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The Synthesis and Spectroscopic Study of Some Bis(tertiary-phosphine)bis(*N*,*N*-dialkylselenocarbamate) Complexes of Palladium(II) and Platinum(II)

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Ten *N*,*N*-dialkylselenocarbamate complexes of palladium(II) and platinum(II), $[(C_6H_5)_3P]_2Pd[SeC(O)NR_2]_2$ (**1**), $[(C_6H_5)_3P]_2Pt[SeC(O)NR_2]_2$ (**2**) (R=CH_3, C_2H_5, n-C_3H_7, and n-C_4H_9), $[CH_3(C_6H_5)_2P]_2Pd[SeC(O)N(CH_3)_2]_2$ (**3**), and $[CH_3(C_6H_5)_2P]_2Pt[SeC(O)N(CH_3)_2]_2$ (**4**), have been prepared. The infrared spectra and molecular-weight determinations indicate that the selenocarbamate ligand is bonded to the palladium(II) or platinum(II) through the selenium atom, with a free carbonyl group in the solid state, while in **1** and **2** two and one triphenylphosphine dissociate in a dilute solution to exist as compounds with bidentate selenocarbamate, $Pd[SeC(O)NR_2]_2$ and $[(C_6H_5)_3P]Pt[SeC(O)NR_2]_2$, respectively. The ^1H- and ^{31}P-NMR spectra of **3** and **4** reveal that they have a *trans*-configuration. The same configuration is suggested for the *N*,*N*-dibutyl derivative of **2** on the basis of the spin-spin coupling constant between the ^{31}P and ^{195}Pt nuclei.

Although *N*,*N*-dialkyldithiocarbamate- and -diselenocarbamate-metal complexes have widely been investigated, there have not been many studies of metal complexes of carbamate with hetero ligand atoms.[1-5] They have been limited only to the *N*,*N*-dialkylthiocarbamate and *N*,*N*-dialkylthioselenocarbamate complexes, and a little attention has been paid to the difference in coordination ability to metal between oxygen and sulfur[6] or between sulfur and selenium.[7]

The present work was undertaken in an attempt to prepare a series of *N*,*N*-dialkylselenocarbamate complexes of palladium and platinum, $[(C_6H_5)_3P]_2M[SeC(O)NR_2]_2$ and $[CH_3(C_6H_5)_2P]_2M[SeC(O)N(CH_3)_2]_2$ (M=Pd(II) and Pt(II); R=CH_3, C_2H_5, and n-C_3H_7), in order to elucidate their configurations by the infrared, ^1H-, and ^{31}P-NMR techniques.

Experimental

Physical Measurements. The molecular-weight determinations were carried out by means of a Hitachi-Perkin-Elmer 115 vapor pressure osmometer in chloroform at 30.5 °C. The infrared spectra were recorded on a Hitachi-Perkin-Elmer 225 spectrophotometer in Nujol mulls, and the electronic spectra were measured on a Hitachi 124 spectrophotometer in a dichloromethane solution, using a 1-cm quartz cell. The proton and P-31 NMR spectra were recorded on a Japan Electron Optics PS-100 spectrometer at 100 and 40.5 MHz respectively. The chemical shifts were measured against tetramethylsilane as the internal standard and 85% H_3PO_4 as the external standard, and were calibrated by the audio-frequency side-band technique.

Preparation. *N*,*N*-Dialkylammonium *N*,*N*-dialkylselenocarbamates were prepared by the reaction of the appropriate dialkylamine with selenium powder and carbon monoxide in tetrahydrofuran, as has been described elsewhere;[8] they were used as the solutions to prepare metal complexes without isolating them.

The method of preparing the complexes, $[(C_6H_5)_3P]_2M[SeC(O)NR_2]_2$ (M=Pd(II) and Pt(II); R=CH_3, C_2H_5, and n-C_3H_7), was basically the same as that for the *N*,*N*-dibutyl derivatives described in a previous paper;[5] the yields were almost quantitative. A suspension of $[(C_6H_5)_3P]_2MCl_2$ (M=Pd(II) and Pt(II)) (0.5 mmol) in dry benzene (20 ml) was stirred, drop by drop, into a tetrahydrofuran solution (10 ml) of dialkylammonium *N*,*N*-dialkylselenocarbamate (1.0 mmol) at room temperature, and then the mixture was further stirred for 4 hr. With the *N*,*N*-dimethyl and *N*,*N*-diethyl derivatives, the precipitates which appeared were filtered and washed with methanol several times to remove the dialkylammonium chloride. The products were then reprecipitated from a large amount of a chloroform-ether mixture.

$[(C_6H_5)_3P]_2Pd[SeC(O)N(CH_3)_2]_2$ (**1a**), mp 207 °C(decomp).

Found: C, 53.30; H, 4.51; N, 3.01%. Calcd for $C_{42}H_{42}N_2O_2P_2Se_2Pd$: C, 54.06; H, 4.53; N, 3.02%.

$[(C_6H_5)_3P]_2Pd[SeC(O)N(C_2H_5)_2]_2$ (**1b**), mp 202—203 °C (decomp).

Found: C, 56.05; H, 5.23; N, 2.72%. Calcd for $C_{46}H_{50}N_2O_2P_2Se_2Pd$: C, 55.86; H, 5.01; N, 2.83%.

$[(C_6H_5)_3P]_2Pt[SeC(O)N(CH_3)_2]_2$ (**2a**), mp 203—204 °C.

Found: C, 48.68; H, 4.24; N, 2.52%. Calcd for $C_{42}H_{42}N_2O_2P_2Se_2Pt$: C, 49.37; H, 4.14; N, 2.74%.

$[(C_6H_5)_3P]_2Pt[SeC(O)N(C_2H_5)_2]_2$ (**2b**), mp 217—220 °C.

Found: C, 50.79; H, 4.52%. Calcd for $C_{46}H_{50}N_2O_2P_2Se_2Pt$: C, 51.26; H, 4.68%.

In the case of the *N*,*N*-di-*n*-propyl derivatives, the ammonium chloride appearing in the reaction was filtered off, and the filtrate was evaporated to dryness under reduced pressure at room temperature. The resulting product was washed with a small amount of methanol and was recrystallized from benzene.

$[(C_6H_5)_3P]_2Pd[SeC(O)N(n\text{-}C_3H_7)_2]_2$ (**1c**), mp 185 °C.

Found: C, 57.45; H, 5.59; N, 2.68%; mol wt, 624 (6.83×10^{-3} M), 465 (4.12×10^{-3} M). Calcd for $C_{50}H_{58}N_2O_2P_2Se_2Pd$: C, 57.46; H, 5.59; N, 2.86%; mol wt, 1045.

$[(C_6H_5)_3P]_2Pt[SeC(O)N(n\text{-}C_3H_7)_2]_2$ (**2c**), mp 225 °C.

Found: C, 52.78; H, 5.27; N, 2.52%; mol wt, 832 (5.76×10^{-3} M), 764 (4.61×10^{-3} M). Calcd for $C_{50}H_{58}N_2O_2P_2Se_2Pt$: C, 52.96; H, 5.16; N, 2.47%; mol wt, 1134.

The characterization of the di-*n*-butyl derivatives, $[(C_6H_5)_3P]_2M[SeC(O)N(n\text{-}C_4H_9)_2]_2$ (M=Pd(**1d**) and Pt(**2d**)), was previously reported.[5]

Into $[(CH_3)_2NH_2][SeC(O)N(CH_3)_2]$ (1.0 mmol) in tetrahydrofuran (10 ml), we stirred a suspension of $[CH_3(C_6H_5)_2P]_2PdCl_2$ (0.5 mmol) in benzene (20 ml) over a 3 hr period at room temperature. The resulting dark red solution was filtered to remove the dimethylammonium chloride precipitated, and the solution was evaporated under reduced pressure to yield a red solid. Recrystallization from toluene gave orange crystals of $[CH_3(C_6H_5)_2P]_2Pd[SeC(O)N(CH_3)_2]_2$ (**3**) (0.47 mmol), mp 186—188 °C.

Found: C, 47.61; H, 4.92; N, 3.68%; mol wt, 701 (4.98×10^{-3} M), 745 (1.42×10^{-2} M). Calcd for $C_{32}H_{38}N_2O_2P_2$-

Se_2Pd: C, 47.51; H, 4.74; N, 3.46%; mol wt, 809.

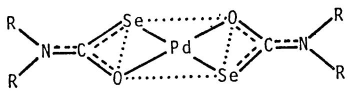
The $[CH_3(C_6H_5)_2P]_2Pt[SeC(O)N(CH_3)_2]_2$ (**4**) was similarly prepared by the reaction of $[CH_3(C_6H_5)_2P]_2PtCl_2$ (0.5 mmol) with the *N*,*N*-dimethylselenocarbamate salt (1.0 mmol); it was recrystallized from toluene to give light yellow crystals (0.45 mmol), mp 182—184 °C.

Found: C, 43.26; H, 4.45; N, 3.18%; mol wt, 800 (3.99×10^{-3} M), 841 (1.33×10^{-2} M). Calcd for $C_{32}H_{38}N_2O_2P_2$-Se_2Pt: C, 42.82; H, 4.27; N, 3.12%; mol wt, 898.

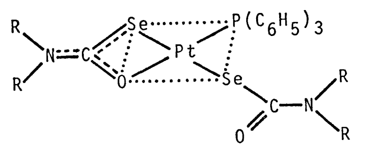
Results and Discussion

Properties. The palladium(II) and platinum(II) complexes obtained are stable in air; their solubilities are dependent on the nature of the *N*-alkyl group as well as on the phosphine coordinated. Among the triphenylphosphine complexes, **1d** and **2d** are fairly soluble in non-polar solvents, but less soluble in polar ones, such as acetone, alcohol, and water. **1c** and **2c** are somewhat soluble only in non-polar solvents, but **1a**, **1b**, **2a**, and **2b** are not sufficiently soluble to undergo spectroscopic study. On the other hand, both **3** and **4** are fairly soluble in common organic solvents.

In a previous communication,[5] the molecular-weight determination and the infrared spectra of **1d** and **2d** at various concentrations in solution have been reported to establish that: (i) the selenocarbamate ligand acts as a monodentate through the selenium atom in the solid state, (ii) in solution, partial dissociations of triphenylphosphine result in the ligand acting in a bidentate manner, and (iii) in a dilute solution, the palladium(II) and platinum(II) complexes dissociate into three and two species, and mainly exist as the following species, A and B respectively. Although the molecular-weights of **1c** and **2c** could not be determined at high concentrations due to their limited solubility, they exhibit a concentration dependence of the molecular weight similar to the cases of **1d** and **2d**, as is shown in Fig. 1.



A



B

The infrared spectra of **1c** and **2c** in the solid state show a strong band due to the ν(C=O) at about 1600 cm^{-1}, while in dichloromethane solution an additional weak band appears around 1540 cm^{-1}, as is listed in Table 1. The band in the 1540 cm^{-1} region is intensified by a decrease in the concentration of the solution, and at the same time the 1600 cm^{-1} band is weakened; these bands may be assigned to the carbonyl groups coordinated and uncoordinated to the metal atom. This infrared behavior is coincident with that of **1d** and **2d**.[5] Thus, conclusions (i)—(iii) for **1d** and **2d** presented above are reasonable for **1c** and **2c** also.

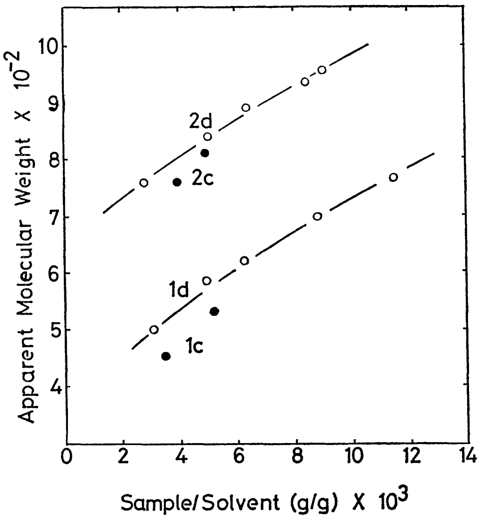


Fig. 1. Apparent molecular weights of $[(C_6H_5)_3P]_2Pd[SeC(O)N(n\text{-}C_3H_7)_2]_2$ (**1c**), $[(C_6H_5)_3P]_2Pt[SeC(O)N(n\text{-}C_3H_7)_2]_2$ (**2c**), $[(C_6H_5)_3P]_2Pd[SeC(O)N(n\text{-}C_4H_9)_2]_2$ (**1d**), and $[(C_6H_5)_3P]_2Pt[SeC(O)N(n\text{-}C_4H_9)_2]_2$ (**2d**) at various concentrations in chloroform.

TABLE 1. ν(C=O) FREQUENCY (cm^{-1}) OF THE COMPLEXES

Complex[a]		ν(C=O)[b]
$[(C_6H_5)_3P]_2Pd(dmsc)_2$	(**1a**)	1599 s
$[(C_6H_5)_3P]_2Pd(desc)_2$	(**1b**)	1589 s
$[(C_6H_5)_3P]_2Pd(dpsc)_2$	(**1c**)	1590 s (1589 s, 1537 m)
$[(C_6H_5)_3P]_2Pd(dbsc)_2$	(**1d**)	1600 s (1592 s, 1532 m)
$[CH_3(C_6H_5)_2P]_2Pd(dmsc)_2$	(**3**)	1599 s (1592 s, 1540 vw)
$[(C_6H_5)_3P]_2Pt(dmsc)_2$	(**2a**)	1603 s
$[(C_6H_5)_3P]_2Pt(desc)_2$	(**2b**)	1595 s
$[(C_6H_5)_3P]_2Pt(dpsc)_2$	(**2c**)	1598 s (1599 s, 1540 sh)
$[(C_6H_5)_3P]_2Pt(dbsc)_2$	(**2d**)	1603 s (1595 s, 1540 sh)
$[CH_3(C_6H_5)_2P]_2Pt(dmsc)_2$	(**4**)	1603 s (1603 s)

a) dmsc: $SeC(O)N(CH_3)_2$, desc: $SeC(O)N(C_2H_5)_2$, dpsc: $SeC(O)N(n\text{-}C_3H_7)_2$, and dbsc: $SeC(O)N(n\text{-}C_4H_9)_2$. b) s, strong; m, medium; sh, shoulder; vw; very weak. The wave number in parentheses are those in dichloromethane solution (1.0 mm cell, 0.8 wt%).

On the other hand, the molecular-weight determination indicates that both **3** and **4** are less dissociated than the triphenylphosphine complexes in solution. In accordance with this, the infrared spectra of these complexes show little change between the solid state and in solution, even in a very dilute solution.

NMR Spectra. As is shown in Table 2, the complexes of **3** and **4** in dichloromethane exhibit two N–CH_3 proton signals resulting from the restricted rotation around the carbamate C$\overset{...}{=}$N bond at low temperatures, although at room temperature broad singlets due to the N–CH_3 are observed. The approximate coalescence temperature was about −5 °C for both complexes. This temperature is considerably lower than that of $(CH_3)_2Sn[SeC(O)N(CH_3)_2]_2$ (50 °C) in nitrobenzene, which has a bidentate selenocarbamate, though the coordination of the carbonyl oxygen to the tin atom is weak.[4] This result suggests that the

TABLE 2. ^{1}H- AND ^{31}P-NMR PARAMETERS OF THE COMPLEXES IN CHLOROFORM SOLUTION; CONCD. 5.0 AND 12 wt%, RESPECTIVELY

Complex		δ(N-CH$_3$) ppm		δ(P-CH$_3$) ppm	$\Delta(^{31}\text{P})$[a] ppm
$[(C_6H_5)_3P]_2Pd(dbsc)_2$	(**1d**)				−29.0
$[CH_3(C_6H_5)_2P]_2Pd(dmsc)_2$	(**3**)	2.56	2.57[b] 2.46	2.35	−35.2
$[(C_6H_5)_3P]_2Pt(dbsc)_2$	(**2d**)				−25.6
$[CH_3(C_6H_5)_2P]_2Pt(dmsc)_2$	(**4**)	2.57	2.56[b] 2.49	2.43	−31.2

a) $\Delta=\delta(^{31}\text{P})_{\text{complexed}}-\delta(^{31}\text{P})_{\text{free}}$; $\delta(^{31}\text{P})_{(C_6H_5)_3P}=5.6$ and $\delta(^{31}\text{P})_{CH_3(C_6H_5)_2P}=28.1$ ppm from 85% H_3PO_4. b) Measured at −15°C.

double-bond character of the carbamate C–N bond of **3** and **4** is small, resulting from the fact that only the selenium atom attaches to the palladium(II) or platinum(II).

The P–CH$_3$ signal of **3** and **4** appears as a triplet, and the latter compound exhibits an additional triplet of the satellite in the higher magnetic field (this triplet results from spin interaction between the ^{195}Pt and (P-)CH$_3$ protons), whereas the lower satellite is obscured by the N-CH$_3$ signal, as is depicted in Fig. 2. This kind of "virtual coupling" phenomenon[9] establishes a *trans* disposition of the phosphine in the square-planar complexes of **3** and **4**.

Fig. 3 shows the ^{31}P-NMR spectra of the complexes, together with those of the free phosphines. **1d** shows a broad signal of the ^{31}P nucleus, which may be due to a dissociative exchange of $(C_6H_5)_3P$ in solution. On the other hand, a sharp signal of the ^{31}P is observed in the remaining complexes. In addition, the Pt(II) complexes exhibit the satellite due to a spin-spin interaction with the ^{195}Pt nucleus, while no coupling between the ^{31}P and ^{77}Se nuclei has been observed. Moreover, no appreciable change in the ^{31}P chemical shift occurred, even when a large excess of the phosphines was added to the solution, in contrast to the the case of **1d**. That the $J(^{195}\text{Pt}—^{31}\text{P})$ value of **2d** is comparable to those of **4** and some *trans*-bis(tertphosphine)platinum(II) dichlorides (J=2385—2531 Hz)[10,11] leads us to the conclusion that **2d** is also of a *trans* configuration.

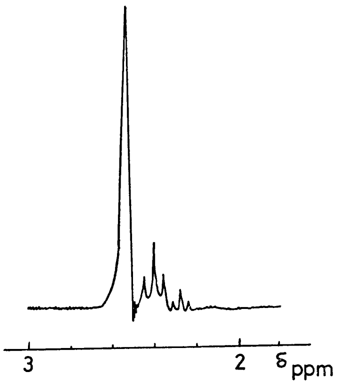


Fig. 2. PMR spectrum of $[CH_3(C_6H_5)_2P]_2Pt(dmsc)_2$ (**4**); 5wt% in CHCl$_3$.

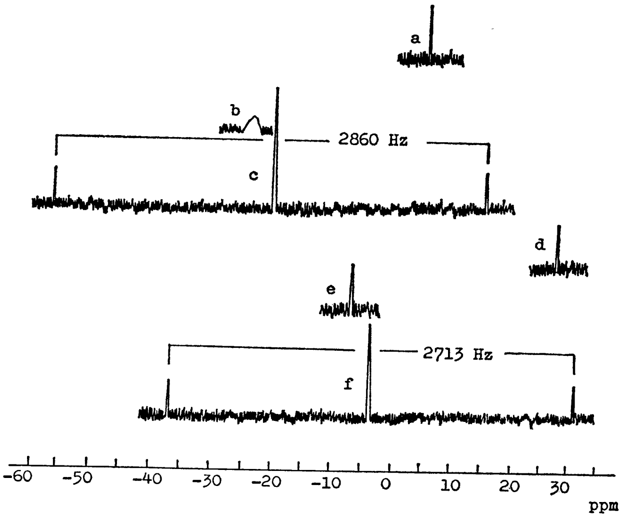


Fig. 3. ^{31}P-NMR spectra of $(C_6H_5)_3P$ (a), $[(C_6H_5)_3P]_2M(dbsc)_2$ (M=Pd (b), Pt (c)), $CH_3(C_6H_5)_2P$ (d), and $[CH_3(C_6H_5)_2P]_2M(dmsc)_2$ (M=Pd (e), Pt (f)) in CHCl$_3$; conc. 12 wt%.

Table 2 also lists the coordination chemical shifts, which are defined as the ^{31}P chemical shifts (relative to 85% H_3PO_4) of the complexes minus that of the free phosphine.[12] It may be noted that the coordination chemical shifts of the methyldiphenylphosphine complexes are larger than those of the triphenylphosphine complexes, while the reverse is true for the $J(^{195}\text{Pt}—^{31}\text{P})$ value. A similar finding with regard to the ^{31}P-NMR spectra has been reported on *cis*-bis-(triphenylphosphine)-[13] and bis(methyldiphenylphosphine)-platinum(II) dichloride,[10] in which the phosphines acting as good σ donors produce a large down-field shift upon coordination, whereas the π bonding with the platinum(II) causes an up-field shift. Thus, the difference in coupling constants between **2d** and **4** may be ascribed to an increase in the π bonding character of the Pt–P bond in the former complex.

Electronic Spectra. The electronic spectra of some complexes are summarized in Table 3. The apparent spectrum of **1d** changes gradually with an increase in the amounts of triphenylphosphine added to the solution, possibly because of a considerable dissociation of triphenylphosphine of **1d** in the measured concentration. Thus, the data for **1d** are those measured in the presence of a large excess of triphenylphosphine.

TABLE 3. ELECTRONIC SPECTRA OF SOME COMPLEXES IN DICHLOROMETHANE; BAND MAXIMA IN nm AND log ε IN PARENTHESES

		CT band	d-d band	
$[(C_6H_5)_3P]_2Pd(dbsc)_2$	(**1d**)	340 (4.12)	494 (2.52)	410 (3.47)
$[CH_3(C_6H_5)_2P]_2Pd(dmsc)_2$	(**3**)	325 (4.20)	474 (2.52)	390 (3.40)
$[(C_6H_5)_3P]_2Pt(dbsc)_2$	(**2d**)	280 (4.23)	398 (2.50)	336 (3.46)
$[CH_3(C_6H_5)_2P]_2Pt(dmsc)_2$	(**4**)	273 (4.35)	383 (2.68)	322 (3.45)

On the contrary, there was no appreciable change in the spectra of the remaining complexes when an excess amount of the phosphines was added to the solution. As may be seen in Table 3, the d-d bands of **3** and **4** appear at wavelength shorter by about 20 nm than those of **1d** and **2d**, indicating a stronger ligand field for methyldiphenylphosphine than for triphenylphosphine.

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