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HYDRIDOCYANOALKYL COMPLEXES OF PLATINUM(II). INSERTION OF OLEFINS INTO THE Pt—H BOND

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Summary

The preparation and spectroscopic properties are described of some platinum(II) complexes having a hydride ligand *cis* or *trans* to an sp^3 carbon, viz. *trans*-PtH(YCN)$(PPh_3)_2$ and *cis*-PtH(YCN)(L—L) with YCN = C_2H_4CN, n-C_3H_6CN, *o*-$CH_2C_6H_4CN$ and L—L = bis(diphenylphosphino)-ethene or -ethane. The complexes *trans*-PtH(YCN)$(PPh_3)_2$ can add a fifth ligand in solution; the resulting five-coordinate complex was observed by ^{31}P NMR in the case of PtH$(C_3H_6CN)(PPh_3)_3$. Insertion of olefin (ethene, 1-cyanoethene, norbornadiene, allene) into the Pt—H bond of the *trans*-hydrido complexes occurs to give *cis*-dialkyl complexes, but the *cis*-hydrido complexes are unreactive. The mechanism of insertion is discussed in terms of the kinetics and the geometries of reactants and products.

Introduction

Several studies on hydrido and alkyl complexes of platinum(II) have shed light on the mechanism of olefin insertion into the Pt—H bond [1—5], on π-complex formation [6], and on ligand elimination reactions [7—11]. Complexes of the type PtH(R)L_2 contain a hydride and an alkyl ligand, and are thought to be intermediates in the catalytic activation of C—H bonds [12]. These complexes are generally unstable, and only a few have been sofar isolated [13—17]. We recently reported the preparation of hydridocyanomethyl complexes *trans*-$PtH(CH_2CN)(PPh_3)_2$ and *cis*-$PtH(CH_2CN)(L—L)$ (L—L = diphosphine, diarsine) [16] and thought they would be good subjects for a study of olefin insertion into a Pt—H bond for three reasons: (i) the complexes $PtHXL_2$ used so far contain a rather weakly bonded fourth ligand (X = Cl, NO_3, acetone, etc.); this increases the number of available coordination sites for the entering olefin and the role of the solvent in the overall process, whereas in $PtH(YCN)L_2$ the fourth ligand is the strongly bonded cyanoalkyl, which cannot be reversibly displaced, (ii) the *cis*-complexes bear a bidentate ligand whose dissociation should be entropically disfavored and which should preclude problems of *cis—trans*-isomerization, and (iii) the complexes contain an NMR probe (^{31}P) to aid the search for intermediates and an IR probe (the CN group) for the detection of eventual elimination products.

We report now the preparation and spectroscopic properties of hydridocyanoalkyl complexes $PtH(YCN)L_2$ (YCN = C_2H_4CN, n-C_3H_6CN, *o*-$CH_2C_6H_4CN$; L_2 = $(PPh_3)_2$, $Ph_2PCH{=}CHPPh_2$, $Ph_2PC_2H_4PPh_2$) and the results of an NMR study of their reaction with olefins. The reactions with other nucleophiles have been described elsewhere [16].

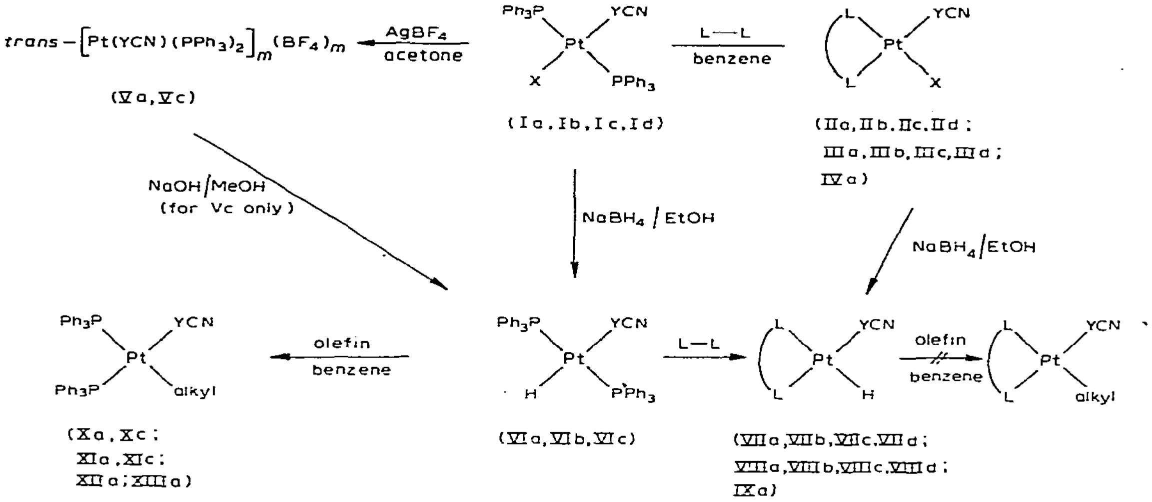
Results and discussion

The complexes *trans*-$PtH(YCN)(PPh_3)_2$ were obtained by treating *trans*-$PtX(YCN)(PPh_3)_2$ (X = Cl, Br) with $NaBH_4$ in warm ethanol or, in the case of YCN = n-C_3H_6CN, by heating the cationic derivative *trans*-$[Pt(n\text{-}C_3H_6CN)(PPh_3)_2]_m(BF_4)_m$ [18] with methanolic NaOH. *cis*-Hydrido complexes were prepared by displacing triphenylphosphine from *trans*-$PtH(YCN)(PPh_3)_2$ by various diphosphines, or by displacing PPh_3 from *trans*-$PtX(YCN)(PPh_3)_2$ by a diphosphine and treating the product with $NaBH_4$ in ethanol.

No insertion of olefins into the Pt—H bond of the *cis* complexes occurred, whereas the *trans*-hydrido complexes reacted cleanly with olefins (ethene, acrylonitrile, norbornadiene and allene), yielding the corresponding dialkyl complexes as the sole products. (No elimination of cyanoalkanes was observed when the reaction was monitored by IR and GLC.) (Scheme 1).

The complexes were characterized by ^1H and ^{31}P NMR spectra (Table 1), IR spectra and elemental analyses (Table 2). The hydrido complexes VIa—VIIId are white crystalline solids stable in air, soluble in benzene and chloroalkanes, and insoluble in alcohols. The *trans*-geometry of VIa [16] and VIb, VIc is deduced from their NMR spectra: a triplet for the hydride resonance due to coupling with two equivalent phosphorus nuclei, and a single ^{31}P resonance (with additional coupling due to ^{195}Pt). All the other hydrido complexes VIIa—VIIId, as well as the dialkyl complexes Xa—XIIIa have a *cis*-geometry: the $^{31}P\{^1H\}$ FT NMR spectra show two doublets. For VIIIa—VIIId, the resonance attributed to the phosphorus atom *trans* to the hydride ligand is that associated with a large additional $^2J(PPtH)$ of ca. 200 Hz in the coupled ^{31}P NMR spectra. Comparison of the coupling constants $^1J(PtP)$ shows that the *trans*-influence of the hydride is about the same as that of a cyanoalkyl ligand. The comparison of related coupling constants $^1J(PtP)$, as well as of $^1J(PtH)$ and $\nu(PtH)$, leads

SCHEME 1



Compound	X	L—L	YCN	Reference
Ia	Cl		CH_2CN	18
Ib	Br		C_2H_4CN	18
Ic	Br		n-C_3H_6CN	18
Id	Cl, Br		*o*-$CH_2C_6H_4CN$	19
IIa	Cl	*cis*-$Ph_2PCH{=}CHPPh_2$	CH_2CN	16
IIb	Cl	*cis*-$Ph_2PCH{=}CHPPh_2$	C_2H_4CN	this work
IIc	Cl, Br	*cis*-$Ph_2PCH{=}CHPPh_2$	n-C_3H_6CN	this work
IId	Cl	*cis*-$Ph_2PCH{=}CHPPh_2$	*o*-$CH_2C_6H_4CN$	19
IIIa	Cl	$Ph_2PC_2H_4PPh_2$	CH_2CN	16. 20
IIIb	Cl, Br	$Ph_2PC_2H_4PPh_2$	C_2H_4CN	this work
IIIc	Cl, Br	$Ph_2PC_2H_4PPh_2$	n-C_3H_6CN	this work
IIId	Cl	$Ph_2PC_2H_4PPh_2$	*o*-$CH_2C_6H_4CN$	this work
IVa	Cl	$Ph_2PC_3H_6PPh_2$	CH_2CN	16
Va			n-C_3H_6CN	this work
Vc			n-C_3H_6CN	this work
VIa			CH_2CN	16
VIb			C_2H_4CN	this work
VIc			n-C_3H_6CN	this work

Compound	Alkyl	X	L—L	YCN	References
VIIa			*cis*-$Ph_2PCH{=}CHPPh_2$	CH_2CN	16
VIIb			*cis*-$Ph_2PCH{=}CHPPh_2$	C_2H_4CN	this work
VIIe			*cis*-$Ph_2PCH{=}CHPPh_2$	n-C_3H_6CN	this work
VIId			*cis*-$Ph_2PCH{=}CHPPh_2$	*o*-$CH_2C_6H_4CN$	this work
VIIIa			$Ph_2PC_2H_4PPh_2$	CH_2CN	16
VIIIb			$Ph_2PC_2H_4PPh_2$	C_2H_4CN	this work
VIIIc			$Ph_2PC_2H_4PPh_2$	n-C_3H_6CN	this work
VIIId			$Ph_2PC_2H_4PPh_2$	*o*-$CH_2C_6H_4CN$	this work
IXa			$Ph_2PC_3H_6PPh_2$	CH_2CN	16
IXc				n-C_3H_6CN	this work
Xa	C_2H_5	CH_2CH_2CN		CH_2CN	this work
Xc	C_2H_5	CH_2CH_2CN		n-C_3H_6CN	this work
XIa	C_2H_5	C_7H_9(norbornenyl)		CH_2CN	this work
XIc	C_2H_5	C_7H_9(norbornenyl)		n-C_3H_6CN	this work
XIIa	C_2H_5	$CH_2CH{=}CH_2$		CH_2CN	this work
XIIIa	C_2H_5	$CH_2CH{=}CH_2$		CH_2CN	this work

TABLE 1

^{1}H AND ^{31}P NMR SPECTRAL DATA FOR CYANOALKYL COMPLEXES OF PLATINUM(II)

Complex		$\delta(CH_2)$ [a] (ppm)	$\delta(H)$ (ppm)	$^1J(PtH)$ (Hz)	$^2J(PPtH)$ (Hz)	$\delta(P)$ [b] (ppm)	$^1J(PtP)$ (Hz)	$^2J(PP)$ (Hz)
Ib	*trans*-$PtCl(C_2H_4CN)(PPh_3)_2$	1.2m				27.3s	3124	—
IIb	$PtBr(C_2H_4CN)(Ph_2PCH{=}CHPPh_2)$	1.9m [c]				49.3d	4159 [d]	10
						55.3d	1757	
IIc	$PtBr(n\text{-}C_3H_6CN)(Ph_2PCH{=}CHPPh_2)$	1.57m				49.1d	4734	10
		1.98m				55.3d	1679	
VIb	*trans*-$PtH(C_2H_4CN)(PPh_3)_2$	1.0m	−5.07t	533	18	34.4s	3121	—
VIc	*trans*-$PtH(n\text{-}C_3H_6CN)(PPh_3)_2$	0.4—1.1bm	−4.51t	636	18	35.1s	3160	—
VIIb	$PtH(C_2H_4CN)(Ph_2PCH{=}CHPPh_2)$	2.35m	−0.89dd	1275	201 *trans*	60.6d	1771 [e] *trans*	13
					18 *cis*	63.4d	1766 *cis*	
VIIc	$PtH(n\text{-}C_3H_6CN)(Ph_2PCH{=}CHPPh_2)$	1.9m	−1.66dd	1290	201 *trans*	60.2d	1806 *trans*	15
					19 *cis*	63.3d	1674 *cis*	
VIId	$PtH(o\text{-}CH_2C_6H_4CN)(Ph_2PCH{=}CHPPh_2)$	3.45dd [f]	−1.42dd	1217	204 *trans*	61.2d	1759 *trans*	14
					18 *cis*	59.5d	1974 *cis*	
VIIIb	$PtH(C_2J_4CH)(Ph_2PC_2H_4PPh_2)$	2.33m	−1.14dd	1251	195 *trans*	49.0bs	1973 *trans*	<2
					16 *cis*	52.6bs	1806 *cis*	
VIIIc	$PtH(n\text{-}C_3H_6CN)(Ph_2PC_2H_4PPh_2)$	2.1m	−1.07dd	1260	195 *trans*	48.2bs	1824 *trans*	<2
					17 *cis*	52.7bs	1712 *cis*	
VIIId	$PtH(o\text{-}CH_2C_6H_4CN)(Ph_2PC_2H_4PPh_2)$	3.33dd [g]	−1.52dd	1195	199 *trans*	43.8bs	1771 *trans*	<2
					17 *cis*	49.9bs	1900 *cis*	
Xa	*cis*-$Pt(CH_2CN)(CH_2CH_3)(PPh_3)_2$	1.4bm				24.0d	1603	10
		0.9bm(CH_3)				26.9d	2652	
Xc	*cis*-$Pt(n\text{-}C_3H_6CN)(CH_2CH_3)(PPh_3)_2$	1.55bm				26.2d	1684	8
		0.8bm(CH_3)				26.6d	1872	
XIa	*cis*-$Pt(CH_2CN)(CH_2CH_2CN)(PPh_3)_2$	1.6bm				21.1d	2220	15
		1.1bm				22.0d	2290	
XIc	*cis*-$Pt(n\text{-}C_3H_6CN)(CH_2CH_2CN)(PPh_3)_2$	1.5bm				23.3d	1653	11
						24.7d	2445	
XIIa	*cis*-$Pt(CH_2CN)(C_7H_9)(PPh_3)_2$	1.4dd [h]				23.9d	1565	12
		C_7H_9 [i]				27.2d	2636	
XIIIa	*cis*-$Pt(CH_2CN)(CH_2CH{=}CH_2)(PPh_3)_2$	1.5m				23.5	1850	~10
		4.4m [j]				25.3	2570	

[a] In CD_2Cl_2 at room temperature; TMS as internal standard. [b] In CD_2Cl_2 at room temperature; a positive sign denotes a resonance at lower field than 85% H_3PO_4 (external reference). [c] δ(CH=) 6.8m ppm. [d] P *trans* to Br. [e] P *trans* to H: this resonance is split into a doublet with ^2J ~200 Hz in the undecoupled spectrum. [f] ^2J(PtCH) 105 Hz; ^3J(PPtCH) 11 Hz (*trans*), 7.3 Hz (*cis*). [g] ^2J(PtCH) 104 Hz; ^3J(PPtCH) 11 Hz (*trans*), 8 Hz (*cis*); $\delta(C_2H_4)$ 2.1 m. [h] ^2J(PtCH) 94 Hz; ^3J(PPtCH) 12 Hz (*trans*), 9 Hz (*cis*). [i] δ(H(1), H(4)) 5.2m, δ(H(2), H(3)) 6.8m, δ(H(5)), H(7)) 1.6m, δ (H(6)) 1.1m ppm (the assignments for the norbornenyl moiety follow those of Stille [24]. [j] $\delta(CH{=}CH_2)$.

TABLE 2

ANALYTICAL AND IR SPECTRAL DATA

Complex	M.p. (dec.) (°C)	Analysis (found (calcd.) (%))				ν(CN) [d] (cm^{-1})	Others (cm^{-1})	
		C	H	N	P			
Ib	211—213	57.81 [a] (57.89)	4.30 (4.23)	1.67 (1.73)	7.66 (6.66)	2248s	278m	ν(PtCl)
IIb	235—236	48.17 [b] (48.08)	3.65 (3.62)	1.99 (1.92)	8.29 (8.55)	2238s	189s	ν(PtBr) [e]
IIc	117—178	49.01 [c] (48.73)	3.94 (3.82)	1.79 (1.89)		2235s	188s	ν(PtBr) [e]
VIb	168—170	60.56 (60.46)	4.62 (4.55)	1.79 (1.81)	8.05 (8.00)	2238s	2019s 800m	ν(PtH) δ(PtH)
VIc	153—154	60.79 (60.91)	4.75 (4.73)	1.89 (1.78)	7.48 (7.85)	2245s	1950s 827m	ν(PtH) δ(PtH)
VIIb	149—150	53.90 (53.87)	4.25 (4.21)	2.08 (2.17)	9.38 (9.58)	2233s	1990s	ν(PtH)
VIIc	134—135	54.45 (54.54)	4.42 (4.42)	2.14 (2.12)	8.99 (9.38)	2245s	1942s	ν(PtH)
VIId	165—170	57.50 (57.63)	4.11 (4.12)	2.00 (1.98)	8.69 (8.74)	2218s	1988s	ν(PtH)
VIIIb	138—142	53.57 (53.70)	4.56 (4.51)	2.24 (2.16)	9.42 (9.55)	2226s	1967s	ν(PtH)
VIIIc	130—131	54.31 (54.38)	4.75 (4.72)	2.03 (2.11)	9.18 (9.35)	2240s	1995s	ν(PtH)
VIIId	180—183	57.06 (57.46)	4.33 (4.04)	2.01 (1.97)	8.52 (8.72)	2216s	2000s	ν(PtH)
Xa	146—147	60.88 (60.90)	4.99 (4.73)	1.77 (1.77)	7.20 (7.85)	2202s	547s [f]	
Xc	139—141	60.68 (61.74)	5.00 (5.06)	1.54 (1.71)	7.62 (7.58)	2248s	547a	
XIa	181—182	58.98 (60.51)	4.45 (4.46)	3.20 (3.44)	7.43 (7.61)	2208s 2218s	544m	
XIc	158—159	60.48 (61.35)	4.99 (4.79)	3.24 (3.33)	6.80 (7.36)	2247s 2199s	544m	
XIIa	173—175	63.21 (63.37)	4.77 (4.85)	1.66 (1.64)	7.04 (7.26)	2208s	1555w	ν(C=C)
XIIIa	144—147	61.15 (61.49)	4.77 (4.65)	1.58 (1.75)		2200s	1608m	ν(C=C)

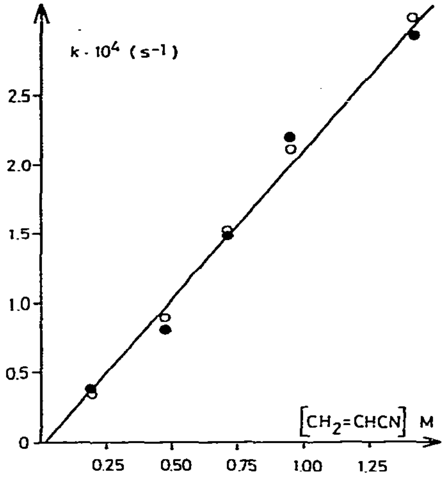
[a] Cl, 4.48 (4.38)%. [b] Br, 11.29 (11.03)%. [c] Br, 10.98 (10.81)%. [d] IR in Nujol mulls. [e] Raman of powdered sample. [f] Mastin's rule [25]: the presence of a band around 550 cm^{-1} is indicative of a *cis*-geometry for bis(triphenylphosphine)platinum(II) complexes.

to the sequence of increasing *trans*-influence $Cl < P < CH_2CN < C_2H_4CN <$ n-C_3H_6CN and to that of decreasing *cis*-influence $CH_2CN > C_2H_4CN >$ n-C_3H_6CN. The *cis*-influence is ca. 10% of that of the *trans*-influence, as judged by the magnitudes of the corresponding ΔJ's. (These sequences have now been verified over more than 40 cyanoalkyl complexes.) The inversion of *cis*- and *trans*-influence sequences has been noted for other ligands [21—23].

The kinetics of the insertion reaction 1 were studied by preparing on a vacuum

$$\underset{\text{(VIc)}}{trans\text{-}PtH(C_3H_6CN)(PPh_3)_2} + CH_2{=}CHCN \rightarrow \underset{\text{(XIc)}}{cis\text{-}Pt(C_3H_6CN)(CH_2CH_2CN)(PPh_3)_2} \qquad (1)$$

line a series of sealed NMR tubes containing VIc and acrylonitrile in varying



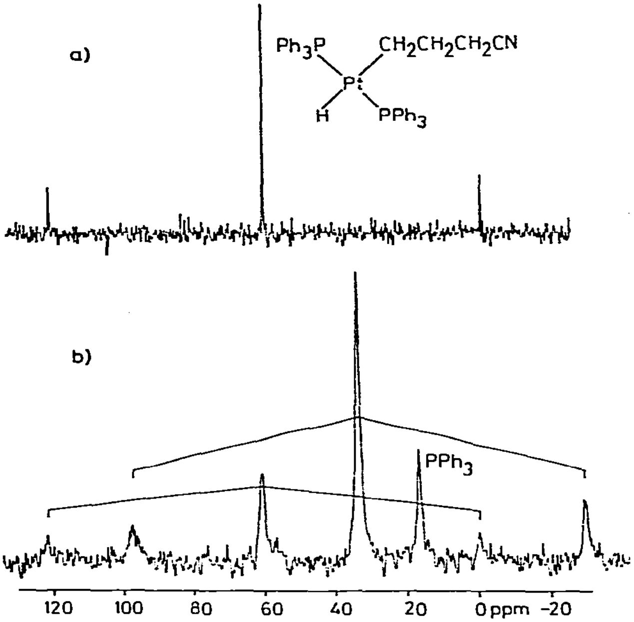


Fig. 1. Reaction 1 in benzene-d_6 at 30°C. [VIc] 0.095 *M*. (The white and black dots refer to the integration of the ^{31}P signals of VIc and XIc, respectively).

Fig. 2. (a) $^{31}P\{^1H\}$ FT NMR spectrum of VIc in $CD_2Cl_2/CHClF_2$ at —130°C (PEt_3 as external reference). (b) Spectrum of a solution of VIc and PPh_3 (molar ratio 1/1) in $CD_2Cl_2/CHClF_2$ at —130°C. ($[VIc]_0$ 0.0634 *M*; $[PPh_3]_0$ 0.0629 *M*).

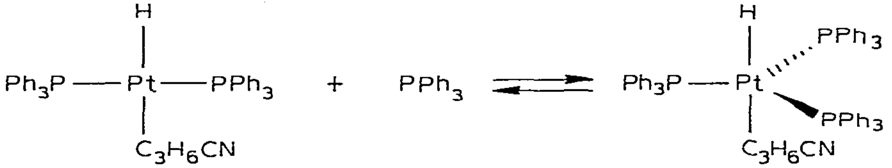
molar ratio in benzene-d_6, and following the reaction at 30.0 ± 0.5°C by periodically integrating the respective ^{31}P signals of the starting hydrido complex and the final product XIc. The reaction is of first order for the hydrido complex and for the olefin (Fig. 1):

$$-d[VIc]/dt = +d[XIc]/dt = k[VIc][CH_2{=}CHCN] \text{ with } k = 2.1 \times 10^{-3}\ M^{-1}\ s^{-1}$$

In the case of platinum(II), an associative type of mechanism is thought to involve a five coordinate intermediate (or transition state) [26]. We tried to get spectral evidence of five-coordinated species in solutions of VIc with an added π-acceptor ligand (PPh_3 or CH_2=CHCN):

1. With PPh_3: $CHClF_2$ was distilled into an NMR tube containing VIc and PPh_3 (molar ratio 1/1) in CD_2Cl_2. A clear solution was obtained by warming to —40°C. Its $^{31}P\{^1H\}$ NMR spectrum indicated that a fast exchange of phosphine was taking place at that temperature. However, a comparison of its spectrum at —130°C with that of VIc revealed the presence of a new complex (Fig. 2). Knowing the total concentration of platinum (c_M = 0.0634 *M*) and of PPh_3 (c_L = 0.190 *M*) and the areas of the ^{31}P signals, the concentration of uncoordinated phosphine is given by $[L]_{free} = c_L\ cs_3/(s_1 + s_2 + s_3) = 0.03\ M$ where s_1, s_2 and s_3 are the relative areas of the signals of VIc, the new species and PPh_3, respectively (the experimental ratios $s_1/s_2/s_3$ are 47/95/27). Thus, the mean number of PPh_3 groups coordinated to the metal is $\bar{n} = (c_L - [L]_{free})/c_m = 2.51$. As $\frac{1}{\bar{n}} = \frac{s_1}{2(s_1 + s_2)} + \frac{s_2}{x(s_1 + s_2)} = 0.4$, the number x of coordinated PPh_3

groups in the new species was found to be 2.9 ± 0.2. The ^{1}H NMR spectrum of the same solution at −80°C presents in the hydride region a single sharp resonance with two satellites due to $^{1}J(PtH)$. The loss of the ^{31}P—^{1}H coupling indicates a rapid exchange of phosphine. On lowering the temperature to −110°C, the sharp resonance at −4.5 ppm corresponding to the hydride of VIc (cf. Table 1) broadens and undergoes an upfield shift to −6.3 ppm. (It was not possible to block the exchange of PPh_3 by further lowering of the temperature as VIc is insoluble in pure $CHClF_2$.) If VIc were the sole species exchanging with free PPh_3, the resonance of the hydride would maintain a constant chemical shift on lowering of the temperature. As this is not the case, we conclude that the new species observed in the ^{31}P NMR spectrum contains a Pt—H bond in addition to three magnetically equivalent PPh_3 groups, and exchanges with free PPh_3 in equilibrium 2.

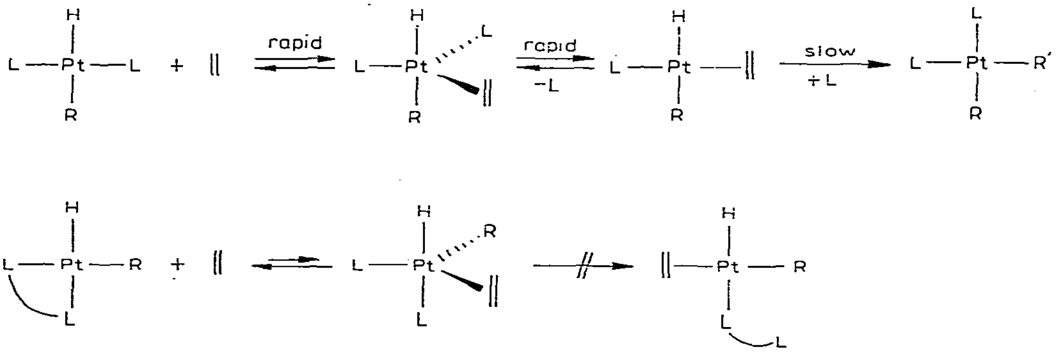


(2)

$K = 70 \pm 10\ M^{-1}$ (at −130°C)

The choice of an axial position of the trigonal bipyramid for the hydride is also in accord with observations made by Jesson et al. [27] for the system HML_3^+/L (M = Ni, Pd, Pt; L = PEt_3), and by Tolman et al. [28] for $HNiL_3CN$ (L = PR_3, $P(OR)_3$).

2. With CH_2=CHCN: addition of acrylonitrile to a solution of VIc in CD_2Cl_2 at −70°C (molar ratio 5/1) causes a broadening of the ^{31}P signals of VIc, suggesting an exchange process of phosphine. (At this temperature, reaction 1 itself is too slow for XIc to be formed in any significant amount in the time of measurement.) However, the ^{31}P NMR spectrum of a solution of VIc and acrylonitrile (molar ratio 1/1) in $CD_2Cl_2/CHClF_2$ at −120°C did not show any signals attributable to the substitution product $PtH(C_3H_6CN)(CH_2{=}CHCN)(PPh_3)$. If the substitution of PPh_3 by acrylonitrile takes place in a fast preequilibrium prior to the rate-determining step of the insertion, an excess of PPh_3 should decrease the rate of the reaction. By monitoring reaction 1 by ^{31}P NMR in two solutions containing VIc + CH_2=CHCN (1/10) and VIc + CH_2=CHCN + PPh_3 (1/10/2), we found that the rate constant was, indeed, smaller in the presence of added PPh_3. Scheme 2 takes into account the preceding observations.



The cis hydrido complexes VIIc or VIIIc, which contain a bidentate diphosphine, did not react with olefins under the conditions used for VIc or under more drastic conditions. In Scheme 2, the formation of the five-coordinated intermediate (or transition state) would indeed be disfavoured, as the metal—carbon bond tends to be in an axial position [28] and that of the four-coordinated substitution product would be entropically disfavoured as one tooth of the bidentate ligand has to become loose.

Experimental

The spectroscopic techniques were described earlier [18]; W. Manser (Mikrolabor ETH, Zürich) and the Institute of Organic Chemistry (University of Padua) carried out the microanalyses. References for the preparation of complexes reported earlier are given in Scheme 1.

Preparation of complexes

trans-PtCl(C_2H_4CN)(PPh_3)$_2$ (IIb). AgCl (2.7 g) was added to a solution of *trans*-PtBr(C_2H_4CN)(PPh_3)$_2$ (3.0 g) [18] in dichloromethane/acetone (4/1, 80 ml) and the suspension stirred at room temperature for 24 h. The excess of AgCl and the AgBr were filtered off and the solution concentrated to 20 ml. The white complex was precipitated by adding ethanol, and recrystallized from dichloromethane/ether. Yield 92%.

PtBr(C_2H_4CN)($Ph_2PCH=CHPPh_2$) (IIb) and PtBr(C_2H_4CN)($Ph_2PC_2H_4PPh_2$) (IIIb). *cis*-Bis(diphenylphosphino)ethene (1.4 g) or 1,2-bis(diphenylphosphino)ethane (0.9 g) was added in small portions to warm solution of *trans*-PtBr(C_2H_4CN)(PPh_3)$_2$ (2.0 and 1.7 g, respectively) in benzene (30 ml), and the solution stirred at 50°C for 30 min. After cooling, diethyl ether (100 ml) was added and the suspension stirred overnight. The solid product was filtered off and redissolved in dichloromethane; a small quantity of $PtBr_2$(L—L) formed remained insoluble and was filtered off. The volume of the filtrate was reduced to 50% and methanol added. The rest of dichloromethane was slowly distilled off and the methanolic suspension filtered to leave a white powder. Yields 88 and 85%, respectively.

PtBr(n-C_3H_6CN)($Ph_2PCH=CHPPh_2$) (IIc), PtBr(n-C_3H_6CN)($Ph_2PC_2H_4PPh_2$) (IIIc) and PtCl(o-$CH_2C_6H_4CN$)($Ph_2PC_2H_4PPh_2$) (IIId). The same method was used but with the following starting materials; IIc and IIIc: *trans*-PtBr(n-C_3H_6CN)(PPh_3)$_2$ [18] (2 and 1.7 g, respectively) and *cis*-$Ph_2PCH=CHPPh_2$ (1.4 g) or $Ph_2PC_2H_4PPh_2$ (0.94 g) in benzene (20 ml, 50°C, 30 min and 50 ml, 25°C, 18 h, respectively). Yields 86 and 88%. IIId: *trans*-PtCl(*o*-$CH_2C_6H_4CN$)(PPh_3)$_2$ [19] (0.9 g) and $Ph_2PC_2H_4PPh_2$ (0.5 g) in benzene (20 ml, 50°C, 40 min). Yield 82%. For PtCl(*o*-$CH_2C_6H_4CN$)($Ph_2PCH=CHPPh_2$) (IId), see [19].

trans-PtH(C_2H_4CN)(PPh_3)$_2$ (VIb). A solution of $NaBH_4$ (0.3 g) in ethanol (60 ml) was added over a period of 12 h to a stirred solution of *trans*-PtCl(C_2H_4CN)(PPh_3)$_2$ [19] in dichloromethane (30 ml) at −10°C. The mixture was kept overnight at −25°C and dichloromethane was then distilled off under vacuum (15 Torr). The white product was precipitated from the ethanolic solution by adding water, and recrystallized from dichloromethane/ether. Yield 35%.

trans-PtH(n-C_3H_6CN)(PPh_3)$_2$ (VIc). A solution of NaOH (0.4 g) in methanol (5 ml) was added to a suspension of *trans*-[Pt(n-C_3H_6CN)(PPh_3)$_2$]$_m$(BF_4)$_m$ (1 g) [18] in methanol (50 ml) and the mixture stirred at 50°C for 90 min. The white product slowly precipitated. The crude complex was filtered off after reduction of the volume of methanol by 50%, and was washed thoroughly with water then with methanol, and recrystallized from dichloromethane/methanol. Yield 70%. Upon monitoring the reaction by IR, we noticed that an hydroxo complex was formed before the hydride [16].

PtH(C_2H_4CN)($Ph_2PCH=CHPPh_2$) (VIIb), PtH(C_2H_4CN)($Ph_2PC_2H_4PPh_2$) (VIIIb), PtH(n-C_3H_6CN)($Ph_2PCH=CHPPh_2$) (VIIc), PtH(n-C_3H_6CN)($Ph_2PC_2H_4PPh_2$) (VIIIc), PtH(o-$CH_2C_6H_4CN$)($Ph_2PCH=CHPPh_2$) (VIId) and PtH(o-$CH_2C_6H_4CN$)($Ph_2PC_2H_4$-PPh_2) (VIIId). A typical procedure is given for VIIIb: a solution of $NaBH_4$ (0.08 g) in ethanol (50 ml) was added during 40 min to a solution of PtBr(C_2H_4CN)-($Ph_2PC_2H_4PPh_2$) (0.36 g) in ethanol (100 ml), which turned pale yellow. Water (3 ml) was added and ethanol distilled off until the hydride began to precipitate; the temperature being kept below 30°C. The suspension was stirred for 30 min in an ice bath then filtered, and the white hydrido complex recrystallized from dichloromethane/methanol. In the case of VIIId, the ethanolic solution was heated at 50°C for 10 min before adding water. Yields between 30% (VIIIb) and 70% (VIIId).

cis-Pt(CH_2CN)(C_2H_5)(PPh_3)$_2$ (Xa) and cis-Pt(n-C_3H_6CN)(C_2H_5)(PPh_3)$_2$ (Xc). A Pyrex test tube containing a solution of *trans*-PtH(CH_2CN)(PPh_3)$_2$ (1.2 g VIa [16]) or *trans*-PtH(n-C_3H_6CN)(PPh_3)$_2$ (1.7 g VIc) in THF (15 and 30 ml, respectively) was introduced into a stainless steel autoclave and the solution stirred under ethylene (25 atm) at room temperature for 20 h. Xa: the suspension of product formed was concentrated to 8 ml and methanol added to complete precipitation. The white dialkyl complex was filtered and recrystallized from dichloromethane/methanol. Yield 66%. Xc: the solution turned pale yellow and was concentrated to 6 ml. Diethyl ether (40 ml) was added and the suspension of product kept overnight at —25°C. Filtration yielded 0.89 g of dialkyl complex. A second crop of product (0.39 g) was obtained by adding pentane to the filtrate. Yield 80%. VIb was found to react in the same way with ethylene. No elimination products (alkanes or cyanoalkanes) were found on analysing the reaction mixture by GLC.

cis-Pt(CH_2CN)(C_2H_4CN)(PPh_3)$_2$ (XIa) and cis-Pt(n-C_3H_6CN)(C_2H_4CN)(PPh_3)$_2$ (XIc). A solution of *trans*-PtH(CH_2CN)(PPh_3)$_2$ (0.15 g) or *trans*-PtH(n-C_3H_6CN)-(PPh_3)$_2$ (0.5 g) and acrylonitrile (0.4 g) in benzene (6 and 15 ml, respectively) was stirred at 50°C for 15 h under nitrogen. The volume of the solution was reduced to 50% and methanol added. The bis(cyanoalkyl) complex started to crystallize on scratching the wall of the Pyrex flask with a glass rod, and was recrystallized from benzene/methanol. Yields 75 and 66%, respectively.

cis-Pt(CH_2CN)(C_7H_8)(PPh_3)$_2$ (XIIa). A suspension of *trans*-PtH(CH_2CN)-(PPh_3)$_2$ (0.3 g) in norbornadiene (10 ml) was stirred at 70°C for 3 h under nitrogen. The suspension was filtered and the beige product redissolved in dichloromethane and treated with active carbon. The filtrate was evaporated to dryness and the residue was recrystallized from dichloromethane/methanol as colorless needles. Yield 90%.

cis-Pt(CH_2CN)($CH_2CH=CH_2$)(PPh_3)$_2$ (XIIIa). A solution of *trans*-PtH(CH_2CN)-

$(PPh_3)_2$ (0.2 g) in 1,2-dichloroethane (5 ml) was stirred under an atmosphere of allene at 60°C for 4 h. The white product was precipitated by adding n-hexane, filtered off and washed with n-hexane. Yield 62%.

The *cis*-hydrido complexes VIIa, VIIc and VIIIa, VIIIc did not react with ethylene or other olefins under similar or more drastic conditions.

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