ordination chemistry, except that solvation of monoanions and neutrals is so weak that the concept of ligand substitution is not very meaningful. The reaction between SO_2^- and O_2 may be the limiting case in which strong overlap leads to adduct formation rather than electron transfer, although Wilkins and co-workers rationalize the data in terms of outer-sphere electron transfer by using very large self-exchange rate constants for both couples.[28] The argument in favor of adduct formation is supported by the observation that SO_2^- supported on TiO_2 binds O_2.[29] Despite the apparent inapplicability of the outer-sphere model to main-group electron-transfer reactions, it is still notable that the title reaction does have a substantial kinetic barrier and thus displays vestiges of the cross relationship of Marcus' theory.

Acknowledgment. Support of this research by the NSF and the Robert A. Welch Foundation is gratefully acknowledged.

Registry No. NO_2^-, 14797-65-0; ClO_2, 10049-04-4.

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[28] Atherton, S. J.; Tsukahara, K.; Wilkins, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 3380-3385.

[29] Gonzalez-Elipe, A. R.; Soria, J. *J. Chem. Soc., Faraday Trans. 1* **1986**, *82*, 739-745.

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Oxidative Addition of Thiols to a Coordinatively Unsaturated Triplatinum Cluster Complex

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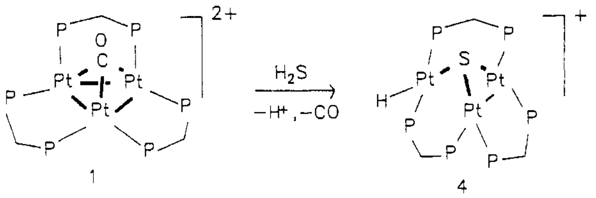
Reaction of RSH with $[Pt_3(\mu_3\text{-CO})(\mu\text{-dppm})_3][PF_6]_2$ (**1**, dppm = $Ph_2PCH_2PPh_2$) gave CO and $[Pt_3H(\mu_3\text{-SR})(\mu\text{-dppm})_3][PF_6]_2$ (**2a**, R = Me; **2b**, R = Et; **2c**, R = CH_2Ph; **2d**, R = CH_2CO_2Et; **2e**, R = Ph; **2f**, R = 4-MeC_6H_4) and, when R = aryl, $[Pt_3(SR)(\mu_3\text{-SR})(\mu\text{-dppm})_3][PF_6]_2$ (**3a**, R = Ph; **3b**, R = 4-MeC_6H_4). Reaction of *t*-BuSH with **1** gave the known complex $[Pt_3H(\mu_3\text{-S})(\mu\text{-dppm})_3][PF_6]$ (**4**). Mixed-thiolate derivatives $[Pt_3(SR)(\mu_3\text{-SR}')(\mu\text{-dppm})_3][PF_6]_2$ (**3c**, R = Me, R′ = Ph; **3d**, R = Ph, R′ = Me) were formed by reaction of **2a** with PhSH. In some cases, thiolate-exchange reactions were observed; for example, **2e** with excess MeSH gave mostly **2a**. PhSeH reacted with **1** to give a mixture of $[Pt_3H(\mu_3\text{-SePh})(\mu\text{-dppm})_3][PF_6]_2$ (**5**) and $[Pt_3(SePh)(\mu_3\text{-SePh})(\mu\text{-dppm})_3][PF_6]_2$ (**6**). In the reactions of **1** with EtSH or PhSH, low-temperature ^{31}P and ^{13}C NMR experiments showed the formation of a rapid preequilibrium between the reagents and $[Pt_3(\mu_3\text{-CO})(RSH)(\mu\text{-dppm})_3]^{2+}$ (**7a**, R = Et; **7b**, R = Ph) with $\Delta H° = -27 \pm 1$ and -24 ± 1 kJ mol^{-1} and $\Delta S° = -110 \pm 5$ and -73 ± 5 J K^{-1} mol^{-1} for formation of **7a** and **7b**, respectively. These reacted further to give **2b** or **2e** on warming to ~0 °C. PhSeH gave the analogous intermediate $[Pt_3(\mu_3\text{-CO})(PhSeH)(\mu\text{-dppm})_3]^{2+}$ and, with excess PhSeH, another species, which is probably $[Pt_3H_2(\mu\text{-SePh})(\mu\text{-dppm})_3]^{3+}$.

Introduction

The coordinatively unsaturated cluster complex $[Pt_3(\mu_3\text{-CO})(\mu\text{-dppm})_3]^{2+}$ (**1**,[1] dppm = $Ph_2PCH_2PPh_2$) is able to mimic several reactions of a Pt(111) surface.[2] In particular, the reaction with H_2S gives $[Pt_3H(\mu_3\text{-S})(\mu\text{-dppm})_3]^+$ (**4**, eq 1[3]), a reaction that models the poisoning of a platinum surface catalyst by H_2S.[4]



(1)

It was suggested that formation of **4** involved coordination of H_2S to **1** followed by oxidative addition to give $[Pt_3H(\mu_3\text{-SH})(\mu\text{-dppm})_3]^{2+}$ and then rapid deprotonation of the μ_3-SH ligand to give **4**. However, no intermediates could be detected.[3] The analogous reactions of RSH and RSeH (R = alkyl or aryl) with complex **1** have now been studied, and intermediate RSH complexes have been detected; the mechanisms of these reactions thus lend support to the proposed mechanism of the reaction of **1** with H_2S. A preliminary account of parts of this work has been published.[5]

Results

Synthesis of New Complexes. The major results from the reaction of $[Pt_3(\mu_3\text{-CO})(\mu\text{-dppm})_3]^{2+}$ (**1**) are shown in Scheme I. When R = alkyl, the thiols RSH gave $[Pt_3H(\mu_3\text{-SR})(\mu\text{-dppm})_3]^{2+}$ (**2**) as the product obtained at room temperature. The only exception was in the reaction of *t*-BuSH with **1**, which gave $[Pt_3H(\mu_3\text{-S})(\mu\text{-dppm})_3]^+$ (**4**), presumably as a result of the relatively good leaving group *t*-Bu^+ being lost from the intermediate **2**. When R = aryl, reaction with excess RSH gave $[Pt_3(SR)(\mu_3\text{-SR})(\mu\text{-dppm})_3]^{2+}$, and it was difficult to isolate the product **2** in pure form from the reaction of equimolar amounts of **1** and RSH due to partial formation of **3** even under these conditions.

The formation of **3** from **2** requires the more acidic arenethiol reagent. For example, **2a** with PhSH gave a mixture of **3c** and **3d** with a trace of **3a**. Reaction of **2e** with MeSH did not yield the above products but gave thiol exchange, with formation of **2a** as major product. Complex **2a** at 0 °C with PhSH gave some **2e**. Thus, it is clear that thiol-exchange reactions are faster than reaction of **2** with RSH to give **3**.

Benzeneselenol behaved in a manner similar to that of PhSH and gave a mixture of $[Pt_3H(\mu_3\text{-SePh})(\mu\text{-dppm})_3]^{2+}$ (**5**) and $[Pt_3(SePh)(\mu_3\text{-SePh})(\mu\text{-dppm})_3]^{2+}$ (**6**), as characterized by NMR spectroscopy. In this case the mixture could not be separated,

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[1] Ferguson, G.; Lloyd, B. R.; Puddephatt, R. J. *Organometallics* **1986**, *5*, 344.

[2] (a) Lloyd, B. R.; Bradford, A.; Puddephatt, R. J. *Organometallics* **1987**, *6*, 424. (b) Rashidi, M.; Puddephatt, R. J. *J. Am. Chem. Soc.* **1986**, *108*, 7111.

[3] Jennings, M. C.; Payne, N. C.; Puddephatt, R. J. *Inorg. Chem.* **1987**, *26*, 3776.

[4] Koestner, R. J.; Salmeron, M.; Kollin, E. B.; Gland, J. L. *Surf. Sci.* **1986**, *172*, 668 and references therein.

[5] Jennings, M. C.; Payne, N. C.; Puddephatt, R. J. *J. Chem. Soc., Chem. Commun.* **1986**, 1809.

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Scheme I

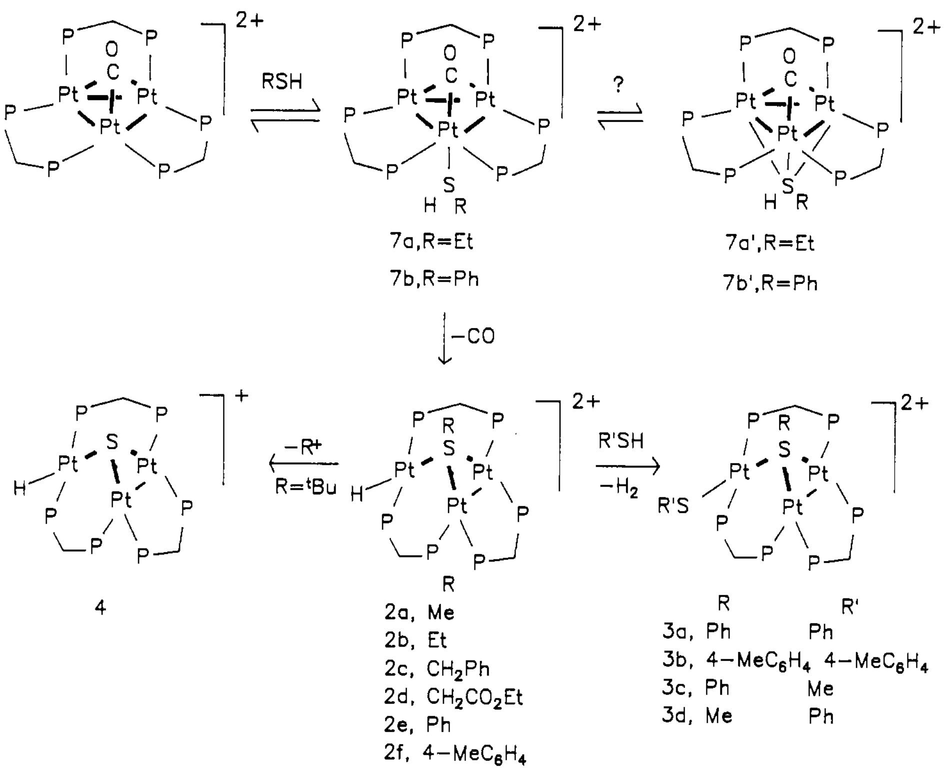


Table I. ^{1}H, ^{31}P, and ^{195}Pt NMR Data for $[Pt_3(\mu_3\text{-}X)(Y)(\mu\text{-dppm})_3]^{n+}$ Complexes

μ_3-X	Y	P^a δ/ppm	$^2J(P^aP^b)$/Hz	$^1J(Pt^1P^a)$/Hz	P^b δ/ppm	$^1J(Pt^2P^b)$/Hz	$^3J(P^bP^b)$/Hz	$^2J(Pt^2P^b)$/Hz
S	H	22.8	27	2992	2.6	3110	181	161
MeS	H	26.2	17	2832	–0.3	3140	160	140
EtS	H	25.3	19	2836	0	3160	151	150
$PhCH_2S$	H	26.0	18.7	2856	1.6	3200	162	140
$EtCO_2CH_2S$	H	27.2	20	2838	1.1	3150	160	130
PhS	H	24.4	18.5	2788	–0.6	3164	156	144
PhS	PhS	16.1		2558	–8.8	3106	153	147
MeS	PhS	18.5		2610	–7.9	3096	150	134
PhS	MeS	18.7		2670	–8.6	3260	140	
MeC_6H_4S	H	24.2	17.5	2780	–0.65	3180	160	140
MeC_6H_4S	MeC_6H_4S	16.3		2558	–8.8	3106	148	188
PhSe	H	13.6		2996	–2.2	3000	184	164
PhSe	PhSe	9.3		2760	–0.6	2970	180	

μ_3-X	Y	P^c δ/ppm	$^1J(Pt^2P^c)$/Hz	Pt^1 δ/ppm	Pt^2 δ/ppm	H δ/ppm	$^2J(PH)$/Hz	$^1J(PtH)$/Hz
S	H	–15.1	3840	–3181	–3172	–9.24	13.5	1106
MeS	H	–11.4	4158	–3387	–3417	–10.0	11.8	1263
EtS	H	–11.4	4149	–3399	–3422	–9.96	12.3	1256
$PhCH_2S$	H	–11.4	4150	–3428	–3434	–9.76	11.8	1249
$EtCO_2CH_2S$	H	–11.4	4204	–3371	–3410	–7.11	12.7	1293
PhS	H	–10.1	4240	–3430	–3405	–9.3	11.6	1314
PhS	PhS	–10.1	4248	–3090	–3388			
MeS	PhS	–11.5	4150	–3064	–3413			
PhS	MeS	–10.4	4200	–3221	–3392			
MeC_6H_4S	H	–10.0	4210			–9.3	11.9	1310
MeC_6H_4S	MeC_6H_4S	–10.0	4212	–3091	–3389			
PhSe	H	–22.4	3980	–2928	–3175	–10.1		1300
PhSe	PhSe	–22.3	3980	–2478	–3200			

but the NMR characterization is definitive (see below).

All of the above complexes are air-stable, yellow solids and were isolated as the PF_6^- salts.

Characterization. The products **2** and **3** were characterized by elemental analysis, FAB MS, and IR and NMR spectroscopies; the comparison to complex **4**, which was characterized crystallographically, was particularly useful. For example, complex **2a** gave a peak in the mass spectrum for $\{Pt_3H(SMe)(dppm)_3PF_6\}^+$, which is the parent less one PF_6^- group, and this was typical behavior for complexes **2** and **3**. The PtH stretching frequencies in the IR spectra for complexes **2** were in the range 2143–2155 cm^{-1}, but no bands in this region were observed for **3**.

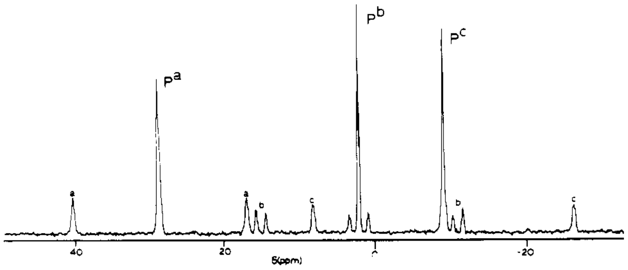


Figure 1. $^{31}P\{^1H\}$ NMR spectrum (121.4 MHz) of $[Pt_3(SPh)(\mu_3\text{-}SPh)(\mu\text{-dppm})_3]^{2+}$ (**3a**).

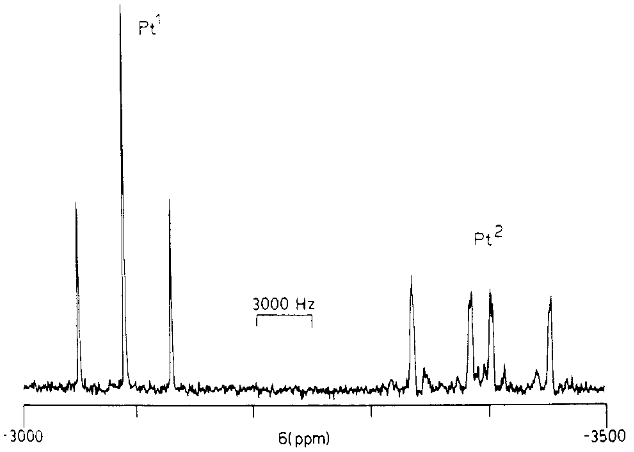
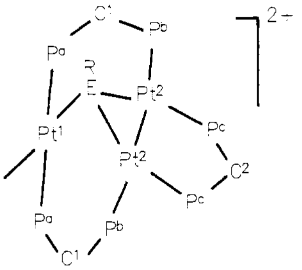


Figure 2. $^{195}Pt\{^1H\}$ NMR spectrum (64.3 MHz) of $[Pt_3H(\mu_3\text{-}SMe)(\mu\text{-}dppm)_3]^{2+}$ (**2a**).

Table II. Equilibrium Constants for Formation of Complexes **7a** and **7b** as a Function of Temperature

T/K	K(**7a**)/L mol^{-1}	K(**7b**)/L mol^{-1}	T/K	K(**7a**)/L mol^{-1}	K(**7b**)/L mol^{-1}
193	31.7	503	233		41.4
213	6.58	141	253	0.61	14.0

The major structural information was obtained from the ^1H, ^{31}P, and ^{195}Pt NMR spectra. Selected data are in Table I, while the remaining NMR data are given in the Experimental Section. The ^{31}P and ^{195}Pt NMR data for **2** and **3** are similar to those discussed earlier for **4** and are very characteristic of the structure with a single Pt–Pt bond (Figures 1 and 2, Table I).[3] The NMR labeling scheme is shown as follows:



The observation of significant couplings $^3J(P^bP^{b'})$ and $2J(Pt^2P^b)$ in the ^{31}P NMR spectra are characteristic of approximately linear PPtPtP groups[3] and confirm the presence of the Pt^2Pt^2 bond (Figure 1, Table I). The ^{31}P assignments were confirmed by correlation of the $^{31}P^{195}Pt$ coupling constants in the ^{31}P and ^{195}Pt NMR spectra (Figure 2). In the ^1H NMR spectra, the PtH resonances for **2** were very similar to that for **4**, with ^1J(PtH) being typical of a terminal hydride trans to sulfur. At room temperature, complex **4** gave two resonances due to the CH_2P_2 protons, and each split into an AB quartet at low temperature.[3] This behavior is due to inversion at sulfur, leading to an effective plane of symmetry containing the $Pt_3(dppm)_3$ unit. This inversion is not possible for the $Pt_3(\mu_3\text{-}SR)$ group, and so the CH_2P_2 protons appeared as two AB quartets at all temperatures.

Characterization of Reaction Intermediates. Complex **1** reacted with EtSH at −78 °C, with a color change from orange to red, forming a complex **7**, whose structure could be **7a** or **7a′**. Evidence for reaction included a shift in the ^{31}P NMR resonance and the ^{13}CO resonance and a change in the associated ^1J(PtP) and ^1J(PtC) couplings. However, the extent of these changes depended on the concentration of EtSH added and also on the temperature (see Experimental Section) and indicated a rapid equilibrium between **1** and **7**, such that an average signal was observed.

On the basis of the known structure of the thiocyanate adduct of **1**[6] and the lack of precedent for μ-RSH ligands,[7] the probable structure of the adduct is **7a**, but the RSH group is expected to migrate rapidly around the Pt_3 triangle perhaps by way of an intermediate **7a′**.[8] From the average $\delta(^{31}P)$ values at varying temperatures, under conditions where the initial concentrations of **1** and EtSH were known, the equilibrium constants for formation of **7a** at different temperatures, and hence the thermodynamic parameters, could be determined (Table II, Figure 3). This treatment gave $\Delta H° = -27$ kJ mol^{-1} and $\Delta S° = -110$ J K^{-1} mol^{-1}. At temperatures above −20 °C, the irreversible reaction to give **2b** occurred, and no further intermediates were detected.

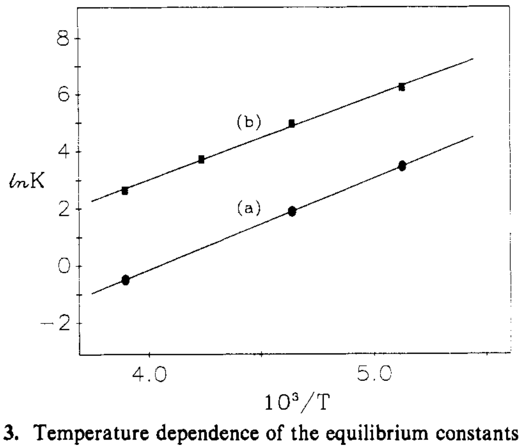
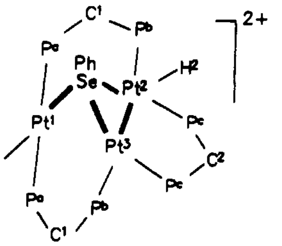


Figure 3. Temperature dependence of the equilibrium constants, K/L mol^{-1}, for formation of complexes **7** by the addition of the thiols (a) EtSH and (b) PhSH.

The behavior of benzenethiol was similar except that separate NMR signals were observed for **1** and **7b** at temperatures from −80 to −20 °C, above which temperature reaction occurred to give **2e**. The ^{31}P NMR spectrum of **7b** gave a singlet only, and we again interpret this in terms of rapid fluxionality involving migration of PhSH between the platinum atoms of the cluster. This is consistent with the case of $[Pt_3(SCN)(\mu_3\text{-}CO)(\mu\text{-}dppm)_3]^+$, in which the thiocyanate binds to a single platinum atom, but the ^{31}P NMR spectrum contains only a singlet down to −80 °C.[7,8] Structure **7b′**, with a rapidly rotating μ_3-PhSH ligand, is consistent with the NMR data but is improbable. The equilibrium constant K at each temperature could be determined by integration of the ^{31}P NMR spectrum (Table II), and these values gave $\Delta H° = -24$ kJ mol^{-1} and $\Delta S° = -73$ J K^{-1} mol^{-1} (Figure 3), similar to the values for formation of complex **7a**. It is not obvious why the equilibration between **1**, PhSH, and **7b** is slower than the analogous reaction with EtSH.

Finally, PhSeH was more reactive and gave two intermediates that were spectroscopically observable. At −80 °C, $[Pt_3(\mu_3\text{-}CO)(PhSeH)(\mu\text{-}dppm)_3]^{2+}$, which is analogous to **7** (again giving only a single ^{31}P resonance), was observed. When excess PhSeH was used, a second species tentatively characterized as $[Pt_3H_2(SePh)(\mu\text{-}dppm)_3]^{3+}$ (**8**) gave six resonances at −60 °C, which coalesced to three resonances at −20 °C. At this temperature, the spectrum was similar to that of **5**. In the ^1H NMR spectrum of **8**, two hydride resonances were observed. One of these at $\delta(H^1)$



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[6] Ferguson, G.; Lloyd, B. R.; Manojlović-Muir, Lj; Muir, K. W.; Puddephatt, R. J. *Inorg. Chem.* **1986**, *25*, 4190.

[7] For relevant reviews, see: Dance, I. G. *Polyhedron* **1986**, *5*, 607. Adams, R. D. *Polyhedron* **1985**, *4*, 2003.

[8] The related fluxionality of phosphine adducts of complex **1** has been described recently: Bradford, A. M.; Jennings, M. C.; Puddephatt, R. J. *Organometallics* **1988**, *7*, 792.

−10.4 [s, $^1J(\mathrm{PtH^1})$ = 1200 Hz] resembled the hydride resonance of **5** and did not change at −20 °C. However, the second hydride resonance at $\delta(\mathrm{H^2})$ −15.8 gave a 1:4:1 triplet at −80 °C, $^1J(\mathrm{PtH^2})$ = 894 Hz, but this had changed to a 1:8:18:8:1 quintet at −20 °C, with $J(\mathrm{PtH})$ = 445 Hz, that is half of the value at −80 °C. This indicates that the hydride is fluxional at −20 °C, migrating rapidly between Pt^2 and Pt^3 and hence giving apparent 2-fold symmetry. This species decayed with formation of **5** and, if excess PhSeH was added, then **6** on warming above −20 °C.

Discussion

This work provides strong support for the proposed mechanism of reaction of H_2S with complex **1** since the isolated products **2** are analogous to the proposed intermediate $[\mathrm{Pt_3H}(\mu_3\text{-SH})(\mu\text{-dppm})_3]^{2+}$ in the H_2S reaction.[3] It is also reasonable that the reaction of **1** with H_2S occurs via a preliminary coordination complex $[\mathrm{Pt_3}(\mu_3\text{-CO})(\mathrm{H_2S})(\mu\text{-dppm})_3]^{2+}$, analogous to $[\mathrm{Pt_3}(\mu_3\text{-CO})(\mathrm{RSH})(\mu\text{-dppm})_3]^{2+}$ (**7**) identified in this work. However, the exact mechanism by which **7** reacts to give **2** is not clear. One possibility is that intramolecular oxidative addition of the SH bond occurs, but this should give a complex with the RS and H ligands mutually cis, and so a rapid isomerization to the observed trans stereochemistry must be invoked. Alternatively, it is possible that protonation of **7** at platinum by a second molecule of RSH occurs, followed by deprotonation of the coordinated RSH group. This mechanism is suggested in particular by the observation of the intermediate **8** in the reaction of **1** with excess PhSeH. In principle, these mechanisms can be distinguished by labeling experiments, but in practice, thiol-exchange reactions frustrate such experiments. Nevertheless, this work has yielded the first complexes containing $\mathrm{Pt_3}(\mu_3\text{-SR})$ groups and a metal–metal bond[9] and has provided further insight into the interaction of H_2S with the coordinatively unsaturated cluster, **1**, and, by analogy, with a Pt(111) surface. Oxidative addition of S–H bonds to mononuclear platinum(0) complexes has been observed previously and is also thought to involve an intermediate RSH complex.[10]

Experimental Section

NMR spectra were recorded with Varian XL200 (^{1}H) and XL300 (^{31}P, ^{13}C, ^{195}Pt) spectrometers using acetone-d_6 as solvent. Chemical shifts were quoted with respect to $\mathrm{Me_4Si}$ (^{1}H, ^{13}C), 85% phosphoric acid (^{31}P), or $\mathrm{K_2PtCl_4}$ (^{195}Pt). The IR data were collected on a Bruker IR/32 FTIR spectrometer as a Nujol mull between NaCl windows. The FAB mass spectra were recorded by using a Finnigan MAT 8230 mass spectrometer on mulls in oxalic acid/3-mercapto-1,2-propanediol. Elemental analyses were carried out by Guelph Chemical Laboratories. Methyl mercaptan was obtained from the Matheson Gas Co. The remaining thiols were obtained from Eastman or Aldrich and were used without purification. The ^{13}C-enriched carbon monoxide was purchased from MSD Isotopes. The preparation of the platinum cluster **1** has been reported previously.[1]

$[\mathrm{Pt_3}(\mu\text{-dppm})_3(\mu_3\text{-SMe})\mathrm{H}][\mathrm{PF_6}]_2$ (2a). To a solution of complex **1** (0.0553 g, 2.68 × 10^{-5} mol) stirring in acetone (10 mL) was admitted a slow flow of methyl mercaptan. The orange solution turned yellow within 30 s. Acetone was evaporated, and the oily product was washed with ether, affording a yellow microcrystalline solid (92% yield). Anal. Calc for $[\mathrm{Pt_3(dppm)_3(SMe)H}][\mathrm{PF_6}]\cdot1.5\mathrm{Et_2O}$: C, 45.02, H, 3.92. Found: C, 45.05; H, 3.92. Mp: 210 °C (dec). IR: $\nu(\mathrm{PtH})$ = 2146 cm^{-1}. FAB MS *m/e* calc (found): $[\mathrm{Pt_3(dppm)_3(SMe)H}][\mathrm{PF_6}]$, 1931 (1931); $[\mathrm{Pt_3(dppm)_3(SMe)}]$, 1785 (1785); $[\mathrm{Pt_3(dppm)_3S}]$, 1770 (1770). ^{1}H NMR (all *J* values in hertz): δ 3.4 [m, 3 H, $^4J(\mathrm{PH})$ = 5.4, $^4J(\mathrm{HH})$ = 1, $^3J(\mathrm{PtH})$ = 33.2, $\mathrm{SCH_3}$], 3.8 [m, 2 H, $^2J(\mathrm{HH})$ = 14, $^2J(\mathrm{PH})$ = 4.8, $^3J(\mathrm{PtH})$ = 9.6, $\mathrm{C^1}\mathit{H}^a\mathrm{H^b}$], 4.4 [d, 2 H, $^2J(\mathrm{HH})$ = 14, $^3J(\mathrm{PtH})$ = 52, $\mathrm{C^1H^a}\mathit{H}^b$], 5.7 [AB, 2 H, $^2J(\mathrm{HH})$ = 13, $^3J(\mathrm{PtH})$ = 37, $\mathrm{C^2H^aH^b}$].

$[\mathrm{Pt_3}(\mu\text{-dppm})_3(\mu_3\text{-SEt})\mathrm{H}][\mathrm{PF_6}]_2$ (2b). To an acetone (10 mL) solution of **1** (0.0845 g, 4.10 × 10^{-5} mol) was added ethanethiol (15 μL, 20.3 × 10^{-5} mol). After the solution was stirred for 2 h, the solvent was evaporated at reduced pressure, giving a yellow powder in 90% yield. Anal. Calc for $[\mathrm{Pt_3(dppm)_3(SEt)H}][\mathrm{PF_6}]_2$: C, 44.24; H, 3.47. Found: C, 44.44; H, 3.61. Mp: 230 °C (dec). IR: $\nu(\mathrm{PtH})$ = 2143 cm^{-1}. FAB MS *m/e* calc (found): $[\mathrm{Pt_3(dppm)_3(SEt)H}][\mathrm{PF_6}]$, 1945 (1945); $[\mathrm{Pt_3(dppm)_3(SEt)}][\mathrm{PF_2}]$, 1878 (1878); $[\mathrm{Pt_3(dppm)_3(S)}]$, 1770 (1770). ^{1}H NMR: δ 1.04 [t, 3 H, $^3J(\mathrm{HH})$ = 7.4, $\mathrm{CH_3}$], 3.90 [q, 2 H, $^3J(\mathrm{HH})$ = 7.4, $\mathrm{CH_2}$], 3.77 [m, 2 H, $^2J(\mathrm{HH})$ = 14, $\mathrm{C^1}\mathit{H}^a\mathrm{H^b}$], 4.35 [d, 2 H, $^2J(\mathrm{HH})$ = 14, $^3J(\mathrm{PtH})$ = 54, $\mathrm{C^1H^a}\mathit{H}^b$], 6.0 [AB, 2 H, $^2J(\mathrm{HH})$ = 15, $^3J(\mathrm{PtH})$ = 56, $\mathrm{C^2H^aH^b}$].

$[\mathrm{Pt_3}(\mu\text{-dppm})_3(\mu_3\text{-SCH_2Ph})\mathrm{H}][\mathrm{PF_6}]_2$ (2c). Benzyl mercaptan (20 μL, 17.0 × 10^{-5} mol) was introduced into an acetone (5 mL) solution of complex **1** (0.064 g, 3.11 × 10^{-5} mol). After 30 min, the orange solution became yellow and the solvent was removed under reduced pressure. The green-tinged product was obtained in good yield (80%). Anal. Calc for $[\mathrm{Pt_3(dppm)_3(SCH_2Ph)H}][\mathrm{PF_6}]_2$: C, 45.75; H, 3.47. Found: C, 45.59; H, 3.57. Mp: 210 °C. IR: $\nu(\mathrm{PtH})$ = 2145 cm^{-1}. FAB MS *m/e* calc (found): $[\mathrm{Pt_3(dppm)_3(S)}]$, 1770 (1770). ^{1}H NMR: δ 3.01 [m, 2 H, $^2J(\mathrm{HH})$ = 14.4, $^2J(\mathrm{PH})$ = 5, $\mathrm{C^1}\mathit{H}^a\mathrm{H^b}$], 4.29 [d, $^2J(\mathrm{HH})$ = 14.4, $^3J(\mathrm{PtH})$ = 56, $\mathrm{C^1H^a}\mathit{H}^b$], 4.92 [br t, 2 H, $^4J(\mathrm{PH})$ = 4, $^3J(\mathrm{PtH})$ = 28, $\mathrm{CH_2}$], 6.02 [AB, 2 H, $^2J(\mathrm{HH})$ = 12, $^3J(\mathrm{PtH})$ = 38, $\mathrm{C^2H^aH^b}$)].

$[\mathrm{Pt_3}(\mu\text{-dppm})_3(\mu_3\text{-SCH_2CO_2CH_2CH_3})\mathrm{H}][\mathrm{PF_6}]_2$ (2d). To an acetone (10 mL) solution of complex **1** (0.0538 g, 2.61 × 10^{-5} mol) was added an excess of ethyl 2-mercaptoacetate (9 μL, 8.21 × 10^{-5} mol). After being stirred for 4.5 h, the orange solution had become paler. The solvent was removed on a rotary evaporator, and the mustard brown solid was washed with ether. Yield: 96%. Anal. Calc for $[\mathrm{Pt_3(dppm)_3(SCH_2CO_2CH_2CH_3)H}][\mathrm{PF_6}]_2$: C, 44.16; H, 3.47. Found: C, 43.88; H, 3.81. Mp: 170 °C (dec). IR: $\nu(\mathrm{PtH})$ = 2155 cm^{-1}, ν (CO) = 1727 cm^{-1}. ^{1}H NMR: δ 0.89 [t, 3 H, $^3J(\mathrm{HH})$ = 6.8, $\mathrm{CH_3}$], 3.6 [q, 2 H, $^3J(\mathrm{HH})$ = 6.8, $\mathrm{CH_2}$], 3.9 [br m, 2 H, $^2J(\mathrm{HH})$ = 12, $\mathrm{C^1}\mathit{H}^a\mathrm{H^b}$], 4.3 [br d, 2 H, $^2J(\mathrm{HH})$ = 12, $\mathrm{C^1H^a}\mathit{H}^b$], 4.6 [t, 2 H, $^4J(\mathrm{PH})$ = 4.5, $^4J(\mathrm{HH})$ = 2.0, $^3J(\mathrm{PtH})$ = 26, $\mathrm{SCH_2}$], 5.7 [AB, 2 H, $^2J(\mathrm{HH})$ = 12, $^3J(\mathrm{PtH})$ = 70, $\mathrm{C^2H^aH^b}$].

$[\mathrm{Pt_3}(\mu\text{-dppm})_3(\mu_3\text{-SPh})\mathrm{H}][\mathrm{PF_6}]_2$ (2e). To a solution of cluster **1** (0.037 g, 1.79 × 10^{-5} mol) in acetone at −78 °C was added 1 molar equiv of thiophenol (1.85 μL, 1.80 × 10^{-5} mol). The orange solution turned red and was allowed to warm slowly to room temperature, affording a yellow solution. The product was obtained as an orange powder in 83% yield. Anal. Calc for $[\mathrm{Pt_3(dppm)_3(SPh)H}][\mathrm{PF_6}]_2$: C, 45.49; H, 3.39. Found: C, 45.52; H, 3.36. Mp: 220 °C (dec). IR: $\nu(\mathrm{PtH})$ = 2145 cm^{-1}. FAB MS *m/e* calc (found): $[\mathrm{Pt_3(dppm)_3(SPh)}][\mathrm{PF_6}]$, 1992 (1992); $[\mathrm{Pt_3(dppm)_3(SPh)}]$, 1847 (1845). ^{1}H NMR: δ 3.15 [m, 2 H, $^2J(\mathrm{HH})$ = 14.6, $^2J(\mathrm{PH})$ = 4, $\mathrm{C^1}\mathit{H}^a\mathrm{H^b}$], 4.36 [d, 2 H, $^2J(\mathrm{HH})$ = 14.6, $^3J(\mathrm{PtH})$ = 55, $\mathrm{C^1H^a}\mathit{H}^b$], 5.8 [AB, 2 H, $^2J(\mathrm{HH})$ = 12.8, $^3J(\mathrm{PtH})$ = 52, $\mathrm{C^2H^aH^b}$].

$[\mathrm{Pt_3}(\mu\text{-dppm})_3(\mu_3\text{-SPh})(\mathrm{SPh})][\mathrm{PF_6}]_2$ (3a). The platinum cluster **1** (0.070 g, 3.40 × 10^{-5} mol) was dissolved in acetone (10 mL), and thiophenol (25 μL, 24.3 × 10^{-5} mol) was added. The orange solution turned yellow within 10 min but was stirred for another 1 h. The acetone solution was concentrated under reduced pressure and layered with pentane. This afforded an orange crystalline powder in good yield (85%). Anal. Calc for $[\mathrm{Pt_3(dppm)_3(SPh)_2}][\mathrm{PF_6}]_2$: C, 46.50; H, 3.41. Found: C, 46.35; H, 3.59. Mp: 240 °C. FAB MS *m/e* calc (found): $[\mathrm{Pt_3(dppm)_3(SPh)_2}]$, 1956 (1955); $[\mathrm{Pt_3(dppm)_3(SPh)S}]$, 1879 (1879); $[\mathrm{Pt_3(dppm)_3(SPh)}]$, 1847 (1847). ^{1}H NMR: δ 3.58 [m, 2 H, $^2J(\mathrm{HH})$ = 14, $^2J(\mathrm{PH})$ = 4.5, $\mathrm{C^1}\mathit{H}^a\mathrm{H^b}$], 4.01 [d, 2 H, $^2J(\mathrm{HH})$ = 14, $^3J(\mathrm{PtH})$ = 51, $\mathrm{C^1H^a}\mathit{H}^b$], 5.86 [AB, 2 H, $^2J(\mathrm{HH})$ = 12.8, $^3J(\mathrm{PtH})$ = 51, $\mathrm{C^2H^aH^b}$].

$[\mathrm{Pt_3}(\mu\text{-dppm})_3(\mathrm{SMe})(\mathrm{SPh})][\mathrm{PF_6}]_2$ (3c,d). Through an acetone (10 mL) solution of **1** (0.067 g, 3.25 × 10^{-5} mol) was bubbled methanethiol, giving product **2a**. Benzenethiol (3.4 μL, 3.31 × 10^{-5} mol) was added, and the solution was allowed to stir for 2 h. The yellow solution gradually turned gold and then pale orange. The solvent was removed on a rotary evaporator, and a yellow-orange powder was obtained in 87% yield. Anal. Calc for $[\mathrm{Pt_3(dppm)_3(SMe)(SPh)}][\mathrm{PF_6}]_2$: C, 45.08; H, 3.41. Found: C, 44.90; H, 3.56. Mp: 205 °C. FAB MS *m/e* calc (found): $[\mathrm{Pt_3(dppm)_3(SPh)S}]$, 1879 (1879).

$[\mathrm{Pt_3}(\mu\text{-dppm})_3(\mu_3\text{-SC_6H_4CH_3})\mathrm{H}][\mathrm{PF_6}]_2$ (2f). A 4.06 × 10^{-3} M solution of *p*-thiocresol (0.0504 g) in acetone (100 mL) was prepared. The *p*-thiocresol solution (6.5 mL, 2.63 × 10^{-5} mol) was added via a dropping funnel to an acetone solution of **1** (0.0521 g, 2.53 × 10^{-5} mol) at 0 °C. The solution was stirred for 16 h at ambient temperature. The solvent was removed under reduced pressure and the product was washed with ether, giving an orange solid. ^{1}H NMR: δ 3.2 [m, 2 H, $^2J(\mathrm{HH})$ = 14.9, $\mathrm{C^1}\mathit{H}^a\mathrm{H^b}$], 4.3 [d, 2 H, $^2J(\mathrm{HH})$ = 14.9, $^3J(\mathrm{PtH})$ = 56, $\mathrm{C^1H^a}\mathit{H}^b$] 6.1 [m, 2 H, $^2J(\mathrm{HH})$ = 8, $\mathrm{C^2H^aH^b}$], 2.6 [s, 3 H, $\mathrm{CH_3}$].

$[\mathrm{Pt_3}(\mu\text{-dppm})_3(\mu_3\text{-SC_6H_4CH_3})(\mathrm{SC_6H_4CH_3})][\mathrm{PF_6}]_2$ (3b). To an acetone (10 mL) solution of **1** (0.050 g, 2.43 × 10^{-5} mol) was added 12 mL (4.87 × 10^{-5} moles) of the above *p*-thiocresol solution. The solution was stirred for 24 h and the solvent removed. The product was washed with ether, giving an orange-yellow solid (75% yield). Mp: 230 °C (dec). FAB MS *m/e* calc (found): $[\mathrm{Pt_3(dppm)_3(SC_6H_4CH_3)_2}][\mathrm{PF_6}]$, 2129 (2126); $[\mathrm{Pt_3(dppm)_3(SC_6H_4CH_3)_2}]$, 1984, (1981). ^{1}H NMR: δ 1.9 [s, 3 H,

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[9] For a recent review, see: Roundhill, D. M. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon: London, 1987; Vol. 5, Chapter 52. The complexes $[\{\mathrm{PtMe_3}(\mu_3\text{-SR})\}_4]$ contain μ_3-SR groups but have no metal–metal bonding.

[10] Ugo, R.; LaMonica, G.; Cenini, S.; Segre, A.; Conti, F. *J. Chem. Soc. A* **1971**, 522.

CH_3], 2.5 [s, 3 H, CH_3], 3.6 [m, 2 H, $^2J(HH)$ = 14, $\mathrm{C^1}H^{a}\mathrm{H^b}$], 4.0 [d, 2 H, $^2J(HH)$ = 14, $^3J(PtH)$ = 52, $\mathrm{C^1H^a}H^{b}$], 5.9 [AB, 2 H, $^2J(HH)$ = 8, $\mathrm{C^2H^aH^b}$].

[$Pt_3(\mu$-dppm$)_3(\mu_3$-$^{13}CO)][PF_6]_2$ (1b). The triplatinum cluster **1** (0.130 g) was dissolved in acetone (5 mL) in a 15-mL round-bottom flask and the solution degassed by using three freeze–pump–thaw cycles. The ^{13}C-enriched carbon monoxide was frozen on top of the acetone solution at 77 K, and the flask was sealed. The reaction flask was warmed to room temperature, and the solution was allowed to stir for 16 h. Evaporation of excess carbon monoxide and solvent yielded the enriched species, **1b**.

Variable-Temperature Multinuclear NMR Experiment. (a) With EtSH. Compound **1b** (0.0313 g, 1.52×10^{-5} mol) was dissolved in acetone-d_6 (0.5 mL) in an NMR tube that was sealed with a septum cap. This tube was inserted into the NMR probe and cooled to −80 °C. NMR: $\delta(^{13}C)$ 208.5 [sept, 1 C, $^2J(PC)$ = 26.4, $^1J(PtC)$ = 762, Pt_3CO], $\delta(^{31}P)$ −8.9 [br s, 6 P, $^1J(PtP)$ = 3700, P]. Then the NMR tube was ejected from the probe and kept at −78 °C while 1 molar equiv of ethanethiol (1.2 μL, 1.62×10^{-5} mol) was added. The solutions were quickly mixed, turning the orange solution red, and returned to the probe. $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR spectra were recorded at various temperatures as follows. −80 °C: $\delta(^{31}P)$ −13.0 [br s, 6 P, $^1J(PtP)$ = 3570, P], $\delta(^{13}C)$ 203.5 [br s, 1 C, $^1J(PtC)$ = 800, Pt_3CO]. −60 °C: $\delta(^{31}P)$ −10.5 [s, 6 P, $^1J(PtP)$ = 3650, P]. −20 °C: $\delta(^{31}P)$ −9.1 [s, 6 P, $^1J(PtP)$ = 3650, P]. 0 °C: spectrum of **2b** (Table I).

(b) With PhSH. The triplatinum cluster **1** (0.037 g, 1.80×10^{-5} mol) was dissolved in acetone-d_6 (0.5 mL) in an NMR tube that was sealed under N_2 with a septum cap. The tube was inserted into the probe of the Varian XL300, and the probe temperature was lowered to −80 °C. NMR: $\delta(^{31}P)$ −8.9 [br s, 6 P, $^1J(PtP)$ = 3700, P]. The NMR tube was ejected and kept at −78 °C. Benzenethiol (2 μL, 1.95×10^{-5} mol) was added via syringe through the septum cap, causing a change from orange to red. The NMR reaction tube was then returned to the spectrometer, and $^{31}P\{^1H\}$ and ^{1}H spectra were recorded at various temperatures. NMR at −80 °C: $\delta(^{31}P)$ −8.8 [s, $^1J(PtP)$ = 3700, complex **1**], −22.2 [s, $^1J(PtP)$ = 3720, $^3J(PP)$ = 160, complex **7b**]. Integration gave the relative concentrations of these species. Similar spectra were observed at −60, −40, and −20 °C. At 0 °C, further reaction occurred to give **2e**.

The experiment was repeated with the ^{13}CO-enriched triplatinum cluster **1b**. NMR at −80 °C: $\delta(^{13}C)$ 209 [sept, 1 C, $^2J(PC)$ = 26.4 $^1J(PtC)$ = 762, Pt_3CO]. The NMR tube was ejected, benzenethiol (1 μL, 9.74×10^{-6} mol) was added at −78 °C, and the tube was reinserted into the probe at −80 °C. NMR δ (^{31}P) −22.3 [br, s, $^1J(PtP)$ = 3720, $^3J(PP)$ = 160], −8.8 [br s, $^1J(PtP)$ = 3700]; $\delta(^{13}C)$ 195 [br s, $^1J(PtC)$ = 762, Pt_3CO]. At temperatures above −20 °C, a ^{13}C signal due to free CO appeared at δ 185 [s, free CO]. After 24 h, a $^{31}P\{^1H\}$ spectrum was recorded that showed only the product **2e** in solution.

(c) With PhSeH. Complex **1** (0.033 g, 1.60×10^{-5} mol) was dissolved in acetone-d_6, and the solution was sealed in an NMR tube under N_2. At dry ice temperature, benzeneselenol (2.8 μL, 1.96×10^{-5} mol) was added via syringe to the NMR tube. The solution color changed from orange to red, and the tube was inserted into the probe at −80 °C. $^{31}P\{^1H\}$ and ^{1}H spectra were recorded at various temperatures. ^{31}P NMR at −80 °C: for **7**, δ −21.6 [s, 6 P, $^1J(PtP)$ = 3750, $^3J(PP)$ = 160]; for **8** (assignments for pairs of phosphorus atoms a,a′, b,b′, and c,c′ may be reversed), δ 18.1 [s, 1 P, $^1J(PtP)$ = 2860, P^a], 14.1 [s, 1 P, $^1J(PtP)$ = 2960, $P^{a'}$], 10.5 [s, 1 P, $^1J(PtP)$ = 2960, P^b], 9.3 [s, 1 P, $^1J(PtP)$ = 2964, $P^{b'}$], −18.2 [br, s, 1 P, $^1J(PtP)$ = 3490, P^c], −26.5 [br s, 1 P, $^1J(PtP)$ = 3220, $P^{c'}$] ^{195}Pt NMR at −80 °C: for **7**, δ −2720 [t, $^1J(PtP)$ = 3700]; for **8**, δ −3200 [t, 1 Pt, $^1J(PtP)$ = 2920, Pt^1], −3227 [t, 1 Pt, $^1J(PtP)$ = 3451, Pt^2], −3280 [t, 1 Pt, $^1J(PtP)$ = 2925, Pt^3]. In addition, there was an unassigned resonance of low intensity at δ −3023 [br ddd, $^1J(PtP)$ = 2200, $^1J(PtP)$ = 3250, $J(PtP)$ = 700]. ^1H NMR at −80 °C: for **8**, δ −10.4 [s, $^1J(PtH)$ = 1200], −15.8 [s, $^1J(PtH)$ = 894]. As the sample was warmed to −60, −40, and finally −20 °C, the six phosphorus signals for **8** coalesced to three signals. By this temperature the phosphorus signal at δ −21.6 had almost disappeared. NMR data for **8** at −20 °C: $\delta(^{31}P)$ 16.0 [s, 2 P, $^1J(PtP)$ = 2906, P^a], 9.5 [br s, 2 P, $^1J(PtP)$ = 2992, P^b], −22.5 [s, 2 P, $^1J(PtP)$ = 3360, P^c]; $\delta(^1H)$ −10.5 [t, $^2J(PH)$ = 12, $^1J(PtH)$ = 1209], −15.9 [s, $^1J(PtH)$ = 445]. At 0 °C signals due to **5** (Table I) were observed. Then more benzeneselenol was added (2.6 μL, 1.82×10^{-5} mol) to the NMR tube at room temperature. This gave the final reaction product **6**, and NMR data are in Table I.

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Synthesis, Crystal Structure, Electrical Properties, and Band Electronic Structure of Bis(1,3-propanediyldithio)tetrathiafulvalenium Tetraiodoindate(III), $(BPDT\text{-}TTF)_3(InI_4)_2$

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We have obtained a 3:2 salt $(BPDT\text{-}TTF)_3(InI_4)_2$ by electrocrystallization and determined its structure by single-crystal X-ray diffraction (triclinic, space group $P\bar{1}$, a = 7.403 (2) Å, b = 9.170 (2) Å, c = 25.883 (7) Å, α = 89.29 (2)°, β = 96.34 (2)°, γ = 92.83 (2)°, V = 1774.2 (8) Å^3, Z = 1). Analysis of the C=C and C—S bond lengths in the PT (i.e., BPDT-TTF) molecules suggests that this salt consists of donor molecules PT in two different oxidation states (i.e., BPDT-TTF$^+$ and BPDT-TTF$^{0.5+}$). This oxidation assignment is consistent with our ESR measurements and band electronic structure calculations. The $(BPDT\text{-}TTF)_3(InI_4)_2$ salt is a semiconductor at room temperature and below, which can be rationalized in terms of electron localization in the stacks of BPDT-TTF$^+$ cations and the electronic instability associated with the well-nested Fermi surface for the layers of $(BPDT\text{-}TTF)_2{}^+$ dimers. Preliminary X-ray diffraction experiments indicate that $(BPDT\text{-}TTF)_3(TlI_4)_2$ is isostructural with $(BPDT\text{-}TTF)_3(InI_4)_2$.

Introduction

A large number of salts of the donor radical cation BEDT-TTF (bis(ethylenedithio)tetrathiafulvalene, also known as ET) have been found with electrical conductivities ranging from insulators to superconductors.[1] Numerous investigators have recently attempted to match the success of using ET in the design of novel conducting materials by introducing slight modifications into the donor molecule. In particular, the saturated ethylene end groups have been replaced by methylene and propylene groups, and all combinations (M = methylene, E = ethylene, P = 1,3-propanediyl)—MT, ET, PT, MET, MPT, and EPT—can be selectively synthesized.[2] PT (or BPDT-TTF, bis(1,3-propane-

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(1) For a review, see: Williams, J. M.; Wang, H. H.; Emge, T. J.; Geiser, U.; Beno, M. A.; Leung, P. C. W.; Carlson, K. D.; Thorn, R. J.; Schultz, A. J.; Whangbo, M.-H. *Prog. Inorg. Chem.* **1987**, *35*, 51.

(2) (a) Kini, A. M.; Beno, M. A.; Williams, J. M. *J. Chem. Soc., Chem. Commun.* **1987**, 335. (b) Kini, A. M.; Tytko, S. F.; Hunt, J. E.; Williams, J. M. *Tetrahedron Lett.* **1987**, *28*, 4153.

0020-1669/88/1327-4284$01.50/0