conversion is not direct. Rather, oxidation appears to proceed through the dissociation of an ACAC moiety to give the green VO(SHED), the only isolated complex in which the ligand is tetradentate with a coordinated alkoxide. The pervanadyl dimers most likely dissociate into monomeric units when dissolved in DMF or DMSO. It is difficult to establish whether monomers are formed in acetonitrile due to the low solubility in this solvent. When anhydrous acid is added to an acetonitrile solution of **1** or **2**, the red $VO(OH)HSHED^+$ complex is formed. This compound is stable, and the acid-base chemistry is reversible, up to 0.8 equiv. Beyond this point, a deep blue monooxovanadium(V)-$HSHED^{2+}$ complex is observed, which is too unstable to be isolated.

Potential Biological Relevance. The vanadium bromoperoxidases are known to contain vanadium(V) in the resting oxidation level of the enzyme, and no evidence has been forwarded to suggest vanadium(IV) as a participant in catalysis. To date, every well-characterized monooxovanadium(V)[31-34] and bare vanadium(V)[36] complexes containing phenolates exhibit strong ligand to metal charge-transfer absorption spectra in the 600-nm range. Clearly such an absorbance is not present, at least in the isolated forms, in the vanadium peroxidases. This leads to the conclusion that bare vanadium(V) or monooxovanadium(V) coordinated to a phenolate is not an appropriate description for this enzyme's resting state. The following possibilities for the metal site then results: (1) tyrosine may not be a ligand to vanadium in these enzymes; (2) active-site vanadium may be in the form of the pervanadyl moiety rather than bare V(V) or VO^{3+}; (3) possibilities 1 and 2 both may be operable. Given the strong aqueous reactivity of bare V(V) or VO^{3+}, it is most likely that at least point 2 is correct.

Floriani[20] has suggested the vanadate/carboxylate analogy to understand the reactivity and structural possibilities for the pervanadyl unit. Support for this notion comes from the facile protonation of the VO_2^+ unit and the isolation of vanadate esters such as $VO(OC(CH_3)_3)(8\text{-}Q)_2$.[21] One possible intermediate in the enzymatic reaction is hypobromite coordinated to V(V), $VO(OBr)^{2+}$. The corresponding acyl hypobromite, RCO(OBr), is an excellent reagent for bromodecarboxylation of aliphatic or aromatic carboxylic acids in the Hunsdiecker reaction[37] and, more interestingly, can brominate directly activated aromatics in a "non-Hunsdiecker" halogenation.[38] Thus, extension of this analogy to the enzymatic system may prove fertile. The SHED complexes described herein may provide an useful entry into the reactivity of these complexes due to the open sixth coordination site. Thus, direct reaction with hydrogen peroxide to generate materials similar to those described by Stomberg[24-26] or the joint reaction of hydrogen peroxide and bromide with $[VO_2(HSHED)]_2$ may provide reactivity analogues for the enzymatic process. In addition, the ^{51}V NMR spectra of these and related complexes may be useful in defining the first coordination sphere ligands of the peroxidase.[39-42] The value of -529 ppm in DMSO vs $VOCl_3$ indicates that the $VO_2(HSHED)$ complex does not model well the extraordinarily large shift seen for the enzyme[40] (-1200 ppm). The NMR behavior of other analogues of these complexes is presently being explored.

Acknowledgment. We thank Prof. Alison Butler (UCSB) for allowing us to quote her values for the ^{51}V NMR spectra of the vanadium SHED complexes prior to publication. Dr. Joseph Bonadies is thanked for a very useful discussion relating to this and the EHPG work described in this paper. V.L.P. thanks the G. D. Searle Family/Chicago Community Trust for a Biomedical Research Scholar's Award (1986-1989).

Supplementary Material Available: Tables 9, 14, and 19, listing anisotropic thermal parameters, Tables 10, 15, and 20, listing fractional atomic positions for hydrogen atoms, Tables 11, 16, and 21, listing the complete set of bond distances, Tables 12, 17, and 22, listing the complete set of bond angles, and Figures 7, 8, and 9, providing complete numbering schemes for **1**, **2**, and **5**, respectively (15 pages); Tables 13, 18, and 23, listing observed and calculated structure factors (20 pages). Ordering information is given on any current masthead page.

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Synthesis and Characterization of the Disulfanoplatinum Complexes *cis*-$(PPh_3)_2Pt(phth)SSR$, Where phth = Phthalimido and R = CH_2Ph, $CH_2CH_2CH_3$, $CHMe_2$, *p*-C_6H_4Me, phth

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Disulfano complexes of the type *cis*-$(PPh_3)_2Pt(phth)SSR$, where phth = phthalimido and R = CH_2Ph, $CH_2CH_2CH_3$, $CHMe_2$, 4-C_6H_4Me, phth, have been prepared via oxidative addition of RSS(phth) to $(PPh_3)_2Pt(C_2H_4)$, wherein S-N bond cleavage occurs. Similarly, the thiolato analogues *cis*-$(PPh_3)_2Pt(phth)SR$ were obtained by using RS(phth). *cis*-$(PPh_3)_2Pt(phth)SSR$ complexes, where R = CH_2Ph, phth, are desulfurized by PPh_3 to give *cis*-$(PPh_3)_2Pt(phth)SCH_2Ph$ and *cis*-$(PPh_3)_2Pt(phth)_2$, respectively. Treatment of *cis*-$L_2Pt(SCH_2Ph)_2$, where L = PPh_3, $PMePh_2$, PMe_2Ph, with (phth)SS(phth) resulted in stepwise displacement of the phenylmethanethiolato ligands by phthalimido groups to give first *cis*-$L_2Pt(phth)SCH_2Ph$ and upon further reaction *cis*-$L_2Pt(phth)_2$ for L = PPh_3, $PMePh_2$ accompanied by the formation of organic polysulfanes RS_xR, where x = 2-4. At -20 °C *trans*-$(PMe_2Ph)_2Pt(phth)SCH_2Ph$ was isolated. The complexes *cis*-$L_2Pt(phth)_2$ were also prepared from *cis*-L_2PtCl_2 and potassium phthalimide.

Introduction

Organic sulfides, disulfides, and trisulfides are common and important species. While thiolato ligands (RS^-) are well-known,[1] simple disulfano (RSS^-) ligands are rare. In view of the propensity of sulfur to catenate, it would not be surprising if such species had an extensive chemistry with transition metals. Recently, a CuSSR species[2] and a RSS^- ligand[3] bridging two molybdenum atoms were reported in model studies of copper enzymes and

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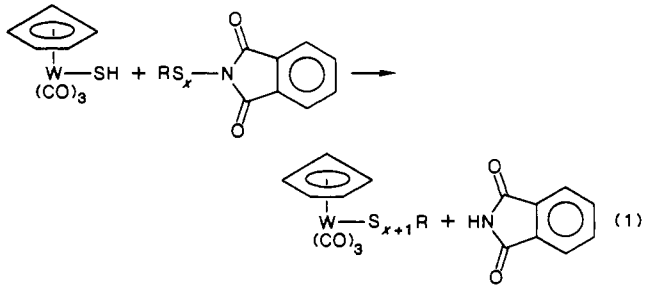
Table I. Analytical and Physical Data

compd	no.	yield, %	mp, °C	%C calcd	%C found	% H calcd	% H found	% S (% N) calcd	% S (% N) found
cis-$(PPh_3)_2Pt(phth)SSCH_2Ph$	**1a**	81	190–192	60.0	59.3	4.02	4.21	6.27	5.87
cis-$(PPh_3)_2Pt(phth)SSCH_2CH_2CH_3$	**1b**	90	160–162	58.0	57.3	4.22	4.22	6.58	5.91
cis-$(PPh_3)_2Pt(phth)SSCHMe_2$	**1c**	79	181–183	58.0	58.6	4.22	4.43	6.58	6.93
cis-$(PPh_3)_2Pt(phth)SS\text{-}4\text{-}C_6H_4Me$	**1d**	84	184–185	60.0	60.9	4.02	4.13	6.27	5.81
cis-$(PPh_3)_2Pt(phth)SSphth$	**1e**	90	206–207	58.1	58.2	3.53	3.04	5.95	5.23
cis-$(PPh_3)_2Pt(phth)SCH_2Ph$	**2a**	83	210–211	61.9	59.7	4.15	4.13	3.24	3.01
cis-$(PPh_3)_2Pt(phth)SCH_2CH_2CH_3$	**2b**	77	205–207	60.0	59.5	4.36	4.32	3.40	3.30
cis-$(PPh_3)_2Pt(phth)SCHMe_2$	**2c**	85	202–203	60.0	59.4	4.36	4.62	3.40	2.98
cis-$(PPh_3)_2Pt(phth)S\text{-}4\text{-}C_6H_4Me$	**2d**	77	224–226	61.9	62.3	4.15	4.27	3.24	3.81
cis-$(PPh_3)_2Pt(phth)Sphth$	**2e**	91	257–259	59.8	59.0	3.64	3.72	3.07	3.09
cis-$(PMePh_2)_2Pt(phth)SCH_2Ph\cdot CH_2Cl_2$[a]	**4**	52	180–182	53.1	53.0	4.11	4.40	3.37	3.69
trans-$(PMe_2Ph)_2Pt(phth)SCH_2Ph$	**5**	82	125–127	50.3	50.2	4.46	4.48	4.32	4.60
cis-$(PPh_3)_2Pt(phth)_2\cdot CH_2Cl_2$[a]	**3a**	94	>250	58.0	57.2	3.65	3.76	(2.55)	(2.37)
cis-$(PMePh_2)_2Pt(phth)_2$	**3b**	88	>250	56.8	56.7	3.83	3.94	(3.16)	(3.74)
cis-$(PMe_2Ph)_2Pt(phth)_2$	**3c**	88	117–119	50.3	50.3	3.93	3.88	(3.67)	(4.05)

[a] A peak due to the appropriate amount of CH_2Cl_2 was detected in the NMR spectra of these complexes.

nitrogenase, respectively. Successive insertion by sulfur atoms into a tungsten–carbon bond has been reported,[4] leading to a η^2-disulfano ligand. In earlier work we adapted the methodology[5] used to prepare unsymmetrical organic di- and trisulfanes to the synthesis of complexes containing disulfano and trisulfano ligands. Treatment of sulfur-transfer reagents of the type $RS_x(phth)$, where phth = phthalimido-*N* and x = 1, 2 with the metal mercapto complex $CpW(CO)_3SH$ gave polysulfanotungsten species of the type $CpW(CO)_3S_xR$,[6] where x = 2,3 (eq 1). Complexes of the



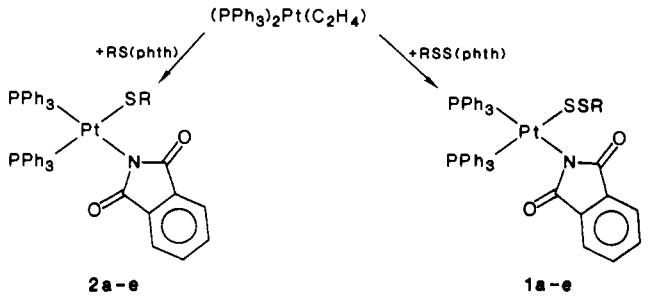
(1)

type $Cp_2Ti(SSR)_2$ and $Cp_2Ti(SR)(SSSR)$ have also been prepared[7] by using this class of sulfur-transfer reagent.

Organic disulfides have been reported to oxidatively add to low-valent platinum complexes with cleavage of the sulfur–sulfur bond.[8] This suggested that RSS(phth) might be a precursor to platinum complexes containing the PtS(phth) moiety. Such a species might, in analogy with the case for RS(phth),[5] react with thiols (R′SH) to give platinum disulfanes (PtSSR′). The reaction of $S_2(Nfl)_2$, where Nfl = fluoren-9-ylideneamino, with $(PPh_3)_2Pt(C_2H_4)$ to give *cis*-$(PPh_3)_2Pt(S(Nfl))_2$ has been briefly reported.[8e] The reactions of $(PPh_3)_2Pt(C_2H_4)$ with RSS(phth) are reported below. In addition Deutsch et al. have shown that the sulfur-transfer reagents RS(phth) react with cobalt thiolate complexes (CoSR′) to give rare coordinated disulfide species (Co-SR′SR).[9] Thus, the reactions of *cis*-$L_2Pt(SR)_2$, where L = PPh_3, $PMePh_2$, PMePh and R = CH_2Ph, with sulfur-transfer reagents were also investigated and are reported herein.

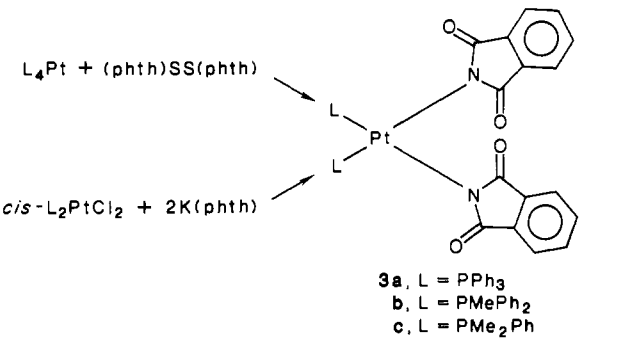
Results

Treatment of $(PPh_3)_2Pt(C_2H_4)$ with sulfur-transfer reagents of the type RSS(phth), where R = alkyl, aryl, phthalimido, gave high yields of disulfanoplatinum complexes (**1a–e**). The thiolato analogues *cis*-$(PPh_3)_2Pt(phth)SR$ (**2a–e**) were prepared from



a, R = CH_2Ph; **b**, R = $CH_2CH_2CH_3$; **c**, R = $CHMe_2$; **d**, R = 4-C_6H_4Me; **e**, R = phth

thiophthalimides, RS(phth). $(PPh_3)_4Pt$ and $(PMePh_2)_4Pt$ reacted with (phth)SS(phth) to give *cis*-$(PPh_3)_2Pt(phth)_2$ (**3a**) and *cis*-$(PMePh_2)_2Pt(phth)_2$ (**3b**), respectively. **3a**, **3b**, and *cis*-



3a, L = PPh_3
b, L = $PMePh_2$
c, L = PMe_2Ph

$(PMe_2Ph)_2Pt(phth)_2$ (**3c**) were also prepared via simple displacement reactions between the appropriate dichloro complexes and potassium phthalimide. On the other hand $(PPh_3)_4Pt$ and (phth)S(phth) gave a mixture of **2e** and **3a**. The compounds are cream to light orange and dissolve in CH_2Cl_2 to give air-stable yellow or orange solutions. Analytical and spectroscopic data are given in Tables I and II, respectively. The X-ray structure of **1c** has been determined and confirms the disulfane linkage.[6a]

The isolation of sulfur-free **3a** from $(PPh_3)_4Pt$ and (phth)SS(phth) prompted treatment of the expected product **1e** with excess PPh_3. This did give **3a**. The desulfurization of **1a** by $PMePh_2$

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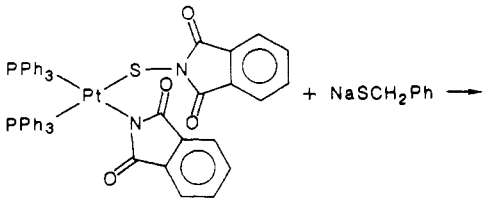
Table II. Selected Spectroscopic Data (IR, NMR) for **1a–e**, **2a–e**, **3a–c**, **4**, and **5**[a]

compd	no.	ν(CO), cm^{-1}	^{1}H[b] τ	^{31}P[c] trans to S α	trans to S J(Pt–P)	trans to N α	trans to N J(Pt–P)	J(P–P)
cis-$(PPh_3)_2Pt(phth)SSCH_2Ph$	**1a**	1660	6.19 (bs)	−19.3	2753	−12.4	3391	21
cis-$(PPh_3)_2Pt(phth)SSCH_2CH_2CH_3$	**1b**	1660	9.30 (t)[d]	−19.4	2732	−12.5	3406	22
cis-$(PPh_3)_2Pt(phth)SSCHMe_2$	**1c**	1660	9.18 (d)[e]	−19.2	2723	−12.8	3407	22
cis-$(PPh_3)_2Pt(phth)SS$-4-C_6H_4Me	**1d**	1660	7.94 (s)	−19.2	2789	−11.4	3377	20
cis-$(PPh_3)_2Pt(phth)SSphth$	**1e**	1660 1730		−18.7	2844	−9.8	3328	19
cis-$(PPh_3)_2Pt(phth)SCH_2Ph$	**2a**	1660	6.39 (td)[f]	−22.2	2785	−11.9	3405	18
cis-$(PPh_3)_2Pt(phth)SCH_2CH_2CH_3$	**2b**	1660	9.45 (t)[g]	−22.3	2775	−12.2	3422	19
cis-$(PPh_3)_2Pt(phth)SCHMe_2$	**2c**	1660	9.02 (d)[h]	−22.3	2775	−11.9	3424	19
cis-$(PPh_3)_2Pt(phth)S$-4-C_6H_4Me	**2d**	1660	7.63 (s)	−20.0	2884	−10.6	3368	21
cis-$(PPh_3)_2Pt(phth)Sphth$	**2e**	1665 1725		−19.6	2882	−9.5	3319	20
cis-$(PMePh_2)_2Pt(phth)SCH_2Ph$	**4**	1660	6.32 (td)[i]	−2.3	2688	5.7	3306	22
trans-$(PMe_2Ph)_2Pt(phth)SCH_2Ph$	**5**	1660	7.17 (t)[j]					
cis-$(PPh_3)_2Pt(phth)_2$	**3a**	1665				−2.3 (t)	3340	
cis-$(PMePh_2)_2Pt(phth)_2$	**3b**	1670	*k*			9.8 (t)	3215	
cis-$(PMe_2Ph)_2Pt(phth)_2$	**3c**	1670	*l*			20.6 (t)	3223	
cis-$(PPh_3)_2Pt(SCH_2Ph)_2$[m]			5.62 (td)[n]	−24.1	2888 (t)			

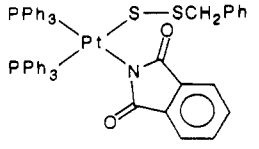
[a] IR samples were taken as KBr disks, ±5 cm^{-1}. NMR samples were in $CDCl_3$ solvent. All J values are in Hz. Abbreviations: s = singlet; d = doublet; t = triplet; m = multiplet; td = triplet of doublets; b = broad. [b] Resonances of the following thiolato or disulfano protons: CH_2Ph, $(CH_2CH_2CH_3)_2$, 4-$C_6H_4CH_3$. Phenyl and phthalimido resonances were observed in the range τ 7–8 (m). [c] ^{31}P chemical shifts in ppm upfield (negative) from 85% H_3PO_4. All the complexes displayed a pattern of two overlapping triplets of doublets except where noted. [d] J(H–H) = 7 Hz. $\tau(CH_2CH_2CH_3)$: 2.39 (t, J(H–H) = 7 Hz), 1.21 (m). [e] J(H–H) = 7 Hz. $\tau(CHMe_2)$: 2.75 (m, J(H–H) = 7 Hz). [f] J(Pt–H) = 29 Hz; J(P–H) = 5 Hz. [g] J(H–H) = 7 Hz. $\tau(CH_2CH_2CH_3)$: 4.40 (m), 1.34 (m). [h] J(H–H) = 7 Hz. $\tau(CHMe_2)$: 5.05 (m). [i] J(Pt–H) = 33 Hz; J(P–H) = 5 Hz. $\tau(PCH_3Ph_2)$: 1.99 (td, J(Pt–H) = 29 Hz, J(P–H) = 10 Hz, trans to phth), 1.49 (td, J(Pt–H) = 32 Hz, J(P–H) = 10 Hz, trans to SCH_2Ph). [j] J(Pt–H) = 34 Hz. $\tau(P(CH_3)_2Ph)$: 1.70 (tt, J(Pt–H) = 29 Hz, J(P–H) = 4 Hz). $\alpha(PMe_2Ph)$: 5.4 (t, J(Pt–P) = 2649 Hz). [k] $\tau(PCH_3Ph_2)$: 1.72 (td, J(Pt–H) = 34 Hz, J(P–H) = 10 Hz). [l] $\tau(P(CH_3)_2Ph)$: 1.48 (td, J(Pt–H) = 32 Hz, J(P–H) = 11 Hz). [m] Data from ref 14. [n] J(Pt–H) = 47 Hz; J(P–H) = 6 Hz.

was followed by NMR. The singlet due to the benzyl methylene protons was replaced by the triplet of doublets due to the thiolato complex **2a**. Concomitantly, the signal due to the methyl group of free $PMePh_2$[10] decreased in intensity accompanied by the appearance and growth of a band corresponding to the methyl group of $SPMePh_2$.[11]

The presence of sulfur–nitrogen bonds in **1e** and **2e** suggested that these might be precursors to tri- and disulfano complexes via treatment with thiols as originally designed. However, both are unreactive to thiols under a variety of conditions, starting materials being recovered or decomposition occurring. Treatment of **2e** with $NaSCH_2Ph$ in THF gave **1a**, but the sulfur chain in **1e** could not be extended in this way.



2e



1a

Complexes of the type *cis*-$L_2Pt(SCH_2Ph)_2$, where L = PPh_3, $PMePh_2$, PMe_2Ph, react in air with (phth)SS(phth), resulting in stepwise replacement of the thiolato ligands by phthalimido groups. For L = PPh_3, **2a** was isolated from the reaction after 25 h, while after 72 h the disubstituted complex **3a** was isolated. For L = $PMePh_2$, reaction at room temperature gave **3b** but reaction at −20 °C gave the monothiolate *cis*-$(PMePh_2)_2Pt(phth)SCH_2Ph$ (**4**). The stepwise nature of the process was observed by following the reaction at −20 °C by proton NMR. Two triplets of doublets due to the phosphine methyl groups rapidly displaced the one due to the starting bis(thiolato) complex, indicating the formation of monosubstituted **4**. Within 1 h, these peaks began to decrease in intensity in favor of the triplet of doublets characteristic of **3b**. A resonance at τ 5.85 appeared immediately, consistent with the formation of $PhCH_2S(phth)$ and/or $PhCH_2S_4CH_2Ph$.[12] For L = PMe_2Ph the product at −20 °C was *trans*-$(PMe_2Ph)_2Pt(phth)SCH_2Ph$ (**5**), while an intractable mixture resulted at room temperature. Treatment of *cis*-$(PMePh_2)_2Pt(SCH_2Ph)_2$ with $PhCH_2S(phth)$ at room temperature gave only **3b**. Reasonable yields (50–80%) were achieved when the reactions were conducted in air; however, use of a nitrogen atmosphere gave black tars and no isolable products. $PhCH_2S_xCH_2Ph$, where x = 2–4, and $PhCH_2S_y(phth)$, where y = 1, 2, were detected in the NMR spectra of the residues obtained by evaporation of the mother liquors of the reactions in air.

In the IR spectra of organic phthalimido compounds and of the sulfur-transfer reagents the ketonic stretching vibration ν(CO, phth) appears as a broad band in the region[13] 1720–1750 cm^{-1}. It shifts to 1585–1620 cm^{-1} in the phthalimido anion.[13a] The bands observed between 1660 and 1670 cm^{-1} for **1a–e**, **2a–e**, **3a–c**, **4**, and **5** (Table II) are assigned to the presence of the Pt–phth moiety. In addition to this band, the complexes **1e** and **2e** displayed a band in the region 1725–1730 cm^{-1}, which is assigned to the sulfur-bonded phthalimido group. Thus ν(CO, phth) is a sensitive indicator of the presence of anionic, metal-bound, or sulfur-bound phthalimido residues.

The patterns observed for the benzyl methylene and phosphine methyl protons in the ^{1}H NMR spectra (Table II) are similar to those observed for similar bis(thiolato) complexes[14] and allows

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unambiguous assignment of cis geometry to **2a**, **3b,c**, and **4** and trans to **5**. Since the two phosphine ligands in the asymmetrical complex *cis*-$(PMePh_2)_2Pt(SCH_2Ph)(phth)$ (**4**) are in different environments (trans to different ligands), two overlapping triplets of doublets are obtained for the phosphine methyl group. Inspection of the values of $J(Pt-CH_3)$ for symmetrical cis complexes containing the ligands $PMePh_2$ and PMe_2Ph indicates that they are above 30 Hz in the diphthalimido complexes **3b,c** but below this in bis(thiolato) derivatives.[14] On this basis, the upfield signal in the spectrum of **4** may be assigned to the phosphine ligand trans to the phenylmethanethiolato ligand.

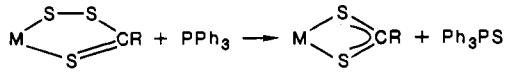
Cis geometry is assigned to **1a–e**, **2a–e**, and **4** on the basis of their ^{31}P NMR spectra. Two signals with the appropriate satellites due to coupling to ^{195}Pt are further split by phosphorus–phosphorus coupling. The NMR trans influence[15] of the phthalimido ligand is clearly smaller than that of the thiolato ligand, as indicated by comparison of the $^1J(Pt-P)$ coupling constants of the *cis*-diphthalimido complexes **3a–c** (ca. 3300 Hz) and those of the *cis*-bis(thiolato) analogues (ca. 2800 Hz).[14] Thus, in all cases the downfield signal is assigned to the phosphine trans to the phthalimido ligand.

Two carbonyl carbon peaks were observed in the ^{13}C NMR spectra of **1e** (176.0 and 167.4 ppm) and **2e** (175.8 and 170.0 ppm), as expected. This resonance occurs at 167.8 ppm in $PhCH_2Sphth$ and at 169.7 ppm in phthalimide. Thus, as the number of intervening sulfur atoms between the phthalimido group and the platinum atom increases, the chemical shift of the carbonyl carbon approaches that of the sulfur-transfer reagent.

Discussion

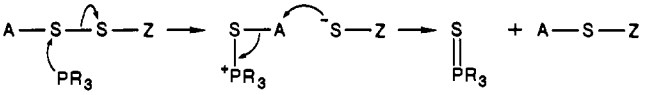
The sulfur-transfer reagents RSS(phth) oxidatively add to $(PPh_3)_2Pt(C_2H_4)$ with cleavage of the S–N bond and not the S–S bond. The result is a direct synthesis of the series of platinum disulfano complexes **1a–e**. This is similar to the reported oxidative addition of C_6F_5SSCl to Vaska's compound,[16] where cleavage of the S–Cl bond is observed. Considerable reactivity of the S–N bond in sulfur-transfer reagents has been observed with $Fe_2(CO)_9$.[17] These reagents also oxidatively add to $Cp_2Ti(CO)_2$ with S–N bond cleavage.[18] This reaction may be a general route to metallodisulfanes.

The platinum disulfanes **1a–e** are stable with respect to spontaneous loss of sulfur, unlike disulfanes of the type $CpW(CO)_3SSR$, which lose sulfur in solution to give the thiolato complexes.[6] However, **1a** was desulfurized by PPh_3 to give **2a**. Interestingly **1e** lost both sulfur atoms upon treatment with PPh_3 to give **3a**. The tungsten disulfanes are also easily desulfurized by PPh_3, and abstraction of a sulfur from metal trithio cumates has been reported:[19]



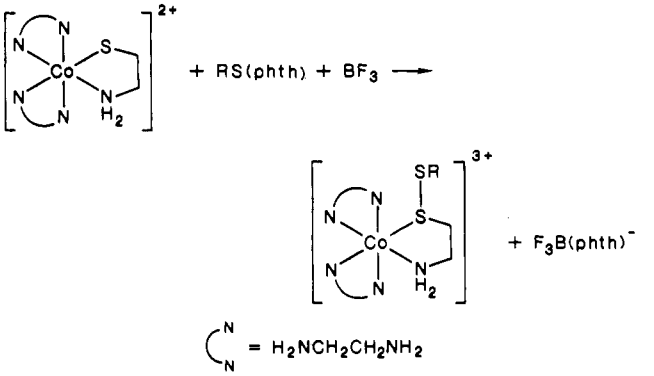
Organic disulfides are normally not desulfurized by PPh_3 unless "activating" terminal groups such as acyl or 2-alkynyl[20] are present. Thus, transition-metal substituents appear to activate the S–S bond.

The desulfurization of "activated" organic disulfides by phosphines is thought to involve the formation of a phosphonium salt[20b,21] with subsequent "backside" attack by the thiolato anion to eliminate the phosphine sulfide. In the case of an unsymmetrical disulfide ASSZ attack is thought to occur on the more negatively polarized sulfur atom:



In **1a** this is expected to be the sulfur atom adjacent to the benzyl group. This is supported by labeling studies of metal trithio cumates, which showed that the sulfur atom adjacent to the carbon atom was abstracted by PPh_3.[19c] Similar studies are required to determine which sulfur in **1a** is lost. In the case of phthalimidodisulfanes (A = R, Z = phth) desulfurization is thought[22] to involve attack on the sulfur atom attached to the nitrogen atom with displacement of the phthalimido anion. Extrapolating to **1e**, one might expect the phthalimido anion generated to attack the metal center, leading to the formation of a stable Pt–phth bond and loss of both sulfur atoms as observed.

A similar tendency is observed in the reactions of *cis*-$L_2Pt(SCH_2Ph)_2$, where L = PPh_3, $PMePh_2$, PMe_2Ph, with sulfur-transfer reagents, which gave complexes containing Pt–phth bonds (**3a–c**) and polysulfides that were identified in solution. The conversion of chelating thiolato ligands to disulfide moieties via reaction with RS(phth) has been reported:[9]



The probable mechanism was described in terms of displacement of the phthalimido anion and formation of a S–S bond, the final coordinated disulfide being stabilized by the chelate effect. The presence of BF_3 led to the formation of an adduct with $phth^-$, which also inhibited displacement of the disulfide ligand. In the platinum systems these factors are not present and displacement is observed.

The role of the phosphine ligands in governing the outcome of these reactions is worthy of brief comment. At room temperature complexes **2a**, **3b**, and **5** are formed, for L = PPh_3, $PMePh_2$, and PMe_2Ph, respectively (although the last mentioned is not a clean reaction). That dual substitution occurs at room temperature in the case of $PMePh_2$ to give **3b** and not **4** may be attributed to the higher trans effect of this phosphine over PPh_3. The isomerization that leads to **5** is less easy to explain. Theoretical considerations suggest that ligands with high trans effects stabilize a 5-coordinate trigonal-bipyramidal transition state.[23] Its lifetime may be long enough in the case of PMe_2Ph to permit rearrangment of the ligands so as to give a trans isomer. Calculations indicate that the intermediate with the stronger σ-donors in the axial positions has the lowest energy.[24] Hence, it may be that the difference between the σ-donating abilities of the phosphines and the phenylmethanethiolato ligand is significant enough to affect the stereochemistry of the product only when L = PMe_2Ph.

Experimental Section

The general experimental techniques have been described previously.[14] ^1H nuclear magnetic resonance (NMR) spectra were obtained on a Varian XL-200 FTNMR spectrometer. Chemical shifts are reported in τ units relative to tetramethylsilane (TMS) as internal standard, with $CDCl_3$ as solvent unless otherwise noted. Phosphorus NMR spectra were

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recorded on the XL-200 or a Bruker WH-90 spectrometer, operating in the pulsed Fourier transform mode, the samples being in $CDCl_3$ or C_6D_6 solution. Chemical shifts (α) are reported in ppm downfield (positive) from 85% H_3PO_4 as external standard, with D_2O as the lock signal. Midrange infrared spectra were recorded on a Perkin-Elmer Model 297 grating spectrophotometer, calibrated with the 1601-cm^{-1} band of polystyrene. Far-IR spectra were obtained on a Nicolet 7199 FTIR instrument. Reactions were monitored and the purity of products was checked by thin-layer chromatography on Eastman "Chromagram" sheets (6063 alumina with fluorescent indicator). Column chromatography was carried out in air by using 80–200-mesh activated alumina from Anachemia Chemicals Ltd., Montreal.

The following complexes were prepared by published methods: $(PPh_3)_2Pt(C_2H_4)$,[25] $(PPh_3)_4Pt$[26] $(PMePh_2)_4Pt$[27] and *cis*-$L_2Pt(SCH_2Ph)_2$,[14] where L = PPh_3, $PMePh_2$, PMe_2Ph. The sulfur-transfer reagents RS_xphth, where phth = phthalimido, R = alky, aryl, phth, and x = 1, 2, were prepared according to literature methods.[12a,28]

A. Preparation of *cis*-$(PPh_3)_2Pt(phth)SSR$ (1a–e). *cis*-((Phenylmethyl)disulfano)(phthalimido)bis(triphenylphosphine)platinum(II), *cis*-$(PPh_3)_2Pt(phth)SSCH_2Ph$ (1a). The preparation of **1a–e** are very similar to that of **1a**, which follows. *N*-((phenylmethyl)dithio)phthalimide (0.12 g, 0.40 mmol) in 15 mL of toluene was added dropwise under N_2 to $(PPh_3)_2Pt(C_2H_4)$ (0.31 g, 0.41 mmol) in 15 mL of toluene. The reaction mixture was stirred under N_2 at room temperature for 7 h. The white precipitate that formed was filtered and redissolved in CH_2Cl_2 and the solution filtered through Celite. Recrystallization (from CH_2Cl_2/ether) of the residue obtained after evaporation of the solvent gave white crystals (0.33 g, 81%).

1d was recrystallized from toluene/ether, and for **1e** the appropriate reagents were added as solids to toluene to give the orange precipitate after 1 h.

B. Preparation of *cis*-$(PPh_3)_2Pt(phth)SR$ (2a–e). *cis*-(Phenylmethanethiolato)(phthalimido)bis(triphenylphosphine)platinum(II), *cis*-$(PPh_3)_2Pt(phth)SCH_2Ph$ (2a). The preparations of **2b–e** are essentially identical with the preparation of **2a** described herein. $(PPh_3)_2Pt(C_2H_4)$ (0.19 g, 0.25 mmol) and *N*-((phenylmethyl)thio)phthalimide (0.07 g, 0.26 mmol) were stirred for 6 h in 20 mL of toluene, under N_2, at room temperature. The reaction mixture was dried in vacuo, the residue was extracted with CH_2Cl_2 in air, and the solution was filtered through Celite. The volume of the filtrate was reduced by vacuum distillation and ether added. Crystallization at −12 °C gave yellow crystals, which were washed with ether and dried in vacuo for 24 h (0.21 g, 83%).

2b was recrystallized from CH_2Cl_2/ether, while **2e** precipitated from solution, was collected on a filter, and was washed with hexane.

C. Reaction of *cis*-(Phthalimidothio)(phthalimido)bis(triphenylphosphine)platinum(II) (2e) with Sodium Phenylmethanethiolate. Excess sodium metal (0.05 g, 2,2 mmol) was treated with $PhCH_2SH$ (0.03 mL, 0.25 mmol) in 10 mL of dry THF. The solution was separated from the unreacted sodium metal by means of a syringe and added dropwise under N_2 to a suspension of *cis*-$(PPh_3)_2Pt(phth)(Sphth)$ (0.24 g, 0.23 mmol) in 20 mL of THF. The reaction mixture was stirred for 1 h and then filtered (under N_2) through Celite. The filtrate was concentrated to about 5 mL under vacuum, and crystallization was induced by the addition of ether. Yellow crystals (0.10 g, 43%) of *cis*-$(PPh_3)_2Pt(phth)$-$SSCH_2Ph$ (**1a**) formed, which were slightly contaminated by phthalimide.

D. Reaction of *cis*-(Phthalimidodisulfano)(phthalimido)bis(triphenylphosphine)platinum(II) (1e) with Triphenylphosphine. A suspension of *cis*-$(PPh_3)_2Pt(phth)SSphth$ (0.13 g, 0.12 mmol) and PPh_3 (0.033 g, 0.13 mmol) in 10 mL of acetone was stirred under N_2 at room temperature for 40 h. The precipitate was collected on a filter and dried in vacuo to give 0.07 g (58%) of *cis*-$(PPh_3)_2Pt(phth)_2$, identified by comparison of its infrared spectrum to that of an authentic sample.

E. Preparation of *cis*-$L_2Pt(phth)_2$ (3a–c). *cis*-Diphthalimidobis(triphenylphosphine)platinum(II), *cis*-$(PPh_3)_2Pt(phth)_2$ (3a). A suspension of *cis*-$(PPh_3)_2PtCl_2$ (0.32 g, 0.41 mmol) in 20 mL of CH_2Cl_2 was treated with potassium phthalimide (0.16 g, 0.86 mmol) and stirred in air at room temperature for 24 h. The resulting suspension was filtered through Celite and the filtrate taken to dryness under vacuum. The residue was recrystallized from CH_2Cl_2/hexane to give white crystals (0.39 g, 94%).[29] **3b** and **3c** were prepared in the same manner.

F. Reaction of *cis*-$L_2Pt(SCH_2Ph)_2$, Where L = PPh_3, $PMePh_2$, PMe_2Ph, with phthSSphth. L = PPh_3. *cis*-$(PPh_3)_2Pt(SCH_2Ph)_2$ (1.0 g, 1.0 mmol) and *N,N'*-dithiobis(phthalimide) (0.34 g, 0.95 mmol) were stirred together in 20 mL of toluene at room temperature for 25 h. The cream-colored precipitate was filtered off and recrystallized from CH_2Cl_2/ether to give off-white crystals of *cis*-$(PPh_3)_2Pt(phth)SCH_2Ph$ (**2a**), which were washed with ether and dried in vacuo for 24 h (0.60 g, 61%). When the reaction time was extended to 72 h, the disubstituted complex *cis*-$(PPh_3)_2Pt(phth)_2$ (**3a**) was obtained in the same manner in 48% yield. Refluxing the reaction mixture over a shorter period led to decomposition.

L = $PMePh_2$. *cis*-$(PMePh_2)_2Pt(SCH_2Ph)_2$ (0.71 g, 0.84 mmol) and *N,N'*-dithiobis(phthalimide) (0.30 g, 0.84 mmol) were stirred together in 30 mL of toluene at −20 °C for 0.5 h. The yellow solution was quickly filtered and the filtrate evaporated to dryness on a rotary evaporator. Recrystallization of the residue from CH_2Cl_2/ether afforded yellow crystals of *cis*-$(PMePh_2)_2Pt(phth)SCH_2Ph{\cdot}CH_2Cl_2$ (**4**), which were washed and dried as before (0.38 g, 52%). Extending the reaction time or performing the reaction at room temperature led to formation of the disubstituted product *cis*-$(PMePh_2)Pt(phth)_2$ (**3b**; 78%).

L = PMe_2Ph. $(PMe_2Ph)_2Pt(SCH_2Ph)_2$ (85% cis, 15% trans; 0.50 g, 0.70 mmol) and *N,N'*-dithiobis(phthalimide) (0.25 g, 0.69 mmol) were stirred together in 25 mL of toluene at −20 °C for 1.5 h. The mixture was filtered and the filtrate evaporated to dryness under vacuum. Recrystallization from CH_2Cl_2/ether gave *trans*-$(PMe_2Ph)_2Pt(phth)$-SCH_2Ph (**5**) as yellow crystals (0.42 g, 82%). Increasing the reaction time or warming led to decomposition.

G. Reaction of *cis*-$(PMePh_2)_2Pt(SCH_2Ph)_2$ with $PhCH_2Sphth$. *cis*-$(PMePh_2)_2Pt(SCH_2Ph)_2$ (0.36 g, 0.43 mmol) was stirred at room temperature with $PhCH_2Sphth$ (0.23 g, 0.87 mmol) in 15 mL of toluene for 18 h. The reaction mixture was concentrated under vacuum to a pale yellow oil, which was recrystallized from CH_2Cl_2/Et_2O. White crystals (0.32 g, 84%) of *cis*-$(PMePh_2)_2Pt(phth)_2$ (**3b**) were obtained. The compounds $PhCH_2S_xCH_2Ph$, x = 2, 3, were detected in the ^1H NMR spectrum of the mother liquors.

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Registry No. **1a**, 85882-94-6; **1b**, 85882-90-2; **1c**, 85882-92-4; **1d**, 85882-96-8; **1e**, 85882-98-0; **2a**, 85882-93-5; **2b**, 85882-89-9; **2c**, 85882-91-3; **2d**, 85882-95-7; **2e**, 85882-97-9; **3a**, 117306-60-2; **3b**, 117226-77-4; **3c**, 117226-78-5; **4**, 117250-90-5; **5**, 117251-11-3; $(PPh_3)_2Pt(C_2H_4)$, 12120-15-9; *cis*-$(PPh_3)_2PtCl_2$, 15604-36-1; $PhCH_2SS(phth)$, 33704-38-0; $CH_3CH_2CH_2SS(phth)$, 30912-77-7; $(CH_3)_2CHSS(phth)$, 33704-40-4; $(4\text{-}C_6H_4\text{-}Me)SS(phth)$, 33704-37-9; $(phth)SS(phth)$, 7764-30-9; $PhCH_2S(phth)$, 14204-26-3; $CH_3CH_2CH_2S(phth)$, 17796-71-3; $(CH_3)_2CHS(phth)$, 17796-72-4; $(4\text{-}C_6H_4\text{-}Me)S(phth)$, 15199-26-5; $(phth)S(phth)$, 7764-29-6; $(phth)SH$, 91565-68-3; $(phth)SSH$, 117226-79-6; *cis*-$(PPh_3)_2Pt(SCH_2Ph)_2$, 75365-64-9; *cis*-$(Ph_2MeP)_2Pt(SCH_2Ph)_2$, 75365-65-0; *cis*-$(PhMe_2P)_2Pt(SCH_2Ph)_2$, 75365-66-1; $PhCH_2SSCH_2Ph$, 150-60-7; $PhCH_2SSSCH_2Ph$, 6493-73-8.

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