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METHYL- AND PHENYL-BIS(TERTIARY PHOSPHINE) *N*-BONDED CARBOXAMIDO COMPLEXES OF PLATINUM(II)

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Summary

Methyl- or phenyl-*N*-carboxamido-complexes of platinum(II) $Pt(NHCOR')RL_2$ ($L = PEt_3$, R = Me, R′ = Me, $CH{=}CH_2$; $L = PEt_3$, R = Ph, R′ = Me; $L = PMe_2Ph$, R = Ph, R′ = Me, Ph; $L = PMePh_2$, R = Ph, R′ = Me; $L = PPh_3$, R = Ph, R′ = Me) * have been prepared by the reaction of KOH with cationic nitrile complexes $[PtR(NCR')L_2]BF_4$. Thermally unstable hydrido-*N*-carboxamido-complexes could be detected spectroscopically. IR and NMR (^1H, ^{31}P) spectra of some of the complexes indicate the existence of a solvent- and temperature-dependent equilibrium between *syn*- and *anti*-isomers arising from restricted rotation about the N—C bond of the carboxamido-group. The *anti*-isomer is favoured by nonpolar solvents and by increasing bulk of L. In the complex $[PtH(NCCH{=}CH_2)(PEt_3)_2]BF_4$, IR and NMR spectra show acrylonitrile to be bound through nitrogen, not through the olefinic C=C bond.

Introduction

Monomeric hydroxoplatinum(II) complexes stabilized by tertiary phosphines catalyse homogeneously the addition of water to nitriles to give carboxamides [1—3], and it has been shown that *N*-bonded carboxamido complexes containing the moiety Pt—NHCOR′ (R′ = alkyl or aryl) are important intermediates in the catalytic cycle. Representatives of this class of compound which have been characterized include the monomeric complexes *trans*-$PtCl(NHCOPh)(PEt_3)_2$ [4], *trans*-$Pt(NHCOMe)R(PPh_3)_2$ (R = Me, C_6H_9) [1,2], Pt(NHCOMe)Me(dppe) [5] and $Pt(NHCOR')(C_6H_9)$(dppe) (R′ = Me, Ph) [2] and the dimeric complexes $[Pt(CH_2CONH)(PPh_3)_2]_2$ [6] and $[Pt(CH_2C_6H_4CONH)(PPh_3)_2]_2$ [7].

* Abbreviations: Me, methyl; Et, ethyl, Ph, phenyl; C_6H_9, 1-cyclohexenyl; dppe, 1,2-bis(diphenylphosphino)ethane; COD, 1,5-cyclooctadiene.

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We report here the preparation of a series of *N*-carboxamido-complexes containing a variety of tertiary phosphines.

Results and discussion

Treatment of *trans*-$PtClRL_2$ (R = Me, Ph; L = various tertiary phosphines) or *trans*-$PtHClL_2$ with $AgBF_4$ in the presence of a nitrile (R'CN) gives the corresponding cationic nitrile complexes *trans*-$[PtR(NCR')L_2]^+$ [8] and *trans*-$[PtH(NCR')L_2]^+$. The former can usually be isolated as hygroscopic BF_4^- salts which are stable under dry nitrogen for several hours and are very soluble in dichloromethane; the salts $[PtPh(NCMe)L_2]BF_4$ (L = PMe_2Ph, $PMePh_2$) form viscous uncrystallizable oils. Owing to their instability the corresponding hydrido cations have been less extensively studied than the phenyl and methyl analogues. However, the *p*-toluonitrile and acrylonitrile salts $[PtH(NCR')(PEt_3)_2]BF_4$ (R' = *p*-C_6H_4Me, CH_2=CH) form colourless crystals which were identified spectroscopically. In all the complexes the ν(CN) band is at higher frequency than that in the free nitrile, indicative of *N*-bonding. The olefinic proton resonances of $[PtMe(NCCH{=}CH_2)(PEt_3)_2]BF_4$ and of $[PtH(NCCH{=}CH_2)(PEt_3)_2]BF_4$ are shifted downfield with respect to free acrylonitrile, again indicative of *N*-bonding rather than η^2-olefin bonding in both cases. The same conclusion has been reached for the analogous dimethylphenylphosphine-containing cation $[PtMe(NCCH{=}CH_2)(PMe_2Ph)_2]^+$ [8]. Moreover, the magnitude of ^1J(PtH) in $[PtH(NCCH{=}CH_2)(PEt_3)_2]BF_4$ (1234 Hz) equals that in the corresponding *p*-toluonitrile species and is much larger than that reported for the ethylene complex *trans*-$[PtH(C_2H_4)(PEt_3)_2]^+$ (908 Hz) [9]. Likewise, the magnitude of $^2J(PtCH_3)$ in *trans*-$[PtMe(NCCH{=}CH_2)(PEt_3)_2]^+$ (79 Hz) is very similar to that of the corresponding acetonitrile cation and is larger than that of the ethylene cation *trans*-$[PtMe(C_2H_4)(PMe_2Ph)_2]^+$ (74.2 Hz) [10].

Reaction of the methyl- or phenyl-platinum(II) nitrile salts with aqueous KOH gives *N*-carboxamido-complexes $Pt(NHCOR')RL_2$ (L = PEt_3, R = Me, R' = Me, CH=CH_2; L = PEt_3, R = Ph, R' = Me; L = PMe_2Ph, R = Ph, R' = Me, Ph; L = $PMePh_2$, R = Ph, R' = Me; L = PPh_3, R = Ph, R' = Me) as hygroscopic, microcrystalline, white or pale cream solids. Even after recrystallization and drying in vacuo, the complexes retain ca. 0.3 mol of water as shown by ^{1}H NMR spectroscopy (see Table 2). The triethylphosphine complex $Pt(NHCOMe)Me(PEt_3)_2$ liquefies immediately on exposure to moist air and can only be obtained as a solid after recrystallization from n-pentane/isopentane. Most of the complexes decompose slowly on storage, even under nitrogen, but the benzamido-complexes appear to be stable indefinitely in air.

Reaction of the hydrido-platinum(II) nitrile salts with aqueous KOH results in decomposition, but spectroscopic evidence for unstable species $PtH(NHCOMe)(PPh_3)_2$ and $PtH(NHCOC_6H_4Me)(PEt_3)_2$ was obtained (see Experimental).

The solid state IR spectra of the new complexes show a very weak ν(NH) band in the 3300—3500 cm^{-1} region; in chloroform, two such bands are observed in some cases owing to the presence of isomers (see below). A broad, intense amide ν(C=O) band appears in the region 1578—1612 cm^{-1}, sometimes overlapping with bands due to aromatic ring vibrations. The $^{31}P\{^1H\}$ NMR spectra consist of singlets with ^{195}Pt satellites [^1J(PtP) ca. 3000 Hz] and confirm

TABLE 1

SELECTED ^{1}H NMR AND IR SPECTROSCOPIC DATA FOR [PtR(NCR')L_2]BF_4 COMPLEXES [a]

R	R'	L	^{1}H NMR		IR	
			δ_R [J(PtH), J(PH)]	$\delta_{R'}$ [J(PtH)]	ν(CN)	ν(BF)
Ph	Ph	PMe_2Ph			2250s	1060s(br)
Ph	Me	PMe_2Ph		3.03s(br)	2250s, 2130w	1060s(br)
Ph	Me	PPh_3		1.43s (6.5)	2280w, 2130w	1060s(br)
Me	Me	PEt_3	0.33 (79, 7)	2.40s (7)	2290w, 2310w	1040s(br)
Me	CH_2=CH	PEt_3	0.42 (79.7)	6.0—6.8m	2255m	1050s(br)
H	Me	PPh_3	−15.7 (1152, 12)	1.66br s	2250vw [c]	1050s(br)
H [b]	p-MeC_6H_4	PEt_3	−17.3 (1234, 14.5)	2.42s (Me), 7.38—7.70m (C_6H_4)	2235s [d]	1050s(br)
H [b]	CH_2=CH	PEt_3	−17.0 (1234, 14.5)	5.8—6.8m	nm	nm

[a] ^{1}H NMR spectra (chemical shifts in ppm, J in Hz) measured in $CDCl_3$ except where stated; IR data (cm^{-1}) refer to Nujol mulls. Abbreviations: (^{1}H NMR) br, broad; s, singlet; m, multiplet; (IR) s, strong; m, medium; w, weak; nm, not measured. [b] ^{1}H NMR spectra measured in CD_2Cl_2. [c] ν(PtH) 2270 cm^{-1} (vw). [d] ν(PtH) 2260 cm^{-1} (vw).

that all the complexes have mutually *trans*-phosphine ligands. In the case of the complexes containing PMe_2Ph or $PMePh_2$, the P—CH_3 resonances in the ^{1}H NMR spectra consist of a 1 : 2 : 1 triplet with ^{195}Pt satellites, as expected for *trans*-phosphines. The ^{1}H NMR spectra of all the complexes exhibit broad resonances in the region δ 3.1—4.5 ppm assignable to N*H* and the *N*-acetamido-complexes also show singlets in the range δ 0.9—2.1 ppm due to COCH_3. In the case of the complexes Pt(NHCOMe)PhL_2 (L = PMe_2Ph, $PMePh_2$, PEt_3) and Pt(NHCOR')Me$(PEt_3)_2$ (R' = Me, CH=CH_2), there is ^{1}H and ^{31}P NMR spectroscopic evidence for the presence of two isomers in solution, whereas Pt(NHCOMe)Ph$(PPh_3)_2$, Pt(NHCOPh)Ph$(PMe_2Ph)_2$, and the previously reported *N*-carboxamido-complexes Pt(NHCOR')(C_6H_9)(dppe) (R' = Me, Ph) [2,4] and *trans*-Pt(NHCOCH_3)R$(PPh_3)_2$ (R = Me, C_6H_9) show only one isomer. The similarity of the N*H* chemical shifts in each case, and of the COCH_3 chemical shifts in the isomers of the *N*-acetamido complexes, rules out the possibility of an amide ⇌ imino-enol tautomerism, Pt—NHCOR' ⇌ Pt—N=C(OH)R'. Moreover, no signals are observed in the region δ 9—11 ppm, where the OH resonance of imino-enol complexes of planar platinum(II) and octahedral platinum(IV) is reported to appear [11]. The isomers are therefore believed to be *anti*- and *syn*-rotamers (I and II, respectively) arising from restricted rotation about the N⁻C bond of the carboxamido group.

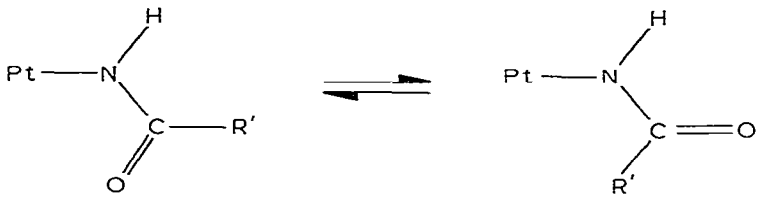
Irradiation of the ^{14}N nuclei in Pt(NHCOMe)Ph$(PMe_2Ph)_2$ enabled the ^{195}Pt satellites of the NH resonance of each isomer to be located. The similarity of the values of ^2J(PtNH) for the two isomers (ca. 16 Hz, 13 Hz) provides clear evidence against the existence of amide ⇌ imino-enol tautomerism. The isomer ratios estimated from ^{1}H or ^{31}P{^{1}H} NMR spectra vary with solvent (Table 3); in the case of Pt(NHCOMe)PhL_2 (L = PMe_2Ph, $PMePh_2$), only one isomer is observed in toluene-d_8, whereas two isomers are observed in $CDCl_3$. In all

TABLE 2

SELECTED NMR (^1H, ^{31}P) AND IR DATA FOR *N*-CARBOXAMIDO COMPLEXES OF PLATINUM(II), $Pt(NHCOR')RL_2$ [a]

Complex	NMR				IR		
	δ(R')	δ(NH)	δ(P)	^1J(PtP)	ν(C=O)	ν(NH)	
						Nujol	$CHCl_3$
$Pt(NHCOMe)Ph(PMe_2Ph)_2$ [b]	1.72(2)	3.66(2) [c]	−5.2(2)	2876	1608s	3492vw	3316vw
	1.75(1)	3.92(1) [d]	−6.7(1)	2832			3370vw
$Pt(NHCOPh)Ph(PMe_2Ph)_2$ [e]		4.55	−5.0	2874	1600s	3385vw	
$Pt(NHCOMe)Ph(PMePh_2)_2$ [f]	1.31(3)	3.30(3)	7.8(3)	3025			
	1.23(1)	3.76(1)	6.4(1)	2991	1595s	3375vw	
$Pt(NHCOMe)Ph(PPh_3)_2$	0.91	3.07 [g]	22.1	3176	1612m	3375vw	3380w
					(1600m) [h]	(3380vw) [h]	
$Pt(NHCOMe)Ph(PEt_3)_2$	2.07(4)	3.94(4)	12.9(4)	2776	1600(sh)	3315w	3412vw
					1585s		
	1.94(1)	3.67(1)	12.7(1)	2815	(1578s) [i]		3315vw
$Pt(NHCOMe)Me(PEt_3)_2$ [j]	1.90(3.5)	3.83(3.5)	15.9(3.5)	2810			3319vw
	1.91(1)	3.68(1)	14.9(1)	2847	1565s(br) [i]		3372vw
$Pt(NHCOCH{=}CH_2)Me(PEt_3)_2$ [k]	5.0–6.2	3.82(4)					
	(ABC)	3.14(1)			1578s [h]	3240w(br) [h]	

[a] Abbreviations as in Table 1. ^{31}P chemical shifts (δ(P), $CHCl_3$) are in ppm downfield (positive) of external 85% H_3PO_4. Isomer ratios ($CDCl_3$) are in parentheses. All N*H* resonances are broad singlets, all NHCO*CH*$_3$ resonances are singlets. Most spectra show a broad peak due to H_2O in the range δ 2–4 ppm, the exact chemical shift depending on solvent and temperature. Addition of D_2O causes the H_2O and NH signals to broaden and then disappear. IR data refer to Nujol mulls except where stated otherwise. [b] δ 1.46t, 1.43t (P*Me*$_2$Ph for 2 isomers in 2 : 1 ratio), ^2J(PH) + ^4J(PH) 7 Hz, ^3J(PtH) 32.8 Hz. [c] ^2J(PtNH) ca. 16 Hz. [d] ^2J(PtNH) ca. 13 Hz. [e] δ 1.51t (P*Me*$_2$Ph), ^2J(PH) + ^4J(PH) 7 Hz, ^3J(PtH) 33.4 Hz. [f] δ 1.62t, 1.54t (P*Me*Ph$_2$ for 2 isomers in 3 : 1 ratio), ^2J(PH) + ^4J(PH) 7.5 Hz, ^3J(PtH) 35.5 Hz. [g] ^2J(PtNH) ca. 13 Hz. [h] CsI disc. [i] $CHCl_3$ solution. [j] δ 0.02t [^2J(PtH) 70.5 Hz, ^3J(PH) 7.5 Hz], −0.04t [^2J(PtH) 69.5 Hz, ^3J(PH) 7.5 Hz], PtC*H*$_3$ for 2 isomers in 3.5 : 1 ratio. [k] δ 0.01t [^2J(PtH) 69 Hz, ^3J(PH) 6.5 Hz], 0.04t [^2J(PtH) 69 Hz, ^3J(PH) 6.0 Hz], PtC*H*$_3$ for 2 isomers in 4 : 1 ratio.



anti. (I) *syn.* (II)

cases, evaporation of one solvent and dissolution in another gives the isomer ratio characteristic of the second solvent, so that irreversible processes are not occurring. The predominant isomer probably has the platinum atom and the amide substituent R′ in an *anti*-orientation, since in *N,N′*-disubstituted amides the more bulky *N*-bound group tends to be *cis* to the carbonyl oxygen atom [12]. The chemical shifts of both the N*H* and COC*H*$_3$ signals also vary markedly with solvent and temperature. Similar phenomena have been reported for imidoyl complexes such as *trans*-PtCl(CH=NC$_6$H$_4$Me-*p*)(PEt$_3$)$_2$, in which the equilibrium between *syn*- and *anti*-isomers is delicately balanced and sensitive to small changes in solvation energies [13]. The appearance of only one isomer in some cases (see above), which appears to be favoured by non-polar solvents, could be attributed to rapid rotation about the N···C bond leading to a time-averaged signal. However, the fact that the complexes involved contain the bulkiest ligand suggests sterically promoted destabilization of one isomer as a more likely explanation. In the case of Pt(NHCOMe)Me(PEt$_3$)$_2$, a variable temperature NMR study, using toluene-d_8 as solvent and hexamethyldisiloxane as internal lock, showed that the N*H* and COC*H*$_3$ signals for the two rotamers coalesce at 80°C and give rise to a broad, averaged signal at 113°C. The original spectrum is observed on cooling to 30°C.

We have noted previously [3] that the chemical shifts of the NH protons in carboxamido complexes containing dppe are 3—4 ppm to lower field than those of similar complexes containing *trans*-triphenylphosphine ligands. In the series *trans*-Pt(NHCOMe)Ph(PMe$_{3-n}$Ph$_n$)$_2$ (n = 1—3), the values of δ(N*H*) and δ(COC*H*$_3$) in CDCl$_3$ for the most abundant rotamer shift linearly to higher field with

TABLE 3

NMR PARAMETERS AND ISOMER RATIOS IN DIFFERENT SOLVENTS

Complex	Solvent	δ(COC*H*$_3$)	Isomer ratio [a]
Pt(NHCOMe)Me(PEt$_3$)$_2$	cyclo-C$_6$D$_{12}$	1.81	one isomer
	C$_6$D$_5$CD$_3$	2.14, 2.24	4 : 1
	CD$_3$CN	1.83, 1.89	2.25 : 1
	CDCl$_3$	1.90, 1.91	3.5 : 1
Pt(NHCOMe)Ph(PMe$_2$Ph)$_2$	C$_6$D$_5$CD$_3$	2.10	one isomer
	CDCl$_3$	1.72, 1.75	2 : 1
Pt(NHCOMe)Ph(PMePh$_2$)$_2$	C$_6$D$_5$CD$_3$	1.27	one isomer
	CDCl$_3$	1.31, 1.23	3 : 1

[a] Estimated from ^{1}H NMR peak heights or by integration.

increasing *n* (Table 2). This correlation suggests that the N-carboxyamido ligand adopts the same configuration (presumably *anti*) in all three cases. The trend can probably be attributed to anisotropic shielding by the phenyl rings of mutually *trans*, phenyl-substituted tertiary phosphines, since a similar effect has been observed on alkyl group (R) proton resonances in octahedral iridium(III) complexes *trans*-$IrCl_2R(CO)(PPh_3)_2$ [14].

Experimental

IR spectra were measured on PE457 or 225 spectrometers calibrated with polystyrene. ^1H NMR spectra were obtained on Jeol PMX-60, Jeol MH-100 or Varian HA-100 instruments using TMS or CH_2Cl_2 as internal reference. $^{31}P\{^1H\}$ spectra were obtained on a modified Bruker 322S instrument. Microanalyses and osmometric molecular weight determinations were performed in the Microanalytical Laboratories of the Research School of Chemistry and the John Curtin School of Medical Research, The Australian National University. Spectroscopic data for the nitrile and carboxamido complexes are given in Tables 1 and 2 respectively, analytical data are in Table 4.

AR grade solvents were used without further purification. The complexes $PtHClL_2$ (L = PEt_3, PPh_3) [15] and $PtIMe(PPh_3)_2$ [16] were prepared by literature methods. Other complexes of formula *trans*-$PtClRL_2$ were prepared by displacement of 1,5-cyclooctadiene from PtClR(COD) (R = Me, Ph) [5,17] by two molar equivalents of the tertiary phosphine (L) in dichloromethane, as described previously [18].

TABLE 4

ANALYTICAL DATA AND MELTING POINTS FOR NEW PLATINUM COMPLEXES

Complex	Melting point °C	Analysis found (calcd.) (%)			
		C	H	P	N
$[PtPh(NCPh)(PMe_2Ph)_2]BF_4$	134—136(d)	47.3 (47.2)	4.1 (4.4)	8.25 (8.4)	1.7 (1.9)
$[PtPh(NCMe)(PPh_3)_2]BF_4$	196—200(d)	57.1 (57.2)	4.15 (4.1)	6.6 (6.7)	1.3 (1.5)
$Pt(NHCOMe)Ph(PMe_2Ph)_2$	107—109	47.9 (47.5)	5.1 (5.15)	10.3 (10.2)	2.15 (2.3)
$Pt(NHCOPh)Ph(PMe_2Ph)_2$	130—134	52.25 (52.1)	4.9 (5.0)	9.1 (9.3)	1.9 (2.1)
$Pt(NHCOMe)Ph(PMePh_2)_2$	160—165(d)	56.0 (55.9)	4.9 (4.8)	8.6 (8.5)	1.7 (1.9)
$Pt(NHCOMe)Ph(PPh_3)_2$ [a]	167—172(d)	62.15 (61.8)	4.8 (4.6)	7.35 (7.25)	1.5 (1.6)
$Pt(NHCOMe)Ph(PEt_3)_2$	120—125(d)	42.4 (42.4)	6.8 (6.9)	10.8 (10.9)	2.5 (2.5)
$Pt(NHCOMe)Me(PEt_3)_2$	35—38	36.5 (35.7)	7.8 (7.4)	11.7 (12.3)	
$Pt(NHCOCH{=}CH_2)Me(PEt_3)_2$	72—76(d)	37.4 (37.2)	7.2 (7.2)	11.8 (12.0)	

[a] Mol. wt. (osmometry, CH_2Cl_2, 35°C): found, 795; calcd. 855.

Preparations

(1) Nitrilebis(tertiary phosphine)phenyl- or methyl-platinum(II) tetrafluoroborates, trans-[PtR(NCR')L_2]BF_4, and N-carboxamidobis(tertiary phosphine)-phenyl- or methyl-platinum(II) complexes trans-Pt(NHCOR')RL_2. (i) A solution of PtClPh(PMe_2Ph)$_2$ (0.29 g, 0.5 mmol) in acetonitrile (3 ml) was treated with silver tetrafluoroborate (0.097 g, 0.5 mmol) dissolved in acetonitrile (1 ml). The mixture was stirred for 5 min at room temperature, then the precipitated silver chloride was filtered off and washed with dichloromethane (3 ml). Evaporation of the combined filtrate and washings to dryness gave a clear, colourless oil. Dissolution in dichloromethane (1 ml) and addition of ether gave *trans*-[PtPh(NCMe)(PMe_2Ph)$_2$]BF_4 quantitatively as an oil which foamed in vacuo and was identified by its ^{1}H NMR spectrum (Table 1).

The salt was dissolved in acetonitrile (4 ml) and was stirred for 2 h with a solution of potassium hydroxide (0.028 g, 0.5 mmol) in water (1 ml). Solvents were evaporated and the residual brown oil was dissolved in dichloromethane (3 × 2 ml), filtered through Celite and concentrated in vacuo. Addition of ether/n-pentane (1/1) precipitated some brown oily material. After cooling to 0°C, the clear supernatant liquid was decanted and further concentrated to give colourless crystals of *trans*-Pt(NHCOMe)Ph(PMe_2Ph)$_2$, which were washed with n-pentane and dried in vacuo. The yield was 0.18 g (60% based on PtClPh-(PMe_2Ph)$_2$).

The following carboxamido complexes were prepared similarly, with variations and yields based on the starting PtClRL_2 complex as indicated. (ii) *trans*-Pt-(NHCOPh)Ph(PMe_2Ph)$_2$ was prepared from PtClPh(PMe_2Ph)$_2$ in benzene/dichloromethane containing a fourfold excess of benzonitrile and was recrystallized from dichloromethane/ether/n-pentane as shiny colourless crystals (84%). The intermediate [PtPh(NCPh)(PMe_2Ph)$_2$]BF_4 formed fine colourless needles from dichloromethane/ether. (iii) *trans*-Pt(NHCOMe)Ph($PMePh_2$)$_2$ was prepared as off-white crystals (43%) as in (i). (iv) *trans*-Pt(NHCOMe)Ph(PPh_3)$_2$: colourless crystals (66%), prepared as in (i). The intermediate [PtPh(NCMe)(PPh_3)$_2$]BF_4 formed colourless crystals from dichloromethane/ether. (v) *trans*-PtPh(NHCOMe)-(PEt_3)$_2$. The crude product from dichloromethane, prepared as in (i), was kept at 30°C/10^{-5} mm to remove acetamide. It was redissolved in dichloromethane and n-pentane was added to the solution to precipitate some coloured impurity. Evaporation of the decanted supernantant liquid gave the product as shiny, colourless crystals (67%). (vi) *trans*-Pt(NHCOMe)Me(PEt_3)$_2$ was prepared as in (i). The crude product was extracted with ether/isopentane (1/10) and the extract was evaporated to dryness to afford a turbid oil which slowly crystallized in vacuo. Recrystallization from n-pentane/isopentane at −40°C gave waxy colourless crystals (ca. 70% yield) which liquefied immediately in moist air. (vii) *trans*-Pt(NHCOCH=CH_2)Me(PEt_3)$_2$ was prepared as in (i), using acrylonitrile as solvent for the first step and dichloromethane for the reaction with KOH. The yellow oil obtained after removal of dichloromethane was taken up in the minimum volume of ether. Isopentane was added to precipitate some coloured oil. The supernantant liquid was decanted and treated with more isopentane to precipitate more oil. Finally, a colourless solution was obtained which, on concentration and cooling to −20°C, gave pale yellow crystals of the product (26%).

(2) Attempted preparation of PtH(NHCOMe)(PPh_3)$_2$. The salt [PtH(NCMe)-

$(PPh_3)_2]BF_4$, prepared from $PtHCl(PPh_3)_2$ and $AgBF_4$ as in (1) (i), was treated with an equimolar quantity of aqueous KOH. The dark oil obtained after removal of solvents gave a pale cream solid after recrystallization from dichloromethane/n-hexane at −20°C; its IR spectrum showed bands at 2192w cm^{-1} due to ν(PtH) and at 3380vw and 1580m(br) cm^{-1} due to Pt—$NHCOCH_3$, but rapid decomposition prevented analytical or ^1H NMR spectroscopic characterization.

(3) Attempted preparation of $PtH(NHCOC_6H_4Me\text{-}p)(PEt_3)_2$. Treatment of $PtHCl(PEt_3)_2$ with $AgBF_4$ in acetone containing a 50% excess of *p*-toluonitrile gave colourless crystals of *trans*-$[PtH(NCC_6H_4Me\text{-}p)(PEt_3)_2]BF_4$ from ether/n-pentane, which were identified by IR and ^1H NMR spectra (Table 1). Reaction of this salt, dissolved in dichloromethane, with aqueous KOH at 0°C gave an inseparable mixture of unstable products. The dichloromethane was evaporated at low temperature and the solid residue was redissolved in $CDCl_3$. The ^1H NMR spectrum showed peaks at δ (ppm) −14.8 (br s, PtH), 2.3 (s, $C_6H_4CH_3$) and 5.0 (br s, NH) which may be due to $PtH(NHCOC_6H_4Me\text{-}p)(PEt_3)_2$.

(4) Acrylonitrilebis(triethylphosphine)hydridoplatinum(II) tetrafluoroborate, trans-[PtH(NCCH=CH$_2$)(PEt$_3$)$_2$]BF$_4$. Silver tetrafluoroborate (0.049 g, 0.25 mmol) was added to a solution of $PtHCl(PEt_3)_2$ (0.117 g, 0.25 mmol) in acrylonitrile (2 ml). After removal of AgCl by filtration, the solvent was evaporated to yield a colourless oily solid. Trituration with n-pentane (1 ml) containing a few drops of ether gave colourless crystals of the product which were stable under nitrogen for several hours and were identified by their ^1H NMR and IR spectra (Table 1).

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