

## OXIDATIVE ADDITION REACTIONS OF CARBON DISELENIDE AND ARENESELENOLS TO SOME IRIDIUM(I) AND PLATINUM(0) COMPLEXES

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### Summary

Reaction of carbon diselenide in 3 to 1 molar ratio, and areneselenols in equimolar ratio, with *trans*-IrCl(CO)(PPh<sub>3</sub>)<sub>2</sub> and PtL<sub>4</sub>, gives oxidative addition products, IrCl(CO)(CSe<sub>2</sub>)(PPh<sub>3</sub>)<sub>2</sub>, Pt(CSe<sub>2</sub>)L<sub>2</sub>, IrHCl(CO)(SeC<sub>6</sub>H<sub>4</sub>Me-*p*)(PPh<sub>3</sub>)<sub>2</sub>, and PtH(SeR)L<sub>2</sub>, respectively (R = Ph and *p*-MeC<sub>6</sub>H<sub>4</sub>; L = PPh<sub>3</sub> and PPh<sub>2</sub>Me). However, reactions of PtL<sub>4</sub> with an excess of areneselenols afford bis(arylsele- nide) complexes Pt(SeR)<sub>2</sub>L<sub>2</sub>. The configurations of these complexes are dis- cussed on the basis of their IR and PMR spectra. The carbon diselenide adducts are suggested to have configurations similar to the corresponding carbon disul- fide adducts. The platinum hydrides are found to exist as a mixture of *cis* and *trans* isomers in solution, both the isomers being labile with regard to dissocia- tive exchange of the tertiary phosphine ligands. The *trans* configurations of Pt(SeR)<sub>2</sub>(PPh<sub>2</sub>Me)<sub>2</sub> are unambiguously shown by the virtually coupled triplet pattern of the PPh<sub>2</sub>Me signals.

### Introduction

A large variety of compounds has been shown to add oxidatively to low- valent transition metal complexes, two representatives of which are Vaska's complex, *trans*-IrCl(CO)(PPh<sub>3</sub>)<sub>2</sub>, and tetrakis(triphenylphosphine)platinum, Pt(PPh<sub>3</sub>)<sub>4</sub> [1, 2]. It has recently been reported that sulfur-containing com- pounds such as carbon disulfide [3] and arenethiols [4, 5] oxidatively add to these low-valent transition metal complexes. This work was undertaken to study oxidative addition reactions of some selenium-containing compounds, carbon diselenide and areneselenols RSeH (R = Ph and *p*-MeC<sub>6</sub>H<sub>4</sub>), to *trans*- IrCl(CO)(PPh<sub>3</sub>)<sub>2</sub> and PtL<sub>4</sub> (L = PPh<sub>3</sub> and PPh<sub>2</sub>Me) for the purpose of compar- ison with the analogous sulfur compounds.

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## Experimental

$(\text{NH}_4)_2\text{IrCl}_6$  and  $\text{K}_2\text{PtCl}_4$  were of reagent grade and used as supplied. Carbon diselenide [6] and areneselenols [7] were prepared by the methods described in the literature. *trans*- $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$  [8] and  $\text{Pt}(\text{PPh}_3)_4$  [9] were synthesized according to the literature methods.  $\text{Pt}(\text{PPh}_2\text{Me})_4$  was prepared in a manner similar to that used for  $\text{Pt}(\text{PPh}_3)_4$ . All reactions involving the low-valent transition metal complexes were carried out under an atmosphere of nitrogen at room temperature, but work-up was carried out in open air except in the case of the metal hydride derivatives.

### Preparation of the carbon diselenide complexes

*Chlorocarbonyl(carbon diselenide)bis(triphenylphosphine)iridium(III)*,  $\text{IrCl}(\text{CO})(\text{CSe}_2)(\text{PPh}_3)_2$ . To a stirred suspension of *trans*- $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$  (0.25 g, 0.32 mmol) in benzene (20 ml) was added dropwise  $\text{CSe}_2$  (0.17 g, 1.0 mmol) in benzene (10 ml), when the color of the solution changed from yellow to dark brown. The solution was concentrated under reduced pressure. Addition of petroleum ether precipitated a red brown solid which was washed with petroleum ether and dried in vacuo (0.27 g, 100%):  $\nu(\text{CO})$  2025,  $\nu(\text{Ir}-\text{Cl})$  265,  $\nu(\text{C}=\text{Se})$  1008  $\text{cm}^{-1}$  (Nujol).

*Bis(triphenylphosphine)(carbon diselenide)platinum(II)*,  $\text{Pt}(\text{CSe}_2)(\text{PPh}_3)_2$ . To a stirred suspension of  $\text{Pt}(\text{PPh}_3)_4$  (0.32 g, 0.26 mmol) in *n*-hexane (20 ml) was added dropwise  $\text{CSe}_2$  (0.10 g, 0.59 mmol) in *n*-hexane (10 ml). The color of the suspension changed from yellow to green and then to brown. After stirring for 1 h, the resulting precipitate was filtered, washed with petroleum ether, and dried in vacuo (0.23 g, 100%):  $\nu(\text{C}=\text{Se})$  999  $\text{cm}^{-1}$  (Nujol).

*Bis(diphenylmethylphosphine)(carbon diselenide)platinum(II)*,  $\text{Pt}(\text{CSe}_2)(\text{PPh}_2\text{Me})_2$ . A reaction between  $\text{Pt}(\text{PPh}_2\text{Me})_4$  (0.30 g, 0.30 mmol) and  $\text{CSe}_2$  (0.15 g, 0.90 mmol) was carried out in a manner similar to that described above to yield a red brown complex (0.21 g, 90%):  $\nu(\text{C}=\text{Se})$  985  $\text{cm}^{-1}$  (Nujol).

### Preparation of the metal hydrides

*Hydridochlorocarbonyl(p-tolylselenido)bis(triphenylphosphine)iridium(III)*,  $\text{IrHCl}(\text{CO})(\text{SeC}_6\text{H}_4\text{Me-p})(\text{PPh}_3)_2$ . To a stirred suspension of *trans*- $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$  (0.38 g, 0.49 mmol) in benzene (20 ml) was added *p*- $\text{MeC}_6\text{H}_4\text{SeH}$  (0.10 g, 0.58 mmol). After stirring for 1 week, one half of the solvent was removed under reduced pressure at room temperature. Addition of petroleum ether precipitated a yellow solid which was washed with the same solvent and dried in vacuo (0.24 g, 52%):  $\nu(\text{Ir}-\text{H})$  2242,  $\delta(\text{Ir}-\text{H})$  810,  $\nu(\text{CO})$  2028,  $\nu(\text{Ir}-\text{Cl})$  270  $\text{cm}^{-1}$  (Nujol);  $\tau(\text{Ir}-\text{H})$  19.52 ppm (triplet,  $J(\text{P}-\text{H})$  12.0 Hz) (benzene).

*Hydrido(phenylselenido)bis(triphenylphosphine)platinum(II)*,  $\text{PtH}(\text{SePh})(\text{PPh}_3)_2$ . Preparation of this compound was briefly described in the literature [5]. To a stirred solution of  $\text{Pt}(\text{PPh}_3)_4$  (0.40 g, 0.32 mmol) in benzene (20 ml) was added  $\text{PhSeH}$  (0.60 g, 0.38 mmol). After stirring for 2 h, the solution was concentrated under reduced pressure, and to this was added petroleum ether. The solution was cooled to give a yellow precipitate which was filtered and washed with petroleum ether (0.17 g, 60%):  $\nu(\text{Pt}-\text{H})$  2147,  $\delta(\text{Pt}-\text{H})$  825, 821  $\text{cm}^{-1}$  (Nujol);  $\nu(\text{Pt}-\text{H})$  2115 (broad),  $\delta(\text{Pt}-\text{H})$  806 (broad)  $\text{cm}^{-1}$  ( $\text{CH}_2\text{Cl}_2$ ).

TABLE 1  
MELTING POINTS, ANALYTICAL DATA, AND MOLECULAR WEIGHTS OF THE COMPLEXES

Compound	M.p. (°C)	Analysis found (calcd.) (%)		Mol. wt. Found (Calcd.)
		C	H	
$\text{IrCl}(\text{CO})(\text{CSe}_2)(\text{PPh}_3)_2$	> 250	48.45 (48.03)	3.56 (3.19)	870 (950)
$\text{IrHCl}(\text{CO})(\text{SeC}_6\text{H}_4\text{Me-}p)(\text{PPh}_3)_2$	235–237	55.75 (55.55)	4.11 (4.03)	
$\text{Pt}(\text{CSe}_2)(\text{PPh}_3)_2$	120–122 (dec)	50.14 (49.95)	3.62 (3.41)	790 (889)
$\text{Pt}(\text{CSe}_2)(\text{PPh}_2\text{Me})_2$	80–83 (dec)	42.41 (42.36)	3.31 (3.43)	
$\text{PtH}(\text{SePh})(\text{PPh}_3)_2^a$	130 (dec)	58.36 (57.50)	4.18 (4.14)	
$\text{PtH}(\text{SeC}_6\text{H}_4\text{Me-}p)(\text{PPh}_3)_2$	110–114 (dec)	58.26 (57.97)	4.34 (4.34)	
$\text{PtH}(\text{SePh})(\text{PPh}_2\text{Me})_2$	107–108 (dec)	50.83 (51.06)	4.25 (4.29)	
$\text{PtH}(\text{SeC}_6\text{H}_4\text{Me-}p)(\text{PPh}_2\text{Me})_2$	116–118 (dec)	51.90 (51.70)	4.51 (4.48)	
$\text{Pt}(\text{SePh})_2(\text{PPh}_3)_2$	178–179	56.32 (55.84)	4.01 (3.99)	920 (1031)
$\text{Pt}(\text{SeC}_6\text{H}_4\text{Me-}p)_2(\text{PPh}_3)_2$	140–143	56.50 (56.63)	4.20 (4.19)	940 (1060)
$\text{Pt}(\text{SePh})_2(\text{PPh}_2\text{Me})_2$	195–196	50.51 (50.26)	4.08 (4.00)	760 (908)
$\text{Pt}(\text{SeC}_6\text{H}_4\text{Me-}p)_2(\text{PPh}_2\text{Me})_2$	187–189	51.14 (51.31)	4.36 (4.32)	910 (937)

<sup>a</sup> Reported m.p. 141°C [5].

*Hydrido(p-tolylselenido)bis(triphenylphosphine)platinum(II)*,  $\text{PtH}(\text{SeC}_6\text{H}_4\text{Me-}p)(\text{PPh}_3)_2$ . A reaction between  $\text{Pt}(\text{PPh}_3)_4$  (0.50 g, 0.40 mmol) and  $p\text{-MeC}_6\text{H}_4\text{SeH}$  (0.07 g, 0.41 mmol) was carried out in a manner similar to that described above to yield the yellow complex (0.24 g, 66%):  $\nu(\text{Pt-H})$  2110, 2085, 2070,  $\delta(\text{Pt-H})$  800, 797  $\text{cm}^{-1}$  (Nujol);  $\nu(\text{Pt-H})$  2112 (broad),  $\delta(\text{Pt-H})$  802 (broad)  $\text{cm}^{-1}$  ( $\text{CH}_2\text{Cl}_2$ ).

*Hydrido(phenylselenido)bis(diphenylmethylphosphine)platinum(II)*,  $\text{PtH}(\text{SePh})(\text{PPh}_2\text{Me})_2$ . A reaction of  $\text{Pt}(\text{PPh}_2\text{Me})_4$  (0.56 g, 0.56 mmol) with  $\text{PhSeH}$  (0.09 g, 0.57 mmol) was carried out as above to give the yellow complex (0.32 g, 76%):  $\nu(\text{Pt-H})$  2110,  $\delta(\text{Pt-H})$  785  $\text{cm}^{-1}$  (Nujol);  $\nu(\text{Pt-H})$  2098 (broad),  $\delta(\text{Pt-H})$  806 (broad)  $\text{cm}^{-1}$  ( $\text{CH}_2\text{Cl}_2$ ).

*Hydrido(p-tolylselenido)bis(diphenylmethylphosphine)platinum(II)*,  $\text{PtH}(\text{SeC}_6\text{H}_4\text{Me-}p)(\text{PPh}_2\text{Me})_2$ . An identical procedure with that described above was carried out using  $\text{Pt}(\text{PPh}_2\text{Me})_4$  (0.35 g, 0.35 mmol) and  $p\text{-MeC}_6\text{H}_4\text{SeH}$  (0.06 g, 0.35 mmol) to afford the yellow complex (0.19 g, 70%):  $\nu(\text{Pt-H})$  2110,  $\delta(\text{Pt-H})$  788  $\text{cm}^{-1}$  (Nujol);  $\nu(\text{Pt-H})$  2095 (broad),  $\delta(\text{Pt-H})$  804  $\text{cm}^{-1}$  ( $\text{CH}_2\text{Cl}_2$ ).

### Preparation of bis(arylselenide) complexes

*Bis(phenylselenido)bis(triphenylphosphine)platinum(II), Pt(SePh)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>.* To a solution of Pt(PPh<sub>3</sub>)<sub>4</sub> (0.41 g, 0.33 mmol) in benzene (20 ml) was added a five-fold excess of PhSeH (0.26 g, 1.65 mmol). After stirring for 24 h, the solution was concentrated under reduced pressure to one half of the initial volume. Addition of petroleum ether to the solution gave an orange solid which was recrystallized from benzene/petroleum ether (0.19 g, 55%).

*Bis(p-tolylselenido)bis(triphenylphosphine)platinum(II), Pt(SeC<sub>6</sub>H<sub>4</sub>Me-p)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>.* A reaction of Pt(PPh<sub>3</sub>)<sub>4</sub> (0.41 g, 0.33 mmol) with *p*-MeC<sub>6</sub>H<sub>4</sub>SeH (0.29 g, 1.70 mmol) was carried out in a manner similar to that described above to give yellow crystals (0.22 g, 63%):  $\tau(\text{C-Me})$  7.84 ppm (CDCl<sub>3</sub>).

*Bis(phenylselenido)bis(diphenylmethylphosphine)platinum(II), Pt(SePh)<sub>2</sub>(PPh<sub>2</sub>Me)<sub>2</sub>.* A reaction of Pt(PPh<sub>2</sub>Me)<sub>4</sub> (0.38 g, 0.38 mmol) with PhSeH (0.30 g, 1.90 mmol) was carried out as above to give yellow crystals (0.20 g, 58%):  $\tau(\text{P-Me})$  7.91 ppm (triplet of triplets;  $J(\text{Pt-P-Me})$  29.4,  $|^2J(\text{P-H}) + ^4J(\text{P-H})|$  7.2 Hz) (CDCl<sub>3</sub>).

*Bis(p-tolylselenido)bis(diphenylmethylphosphine)platinum(II), Pt(SeC<sub>6</sub>H<sub>4</sub>Me-p)<sub>2</sub>(PPh<sub>2</sub>Me)<sub>2</sub>.* A preparation identical with that above was carried out employing Pt(PPh<sub>2</sub>Me)<sub>4</sub> (0.28 g, 0.28 mmol) and *p*-MeC<sub>6</sub>H<sub>4</sub>SeH (0.24 g, 1.40 mmol) to afford yellow crystals (0.17 g, 65%):  $\tau(\text{P-Me})$  7.93 ppm (triplet of triplets;  $J(\text{Pt-P-Me})$  29.4,  $|^2J(\text{P-H}) + ^4J(\text{P-H})|$  7.2 Hz);  $\tau(\text{C-Me})$  7.86 ppm (CDCl<sub>3</sub>).

Melting points, analytical data, and molecular weights of the complexes are shown in Table 1.

### Physical measurements

Molecular weights were determined in CHCl<sub>3</sub> using a Hitachi-Perkin-Elmer 115 vapor pressure osmometer. IR spectra were recorded on Hitachi-Perkin-Elmer 225 (4000–400 cm<sup>-1</sup>) and Hitachi EPI-L (700–200 cm<sup>-1</sup>) Grating Spectrophotometers. PMR spectra were obtained on a JEOL JNM-PS-100 spectrometer equipped with a JNM-VT-3B variable temperature controller. Sample tubes containing the metal hydrides were sealed under high vacuum to avoid decomposition of the air-sensitive complexes. Tetramethylsilane was used as internal standard.

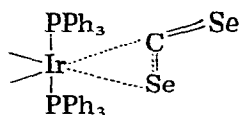
## Results and discussion

### The carbon diselenide complexes

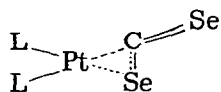
IrCl(CO)(CSe<sub>2</sub>)(PPh<sub>3</sub>)<sub>2</sub> and Pt(CSe<sub>2</sub>)L<sub>2</sub> (L = PPh<sub>3</sub> and PPh<sub>2</sub>Me) are fairly stable in air, but the odor of CSe<sub>2</sub> is perceptible even in the solid complexes. Molecular weight determinations indicate that these complexes are essentially monomeric in CHCl<sub>3</sub>, although a slight dissociation of ligands is possible (Table 1).

In the IR spectra, the  $\nu(\text{CO})$  and  $\nu(\text{Ir-Cl})$  of the Ir complex are found at 2025 and 265 cm<sup>-1</sup>, respectively. The former frequency is higher and the latter is lower than those of the parent complex; 1960 and 317 cm<sup>-1</sup>, respectively, which indicates the occurrence of the oxidative addition reaction of CSe<sub>2</sub>. In addition, the complex exhibits a strong band due to the  $\nu(\text{C=Se})$  at 1008 cm<sup>-1</sup>,

which is considerably lower than the asymmetric  $\nu(\text{Se}=\text{C}=\text{Se})$  of the free  $\text{CSe}_2$  molecule ( $1275 \text{ cm}^{-1}$ ) [10].  $\text{Pt}(\text{CSe}_2)\text{L}_2$  also show strong  $\nu(\text{C}=\text{Se})$  bands at  $999$  ( $\text{L} = \text{PPh}_3$ ) and  $985 \text{ cm}^{-1}$  ( $\text{L} = \text{PPh}_2\text{Me}$ ), respectively. The low  $\nu(\text{Ir}-\text{Cl})$  value of the Ir complex suggests that the chlorine atom is not located *trans* to CO; the  $\text{Cl}-\text{Ir}-\text{CO}$  portion is bent upon adduct formation [11], although the absolute location of the chlorine and CO ligands cannot be decided. These IR results are consistent with the configurations I and II for the Ir and Pt complexes, respectively, which are analogous to those of the previously reported carbon disulfide complexes,  $\text{IrCl}(\text{CO})(\text{CS}_2)(\text{PPh}_2\text{Me})_2$  [11] and  $\text{Pt}(\text{CS}_2)(\text{PPh}_3)_2$  [3], respectively. The structure of the latter has been determined by an X-ray crystallographic analysis [12].

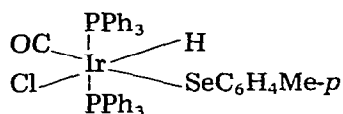


(I)

(II)  $\text{L} = \text{PPh}_3$  and  $\text{PPh}_2\text{Me}$ 

#### The metal hydrides

The reaction of *trans*- $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$  with a slight excess of *p*-tolueneselenol gives the yellow complex,  $\text{IrHCl}(\text{CO})(\text{SeC}_6\text{H}_4\text{Me-}p)(\text{PPh}_3)_2$ , which is rapidly oxidized in solution. In the PMR spectra of this compound in benzene, the  $\text{Ir}-\text{H}$  resonance consists of a triplet at  $\tau$  19.52 ppm ( $J(\text{P}-\text{H})$  12.0 Hz), which indicates that the two phosphine ligands are *cis* to the hydride ligand and *trans* to each other. The low value of  $\nu(\text{Ir}-\text{Cl})$  ( $270 \text{ cm}^{-1}$ ) suggests that the  $\text{Cl}-\text{Ir}-\text{CO}$  portion of the parent complex is bent upon adduct formation [11]. The value of  $2025 \text{ cm}^{-1}$  for  $\nu(\text{CO})$  is too high to assign the CO ligand *trans* to the hydride ligand. Moreover, the value of  $2242 \text{ cm}^{-1}$  for the  $\nu(\text{Ir}-\text{H})$  is reasonable to assign to the hydride ligand *trans* to the chlorine atom [13]. Thus, the configuration of  $\text{IrHCl}(\text{CO})(\text{SeC}_6\text{H}_4\text{Me-}p)(\text{PPh}_3)_2$  is suggested as III which may result from *cis* addition of the selenol. This configuration is common to the analogous benzenethiol adducts reported [4].



(III)

Equimolar reactions of the zerovalent Pt complexes with areneselenols give the yellow hydrides which are soluble in common organic solvents except for petroleum ether and which are sensitive to air oxidation in solution. These hydrides exhibit IR bands assignable to  $\nu(\text{Pt}-\text{H})$  and  $\delta(\text{Pt}-\text{H})$  around  $2100$  and  $800 \text{ cm}^{-1}$ , respectively. Although two or three  $\nu(\text{Pt}-\text{H})$  and  $\delta(\text{Pt}-\text{H})$  bands appear in some of the spectra in Nujol mulls, only one broad band is observed in  $\text{CH}_2\text{Cl}_2$  solution in the corresponding regions.

Table 2 gives the relevant PMR data, which indicate that these hydrides exist as a mixture of *cis* and *trans* isomers in  $\text{CH}_2\text{Cl}_2$  solution, the latter being predominant. The existence of the *cis* isomer, which is found to be a rather gen-

TABLE 2  
CHEMICAL SHIFTS (ppm) AND COUPLING CONSTANTS (Hz) OF THE ARYLSELENIDE HYDRIDES OF PLATINUM(II)

Temperature (°C)	<i>trans</i> isomer			<i>cis</i> isomer <sup>a</sup>		
	$\tau$ (Pt—H)	$J$ (Pt—H)	$J$ (P—H)	$\tau$ (Pt—H)	$J$ (P—H) ( <i>trans</i> )	$J$ (P—H) ( <i>cis</i> )
<i>PtH(SePh)(PPh<sub>3</sub>)<sub>2</sub></i>						
24	19.67	1018	<i>b</i>	16.15	182	16.5
-20	19.57	1013	12.6	16.19	182	16.5
-50	19.46	1013	13.2	15.90	182	16.2
<i>PtH(SeC<sub>6</sub>H<sub>4</sub>Me-<i>p</i>)(PPh<sub>3</sub>)<sub>2</sub></i>						
24	19.65	1000	<i>b</i>	16.10	180	17.4
-10	19.57	997	<i>b</i>	16.02	179	17.4
-32	19.44	993	12.3	15.85	179	17.5
<i>PtH(SePh)(PPh<sub>2</sub>Me)<sub>2</sub></i> <sup>c</sup>						
-50	19.58	1048	<i>b</i>	15.63	176	18.3
<i>PtH(SeC<sub>6</sub>H<sub>4</sub>Me-<i>p</i>)(PPh<sub>2</sub>Me)<sub>2</sub></i> <sup>d</sup>						
-52	19.68	1060	<i>b</i>	15.68	179	18.3

<sup>a</sup>  $J$ (Pt—H) could not be obtained because of too weak intensity. <sup>b</sup> Splitting due to the two <sup>31</sup>P nuclei was not clear. <sup>c</sup> At 24° only broad P—CH<sub>3</sub> and Pt—H signals assignable to the *trans* isomer could be observed at  $\tau$  8.12 and 19.82 ppm, respectively. At -50°  $\tau$ (P—CH<sub>3</sub>) 8.02 (complex multiplet) and 8.43 ppm (doublet,  $J$ (P—H) 8.6 Hz) for the *trans* and *cis* isomers, respectively. <sup>d</sup> At 24° only broad P—CH<sub>3</sub> and Pt—H signals assignable to the *trans* isomer could be observed at  $\tau$  8.02 and 19.81 ppm, respectively. At -52°  $\tau$ (P—CH<sub>3</sub>) 7.97 and 8.35 ppm (broad singlets) for the *trans* and *cis* isomers, respectively.

eral tendency of this class of compounds, has not been referred to by Ugo et al. [5], who reported the IR and PMR spectral data of *PtH(SePh)(PPh<sub>3</sub>)<sub>2</sub>*. Thus, at 24°C this compound shows a pair of slightly broad doublets at  $\tau$  16.15 for the *cis* isomer and a broad singlet at  $\tau$  19.67 for the *trans* isomer. Side bands due to coupling with the <sup>195</sup>Pt nucleus could not be observed with the *cis* isomer owing to the weak intensity. On the contrary, side bands are observable with the *trans* isomer, and the value of  $J$ (Pt—H) is very similar to those obtained for stable PPh<sub>3</sub> hydride complexes of Pt<sup>II</sup> [14]. However, the signal does not show split due to coupling with the two *cis* <sup>31</sup>P nuclei. These results can be explained in terms of dissociative exchange of PPh<sub>3</sub> in the *trans* isomer. Similar results are commonly observed in tertiary phosphine hydride complexes of Pt<sup>II</sup> [14]. On cooling, these signals become clearer with a slight shift to the lower field, probably because of a temperature effect, and at -20°C the *trans* isomer's signal is split into triplet, as was reported by Ugo et al. [5]. Therefore, at low temperature both isomers are rigid with regard to PPh<sub>3</sub> dissociation on the NMR time scale. Similarly, *PtH(SeC<sub>6</sub>H<sub>4</sub>Me-*p*)(PPh<sub>3</sub>)<sub>2</sub>* exists as a mixture of two isomers in CH<sub>2</sub>Cl<sub>2</sub> and the *trans/cis* ratio is found to be about 2.0 by the integrated intensity ratio of the *p*-Me signals.

On the other hand, the PPh<sub>2</sub>Me complexes represent the more labile systems (compared to the PPh<sub>3</sub> complexes) with regard to dissociative exchange of the tertiary phosphine ligands, as is shown in Fig. 1 and Table 2. At 24°C *PtH(SePh)(PPh<sub>2</sub>Me)<sub>2</sub>* exhibits only a very broad Pt—H signal at  $\tau$  19.69 with neither satellites due to the <sup>195</sup>Pt nor the <sup>31</sup>P nuclei observed in CH<sub>2</sub>Cl<sub>2</sub>. This signal can be assigned as due to the *trans* isomer in view of the chemical shift value in analogy with those of the PPh<sub>3</sub> analogs. On cooling, the *trans* isomer's signal exhibits satellites due to the Pt nucleus but no splitting due to the P

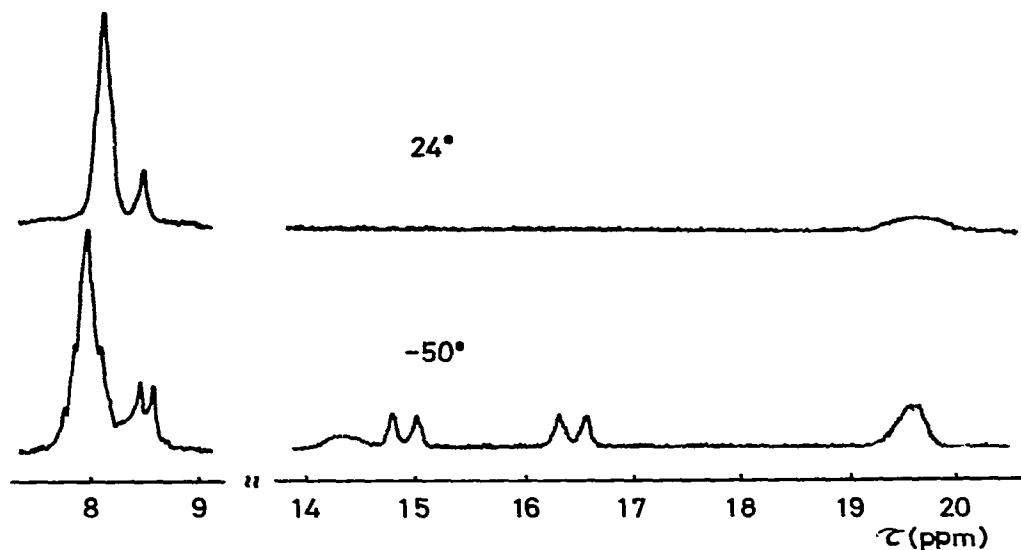


Fig. 1. Temperature-dependent PMR spectra of  $\text{PtH(SePh)(PPh}_2\text{Me)}_2$  in  $\text{CH}_2\text{Cl}_2$ . The aromatic proton signals and the high field satellite of the Pt—H signal are omitted.

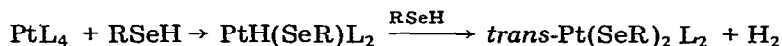
nuclei at  $-50^\circ\text{C}$ . The Pt—H signal due to the *cis* isomer appears as a faint one at  $-15^\circ\text{C}$  and becomes two pairs of clear doublets at  $\tau$  15.63 at  $-50^\circ\text{C}$ . In accordance with the change of the Pt—H signals, the P—Me signals confirm the lability of this hydride. Thus, the *trans* isomer's signal, which is predominant, remains a broad singlet down to  $-15^\circ\text{C}$ , and becomes a complex multiplet at  $-50^\circ\text{C}$ . The *cis* isomer's signal is observed as a broad singlet down to  $-15^\circ\text{C}$ ; however, at  $-50^\circ\text{C}$  it is a doublet, indicating the "rigidity" of the  $\text{PPh}_2\text{Me}$  ligand on the NMR time scale. Similarly,  $\text{PtH(SeC}_6\text{H}_4\text{Me-}p\text{)(PPh}_2\text{Me)}_2$ , which shows only a broad Pt—H signal at  $24^\circ\text{C}$ , exists as a mixture of almost rigid *cis* and still labile *trans* isomers at  $-52^\circ\text{C}$ . Thus, two distinct pairs of doublets and a broad singlet are observed for the Pt—H signals of the *cis* and *trans* isomers, respectively. However, the P—Me signals, even at  $-52^\circ\text{C}$ , are still observed as a broad singlet and complex multiplet for both the isomers. It is noteworthy that virtually coupled P—Me signals often show a singlet or complex multiplet, which is also explained in terms of phosphine exchange [15].

Roundhill et al. [16] have suggested that the driving force for addition of any protonic acid to  $\text{Pt(PPh}_3)_4$  is dependent on the acid strength or the coordinating capacity of the conjugate base to the Pt atom. Although the quantitative acid strength of areneselenols is not known, these compounds seem to be weak acids judging from the fact that dilution in  $\text{CCl}_4$  has no effect on the proton chemical shift of the SeH group [17]. On the other hand, the conjugate base  $\text{PhSe}^-$  is shown to be a good ligand to  $\text{Rh}^{\text{I}}$  and  $\text{Ir}^{\text{I}}$  [18], which are isoelectronic to  $\text{Pt}^{\text{II}}$ . Therefore, the hydride formation in the reactions of  $\text{PtL}_4$  with  $\text{RSeH}$  ( $\text{R} = \text{Ph}$  and  $p\text{-MeC}_6\text{H}_4$ ) is probably induced by strong conjugate bases  $\text{RSe}^-$ .

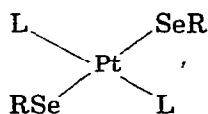
A reasonable correlation has been found to exist between the  $\tau(\text{Pt-H})$  value of *trans*-PtHX(PPh<sub>3</sub>)<sub>2</sub> in CDCl<sub>3</sub> and the *trans* effect of the ligands; it increases in the order of CO<sub>2</sub>CF<sub>3</sub> < Cl < Br < (CH<sub>2</sub>)<sub>2</sub>(CO)<sub>2</sub>N < SCOCH<sub>3</sub> < CN [16]. According to the correlation, the *trans* effect of PhSe<sup>-</sup> in *trans*-PtH-(SePh)(PPh<sub>3</sub>)<sub>2</sub> ( $\tau(\text{Pt-H})$  19.67 ppm (CH<sub>2</sub>Cl<sub>2</sub>)) is as large as that of the thioacetate group, whose complex shows  $\tau(\text{Pt-H})$  at 19.8 ppm, and smaller than CN ( $\tau(\text{Pt-H})$  17.5 ppm) [16]. The  $\tau(\text{Pt-H})$  value of the selenol adduct is also close to that of the thiol adduct *trans*-PtH(SPh)(PPh<sub>3</sub>)<sub>2</sub> in CH<sub>2</sub>Cl<sub>2</sub> (19.93 ppm) [5], suggesting that selenium and sulfur have a similar *trans* effect in square-planar Pt<sup>II</sup> complexes. In this respect, it is of interest to note that in *N,N*-dialkylthioselenocarbamate-palladium(II) and -platinum(II), only a slight difference is observed in coordinating ability of sulfur and selenium [19].

#### The bis(arylselenide) complexes

Reactions of zerovalent platinum complexes with a five-fold excess of areneselenols give orange or yellow crystals of Pt(SeR)<sub>2</sub>L<sub>2</sub> (R = Ph and *p*-MeC<sub>6</sub>H<sub>4</sub>; L = PPh<sub>3</sub> and PPh<sub>2</sub>Me), which are stable in air and soluble in common organic solvents other than saturated hydrocarbons. These complexes are essentially monomeric in CHCl<sub>3</sub> (Table 1). The compositions of these complexes are confirmed by the integrated intensity ratio in the PMR spectra. In the PPh<sub>2</sub>Me complexes, the P-Me signals appear as triplet of triplets due to coupling with <sup>195</sup>Pt nucleus and the virtual coupling [20], which indicates the *trans* configuration IV for the complexes. This type of bis(arylselenide) complex would be produced by reductive elimination of H<sub>2</sub> from a six-coordinate Pt<sup>IV</sup> complex, which may be formed by oxidative addition reaction of the Pt<sup>II</sup> hydride complex with another molecule of selenol as is indicated in the equation.



A similar result is reported with the reaction between Pt(PPh<sub>3</sub>)<sub>4</sub> and dichloromethylsilane [21].



(IV) L = PPh<sub>3</sub> and PPh<sub>2</sub>Me; R = Ph and *p*-MeC<sub>6</sub>H<sub>4</sub>

#### References

- 1 J.P. Collman and W.R. Roper, *Advan. Organometal. Chem.*, **7** (1968) 53.
- 2 R. Ugo, *Coord. Chem. Rev.*, **3** (1968) 319.
- 3 M.C. Baird and G. Wilkinson, *J. Chem. Soc. (A)*, (1967) 865.
- 4 (a) H. Singer and G. Wilkinson, *J. Chem. Soc. (A)*, (1968) 2516;  
(b) C.V. Senoff, *Can. J. Chem.*, **48** (1970) 2444;  
(c) A.K. Keskin and C.V. Senoff, *J. Organometal. Chem.*, **37** (1972) 201.
- 5 R. Ugo, G. La Monica and S. Cenini, *J. Chem. Soc. (A)*, (1971) 522.
- 6 D.J.G. Ives, R.W. Pittman and W. Wardlaw, *J. Chem. Soc.*, (1947) 1080.
- 7 D.G. Foster, *Org. Synth. Coll. Vol.*, **3** (1955) 771.
- 8 K. Vrieze, J.P. Collman, C.T. Sears, Jr. and M. Kubota, *Inorg. Synth.*, **11** (1968) 101.
- 9 R. Ugo, F. Cariatì and G. La Monica, *Inorg. Synth.*, **11** (1968) 105.
- 10 G. Gattow and M. Draeger, *Z. Anorg. Allgem. Chem.*, **343** (1966) 11.



- 11 A.J. Deeming and B.L. Shaw, *J. Chem. Soc. (A)*, (1969) 1128.
- 12 R. Mason and A.I.M. Rae, *J. Chem. Soc. (A)*, (1970) 1767.
- 13 L. Vaska, *J. Amer. Chem. Soc.*, 88 (1966) 5325.
- 14 Pi-Chang Kong and D.M. Roundhill, *Inorg. Chem.*, 11 (1972) 749.
- 15 (a) J.P. Fackler, Jr., J.A. Fetchin, J. Mayhew, W.C. Seidel, T.J. Swift and M. Weeks, *J. Amer. Chem. Soc.*, 91 (1969) 1941;  
(b) A.J. Deeming and B.L. Shaw, *J. Chem. Soc. (A)*, (1969) 597.
- 16 D.M. Roundhill, P.B. Tripathy and B.W. Renoe, *Inorg. Chem.*, 10 (1971) 727.
- 17 (a) N. Shargi and I. Lalezari, *Spectrochim. Acta*, 20 (1964) 237;  
(b) I. Lalezari and N. Shargi, *ibid.*, 23A (1967) 1948.
- 18 L. Vařka and J. Peone, Jr., *Chem. Commun.*, (1971) 418.
- 19 T. Tanaka and N. Sonoda, *Inorg. Chem.*, 10 (1971) 2337.
- 20 J.M. Jenkins, J.R. Moss and B.L. Shaw, *J. Chem. Soc. (A)*, (1969) 2796.
- 21 W. Fink and A. Wenger, *Helv. Chim. Acta*, 54 (1971) 2186.