all the spectra, there is no evidence for observable isomers of IV in solution.

Preliminary T_1 measurements on I and III indicate that they have fast relaxation times of 16 and 23 ms, respectively, and spectra were obtained with no pulse delay. Despite this, the peaks of I and II were still somewhat broadened (about 140 Hz at half height). Since III and IV also had short relaxation times but had sharp peaks, we attribute the broadening of I and II to some molecular fluxionality in solution. The low solubility of I and II precludes variable-temperature studies. The low-field shift for II suggests some slight paramagnetic nature to the molecule in solution. The extremely long Cr-Cr bond may allow some thermal population of the low-lying metal-metal antibonding orbital. However, the obvious stability of compound II, along with the fact that a ^{125}Te NMR signal could be easily observed, leads us to conclude that there is no substantial dissociation occurring in solution.

Bonding. The bonding in I and II is fairly straightforward. Each telluride can be viewed as donating one lone pair of electrons to each metal tetracarbonyl fragment in the ring. If each telluride is considered to bear a 2- charge, then each ring metal center is formally 1+. This leads to the formation of the metal-metal bond, completing the 18-electron count around each metal center and rendering the molecule diamagnetic, as observed from Gouy measurements of I and II in the solid state. One of the remaining lone pairs of each telluride is donated to a neutral metal pentacarbonyl fragment exo to the ring.

Similarly, the bonding in III and IV can be explained by classical valence arguments. The Te_2^{2-} and Te_3^{2-} chains have three lone pairs and formal charges of 2- localized on the terminal tellurides. These terminal atoms each donate two lone pairs to $Cr(CO)_5$ fragments, completing the 18-electron count around the metal centers.

Conclusions

We have shown that the reaction of excess group 6 carbonyls with various polytellurides in solution is quite complex and leads to variety of unusual metal-rich products. We had previously demonstrated that equimolar amounts of metal carbonyl and polytelluride leads to simple substitution products and that excess tungsten carbonyl is susceptible to oxidation by Te_4^{2-}, leading to cluster formation.[13] In this paper we extend this chemistry using excess metal carbonyls and a variety of polytelluride starting materials. The identity of the products is extremely sensitive to the reaction conditions and stoichiometry employed, which is understandable given the complexity of the polytelluride equilibria in solution. The nature of these products highlights the ability of tellurides to act as excellent cluster building species.

The polytellurides can induce some oxidation of the low-valent metal centers upon coordination. However there is significantly less electron transfer than is the case with polyselenides or polysulfides, presumably because of the lower electron affinity of tellurium. However it is clear that under the proper conditions a large number of stable and interesting metal tellurides can be prepared.

Acknowledgment. We are indebted to the National Science Foundation for support of this work (Grant CHE-9102548). We are also grateful to Dr. Dan Bearden for assistance in obtaining ^{125}Te NMR data.

Supplementary Material Available: Tables of complete crystallographic data and complete listings of distances and angles, atomic coordinates, anisotropic thermal parameters, and hydrogen atom coordinates for structures I, II, III, IVa, and IVb (30 pages); tables of observed and calculated structure factors for all five structures (110 pages). Ordering information is given on any current masthead page.

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Reactions of [Pt(dien)Cl]Cl and [Pt(trpy)Cl]Cl with Thiols, Thioethers, and Dialkyl Disulfides: A ^{195}Pt NMR Study

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The reactions of monofunctional platinum compounds [Pt(dien)Cl]Cl (dien = 1,5-diamino-3-azapentane) and [Pt(trpy)Cl]Cl (trpy = 2,2′,2″-terpyridine) with thiols (RSH), thioethers (RSR), and disulfides (RSSR) have been investigated by ^{1}H, ^{13}C, and ^{195}Pt NMR spectroscopy. Empirical trends in ^{195}Pt NMR chemical shifts are noted in terms of the classes sulfur functional groups coordinated to platinum. It appears that neither the steric bulk nor the electronic character of the alkyl group makes a significant contribution to the ^{195}Pt nuclear shielding. Reactions of dialkyl disulfides with [Pt(dien)Cl]Cl initially lead to a monodentate complex $[Pt(dien)(RSSR)]^{2+}$ which can be isolated as the ClO_4^- or PF_6^- salts. In the presence of [Pt(dien)Cl]Cl, the monodentate disulfido complex undergoes further reaction to cleave the S-S bond in the disulfide ligand, via a redox process.

Introduction

The chemistry of transition metal complexes containing metal-sulfur bonds has become of considerable biological, environmental, and industrial importance during the past decade.[1-3] Organosulfur compounds are present in kerogens and crude oils, and they play an important role in coal processing. A knowledge of the distribution of various sulfur functional groups in petroleum fractions, coal, and coal-derived liquids is also very important to further our understanding of the role of sulfur in the generation of oil and natural gas.[4] A motivation behind our current interest in sulfur coordination to platinum is the possibility of developing a ^{195}Pt NMR method to identify organically bound sulfur (thiols, thiophenes, thioethers, disulfides) in coal materials.[5] As part of our strategy to make model complexes with sulfur ligands for ^{195}Pt

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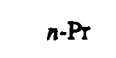
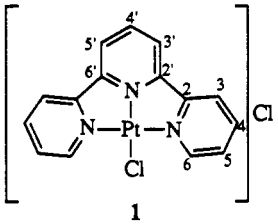
Chart I

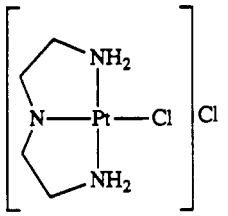
[Pt(trpy)(SR)]PF_6				[Pt(dien)(SR)]ClO_4				[Pt(dien)(SR_2)]$(ClO_4)_2$				[Pt(dien)$(SR)_2$]$(ClO_4)_2$	
	R		R		R		R		R		R		R
3	Et	7	allyl	10	Et	13	allyl	17	Me	20	*i*-Pr	23	Me
4	*n*-Pr	8	*c*-Pent	11	*n*-Pr	14	benzyl	18	Et	21	*n*-Bu	24	Et
5	*i*-Pr	9	*c*-Hex	12	*i*-Pr	15	Ph	19	*n*-Pr	22		25	*n*-Pr
6	benzyl					16	*c*-Pent					26	*i*-Pr

NMR studies, we began with the relatively simple and well-known monofunctional tagging cations **1** and **2** to avoid bifunctional coordination and geometrical complexity.[6]



1

[Pt(trpy)Cl]Cl



2

[Pt(dien)Cl]Cl

Because it is generally accepted that the interaction of DNA molecules with *cis*-platin [*cis*-diaminodichloroplatinum(II)] is responsible for its antitumor activity, the reactivities of both **1**[7] and **2**[8] with sulfur-containing protein molecules have been studied. Furthermore, the kinetics of the displacement of bromide ion from $[Pt(dien)Br]^+$ by thioethers has been elucidated.[9] There are, however, no reports on the ^{195}Pt NMR resonance spectra of these compounds in the literature. ^{195}Pt NMR studies involving sulfur-bound ligands are virtually limited to *cis*- and *trans*-PtL_2X_2, PtL_2X_4, PtL_2X_4, and $Pt_2L_4X_6$ (where L = thioether,[10,11] thiourea,[12] thioamid,[12] thiocyanate[13,14] and X = Cl, Br, I).

In this paper the synthesis and isolation of the thiolato complexes **3–16**, the thioether complexes **17–22** and the disulfide complexes **23–26** are reported (see Chart I).

Although organic disulfides coordinate to other transition metal ions such as Mn(II),[15] Re(II),[15] Ru(II),[16] Pd(II),[17] Co(III),[18] and Cu,[19,20] no such example has been described for Pt(II). The cleavage of the sulfur–sulfur bond in organic disulfides is a well-known organic reaction which can be effected by nucleophilic, electrophilic, and radical processes.[21] In the case of zerovalent platinum, organic disulfides have been reported to add oxidatively with cleavage of the sulfur–sulfur bond.[22] This suggests that $[Pt(dien)(RSSR)]^{2+}$ may undergo further reaction to form thiolato complexes, a point we address in the present paper. ^{195}Pt NMR chemical shifts are reported for 53 complexes of the types represented by **3–26**, including eight of the type $\{[Pt(dien)_2SR]^{3+}$.

Experimental Section

Materials and Methods. All thiols, disulfides, and thioethers were obtained from Aldrich Chemical Co., except 2,5-dihydrothiophene, which was synthesized according to a literature procedure.[23] K_2PtCl_4 was either obtained from Johnson Matthey or synthesized from $H_2Pt(OH)_6$.[24] The platinum compounds [Pt(dien)Cl]Cl[25] and [Pt(trpy)Cl]Cl[26] were prepared as previously described.

All pH measurements were carried out at room temperature and were standardized with Fischer certified buffer solutions before each measurement. The ^{1}H NMR (300-MHz) and ^{13}C NMR (75.3-MHz) spectra were recorded with Varian 300 VXR instruments. For the ^{195}Pt NMR measurements, 0.01 mol of complex was dissolved in 2 mL of solvent in a 10-mm NMR tube. All reactions were performed at room temperature over a pH range of 2–3 for thiols and 5–8 for thioethers and disulfides. ^{195}Pt NMR (43.8-MHz) spectra were recorded with a Bruker WM 200 spectrometer. References were K_2PtCl_6 (external) for ^{195}Pt, D_2O (99.8%, internal) for ^{1}H, and 1,3-dioxane for (internal) ^{13}C spectra.

Preparation of [Pt(trpy)(SR)]PF_6. In a typical procedure, a solution of [Pt(trpy)Cl] Cl (200 mg, 0.37 mmol) in water (10 mL) was combined with $AgPF_6$ (4.0 mmol). After stirring for 4–6 h, the AgCl precipitate was centrifuged off. To the deep yellow solution was added the desired thiol (~0.4–0.5 mL), and the pH of the solution was adjusted to ~5–6. Ether was added, and the deep red precipitate was filtered and washed with cold water and ether, and dried over P_4O_{10}. The yields of these compounds are **3** (R = Et) 82%, **4** (R = *n*-Pr) 62%, **5** (R = *i*-Pr) 64%, **6** (R = $CH_2C_6H_5$) 54%, **7** (R = $CH_2CH{=}CH_2$) 57%, **8** (R = *c*-Pent) 70%, and **9** (R = *c*-Hex) 65%. Pure samples were obtained by recrystallization from H_2O/acetone. ^{1}H and ^{13}C NMR data of the complexes are reported in Table I.

Preparation of [Pt(dien)(SR)]ClO_4. In a typical reaction, a solution of $AgClO_4$ (120 mg, 0.57 mmol) in 5 mL of water was added to [Pt(dien)Cl]Cl (100 mg, 0.27 mmol) in 20 mL of water, and the reaction mixture stirred for 16–18 h. After the removal of the AgCl precipitate, the desired thiol (RSH 0.2 mL) was added to the solution. After the pH of the solution was adjusted to 5–6 with 0.01 N NaOH, the reaction mixture was stirred for an additional 2 h. The product was obtained as yellow precipitate, which was isolated by filtration and washed with ether and dried over P_4O_{10}. *Caution*: Perchlorates containing organic moieties can be explosive. Although no problems were encountered with this product, proper precautions are to be taken. The yields of the complexes

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Table I. ^1H and ^{13}C NMR Spectroscopic Data for $[Pt(trpy)SR]PF_6$ Complexes[a]

	^1H		^{13}C	
compound	Pt(trpy)	S–R	Pt(tryp)	S–R
$[Pt(tryp)(SEt)]^+$, **3**	8.08 (m, 4′4)[b]	2.29 (q, 2 H, CH_2)	157.34 (3),[b] 128.78 (5)[b]	22.34 (CH_2)
	7.85 (m, 3,3′)	1.20 (t, 3 H, CH_3)	154.01 (3′), 125.62 (2)	15.34 (CH_3)
	7.82 (m, 6)		151.07 (6), 124.30 (2′)	
	7.50 (m, 5)		143.04 (4), 142.75 (4′)	
$[Pt(trpy)(S-n-Pr)]^+$, **4**	8.35 (m, 4′,4)	2.35 (m, 2 H, CH_2)	157.96 (3), 128.88 (5)	26.42 (α-CH_2)
	8.28 (m, 3,3)	2.00 (m, 2 H, CH_2)	152.29 (3′), 125.24 (2)	25.87 (β-CH_2)
	7.93 (m, 6)	1.27 (m, 2 H, CH_3)	151.41 (6), 123.69 (2′)	13.15 (γ-CH_3)
	7.41 (m, 5)		142.08 (4), 141.51 (4′)	
$[Pt(trpy)(S-i-Pr)]^+$, **5**	8.77 (m, 4.4)	2.98 (m, 1 H, CH_2)	158.23 (3), 128.93 (5)	30.18 (α-CH)
	8.11, 8.07 (m, 3,3′)	10.7 (d, 6 H, CH_3)	153.10 (3′), 125.17 (2)	28.01 (β-CH_3)
			152.16 (6), 123.64 (2′)	26.51 (β-CH_3)
	7.95 (m, 6)		142.09 (4), 141.67 (4′)	
	7.52 (m, 5)			
$[Pt(trpy)(SCH_2Ph)]^+$, **6**	8.14 (m, 4′4)	7.13, 6.90 (5 H, C_6H_5)	157.26 (3), 128.65 (5)	128.31, 128.15, 126.35 (C_6H_5)
	7.85 (m, 3,3)		151.69 (3′,6), 125.25 (2)	
	7.63 (m, 6)	2.97 (m, 2 H, CH_2)	142.36 (4), 123.64 (2′)	
	7.57 (m, 5)		141.83 (4′)	34.15 (CH_2)
$[Pt(tryp)(S-allyl)]^+$, **7**	8.59 (m, 4′,4)	5.47 (m, 1 H, H_c)[c]	157.99 (3), 128.96 (5)	138.83 (=CH)
	8.06 (m, 3,3′)	4.94 (m, J = 4 Hz, H_b)[c]	152.76 (3′), 125.23 (2)	114.27 (=CH_2)
	7.89 (m, 6′)	4.85 (d, J = 12 Hz, H_a)[c]	151.92 (6), 123.71 (2′)	26.51 (CH_2)
	7.49 (m, 5)	2.81 (m, 2H, CH_2)	142.14 (4), 141.97 (4′)	
$[Pt(tryp)(S-c-Pent)]^+$, **8**	8.69 (m, 4,4′)	3.14 (m, 1 H, α-H)	158.22 (3), 128.90 (5)	50.15 (α-C)
	8.08 (m, 3)	1.88 (m, 2 H, β-H)	152.98 (3′), 125.90 (2)	34.08, 33.10 (β-C)
	7.90 (m, 3′)	1.69 (2 H, β-H)	152.03 (6), 123.66 (2′)	
	7.88 (m, 6)	1.43 (m, 4 H, γ-H)	142.08 (4)	24.02, 23.90 (γ-C)
	7.51 (m, 5)		141.87 (4′)	
$[Pt(trpy)(S-c-Hex)]^+$, **9**	8.67 (m, 4,4′)	2.82 (m, 1 H, α-H)	157.95 (3), 128.3 (5)	47.74 (α-C)
	8.05 (m, 3)	1.81 (m, 8 H, β-H)	153.9 (3′), 125.7 (2)	32.43, 30.1 (β, γ-C)
	7.98 (m, 3′)	1.53 (m, 2 H, γ-H)	151.1 (6), 124.01 (2′)	
	7.78 (m, 6)		142.5 (4)	28.01
	7.47 (m, 5)		142.0 (4′)	26.53 (δ-C)

[a] Chemical shifts are in ppm. ^1H and ^{13}C NMR assignments were made following reference 7c. ^1H and ^{13}C NMR data were recorded in solutions made by dissolving about 5 mg of sample in ca. 0.8 mL of D_2O at room temperature. [b] These numbers refer to the atoms indicated by the numbering system shown in **1** (Jennette, K. W.; Gill, J. J.; Sadowick, J. A.; Lippard, S. J. *J. Am. Chem. Soc.* **1976**, *98*, 6159). [c] The numbering for the allyl protons is

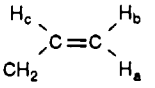

Table II. ^1H and ^{13}C NMR Data for $[Pt(dien)(SR)]ClO_4$ Complexes[a]

	^1H		^{13}C	
compound	Pt(dien)	SR	Pt(dien)	SR
$[Pt(dien)(SEt)]^+$, **10**	3.44–3.29 (m, 8 H)	2.32 (m, 2 H, CH_2)	44.37	22.37 (CH_2)
		1.27 (m, 3 H, CH_3)	35.64	14.19 (CH_3)
$[Pt(dien)(S-n-Pr)]^+$, **11**	3.45–3.32 (m, 8 H)	2.50 (m, 2 H, CH_2)	44.57	27.29 (CH_2)
		1.64 (m, 2 H, CH_2)	35.34	26.52 (CH_2)
		1.04 (m, 3 H, CH_3)		13.32 (CH_3)
$[Pt(dien)(S-i-Pr)]^+$, **12**	3.47–3.31 (m, 8 H)	1.98 (m, 1 H, CH)	44.49	34.39 (CH)
		0.93 (m, 6 H, CH_3)	35.64	23.67 (CH_3)
$[Pt(dien)(S-allyl)]^+$, **13**	3.49–3.31 (m, 8 H)	3.03 (m, br, CH_2)	44.54	134.58 (=CH)
		5.2–4.7 (m, 3 H, CH, CH_2)	35.31	116.75 (=CH_2)
				27.49 (CH_2)
$[Pt(dien)(SCH_2Ph)]^+$, **14**	3.40–3.30 (m, 8 H)	3.06 (CH_2)	44.52	141.01, 128.54, 126.69 (C_6H_5)
		6.77 (C_6H_5)	35.29	
				28.55 (CH_2)
$[Pt(dien)(SPh)]^+$, **15**	3.52–3.29 (m, 8 H)	6.74 (m, 5 H, C_6H_5)	44.57	129.00, 128.93, 125.27, 125.21 (C_6H_5)
			36.59	
$[Pt(dien)(S-c-Pent)]^+$, **16**	3.95–3.23 (m, 8 H)	1.87 (m, 1 H, αH)	44.57	48.74 αC
		1.64 (m, 2 H, βH)	35.39	37.66 βC
		1.39 (m, 2 H, γH)		25.56 γC

[a] Chemical shifts are in ppm. ^1H and ^{13}C NMR spectra were recorded at room temperature in solutions made by dissolving ca. 5 mg of sample in about 0.8 mL of D_2O.

Table III. ^{1}H and ^{13}C NMR Data for $[Pt(dien)SR_2](ClO_4)_2$ and $[Pt(dien)(RSSR)](ClO_4)_2$ Complexes[a]

complex	^{1}H NMR		^{13}C NMR	
	Pt(dien)	RSR or RSSR	Pt(dien)	RSR or RSSR
$[Pt(dien)SMe_2)]^{2+}$, **17**	3.43–3.32 (m, 8 H)	1.53 (s, 6 H, CH_3)	45.27, 35.23	13.7
$[Pt(dien)SEt_2]^{2+}$, **18**	3.44–3.30 (m, 8 H)	2.56 (m, 4 H, CH_2) 1.84 (m, 6 H, CH_3)	45.31, 35.17	19.5 (CH_2) 13.5 (CH_3)
$[Pt(dien)S(n\text{-}Pr)_2]^{2+}$, **19**	3.41–3.31 (m, 8 H)	7.65 (m, 2 H, CH_2) 1.48 (m, 2 H, CH_2) 0.89 (m, 3 H, CH_3)	44.54, 35.30	24.02 (CH_2) 22.98 (CH_2) 13.15 (CH_3)
$[Pt(dien)S(i\text{-}Pr)_2]^{2+}$, **20**	3.57–3.15 (m, 8 H)	2.69 (m, 1 H, CH) 1.17 (d, 6 H, CH_3)	46.46, 33.35	36.60 (CH) 13.82 (CH_3)
$[Pt(dien)S(n\text{-}Bu)_2]^{2+}$, **21**	3.42–32.23 (m, 8 H)	2.58 (m, 2 H) 1.57 (m, 4 H) 0.83 (m, 3 H)	44.37, 35.39	38.60 (CH_2) 31.34 (CH_2) 21.65 (CH_2) 13.72 (CH_3)
$[Pt(dien)(2,5\text{-dihydrothiophene})]^{2+}$, **22**	3.42–3.30 (m, 8 H)	5.58 (m, 2 H) 4.63 (m, 2 H) 2.56 (m, 2 H)	44.56, 38.73	125.97 (C=C) 56.93 (CH_2)
$[Pt(dien)(MeSSMe)]^{2+}$, **23**	3.42–3.30 (m, 8 H)	1.32 (6 H, CH_3)	44.71, 37.21	14.2 (CH_3) 14.15 (CH_3)
$[Pt(dien)(EtSSEt)]^{2+}$, **24**	3.38–3.28 (m, 8 H)	1.90 (4 H, CH_2) 1.28 (6 H, CH_3)	45.01, 36.28	22.10 (CH_2) 15.15 (CH_3)
$[Pt(dien)(n\text{-}PrSS\text{-}n\text{-}Pr)]^{2+}$, **25**	3.36–3.29 (m, 8 H)	1.75 (m, 4 H, CH_2) 1.25 (m, 4 H, CH_2) 0.85 (m, 6 H, CH_3)	44.52, 35.43	28.69 (CH_2) 22.98 (CH_2) 13.12 (CH_3)
$[Pt(dien)(i\text{-}PrSS\text{-}i\text{-}Pr)]^{2+}$, **26**	3.38–3.32 (m, 8 H)	2.32 (m, 2 H, CH) 1.20 (m, 12 H, CH_3)	44.77, 35.48	40.46 (CH) 25.35 (CH_3)

[a] Chemical shifts are in ppm. NMR spectra were recorded at room temperature in solutions made by dissolving ca. 5 mg of sample in about 0.8 mL of D_2O.

are **10** (R = Et) 78%, **11** (R = *n*-Pr) 58%, **12** (R = *i*-Pr) 54%, **13** (R = $CH_2CH{=}CH_2$) 62%, **14** (R = $CH_2C_6H_5$) 67%, **15** (R = Ph) 65%, and **16** (R = *c*-Pent) 59%. The ^{1}H and ^{13}C NMR data of the complexes are reported in Table II.

Preparation of $[Pt(dien)SR_2](ClO_4)_2$. To a solution of [Pt(dien)Cl]Cl (200 mg, 0.54 mmol) in 20 mL of water was added $AgClO_4$ (200 mg, 1.01 mmol). The reaction mixture was stirred for 16 h, and the AgCl which formed was centrifuged. To the centrifugate was added dihydrothiophene (100 mg, 1.16 mmol), and the mixture was stirred for 4 days to obtain the cream solid **22**. This solid was recrystallized from methanol and water to give 310 mg of light yellow microcrystals. Yield, 72%; Anal. Calcd (Found) for $C_8H_{17}N_3Cl_2O_8SPt$: C, 16.52 (16.37); H, 2.92 (2.89); N, 7.22 (7.24); S, 5.50 (5.57). Analogous procedures gave **17** (R = Me), 58% yield; **18** (R = Et), 59% yield; **19** (R = *n*-Pr), 47% yield; **20** (R = *i*-Pr), 54% yield; and **21** (R = *n*-Bu), 55% yield. The ^{1}H and ^{13}C NMR data of the complexes are reported in Table III.

Preparation of $[Pt(dien)(RSSR)](ClO_4)_2$. $[Pt(dien)(H_2O)](ClO_4)_2$ was prepared from [Pt(dien)Cl]Cl (100 mg, 0.27 mmol) and $AgClO_4$ (110 mg, 0.54 mmol), as described in the preceding preparation. To the aqueous filtrate containing the $[Pt(dien)(H_2O)](ClO_4)_2$ was added MeSSMe (40 mg, 0.64 mmol) in 1 mL of MeOH. The reaction mixture was stirred for 72 h. Addition of ether gave a yellow solid **23** (R = Me) which was washed with cold MeOH and dried over P_4O_{10}. Yield: 52 mg, 42%; Anal. Calcd (Found) for $C_6H_{19}N_3O_8Cl_2S_2Pt$: C, 12.8 (11.97); H, 3.21 (3.25); N, 7.10 (7.10); S, 10.82 (11.14). Using analogous procedures, **24** (R = Et) 47% yield, **25** (R = *n*-Pr) 49% yield, and **26** (R = *i*-Pr) 42% yield were prepared. The ^{1}H and ^{13}C NMR data for the complexes are reported in Table III.

Discussion

The thiolato, thioether, and disulfide complexes described herein were synthesized according to reactions 1–4. All of the [Pt-

$$[Pt(trpy)Cl]^+ \xrightarrow[2.\ RSH]{1.\ AgPF_6} [Pt(trpy)(SR)]^+ + H^+ + Cl^- \quad (1)$$
1 → **3–9**, 57–82%

$$[Pt(dien)Cl]^+ \xrightarrow[2.\ RSH]{1.\ AgClO_4} [Pt(dien)(SR)]^+ + H^+ + Cl^- \quad (2)$$
1 → **10–16**, 54–78%

$$[Pt(dien)Cl]^+ \xrightarrow[2.\ RSR]{1.\ AgClO_4} [Pt(dien)(SR_2)]^{2+} + 2Cl^- \quad (3)$$
2 → **17–22**, 47–72%

$$[Pt(dien)Cl]^+ \xrightarrow[2.\ RSR]{1.\ AgClO_4} [Pt(dien)(SR)_2]^{2+} + 2Cl^- \quad (4)$$
2 → **23–26**, 42–49%

$(trpy)(SR)]^+$ complexes are red to brick red while $[Pt(dien)(SR)]^+$ complexes are cream to light yellow. Most of the thiolato complexes are soluble in acetonitrile but sparingly soluble in H_2O. The thioether and disulfide complexes are also sparingly soluble in H_2O.

[Pt(trpy)Cl]Cl is more reactive toward thiols compared with [Pt(dien)Cl]. The ^{195}Pt NMR spectra recorded during the reaction between [Pt(trpy)Cl]Cl and thiols show the decline of signal at −2694 ppm due to [Pt(trpy)Cl]Cl and the growth of a signal at ∼−3150 ppm due to $[(Pt(trpy)(SR)]^+$, almost instantaneously. Within 3–4 h the signal due to $[Pt(trpy)Cl]^+$ diminishes. Similar reactions with $[Pt(dien)Cl]^+$ proceed very slowly as is evident from the slow decline of the ^{195}Pt NMR signal at −2732 ppm due to $[Pt(dien)Cl]^+$ and the slow appearance of a signal at ∼−3180 ppm due to $[Pt(dien)(SR)]^+$. In this case, it takes 16–18 h for the reaction to go to completion. The difference in reactivity between **1** and **2** with thiols is attributed to the difference in lability of the chloride ion. The more labile chloride ion in $[Pt(trpy)Cl]^+$ is due to the presence of the aromatic terpyridine ligand. It has been shown that the chloride ion is displaced from $[Pt(trpy)Cl]^+$ approximately 10^3–10^4 times faster than from $[Pt(dien)Cl]^+$.[27]

In NMR tube experiments, the ^{195}Pt NMR resonances of [Pt(trpy)Cl]Cl and [Pt(dien)Cl]Cl were used as an indication of reaction completion. The data reported in Tables IV and V strongly suggest the formation of a Pt–S bond with the Pt(II) complexes **1** and **2**, since in all cases the ^{195}Pt resonance is substantially shifted to high field with respect to the chemical shift of the starting materials, a phenomenon that has been noted earlier.[28] The rate of the sulfur coordination to **2** depends mainly on the nature of the sulfur functional group (i.e., RSH, RSR) and the steric bulk of the ligand. In all cases, a 1:1 molar ratio of Pt(II) reagents to sulfur ligand was used. Reactions of $[Pt(dien)Cl]^+$ with thiols went to completion within 14–16 h (pH 2–3), whereas in the case of thioether and disulfide ligands the reactions are not complete even after 3 weeks. This rate difference is not surprising, however, since thioethers and disulfides are neutral and bulkier compared with negatively charged thiolato groups. In the case of thioether ligands, a significant retardation by steric hindrance and an insensitivity to inductive effects on rates has been noted.[9b]

The NMR data in Tables IV and V reveal that the ^{195}Pt chemical shifts of platinum(II) complexes are very dependent upon

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Table IV. ^{195}Pt NMR Chemical Shift Data[a] for $[Pt(trpy)(SR)]^+$, $[Pt(dien)(SR)]^+$, and $[Pt(dien)(SR_2)]^+$ Complexes

R	$[Pt(trpy)(SR)]^+$[b]	$[Pt(dien)(SR)]^+$[b]	$[Pt(dien)(RSR)]^{2+}$[c]
Et	−3105	−3180	−3372
Pr	−3120	−3186	−3375
i-Pr	−3167	−3187	−3355
n-Bu	−3130	−3189	−3355
n-Hex	−3124	−3187	
n-Pent	−3125	−3188	
allyl	−3128	−3185	−3351
phenyl	−3150	−3196	
2-methyl-2-butyl[d]	−3129	−3176	
3-methyl-1-butyl[d]	−3127	−3172	
2-methyl-1-butyl[d]	−3125	−3178	
benzyl	−3140	−3192	−3360
t-Bu[d]			−3386
c-Pent	−3151	−3154	
c-Hex	−3161	−3166	
$CH_2CH{=}CHCH_2$			−3351

[a] Chemical shifts in ppm. Line widths are in the range of 250–400 Hz. [b] All measurements were carried out at pH 2–3. [c] All measurements were carried out at pH 6–8. [d] All ^{195}Pt NMR measurements were carried out by adding 1 equiv of the sulfur ligand to **1** or **2** at room temperature. In a typical experiment 0.10 mmol of **1** or **2** were used in 2 mL of D_2O in a 10-mm NMR tube.

Table V. ^{195}Pt Chemical Shifts of $[Pt(dien)(RSSR)]^{2+}$ and $[Pt(dien)]_2SR]^{3+}$ Complexes[a]

ligand R	$[Pt(dien)(RSSR)]^{2+}$	$\{[Pt(dien)]_2SR\}^{3+}$
Me	−3294	−3124
Et	−3290	−3190
Pr	−3282	−3185
i-Pr	−3313	
n-Bu	−3284	−3186
n-Bu	−3309	
CH_2Ph	−3287	−3191
Ph		−3212
allyl	−3323	−3187
benzyl, methyl	−3252, −3282	−3197, −3207

[a] ^{195}Pt NMR chemical shifts in ppm were recorded in D_2O using K_2PtCl_6 as an external standard. One equivalent of RSSR was added to an equimolar water solution of [Pt(dien)Cl]Cl. The $[Pt(dien)(RSSR)]^{2+}$ and $\{[Pt(dien)]_2(SR)\}^{3+}$ complexes in these experiments were observed in a reaction mixture.

the type of sulfur ligand present (i.e., SR^-, RSR, RSSR); however, there are no significant changes in the ^{195}Pt chemical shift values upon varying the alkyl groups within the same sulfur functionality. When the ^{195}Pt NMR spectrum was recorded for a mixture of **3**, **4**, and **5**, only a single broad signal could be observed (width at a half-height ~400 Hz). This broadening of the signal may be due to the fast relaxation of the ^{195}Pt nucleus by the quadrupolar ^{14}N nucleus in the dien ligand[10] and/or fast exchange of the SR group at the platinum center. It is apparent that modification of the substituents on the sulfur ligands has a less dramatic effect on the ^{195}Pt resonance than replacement of a Cl by Br (120–150 ppm) or Br by I (240–300 ppm).[14] The effect of replacing of a methyl group on a sulfur ligated to platinum(II) by phenyl is more difficult to assess with the limited data available. This process results in an increase in shielding in the case of the thiolate ligand by ~40 ppm (Table IV). In the case of thioether and disulfide ligands, however, no such information could be obtained due to the lack of reactivity of diphenyl sulfide and diphenyl disulfide with **1** and **2** in aqueous media.

The lack of reactivity of thioethers, disulfides, and sterically bulky thiolates with $[Pt(trpy)Cl]^+$ was surprising in view of the affinity of sulfur ligands for platinum. Repeated attempts including prolonged stirring and heating failed to effect the displacement of chloride from this complex by thioether and disulfide ligands. Kostić and co-workers[29] have shown from molecular

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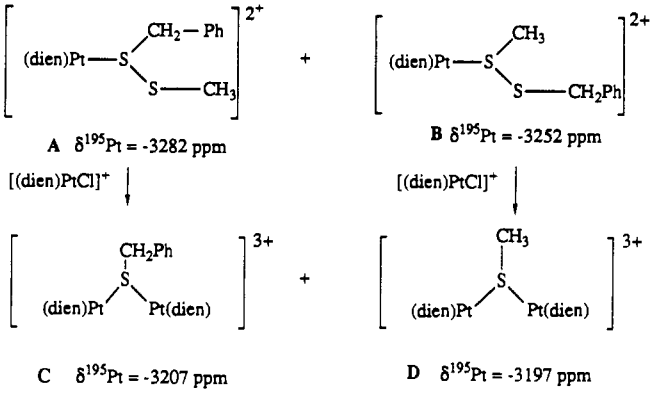
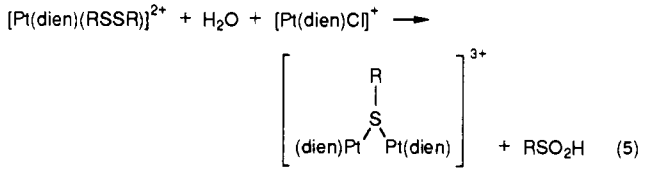
Scheme I



orbital calculations on $[Pt(trpy)SMe_2]^{2+}$ that there exists a strong repulsion between methyl groups in SMe_2 and an ortho H atom in the terpyridine ring that accounts for our results. This repulsion does not disappear on rotation of the pyramidal thioether ligand about the Pt–S bond.

Although $[Pt(trpy)(H_2O)]^{2+}$ is unreactive to disulfide ligands, treatment of $[Pt(dien)(H_2O)]^{2+}$ with dialkyl disulfides in a 1:1 molar ratio gave $[Pt(dien)(RSSR)]^{2+}$ complexes which are initially similar to those obtained with thioether ligands. The ^{195}Pt NMR chemical shifts for these disulfido complexes are normally observed as a singlet in the −3280 ppm region (Table V), in addition to the line at −2732 ppm due to unreacted [Pt(dien)Cl]Cl. After 10–12 days at room temperature, however, an additional resonance in the −3180 ppm region appears. This suggests that the coordinated disulfide ligand undergoes further reaction to form bridged thiolato complexes as shown in reaction 5. In the first step,



coordination of RSSR to [Pt(dien)Cl]Cl takes place ($t_{1/2}$ = 7 days) to give a thioether-type coordination linkage. In the second step, the coordinated disulfide undergoes a redox reaction, wherein cleavage of the S–S bond occurs. Although the cleavage of S–S bonds has previously been observed during the reaction of GSSG with the $[Pt(dien)]^{2+}$ unit,[8a] the observation of the initial binding of RSSR to the dicationic platinum center as a monodentate ligand has not been previously reported. Although the coordinated dialkyl disulfide complexes **23**–**26** shown in reaction 4 can be isolated, their dinuclear thiolato analogues formed in reaction 5 could not be purified because they precipitate out as an intractable mixture with the analogous complexes formed in reaction 4.

The isolated disulfide complexes **23**–**26**, however, do not form the thiolato species even after 3–4 weeks in solution. This indicates that unreacted $[Pt(dien)]^{2+}$ cation is required to facilitate the cleavage of the S–S bond, as described by Reedjik and Lempers.[8a] Although oxidative addition of dialkyl disulfides to Pt(0) complexes has been observed,[22] we do not observe such a reaction of this type of ligand to **1** and **2** [which contain Pt(II)] to give Pt(IV) complexes. In the case of benzyl methyl disulfide, a pair of isomers was detected, as indicated by the two ^{195}Pt resonances (−3252 and −3282 ppm) ascribed to isomer A and B, respectively, which in turn collapse to their respective bridged thiolato complexes C and D in Scheme I. The combined yields of A and B, as judged by rough integration of the ^{195}Pt NMR peaks was 25%, with a ratio of B to A of about 2:1.

Conclusions. The data reported in Table IV reveal that the ^{195}Pt nucleus is more shielded for $[Pt(dien)(SR)]^+$ compounds than for their $[Pt(trpy)(SR)]^+$ analogues, with differences ranging from 75 ppm for R = Et to 3 and 5 ppm for R = *c*-Pent and *c*-Hex, respectively. Comparing the shift data in Tables IV and V for $[Pt(dien)(SR)]^+$ and $\{[Pt(dien)]_2SR\}^{3+}$, respectively, it is seen that,

for a given R group, the Pt nuclei are about equally shielded despite the charge difference and the change in sulfur coordination number. The similar δ ^{195}Pt ranges of these two types of compounds (ca. −3100 to −3200 ppm) are more deshielded than that of $[Pt(dien)(RSSR)]^{2+}$ complexes (ca. −3250 to −3320 ppm), which are in turn more deshielded than the range for $[Pt(dien)(RSR)]^{2+}$ complexes (ca. −3351 to −3375 ppm). The δ ^{195}Pt shielding order $RS^- < RSSR < RSR$ may reflect a decrease in the paramagnetic shielding term resulting from an increase in the ligand field splitting parameter ΔE.[30] A rationale for this order is not obvious, however. These data demonstrate that any of these classes of compounds can be identified in a mixture (provided the chemical shifts are not too near a boundary of the range for a given class). However, speciation of members within a class is not feasible owing to the width of the ^{195}Pt chemical shifts in these reagents, to which sulfur inversion[31-33] processes can also contribute in the case of $[Pt(dien)(SR_2)]^{2+}$, $[Pt(dien)(RSSR)]^{2+}$, and $\{[Pt(dien)]\}_2SR$ complexes.

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Cleavage of a Cyclotriphosphine Ring by Iron Carbonyls[1]

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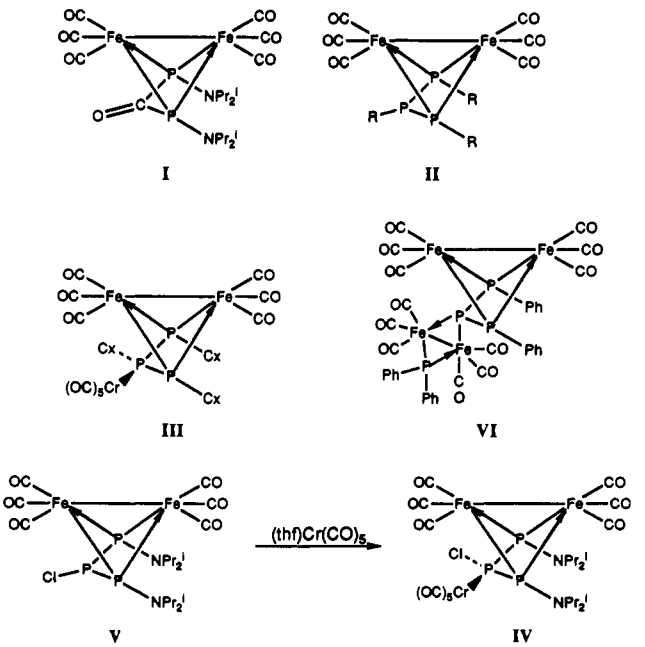
Reaction of tri-*tert*-butylcyclotriphosphine, *t*-Bu_3P_3, with $Fe(CO)_5$ in boiling toluene or with $Fe_3(CO)_{12}$ in boiling benzene gives yellow-brown crystalline *t*-$Bu_3P_3Fe_2(CO)_6$. An X-ray diffraction study of *t*-$Bu_3P_3Fe_2(CO)_6$ (orthorhombic, $P2_12_12_1$; a = 10.522 (5) Å, b = 12.188 (4) Å, c = 19.807 (8) Å, Z = 4) indicates an Fe–Fe bond (Fe–Fe = 2.602 (3) Å) and opening of the cyclotriphosphine P_3 triangle to give a P_3 chain (P1–P3 = 2.226 (6) Å, P2–P3 = 2.209 (6) Å) with an essentially nonbonding P1···P2 distance of 2.499 (6) Å between the end phosphorus atoms of this P_3 chain; the center atom of the P_3 chain is trivalent and not bonded directly to any iron atoms. Reaction of *t*-Bu_3P_3 with $Fe_2(CO)_9$ at room temperature gives not only this binuclear complex *t*-$Bu_3P_3Fe_2(CO)_6$ but also a trinuclear complex *t*-$Bu_3P_3[Fe(CO)_4]Fe_2(CO)_6$. X-ray diffraction of this trinuclear complex (monoclinic, $P2_1/n$; a = 9.180 (5) Å, b = 16.923 (7) Å, c = 19.186 (9) Å, β = 93.27 (4)°, Z = 4) indicates a structure similar to that of the binuclear complex *t*-$Bu_3P_3Fe_2(CO)_6$ but with an $Fe(CO)_4$ group bonded to the center phosphorus atom of the P_3 chain. Reaction of *t*-$Bu_3P_3Fe_2(CO)_6$ with hydrogen peroxide in ethanol and with sulfur in boiling toluene gives the corresponding oxide *t*-$Bu_3P_3OFe_2(CO)_6$ and sulfide *t*-$Bu_3P_3SFe_2(CO)_6$, respectively.

Introduction

In recent years the reaction of $Na_2Fe(CO)_4$ with *i*-Pr_2NPCl_2 has been found to give as the major product the phosphorus-bridging carbonyl derivative $(i\text{-}Pr_2NP)_2COFe_2(CO)_6$ (I) in diethyl ether solution but the triphosphine derivative $(i\text{-}Pr_2NP)_3Fe_2(CO)_6$ (II; R = *i*-Pr_2N) in tetrahydrofuran solution.[2] The formation of II (R = *i*-Pr_2N) from the $Na_2Fe(CO)_4$/*i*-Pr_2NPCl_2 reaction is of interest because of the formation of a chain of three phosphorus atoms from the reductive coupling of three *i*-Pr_2NP units upon reaction of *i*-Pr_2NPCl_2 with the $Na_2Fe(CO)_4$. A related reductive coupling reaction occurs upon treatment of $(CxPCl_2)Fe(CO)_4$ (Cx = cyclohexyl) with $Na_2Cr_2(CO)_{10}$ to give the derivative $Cx_3P_3[Cr(CO)_5]Fe_2(CO)_6$ (III),[3] in which not only the outer phosphorus atoms of the triphosphine chain are bonded to iron atoms but also the central phosphorus atom of the triphosphine chain is coordinated to a $Cr(CO)_5$ group. This compound is closely related to the product $(i\text{-}Pr_2NP)_2P(Cl)[Cr(CO)_5]Fe_2(CO)_6$ (IV) obtained by complexation of the central phosphorus atom in $(i\text{-}Pr_2NP)_2P(Cl)Fe_2(CO)_6$ (V) by reaction with $(thf)Cr(CO)_5$.[4] Other compounds containing a triphosphine hexacarbonyldiiron P_3Fe_2 unit have been obtained by the following methods:



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