Ligand Dissociation as a Preliminary Step in Methyl for Halogen Exchange Reactions of Platinum(II) Complexes

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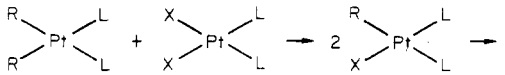
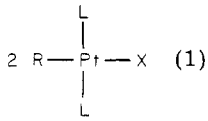
The complex *cis*-$[PtMe_2(SMe_2)_2]$ exists in solution in equilibrium with $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ and free SMe_2. Methyl for halogen exchange occurs on reaction of *cis*-$[PtMe_2(SMe_2)_2]$ with *cis*- or *trans*-$[PtCl_2(SMe_2)_2]$ to give *trans*-$[PtClMe(SMe_2)_2]$ as the only product, with *trans*-$[PtI_2(SMe_2)_2]$ to give *trans*-$[PtIMe(SMe_2)_2]$, and with *trans*-$[PtI_2(PMePh_2)_2]$ to give isomers of $[PtIMe(SMe_2)(PMePh_2)]$ as major projects, whereas *cis*-$[PtMe_2(PMe_2Ph)_2]$ reacts with *trans*-$[PtI_2(SMe_2)_2]$ to give *trans*-$[PtIMe(PMe_2Ph)_2]$ and *trans*-$[PtIMe(SMe_2)_2]$ with no scrambling of neutral ligands. Kinetic studies show that the reaction of *cis*-$[PtMe_2(SMe_2)_2]$ with *trans*-$[PtCl_2(SMe_2)_2]$ follows second-order kinetics (first order in each reagent) and the reaction is strongly retarded in the presence of free SMe_2. From these results, it is deduced that the methyl for halogen exchange reactions of *cis*-$[PtMe_2(SMe_2)_2]$ occur after dissociation of SMe_2 to give a reactive intermediate, $[PtMe_2(SMe_2)]$.

Introduction

Although alkyl transfer from a main-group metal to a transition metal is one of the most useful synthetic routes to alkyl derivatives of transition metals, the related alkyl transfer between two transition-metal centers has not yet been exploited extensively.[1-4] There is however a growing recognition that such reactions may be synthetically useful and that they must be considered in many apparently unrelated reactions of transition-metal alkyls.[1,2,5] Both alkyl for alkyl and alkyl for halogen exchange reactions between transition-metal centers have been identified.[1-4]

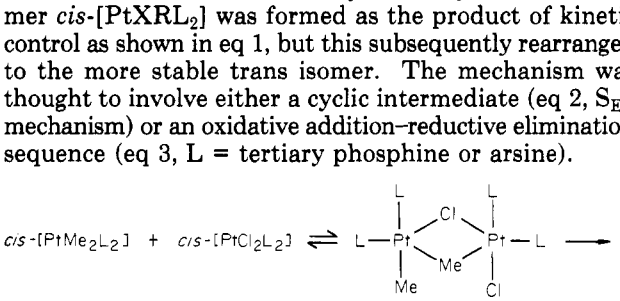
A systematic study of the symmetrization reactions of eq 1 has been reported previously[4,6] (R = alkyl or aryl; X = halide or other anionic ligand; L = tertiary phosphine or arsine).





(1)

In several cases the thermodynamically less stable isomer *cis*-$[PtXRL_2]$ was formed as the product of kinetic control as shown in eq 1, but this subsequently rearranged to the more stable trans isomer. The mechanism was thought to involve either a cyclic intermediate (eq 2, S_E2 mechanism) or an oxidative addition–reductive elimination sequence (eq 3, L = tertiary phosphine or arsine).



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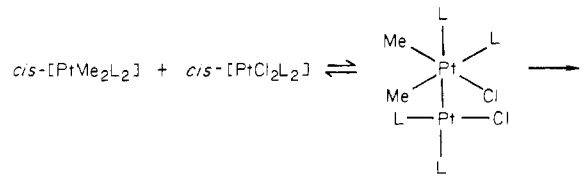

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These reactions were considered to occur without prior dissociation of a ligand, L, for the following reasons:[4] 1. Some loss of stereochemistry at platinum would be expected if 3-coordinate platinum complexes were involved, since such T-shaped molecules are expected to isomerize rapidly,[7] but this was not observed in many (though not all) cases. 2. Similar complexes with L = PMe_3 or $AsMe_3$ reacted at similar rates; the arsine complexes would be expected to give much higher reactivity if ligand dissociation were involved, since the Pt–AsR_3 bond is much more labile than the Pt–PR_3 bond. 3. Several reactions were shown to follow second-order kinetics, whereas a mechanism involving rate-determining loss of ligand from one reagent would give first-order kinetics. 4. Reactions carried out between complexes $PtMe_2L_2$ and $PtCl_2L'_2$, where L and L′ are different tertiary phosphines, occurred without scrambling of the ligands L and L′.

We have now discovered a system that reacts according to eq 1, with L = Me_2S. The ligand dimethyl sulfide does not displace chloride from platinum to form ionic complexes $[PtClL_3]^+Cl^-$ or $[PtMeL_3]^+Cl^-$, even when present in large excess.[8] It is shown that the exchange reaction of eq 1, L = Me_2S, is significantly retarded in the presence of free ligand, L, and a mechanism involving preliminary dissociation of L from *cis*-$[PtMe_2L_2]$ is proposed in this case.

Results

Synthesis and Characterization of Reagents and Products. The isomers *cis*- and *trans*-$[PtCl_2(SMe_2)_2]$ are easily prepared and purified. In $CDCl_3$ solution the trans isomer is thermodynamically stable, but the less stable cis

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(2) Tamaki, A.; Kochi, J. K. *J. Organomet. Chem.* **1974**, *64*, 411.
(3) Rice, G. W.; Tobias, R. S. *J. Organomet. Chem.* **1975**, *86*, C37.
(4) Puddephatt, R. J.; Thompson, P. J. *J. Chem. Soc., Dalton Trans.* **1975**, 1810. Thompson, P. J.; Puddephatt, R. J. *J. Organomet. Chem.* **1975**, *120*, C51. Puddephatt, R. J.; Thompson, P. J. *J. Chem. Soc., Dalton Trans.* **1977**, 1219.
(5) Puddephatt, R. J.; Thompson, P. J. *J. Chem. Soc., Dalton Trans.* **1976**, 2091. Johnson, A.; Puddephatt, R. J. *Ibid.* **1976**, 1360. Johnson, A.; Puddephatt, R. J. *Ibid.* **1975**, 115.
(6) Visser, J. P.; Jager, W. W.; Masters, C. *Recl. Trav. Chim. Pays-Bas* **1975**, *94*, 61.
(7) Komiya, S.; Morimoto, Y.; Yamamoto, A.; Yamamoto, T. *Organometallics*, **1982**, *1*, 1528. Tatsumi, K.; Hoffmann, R.; Yamamoto, A.; Stille, J. K. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1857 and references therein. Note, however, that T-shaped palladium(II) complexes isomerize relatively slowly.
(8) Roulet, R.; Barbey, C. *Helv. Chim. Acta* **1973**, *56*, 2179.

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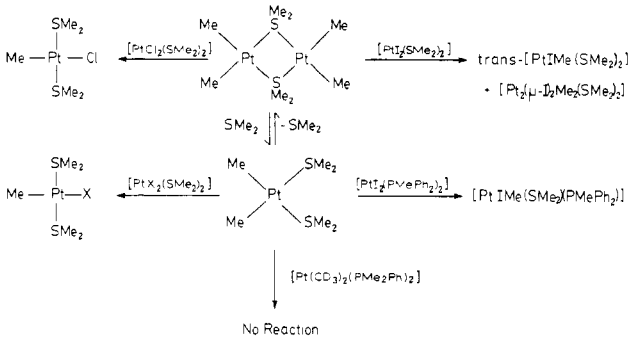
Scheme I



isomer isomerizes only very slowly. This isomerization is catalyzed by added dimethyl sulfide, as originally reported by Roulet and Barbey who proposed that a consecutive displacement mechanism operated.[8] We have confirmed that the rate of isomerization in $CDCl_3$ solution at 20 °C is given by the expression

$$-d/dt[cis] = k\{[cis] - [cis]^{\infty}\}[SMe_2]$$

and $k = 0.21$ L mol^{-1} s^{-1}. In $CDCl_3$ at 30 °C, we find the equilibrium constant for cis–trans isomerization is 6.4 and in CD_2Cl_2 it is 2.3, while Roulet and Barbey report 6.4 and 1.9, respectively, at 28 °C. Most of our studies were carried out in $CDCl_3$ solution where the trans isomer is dominant in the equilibrium mixtures. Treatment of either isomer of $[PtCl_2(SMe_2)_2]$ with methyllithium gave the binuclear $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$, which was characterized unambiguously by the ^{1}H NMR spectrum. Thus the MePt resonance appeared as a singlet with quarter intensity satellites due to coupling with ^{195}Pt, while the equal intensity Me_2S resonance appeared as a 1:8:18:8:1 multiplet due to ^{195}Pt coupling, proving the bridging nature of the Me_2S ligands (Figure 1).[9] The related $[Pt_2Me_4(\mu\text{-}SEt_2)_2]$ has been characterized previously.[10] Some of the chemistry developed from $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ is shown in the flow diagram of Scheme I and is described below.

Addition of Me_2S to solutions of $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ in CH_2Cl_2 solution gave *cis*-$[PtMe_2(SMe_2)_2]$, characterized by its ^{1}H NMR spectrum (Figure 1). The cis stereochemistry, which is always seen in complexes $PtMe_2L_2$, is proved by the very low coupling $^3J(PtSCH_3)$ of 23 Hz (Table I), indicating that dimethyl sulfide is trans to methyl.[11] Separate signals were observed due to free and coordinated SMe_2, and the coordinated SMe_2 resonance gave clearly defined satellites due to coupling with ^{195}Pt, thus proving that exchange of these groups is slow on the NMR time scale. However, evaporation of solutions containing *cis*-$[PtMe_2(SMe_2)_2]$, even at low temperature, always led to partial loss of SMe_2 and formation of $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$. It is therefore clear that dissociation of Me_2S from *cis*-$[PtMe_2(SMe_2)_2]$ is a facile reaction. Similarly, reaction of $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ with SMe_2 to give *cis*-$[PtMe_2(SMe_2)_2]$ is also rapid. If this reaction was carried out in an NMR tube, reaction was complete before the NMR spectrum could be recorded. When approximately the calculated quantity of SMe_2 was added to $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$, according to the stoichiometry of eq 4, NMR signals due to $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$, *cis*-$[PtMe_2(SMe_2)_2]$, and free SMe_2 were observed (Figure 1), showing that eq 4 is an equilibrium.

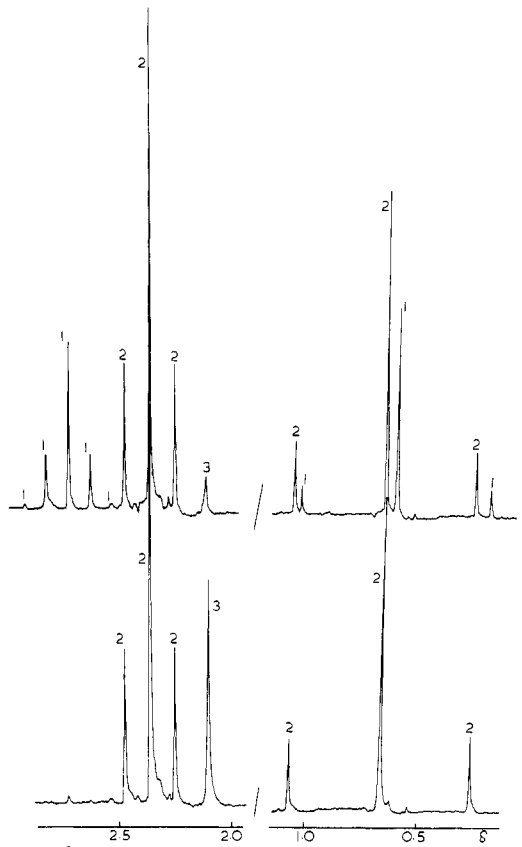


Figure 1. ^{1}H NMR spectra (100 MHz) of, above, equilibrium mixture of $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$, *cis*-$[PtMe_2(SMe_2)_2]$, and free SMe_2 and, below, with excess SMe_2 added to give almost complete conversion to *cis*-$[PtMe_2(SMe_2)_2]$. Peaks labeled 1 due to $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$, 2 due to *cis*-$[PtMe_2(SMe_2)_2]$, and 3 due to SMe_2.

$$[Pt_2Me_4(\mu\text{-}SMe_2)_2] + 2SMe_2 \rightleftharpoons 2\,cis\text{-}[PtMe_2(SMe_2)_2] \quad (4)$$

From eight separate NMR experiments involving integration of signals due to each complex and free SMe_2, the equilibrium constant was found to be 1300 ± 200 L mol^{-1} at 30 °C. Because it was not possible to isolate pure *cis*-$[PtMe_2(SMe_2)_2]$, solutions containing this complex were prepared as needed by adding the calculated quantity of SMe_2 to $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ in CH_2Cl_2 solution.

The symmetrization reaction between *cis*-$[PtMe_2(SMe_2)_2]$ and either *cis*- or *trans*-$[PtCl_2(SMe_2)_2]$ occurred readily to give *trans*-$[PtClMe(SMe_2)_2]$ as the only product. No *cis*-$[PtClMe(SMe_2)_2]$ was detected at any stage when reactions were monitored by NMR spectroscopy. Because the stereochemistry of the exchange reactions can give useful mechanistic insights, we have attempted to prepare *cis*-$[PtClMe(SMe_2)_2]$ by an independent method, in order that the rate of its rearrangement to the trans isomer might be studied. Generally, reaction of anhydrous HCl with *cis*-$[PtMe_2L_2]$ yields *cis*-$[PtClMeL_2]$ only,[12] but addition of HCl to a cold solution of *cis*-$[PtMe_2(SMe_2)_2]$ in ether led to rapid precipitation of *trans*-$[PtClMe(SMe_2)_2]$ only, as identified by IR and NMR spectroscopy. We conclude that *cis*-$[PtClMe(SMe_2)_2]$ isomerizes very rapidly to the trans isomer. Hence it is not possible to determine whether the loss of stereochemistry seen for the exchange reaction occurs during the actual methyl for chloro exchange or in

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Table I. ^{1}H NMR Spectra of the Complexes in $CDCl_3$

complex	δ(MePt)	^2J(PtH), Hz	δ(MeS)	^3J(PtH), Hz
$[Pt_2Me_4(\mu\text{-}SMe_2)_2]$	0.63	85	2.75	20[a]
cis-$[PtMe_2(SMe_2)_2]$	0.68	81	2.39	23
cis-$[PtCl_2(SMe_2)_2]$			2.55	50
trans-$[PtCl_2(SMe_2)_2]$			2.44	42
trans-$[PtClMe(SMe_2)_2]$	0.46	80	2.51	54
trans-$[PtI_2(SMe_2)_2]$			2.66	44
trans-$[PtIMe(SMe_2)_2]$	0.66	77	2.58	56
$[Pt_2(\mu\text{-}I)_2Me_2(SMe_2)_2]$[b]	0.70	76	2.42	72
	0.74	80	2.43	72
$Na[PtIMe_2(SMe_2)]$	0.25[c]	82	2.12	24
$[PtI(SMe_2)_3][BF_4]$			2.88[d]	44
			2.66[e]	46

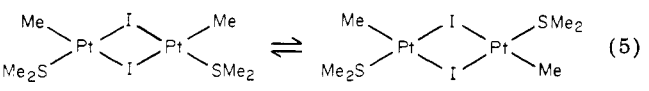
[a] 1:8:18:8:1 quintet. [b] Two isomers present; see text. [c] Two resonances not resolved. [d] SMe_2 trans to S. [e] SMe_2 trans to I.

a very rapid subsequent isomerization of initially formed *cis*-$[PtClMe(SMe_2)_2]$.

The methyl exchange reactions were much faster than in similar reactions with phosphine or arsine ligands. For example, the exchange between *cis*-$[PtMe_2(SMe_2)_2]$ and *trans*-$[PtCl_2(SMe_2)_2]$ was half complete in ~20 min at room temperature, whereas that between *cis*-$[PtMe_2(PMe_2Ph)_2]$ and *cis*-$[PtCl_2(PMe_2Ph)_2]$ was half complete in ~3 weeks under similar conditions (concentrations of ~0.06 M in CH_2Cl_2 solution).[4]

Reaction of $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ with either *cis*- or *trans*-$[PtCl_2(SMe_2)_2]$ gave *trans*-$[PtClMe(SMe_2)_2]$ as the only identified platinum complex. The other expected product $[Pt_2Cl_2Me_2(\mu\text{-}SMe_2)_2]$ was not detected at any stage, but an insoluble brown-black precipitate was formed. The complex $[Pt_2Cl_2Me_2(\mu\text{-}SMe_2)_2]$ appears to be very unstable and decomposes to *trans*-$[PtClMe(SMe_2)_2]$ and "PtClMe"; the insoluble product may be a mixture of $PtCl_2$ and Pt metal formed by decomposition of "PtClMe". Attempts have been made to prepare $[Pt_2Cl_2Me_2(SMe_2)_2]$ by other methods, for example by methylation of $[Pt_2Cl_4(\mu\text{-}SMe_2)_2]$, and in all cases *trans*-$[PtClMe(SMe_2)_2]$ was formed along with methane and the dark insoluble material. The exchange reactions between $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ and $[PtCl_2(SMe_2)_2]$ were too rapid to allow monitoring by ^{1}H NMR spectroscopy, being complete within 5–10 min at room temperature.

The reaction between *cis*-$[PtMe_2(SMe_2)_2]$ and *trans*-$[PtI_2(SMe_2)_2]$ gave *trans*-$[PtIMe(SMe_2)_2]$, and this reaction was complete in 5–10 min at room temperature. A still faster reaction occurred between $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ and *trans*-$[PtI_2(SMe_2)_2]$ to give *trans*-$[PtIMe(SMe_2)_2]$ and $[Pt_2(\mu\text{-}I)_2Me_2(SMe_2)_2]$. This dimer was sufficiently stable to allow identification by NMR spectroscopy though it could not be isolated. In the low-temperature spectra (0 °C or less) two isomers were detected. Each contained MePt and Me_2S resonances in a 1:2 ratio and each gave 1/4 intensity satellites due to coupling to ^{195}Pt. The results show that the Me_2S ligands occupy terminal coordination sites and hence that iodide bridges are formed. Data are given in Table I and the relative abundances of the two isomers characterized by δ(MePt) 0.70 and 0.74 was ~ 60:40. At 30 °C the two Me_2S singlets had coalesced in the 100-MHz spectra and the two MePt peaks were broad but not quite coalesced. It is thus apparent that the cis and trans isomers interconvert readily (eq 5).



(5)

We cannot assign the NMR spectra to the specific isomer. Presumably, the iodide bridges are more stable than chloride or dimethyl sulfide bridges and the dimers are therefore long-lived in solution.

In the exchange reactions with iodoplatinum complexes, minor species were detected by NMR spectroscopy in reaction mixtures but could not be identified. We have prepared $[PtI(SMe_2)_3][BF_4]$ and Na *cis*-$[PtMe_2I(SMe_2)]$ in solution by independent methods, and the absence of either complex cation $[PtI(SMe_2)_3]^+$ or anion *cis*-$[PtMe_2I(SMe_2)]^-$ in the reaction mixtures was established by comparison of the NMR data (Table I).

As a further check on ligand dissociation, some further experiments with mixed ligands, L, were carried out. The reaction of *trans*-$[PtI_2(SMe_2)_2]$ with *cis*-$[PtMe_2(PMe_2Ph)_2]$ occurred without scrambling of neutral ligands to give *trans*-$[PtIMe(SMe_2)_2]$ and *trans*-$[PtIMe(PMe_2Ph)_2]$, being half complete in 4 days. The lack of scrambling of neutral ligands is evidence against a dissociative mechanism. However, reaction of mostly *trans*-$[PtI_2(PMePh_2)_2]$ with *cis*-$[PtMe_2(SMe_2)_2]$ gave extensive scrambling with the major products being isomers of $[PtIMe(SMe_2)(PMePh_2)]$, characterized by doublet signals for the MePt groups in the ^{1}H NMR spectra due to $^{31}P^1H$ coupling, and no *trans*-$[PtIMe(PMePh_2)_2]$ was formed. This reaction was complete in 2 days. Similarly, the reaction of *cis*-$[PtCl_2(PMe_2Ph)_2]$ with *cis*-$[PtMe_2(SMe_2)_2]$ gave extensive scrambling of the neutral ligands, with the major products being *trans*-$[PtClMe(SMe_2)_2]$ and isomers of $[PtClMe(SMe_2)(PMe_2Ph)]$, characterized by doublet signals for the MePt groups due to $^{31}P^1H$ coupling and no *trans*-$[PtClMe(PMe_2Ph)_2]$ was formed. This reaction was half complete in 3 days at room temperature and hence is slower than the analogous reactions with the iodoplatinum complex. The mixture of *trans*-$[PtCl_2(SMe_2)_2]$ with *cis*-$[PtMe_2(PMe_2Ph)_2]$ in solution gave no reaction after 5 days. These data suggest that dissociation of SMe_2 from *cis*-$[PtMe_2(SMe_2)_2]$ occurs and leads to the ligand scrambling reaction as well as to the increased rate of reaction.[13]

No reaction occurred between *cis*-$[PtMe_2(SMe_2)_2]$ and *cis*-$[Pt(CD_3)_2(PMe_2Ph)_2]$ over a period of several days, showing that methyl for methyl exchange in these systems does not occur readily.

Kinetic Studies. Kinetic studies were carried out on the reaction of *trans*-$[PtCl_2(SMe_2)_2]$ with *cis*-$[PtMe_2(SMe_2)_2]$ in $CDCl_3$ solution. Concentrations were determined for both reagents and the product *trans*-$[PtClMe(SMe_2)_2]$ by comparison of the peak heights of the Me_2S singlets for each species in the 60-MHz ^{1}H NMR spectra with that for benzene, added as internal reference, after calibration with known concentrations. In this way, in-

(13) As a cautionary note, we found that exchange between *cis*-$[PtMe_2(PMe_2Ph)_2]$ and $[PtI_2(PMePh_2)_2]$ gave extensive ligand scrambling with formation of *trans*-$[PtIMe(PMe_2Ph)(PMePh_2)]$ as well as the symmetrical products.

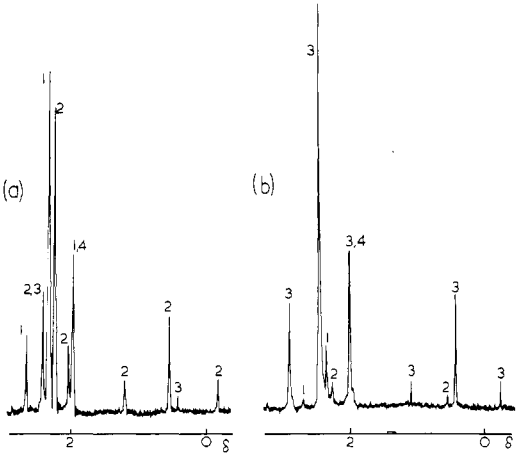


Figure 2. ^{1}H NMR spectra (60 MHz) recorded during reaction of *trans*-$[PtCl_2(SMe_2)_2]$ with *cis*-$[PtMe_2(SMe_2)_2]$ in the presence of SMe_2 (0.031 M). Spectra were recorded after (a) 3 min and (b) 300 min. Peaks are labeled: 1, *trans*-$[PtCl_2(SMe_2)_2]$; 2, *cis*-$[PtMe_2(SMe_2)_2]$; 3, *trans*-$[PtClMe(SMe_2)_2]$; 4, SMe_2.

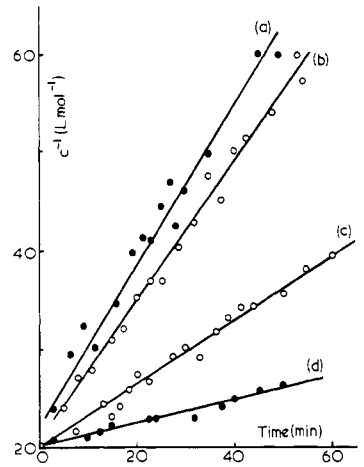


Figure 3. Second-order plots for reaction of *trans*-$[PtCl_2(SMe_2)_2]$ with *cis*-$[PtMe_2(SMe_2)_2]$. Concentration of SMe_2 added: (a) 0, (b) 0.0131 M, (c) 0.0476 M, (d) 0.131 M.

dependent measures of rate constants were obtained in each experiment. Some typical spectra are shown in Figure 2. The reaction followed overall second-order kinetics as shown by the plots in Figure 3, when equal concentrations of reagents were used. Further experiments, using relative concentrations of reagents *cis*-$[PtMe_2(SMe_2)_2]$ and *trans*-$[PtCl_2(SMe_2)_2]$ in the range 0.25–2.0 and measuring initial rates clearly showed that the rate of the reactions showed a first-order dependence on the concentration of each reagent.

Next, kinetic experiments were carried out by using equal concentrations of *cis*-$[PtMe_2(SMe_2)_2]$ and *trans*-$[PtCl_2(SMe_2)_2]$ but with excess dimethyl sulfide present. Again the reactions followed second-order kinetics, but the reactions were retarded by added dimethyl sulfide, as shown by the data in Table II and Figure 3. The NMR spectra showed only the presence of reagents, the product *trans*-$[PtClMe(SMe_2)_2]$, and free Me_2S, so that the retardation by Me_2S was not due to interaction with either starting reagent but by interception of a reaction intermediate. Attempts were made to study the kinetics with a deficiency of dimethyl sulfide when the reagents were *cis*-$[PtMe_2(SMe_2)_2]$, $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$, and *trans*-$[PtCl_2(SMe_2)_2]$. The reactions were too fast to monitor satisfactorily by the NMR method, but it was possible to show that at intermediate stages of reaction both *cis*-

Table II. Second-Order Rate Constants (L mol^{-1} s^{-1}) for Reaction of *cis*- or *trans*-$[PtCl_2(SMe_2)_2]$ with *cis*-$[PtMe_2(SMe_2)_2]$ in $CDCl_3$ at 20 °C

reagent	$[SMe_2]$, mol L^{-1}	$[SMe_2]_{corr}$,[a] mol L^{-1}	$10^3 k_{obsd}$, L mol^{-1} s^{-1}
cis-$[PtCl_2(SMe_2)_2]$	0	0.016	7.5
trans-$[PtCl_2(SMe_2)_2]$	0	0.016	13.7 ± 0.7
	0.0131	0.020	12.2 ± 0.6
	0.0381	0.039	6.3 ± 0.5
	0.0476	0.048	5.2 ± 0.4
	0.131	0.131	1.8 ± 0.2

[a] Corrected to allow for the equilibrium of eq 4.

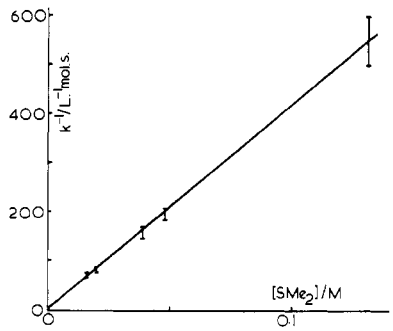


Figure 4. Graph of reciprocal of the second-order rate constants for reaction of *trans*-$[PtCl_2(SMe_2)_2]$ with *cis*-$[PtMe_2(SMe_2)_2]$ vs. the concentration of dimethyl sulfide, corrected for the equilibrium of eq 4.

$[PtMe_2(SMe_2)_2]$ and $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ were present. It is probable, although our data are not accurate enough to prove this, that the equilibrium of eq 4 is maintained during the exchange reaction.

The kinetic data are most readily rationalized in terms of the mechanism shown in eq 6–8. This leads to the rate expression of eq 9.

$$cis\text{-}[PtMe_2(SMe_2)_2] \underset{k_2}{\overset{k_1}{\rightleftharpoons}} [PtMe_2(SMe_2)] + SMe_2 \quad (6)$$

$$[PtMe_2(SMe_2)] + trans\text{-}[PtCl_2(SMe_2)_2] \xrightarrow{k_3} trans\text{-}[PtClMe(SMe_2)_2] + [PtClMe(SMe_2)] \quad (7)$$

$$[PtClMe(SMe_2)] + SMe_2 \xrightarrow{\text{fast}} trans\text{-}[PtClMe(SMe_2)_2] \quad (8)$$

$$-\frac{d}{dt}[PtMe_2(SMe_2)_2] = -\frac{d}{dt}[PtCl_2(SMe_2)_2] = \frac{k_1 k_3 [PtMe_2(SMe_2)_2][PtCl_2(SMe_2)_2]}{\{k_2[SMe_2] + k_3[PtCl_2(SMe_2)_2]\}} \quad (9)$$

This expression is complex but is considerably simplified under conditions where $k_2[SMe_2] \gg k_3[PtCl_2(SMe_2)_2]$. Now a simple expression giving second-order kinetics and with $k_{obsd} = k_1k_3/k_2[SMe_2]$ is obtained. A graph of k_{obsd} vs. $1/[SMe_2]$ is a straight line passing through the origin at higher concentrations of added SMe_2, indicating that this is a good approximation under these conditions. However, eq 9 predicts that a better straight line should be obtained by plotting $1/k_{obsd}$ vs. $[SMe_2]$ and this is indeed found (Figure 4). Although the expression is a rough approximation, so long as $k_3[PtCl_2(SMe_2)_2] \ll k_2[SMe_2]$ approximate second-order kinetics are expected with $1/k_{obsd} = k_2[SMe_2]/k_1k_3 + [PtCl_2(SMe_2)_2]/k_1$. Analysis gave $k_2/k_1k_3 = 4.0 \times 10^3$ s and $[PtCl_2(SMe_2)_2]/k_1 = 6$ mol L^{-1} s and hence $k_1 \approx 9 \times 10^{-3}$ s^{-1} if we use the initial concentration of $[PtCl_2(SMe_2)_2]$. This figure for k_1 is at best an

approximation, but it does allow an estimation of the half-life for dissociation of Me_2S from *cis*-$[PtMe_2(SMe_2)_2]$ of about 1.5 min to be estimated. In addition it gives $k_2/k_3 \approx 36$. Now, under the most adverse conditions for the approximations made in the kinetic scheme, that is when no excess SMe_2 was added, this gives $k_2[SMe_2]/k_3[PtCl_2(SMe_2)_2]^0 \approx 12$. The approximation that the reversible dissociation of Me_2S from *cis*-$[PtMe_2(SMe_2)_2]$ is fast compared to the subsequent exchange reaction is therefore reasonable.[14]

The reaction between *cis*-$[PtCl_2(SMe_2)_2]$ and *cis*-$[PtMe_2(SMe_2)_2]$ also gave good second-order kinetics (Table II) and was a little slower than the corresponding reaction of *trans*-$[PtCl_2(SMe_2)_2]$. In the presence of free SMe_2, the exchange reaction was slower but was complicated by the catalysis by free SMe_2 of the isomerization of *cis*-$[PtCl_2(SMe_2)_2]$ to the more stable trans isomer. Hence a detailed study was not attempted.

The reaction of *trans*-$[PtI_2(SMe_2)_2]$ with *cis*-$[PtMe_2(SMe_2)_2]$ to give *trans*-$[PtIMe(SMe_2)_2]$ was complete in 5 min at room temperature, and hence it was not possible to follow the kinetics. A solution containing 0.05 M excess dimethyl sulfide and the same concentrations of reagents was made up and reacted much more slowly, being half complete in ~100 min, while a similar solution containing 0.025 M excess dimethyl sulfide was half reacted after ~40 min. The reactions were more complex than those using *trans*-$[PtCl_2(SMe_2)_2]$ as reagent and gave rather poor second-order kinetics. Part of the problem arises due to broadening of the resonance in NMR spectra due to free SMe_2 as the reaction proceeds. In this case, it seems probably that exchange with product *trans*-$[PtIMe(SMe_2)_2]$ may occur at high dimethyl sulfide concentrations, perhaps according to

$$trans\text{-}[PtIMe(SMe_2)_2] + SMe_2 \rightleftharpoons [PtMe(SMe_2)_3]I$$

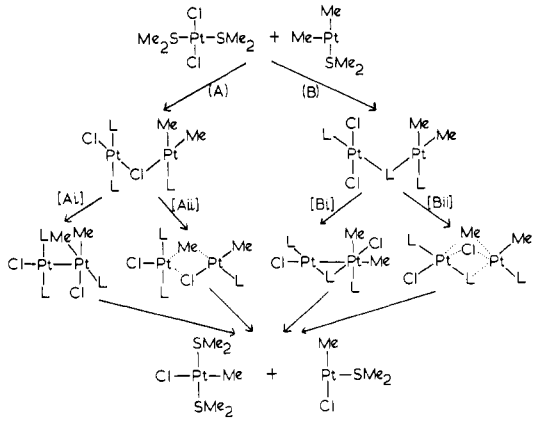
The marked retardation of the exchange reaction by excess SMe_2 certainly indicates that the reaction occurs after dissociation of SMe_2 from *cis*-$[PtMe_2(SMe_2)_2]$ to give $[PtMe_2(SMe_2)]$.[15]

Discussion

The most significant aspect of this work is the clear demonstration that the methyl for chloro exchange reaction between *cis*-$[PtMe_2(SMe_2)_2]$ and *trans*-$[PtCl_2(SMe_2)_2]$ occurs after preliminary dissociation of dimethyl sulfide to give a coordinatively unsaturated intermediate $[PtMe_2(SMe_2)]$, which we assume has the cis T-shaped stereochemistry.[16,17]

There is still a problem in understanding the mechanism by which the exchange reaction of eq 7 occurs. Some probable mechanisms are shown in Scheme II. We assume that the first step involves donation of a lone pair from either the chloride (route A) or dimethyl sulfide (route B)

Scheme II



of *trans*-$[PtCl_2(SMe_2)_2]$ to the electron-deficient platinum center in $[PtMe_2(SMe_2)]$. In route A, the chloride is now bridging and the methyl group is transferred by the oxidative addition–reductive elimination sequence (Ai) or the S_E2 mechanism (Aii). In route B, the μ-SMe_2 simply acts as a bridging ligand leading to a template effect in enhancing the rate of methyl for chloro exchange by the oxidative addition–reductive elimination mechanism (Bi) or the S_E2 mechanism (Bii, Scheme II). Inspection of molecular models indicates that the intermediates in route A are less strained, but, since dialkyl sulfides are better bridging ligands than is chloride in diplatinum complexes, route B must be considered possible.[18] Recent evidence strongly favors the oxidative addition–reductive elimination sequence for alkyl for halogen exchange in related systems,[19] but data from the present work cannot distinguish between this mechanism and the S_E2 mechanism. We note that iodide is a better bridging ligand than dimethyl sulfide in diplatinum complexes (see for example eq 5)[18] and hence route A is likely to be strongly favored in the reactions with *trans*-$[PtI_2(SMe_2)_2]$. In this regard, it is relevant that the iodoplatinum complexes undergo exchange more rapidly than the chloroplatinum complexes.

Finally, the problem of whether or not ligand dissociation is always necessary in exchange reactions of $[PtR_2L_2]$ with $[PtX_2L_2]$ should be addressed. We believe that ligand dissociation is not a necessary condition for exchange for reasons outlined in the introduction. However, it is apparent from this work that the exchange can occur very much more rapidly if easy ligand dissociation from *cis*-$[PtMe_2L_2]$ can generate the coordinatively unsaturated 14-electron species $[PtMe_2L]$ as a reaction intermediate. Such 14-electron species have been implicated in many reactions of d^8 transition-metal complexes, for example in reductive elimination of ethane from $[AuMe_3L]$ or $[PdMe_2L_2]$,[16] in β elimination from $[PtEt_2L_2]$[20] and γ elimination from $[Pt(CH_2CMe_3)_2L_2]$,[21] and in thermolysis of metallacyclopentanes $[M(CH_2)_4L_2]$,[22] all of which may involve preliminary dissociation of a ligand L. Now alkyl for halogen exchange reactions must be added to this list.[23]

(14) It is surprising that such good second-order kinetics were observed in cases where no excess SMe_2 was present, since the stationary state concentration of SMe_2 might be expected to decrease as the concentration of *cis*-$[PtMe_2(SMe_2)_2]$ decreases.

(15) It is possible that the dissociation of SMe_2 from *cis*-$[PtMe_2(SMe_2)_2]$ could be rate determining in this case, when no excess SMe_2 is present.

(16) For a theoretical discussion of T-shaped d^8 complexes see: Komiya, S.; Albright, T. A.; Hoffmann, R.; Kochi, J. K. *J. Am. Chem. Soc.* **1977**, *99*, 8440 and ref 7.

(17) The only other reasonable explanation for the retardation of the exchange reaction by added dimethyl sulfide would be that the dimer $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ was the reactive species, but this mechanism would lead to kinetics showing a 0.5 order dependence on $[PtMe_2(SMe_2)_2]$ and so is inconsistent with the observed results.

(18) For example the complexes $[Pt_2X_4(SMe_2)_2]$ contain μ-SMe_2 and terminal X groups when X = Cl or Br, but terminal SMe_2 and μ-X groups when X = I. In $[Pd_2X_4(SMe_2)_2]$ the latter structure is found for X = Cl, Br, and I.[9]

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Experimental Section

NMR spectra were recorded by using Varian T60 or XL100 spectrometers. Complexes *cis*- and *trans*-$[PtCl_2(SMe_2)_2]$ and *trans*-$[PtI_2(SMe_2)_2]$ were prepared by modifications of known procedures.[8,24] *cis*-$[PtMe_2(PMe_2Ph)_2]$, $[PtI_2(PMePh_2)_2]$, *trans*-$[PtIMe(PMe_2Ph)_2]$, and *trans*-$[PtIMe(PMePh_2)_2]$ were prepared as described previously.[4,5] Experiments requiring inert atmosphere were carried out by using standard Schlenk techniques.

$[Pt_2Me_4(\mu\text{-}SMe_2)_2]$. Methyllithium solution (2.5 mL, 1.3 M in ether) was added dropwise to a suspension of $[PtCl_2(SMe_2)_2]$ (0.51 g, mixture of cis and trans) in ether (25 mL) under an atmosphere of N_2 at 0 °C. The solution was then allowed to warm slowly to room temperature. The mixture was hydrolyzed with saturated aqueous ammonium chloride solution (5 mL), and the ether layer was separated, dried, and evaporated under vacuum to give the product (0.27 g, 71%), as an off-white solid; mp 86 °C dec. Anal. Calcd for $C_8H_{24}S_2Pt_2$: C, 16.7; H, 4.2. Found: C, 16.8; H, 4.25.

***trans*-[PtClMe(SMe$_2$)$_2$].** A solution of *cis*-$[PtMe_2(SMe_2)_2]$ was prepared by addition of SMe_2 (0.031 mL, 0.429 mmol) to a solution of $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ (0.123 g, 0.214 mmol) in CH_2Cl_2 (1.5 mL). To this solution was added *trans*-$[PtCl_2(SMe_2)_2]$ (0.167 g, 0.428 mmol), and the course of the reaction was monitored by using ^1H NMR spectroscopy. After 2 h, the reaction was complete and the product was precipitated by addition of hexane and then cooling to −78 °C: yield 0.287 g, 91%; mp 56–60 °C. Anal. Calcd for $[PtClMe(SMe_2)_2]$: C, 16.2; H, 4.1; S, 17.3. Found: C, 16.3; H, 4.0; S, 17.1. A similar reaction using *cis*-$[PtCl_2(SMe_2)_2]$ gave the same product in 94% yield.

$[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ with *trans*-$[PtCl_2(SMe_2)_2]$. *trans*-$[PtCl_2(SMe_2)_2]$ (0.0359 g, 0.092 mmol) was added to a solution of $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ (0.0264 g, 0.046 mmol) in CH_2Cl_2 (1.5 mL). Reaction to give *trans*-$[PtClMe(SMe_2)_2]$ and dark insoluble material was complete in 10 min as determined by ^1H NMR. The solution was filtered to remove insoluble materials, and the filtrate was added to hexane and cooled to −78 °C. The product *trans*-$[PtClMe(SMe_2)_2]$ (0.0464 g, 0.125 mmol) precipitated and was characterized by ^1H NMR (yield 91%). A similar reaction using *cis*-$[PtCl_2(SMe_2)_2]$ gave the same product (94% yield).

***trans*-[PtIMe(SMe$_2$)$_2$].** A solution of *cis*-$[PtMe_2(SMe_2)_2]$ was prepared by reaction of $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ (0.0695 g) in $CDCl_3$ (2 mL) with SMe_2 (17.8 μL). To this solution was added *trans*-$[PtI_2(SMe_2)_2]$ (0.0694 g) in $CDCl_3$ (2 mL). The color changed rapidly from browth to orange. After 24 h, the product was identified by NMR (Table I) as *trans*-$[PtIMe(SMe_2)_2]$. In solution the product decomposed only slowly to a brown solid, but on evaporation of the solvent extensive decomposition occurred and an unidentified brown solid was obtained. Loss of Me_2S with formation of iodide bridges was suspected, and it was thus not possible to obtain analytical data for the product.

$[PtI(SMe_2)_3]BF_4$. To a solution of *trans*-$[PtI_2(SMe_2)_2]$ (0.376 g) in CH_2Cl_2 (15 mL) containing free SMe_2 was added $Ag[BF_4]$ (0.128 g) in methanol (3 mL). The yellow precipitate of AgI was removed, and the solvent was evaporated under vacuum to give the product as a yellow solid, identified by its NMR spectrum (Table I). The complex decomposed on standing to give *trans*-$[PtI_2(SMe_2)_2]$ and unidentified material. It was therefore not possible to obtain analytical data. No reaction occurred between *trans*-$[PtI_2(SMe_2)_2]$ and SMe_2 in the absence of silver salt.

Na[PtMe$_2$I(SMe$_2$)]. To a solution of $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ (0.045 g) in acetone-d_6 (0.5 mL) was added sodium iodide (0.023 g) in acetone-d_6 (0.5 mL). A bright yellow color developed immediately, and the product was identified by its NMR spectrum. The solvent was evaporated to give a yellow solid, but NMR analysis showed that decomposition to $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$, $[PtMe_2(SMe_2)_2]$, *trans*-$[PtIMe(SMe_2)_2]$, and *trans*-$[PtI_2(SMe_2)_2]$ had occurred.

Reaction of *trans*-[PtI$_2$(SMe$_2$)$_2$] with *cis*-[PtMe$_2$(PMe$_2$Ph)$_2$]. Equimolar proportions of these reagents in CH_2Cl_2 (0.03 M) were allowed to react, and the reaction rate was monitored by ^1H NMR spectroscopy. Reaction was half complete in 4 days at 20 °C. Products were identified by NMR as *trans*-$[PtIMe(SMe_2)_2]$ (Table I) and *trans*-$[PtIMe(PMe_2Ph)_2]$ [δ 0.28 (t, $^3J(PH) = 7$ Hz, $^2J(PtH) = 81$ Hz (MePt)), 1.91 (t, $^2J + {}^4J(PH) = 7$ Hz, $^3J(PtH) = 29$ Hz (MeP))], by comparison with the spectra of authentic samples.[4] No doublet MePt signals were observed (cf. next reaction).

Reaction of *cis*-[PtMe$_2$(SMe$_2$)$_2$] with [PtI$_2$(PMePh$_2$)$_2$]. When equimolar proportions of these reagents in CH_2Cl_2 (0.03 M) were allowed to react, the products after 2 days were a complex mixture. In the MePt region of the NMR spectrum were seen doublet resonances at δ 0.83 [$J(PMe) = 5.5$ Hz, $J(PtMe) = 73$ Hz] and 0.29 [$J(PMe) = 4$ Hz, $J(PtMe) = 69$ Hz] assigned to isomers of $[PtIMe(SMe_2)(PMePh_2)]$ but no triplet due to *trans*-$[PtIMe(PMePh_2)_2]$.[4] When the solvent was removed and then the mixture redissolved in CD_2Cl_2, additional doublets were observed at δ 0.47 [$J(PMe) = 4$ Hz] and 0.33 [$J(PMe) = 3$ Hz], tentatively assigned to $[Pt_2(\mu\text{-}I)_2Me_2(PMePh_2)_2]$ formed by loss of SMe_2.

Reaction of [PtI$_2$(PMePh$_2$)$_2$] with *cis*-[PtMe$_2$(PMe$_2$Ph)$_2$]. Reaction was carried out in the same way as above. Reaction was half complete in 4 days. Products were *trans*-$[PtIMe(PMe_2Ph)_2]$ [δ 0.29 (t, $^3J(PH) = 7$ Hz, $^2J(PtH) = 81$ Hz (MePt)],[4] *trans*-$[PtIMe(PMePh_2)_2]$ [δ −0.01 (t, $^3J(PH) = 7$ Hz, $^2J(PtH) = 79$ Hz, (MePt)],[4] and *trans*-$[PtIMe(PMe_2Ph)(PMePh_2)]$ [δ 0.13 (t, $^3J(PH) = 7$ Hz, $^2J(PtH) = 80$ Hz, (MePt)], in relative amounts 1:1:2 as determined by integration of the NMR spectra. The first two compounds were identified by direct comparison with known compounds,[4] and the NMR parameters of the mixed ligand complex are exactly as expected.[4,5]

Kinetic Studies. The procedure for a typical experiment is given. A solution containing *cis*-$[PtMe_2(SMe_2)_2]$ (0.050 M), benzene (0.025 M), and excess SMe_2 (0.038 M) in $CDCl_3$ was prepared by addition of SMe_2 to $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ and C_6H_6 in $CDCl_3$. An aliquot of this solution (2.0 mL) containing *cis*-$[PtMe_2(SMe_2)_2]$ (0.10 mmol) was added to solid *trans*-$[PtCl_2(SMe_2)_2]$ (0.039 g, 0.10 mmol), and the resulting solution was transferred to an NMR tube. NMR spectra (60 MHz) were recorded at intervals of 2–10 min over a period of 2 h until reaction was complete. Concentrations of all species were calculated by comparison of peak heights of the Me_2S resonance of each species vs. the peak height for the C_6H_6 resonance, after calibration. Graphs of $1/c$ vs. time where c was either the concentration of *cis*-$[PtMe_2(SMe_2)_2]$ or *trans*-$[PtCl_2(SMe_2)_2]$ gave straight lines from the slope of which independent measures of the second-order rate constants were calculated.

Registry No. $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$, 79870-64-7; *cis*-$[PtMe_2(SMe_2)_2]$, 87145-38-8; *cis*-$[PtCl_2(SMe_2)_2]$, 17836-09-8; *trans*-$[PtCl_2(SMe_2)_2]$, 17457-51-1; *trans*-$[PtClMe(SMe_2)_2]$, 87145-39-9; *trans*-$[PtI_2(SMe_2)_2]$, 18534-69-5; *trans*-$[PtIMe(SMe_2)_2]$, 87145-40-2; *trans*-$[Pt_2(\mu\text{-}I)_2Me_2(SMe_2)_2]$, 87145-41-3; *cis*-$[Pt_2(\mu\text{-}I)_2Me_2(SMe_2)_2]$, 87173-71-5; $Na[PtIMe_2(SMe_2)]$, 87145-42-4; $[PtI(SMe_2)_3][BF_4]$, 87145-43-5; *trans*-$[PtIMe(PMe_2Ph)_2]$, 24882-77-7; *trans*-$[PtIMe(PMePh_2)_2]$, 24858-62-6; $[Pt_2(\mu\text{-}I)_2Me_2(PMePh_2)_2]$, 87145-44-6; *trans*-$[PtIMe(PMe_2Ph)(PMePh_2)]$, 87145-45-7; *cis*-$[PtMe_2(PMe_2Ph)_2]$, 24917-48-4; $[PtI_2(PMePh_2)_2]$, 53585-57-2; $[PtIMe(SMe_2)(PMePh_2)]$, 87145-46-8.

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