Cationic Organometallic Complexes with Unsaturated Systems. III. Nickel(II) and Palladium(II) Isocyanide and Related Complexes

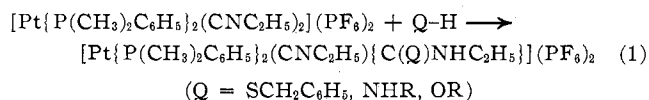BY W. J. CHERWINSKI, H. C. CLARK,* AND L. E. MANZER

Cationic nickel(II) and palladium(II) complexes of the type [MClL'L₂][Z] (where M = Pd or Ni; L' = phosphine, phosphite, arsine, pyridine, carbon monoxide, or isocyanide; L = phosphine or arsine; Z = noncoordinating anion) have been prepared and characterized by infrared and nmr spectroscopy. For M = Ni only the complexes where L' = isocyanide could be prepared and the stability of these complexes is discussed in terms of the relative σ and π properties of L'. The change in isocyanide stretching frequency $\Delta\nu_{N\equiv C}$ on coordination is discussed for the triad where M = Pt, Pd, Ni and related to the electronegativity of the metal. The cationic nickel(II) complexes exhibit rapid exchange of phosphines at room temperature due to a delocalization of the positive charge from the metal onto the nitrogen. The palladium–chlorine stretching frequency varies with the trans influence of the ligand L'.

Introduction

In recent years the preparation and reactivity of a wide variety of cationic organoplatinum(II) complexes of the type *trans*-[PtXL'L₂]⁺ (where X = anionic ligand such as CH₃, CF₃, Cl, H; L' = neutral ligand; L = tertiary phosphine or arsine) have been investigated,[1-3] but similar studies have been very limited for palladium(II) and nickel(II).

In particular, isocyanide complexes of platinum(II) have been shown to be remarkably stable and reactive toward nucleophilic attack by alcohols, amines, and thiols to give a wide variety of carbene complexes (eq 1).[4-6] Knebel and Treichel[7] have recently studied

$$[Pt\{P(CH_3)_2C_6H_5\}_2(CNC_2H_5)_2](PF_6)_2 + Q-H \longrightarrow$$
$$[Pt\{P(CH_3)_2C_6H_5\}_2(CNC_2H_5)\{C(Q)NHC_2H_5\}](PF_6)_2 \quad (1)$$
$$(Q = SCH_2C_6H_5, NHR, OR)$$

nucleophilic addition reactions to cationic platinum(II) isocyanide complexes to give metal carboxamido complexes (eq 2).

$$[Pt\{P(C_6H_5)_3\}_2(CNCH_3)_2](BF_4)_2 + XH^- \longrightarrow$$
$$[Pt\{P(C_6H_5)_3\}_2(CNCH_3)\{C(X)NHCH_3\}](BF_4) \quad (2)$$
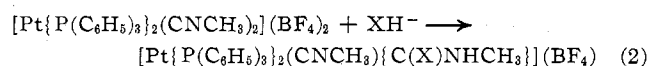
Most of the early work on isocyanide complexes of the platinum group metals[8] dealt with compounds of the type MX₂(CNR)₂ or of the Magnus salt type [M(CNR)₄][Z]₂ (M = Pt, Pd, Ni; Z = noncoordinating anion) and in these complexes it was shown that the metal–isocyanide bond was particularly stable in contrast to the corresponding metal–carbonyl bond. Many authors[9,10] have compared the structural and bonding properties of carbonyl and isocyanide metal complexes and have shown that isocyanides are stronger σ donors and weaker π acceptors than carbon monoxide. Thus these ligand properties of isocyanides compared to

carbon monoxide presented the possibility of isolating stable cationic nickel(II) and palladium(II) isocyanide complexes whereas the analogous carbonyl complexes are unknown for nickel and rare for palladium.[11] In the latter case it was also hoped that infrared parameters such as ν_{Pd-Cl} would be sensitive to the trans influence of various other neutral ligands L' in the complexes [PdClL'L₂]⁺Z⁻.

Results and Discussion

Analytical and physical data of the new compounds obtained are shown in Table I.

(i) Preparation of [MClL'L₂][Z].—The palladium-(II) derivatives [PdClL'L₂][Z] were prepared by the reaction of PdCl₂L₂, where L = tertiary phosphine, arsine, or stibine, with the appropriate neutral ligand L', where L' = phosphine, arsine, phosphite, pyridine, isocyanide, or carbon monoxide, in the presence of AgZ, the silver salt of a noncoordinating anion (Z) (eq 3).

$$MCl_2L_2 + L' + AgZ \longrightarrow [MClL'L_2][Z] + AgCl \quad (3)$$
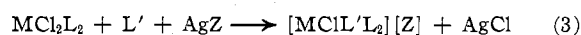
Similarly for M = Ni and L' = isocyanide the cationic derivatives [NiCl(CNR)L₂][Z] were prepared by the addition of 1 molar equiv of isocyanide to NiCl₂L₂ in the presence of the silver salt AgZ. The basic reaction involved (eq 4) was recognized previously by Basolo,

$$MXX'L_2 + L' \rightleftharpoons [MX'L'L_2][X] \quad (4)$$
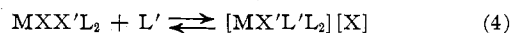
et al.,[12] for M = Pt. This equilibrium generally favors the reactants and in fact those ionic complexes reported for X = halide, [PtCl{P(CH₃)₂C₆H₅}₃]⁺ [13] or [PtH{P(C₂H₅)₃}(diphos)]⁺,[14] were only isolated by virtue of their insolubility in the particular solvent employed. Treichel and Hess[15] have recently reported the stable complexes [PtCl(CNCH₃){P(C₆H₅)₃}₂]⁺Cl⁻ formed from the reaction of PtCl₂{P(C₆H₅)₃}₂ with methyl isocyanide in acetone solution. We have similarly reported[6] that the addition of *p*-methoxyphenyl isocyanide to *trans*-PtCH₃Cl{P(CH₃)₂C₆H₅}₂ in benzene solution leads to a precipitate of PtCH₃Cl{P(CH₃)₂C₆H₅}₂(CNC₆H₄OCH₃) which may be five-coordinate in

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TABLE I
ANALYTICAL, PHYSICAL, AND INFRARED DATA FOR CATIONIC NICKEL(II) AND
PALLADIUM(II) COMPLEXES, [MClLQ$_2$]$^+$[Z]$^-$

Metal (M)	Ligand (L)	Ligand (Q)^f	Anion (Z)	% carbon Calcd	Found	% hydrogen Calcd	Found	Mp, °C	Recrystn solvents^g	Color	$\nu_{N\equiv C}$ (complex), cm^{-1}	$\Delta\nu_{N\equiv C}$,^{a} cm^{-1}
Ni	CNC$_6$H$_4$OCH$_3$	A	PF$_6$	58.93	58.84	4.16	3.99	>188	F	Orange	2170	45
Ni	CNC$_6$H$_4$CH$_3$	A	PF$_6$	60.00	59.58	4.23	4.28	>178	F	Orange	2179	54
Ni	CNC$_6$H$_4$OCH$_3$	B	PF$_6$	39.47	39.61	6.13	5.97	125–134	G	Yellow	2191	66
Ni	CNC$_6$H$_4$CH$_3$	B	PF$_6$	40.54	40.50	6.29	6.14	135–136	F	Yellow	2166	41
Ni	CNC$_6$H$_4$OCH$_3$	C	PF$_6$	44.45	44.73	4.51	4.53	181–182	H	Yellow	2187	62
Ni	CNC$_6$H$_4$CH$_3$	C	PF$_6$	45.57	45.66	4.62	4.76	188–190	F	Yellow	2192	67
Ni	CNC$_6$H$_5$	C	SbF$_6$	38.94	39.08	3.84	3.69	168–169	F	Pale yellow	2186	69
Ni	CNC$_6$H$_4$CH$_3$	D	PF$_6$	53.97	53.76	4.40	4.28	160–165	F	Yellow	2181	56
Ni	CNC$_6$H$_5$	D	SbF$_6$	47.55	47.33	3.75	3.71	168–172	G	Orange	2180	63
Ni	CNC$_6$H$_4$CH$_3$	D	Cl	63.09	62.89	5.15	5.01	>120	F	Green-brown	2160	35
Ni	CNC$_6$H$_5$	D	Cl	61.12	61.33	5.13	4.92	>150	G	Green	2139	12
Pd	CNC$_6$H$_4$CH$_3$	B	PF$_6$	37.52	37.89	5.82	5.66	169–171	F	Yellow	2210	85
Pd	CNC$_6$H$_4$CH$_3$	E	SbF$_6$	29.44	29.27	4.57	4.51	156–158	H	White	2211	86
Pd	CNC$_6$H$_4$CH$_3$	C	PF$_6$	42.40	42.44	4.30	4.12	196–198	F	White	2212	87
Pd	CNC$_6$H$_4$CH$_3$	D	PF$_6$	50.79	50.83	4.14	4.04	215–217	F	White	2226	101
Pd	CNC$_6$H$_4$OCH$_3$	E	SbF$_6$	28.87	28.83	4.48	4.39	155–157	H	Yellow	2212	87
Pd	CNC$_6$H$_4$OCH$_3$	C	PF$_6$	41.40	41.58	4.20	4.09	182–184	F	White	2211	86
Pd	CNC$_6$H$_4$OCH$_3$	D	PF$_6$	49.80	49.86	4.06	3.93	211–212	F	White	2230	105
Pd	CNCH$_3$	E	SbF$_6$	22.62	22.88	4.48	4.21	110–112	H	White	2264	94
Pd	CNCH$_3$	D	SbF$_6$	41.34	41.05	3.59	3.61	195–196	F	White	2261	91
Pd	CNC$_6$H$_5$	B	BF$_4$	40.18	40.02	6.21	6.40	137–139	F	White	2222	105
Pd	CNC$_6$H$_5$	C	SbF$_6$	36.65	36.08	3.61	3.22	183–184	F	White	2225	108
Pd	P(C$_2$H$_5$)$_3$	B	B(C$_6$H$_5$)$_4$	b	...	...	...	136–138	H	Yellow		
Pd	P(CH$_3$)$_2$(C$_6$H$_5$)	B	PF$_6$	c	...	...	...	Oil	F	Yellow		
Pd	P(OC$_2$H$_5$)$_3$	B	SbF$_6$	27.81	28.06	5.82	5.95	118–120	H	White		
Pd	P(OC$_6$H$_5$)$_3$	B	SbF$_6$	39.10	39.32	4.91	4.79	136–138	H	White		
Pd	NC$_5$H$_5$	B	SbF$_6$	29.58	29.56	5.09	5.11	170–172	F	White		
Pd	py'^{d}	B	SbF$_6$	32.80	33.02	5.62	5.50	194–196	F	White		
Pd	P(CH$_3$)$_2$(C$_6$H$_5$)	E	SbF$_6$	28.70	28.75	4.82	4.61	83–87	F	Pale yellow		
Pd	P(CH$_3$)(C$_6$H$_5$)$_2$	E	SbF$_6$	33.40	33.75	4.81	4.77	138–140	F	Pale yellow		
Pd	P(C$_6$H$_5$)$_3$	E	SbF$_6$	37.50	37.52	4.71	4.60	184–186	H	Yellow		
Pd	As(C$_6$H$_5$)$_3$	C	PF$_6$	36.42	36.57	5.14	5.44	Oil	F	Yellow		
Pd	P(CH$_3$)$_2$(C$_6$H$_5$)	C	PF$_6$	41.13	41.10	4.75	4.40	>67	F	Orange-yellow		
Pd	P(CH$_3$)(C$_6$H$_5$)$_2$	C	SbF$_6$	40.81	40.68	4.13	3.90	>83	F	Yellow		
Pd	P(C$_6$H$_5$)$_3$	C	SbF$_6$	46.39	46.60	4.81	4.78	82–103	F	Yellow		
Pd	P(CH$_3$)(C$_6$H$_5$)$_2$^{e}	D	SbF$_6$	48.05	48.23	4.03	3.82	>130	F	Yellow		

^{a} $\nu_{N\equiv C}$(complex) − $\nu_{N\equiv C}$(free ligand). ^{b} Previously reported. ^{c} Not analyzed. ^{d} py' = 2,4,6-trimethylpyridine. ^{e} Isolated as monoetherate. ^{f} A = P(C$_6$H$_5$)$_3$; B = P(C$_2$H$_5$)$_3$; C = P(CH$_3$)$_2$C$_6$H$_5$; D = P(CH$_3$)(C$_6$H$_5$)$_2$; E = As(C$_2$H$_5$)$_3$. ^{g} F = CH$_2$Cl$_2$-(C$_2$H$_5$)$_2$O; G = CH$_2$Cl$_2$-n-C$_5$H$_{12}$; H = (CH$_3$)$_2$CO-(C$_2$H$_5$)$_2$O.

the solid state but dissociated in a polar solvent. A similar equilibrium may occur here for complexes of palladium(II) and nickel(II).

Whereas the postulated five-coordinate species[15] [PtX-(CNCH$_3$)$_2${P(C$_6$H$_5$)$_3$}$_2$][X] has been isolated for X = Br or I, similar derivatives of palladium(II) could not be isolated here. For nickel(II) reaction 3 does not proceed for neutral ligands L' other than isocyanide, even in the presence of silver salts. The absence of a silver chloride precipitate suggests that the equilibrium lies well to the left.

The addition of 1 molar equiv of isocyanide to NiCl$_2$L$_2$ in acetone or methanol causes an immediate color change and we have isolated the complex NiCl$_2$(CN-C$_6$H$_5$){P(CH$_3$)(C$_6$H$_5$)$_2$}$_2$ which is diamagnetic (Gouy method) in the solid state and in solution. The addition of a silver salt AgZ in solution then causes a further color change with a flocculent precipitate of silver chloride and the salt containing the square-planar nickel cation can be isolated.

Infrared Spectroscopic Studies of Palladium and Nickel Complexes.—The N≡C stretching frequency may be used to investigate the nature of the bonding between the metal and isocyanide ligand. For neutral derivatives of metals in low oxidation states, isocyanides are capable of extensive back-bonding of metal d electrons, and, in fact, ν_{NC} values for complexes of chromium

and nickel,[16] *e.g.*, Ni(CNAr)$_4$, are lowered relative to the frequencies of the free isocyanide. Recently, differences in ν_{NC} for the system NiL(CN-t-Bu)$_2$ have been used[17] to evaluate the relative π acidities of various neutral ligands L. However, for isocyanide complexes of metals in higher oxidation states $\Delta\nu_{N\equiv C}$ (=$\nu_{N\equiv C}$ (complex) − $\nu_{N\equiv C}$(free ligand)) is positive.[10]

For the cationic isocyanide derivatives of palladium-(II) (Table I) $\nu_{N\equiv C}$ falls in the range 2210–2264 cm^{-1} while for nickel(II) these values (2139–2206 cm^{-1}) are slightly lower for the same isocyanide. The shifts to higher frequencies, from the values of the free ligands, therefore indicate an increased N–C bond order (more triple-bond character), presumably caused by σ donation of the carbon atom lone pair to the metal which is not counterbalanced by π back-donation into the carbon p$_z$ orbital but rather by delocalization of the nitrogen lone pair into the carbon p$_z$ orbital.[6] In this instance, a resonance hybrid such as I may make a significant contribution compared to II where π bonding is more important as in zerovalent metal complexes.

$$M \leftarrow C \overset{..}{=} N \diagdown R \qquad\qquad -M-C\equiv\overset{+}{N}-R$$

II   I

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(17) S. Otsuka, T. Yoshida, and Y. Tatsuno, *J. Chem. Soc. D*, 67 (1971).

We have found[6] that the greater the positive charge on the metal, the greater will be the delocalization of the nitrogen lone pair due to a significant contribution from I. Indeed, for the series of analogous compounds *trans*-[MCl(CNR)L$_2$]$^+$, where L = phosphine, $\Delta\nu_{N\equiv C}$ falls in the ranges 125–112, 108–85, and 69–12 cm^{-1} for M = Pt, Pd, and Ni, respectively. Typically, for L = P(CH$_3$)$_2$C$_6$H$_5$ and R = *p*-C$_6$H$_4$OCH$_3$ these values are $\Delta\nu_{N\equiv C}$ = 125, 87, and 68 cm^{-1}. The order of decreasing $\Delta\nu_{N\equiv C}$, Pt > Pd > Ni, parallels the relative electronegativities of these metals,[18] and indicates a decreasing contribution from resonance hybrid I. Similar data have been reported[19] for $\nu_{N\equiv C}$ in the series *trans*-[MH(CNR)(depe)$_2$]$^+$ where M = Fe, Ru, or Os, although the relative delocalization of the nitrogen lone pair due to hybrid I decreases in this triad in the order Ru > Os > Fe.

In a related series of compounds,[2] *trans*-[PtX(CNR)-L$_2$]$^+$ (L = P(CH$_3$)$_2$C$_6$H$_5$; X = CH$_3$, CF$_3$, I, Cl), $\Delta\nu$ is lowest in the series for the group X which has the highest trans influence. Such a group tends to reduce the effective (positive) charge on platinum by σ donation resulting in less delocalization of the nitrogen lone pair and a small increase in $\nu_{N\equiv C}$. On the other hand, for dipositive cations of platinum(II),[6] the delocalization arising from the greater positive charge on the metal may give a larger increase in $\Delta\nu$.

Changes in $\nu_{N\equiv C}$ may also be induced by differences in the isocyanide ligands themslves. Belluco, *et al.*,[20] have found that $\nu_{N\equiv C}$ for neutral palladium(II) derivatives PdX$_2$(CNR)L decreases in the order R = cyclohexyl > phenyl > *p*-nitrophenyl, in agreement with a similar trend for the uncoordinated isocyanides. They suggested that the donor carbon of the alkyl isocyanide would be a better σ donor than that of the aryl isocyanide because of the inductive effect of the alkyl group. However in the series of complexes[6] *trans*-[PtCH$_3$(CNR){P(CH$_3$)$_2$C$_6$H$_5$}$_2$]$^+$Z$^-$ we have examined the coupling constant J(Pt–C–H), which gives a measure of the relative σ-donor strength for a neutral ligand trans to the methyl group,[1] and found that the σ-donor strength of the isocyanide is fairly constant. Therefore the inductive effect of the alkyl group may in fact cause a greater delocalization of the nitrogen lone pair into the carbon 2p$_z$ orbital, resulting in a greater $\Delta\nu_{N\equiv C}$, without affecting the donor strength of the isocyanide. Although $\nu_{N\equiv C}$ for the palladium and nickel complexes falls in the order alkyl > aryl, there is no correlation between $\Delta\nu_{N\equiv C}$ and an aromatic substituent.

Other typical bands for isocyanide derivatives have been observed[20] in the range 600–350 cm^{-1} and tentatively assigned to the in-plane deformation δ_{M-CN} and to the stretching vibration ν_{M-C}. However for the complexes considered here, these absorptions are often masked by those of phosphine ligands and could not be assigned with certainty.

For the isocyanide complexes, as well as other derivatives of palladium(II), [PdClL′L$_2$]$^+$, where L′ = neutral ligand and L = phosphine, the infrared Pd–Cl stretching frequencies have been found to vary with changes in L′ (Table II). Apart from pyridine, the

(18) M. Meier, F. Basolo, and R. G. Pearson, *Inorg. Chem.*, **8**, 795 (1969).
(19) G. M. Bancroft, M. J. Mays, B. E. Prater, and F. P. Stefanini, *J. Chem. Soc. A*, 2146 (1970).
(20) B. Crociani, T. Boschi, and U. Belluco, *Inorg. Chem.*, **9**, 2021 (1970).

TABLE II

INFRARED DATA^a FOR CATIONIC COMPLEXES OF PALLADIUM(II), *trans*-[PdClL′{P(C$_2$H$_5$)$_3$}$_2$]$^+$

Ligand L′	ν_{Pd-Cl},^{b} cm^{-1}	Ligand L′	ν_{Pd-Cl},^{b} cm^{-1}
CO[11]	330 w	P(C$_6$H$_5$)$_3$[11]	300 w, b
CH$_3$C$_6$H$_4$NC	323 m	P(C$_2$H$_5$)$_3$[11]	290 w, b
P(OC$_6$H$_5$)$_3$	312 m	py	290 s, b, 275 w, b
P(OC$_2$H$_5$)$_3$	311 m	py′^{c}	275 w, b

^{a} Trans influence; σ-donor strength decreases down the series. ^{b} Run as Nujol mulls. ^{c} 2,4,6-Trimethylpyridine.

trans influence (series A) agrees well with that of Church and Mays[3,21] from platinum complexes: series A: P(C$_2$H$_5$)$_3$ > P(OCH$_3$)$_3$ ∼ P(OC$_6$H$_5$)$_3$ > P(C$_6$H$_5$)$_3$ > ArNC > RNC > CO > py.

Church and Mays[3] have also studied ^{19}F nmr parameters for the series *trans*-[Pt(FC$_6$H$_4$)L′{P(C$_2$H$_5$)$_3$}$_2$]$^+$ and tentatively assigned a "π-acceptor series" to the trans ligands L′. Although the criticism may be made that the optimum conditions for good π overlap between a metal and the *aryl* groups trans to L′ are not known, series B emphasizes the fact that π contributions from isocyanide ligands in platinum(II) cations are indeed very low: series B: CO > P(OC$_6$H$_5$)$_3$ ∼ P(C$_2$H$_5$)$_3$ > P(OCH$_3$)$_3$ > ArNC > RNC. The higher electronegativity of platinum(II), together with its capacity to back-donate π-electron density to coordinated ligands, may explain its greater tendency for complex formation with a variety of σ-donor and π-acceptor ligands. Furthermore for palladium(II), where metal–ligand π back-bonding is somewhat less effective, stable cationic derivatives form with ligands L′ of series A whose σ-donor abilities are sufficiently strong to balance their position in the π-acceptor series B. However, in contrast to the platinum(II) carbonyl cations, those for palladium(II) are far less stable possibly due to the reduced σ-donor capacity of carbon monoxide and the lower π basicity of palladium compared to platinum. Indeed, the stability of the known derivatives[11] *trans*-[PdCl(CO){P(C$_2$H$_5$)$_3$}$_2$]$^+$ may arise mainly from the influence of the triethylphosphine ligands which do not compete strongly with CO for the available electron density of palladium(II). For nickel(II), both its relatively low electronegativity and the reduced size of its 3d orbitals suggest that coordination by weaker σ-donor ligands may not occur and that dπ–pπ bonding with coordinated ligands may be ineffective. In fact no cationic derivatives of nickel(II) are found for ligands L′ of series A since even for strong σ donors some π back-bonding is required for effective bonding. The remarkable stability of cationic nickel(II) isocyanide complexes may well arise from the strong σ-donating power of the isocyanide together with its low position in series B.

^{1}H Nmr Studies. (i) Cationic Nickel(II) and Palladium(II) Isocyanide Complexes.—Proton nmr data for the cationic nickel(II) and palladium(II) isocyanide complexes are listed in Table III. The phosphine methyl resonances for the palladium(II) complexes appear as 1:2:1 triplets due to strong phosphorus–phosphorus coupling, indicative of "virtually" coupled[22] trans phosphines. The coupling ^2J(P–H) + ^4J(P–H) for the palladium complexes is *ca.* 8.2 Hz which is typical

(21) M. J. Church and M. J. Mays, *J. Chem. Soc. A*, 1938 (1970).
(22) R. K. Harris, *Can. J. Chem.*, **42**, 2275 (1964).

TABLE III
1H NMR DATA FOR CATIONIC NICKEL(II) AND PALLADIUM(III) ISOCYANIDE COMPLEXES, [MCl(Is)L2][Z]

Metal (M)	Anion (Z)	Ligand (L)	Isocyanide (Is)	Probe temp,[c] °C	Phosphine methyls $-\delta_{CH_3}{}^a$	$J(P-H)^b$	Isocyanide methyls $-\delta_{CH_3}$
Pd	PF6	P(CH3)2C6H5	CH3C6H4NC	0	2.00	8.32	2.33
Pd	PF6	P(CH3)2C6H5	CH3OC6H4NC	31	2.00	8.20	3.81
Pd	SbF6	P(CH3)2C6H5	C6H5NC	31	2.02	8.32	...
Pd	PF6	P(CH3)(C6H5)2	CH3C6H4NC	31	2.39	8.40	2.31
Pd	PF6	P(CH3)(C6H5)2	CH3C6H4NC	31	2.38	8.20	3.79
Pd	SbF6	P(CH3)(C6H5)2	CH3NC	31	2.34	8.10	2.57
Ni	PF6	P(C2H5)3	CH3C6H4NC	31	1.32	...	2.49
Ni	PF6	P(C2H5)3	CH3OC6H4NC	31	1.33	...	3.86
Ni	PF6	P(CH3)2C6H5	CH3OC6H4NC	-23	1.92	4.5	3.94
Ni	PF6	P(CH3)2C6H5	CH3C6H4NC	-8	1.97	4.3	2.41
Ni	PF6	P(CH3)(C6H5)2	CH3C6H4NC	0	2.87	4.5	2.32
Ni	SbF6	P(CH3)2C6H5	C6H5NC	-20	1.93	4.5	
Ni	SbF6	P(CH3)(C6H5)2	C6H5NC	-20	2.42	4.3	

[a] Chemical shifts are in ppm relative to TMS using dichloromethane as solvent and internal standard. [b] Coupling constants in hertz; $^2J(P-H) + {}^4J(P-H)$ is quoted (see ref 22). [c] Temperature at which $^{31}P-{}^1H$ coupling was clearly resolved.
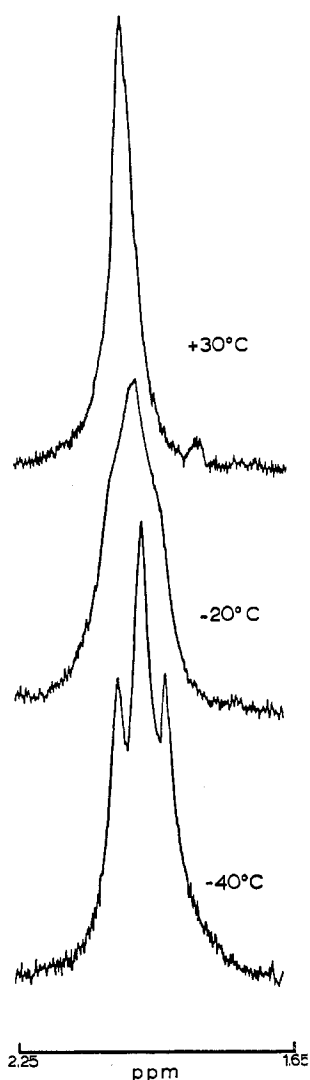

Figure 1.—Variable-temperature nmr spectra of *trans*-[NiCl-(CNC6H4OCH3){P(CH3)2C6H5}2]+SbF6- recorded on a dichloromethane solution.

of most square-planar palladium(II) and platinum(II) complexes. The nickel complexes, on the other hand, using dimethylphenylphosphine or phenyldimethylphosphine exhibit only a singlet in the phosphine methyl region (see Figure 1). However as the temperature is lowered, the singlet broadens and eventually $^{31}P-{}^1H$

coupling is observed. We have observed[2,6,23] similar effects in the 1H nmr spectra of the complexes *trans*-[PtX(CNR)L2]+, where X = CF3, CH3, or H and L = P(CH3)2C6H5 or P(CH3)(C6H5)2, and have attributed the phenomena to rapid exchange of the phosphines between equivalent sites resulting in loss of platinum and phosphorus coupling. Labilization of the phosphines may be induced by the coordinated isocyanide groups which are very effective in reducing the positive charge at the metal[6] (see resonance hybrid I). The observed exchange for the complexes where X = CH3, compared to the absence of exchange for X = Cl, may also arise from a reduction in the effective nuclear charge on platinum(II) by the stronger σ-inductive effect of the CH3 group, which has a higher trans influence than Cl. Although the electronegativity of platinum(II) exceeds that of palladium(II), exchange at room temperature is still absent for *trans*-[PdCl(CN-R){P(CH3)2C6H5}2]+, except where R = C6H4-CH3. However for nickel(II), its low electronegativity together with a further lowering of the effective nuclear charge by the isocyanide ligand may account for the exchange observed for *trans*-[NiCl(CNR)-{P(CH3)2C6H5}2]+. These results are not surprising since the "soft" phosphine ligands are likely to form weaker bonds with nickel(II) which is "hard" compared with platinum(II).

An interesting feature of the 1H nmr spectra is that $^2J(P-H) + {}^4J(P-H)$ for the nickel complexes (~4.4 Hz) is much less than the platinum and palladium analogs. The coupling $J(P-C-H)$ is dependent on the hybridization and character of the phosphorus lone pair of electrons. For example, it has been established[24,25] that the sign of $J(P-C-H)$ is positive for the free phosphine and negative for the coordinated phosphine. Therefore it is possible that phosphorus–hydrogen coupling may be relaxed as a result of phosphine exchange and that an average $^3J(P-H)$ between free and bound phosphine is observed.

(ii) **Complexes of the Type [PdClL'L2]+ (L', L = Tertiary Phosphine or Arsine).**—All of the complexes were obtained with a trans configuration except for the products of reactions involving PdCl2{P(CH3)2C6H5}2

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TABLE IV

PROTON NMR DATA FOR CATIONIC COMPLEXES OF PALLADIUM(II), [PdClL'L₂] [Z]

Anion (Z)	Ligand (L)	Ligand (L')	Config'n	L phosphine methyls −δ$_{CH_3}$^{a}	L phosphine methyls J(B–P)^b	L' phosphine methyls −δ$_{CH_3}$^{a}	L' phosphine methyls J(H–B)^b
PF₆	P(C₂H₅)₃	P(CH₃)₂C₆H₅	Trans	...	...	2.02 d	10.2
SbF₆	As(C₂H₅)₃	P(CH₃)₂C₆H₅	Trans	...	...	1.98 d	10.4
SbF₆	As(C₂H₅)₃	P(CH₃)(C₆H₅)₂	Trans	...	...	2.36 d	10.0
PF₆	P(CH₃)₂C₆H₅	As(C₂H₅)₃	Cis	1.74 d	11.1	...	...
PF₆	P(CH₃)₂C₆H₅	P(CH₃)₂C₆H₅	...	1.88 t	7.10	1.26 d	10.2
SbF₆	P(CH₃)₂C₆H₅	P(C₆H₅)₃	Trans	1.56 t	7.60	...	...
SbF₆	P(CH₃)₂C₆H₅	P(C₆H₅)₃	Cis	1.91 t, 1.70 d	7.60, 12.7	...	...
SbF₆	P(CH₃)(C₆H₅)₂	P(CH₃)(C₆H₅)₂	...	2.08 t	8.84	1.77 d	9.24

^{a} Chemical shifts in ppm relative to TMS using dichloromethane as internal standard; d = doublet, t = triplet. ^{b} Coupling constants in hertz; ^2J(P–H) + ^4J(P–H) is quoted (see ref 22).

with As(C₂H₅)₃ and P(C₆H₅)₃ in the presence of AgX; with triethylarsine the pure cis isomer was isolated, while triphenylphosphine gave a mixture of cis and trans isomers. The proton nmr data for these complexes are given in Table IV. Two dimethylphenyl- or phenyldimethylphosphines in the cis geometry are easily detected since the phosphine methyl resonances appear as a doublet, whereas trans phosphines show a triplet as a result of virtual coupling. Also J(P–C–H) is dependent on the ligand trans to the phosphine. For ligands of low trans influence, i.e., Cl, J(P–C–H) ≈ 12 Hz, whereas when phosphine is trans to phosphine, J(P–C–H) ≈ 7.5 Hz.

Cis isomers are only obtained when L' is a weaker σ donor than L. As a result, the ligands L tend to rearrange placing the stronger σ donor trans to chloride and the weaker σ donor L' trans to L, where there is less competition for "s"-electron density.

Electronic Spectra of Nickel(II) Complexes.—The nickel(II) isocyanide complexes all exhibit only one intense absorption in the visible spectrum in the region ∼25,000 cm⁻¹ with extinction coefficients from 2000 to 10,000 M^{-1} cm⁻¹. Although this is the region where d–d transitions usually occur for square-planar nickel(II) complexes, the large extinction coefficients indicate that this absorption is a charge-transfer band and any d–d bands are probably hidden.

Experimental Section

p-Tolyl isocyanide and phenyl isocyanide were prepared by the phosgene method;[26] *p*-methoxyphenyl isocyanide was prepared by the method of Hertler and Corey[27] and methyl isocyanide by the method of Casanova, Schuster, and Werner.[28] The complexes NiCl₂L₂ and PdCl₂L₂ (L = tertiary phosphine, arsine, or stibine) were prepared by conventional methods.[11,29,30]

All reactions were carried out under a nitrogen atmosphere and Spectro Grade solvents were used without further purification. Microanalyses were performed by Chemalytics Inc., Tempe, Ariz. Visible spectra were recorded on a Beckman DK-1 spectrometer. Infrared spectra were recorded on a Beckman IR-7

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spectrophotometer as 2% by weight KBr disks and were unchanged as Nujol mulls. Proton nmr were recorded on a Varian Associates HA100 spectrometer equipped with variable-temperature accessories. Dichloromethane was used as solvent as well as internal standard.

Many of the complexes were prepared by the same procedures so only a few representative examples are described.

(i) **Preparation of [PdCl{P(CH₃)₂C₆H₅}₃](PF₆).**—Dimethylphenylphosphine (0.069 g) was added to a solution of PdCl₂{P(CH₃)₂C₆H₅}₂ (0.226 g) in dichloromethane (10 ml). A white precipitate of silver chloride formed immediately upon addition of AgPF₆ (0.126 g) in acetone (5 ml). The solution was stirred for 1 hr and the silver chloride was removed by centrifugation to give a clear solution. The addition of diethyl ether yielded orange-yellow crystals of [PdCl{P(CH₃)₂C₆H₅}₃]PF₆ (0.185 g).

(ii) **Preparation of [NiCl{P(CH₃)₂(C₆H₅)}₂(CNC₆H₅)](SbF₆).**—To a solution of NiCl₂{P(CH₃)₂C₆H₅}₂ (0.334 g) in methanol was added phenyl isocyanide (0.085 g). The solution turned immediately green-brown. Upon the addition of AgSbF₆ (0.280 g) in 5 ml of methanol, a flocculent precipitate of silver chloride formed and the solution turned orange. The solvent was then removed under vacuum. The product was extracted from the silver chloride with dichloromethane and filtered, and the addition of diethyl ether yielded pale yellow crystals of [NiCl{P(CH₃)₂(C₆H₅)}₂(CNC₆H₅)](SbF₆) (0.451 g).

(iii) **Preparation of [PdCl{P(C₂H₅)₃}₂(CNC₆H₄CH₃)](PF₆).**—To a solution of PdCl₂{P(C₂H₅)₃}₂ (0.207 g) in dichloromethane was added *p*-tolyl isocyanide (0.059 g). A white precipitate of silver chloride formed immediately upon addition of AgPF₆ (0.126 g) in acetone. The solution was stirred for 1 hr, and the silver chloride was removed by centrifugation. The solvent volume was reduced on a rotary evaporator to about 10 ml and crystallization was induced with diethyl ether. The white crystals were filtered and washed with ether to give [PdCl{P(C₂H₅)₃}₂-(CNC₆H₄CH₃)](PF₆) (0.185 g).

(iv) **Preparation of NiCl₂{P(CH₃)(C₆H₅)₂}₂(CNC₆H₅).**—To a solution of NiCl₂{P(CH₃)₂(C₆H₅)}₂ (0.463 g) in 10 ml of methanol was added phenyl isocyanide (0.090 g). The solution turned green-brown and was stirred magnetically for 10 min. The methanol was removed to give a brown oil which was dissolved in 5 ml of dichloromethane and added dropwise to a stirred solution of pentane. A green-brown precipitate formed immediately so it was filtered and reprecipitated again from dichloromethane and pentane and then dried *in vacuo* to give NiCl₂-{P(CH₃)(C₆H₅)₂}(CNC₆H₅) (0.356 g).