complex by way of reaction 2. Certainly one mechanism is not unique. It is possible to consider still another viewpoint consistent with a large negative enthalpy for reaction 1 and almost zero enthalpy for reaction 2.

In the crystal of $KFe^{III}[Fe^{II}(CN)_6]$ the two different oxidation states show preferential association[5] for the carbon ends (Fe^{II}) and nitrogen ends (Fe^{III}), respectively, of the cyanide ligands. Assuming that this behavior can be extended to the species in solution, the formation of Turnbull's blue, not Prussian blue, would cause a charge-transfer transition (−42.03 kcal/mol of electrons)[5] from Fe^{2+} to $Fe(CN)_6{}^{3-}$, *i.e.*, $Fe^{II}[Fe^{III}(CN)_6]^- \rightarrow Fe^{III}[Fe^{II}(CN)_6]^-$. The effect of this charge-transfer transition should be seen in the $\Delta H°$ value for reaction 1 but not in that for reaction 2. The larger $\Delta H°$ value for reaction 1 compared to that for reaction 2 is consistent with this explanation; however, the difference between the two $\Delta H°$ values (15.9 kcal/mol) is considerably less than the 42.0 kcal/mol expected from the charge-transfer transition. Nevertheless, this viewpoint is not unreasonable since other energy terms besides the charge-transfer transition are undoubtedly important in determining the magnitude of the measured $\Delta H°$ value.

Shriver, *et al.*,[16] found that the ligand field strength of the cyanide ion when bonded through nitrogen was comparable to that of H_2O. This finding is generally supported by the data presented here. In the reaction of ferric ion with ferrocyanide ion the six water molecules surrounding the ferric ion are replaced by the nitrogen ends of six cyanide ions. Since the $\Delta H°$ value for reaction 2 is very close to zero (0.72 kcal/mol), the nitrogen ends of the bonded cyanide ions appear to have essentially the same effect as the water molecules they have replaced.

[16] D. F. Shriver, S. A. Shriver, and S. E Anderson, *Inorg. Chem.*, **4**, 725 (1965).

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Synthesis and Reactivity of Novel Palladium(II)–Isocyanide Complexes

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Novel Pd^{II} complexes of the type $Pd(RNC)_2X_2$ (RNC = cyclohexyl and *p*-nitrophenyl isocyanide; X = Cl, I) and of the type $Pd(RNC)(L)X_2$ (RNC = phenyl, *p*-nitrophenyl, and cyclohexyl isocyanide; L = $P(C_6H_5)_3$, $As(C_6H_5)_3$; X = Cl, Br, I) have been prepared. The configuration of these compounds has been assigned, where possible, on the basis of their near- and far-infrared spectra. The reactions of the above compounds with methanol and *p*-toluidine are also reported and discussed. The products of such reactions have been formulated as carbene derivatives of Pd^{II}. The ir spectra of all complexes have been discussed with special regard to the bonding properties of the isocyanide group.

Introduction

Structural and bonding properties of isocyanide metal compounds have been discussed by many authors.[1] In general, ir studies on the stretching frequencies of CO and NC in mixed carbonyl–isocyanide derivatives have shown that isocyanides are stronger σ donors and weaker π acceptors than carbon monoxide.[2,3]

As far as isocyanide complexes of platinum group metals are concerned, only the compounds of the type $M(RNC)_2X_2$ and the Magnus salt type have been reported in the literature so far.[1] In these derivatives it has been found that the metal–isocyanide bond is particularly stable in contrast to the corresponding metal–carbonyl bond.

In the present work we report the synthesis of some novel complexes of the type $Pd(RNC)_2X_2$ and their substitution reactions of the isocyanide group with mono- and bidentate neutral ligands having N, P, and As donor atoms. The coordinated isocyanide group undergoes also addition reactions with methanol and *p*-toluidine.

An ir study is also reported in order to investigate the bonding properties of the isocyanides (RNC) in relation to the effects of the organic group R on the ν(NC) vibrations and on the corresponding Pd–X stretching frequencies, when X is in the *trans* position to the isocyanide.

Experimental Section

All isocyanides have been prepared according to the methods of Ugi and coworkers.[4,5] $Pd(CH_3CN)_2Cl_2$ has been prepared according to the standard methods of the literature. All other chemicals were reagent grade and were used without further purification.

(I) Preparation of the Complexes $Pd(RNC)_2X_2$ and Pd(RNC)-

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[1] F. Bonati and L. Malatesta "Isocyanide Complexes of Metal," Wiley, New York, N. Y., 1969, p 26, and references therein.

[2] (a) M. Bigorgne, *Bull. Soc. Chim. Fr.*, 295 (1963); (b) M. Bigorgne, *J. Organometal. Chem.*, **1**, 101 (1963).

[3] F. A. Cotton and R. V. Parish, *J. Chem. Soc.*, 1440 (1960).

[4] I. Ugi, U. Fetzer, U. Eholzer, H. Knupfer, and K. Offermann, *Angew. Chem., Int. Ed. Engl.*, **4**, 472 (1965).

[5] I. Ugi, R. Meyr, M. Lipinski, F. Bodesheim, and R. Rosendahl, *Org. Syn.*, **41**, 13 (1961).

TABLE I

ANALYTICAL AND PHYSICAL DATA FOR COMPLEXES OF THE TYPE $Pd(RNC)(L)X_2$

Complex	Color	% C		% H		% N		% X		Mp,[a]
		Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	°C
$Pd(C_6H_5NC)(P(C_6H_5)_3)Cl_2$	Cream	55.33	54.8	3.71	3.7	2.58	2.8	13.06	13.2	248
$Pd(C_6H_5NC)(As(C_6H_5)_3)Cl_2$	Yellow	51.18	50.8	3.44	3.5	2.39	2.6	12.08	11.95	192
$Pd(C_6H_5NC)(P(C_6H_5)_3)Br_2$	Yellow	47.54	48.3	3.19	3.2	2.22	2.3	25.30	25.6	260
$Pd(C_6H_5NC)(P(C_6H_5)_3)I_2$	Red-orange	41.38	41.2	2.78	2.6	1.90	2.0	34.98	35.2	265
$Pd(C_6H_{11}NC)_2Cl_2$	Yellow	42.50	42.3	5.60	5.4	7.08	7.1	17.92	18.1	110
$Pd(C_6H_{11}NC)I_2$	Orange	29.06	28.4	3.83	3.65	4.84	4.9	43.87	44.6	130
$Pd(C_6H_{11}NC)(P(C_6H_5)_3)Cl_2$	Yellow	54.72	54.4	4.78	4.7	2.55	2.6	12.92	13.4	250
$Pd(C_6H_{11}NC)(As(C_6H_5)_3)Cl_2$	Yellow	50.66	50.3	4.42	4.5	2.36	2.5	11.96	12.4	210
$Pd(C_6H_{11}NC)(P(C_6H_5)_3)Br_2$	Yellow	47.09	47.2	4.11	4.0	2.20	2.3	25.06	25.2	250
$Pd(C_6H_{11}NC)(As(C_6H_5)_3)Br_2$	Yellow	44.05	44.2	3.84	3.75	2.05	2.1	23.45	23.7	227
$Pd(C_6H_{11}NC)(P(C_6H_5)_3)I_2$	Red-orange	41.04	41.5	3.58	3.5	1.91	2.0	34.69	34.8	213
$Pd(p\text{-}NO_2C_6H_4NC)_2Cl_2$	Yellow	35.51	35.4	1.70	1.7	11.83	12.0	14.97	15.1	230
$Pd(p\text{-}NO_2C_6H_4NC)_2I_2$	Orange	25.61	25.5	1.23	1.3	8.54	8.3	38.66	38.7	237
$Pd(p\text{-}NO_2C_6H_4NC)(P(C_6H_5)_3)Cl_2$	Yellow	51.09	50.9	3.26	3.3	4.77	4.9	12.06	11.8	210
$Pd(p\text{-}NO_2C_6H_4NC)(P(C_6H_5)_3)Br_2$	Yellow	44.37	43.7	2.83	2.75	4.14	4.0	23.62	22.8	248
$Pd(p\text{-}NO_2C_6H_4NC)(P(C_6H_5)_3)I_2$	Red-orange	38.96	39.0	2.48	2.4	3.64	3.6	32.93	33.8	225
$Pd(p\text{-}NO_2C_6H_4NC)(As(C_6H_5)_3)Cl_2$	Orange	47.53	47.6	3.03	2.9	4.44	4.6	11.22	10.9	190
$Pd(C_6H_5NC)(C_6H_5NHCOCH_3)Cl_2$	Off-white	43.35	42.9	3.39	3.5	6.74	6.65	17.06	17.2	165
$Pd(P(C_6H_5)_3)(C_6H_5NHCOCH_3)Cl_2$	Off-white	54.33	53.8	4.21	4.4	2.44	2.5	12.34	12.5	159
$Pd(C_6H_5NC)(C_6H_5NHCNHC_6H_4CH_3)Cl_2$	Off-white	51.40	50.7	3.90	3.8	8.56	8.4	14.45	14.6	234
$Pd(P(C_6H_5)_3)(C_6H_5NHCNHC_6H_4CH_3)Cl_2$	White	59.14	58.5	4.50	4.5	4.31	4.3	10.91	10.7	249

[a] All melting points are uncorrected.

(L)X_2. **Type $Pd(RNC)_2X_2$.**—The complexes $Pd(C_6H_5NC)_2X_2$ (X = Cl, I) have been prepared according to the methods already described.[6,7] The above compounds have been more conveniently obtained by the following general methods.

(a) **Chloro Derivatives.**—A suspension of $Pd(CH_3CN)_2Cl_2$ (1 g, *ca.* 4 mmol) in 40 ml of acetone or chloroform was stirred and treated with the stoichiometric amount of the corresponding isocyanide. The reaction product precipitates immediately. After 15 min the precipitation was completed by adding an ether–ethanol mixture (20:1). The complexes were purified by dissolving in a large volume of chloroform and reprecipitating with ether, after treatment with charcoal and concentration under reduced pressure. $Pd(p\text{-}NO_2C_6H_4NC)_2Cl_2$ could not be purified, because of its low solubility in common organic solvents (yield 50–60%).

(b) **Iodo Derivatives.**—A 1-g sample of $PdCl_2$ suspended in 100 ml of acetone was treated with an excess of KI (*ca.* 8 g) and then with the stoichiometric amount of the corresponding isocyanide. The resulting suspension was stirred for 24 hr. It was then evaporated to dryness and the residue was extracted with chloroform. The solution was treated with charcoal concentrated under reduced pressure and the complex was precipitated with an ether–ethanol mixture (20:1). The complexes so obtained are sufficiently pure (yield 70–80%).

Type $Pd(RNC)(L)X_2$.—A 1-mmol sample of $Pd(RNC)_2X_2$ (X = Cl, I) suspended in 20 ml of chloroform was treated, under stirring, with $P(C_6H_5)_3$ (1 mmol) or $As(C_6H_5)_3$ (1.5–2 mmol) dissolved in the minimum amount of ether. A clear solution was obtained, from which the reaction product precipitated after a few minutes. $As(C_6H_5)_3$ requires more time (2–3 hr) than $P(C_6H_5)_3$ (1 hr) in order to react completely. The precipitation was completed by diluting with ether. In the case of cyclohexyl isocyanide derivatives, which are more soluble, the precipitation was completed by adding an ether–petroleum ether mixture (1:1). The products, washed several times with ether, did not require further purification (yield 70–80%).

The bromo derivatives have been obtained by metathetical reaction from the corresponding chloro derivatives with an excess of LiBr in acetone.

(II) Reactions of Isocyanide Complexes with Methanol and *p*-Toluidine. **Reaction of $Pd(C_6H_5NC)_2Cl_2$ with Methanol.**—A 300-mg sample of Na_2PdCl_4 (*ca.* 1 mmol) dissolved in 50 ml of methanol was treated with the stoichiometric amount of C_6H_5NC. A yellow precipitate $Pd(C_6H_5NC)_2Cl_2$ was immediately formed. This product slowly redissolved under stirring. After 24 hr the reaction mixture was filtered off and the filtrate was taken to dryness under reduced pressure. The crude product was purified by reprecipitating twice from a large volume of chloroform with ether (yield 65%).

Reaction of $Pd(C_6H_5NC)(P(C_6H_5)_3)Cl_2$ with Methanol.—A 1-mmol sample of the initial product was suspended in 50 ml of methanol and refluxed for 1 hr. The reaction mixture, after treatment with charcoal and filtration, was concentrated and treated with ether to precipitate the product. The off-white product was purified by reprecipitation from a large volume of chloroform with ether (yield 80%).

Reaction of $Pd(C_6H_5NC)_2Cl_2$ with *p*-Toluidine.—A 1-mmol sample of $Pd(C_6H_5NC)_2Cl_2$ suspended in 40 ml of chloroform was treated with 1 mmol of *p*-toluidine. A clear solution was obtained, from which, after refluxing for 10 min, an off-white crystalline product precipitated. This product required no further purification (yield 80%).

Reaction of $Pd(C_6H_5NC)(P(C_6H_5)_3)Cl_2$ with *p*-Toluidine.—A 1-mmol sample of the initial product dissolved in 40 ml of chloroform was treated with 1.5 mmol of *p*-toluidine and refluxed for 1 hr. The reaction mixture, after treatment with charcoal and filtration, was concentrated under reduced pressure and precipitated by diluting with ether. The product was purified by reprecipitation from a large volume of chloroform with ether (yield 70%).

All yields have been calculated on the theoretical amount of the final products of the reactions.

Analytical and physical data for all complexes are reported in Table I.

(III) Infrared Spectra.—Infrared spectra were recorded in the region 4000–250 cm^{-1} with a Perkin-Elmer 621 spectrophotometer and with a Beckmann IR 11 in the region 450–80 cm^{-1}. From 4000 to 1300 cm^{-1} hexachlorobutadiene mulls and NaCl plates were used; from 1700 to 250 cm^{-1} Nujol mulls and CsI plates were used. Nujol mulls and thin polythene sheets were used from 400 to 80 cm^{-1}. Solution spectra were recorded with KBr liquid cells of 1-mm path length. Calibration was performed against a carbon monoxide rotational spectrum, polystyrene film, and a water vapor rotational spectrum. Accuracy is believed to be better than ±1 cm^{-1}.

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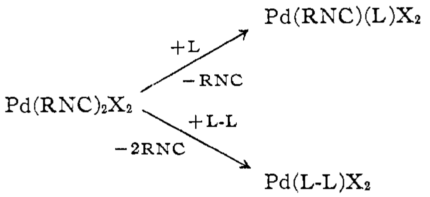
[7] F. Canziani, F. Cariati, and U. Sartorelli, *Rend. Ist. Lomb. Sci. Lett. A*, **98**, 564 (1964).

Results and Discussion

(a) **Complexes of the Type $Pd(RNC)_2X_2$ (RNC = Cyclohexyl and *p*-Nitrophenyl Isocyanide).**—The chloro derivatives have the *cis* configuration (C_{2v} symmetry) since their ir spectrum shows two strong bands ν(NC) in the region 2248–2225 cm^{-1} (see Table III) both in the solid state and in solution. Correspondingly in the region 346–315 cm^{-1} two bands have been detected and assigned to the Pd–Cl stretching vibrations. The same configuration was also attributed to $Pd(C_6H_5NC)_2Cl_2$ on the basis of its ir spectrum.[7]

The ir spectra of the iodo derivatives in the solid state and in solution have only one very strong ν(NC) in the range 2220–2190 cm^{-1}. On this basis they have been assigned a *trans* configuration (D_{2h} symmetry), as was also found for $Pd(C_6H_5NC)_2I_2$.[7]

(b) **Reactions of $Pd(RNC)_2X_2$ with Neutral Mono- and Bidentate Ligands.**—Complexes of the type $Pd(RNC)_2X_2$ (RNC = cyclohexyl, phenyl, and *p*-nitrophenyl isocyanide; X = Cl, I) react with monodentate ligands (L), such as triphenylphosphine and triphenylarsine, and with bidentate ligands (L-L), such as 1,2-bis(diphenylphosphino)ethane and 1,2-bis(diphenylarsino)ethane, according to the scheme

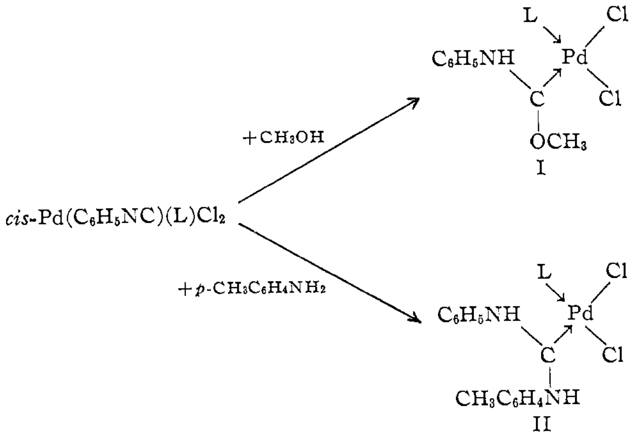


The reactions with triphenylphosphine proceed at milder conditions than with triphenylarsine. In both cases, even with an excess of ligand, only one isocyanide group is replaced except with the iodo derivatives, which do not react with the arsine. Only the bidentate ligands are able to replace both isocyanide groups yielding the well-known complexes $Pd(L\text{-}L)X_2$, owing to the chelating nature of the entering groups. Ligands with aromatic nitrogen, such as pyridine and bipyridyl, give no substitution reactions. All these facts show that the Pd^{II}–NC bond is particularly stable in such complexes.

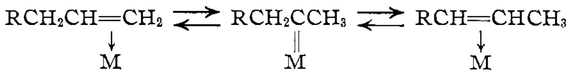
As far as the configuration of the reaction products with monodentate ligands is concerned, chloro derivatives have been assigned a *cis* structure. In fact, their ir spectra in the solid state always show two strong bands attributable to the Pd–Cl stretching vibrations, the higher frequency band falling in the range 341–329 cm^{-1} and the lower frequency one in the range 298–293 cm^{-1} (this is the typical region for ν(Pd–Cl) vibrations when the chloride is in the *trans* position to a phosphine or arsine).[8] It was not possible to determine even tentatively the configuration of the iodo derivatives $Pd(RNC)(P(C_6H_5)_3)I_2$, since no ν(Pd–I) bands could be detected, presumably because of their low intensity.

The bromo derivatives $[Pd(RNC)(L)Br_2]$ have been prepared by metathetical reaction with LiBr from the corresponding chloro derivatives. These complexes also have a *cis* structure, the ν(Pd–Br) bands falling in the range 240–186 cm^{-1} (see Table III). The assignment of the ν(Pd–Br) band at lower frequency was complicated by the occurrence of other bands in the same spectral region.

(c) **Reactions of $Pd(C_6H_5NC)(L)Cl_2$ with Methanol and *p*-Toluidine.**—The complexes of type $Pd(C_6H_5NC)(L)Cl_2$, with L = C_6H_5NC or $P(C_6H_5)_3$, react with methanol and *p*-toluidine according to the scheme



The products obtained from these addition reactions have been formulated as carbene derivatives on the basis of their elemental analysis and ir spectra. A platinum(II)–carbene derivative has been very recently obtained by Chatt, *et al.*, by adding ethanol to $Pt(C_6H_5NC)(P(C_2H_5)_3)Cl_2$. The presence of an ethoxy(phenylamino)carbene group in the product of this reaction has been confirmed by an X-ray investigation.[9] A metal–carbene complex was postulated as an intermediate in the olefin isomerization catalyzed by d^8 metal complexes, the proposed mechanism involving intramolecular migration of hydride within the olefin coordinated to the transition metal[10]



$$\underset{\substack{\downarrow\\ M}}{RCH_2CH{=}CH_2} \rightleftarrows \underset{\substack{\|\\ M}}{RCH_2CCH_3} \rightleftarrows \underset{\substack{\downarrow\\ M}}{RCH{=}CHCH_3}$$

Complexes I and II are poorly soluble in common organic solvents so that nmr and molecular weight measurements were prevented. These compounds are the first examples of palladium(II)–carbene derivatives. The carbene complexes so far reported in the literature were obtained by the action of strong nucleophiles, such as lithium alkyls and phenyls, on the CO unsaturated bond of chromium, molybdenum, and tungsten carbonyls.[11] Nucleophilic attacks by amines or RO^- groups on coordinated CO groups of manganese, rhenium, iridium, and iron carbonyl derivatives are very well recognized.[12,13]

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TABLE II

CHARACTERISTIC IR BANDS OF ADDITION PRODUCTS (CM^{-1})[a]

Complex	ν(N—H)	ν(NC)	δ(N—H)	ν(C$\overline{\cdots}$N)[b]	ν(Pd—Cl)
$Pd(C_6H_5NC)(C_6H_5—NH—C—OCH_3)Cl_2$	3225 m, 3195 sh, 3140 mw	2112 vs	1600 sh, 1595 m	1554 s	328 s, 300 m, 280 ms
$Pd(P(C_6H_5)_3)(C_6H_5—NH—C—OCH_3)Cl_2$	3148 mw, 3103 mw		1591 m	1547 s	302 m, 287 m
$Pd(C_6H_5NC)(C_6H_5—NH—C—NH—C_6H_4—CH_3)Cl_2$	3205 ms, 3180 sh, 3120 w	2206 s	1597 m, 1587 ms	1549 s	319 m, 287 mw, 270 m
$Pd(P(C_6H_5)_3)(C_6H_5—NH—C—NH—C_6H_4—CH_3)Cl_2$	3158 m, 3106 m		1588 m	1538 s	295 m, 285 sh, 273 m

[a] Abbreviations: vs, very strong; s, strong; ms, medium strong; m, medium; mw, medium weak; w, weak; sh, shoulder. [b] Tentative assignments.

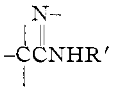
TABLE III

CHARACTERISTIC IR BANDS OF COMPLEXES OF THE TYPE $Pd(RNC)(L)X_2$ (CM^{-1})

Complex	ν(NC)		ν(PdX)	Characteristic absorptions in the region 600–350 cm^{-1}		Characteristic absorptions of NO_2 group	
	Solid	Soln ($CHCl_3$)				Asym ν(NO)	Sym ν(NO)
$Pd(C_6H_5NC)_2Cl_2$	2241 vs	2230 vs	342 ms, 328 sh	531 m	449 m		
	2225 vs	2213 vs	319 s	493 ms	408 m		
$Pd(C_6H_5NC)_2I_2$	2202 s	2200 s	n.r.[b]	524 m	436 m		
$Pd(C_6H_5NC)(P(C_6H_5)_3)Cl_2$	2212 vs	2209 vs	334 s, 294 s	550 m	457 m[a]		
$Pd(C_6H_5NC)(As(C_6H_5)_3)Cl_2$	2210 vs	2209 vs	340 s, 296 s	544 m	430 m		
$Pd(C_6H_5NC)(P(C_6H_5)_3)Br_2$	2210 vs	2204 vs	232 s, 197 m or 186 m	549 m	433 m[a]		
$Pd(C_6H_5NC)(P(C_6H_5)_3I_2$	2181 vs	2196 vs	n.r.	543 m	420 m[a]		
$Pt(C_6H_5NC)_2Cl_2$	2241 vs	2234 vs	340 s, 321 s	568 m	469 m		
	2213 vs	2203 vs		557 s	430 ms		
$[Pt(C_6H_5NC)_4][PtCl_4]$	2249 vs	Insol	307 s	539 ms	464 ms		
C_6H_5NC	2124 vs	2130 vs					
	(liquid film)						
$Pd(C_6H_{11}NC)_2Cl_2$	2248 vs	2247 vs	337 s, 315 s	569 m	453 m		
	2230 vs	2231 vs					
$Pd(C_6H_{11}NC)_2I_2$	2219 vs	2220 vs	n.r.	554 mw	441 m		
$Pd(C_6H_{11}NC)(P(C_6H_5)_3)Cl_2$	2235 vs	2227 vs	329 m, 295 s	n.o.[c]	451 m[a]		
$Pd(C_6H_{11}NC)(As(C_6H_5)_3)Cl_2$	2236 vs	2227 vs	329 m, 298 s	560 w	435 mw		
$Pd(C_6H_{11}NC)(P(C_6H_5)_3Br_2$	2231 s	2223 s	235 s, 198 m	n.o.	450 m[a]		
$Pd(C_6H_{11}NC)(As(C_6H_5)_3)Br_2$	2228 s	2223 s	234 s, 210 m	n.r.	431 m		
$Pd(C_6H_{11}NC)(P(C_6H_5)_3)I_2$	2225 s	2219 s	n.r.	565 w	430 m[a]		
$C_6H_{11}NC$	2135 vs	2143 vs					
	(liquid film)						
$Pd(p\text{-}NO_2C_6H_4NC)Cl_2$	2241 vs	Insol	346 ms, 330 ms	497 m	415 m	1520 vs	1342 vs
	2225 vs			478 mw	405 m		
$Pd(p\text{-}NO_2C_6H_4NC)I_2$	2190 vs	2193 vs	182 m	493 ms	389 ms	1526 vs	1354 vs
						1520 vs	1341 vs
$Pd(p\text{-}NO_2C_6H_4NC)(P(C_6H_5)_3)Cl_2$	2215 vs	2201 vs	332 s, 326 sh, 293 vs	n.o.	426 m[a]	1528 vs	1340 vs
$Pd(p\text{-}NO_2C_6H_4NC)(As(C_6H_5)_3)Cl_2$	2200 vs	2200 vs	334 m, 294 ms	497 w	400 w	1520 s	1340 s
$Pd(p\text{-}NO_2C_6H_4NC)(P(C_6H_5)_3)Br_2$	2195 vs	2196 vs	240 m or 230 m, 200 mw	n.o.	408 m	1521 vs	1343 vs
$Pd(p\text{-}NO_2C_6H_4NC)(P(C_6H_5)_3)I_2$	2181 vs	2187 vs	n.r.	n.o.	370 m	1520 vs	1340 vs
$p\text{-}NO_2C_6H_4NC$	2116 vs	2124 vs				1532 vs	1342 vs

[a] These bands may also belong to $P(C_6H_5)_3$. [b] Not recorded. [c] Not observed because of $P(C_6H_5)_3$ strong absorptions in the same region.

In Table II the most characteristic bands of the products I and II are reported. The ν(NH) vibrations fall in the range 3225–3103 cm^{-1}, which is significantly lower (100–200 cm^{-1}) than the usual range for secondary amines (3500–3300 cm^{-1}). This fact is related to the presence of a strong band in the range 1554–1538 cm^{-1}, attributable to a carbon–nitrogen stretching vibration with a remarkable character of double bond between the two atoms, as in the amidines[14]



$$\begin{array}{l} \quad\;\; N- \\ \;\; | \;\; \| \\ -CCNHR' \\ \;\; | \end{array}$$

The electrophilic character of the coordinated carbon atom in the carbene group is likely to remove electron density from the lone pair of the nitrogen atom in the α position, a partial positive charge being induced on the latter atom. This may account for the lowering of the N–H stretching vibrations.

The presence of at least two ν(Pd–Cl) bands in the range 328–270 cm^{-1} is in favor of a *cis* structure, suggesting that during the addition reaction the initial configuration is retained. The low values of the Pd–Cl stretching frequencies indicate a rather high *trans* influence of the carbene group, even though hydrogen bonds and other interactions in the solid state may contribute to the lowering of such bands. Hydrogen bonding may also account for more than one ν(N–H) band being observed for complexes I, although these contain one single NH group.

(d) **Infrared Data.**—In Table III the most charac-

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[14] N. B. Colthup, L. H. Daly, and S. E. Wiberley, "Introduction to Infrared and Raman Spectroscopy," Academic Press, New York, N. Y., 1964, p 283.

teristic bands of the complexes of the type Pd(RNC)(L)X_2 are reported. The ir data so far reported in the literature for palladium(II)–isocyanide derivatives of the type Pd$(RNC)_2X_2$ (R = phenyl and *p*-tolyl) refer only to the NC stretching vibrations in the region about 2200 cm^{-1}. Such vibrations were discussed in relation either to the structure of the complexes or to the type of Pd^{II}–NC bond.[7] Besides the ν(NC) bands, the data in Table II also include the ν(Pd–X) bands and some typical bands in the range 600–350 cm^{-1}. For the *p*-nitrophenyl isocyanide derivatives the asymmetric and symmetric ν(NO) bands are also reported.

As far as ν(NC) vibrations are concerned, they fall in the range 2248–2181 cm^{-1}. In general, it has been found that ν(NC) decreases in the order: cyclohexyl > phenyl > *p*-nitrophenyl derivatives; this trend has been found also for the uncoordinated isocyanides. This is in agreement with a higher NC bond order due to the higher electron-donor character of the cyclohexyl group compared to the other two groups. A typical effect of coordination on the isocyanide group is the shift to higher frequency of ν(NC), which may be considered as a reliable index of an increased N–C bond order (more "triple-bond" character). This is caused by the σ donation of the carbon atom lone pair to the central metal, which is not counterbalanced by the π back-donation. In this respect, chloro derivatives of the type Pd$(RNC)_2Cl_2$ show the highest $\Delta\nu$(NC) between the coordinated and uncoordinated ligand, because of the higher effective charge on the central metal induced by the more electronegative chloride ligands.

It is interesting also to compare $\Delta\nu$(NC) in a series of analogous compounds (Table IV). Even though the differences are small, the observed trend seems to indicate that there is a decreasing electron drift from the ligand to the metal in the order: cyclohexyl > phenyl > *p*-nitrophenyl isocyanide. This fact is reflected also by the higher *trans* influence of cyclohexyl isocyanide, as can be seen from the Pd–Cl stretching frequency in the *trans* position.[15] In fact all cyclohexyl isocyanide derivatives show lower ν(Pd–Cl) than the corresponding derivatives with the other isocyanides.

TABLE IV

$\Delta\nu$(NC) (CM^{-1}) FOR Pd(RNC)(P$(C_6H_5)_3$)X_2 IN $CHCl_3$

R group	X = Cl	X = Br
Cyclohexyl	84	80
Phenyl	79	74
p-Nitrophenyl	77	72

The complexes Pd(RNC)(L)X_2 have typical bands in the range 600–350 cm^{-1}, which are tentatively assigned to the in-plane deformation δ(Pd–CN) and to the stretching vibration ν(Pd–C). It is to be noted that these bands have been separated from the absorptions that the ligands RNC and L exhibit in the same region. The above assignment is based on the fact that the corresponding vibrations of many carbonyl and cyano derivatives fall in the same range.[16] In support of this assignment it is to be pointed out that the complexes Pt$(C_6H_5NC)_2Cl_2$ and [Pt$(C_6H_5NC)_4$][$PtCl_4$][17,18] have four and two bands, respectively, in the same region. This fact can be accounted for by the group theory, assuming C_{2v} and D_{4h} symmetries, respectively, for the two complexes.

	Symmetry	Ir-active ν(PtC)	Ir-active δ(PtCN)
Pt$(C_6H_5NC)_2Cl_2$	C_{2v} 4 bands:	$A_1 + B_1$	$A_1 + B_1$
Pt$(C_6H_5NC)_4^{2+}$	D_{4h} 2 bands:	E_u	E_u

The complex [Pt$(C_6H_5NC)_4$][$PtCl_4$] shows only one band at 307 cm^{-1} assigned to ν(PtCl). This band is typical for the ion $PtCl_4^{2-}$;[19,20] its frequency is the lowest one so far recorded owing to the large size of the counterion Pt$(C_6H_5NC)_4^{2+}$.

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[15] D. M. Adams, J. Chatt, J. Gerratt, and A. D. Westland, *J. Chem. Soc.*, 734 (1964).

[16] D. M. Adams, "Metal-Ligand and Related Vibrations," E. Arnold, London, 1967, pp 118, 166, and references therein.

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