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Carboxamido and Thiocarboxamido Complexes of Platinum and Palladium

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Carboxamido complexes of the formula $L_2M(Cl)CONRR'$, where L = a phosphine or arsine, M = Pt or Pd, and R and R' are H or alkyl groups, may be prepared by three general methods: I, reaction of the cationic complex $L_2PtCl(CO)^+$ with primary and secondary amines; II, reaction of L_2MCl_2 with CO and amines; and III, the oxidative-addition reaction of L_4M with $ClC(O)N(CH_3)_2$. The thiocarboxamido analogs $L_2M(C\ )CSN(CH_3)_2$ may also be prepared *via* method III using $ClC(S)N(CH_3)_2$. Proton nmr studies indicate that the complexes have a trans stereochemistry and that there is a high barrier to rotation around the C–N bond of the carboxamido group. This barrier appears to be largely steric, depending strongly on the bulk of the L ligands. The thiocarboxamido complexes react with HBF_4 to give cationic complexes $\{L_4M_2[CSN(CH_3)_2]_2\}^{2+}$ which are presumably dimeric and contain bridging thiocarboxamido ligands. The reaction of $Pd[P(OCH_3)_3]_4$ with $ClC(S)N(CH_3)_2$ yields an analogous dimeric complex $[(CH_3O)_3P]_2Pd_2(Cl)_2[CSN(CH_3)_2]_2$ whose Pd atoms are bridged by two thiocarboxamido ligands, as established by an X-ray structural investigation.

Introduction

With few exceptions, cationic metal carbonyl complexes react with primary and secondary alkylamines to yield carboxamido derivatives according to the equation

$$L_nMC{\equiv}O^+ + 2RNH_2 \longrightarrow L_nMC(=O)NHR + RNH_3^+ \quad (1)$$

Such complexes of Fe,[2] Ru,[3] Mn,[4] Re,[5] Mo,[6] and W[6] have been prepared previously by this general method. In the present paper, we report the preparation of carboxamido and thiocarboxamido complexes of platinum and palladium. Depending on the compound desired, their syntheses have been achieved *via* reaction 1, by reaction of noncarbonyl compounds with CO and amines or by oxidative-addition reactions of Pt(0) and Pd(0).

Experimental Section

Materials.—The cationic complexes $[L_2PtCl(CO)]BF_4$, where L = $P(C_6H_5)_3$ or $As(C_6H_5)_3$, were prepared by a modification of the methods of Clark, Dixon, and Jacobs.[7] Approximately 10 mmol of L_2PtCl_2 in 25 ml of $CHCl_3$ was allowed to react with a 1 atm pressure of BF_3 (~50 mmol) at room temperature with stirring for 10–12 hr. The BF_3 was removed by N_2 purging, and the solution was evaporated to dryness under vacuum. The resulting solid was dissolved in a minimum of CH_2Cl_2 under an atmosphere of CO. While maintaining the CO atmosphere the volume of the solution was reduced on a steam bath, and diethyl ether was added to precipitate the $[L_2PtCl(CO)]BF_4$ product. It showed the characteristic C–O stretching absorption at approximately 2120 cm^{-1} and that of BF_4^- at 1050 cm^{-1}, previously reported for these compounds.[7,8]

The L_4Pt compounds were prepared by the hydrazine reduction of L_2PtCl_2 in the presence of excess L in ethanol.[9] The L_4Pd compounds were prepared by the reaction of ~3 mmol of π-allyl-π-cyclopentadienylpalladium[10] with ~15 mmol of the ligand L in ether or pentane as briefly described by Bittler, *et al.*,[11] and later used by Mukhedkar, *et al.*[12]

Carboxamido and Thiocarboxamido Complexes.—The $L_2M(Cl)CONRR'$ and $L_2M(Cl)CSNRR'$ complexes (where M is Pt or Pd and R and R' are H or alkyl groups) were prepared according to three general reactions: method I, reaction of $[L_2PtCl(CO)]BF_4$ with an amine; method II, reaction of L_2MCl_2 with CO and an amine; method III, reaction of L_4M with $ClC(O)N(CH_3)_2$ or $ClC(S)N(CH_3)_2$. The chloro derivatives could be converted to other halogen or pseudohalogen derivatives by ligand exchange (method IV). Table I summarizes conditions used in the synthesis of the compounds. Preparative details for representative complexes by the four general methods are given below.

Method I. $[(C_6H_5)_3P]_2Pt(Cl)CON(CH_3)_2$.—To 1.0 g (1.2 mmol) of $\{[(C_6H_5)_3P]_2PtCl(CO)\}BF_4$ suspended in 50 ml of freshly distilled benzene was added 1 ml of anhydrous $NH(CH_3)_2$. The mixture was stirred under a nitrogen atmosphere at room temperature for about 1 hr. The solution was filtered through Celite filter aid and evaporated to dryness. The oily solid was triturated with diethyl ether to give a pale yellow solid. Recrystallization from CH_2Cl_2–ether gave 0.63 g (65% yield) of the white microcrystalline product. *Anal.* Calcd for $C_{39}H_{36}ClNOP_2Pt$: C, 56.4; H, 4.38; N, 1.69; Cl, 4.29. Found: C, 55.6; H, 4.47; N, 2.07; Cl, 4.49.

Method II. $[(C_6H_5)_3P]_2Pd(Cl)CON(CH_3)_2$.—Carbon monoxide was bubbled into a suspension of 1.0 g (1.4 mmol) of $[(C_6H_5)_3P]_2PdCl_2$ in 25 ml of a 50:50 solution of acetone–dimethylamine at 0°. After 15 min, the yellow mixture turned to a colorless solution which was evaporated to dryness leaving an oily red solid. The residue was extracted with water to remove $[(CH_3)_2NH_2]Cl$ and dried under vacuum. Recrystallization from CH_2Cl_2–ether gave 0.85 g (80% yield) of the white product. *Anal.* Calcd for $C_{39}H_{36}ClNOP_2Pd$: C, 63.4; H, 4.91; N, 1.90. Found: C, 62.7; H, 5.17; N, 2.22.

$[(C_6H_5)_3P]_2Pd(Cl)CONHCH_3$.—To avoid an excess of amine which decreased the yields, the palladium–carboxamido complexes of primary amines were prepared by the following modification of method II. A mixture of 2.4 g (10 mmol) of $(CH_3NH_2)_2PdCl_2$ and 6.0 g (23 mmol) of $P(C_6H_5)_3$ in CH_2Cl_2 was stirred under approximately 0.5 atm pressure of CO for 1 hr. After filtering, the solution was treated with ether to give 1.2 g (16% yield) of the pale yellow product. Subsequent reaction of the residue with additional $P(C_6H_5)_3$ and CO gave more product with overall yields up to 67%. *Anal.* Calcd for $C_{38}H_{34}ClNOP_2Pd$: C, 62.96; H, 4.73; N, 1.93; Cl, 4.90. Found: C, 62.27; H, 4.66; N, 1.90; Cl, 5.54.

Method III. $[(C_6H_5)_3P]_2Pt(Cl)CON(CH_3)_2$.—Dimethylcarbamoyl chloride (0.2 ml, 2 mmol) was added to 2.4 g (2.0 mmol) of $[(C_6H_5)_3P]_4Pt$ in 50 ml of freshly distilled benzene under a nitrogen atmosphere. After 30 min, the white *cis*-$[(C_6H_5)_3P]_2PtCl_2$ which had precipitated was filtered off and the solution volume was reduced under vacuum. On treatment with ether, 0.4 g (25% yield) of the white product precipitated. Its ir and nmr spectra were identical with those obtained for the compound prepared by method I.

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TABLE I
PREPARATION OF CARBOXAMIDO AND THIOCARBOXAMIDO COMPLEXES

Compound[a]	Method[b]	Reaction solvent[c]	Method of product isolation from soln[c]	Recrystn solvent[c]	Color
$(TPP)_2Pt(Cl)CON(CH_3)_2$	I	B	B[i]	D–E	White
	II	A	W[j]	D–E	
	III	B	B[i]	D–E	
$(TPP)_2Pt(I)CON(CH_3)_2$	IV[d]	A	B–C[i]	D–E	Pale orange
$(TPP)_2Pt(NCO)CON(CH_3)_2$	IV[e]	A	W[j]	D–E	White
$(TPA)_2Pt(Cl)CON(CH_3)_2$	I	D	C[i]	C–E	White
$(MDPP)_2Pt(Cl)CON(CH_3)_2$	II	D	B[i]	D–E	White
$(DMPP)_2Pt(Cl)CON(CH_3)_2$	II	A	W[j]	D–E	White
$(TPP)_2Pt(Cl)CON(CH_3)(C_2H_5)$	II	A	W[j]	D–E	White
$(TPP)_2Pt(Cl)CONH(CH_3)$	I	B	B[i]	B–E	White
$(TPP)_2Pt(Cl)CONH(C_2H_5)$	I	D	D–B[i]	D–B–E	White
$(TPP)_2Pt(Cl)CON(C_2H_5)_2$	I	D	W[j]	D–E	White
	II	A	W[j]	A–E	
$(TPA)_2Pt(Cl)CON(C_2H_5)_2$	I	D	C–B[i]	A–E	White
$(TPA)_2Pt(Cl)CONH(i\text{-}C_3H_7)$	I	D	C–B[i]	A–E	White
$(TPP)_2Pd(Cl)CON(CH_3)_2$	II	A	W[k]	D–E	White
	III	B			
$(TPP)_2Pd(Cl)CON(CH_3)(C_2H_5)$	II	A	W[j]	D–E	White
$(TPP)_2Pd(Cl)CSN(CH_3)_2$	III	B			Bright yellow
$(TPP)_2Pd(Br)CSN(CH_3)_2$	IV[f]	A	W[j]	D–E	Bright yellow
$(TPP)_2Pd(I)CSN(CH_3)_2$	IV[g]	A	W[j]	D–E	Red
$\{(TPP)_4Pd_2[CSN(CH_3)_2]_2\}(BF_4)_2$	IV[h]	A	W[j]	D–E	White
$(MDPP)_2Pd(Cl)CON(CH_3)_2$	III	B			Yellow-orange
$(MDPP)_2Pd(I)CSN(CH_3)_2$	IV[g]	A	W[j]	D–E	Red
$(TPP)_2Pt(Cl)CSN(CH_3)_2$	III	B			Yellow-green
$(TPP)_2Pt(I)CSN(CH_3)_2$	IV[g]	A	W[j]	D–E	Orange
$\{(TPP)_4Pt_2[CSN(CH_3)_2]_2\}(BF_4)_2$	IV[h]	A	W[j]	D–E	White
$(MDPP)_2Pt(Cl)CSN(CH_3)_2$	III	B			Yellow
$\{(MDPP)_4Pt_2[CSN(CH_3)_2]_2\}(BF_4)_2$	IV[h]	A	W[j]	D–E	White
$(TMP)_2Pd_2(Cl)_2[CSN(CH_3)_2]_2$	III	E		D–E	Yellow-orange

[a] TPP = $(C_6H_5)_3P$, TPA = $(C_6H_5)_3As$, MDPP = $CH_3(C_6H_5)_2P$, DMPP = $(CH_3)_2(C_6H_5)P$, TMP = $(CH_3O)_3P$. [b] See Experimental Section. [c] B = benzene, A = acetone, D = dichloromethane, W = water, C = chloroform, E = diethyl ether. [d] Reaction with NaI. [e] Reaction with NaNCO. [f] Reaction with $(C_2H_5)_4NBr$. [g] Reaction with $(n\text{-}C_4H_9)_4NI$. [h] Reaction with HBF_4. [i] Evaporated reaction solution to dryness and extracted with this solvent or solvent mixture. [j] Precipitated from reaction solution with this solvent. [k] Evaporated reaction solution to dryness and washed with this solvent.

$[(C_6H_5)_3P]_2Pd(Cl)CSN(CH_3)_2$.—Freshly sublimed dimethylthiocarbamoyl chloride (0.25 g, 1.9 mmol) was added to a solution of 0.79 g (0.68 mmol) of $[(C_6H_5)_3P]_4Pd$ in 50 ml of freshly distilled benzene under a nitrogen atmosphere. A bright yellow solid began to form immediately. The benzene was removed under vacuum and 0.51 g (98% yield) of the product was collected and washed with ether. *Anal.* Calcd for $C_{39}H_{36}ClNSP_2Pd$: C, 62.1; H, 4.81; N, 1.86; Cl, 4.70; S, 4.24. Found: C, 62.1; H, 4.64; N, 2.09; Cl, 4.69; S, 4.33.

Method IV. $[(C_6H_5)_3P]_2Pt(I)CON(CH_3)_2$.—To 0.5 g of $[(C_6H_5)_3P]_2Pt(Cl)CON(CH_3)_2$ in 25 ml of acetone was added an acetone solution of 1.0 g of NaI (or $(n\text{-}C_4H_9)_4NI$). The mixture was stirred at room temperature for 1 hr. It was evaporated to dryness. The resulting residue was extracted with a 50:50 solution of benzene–chloroform. This solution was reduced under vacuum and treated with ether to give pale orange crystals of the product. It was characterized by its ir and nmr spectra and its reaction with trichloroacetic acid to give $[(C_6H_5)_3P]_2Pt(I)(CO)^+$ which was identified by its ir spectrum.[13]

$\{[(C_6H_5)_3P]_4Pd_2[CSN(CH_3)_2]_2\}(BF_4)_2$.—One gram (1.31 mmol) of $[(C_6H_5)_3P]_2Pd(Cl)CSN(CH_3)_2$ was slurried in 25 ml of acetone, and several drops of 40% aqueous fluoroboric acid was added. The mixture immediately produced a colorless solution which upon treatment with water yielded 1.0 g (95% yield) of the white microcrystalline product. It was identified by its spectra and reactions (see Results and Discussion). The analogous Pt compound was prepared in the same manner. *Anal.* Calcd for $C_{39}H_{36}NSP_2BF_4Pt$: C, 52.35; H, 4.1; N, 1.56; S, 3.58. Found: C, 53.37; H, 5.0; N, 1.73; S, 3.95.

$[(CH_3O)_3P]_2Pd_2(Cl)_2[CSN(CH_3)_2]_2$.—Freshly sublimed dimethylthiocarbamoyl chloride (0.24 g, 2.0 mmol) was added to a solution of freshly prepared $[(CH_3O)_3P]_4Pd$ (1.2 g, 2.0 mmol) in anhydrous ether under a nitrogen atmosphere. After stirring for about 10 min, the yellow powder was collected and recrystallized from CH_2Cl_2–ether giving 0.65 g (85% yield) of the product. *Anal.* Calcd for $C_9H_{15}ClNSPO_3Pd$: C, 20.33; H, 4.29; N, 3.95; Cl, 10.01; S, 9.05. Found: C, 20.14; H, 4.09; N, 3.73; Cl, 10.18; S, 9.08. On reaction with excess $P(C_6H_5)_3$, $[(CH_3O)_3P]_2Pd_2(Cl)_2[CSN(CH_3)_2]_2$ is readily converted to $[(C_6H_5)_3P]_2Pd(Cl)CSN(CH_3)_2$.

Infrared spectra were recorded on a Beckman IR-12 spectrophotometer. The proton nmr spectra were recorded on a Varian A-60 or Perkin-Elmer Hitachi R-20B spectrometer. The variable-temperature nmr data were obtained on the latter instrument.

Results and Discussion

Synthetic Routes to Carboxamido and Thiocarboxamido Complexes.—Four general types of reaction have been used to prepare these derivatives (Table I). They are given below.

Method I.—This approach involves the well-established reaction (see Introduction) of cationic metal carbonyl complexes with primary and secondary amines

$$trans\text{-}L_2PtCl(CO)^+ + 2HNRR' \longrightarrow trans\text{-}L_2Pt(Cl)CONRR' + H_2NRR'^+ \quad (2)$$

(where R and R′ are H or alkyl groups). Arylamines, such as aniline, however, do not react with the cations under the mild conditions used in these preparations. Clark, *et al.*,[8,13] previously prepared alkoxycarbonyl complexes, $L_2Pt(Cl)COOR$, from the cations and alcohols in a closely related reaction. The analogous palladium complexes were not prepared by this route because $L_2PdCl(CO)^+$ is known to lose CO rapidly except under a CO atmosphere.[14]

Method II.—This method is by far the best and most general method of preparing carboxamido complexes of

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both platinum and palladium. It simply involves bubbling CO into a solution containing the desired amine and L_2MCl_2 complex

$$cis\text{-}L_2MCl_2 + CO + 2HNRR' \longrightarrow trans\text{-}L_2M(Cl)CONRR' + [H_2NRR']Cl \quad (3)$$

(where M is Pt or Pd, and R and R′ are H or alkyl groups).

Although no mechanistic studies were undertaken, it seems probable that the reaction proceeds by initial formation of $L_2MCl(CO)^+$ which then reacts with the amine as in eq 2. The existence of an intermediate cationic carbonyl complex is supported by the known reaction[15] of *cis*-$[(C_2H_5)_3P]_2PtCl_2$ with CO at room temperature to form *trans*-$[(C_2H_5)_3P]_2PtCl(CO)^+$. This does not rule out the possibility that amine coordination occurs first which is followed by CO insertion into the Pt–N bond; there are, however, no known examples of this type of CO insertion.

The ease of carboxamido complex formation from CO, amines, and Pt(II) or Pd(II) complexes strongly suggests that carboxamido derivatives may occur as intermediates in certain catalytic reactions. Such may be the case for the $PdCl_2$-catalyzed reaction of CO and amines to form ureas, formamides, and oxamides,[16] for the reaction of $PdCl_2$ with CO and amines to form alkyl isocyanates,[17,18] or for the reaction of $Pd(NH_2R)_2Cl_2$ with CO to give alkyl isocyanates.[17]

Method III.—Oxidative-addition reactions of L_4Pt and L_4Pd with dimethylcarbamoyl chloride and dimethylthiocarbamoyl chloride yield the corresponding *N,N*-dimethylcarboxamido complexes

$$L_4M + ClC(=Y)N(CH_3)_2 \longrightarrow trans\text{-}L_2M(Cl)CYN(CH_3)_2 + 2L \quad (4)$$

(where M = Pt or Pd, and Y = O or S).

Yields (~25%) from the reaction of $[(C_6H_5)_3P]_4Pt$ and $[(C_6H_5)_3P]_4Pd$ with $ClC(O)N(CH_3)_2$ are lower than those obtained by methods I or II. In this case much of the product is $[(C_6H_5)_3P]_2MCl_2$, which is apparently not formed from the reaction of *trans*-$[(C_6H_5)_3P]_2M(Cl)CON(CH_3)_2$ with excess $ClC(O)N(CH_3)_2$ since this reaction occurs only very slowly. On the other hand, yields for the reaction of $ClC(S)N(CH_3)_2$ with all of the L_4M complexes studied (Table I) are virtually quantitative, even in the presence of excess $ClC(S)N(CH_3)_2$. Very recently oxidative-addition reactions of L_4Ni with $ClC(S)N(CH_3)_2$ have been reported[19] to yield analogous $L_2Ni(Cl)CSN(CH_3)_2$ complexes.

Method IV.—The chloride ligand in the *trans*-$L_2M(Cl)CONRR'$ complexes may be exchanged readily with other anionic ligands

$$trans\text{-}L_2M(Cl)CONRR' + X^- \longrightarrow trans\text{-}L_2M(X)CONRR' + Cl^- \quad (5)$$

(where M = Pt or Pd; X^- = Br^-, I^-, or NCO).

Still another method of preparing both carboxamido and thiocarboxamido complexes was demonstrated by Knebel and Treichel in the reactions of the isocyanide complex *trans*-$[(C_6H_5)_3P]_2Pt(CNCH_3)^{2+}$ with OH^- and SH^- to give *trans*-$[(C_6H_5)_3P]_2Pt(CNCH_3)CONHCH_3^+$ and *trans*-$[(C_6H_5)_3P]_2Pt(CNCH_3)CSNHCH_3^+$, respectively.[20]

Properties of the Complexes.—Except for $[(C_6H_5)_3P]_2Pd(Cl)CONHCH_3$, which shows some decomposition after several months, all of the carboxamido and thiocarboxamido complexes are air-stable crystalline solids, soluble in $CHCl_3$ and CH_2Cl_2, slightly soluble in acetone and hot benzene, but insoluble in water, diethyl ether, and hexane. They are also surprisingly stable toward water. This contrasts with the similar alkoxycarbonyl complexes, *trans*-$L_2Pt(Cl)COOR$, which react with water[13] in the presence of salts to give the platinum hydride complex ($L_2Pt(Cl)H$), CO_2, and the alcohol.

The carboxamido complexes in CH_2Cl_2 solvent react instantaneously with strong acids

$$L_2M(Cl)CONRR' + 2HX \rightleftharpoons [L_2M(Cl)CO]X + [H_2NRR']X \longrightarrow L_2M(Cl)X + CO \quad (6)$$

to give initially the cationic carbonyl complex which may either react with the anion X^- with displacement of CO or lose CO and dimerize to the chloride-bridged $(L)_4M_2Cl_2^{2+}$ complexes.[14] For platinum, the intermediate cationic carbonyl complex is sufficiently stable that it may be identified in solution by its terminal CO stretching absorption at ~2120 cm^{-1}. This disappears at a rate depending on the nature of X^- to give the final product $L_2M(Cl)X$. As noted previously[14] the palladium cationic carbonyl complex loses CO rapidly; as a result, this intermediate species cannot be detected by ir spectroscopy.

To gain a qualitative idea of what acid strength was required to allow reaction 6 to proceed, $[(C_6H_5)_3P]_2Pd(Cl)CON(CH_3)_2$ was treated with several acids in CH_2Cl_2 solvent. The reaction was followed by the disappearance of the carboxamido methyl resonances (see below) in the proton nmr spectrum of the complex. It was found that HCl, Cl_3CCO_2H (pK_a = 0.70), and $BrCH_2CO_2H$ (pK_a = 2.69) react, but *p*-$NO_2C_6H_4CO_2H$ (pK_a = 3.41), $C_6H_5CO_2H$ (pK_a = 4.19), and CH_3CO_2H (pK_a = 4.75) do not. Thus it appears that a rather strong acid is required to carry out reaction 6. Previously it was observed[2-5] that other carboxamido complexes react with HCl in the same manner. The thiocarboxamido complexes reported in this paper react in quite a different way.

$[(CH_3O)_3P]_2Pd_2(Cl)_2[CSN(CH_3)_2]_2$.—This compound is obtained from the reaction of $Pd[P(OCH_3)_3]_4$ with $ClC(S)N(CH_3)_2$. It presumably results from a two-step reaction involving initial oxidative addition according to eq 4 to form $[(CH_3O)_3P]_2Pd(Cl)CSN(CH_3)_2$ which subsequently loses one $P(OCH_3)_3$ ligand with dimer formation. An X-ray structural investigation[21] of the final product (**1**) shows the coordination around each Pd to be essentially square planar with the plane of the thiocarboxamido ligand roughly (~67°) perpendicular to the coordination plane. The sulfur of each thiocarboxamido group is bound to the other

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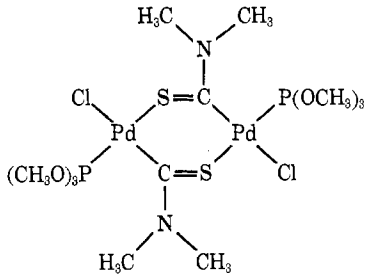

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Pd atom. The geometry of the bridging ligands causes the square planes around the Pd atoms to be at an angle of 57° with respect to each other. Although organic thioamides are known to act as sulfur-donor ligands toward metals,[22] this is the first example of a thiocarboxamido ligand of a metal complex acting as a ligand to another metal.

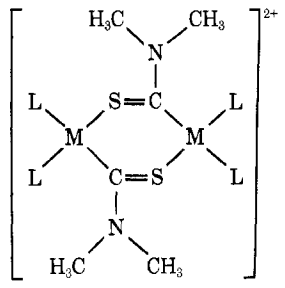
The reaction of $Ni[P(OC_6H_5)_3]_4$ with $ClC(S)N(CH_3)_2$ has been shown[19] to give a dimeric complex, $[(C_6H_5O)_3P]_2Ni_2(Cl)_2[CSN(CH_3)_2]_2$, whose structure is presumably analogous to that of the Pd analog reported here.

$\{L_4M_2[CSN(CH_3)_2]_2\}^{2+}$.—In acetone solution, the $L_2M(Cl)CSN(CH_3)_2$ complexes are unaffected by aqueous HCl but react with aqueous HBF_4 to give $\{L_4M_2[CSN(CH_3)_2]_2\}(BF_4)_2$

$$2L_2M(Cl)CSN(CH_3)_2 + 2HBF_4 \longrightarrow \{L_4M_2[CSN(CH_3)_2]_2\}(BF_4)_2 + 2HCl \quad (7)$$

(where M = Pt or Pd).

Thus, the reaction appears to be one in which the coordinated chloride in the thiocarboxamido complex dissociates to give a three-coordinated complex which dimerizes to yield the product. The product structures (**2**) are presumably analogous to that of $[(CH_3O)_3P]_2$-



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$Pd_2(Cl)_2[CSN(CH_3)_2]_2$, **1**—that is, incorporating bridging thiocarboxamido ligands.

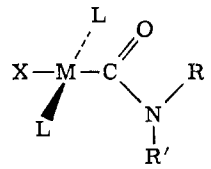
With $[(C_6H_5)_3P]_2Pd(Cl)CSN(CH_3)_2$, Cl^- dissociation and dimerization occur in solution even in the absence of HBF_4. This is indicated by its proton nmr spectrum in $CDCl_3$, which shows four lines for the *N*-methyl resonances. Two of these (τ 6.5 and 7.5) are the same as those observed in the spectrum of $\{[(C_6H_5)_3P]_4Pd_2[CSN(CH_3)_2]_2\}(BF_4)_2$. The other two lines ($\tau$ 7.3 and 7.4) then presumably are those of the starting thiocarboxamido complex. Thus the equilibrium

$$2[(C_6H_5)_3P]_2Pd(Cl)CSN(CH_3)_2 \rightleftharpoons \{[(C_6H_5)_3P]_4Pd_2[CSN(CH_3)_2]_2\}^{2+} + 2Cl^- \quad (8)$$

exists in solution. This has been confirmed by adding Cl^- (as $(C_6H_5)_4AsCl$) to the solution to shift the equilibrium to the left. For the corresponding iodo complex, $[(C_6H_5)_3P]_2Pd(I)CSN(CH_3)_2$, the methyl resonances are observed as a broad singlet suggesting rapid equilibration of the two forms (eq 8) on the nmr time scale.

Proton Nmr Spectra and Structures.—To establish the cis–trans stereochemistry of the carboxamido and thiocarboxamido complexes, the proton nmr spectra of several representative complexes containing the phosphine ligands $CH_3(C_6H_5)_2P$ or $(CH_3)_2(C_6H_5)P$ were examined (Table II).

Jenkins and Shaw[23] had previously shown that *trans*-$(CH_3)_2(C_6H_5)P$ ligands in platinum complexes show a proton nmr spectrum in which an apparent triplet, due to "virtual" coupling of the methyl protons with the trans P atoms, is split further by ^{195}Pt ($I = 1/2$, 34% abundance) into two triplet satellites. The intensity ratio of these three apparent triplet groups is 1:4:1. The spectrum of the phosphine CH_3 group in $[CH_3(C_6H_5)_2P]_2Pt(Cl)CYN(CH_3)_2$ (for Y = O or S) gives precisely this splitting pattern (Table II) indicating that both the carboxamido and thiocarboxamido complexes of Pt are of trans geometry. The spectrum of $[(CH_3)_2(C_6H_5)P]_2Pt(Cl)CON(CH_3)_2$, however, shows two such sets of patterns. This arises from the nonequivalence of the two CH_3 groups in the ligand and has been observed in a variety of other complexes[24] containing *trans*-$(CH_3)_2(C_6H_5)P$ ligands in which there is no plane of symmetry though the two trans phosphorus atoms. In carboxamido complexes, this result suggests that there is restricted rotation around the Pt–C bond. On the basis of the nmr results for these model compounds, it is assumed that the neutral carboxamido and thiocarboxamido complexes reported in this paper have a trans geometry (**3**). This assign-



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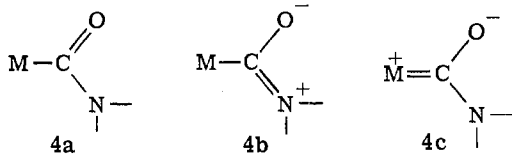
ment is supported by a similar assignment for the related carboalkoxy derivatives, $L_2Pt(Cl)COOR$.[13]

The majority of complexes prepared were those using $P(C_6H_5)_3$ ligands; they showed a multiplet in the region of τ 2–3. In addition, the complexes containing the $CON(CH_3)_2$ ligand exhibited two *N*-methyl resonances due to restricted rotation around the C–N bond. In organic amides[25] such restricted rotation and their planar structures are indicative of the importance of resonance form **4b** to the bonding in the amide group.



4a 4b 4c

The possible π-donor ability of metals, such as Pt and

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TABLE II

PROTON NMR SPECTRA OF $L_2M(X)CYNRR'$ IN $CDCl_3$ AT ROOM TEMPERATURE[a]

M	Y	L	X	R	R'	τ, ppm: α-H of R	α-H of R'	β-H of R	β-H of R'	$^4J_{PtCNCH}$[b] of R, Hz
Pt	O	TPA	Cl	CH_3	CH_3	7.27	8.33			
Pt	O	TPP	I	CH_3	CH_3	7.29	8.40			6.1
Pd	O	TPP	Cl	CH_3	CH_3	7.29	8.27			
Pd	O	TPP	Cl	H	CH_3	5.45[l]	8.46			
Pt	O	TPP	Cl	CH_3	CH_3	7.33	8.40			5.8
Pt	O	DMPP[c]	Cl	CH_3	CH_3	7.45	7.69			6.2[d]
Pt	O	TPP	NCO	CH_3	CH_3	7.45	8.47			5.2
Pt	O	MDPP[e]	Cl	CH_3	CH_3	7.55	8.15			6.3
Pd[f]	O	TPP	Cl	CH_3	C_2H_5	6.87	7.62		9.70	
				C_2H_5	CH_3	6.38	7.95	9.35		
Pt[f]	O	TPP	Cl	CH_3	C_2H_5	6.99	7.73		9.76	5.7
				C_2H_5	CH_3	6.42	8.06	9.44		6.6
Pt	O	TPP	Cl	C_2H_5	C_2H_5	6.16	7.60	9.23	9.67	~6
Pt	O	TPA	Cl	C_2H_5	C_2H_5	7.24	7.84	9.38	9.88	
Pt	O	TPP	Cl	H	CH_3	5.2[l]	8.4			
Pt	O	TPP	Cl	H	C_2H_5	5.3[l]	7.75		9.50	
Pt	O	TPA	Cl	H	i-C_3H_7	5.4[l]	7.02		9.85	
Pd	S	TPP	Cl	CH_3	CH_3	6.5	7.5[g]			
						7.3	7.4			
Pd	S	TPP	Br	CH_3	CH_3	7.39	7.51			
Pd	S	TPP	I	CH_3	CH_3	7.40	7.40			
Pt	S	TPP	Cl	CH_3	CH_3	7.37	7.78			6
Pt	S	TPP	I	CH_3	CH_3	7.41	7.70			7
Pd	S	MDPP[h]	Cl	CH_3	CH_3	7.23	7.68			
Pd	S	MDPP[i]	I	CH_3	CH_3	7.22	7.75			
Pt	S	MDPP[j]	Cl	CH_3	CH_3	7.19	7.64			7
Pt[o]	S	MDPP[k]	BF_4	CH_3	CH_3	6.36	7.25			6
Pt[o]	S	TPP	BF_4	CH_3	CH_3	6.16	7.72			4.5
Pd[o]	S	TPP	BF_4	CH_3	CH_3	6.38	7.51			
Pd	S	TMP	Cl[m]	CH_3	CH_3	6.32	6.79[n]			

[a] Abbreviations are the same as in Table I and 3. [b] Where no value is given, the coupling constant is less than 2 Hz. [c] CH_3 groups of L at τ 8.25 ($^3J_{PtPCH}$ = 31.6 Hz) and τ 8.29 ($^3J_{PtPCH}$ = 35.2 Hz); each is a triplet with triplet satellites due to coupling to ^{195}Pt. [d] For R', $^4J_{PtCNCH}$ = 4.2 Hz. [e] CH_3 group of L at τ 7.84, a triplet with triplet satellites due to coupling to ^{195}Pt ($^3J_{PtPCH}$ = 34.5 Hz). [f] Mixture of isomers. [g] See text. [h] CH_3 group of L at τ 7.98, a singlet. [i] CH_3 group of L at τ 7.68, a singlet. [j] CH_3 group of L at τ 7.86, a triplet with triplet satellites due to coupling to ^{195}Pt ($^3J_{PtPCH}$ = 32 Hz). [k] CH_3 group of L at τ 7.87, a multiplet. [l] Proton on nitrogen. [m] Compound is $[(CH_3O)_3P]_2Pd_2(Cl)_2[CSN(CH_3)_2]_2$. [n] Triplet ($J \cong 1.5$ Hz). Both 60- and 100-MHz spectra show this unexplained pattern. [o] Formulas for these dimeric complexes are $\{L_4M_2[CSN(CH_3)_2]_2\}(BF_4)_2$.

Pd, suggests that form **4c** may also make an appreciable contribution in the metal derivatives. This is supported by the low C–O stretching frequency (~1570 cm^{-1}) of the carboxamido ligand as compared to that in organic amides (~1670 cm^{-1}). On this basis it would be anticipated that the C–N rotational barrier and the nmr coalescence temperature would be lower in carboxamido complexes than in organic amides. Table III presents coalescence temperatures for some inorganic and organic $Z–CON(CH_3)_2$ derivatives. The low value for $CH_3OC(O)N(CH_3)_2$ has been attributed to important contributions by **4c**. As expected for metal complexes, $(\pi\text{-}C_5H_5)M(CO)_3CON(CH_3)_2$ (M = Mo or W) also show a relatively low coalescence temperature.

TABLE III

COALESCENCE TEMPERATURES OF INORGANIC AND ORGANIC CARBOXAMIDO DERIVATIVES, $Z–CON(CH_3)_2$

Z	Solvent	T_c, °C
OCH_3[a]	$CHCl_3$	−13
$(\pi\text{-}C_5H_5)Mo(CO)_3$[b]	$(CD_3)_2CO$	~18
$(\pi\text{-}C_5H_5)W(CO)_3$[b]	$(CD_3)_2CO$	~18
C_6H_5[a]	[c]	12
Cl[a]	Neat	53
C_2H_5[a]	Neat	61
CH_3[a]	Neat	87
H[a]	Neat	116
$[(CH_3)_2(C_6H_5)P]_2PtCl$	[d]	125 ± 5
$[CH_3(C_6H_5)_2P]_2PtCl$	[d]	140–145
$[(C_6H_5)_3P]_2PdCl$	[d]	160 ± 5
$2,4,6\text{-}(CH_3)_3C_6H_2$[a]	[c]	168
$[(C_6H_5)_3P]_2PtCl$	[d]	>200
$2,4,6\text{-}[(CH_3)_3C]_3C_6H_2$[a]	[c]	>200

[a] Reference 25. [b] Reference 6. [c] Chloronaphthalene–benzotrichloride (1:1). [d] *o*-Dichlorobenzene.

The data in Table II also show a large difference in chemical shifts between the two *N*-methyl groups. In contrast, the difference for $(\pi\text{-}C_5H_5)W(CO)_3CON(CH_3)_2$ in acetone-d_6 is only about 6 Hz (τ 7.11 and 7.22), which is also about the same as observed for organic amides.[25] The unusually large difference in the Pt and Pd complexes may be related primarily to the chemical shift of the CH_3 trans to the oxygen. This CH_3 may be shielded by the phenyl groups of the phosphine ligands, thus moving it to higher field. If this is true, it would be expected that phosphines with fewer phenyl groups would reduce this upfield shift and thereby re-

In addition to electronic effects, it has been shown[25] in substituted benzamides (Table III) that bulky groups ortho to the carboxamido group sterically restrict rotation around the C–N bond. Thus a possible reason for the high rotational barriers in the Pd and Pt complexes as compared with those in the Mo and W complexes is the bulkiness of the $P(C_6H_5)_3$ groups which hinder the rotation. This is supported by the observed decreasing coalescence temperature with decreasing bulkiness of the phosphine: $(C_6H_5)_3P > (CH_3)(C_6H_5)_2P > (CH_3)_2(C_6H_5)P$. It should be added, however, that such a trend might also be attributed to the electron-releasing ability of the CH_3 group in the phosphine which would enhance contributions from resonance form **4c**.

duce the separation. Below are given chemical shift differences (R′ − R) for the series of complexes $L_2Pt(Cl)CON(CH_3)_2$ in $CDCl_3$ solvent

	τ, ppm		
L	R = CH_3	R′ = CH_3	R′ − R
$(C_6H_5)_3As$	7.27	8.33	1.06
$(C_6H_5)_3P$	7.33	8.40	1.07
$(CH_3)(C_6H_5)_2P$	7.55	8.15	0.60
$(CH_3)_2(C_6H_5)P$	7.45	7.69	0.24

The assignment of the resonances to R or R′ (**1**) is based on coupling constant arguments (see below). This series of compounds does in fact show that the separation between the methyl resonances decreases with a decrease in the number of phenyl groups in the L ligands.

In organic amides the CH_3 trans to the carbonyl oxygen shows a large upfield shift when benzene is added to the solution.[26] This presumably results from benzene association with the relatively positive nitrogen atom as far away from the negative oxygen as possible. When the spectrum of $[(CH_3)(C_6H_5)_2P]_2Pt(Cl)CON(CH_3)_2$ was taken in benzene solvent, both methyl groups shifted to slightly *lower* field (τ 7.89 and 7.51). There was no evidence of an upfield shift of the trans CH_3 group, possibly due to the already existing association of this CH_3 group with the phenyl groups of the ligands.

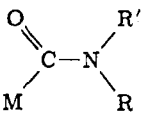
The assignment of R (**3**) to the low-field resonance and R′ to the high-field resonance in the $L_2Pt(Cl)CON(CH_3)_2$ and $L_2Pt(Cl)CSN(CH_3)_2$ complexes is largely based on the splitting of the low-field resonance into a 1:4:1 three-band pattern due to coupling with ^{195}Pt (Table II).

In organic formamides, $HCON(CH_3)_2$, the formyl H couples more strongly to the trans CH_3 group than to the cis.[26] Thus by analogy, the low-field resonance is assigned to the CH_3 group trans to the Pt. This leaves the CH_3 group cis to the Pt for the singlet high-field resonance; this assignment is also consistent with phenyl shielding by the phosphine ligands.

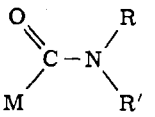
The spectrum of $[(CH_3)_2(C_6H_5)P]_2Pt(Cl)CON(CH_3)_2$ differed slightly from the others in that both carboxamido methyl resonances were split. Nevertheless, the low-field resonance had the greater coupling constant, as expected. One other devivative whose spectrum differed was $[(C_6H_5)_3As]_2Pt(Cl)CON(CH_3)_2$; neither methyl resonance was split. It is not clear why the arsine ligand decreased the coupling to the Pt, but the same phenomenon[8] was previously observed for $L_2Pt(Cl)COOR$, where L = $(C_6H_5)_3P$ or $(C_6H_5)_3As$.

In the *N,N*-diethyl derivatives $L_2Pt(Cl)CON(CH_2CH_3)_2$ both the α and β protons of the ethyl group cis to the Pt are observed at higher field than those of the trans ethyl. That the high-field α and β protons are associated with the same ethyl group has been confirmed by spin-decoupling experiments.

In complexes containing two different substituents on nitrogen, restricted rotation gives rise to cis and trans isomers. La Planche and Rogers[26] found that for a series of organic *N*-monoalkylamides (R′ = H) the predominant configuration was that shown in **5b** and that measurable concentrations of the other isomer existed only for the formamides. With *N,N*-dialkyl-



5a



5b

amides involving two different alkyl groups, both isomers were present in about equal concentrations.[26] For the *N*-monoalkylcarboxamido complexes reported here, the alkyl protons of the R group are unsplit by ^{195}Pt and occur at high fields (Table II) comparable to that assigned above to alkyl groups cis to the metal in the dialkylcarboxamido complexes. This suggests that they have geometry **5a** (R′ = H), in contrast to the organic amides.

For the complexes $[(C_6H_5)_3P]_2M(Cl)CON(CH_3)(C_2H_5)$ with an unsymmetrically substituted *N,N*-dialkylcarboxamido group, the nmr spectra indicate the presence of about equal amounts of the two possible isomers. Hence the distribution of isomers in these complexes is very similar to that found in organic amides.

The nmr spectra of the *N,N*-dimethylthiocarboxamido derivatives are very similar to those of their oxygen analogs, except that the differences between the chemical shifts of the methyl groups in the thio derivatives are significantly smaller (Table II). Also the unusual singlet character of the phosphine methyl groups in $[(CH_3)(C_6H_5)_2P]_2Pd(X)CSN(CH_3)_2$, where X = Cl or I, is not clear although it may be related to rapid exchange of the phosphine ligands as has been observed previously.[27] Finally it should be recalled that the spectrum of $[(C_6H_5)_3P]_2Pd(Cl)CSN(CH_3)_2$ is complicated by Cl^- dissociation as discussed earlier.

The nmr spectrum of $\{[(CH_3)(C_6H_5)_2P]_4Pt_2[CSN(CH_3)_2]_2\}(BF_4)_2$ shows two doublets, with their ^{195}Pt satellites, for the phosphine methyl groups. This is the expected pattern for the two different kinds of phosphines in the proposed structure (**2**). The thiocarboxamido group exhibits a low-field singlet (with ^{195}Pt satellites) attributed to the CH_3 group trans to the Pt and a high-field singlet (no ^{195}Pt coupling) of the cis CH_3 group.

Infrared Spectra.—The C–O stretching absorption in the 1565–1615-cm^{-1} region is characteristic of *N,N*-dimethylcarboxamido complexes. Although this absorption for monoalkylcarboxamido derivatives (CONHR) is also expected in this same general region, these have not been definitely assigned due to the occurrence of the N–H bending mode in the same area. In general, however, the C–O stretching frequencies are slightly higher for the palladium complexes as compared to their platinum analogs (Table IV). This is similar to observations on molybdenum– and tungsten–carboxamido complexes where the frequencies of the second-row transition metal complexes (Mo) are higher than those of the third-row (W) analogs.[6]

Organic compounds containing tertiary thioamide groups exhibit four absorptions which are associated with the thioamide group;[28] for example, for $HC(S)N(CH_3)_2$ in CCl_4 solvent these bands are observed at 1530 (vs), 1401 (s), 1130 (s), and 975 (s) cm^{-1}. Al-

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TABLE IV
INFRARED SPECTRA OF $L_2M(X)CONRR'$ COMPLEXES

M	L[a]	X	R	R'	Sample	ν_{CO}, cm^{-1}	Other
Pt	TPP	Cl	CH_3	CH_3	CH_2Cl_2	1566	Pt–Cl 264
					KBr	1572	
					Nujol	1570	
Pt	MDPP	Cl	CH_3	CH_3	CH_2Cl_2	1565	
					KBr	1570	
Pt	TPA	Cl	CH_3	CH_3	CH_2Cl_2	1585	
					Nujol	1580	
Pd	TPP	Cl	CH_3	CH_3	CH_2Cl_2	1605	
					KBr	1598	
Pd	TPP	Cl	H	CH_3	CH_2Cl_2	1628[b]	ν(NH) 3458
Pt	TPP	I	CH_3	CH_3	CH_2Cl_2	1570	
					Nujol	1574	
Pt	TPP	NCO	CH_3	CH_3	Nujol	1580	NCO 2221
Pt	TPA	Cl	H	i-C_3H_7	KBr	1616[b]	ν(NH) 3425
						1602[b]	
Pt	TPP	Cl	H	C_2H_5	CH_2Cl_2	1601[b]	ν(NH) 3422
Pt	TPP	Cl	H	CH_3	CH_2Cl_2	1600[b]	
					Nujol	1618[b]	
						1602[b]	Pt–Cl 270
					Kel-F		ν(NH) 3400 ± 10

[a] Abbreviations are the same as in Table I. [b] δ(NH) and ν(CO) bands.

TABLE V
INFRARED SPECTRA OF $L_2M(X)CSN(CH_3)_2$ COMPLEXES

M	L[a]	X	Sample	$CSN(CH_3)_2$ bands, cm^{-1}
Pd	TPP	Cl	Nujol	949, 1150, 1230, 1520
			KBr	960, 1145, 1240, 1525
Pd	TPP	Br	KBr	959, 1145, 1241, 1521
			CH_2Cl_2	957, 1144, 1238, 1520
Pd	TPP	I	KBr	954, 1140, 1235, 1515
			CH_2Cl_2	955, 1144, 1233, 1520
Pt	TPP	Cl	KBr	963, 1140, 1250, 1517
			CH_2Cl_2	964, 1131, 1246, 1510
Pt	TPP	I	KBr	960, 1140, 1250, 1522
			CH_2Cl_2	960, 1123, 1245, 1515
Pd	MDPP	Cl	CH_2Cl_2	963, 1137, 1239, 1515

[a] Abbreviations are the same as in Table I.

though there is extensive coupling of the other vibrations, the lowest frequency absorption appears to be due to a relatively pure C–S stretching vibration. In the thiocarboxamido complexes of Pt and Pd (Table V), we have also observed four bands in the region 900–1525 cm^{-1} which are associated with the thiocarboxamido ligand. These occur in approximately the same regions as their organic counterparts.

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Mechanisms of Substitution Reactions of Axially Blocked Palladium(II) Complexes in Different Solvents

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The rates of the reactions of halide ions with $Pd(Et_4dien)X^+$ (Et_4dien = $HN[C_2H_4N(C_2H_5)_2]_2$; X^- = Cl^-, Br^-, I^-) complexes have been investigated as a function of temperature in several different solvents. The activation parameters show that the reactions in protic solvents involve associative activation, whereas in aprotic solvents a dissociative mechanism with leaving-group solvation is probable.

Introduction

The principal pathway of the substitution reactions of the axially blocked, square-planar complexes $Pd(Et_4dien)X^+$ (Et_4dien = $HN[C_2H_4N(C_2H_5)_2]_2$; X^- = Cl^-, Br^-) with most nucleophilic reagents in aqueous solution involves a slow solvolysis step (eq 1), followed by rapid anation (eq 2).[1,2]

$$Pd(Et_4dien)X^+ + H_2O \xrightarrow[k_1]{\text{slow}} Pd(Et_4dien)H_2O^{2+} + X^- \quad (1)$$

$$Pd(Et_4dien)H_2O^{2+} + Y^{n-} \xrightarrow{\text{fast}} Pd(Et_4dien)Y^{(2-n)+} + H_2O \quad (2)$$

Little is known concerning the detailed role of the water molecule in the solvolysis step. For the reactions of unhindered square-planar substrates with a variety of solvent (sol) molecules, a mechanistic model has been developed which features strong associative activation, leading to a five-coordinate transition state containing a solvent molecule attached to the metal.[3,4]

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