation of the bridging sulfide ligand (26).

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