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ALKOXO AND HYDROXO COMPLEXES OF PLATINUM(II). NOVEL INSERTION REACTIONS INTO PLATINUM—OXYGEN BONDS AND CONDENSATIONS WITH COMPOUNDS CONTAINING ACTIVE HYDROGEN ATOMS

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Summary

Hydroxo and alkoxo alkyl complexes of the general formula *cis*- and *trans*-$Pt(OR)(R_x)L_2$ (R = H, CH_3; R_x = CH_2CN, CF_3, CH_2CF_3; L_2 = 2 PPh_3, diphosphine) were prepared by metathesis of $PtCl(R_x)L_2$ or $[Pt(R_x)L_2]BF_4$ with NaOR. The platinum—oxygen bonds undergo facile insertion of CO, COS, CS_2 and SO_2. The hydroxo complexes react with a variety of acids, including fairly weak carbon or nitrogen acids, such as phenylacetylene, acetamide and methylaniline, to give the corresponding condensation complexes.

Introduction

Only a limited number of transition d^8 metal complexes containing metal—oxygen bonds have been reported, at least in the case of monodentate ligands, probably owing to the "hard" character of oxygen. These complexes doubtless play an important role as intermediates in synthetic reactions, particularly in some catalytic processes, viz. hydration of nitriles [1], oxidation of ethylene [2] and alcohols [3].

Much work in this area has been carried out on platinum(II) and palladium(II) complexes. In particular, two outstanding observations have been made in studies on these complexes. Firstly, small molecules such as CO [4,5], SO_2 [6], isocyanides [7] and CO_2 [8] insert into metal—oxygen bonds, M—OH or M—OR, forming stable hydroxy- or alkoxy-carbonyl, -sulfonyl, carbamoyl or alkoxy-

imidoyl, and carbonato complexes. Secondly, condensation reactions of the strongly basic hydroxo complexes with organic compounds containing active hydrogen atoms may occur [9—12].

In order to elucidate the factors governing the stability and nature of the σ-M—OR bonds (R = H, CH_3), a series of square-planar complexes, *cis*- and *trans*-$Pt(OR)(R_x)L_2$ (R = H, CH_3; R_x = CH_2CN, CF_3, CH_2CF_3; L_2 = 2 PPh_3, diphosphine) has been prepared. This paper describes the preparation and spectral features of some novel hydroxo and methoxo organoplatinum complexes, and the insertions of CO, COS, CS_2 and SO_2 into the Pt—O bonds. Some condensation reactions are also described between hydroxo complexes and inorganic or organic acids, including fairly weak nitrogen or carbon acids such as HBF_4, thiophenol, hydrogen sulfide, acetamide, phenylacetylene and methylaniline.

Results and discussion

Synthesis and spectroscopic properties of methoxo and hydroxo complexes

The methoxo—platinum(II) complexes $Pt(OCH_3)(R_x)L_2$ (L_2 = *cis*-Ph_2PCH=$CHPPh_2$: Ia, R_x = CH_2CN, Id, R_x = CF_3; Ie, L_2 = 2 PPh_3, R_x = CF_3) were prepared by metathesis reactions of $PtCl(R_x)L_2$ with $NaOCH_3$, as previously reported [11,12]. These reactions proceed readily at or slightly above room temperature in an anhydrous benzene/methanol mixture, to give colourless products in high yields. Sometimes small amounts of the hydroxo complexes $Pt(OH)(R_x)L_2$ are formed probably by the facile hydrolysis of the corresponding methoxo complexes. The success in preparing $Pt(OCH_3)(R_x)L_2$ complexes seems to be related to the nature of the alkyl ligand R_x: a more electronegative R_x will increase the effective positive charge on the metal, and consequently the electron density on the OCH_3 group will decrease, increasing the covalency of the Pt—OCH_3 bond. The complexes Ia, Id, Ie are thermally stable and can be stored for a long time under nitrogen. In benzene solution prolonged heating does not yield the corresponding well known hydrido complexes $PtH(R_x)L_2$ [13,14] by β-hydrogen abstraction from the methoxo ligand. The infrared spectra (Table 1) of the methoxo complexes show a strong band at ca. 1060 cm^{-1} due to ν(O—CH_3). In the ^1H NMR spectra the methoxy protons appear as a singlet at δ 2.0 for *trans*-$Pt(OCH_3)(CF_3)(PPh_3)_2$ (Ie) and as a doublet at δ 3.65 ppm for $Pt(OCH_3)(CF_3)(Ph_2PCH$=$CHPPh_2)$ (Id). In the analogous cyanomethyl derivatives $Pt(OCH_3)(CH_2CN)(Ph_2PCH$=$CHPPh_2)$ (Ia), however, the doublet is split into an additional doublet, ^4J(PPtOCH) 1.0 Hz (*cis*) and 5.9 Hz (*trans*). This pattern confirms that a negligibly small coupling occurs with the *cis*-phosphorus atom, while the strong coupling observed is due to the *trans*-phosphorus atom in bisphosphine methoxo complexes of platinum(II) [9,11,12]. The *cis* or *trans* configuration of these complexes is confirmed by the resonance patterns shown by the CH_2CN and CF_3 ligands in their ^1H and ^{19}F NMR spectra, respectively: complexes Ia and Id display the usual doublet of doublets, whereas Ie shows a triplet, all with ^{195}Pt satellites.

The methoxo complexes Ia, Id, Ie can be converted into the corresponding hydroxo complexes by hydrolysis with water; however the latter were prepared more conveniently by treating the dimeric $[Pt(CH_2CN)L_2]_2(BF_4)_2$ or the solvato $[Pt(S)(R_x)L_2](BF_4)$ cationic complexes, which are obtained by treating

the parent chlorides $PtCl(R_x)L_2$ (R_x = CH_2CN, CF_3, CH_2CF_3) with $AgBF_4$ in dichloromethane with aqueous KOH. The following hydroxo complexes were prepared by this general procedure: $Pt(OH)(CH_2CN)L_2$ (IIa, L_2 = Ph_2PCH=$CHPPh_2$ [12]; IIb, L_2 = $Ph_2PCH_2CH_2PPh_2$; IIc, L_2 = $Ph_2P(CH_2)_3PPh_2$)$Pt(OH)(CF_3)L_2$ (IId, L_2 = Ph_2PCH=$CHPPh_2$; IIe, L_2 = 2 PPh_3, IIf, L_2 = 2 PPh_2Me) and *cis*-$Pt(OH)(CH_2CF_3)(PPh_3)_2$ (IIg). A similar reaction of *cis*-$PtCl(CH_2NO_2)(PPh_3)_2$ did not give the expected hydroxo complexes, but an uncharacterized pale-yellow product, whose IR and ^1H NMR spectra do not show the typical bands of the nitro group and the resonances of nitromethyl protons; a strong absorption at 2230 cm^{-1} in their IR spectrum suggests the formation of a fulminato derivative by loss of water from the CH_2NO_2 ligand [15].

The hydroxo complexes IIa—IIg are white crystalline solids, which are more stable in air than the corresponding methoxo complexes. The trifluoromethyl derivatives IId—IIf are particularly stable, and can be stored in air for several weeks. The *trans* geometry of IIe and IIf is deduced from their NMR spectra: a triplet for both OH and CF_3 resonances due to coupling with two equivalent phosphorus nuclei. Additional evidence for the *trans* configuration of IIe was provided by the $^{31}P\{^1H\}$ FT NMR spectrum which showed a quartet centered at δ 25.8 ppm, with ^{195}Pt satellites, ^1J(PtP) 3202 Hz. This quartet is due to coupling of the two equivalent PPh_3 in *trans* position with the three fluorine atoms of CF_3 (^3J(FCPtP) 17.0 Hz, as also found in its ^{19}F NMR spectrum). All the other hydroxo complexes have a *cis* geometry: the CH_2CN and the CF_3 resonances show the usual doublet of doublets; the smaller coupling constant ^3J(PPtCH) or ^3J(PPtCF) is due to the phosphorus atom *trans* to the CH_2CN or CF_3 ligands, since these groups have a very high *trans* influence despite their strong electronegativity [14,16,17]. In the ^1H NMR spectra of hydroxo complexes with *cis* configurations we were unable to detect a proton signal in the range δ +5 to —5, perhaps because of hydrogen-bonding association. Only the OH resonance of IIg could be located at δ 0.53 ppm, but it appears unexpectedly as a triplet. The IR spectra of the hydroxo complexes (Table 1) show ν(O—H) in the 3625—3600 cm^{-1} region. This band is broad and weak in Nujol mulls, but sharp and of medium intensity in dichloromethane solution.

Insertion reactions into Pt—OR and Pt—OH bonds

Alkoxycarbonyl complexes of palladium (Pd—COOR) have been postulated as intermediates in carbonylation reactions of alcohols [18] and also in certain palladium(II) catalyzed carbonylations of olefins in the presence of alcohols [19]. Stabilization of the alkoxocarbonyl ligand by phosphines (L) has been accomplished in the synthesis of complexes of type $MX(COOR)L_2$ (M = Pd, Pt), by various methods [20,21]. However, a widely employed procedure involves nucleophilic attack of ROH or RO^- on the metal carbonyl species [22—24]. Recently, Bennett and Yoshida [9] have reported the preparation of $Pt(COOCH_3)(C_6H_9)(Ph_2PCH_2CH_2PPh_2)$ via CO insertion into the Pt—OCH_3 bond.

In order to gain more information on the nature of the Pt—O bond, we have examined the insertion reactions with isocyanides [7], and with CO, COS, CS_2 and SO_2 (vide infra).

The methoxo complexes Ia, Id, Ie suspended in benzene react with CO under ambient conditions to give the methoxycarbonyl derivatives $Pt(COOCH_3)(R_x)$-

(Continued on p. 244)

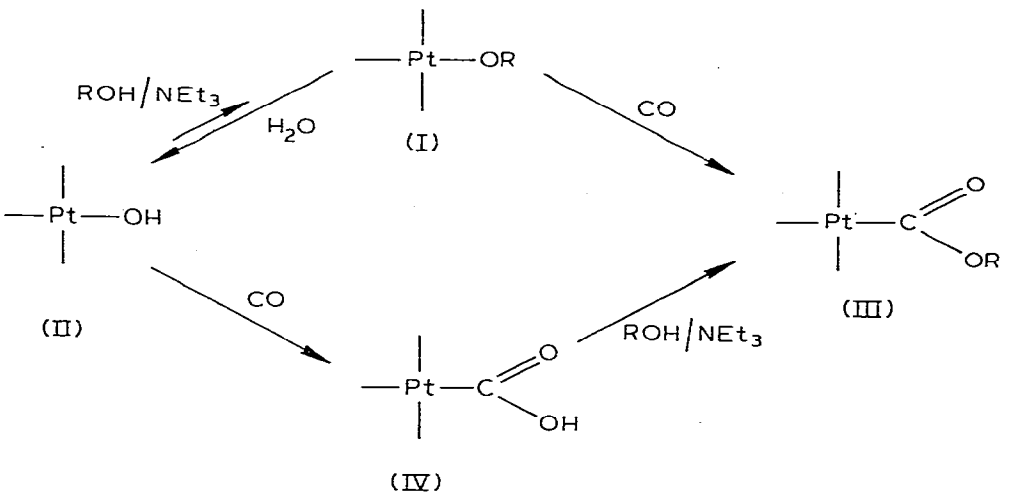
TABLE 1

SELECTED IR AND NMR SPECTROSCOPIC DATA FOR METHOXO AND HYDROXO COMPLEXES

Complex		IR (cm^{-1} ± 3) [a]	^1H [b] and ^{19}F [c] NMR (δ in ppm, J in Hz)
Ia	$Pt(OCH_3)(CH_2CN)(Ph_2PCH{=}CHPPh_2)$	1062s, $\nu(O{-}CH_3)$ 2200s, $\nu(C{\equiv}N)$	$\delta(OCH_3)$ 3.76(dd); $^3J(PtOCH)$ 44.1; $^4J(PPtOCH)$ 1.0(*cis*), 5.9(*trans*) $\delta(CH_2CN)$ 1.61(dd); $^2J(PtCH)$ 78.5; $^3J(PPtCH)$ 4.2(*cis*), 9.9(*trans*)
Id	$Pt(OCH_3)(CF_3)(Ph_2PCH{=}CHPPh_2)$	1055s, $\nu(O{-}CH_3)$	$\delta(OCH_3)$ [d] 3.65(d); $^3J(PtOCH)$ 48.5; $^4J(PPtOCH)$ 7.0 $\delta(CF_3)$ −27.9(dd); $^2J(PtCF)$ 603; $^3J(PPtCF)$ 9(*cis*), 58(*trans*)
Ie	*trans*-$Pt(OCH_3)(CF_3)(PPh_3)_2$	1065s, $\nu(O{-}CH_3)$	$\delta(OCH_3)$ [d] 2.0(s); $^3J(PtOCH)$ 19.7 [e]
IIa	$Pt(OH)(CH_2CN)(Ph_2PCH{=}CHPPh_2)$ [f]	2205s, $\nu(C{\equiv}N)$ 3600m, $\nu(O{-}H)$	$\delta(CH_2CN)$ 1.62(dd); $^2J(PtCH)$ 79; $^3J(PPtCH)$ 4(*cis*), 10(*trans*) [g]
IIb	$Pt(OH)(CH_2CN)(Ph_2PCH_2CH_2PPh_2)$	2196s, $\nu(C{\equiv}N)$ 3599w, $\nu(O{-}H)$	$\delta(CH_2CN)$ 1.41(dd); $^2J(PtCH)$ 77.8; $^3J(PPtCH)$ 3.9(*cis*), 9.8(*trans*) $\delta(CH_2P)$ 2.0–2.8 broad multiplet [g]
IIc	$Pt(OH)(CH_2CN)[Ph_2P(CH_2)_3PPh_2]$	2202s, $\nu(C{\equiv}N)$ 3602w, $\nu(O{-}H)$	$\delta(CH_2CN)$ 1.18(dd); $^2J(PtCH)$ 77.6; $^3J(PPtCH)$ 4.5(*cis*), 9.7(*trans*) $\delta(CH_2)_3$ 1.8–2.9 broad multiplet [g]
IId	$Pt(OH)(CF_3)(Ph_2PCH{=}CHPPh_2)$	3626w, $\nu(O{-}H)$	$\delta(CF_3)$ −28.0(dd); $^2J(PtCF)$ 601; $^3J(PPtCF)$ 9.9(*cis*), 57(*trans*) [g]
IIe	*trans*-$Pt(OH)(CF_3)(PPh_3)_2$	3625w, $\nu(O{-}H)$	$\delta(OH)$ −1.97(t); $^2J(PtOH)$ 21.0; $^3J(PPtOH)$ 4.2 $\delta(CF_3)$ −8.72(t); $^2J(PtCF)$ 578; $^3J(PPtCF)$ 17.0
IIf	*trans*-$Pt(OH)(CF_3)(PPh_2Me)_2$	3602w, $\nu(O{-}H)$	$\delta(OH)$ 1.23(t); $^2J(PtOH)$ 35.0; $^3J(PPtOH)$ 6.9 $\delta(CH_3P)$ 2.05(t); $^3J(PtPCH)$ 31.0; $^2J(PCH) + {}^4J(PPtPCH)$ 6.0 $\delta(CF_3)$ −9.25(t); $^2J(PtCF)$ 629; $^3J(PPtCF)$ 16.3
IIg	*cis*-$Pt(OH)(CH_2CF_3)(PPh_3)_2$	3610w, $\nu(O{-}H)$ [h] 552s [i]	$\delta(OH)$ 0.53(t(br)); $^2J(PtOH)$ ~38; $^3J(PPtOH)$ ~5.5 $\delta(CH_2CF_3)$ 1.60(qdd); $^2J(PtCH)$ 74; $^3J(PPtCH)$ 5.3(*cis*), 8.2(*trans*); $^3J(HCCF)$ 15.9 $\delta(CH_2CF_3)$ −50.56(dt); $^3J(PtCCF)$ 149; $^4J(PPtCCF)$ 15.2(*trans*), <1(*cis*); $^3J(HCCF)$ 15.9

[a] IR spectra measured as Nujol mulls; all trifluoromethyl complexes showed strong bands due to $\nu(CF_3)$ in the 1115–1085 and 1030–975 cm^{-1} regions, partly overlapped with phosphine absorptions. [b] Measured at room temperature in CD_2Cl_2, unless stated otherwise; s, singlet; d, doublet; t, triplet; q, quartet; (br), broad. [c] ^{19}F NMR data in CH_2Cl_2, at room temperature; negative values of chemical shifts, $\delta(CF_3)$, indicate a shift upfield referred to $CFCl_3$ (internal reference). [d] In $CDCl_3$. [e] Too insoluble in CH_2Cl_2 or $CHCl_3$ for ^{19}F NMR. [f] IR and NMR data from ref. [12]. [g] OH resonance could not be located. [h] The IR shows strong bands at 1245, 1237, 1042 and 1005 cm^{-1} due to CH_2CF_3 ligand. [i] The presence of this band around 550 cm^{-1} is indicative of a *cis* geometry for isomers $Pt(PPh_3)_2XY$, according to Mastin's identification method [30].

SCHEME 1



SCHEME 2

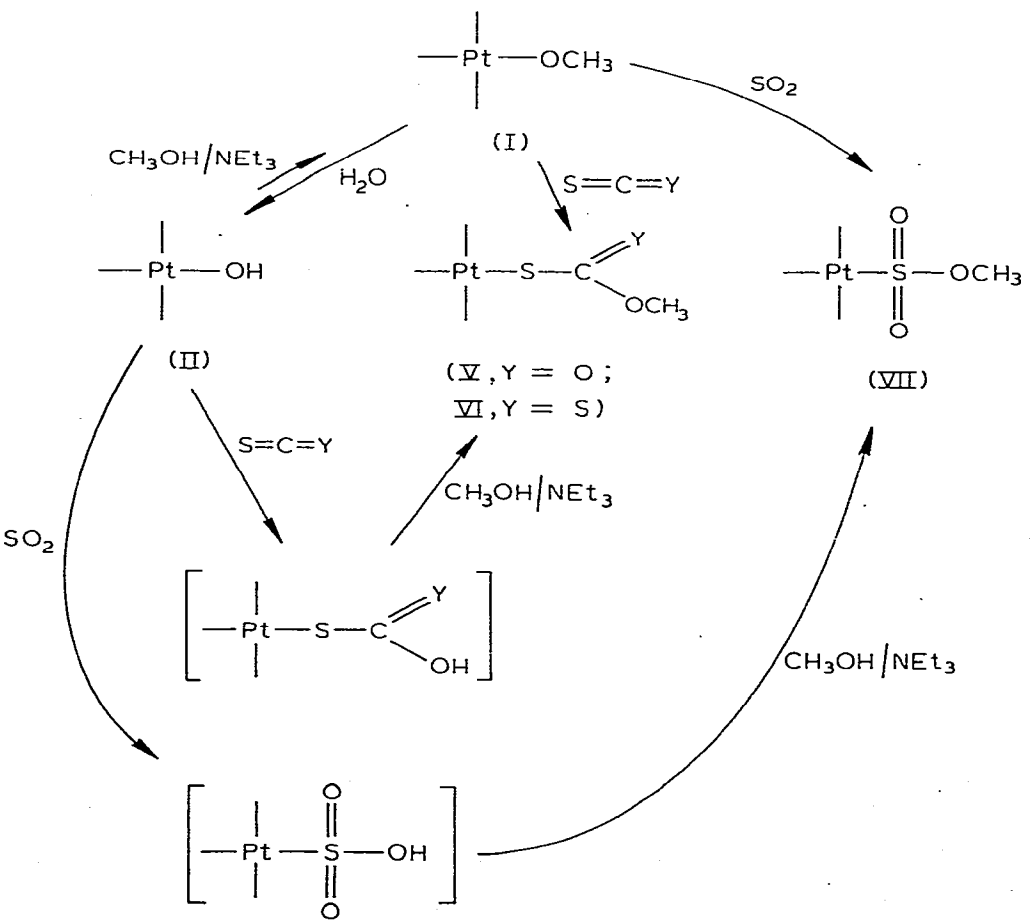


TABLE 2

SPECTRAL DATA FOR INSERTION REACTION PRODUCTS OF CO, COS, CS_2 AND SO_2 INTO Pt–O BONDS

	Complex	IR (cm^{-1} ± 3) [a]
IIIa	$Pt(COOCH_3)(CH_2CN)(Ph_2PCH{=}CHPPh_2)$	2203s, ν(C≡N): 1639vs, ν(C=O); 1045vs, ν(C–OC)
IIIb	$Pt[(COOCH(CH_3)_2](CH_2CN)(Ph_2PCH{=}CHPPh_2)$	2204s, ν(C≡N): 1633vs, ν(C=O); 1040vs, ν(C–OC)
IIIc	$Pt[COOC(CH_3)_3](CH_2CN)(Ph_2PCH{=}CHPPh_2)$	2208s, ν(C≡N): 1638vs, ν(C=O); 1052vs, ν(C–OC)
IIId	$Pt(COOCH_3)(CF_3)(Ph_2PCH{=}CHPPh_2)$	1657vs, 1643vs, ν(C=O) 1055vs, ν(C–OC)
IIIe	*trans*-$Pt(COOCH_3)(CF_3)(PPh_3)_2$	1655s, 1632vs, ν(C=O) 1053s, ν(C–OC)
IVa	$Pt(COOH)(CH_2CN)(Ph_2PCH{=}CHPPh_2)$	2680w, ν(O–H) [f]; 2203m, ν(C≡N) 1604vs, ν(C=O); 1148s, ν(C–OH)
IVd	$Pt(COOH)(CF_3)(Ph_2PCH{=}CHPPh_2)$	2685w, ν(O–H) [f]; 1610vs, ν(C=O) 1170m, 1155w, ν(C–OH)
Va	$Pt(SCOOCH_3)(CH_2CN)(Ph_2PCH{=}CHPPh_2)$	2205s, ν(C≡N) 1655vs, ν(C=O); 1110vs(br), ν(C–OC)
Vd	$Pt(SCOOCH_3)(CF_3)(Ph_2PCH{=}CHPPh_2)$	1655vs, ν(C=O); 1130s, ν(C–OC)
VIa	$Pt(SCSOCH_3)(CH_2CN)(Ph_2CH{=}CHPPh_2)$	2205s, ν(C≡N) 1196s, 1133s, 1057s, CS_2OCH_3 group
VId	$Pt(SCSOCH_3)(CF_3)(Ph_2PCH{=}CHPPh_2)$	1203s, 1147m, 1055vs, CS_2OCH_3 group
VIId	$Pt(SO_2OCH_3)(CF_3)(Ph_2PCH{=}CHPPh_2)$	1238s, $\nu_{as}(SO_2)$; 1115s, $\nu_s(SO_2)$ 605w, δ(O–S–O)

[a] IR measured as Nujol mulls, all trifluoromethyl complexes showed strong bands due to $\nu(CF_3)$ in the 1120–1090 and 1020–980 cm^{-1} regions, partly overlapped with phosphine absorptions. [b] Measured at room temperature in CD_2Cl_2, unless stated otherwise. [c] ^{19}F NMR data at room temperature; $\delta(CF_3)$ as in Table 1. [d] In $CDCl_3$. [e] ^3J-

($Ph_2PCH{=}CHPPh_2$) (IIIa, $R_x = CH_2CN$; IIId, $R_x = CF_3$) and *trans*-$Pt(COOCH_3)(CF_3)(PPh_3)_2$ (IIIe) (see Experimental, Method A). These complexes can be prepared more conveniently by reaction of CO with the corresponding hydroxo complexes suspended in methanol and treated with excess of triethylamine (Method B). By this latter procedure, which cannot be used for the preparation of unstable alkoxo complexes such as isopropoxo and t-butoxo, complexes IIIb and IIIc were prepared. These carbonylation reactions are summarized in Scheme 1. Such a scheme would indicate the two possible roles of the ROH/NEt_3 basic solution, i.e., formation of the alkoxo derivative I by equilibrium II ⇌ I, and/or esterification of the carboxylato intermediate complex IV. The path involving IV, however, seems definitely to operate in fact, the two consecutive steps can be carried out separately (see Experimental).

The hydroxo-complexes IIa and IId also undergo COS, CS_2 and SO_2 insertions readily at room temperature in $MeOH/NEt_3$ solution, producing the stable *O*-methylthiocarbonato (V), *O*-methyldithiocarbonato (VI), and methoxysulfinato (VII), compounds respectively (Scheme 2).

^1H [b] and ^{19}F [c] NMR (δ in ppm, J in Hz)

$\delta(CH_3)$ [^4J(PtCOCH)]	H: F:	$\delta(CH_2CN)$ $\delta(CF_3)$	^2J(PtCH) ^2J(PtCF)	^3J(PPtCH) ^3J(PPtCF)
3.40(s) [d] [5.8]	H:	1.89(dd)	96.6	7.2(*cis*) 9.0(*trans*)
1.02(d) [d] [e]	H:	1.87(dd)	97.3	7.3(*cis*) 8.9(*trans*)
1.18(s)	H:	1.76(dd)	97.5	7.5(*cis*) 8.9(*trans*)
3.31(s) [6.3]	F:	−17.7(dd)	736	16(*cis*) 56(*trans*)
2.16(s) [3.3]	F:	−16.4(t)	406	12.4
—	H:	1.71(dd)	78.5	3.8(*cis*) 10.2(*trans*)
—		[g]		
3.37(s)	H:	1.83(dd)	84.0	5.7(*cis*) 9.3(*trans*)
3.26(s)	F:	−21.5(dd)	[h]	14(*cis*) 60(*trans*)
3.37(s)	H:	1.83(dd)	84.0	5.7(*cis*) 9.3(*trans*)
3.26(s)	F:	−21.3(dd)	[h]	14(*cis*) 59(*trans*)
3.25(s)		[g]	—	—

(HCCH) 6.6 Hz, ^5J(PtCOCCH) 3.1 Hz; δ(CH(CH$_3$)) 4.97 (m). [f] Hydrogen-bonded OH group. [g] Too insoluble in organic solvents for ^{19}F NMR spectra. [h] Not observed, owing to low solubility.

Unlike the above carbonylation reactions, the acid intermediates Pt—SC(=Y)-OH and Pt—SO_3H, which are certainly involved in the insertion reactions with hydroxo complexes II, cannot be isolated pure.

IR and NMR data for all insertion products are given in Table 2. In particular, the alkoxycarbonyl complexes IIIa—IIIe show typical ester bands in their IR spectra, and the ester methyl resonance in the ^1H NMR spectrum is a singlet with ^{195}Pt satellites ^4J(PtCOOH) 3.3—6.3 Hz. For the methylthiocarbonato (Va, Vd), and methyldithiocarbonato (VIa, VId) derivatives, the ^1H NMR and IR data are consistent with the presence of *S*-bonded organic moieties coordinated to platinum. There seems to be no precedents for the vibrational spectral analysis of coordinated SCO_2CH_3 and $SCSOCH_3$ groups. Moreover, these data are significantly different from those of all known metal—CS_2O, —CO_3H, —CO_3R and —SCO_2H associations [8,21,24,26]. The IR spectrum of the methoxysulfonyl complex VIId shows absorptions of the SO_2OCH_3 group in agreement with the previously reported data for analogous derivatives of platinum(II) and palladium-(II) [6].

TABLE 3

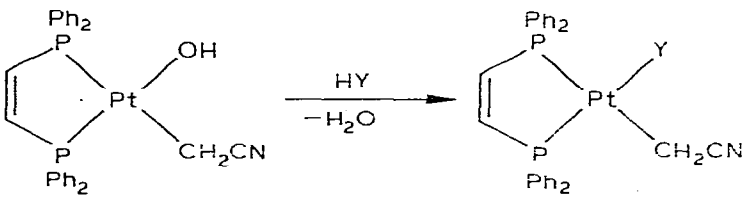
ANALYTICAL DATA FOR NEW PLATINUM COMPLEXES

	Complex	Analysis (found (calcd.) (%))			M.p. (dec) (°C)
		C	H	N or Cl	
	cis-$PtI(CH_2CF_3)(PPh_3)_2$	48.62 (49.10)	3.34 (3.47)		246–249
	cis-$PtCl(CH_2CF_3)(PPh_3)_2$	54.08 (54.46)	3.67 (3.85)	4.37 (4.23)	256–258
	trans-$PtBr(CF_3)(PPh_3)_2$	50.79 (51.16)	3.40 (4.48)		284–286
	trans-$PtCl(CF_3)(PPh_3)_2$	53.52 (53.92)	3.58 (3.67)	4.50 (4.30)	283–285
	trans-$PtBr(CF_3)(PPh_2Me)_2$	43.34 (43.56)	3.36 (3.52)		220–221
	$PtCl(CF_3)(Ph_2PCH{=}CHPPh_2)$	46.17 (46.60)	3.22 (3.19)	5.42 (5.09)	>300
	cis-$PtCl(CH_2NO_2)(PPh_3)_2$	54.78 (54.52)	4.20 (3.96)	1.74 (1.72)N 4.49 (4.35) Cl	258–260
Ia	$Pt(OCH_3)(CH_2CN)(Ph_2PCH{=}CHPPh_2)$	52.08 (52.57)	4.04 (4.10)	2.09 (2.11)	178–182
Id	$Pt(OCH_3)(CF_3)(Ph_2PCH{=}CHPPh_2)$	48.56 (48.63)	3.71 (3.64)		227–230
Ie	*trans*-$Pt(OCH_3)(CF_3)(PPh_3)_2$	54.82 (55.68)	4.20 (4.06)		181–183
IIb	$Pt(OH)(CH_2CN)[Ph_2P(CH_2)_2PPh_2]$	51.24 (51.69)	4.34 (4.18)	2.23 (2.15)	185–188
IIc	$Pt(OH)(CH_2CN)[Ph_2P(CH_2)_3PPh_2]$	52.65 (52.41)	4.53 (4.40)	2.10 (2.11)	192–196
IId	$Pt(OH)(CF_3)(Ph_2PCH{=}CHPPh_2)$	47.72 (47.87)	3.36 (3.42)		222–224
IIe	*trans*-$Pt(OH)(CF_3)(PPh_3)_2$	55.31 (55.16)	3.97 (3.88)		188–191
IIf	*trans*-$Pt(OH)(CF_3)(PPh_2Me)_2$	47.85 (47.58)	3.94 (3.99)		103–106
IIg	*cis*-$Pt(OH)(CH_2CF_3)(PPh_3)_2$	55.23 (55.68)	3.87 (4.06)		152–156

IIIa	$Pt(COOCH_3)(CH_2CN)(Ph_2PCH{=}CHPPh_2)$	52.41	4.16	2.01	190—192
		(52.18)	(3.94)	(2.03)	
IIIb	$Pt[COOCH(CH_3)_2](CH_2CN)(Ph_2PCH{=}CHPPh_2)$	53.00	4.52	1.97	191—193
		(53.48)	(4.35)	(1.95)	
IIIc	$Pt[COOC(CH_3)_3](CH_2CN)(Ph_2PCH{=}CHPPh_2)$	54.29	4.63	1.88	205—208
		(54.10)	(4.54)	(1.91)	
IIId	$Pt(COOCH_3)(CF_3)(Ph_2PCH{=}CHPPh_2)$	48.08	3.50		206—209
		(48.41)	(3.50)		
IIIe	*trans*-$Pt(COOCH_3)(CF_3)(PPh_3)_2$	55.22	4.02		186—188
		(55.26)	(3.92)		
IVa	$Pt(COOH)(CH_2CN)(Ph_2PCH{=}CHPPh_2)$	52.09	3.92	2.12	177—179
		(51.48)	(3.72)	(2.07)	
IVd	$Pt(COOH)(CF_3)(Ph_2PCH{=}CHPPh_2)$	47.60	3.45		188—190
		(47.67)	(3.29)		
Va	$Pt(SCOOCH_3)(CH_2CN)(Ph_2PCH{=}CHPPh_2)$	49.03	3.91	1.90	185—188
		(49.86)	(3.77)	(1.94)	
Vd	$Pt(SCOOCH_3)(CF_3)(Ph_2PCH{=}CHPPh_2)$	46.30	3.42		235—237
		(46.34)	(3.35)		
VIa	$Pt(SCSOCH_3)(CH_2CN)(Ph_2PCH{=}CHPPh_2)$	48.35	3.79	1.76	168—170
		(48.78)	(3.68)	(1.89)	
VId	$Pt(SCSOCH_3)(CF_3)(Ph_2PCH{=}CHPPh_2)$	44.82	3.45		181—184
		(45.37)	(3.28)		
VIId	$Pt(SO_3CH_3)(CF_3)(Ph_2PCH{=}CHPPh_2)$	44.02	3.37		180—182
		(44.51)	(3.33)		
VIII	$Pt(SH)(CH_2CN)(Ph_2PCH{=}CHPPh_2)$	50.28	3.87	2.20	236—238
		(50.60)	(3.79)	(2.11)	
IX	$Pt(p\text{-}CH_3C_6H_4S)(CH_2CN)(Ph_2PCH{=}CHPPh_2)$	55.13	4.36	1.84	237—241
		(55.70)	(4.14)	(1.86)	
Xa	$Pt(PhC{\equiv}C)(CH_2CN)(Ph_2PCH{=}CHPPh_2)$	59.58	4.10	1.90	225—228
		(59.02)	(3.99)	(1.91)	
Xb	$Pt(p\text{-}CH_3C_6H_4C{\equiv}C)(CH_2CN)(Ph_2PCH{=}CHPPh_2)$	59.85	4.23	1.84	259—262
		(59.52)	(4.18)	(1.87)	
Xd	$Pt(PhC{\equiv}C)(CF_3)(Ph_2PCH{=}CHPPh_2)$	55.03	3.78		271—273
		(55.19)	(3.57)		
XI	$Pt(CH_3CONH)(CH_2CN)(Ph_2PCH{=}CHPPh_2)$	51.77	4.31	3.87	198—199
		(52.25)	(4.09)	(4.06)	
XII	$Pt(PhMeN)(CH_2CN)(Ph_2PCH{=}CHPPh_2)$	55.67	4.43	3.45	184—186
		(56.99)	(4.37)	(3.80)	

Condensation reactions promoted by hydroxo—platinum(II) complexes

The hydroxo complex $Pt(OH)(CH_2CN)(Ph_2PCH{=}CHPPh_2)$ (IIa), suspended in benzene, when treated with tetrafluoroboric acid liberates H_2O to give the cationic complex $[Pt(CH_2CN)(Ph_2PCH{=}CHPPh_2)](BF_4)_2$ [12,27] in which the cyano group is linked by a σ-N—Pt bond to another platinum atom. IIa reacts also with weak acids, e.g. hydrogen sulfide, *p*-methylthiophenol, phenylacetylenes and acetamide to give high yields of the corresponding condensation complexes:



(IIa)

(VIII, Y = HS;
IX, *p*-$CH_3C_6H_4S$;
Xa, $PhC{\equiv}C$;
Xb, *p*-$CH_3C_6H_4C{\equiv}C$;
XI, CH_3CONH;
XII, PhMeN)

The strong basic properties of IIa are borne out by reaction with the extremely weak acid, *N*-methylaniline, which gives $Pt(NMePh)(CH_2CN)(Ph_2PCH{=}CHPPh_2)$ (XII), although not quantitatively. Similar condensation reactions were previously described for some hydroxo complexes of platinum(II) and palladium(II) [10—12]. It is noteworthy that condensation reactions on the cyanomethyl derivative IIa are faster than hydrolysis or nucleophilic addition to the CN group, as previously reported [12,28,29].

All the complexes were characterized by elemental analysis, IR and ^1H NMR spectra.

Experimental

Infrared spectra (in nujol mulls and in CH_2Cl_2 solution) were determined with a Perkin—Elmer 457 spectrophotometer. ^1H NMR spectra were recorded with Varian EM-390 and Bruker WP-60 instruments [$(CH_3)_4Si$ or CH_2Cl_2 as internal reference], ^{19}F NMR spectra with a Hitachi Perkin—Elmer R-20A instrument ($CFCl_3$ as an internal reference, negative value of chemical shifts indicate a shift upfield referred to $CFCl_3$) and $^{31}P\{^1H\}$FT NMR spectra with a Bruker WP-60 instrument (85% H_3PO_4 as external reference). Melting points were taken on a hot plate apparatus, and are uncorrected. The Institute of Organic Chemistry (University of Padua) carried out the microanalyses.

All reactions and physical measurements were carried out under dry dinitrogen or argon using conventional Schlenk-tube and glove-bag techniques, although most of the platinum complexes were air stable once isolated as solids. Solvents were distilled under dinitrogen from appropriate drying agents. Oven-dried glassware was used for preparations and reactions of methoxo complexes. The following complexes were prepared according to known methods: $Pt(PPh_3)_4$ [31], *cis*-$PtCl_2(PPh_3)_2$ [32] and $PtCl(CH_2CN)(P{-}P)$ (P—P = 1,2-bis(diphenylphosphino)-ethene [33], -ethane [33] or -propane [13]).

Preparation of complexes

cis-PtI(CH_2CF_3)(PPh_3)$_2$. To a suspension of 9.6 g (7.7 mmol) of $Pt(PPh_3)_4$ in 100 ml of benzene were added 2.2 ml (22.5 mmol) of ICH_2CF_3. The mixture was heated for 10 min at 50°C and then stirred at room temperature for 1 h. Addition of 200 ml of diethyl ether gave a white solid which was recrystallized from dichloromethane/ether (yield 5.8 g, 81%). The assignment of the *cis* configuration is based on the strong IR band at 549 cm^{-1}, attributed to the first overtone of the asymmetric PC_3 deformation mode in bis(triphenylphosphine)-platinum(II) complexes, as proposed by Mastin [30]. The complex was insufficiently soluble in dichloromethane or chloroform for NMR measurements.

cis-PtCl(CH_2CF_3)(PPh_3)$_2$. $AgBF_4$ (0.52 g, 2.67 mmol) was added to a suspension of *cis*-PtI(CH_2CF_3)(PPh_3)$_2$ (2.5 g, 2.7 mmol) in dichloromethane (100 ml). AgI was filtered off, the filtrate reduced to small volume and then treated with 100 ml of methanol and an excess of lithium chloride (ca. 0.8 g). The white product which precipitated immediately was filtered, washed with water and recrystallized from dichloromethane/methanol (yield 1.9 g, 84%). IR (Nujol): 302m, ν(Pt—Cl); 548s cm^{-1}, this band is indicative of a *cis* geometry according to Mastin's rule [30]. The complex was insufficiently soluble for NMR measurements.

trans-PtBr(CF_3)(PPh_3)$_2$. Bromotrifluoromethane was passed through a solution of $Pt(PPh_3)_4$ (13.5 g, 10.8 mmol) in benzene (200 ml), and the mixture was stirred under atmosphere of $BrCF_3$ at room temperature. After 8 days the yellow suspension was concentrated to 120 ml under reduced pressure. The pale yellow crude product which separated was filtered off and suspended in dichloromethane (120 ml), the suspension was stirred for 15 h. The white microcrystals obtained were washed with dichloromethane, then with ether (yield 7.8 g, 83%). Its *trans*-geometry was deduced from the absence of an IR band around 550 cm^{-1} [30].

trans-PtCl(CF_3)(PPh_3)$_2$. $AgBF_4$ (0.39 g, 2.0 mmol) in acetone (5 ml) was added to a suspension of *trans*-PtBr(CF_3)(PPh_3)$_2$ (1.74 g, 2.0 mmol) in dichloromethane (80 ml). AgBr was filtered off, the filtrate reduced to small volume and then treated with 100 ml acetone and an excess of lithium chloride (0.2 g). The white product which precipitated was filtered off and recrystallized from chloroform/ethanol (yield 1.57 g, 95%). IR (Nujol): 307 w-m, ν(Pt—Cl).

trans-PtBr(CF_3)(PPh_2Me)$_2$. To a suspension of *trans*-PtBr(CF_3)(PPh_3)$_2$ (3.50 g, 4.03 mmol) in n-hexane (100 ml) was added an excess of methyldiphenylphosphine (2.0 ml), and the mixture was stirred at room temperature for 20 h. The white product was separated and treated with an additional amount of PPh_2Me (0.3 ml) in n-hexane (100 ml) suspension. After stirring for 12 h, the white crystalline complex was filtered off and recrystallized from dichloromethane/methanol (yield 1.9 g, 63%). ^{19}F NMR in CH_2Cl_2: $\delta(CF_3)$ −10.4 (t) ppm, ^2J(PtCF) 739 Hz, ^3J(PPtCF) 20 Hz. ^1H NMR in CD_2Cl_2: $\delta(PCH_3)$ 2.26 (t) ppm, ^3J(PtPCH) 31 Hz, ^2J(PCH) + ^4J(PPtPCH) 7.8 Hz.

PtCl(CF_3)($Ph_2PCH{=}CHPPh_2$). A suspension of *trans*-PtCl(CF_3)(PPh_3)$_2$ (1.61 g, 1.95 mmol) and *cis*-1,2-bis(diphenylphosphine)ethene (0.95 g, 2.4 mmol) in benzene (130 ml) was stirred at room temperature for 10 h. After addition of diethyl ether (150 ml), the white product was filtered, washed with ether, and recrystallized from dichloromethane/methanol (yield 1.25 g, 92%). IR (Nujol):

312m cm^{-1}, ν(Pt—Cl). The complex was insufficiently soluble for ^{19}F NMR measurements.

cis-PtCl(CH_2NO_2)(PPh_3)$_2$. A suspension of *cis*-$PtCl_2(PPh_3)_2$ (4.2 g, 5.31 mmol) and Ag_2O (0.67 g, 5.8 meq) in nitromethane (150 ml) was stirred at room temperature under argon for 6 days. The grey mixture of solids (AgCl, Ag_2O and the complex) was removed by gravity filtration using a fine-grade filter paper, washed with nitromethane and then with methanol. The residue was extracted with dichloromethane (150 ml); the solution obtained was passed down a short Fluorisil column and then evaporated to small volume. Addition of ethyl ether gave a white solid which was recrystallized from dichloromethane/methanol (yield 3.6 g, 83%). IR (Nujol): 1499s cm^{-1} and 1355s cm^{-1}, $\nu(NO_2)$; 308m cm^{-1}, ν(Pt—Cl); 548vs cm^{-1}, this band is indicative of a *cis*-geometry [30]. ^1H NMR in CD_2Cl_2: $\delta(CH_2NO_2)$ 4.46 (dd) ppm, ^2J(PtCH) 69.3 Hz, ^3J(PPtCH) 5.1 Hz (*cis*) and 7.9 Hz (*trans*).

Preparation of methoxo complexes

Pt(OCH_3)(CH_2CN)($Ph_2PCH{=}CHPPh_2$) (Ia). A solution of $NaOCH_3$ (0.27 g, 5.0 mmol) in methanol (4 ml) was added to a suspension of $PtCl(CH_2CN)$-$(Ph_2PCH{=}CHPPh_2)$ (0.78 g, 1.17 mmol) in benzene (50 ml). The mixture was vigorously stirred at room temperature for 3 h. NaCl and excess of $NaOCH_3$ were filtered off and the filtrate was evaporated to dryness in vacuo. Dichloromethane (30 ml) was added and the solution filtered. Addition of n-heptane (20 ml) and concentration under reduced pressure gave a white solid (yield 0.64 g, 83%).

Pt(OCH_3)(CF_3)($Ph_2PCH{=}CHPPh_2$) (Id). A solution of $NaOCH_3$ (0.35 g, 6.5 mmol) in methanol (5 ml) was added to a suspension of $PtCl(CF_3)(Ph_2PCH{=}$ $CHPPh_2)$ (0.85 g, 1.22 mmol) in benzene (80 ml), and the mixture vigorously stirred at 50° C for 30 min, and then at room temperature. After 4 h, the white complex Id was isolated with similar procedure as Ia (yield 0.61 g, 72%).

This compound suspended in benzene and heated under reflux for 3 h was recovered unchanged. The same reaction with water gave IId in good yield (see below).

trans-Pt(OCH_3)(CF_3)(PPh_3)$_2$ (Ie). A similar procedure as for Id, using $NaOCH_3$ (0.123 g, 2.28 mmol) in methanol (2 ml) and *trans*-$PtCl(CF_3)(PPh_3)_2$ (0.46 g, 0.56 mmol) gave a white product (yield 0.34 g, 74%).

Preparation of hydroxo complexes

The following general procedure (with a few variations in particular cases) was followed in the preparation of complexes of type $Pt(OH)(R_x)L_2$.

Pt(OH)(CH_2CN)($Ph_2PCH_2CH_2PPh_2$) (IIb). $AgBF_4$ (0.113 g, 0.58 mmol) was added to a solution of $PtCl(CH_2CN)(Ph_2PCH_2CH_2PPh_2)$ [33] (0.38 g, 0.57 mmol) in dichloromethane (50 ml). The mixture was stirred for 40 min, AgCl filtered off and the filtrate evaporated in vacuo. The residual solid obtained was suspended in methanol (25 ml) and treated with a solution of KOH (0.064 g, 1.14 mmol) in water (2 ml). After filtration to remove traces of silver compounds, the solution was evaporated to dryness under reduced pressure (30—40° C 10^{-1} mmHg). The residue was extracted with dichloromethane (20 ml), and the solution evaporated give a white product, which was washed with water and

dried. This was dissolved in dichloromethane (10 ml) and treated with a mixture of n-heptane/benzene (2/1, 30 ml). Concentration under reduced pressure gave a white solid which was filtered off, washed with n-heptane and dried in vacuo (yield 0.32 g, 86%).

Pt(OH)(CH_2CN)($Ph_2PCH{=}CHPPh_2$) (IIa). This complex was prepared similarly in good yield. After recrystallization from dichloromethane/ethyl ether, it shows m.p., IR and ^1H NMR spectra identical with those of the same complex as described earlier [12].

Pt(OH)(CH_2CN)[$Ph_2P(CH_2)_3PPh_2$] (IIc). This was prepared similarly, starting from PtCl(CH_2CN)[$Ph_2P(CH_2)_3PPh_2$] [13] (0.35 g, 0.51 mmol). Recrystallization from dichloromethane/benzene gave a white solid (0.29 g, 85%).

Pt(OH)(CF_3)($Ph_2PCH{=}CHPPh_2$) (IId). The complex was prepared from PtCl(CF_3)($Ph_2PCH{=}CHPPh_2$) (0.32 g, 0.46 mmol). After recrystallization from dichloromethane/benzene a white solid was obtained (yield 0.28 g, 90%). $^{31}P\{^1H\}$ FT NMR in CH_2Cl_2/CD_2Cl_2: $\delta(P)_{trans\text{-}OH}$ 38.07 (qd) ppm, ^1J(PtP) 3263 Hz, ^3J(FCPtP) 9.9 Hz, ^2J(PPtP) ~10 Hz; $\delta(P)_{trans\text{-}CF_3}$ 43.92 (qd) ppm, ^1J(PtP) 2073 Hz, ^3J(FCPtP) 57 Hz, ^2J(PPtP) ~ 10 Hz.

trans-Pt(OH)(CF_3)(PPh_3)$_2$ (IIe). A suspension of *trans*-PtCl(CF_3)(PPh_3)$_2$ (1.50 g, 1.82 mmol) in dichloromethane (100 ml) was treated with $AgBF_4$ (0.36 g, 1.85 mmol). After filtration of AgCl, the solution was evaporated to dryness. The residue was suspended in acetone (40 ml) and a solution of KOH (0.105 g, 1.87 mmol) in water (5 ml) was added dropwise. The mixture was stirred at room temperature for 1 h and then evaporated to 20 ml under reduced pressure. The white complex IIe was precipitated by adding water, and recrystallized from dichloromethane/ethyl ether (yield 1.1 g, 75%). $^{31}P\{^1H\}$ FT NMR in CH_2Cl_2/CD_2Cl_2: δ(P) 25.8 (q) ppm, ^1J(PtP) 3202 Hz, ^3J(FCPtP) 17 Hz.

trans-Pt(OH)(CF_3)(PPh_2Me)$_2$ (IIf). This was prepared similarly to IIe starting from *trans*-PtBr(CF_3)(PPh_2Me)$_2$ (0.64 g, 0.86 mmol). Recrystallization from dichloromethane/diethyl ether/n-pentane gave IIf as white microcrystals (yield 0.37 g, 63%).

cis-Pt(OH)(CH_2CF_3)(PPh_3)$_2$ (IIg). The complex was prepared as described for the synthesis of IIb, starting from *cis*-Pt(Cl)(CH_2CF_3)(PPh_3)$_2$ (0.65 g, 0.77 mmol). Recrystallization from dichloromethane/benzene gave a white microcrystalline solid (yield 0.57 g, 90%).

Reactions of alkoxo complexes with carbon monoxide

The following two general procedures were followed in the preparation of the alkoxycarbonyl complexes.

Pt($COOCH_3$)(CH_2CN)($Ph_2PCH{=}CHPPh_2$) (IIIa). Method (A). A solution of Ia (0.20 g, 0.30 mmol) in benzene (20 ml) was stirred for 3 h under CO (1 atm). Precipitation with n-heptane and recrystallization from dichloromethane/n-pentane yielded white microcrystals of IIIa (0.15 g, 72%).

Method (B). A solution of IIa (0.22 g, 0.34 mmol) in methanol (15 ml) was treated with triethylamine (0.1 ml) and kept under CO (1 atm) for 15 h. The white solid obtained was filtered, washed with n-pentane and dried in vacuo (yield 0.18 g, 76%).

Pt[$COOCH(CH_3)_2$](CH_2CN)($Ph_2PCH{=}CHPPh_2$) (IIIb). This was prepared from IIa (0.16 g, 0.25 mmol) in isopropanol (15 ml) by method B as white microcrystals (yield 0.16 g, 89%).

$Pt[COOC(CH_3)_3](CH_2CN)(Ph_2PCH{=}CHPPh_2)$ (IIIc). The complex was prepared from IIa (0.20 g, 0.31 mmol) in t-butanol (20 ml) by method B as white microcrystals (yield 0.18 g, 79%).

$Pt(COOCH_3)(CF_3)(Ph_2PCH{=}CHPPh_2)$ (IIId). The complex was prepared from Id (0.20 g, 0.29 mmol) by method A as a white solid (yield 0.16 g, 77%), and also from IId (0.23 g, 0.34 mmol) by method B (yield 0.19 g, 78%).

trans-$Pt(COOCH_3)(CF_3)(PPh_3)_2$ (IIIe). The complex was prepared from IIe (0.24 g, 0.30 mmol) by method B as a white product (yield 0.21 g, 83%).

Reactions of hydroxo complexes with carbon monoxide

$Pt(COOH)(CH_2CN)(Ph_2PCH{=}CHPPh_2)$ (IVa). A suspension of IIa (0.26 g, 0.40 mmol) in benzene (30 ml) was stirred at room temperature under CO (1 atm) for 2 days. Concentration of the solution and addition of n-pentane gave a white product, which was filtered off, washed with n-pentane and dried in vacuo (yield 0.15 g, 55%).

$Pt(COOH)(CF_3)(Ph_2PCH{=}CHPPh_2)$ (IVd). A suspension of IId (0.32 g, 0.47 mmol) in benzene (30 ml) was stirred at room temperature under CO (1 atm) for 3 h. The white product was filtered off, washed with n-pentane and dried in vacuo (yield 0.30 g, 90%). The complex was insoluble in aromatic hydrocarbons, and insufficiently soluble in chlorinated solvents for NMR measurements.

The complex IVa and IVd are fairly stable in the solid state and do not react with air or water.

The complexes IVa and IVd (ca. 0.25 g) when suspended in methanol (10 ml) and treated with excess of triethylamine (0.1 ml) are readily esterified to the corresponding alkoxycarbonyl complexes IIIa and IIId respectively, in almost quantitative yields.

Reactions of methoxo complexes with carbonyl sulfide

$Pt(SCOOCH_3)(CF_3)(Ph_2PCH{=}CHPPh_2)$ (Vd). Method A. COS was bubbled into a solution of Id (0.30 g, 0.43 mmol) in benzene (30 ml) at 20°C. After 3 min the bubbling was stopped, and the mixture was stirred for 50 min. Precipitation was completed by adding ether (60 ml), and Vd was obtained as white microcrystals by recrystallization from dichloromethane/methanol (yield 0.24 g, 74%).

Method B. COS was bubbled into a solution of IId (0.25 g, 0.37 mmol) and triethylamine (0.1 ml) in methanol (15 ml) at 20°C. After 2 min the bubbling was stopped, and the solution was stirred until cloudy. Precipitation was completed by adding diethyl ether (40 ml). The white complex obtained was filtered off and recrystallized from dichloromethane/methanol (yield 0.22 g, 79%).

$Pt(SCOOCH_3)(CH_2CN)(Ph_2PCH{=}CHPPh_2)$ (Va). This complex was prepared from IIa (0.20 g, 0.31 mmol) by method B described for Vd as white microcrystals (yield 0.17 g, 76%).

Reactions of methoxo complexes with carbon disulfide

$Pt(SCSOCH_3)(CH_2CN)(Ph_2PCH{=}CHPPh_2)$ (VIa). Method A. A solution of Ia (0.26 g, 0.39 mmol) in benzene (15 ml) was treated with CS_2 (0.2 ml) and stirred at room temperature. The pale yellow product which precipitated immediately was filtered off, and recrystallized from dichloromethane/diethyl

ether (white microcrystals, yield 0.21 g, 72%).

Method B. A solution of IIa (0.20 g, 0.31 mmol) in methanol (20 ml) was treated with triethylamine (0.1 ml) and CS_2 (0.5 ml). The mixture was heated at 40°C until cloudy. Precipitation was completed by addition of diethyl ether (40 ml). The white complex was filtered off and recrystallized from dichloromethane/methanol (yield 0.17 g, 74%).

$Pt(SCSCH_3)(CF_3)(Ph_2PCH{=}CHPPh_2)$ (VId). The complex was prepared from Id (0.20 g, 0.29 mmol) by method A described for VIa (yield 0.18 g, 81%), and also from IId (0.23 g, 0.34 mmol) by method B as white microcrystals (0.23 g, 88%).

Reaction of $Pt(OCH_3)(CF_3)(Ph_2PCH{=}CHPPh_2)$ with sulfur dioxide

$Pt(SO_3CH_3)(CF_3)(Ph_2PCH{=}CHPPh_2)$ (VIId). SO_2 was bubbled into a solution of Id (0.25 g, 0.36 mmol) in benzene (30 ml) at room temperature. After 5 min the bubbling was stopped, and the solution was stirred for 8 h. The white product obtained was filtered off, washed with n-pentane and dried (yield 0.23 g, 84%).

Reactions of hydroxo complexes with COS, CS_2 and SO_2

The insertion reactions of COS, CS_2 or SO_2 into Pt—OH bonds of complexes IIa, IId take place readily in non polar solvents under similar experimental conditions as used for the same insertion reactions into Pt—OCH_3 bonds. However elecmental analyses, and IR and ^{1}H NMR spectra of the products do not support definite formulations; presumably these reactions involve incipient formation of the unstable acidic groups (i.e. SO_3H) and/or acid cleavage reactions on the adjacent Pt—R_x bond.

Condensation reactions of hydroxo complexes

$Pt(SH)(CH_2CN)(Ph_2PCH{=}CHPPh_2)$ (VIII). Hydrogen sulfide was passed into a suspension of IIa (0.25 g, 0.39 mmol) in benzene (15 ml) and diethyl ether (15 ml) at room temperature for a few minutes, and then stirred for 30 min. The white product was filtered off and recrystallized from dichloromethane/n-heptane (yield 0.22 g, 86%). IR (Nujol): 2208s cm^{-1}, ν(C≡N). ^{1}H NMR in CD_2Cl_2: δ(SH) —0.14 (dd) ppm, ^2J(PtSH) 56.6 Hz, ^3J(PPtSH) 6.0 (*cis*) and 12.7 Hz (*trans*); $\delta(CH_2CN)$ 1.70 (dd) ppm, ^2J(PtCH) 84.9, ^3J(PPtCH) 6.3 (*cis*) and 9.3 Hz (*trans*).

$Pt(p\text{-}CH_3C_6H_4S)(CH_2CN)(Ph_2PCH{=}CHPPh_2)$ (IX). A stirred suspension of IIa (0.25 g, 0.39 mmol) in methanol (20 ml) was treated with *p*-methylthiophenol (1 ml). After a few minutes the white complex was filtered off, washed with methanol and recrystallized from dichloromethane/ethyl ether (yield 0.24 g, 83%). IR (Nujol): 2208s, ν(C≡N). ^{1}H NMR in $CDCl_3$: $\delta(CH_2CN)$ 1.38 (dd) ppm, ^2J(PtCH) 87.9 Hz, ^3J(PPtCH) 5.7 Hz (*cis*) and 9.6 Hz (*trans*); $\delta(CH_3)$ 2.16 (s) ppm.

$Pt(C_6H_5C{\equiv}C)(CH_2CN)(Ph_2PCH{=}CHPPh_2)$ (Xa). Phenylacetylene (0.4 ml) was added to IIa (0.20 g, 0.31 mmol) in benzene (15 ml), and the mixture stirred at 50°C for 20 min. After evaporation to dryness in vacuo, dichloromethane (30 ml) and methanol (20 ml) were added. Concentration under reduced pressure gave a white product (yield 0.17 g, 75%). IR (Nujol): 2202s ν(C≡N), 2110m cm^{-1} ν(C≡C). ^{1}H NMR in $CDCl_3$: $\delta(CH_2CN)$ 1.98 (dd) ppm, ^2J(PtCH) 91.0 Hz, ^3J(PPtCH) 6.6 Hz (*cis*) and 9.9 Hz (*trans*).

Pt(p-$CH_3C_6H_4C{\equiv}C$)(CH_2CN)($Ph_2PCH{=}CHPPh_2$) (Xb). A similar reaction using *p*-tolylacetylene (0.5 ml) and IIa (0.25 g, 0.38 mmol) in methanol (20 ml) gave, after heating at 60° C for 5 min, a white precipitate (yield 0.23 g, 80%). IR (Nujol): 2209s ν(C≡N), and 2115m cm^{-1} ν(C≡C). The complex was insufficiently soluble in chlorinated solvents for ^{1}H NMR measurements.

Pt($C_6H_5C{\equiv}C$)(CF_3)($Ph_2PCH{=}CHPPh_2$) (Xd). This was similarly prepared from phenylacetylene and IId in methanol. The white product obtained in almost quantitative yield was insoluble in most common organic solvents. IR (Nujol): 2125m, ν(C≡C).

Pt(CH_3CONH)(CH_2CN)($Ph_2PCH{=}CHPPh_2$) (XI). Acetamide (0.10 g, 1.7 mmol) was added to a suspension of IIa (0.20 g, 0.31 mmol) in benzene (15 ml), and the mixture stirred at room temperature for 15 h. After removal of solvent and excess of acetamide at 60° C (10^{-2} mmHg), the white residual solid was crystallized from dichloromethane/petroleum ether (yield 0.15 g, 70%). IR (Nujol): 2203s ν(C≡N), 3375w and 3330w ν(NH), 1597vs cm^{-1} ν(CONH). ^{1}H NMR in CD_2Cl_2: δ($COCH_3$) 1.87 (s) ppm, ^4J(PtNCCH) 6.0 Hz; δ(NH) 5.75 (br) ppm; δ(CH_2CN) 1.59 (dd) ppm, ^2J(PtCH) 77.6 Hz, ^3J(PPtCH) 5.1 Hz (*cis*) and 10.2 Hz (*trans*).

Pt(PhMeN)(CH_2CN)($Ph_2PCH{=}CHPPh_2$) (XII). *N*-Methylaniline (0.5 ml) was added to a suspension of IIa (0.30 g, 0.46 mmol) in benzene (30 ml). A deep red solution was obtained on heating at 60° C for 2 h. Concentration of the solution and addition of diethyl ether gave an orange-yellow solid which was filtered off and dried in vacuo (yield 0.23 g). Spectroscopic characterization of this solid shows in addition to the features characteristic for the starting complex IIa, the following signals: IR (Nujol), 2198s cm^{-1}, ν(C≡N); ^{1}H NMR in $CDCl_3$, δ(NCH_3) 2.70 (d) ppm, ^3J(PtNCH) 30.6 Hz, ^4J(PPtNCH) 3.9 Hz (strong coupling only with the *trans*-phosphorus atom), δ(CH_2CN) 1.64 (dd) ppm, ^2J(PtCH) 86.1 Hz, ^3J(PPtCH) 4.9 (*cis*) and 9.9 Hz (*trans*). Analytical and ^{1}H NMR data indicate that the product contains ca. 70% of XII.

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