

REACTIONS OF ACETYLENES WITH NOBLE-METAL CARBONYL HALIDES

II *. INSERTIONS INTO THE CHLORO—PLATINUM BOND

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Summary

The reaction of dichlorodicarbonylplatinum with $\text{ROOCC}\equiv\text{CCOOR}$ ($\text{R} = \text{CH}_3, \text{C}_2\text{H}_5$) in benzene and toluene gives carbonylchloro(1,2-*trans*-dicarboalkoxy-2-chloroethenyl)platinum compounds by insertion of the active acetylene molecule into the Pt—Cl bond.

These chelated stable square-planar vinyl derivatives react with neutral donor ligands to give simple σ -alkenyl derivatives: $[\text{Pt}(\text{CO})\text{Cl}(\text{ROOCC}=\text{C}(\text{Cl})\text{COOR})\text{L}]$ ($\text{L} = \text{C}_5\text{H}_5\text{N}, \text{CH}_3\text{C}_5\text{H}_4\text{N}$), $[\text{PtCl}(\text{ROOCC}=\text{C}(\text{Cl})\text{COOR})\text{L}_2]$ ($\text{L} = \text{PPh}_3, \text{PCH}_3\text{Ph}_2$), and $[\text{PtCl}(\text{ROOCC}=\text{C}(\text{Cl})\text{COOR})(\text{L}-\text{L})]$ ($\text{L}-\text{L} = \text{DPE}, \text{bipy}, \text{Me}_2\text{bipy}$). The anionic species $[\text{cis-Pt}(\text{CO})\text{X}_2(\text{ROOCC}=\text{C}(\text{Cl})\text{COOR})]^-$ have been isolated as PPN salts by treating the vinyl complexes with Cl^- , I^- or SCN^- . The stereochemistry has been elucidated from spectroscopic data (IR and ^1H NMR).

Introduction

Continuing our investigation of the reactions of acetylenes with dichlorodicarbonylplatinum [1], we have extended our study to acetylenes activated by the presence of electron-withdrawing groups. Olefins and acetylenes bearing electron-withdrawing substituents are known to react readily with platinum hydrides or alkylplatinums to form compounds derived from the insertion

* For part I see ref. 1b.

ary product under the reaction conditions used, but when the reaction was carried out in boiling toluene by gradual addition of dialkylacetylene dicarboxylate, e.g. 1/4 of a mol per mol of dichlorodicarbonylplatinum up to the final ratio 1/1, it was isolated in the same amount as I.

The reaction course did not seem to be temperature dependent; the complete transformation of dichlorodicarbonylplatinum into the compounds indicated above was achieved in 2 h at 100°C but required 10 days at room temperature when the molar ratio of the reagents was 1/1.7, no significant change in the relative amount of the three species formed was observed. The formulation of compounds I as carbonylchloro(1,2-*trans*-dicarboalkoxy-2-chloroethenyl)platinum was inferred from the elemental analysis, molecular weight, spectroscopic characteristics and chemical behaviour. Both compounds IA and IB were isolated as yellow needles, soluble in all the common organic solvents, except hydrocarbons. Osmometric molecular weight measurements showed that both are monomeric in acetone, chloroform and benzene. The mass spectrum of complex IA contained a parent ion at m/e 436, and fragmentation occurred by loss of OCH_3 and CO so that both ions $[PtCl(CH_3OCC=C(Cl)COOCH_3)]^+$ and $[Pt(CO)Cl(CH_3OCC=C(Cl)CO)]^+$ were observed. The IR spectra of the solids (Nujol mulls and Csl discs) showed a strong sharp band in the carbonyl region at ca. 2120 cm^{-1} (terminal CO) and the expected very strong band at ca. 1710 cm^{-1} due to the ester carbonyl groups. This last band was rather broad and sometimes split, particularly in Nujol mull, into separate very strong bands, e.g. for complex IB at 1710 and 1695 cm^{-1} . Both compounds also showed a strong absorption band at ca. 1570 cm^{-1} , which can be ascribed to an ester carbonyl group coordinated to the metal atom [6,7]. This assignment is further supported by the fact that the 1570 cm^{-1} absorption band was also present in the spectra registered in non-donor solvents such as dichloromethane, chloroform and benzene while it disappeared in acetonitrile where it was replaced by a weak band at ca 1580–1560 cm^{-1} , probably due to $\nu(C=C)$. The far IR spectra showed a strong band at ca. 320 cm^{-1} in the Pt–Cl region, and a medium intensity band at ca. 375 cm^{-1} , which could be assigned to $\nu(OCO)$ [7].

The 1H NMR spectrum of IA contained two singlets at δ 4.27 ppm and δ 3.86 ppm in the expected 1/1 intensity ratio; the higher field resonance showed coupling with ^{195}Pt ($J(Pt-H)$ 2 Hz) and could be assigned to the α - CO_2CH_3 group [4], while the lower field signal appeared as a sharp singlet, not coupled with ^{195}Pt , and could be assigned to the β - CO_2CH_3 . Similarly the 1H NMR spectrum of IB contained signals at δ 4.77q, 4.34q, 1.5t and 1.28t in the expected 2/2/3/3 intensity ratio, in agreement with the presence of two inequivalent $CO_2CH_2CH_3$ groups, the δ 4.34 ppm resonance appearing coupled with ^{195}Pt ($J(Pt-H)$ 2.4 Hz). These spectroscopic NMR and IR data are consistent with the cyclic structure shown in Scheme 1 in which the carbonyl oxygen of the β -carboalkoxy group coordinates to the platinum atom. Definite confirmation of this type of structure should come from an X-ray investigation, but to date all attempts with crystals of both IA and IB have failed, owing to molecular disorder.

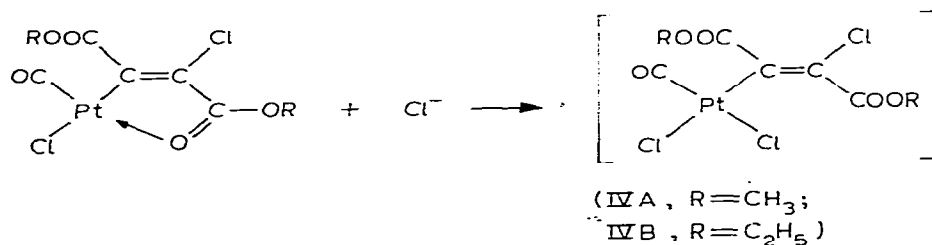
Compounds of type II have also been obtained by treating I with 1–3 mol of dialkylacetylene dicarboxylate in boiling benzene or in toluene at 105°C.

Compound IIA was isolated as pale-yellow powder and recrystallized from toluene/hexane: it was very soluble in all the common organic solvents except hydrocarbons, and attempts to obtain crystals suitable for an X-ray investigation failed. The elemental analysis suggests that two moles of activated acetylenes per platinum atom are present in the molecule, and mol. wt. measurement in benzene showed that it was trimeric in solution. The IR spectrum of IIA in Nujol mull showed the following absorption bands: 2100m, assignable to terminal CO, 1720vs, due to carbonyl ester groups, 1560s(br), due to the chelate carbonyl ester group, and 328w cm^{-1} , due to Pt—Cl stretch. The ^1H NMR spectrum showed two unresolved multiplets centred at ca. δ 4.2 and 3.8 ppm with the relative intensity ratio 1/3, suggesting that two different types of carbomethoxy groups are present. Compound IIB was obtained analogously from IB, it could not be isolated pure from the oily residue, but the spectroscopic data of the crude sample suggest that it has a similar molecular structure to IIA. The chemical properties of these 1/2 adducts are presently under investigation and we suspect that their molecular structure may be related to that proposed for the 1/2 adducts with dialkylacetylene dicarboxylate in the case of palladium [7]. The compounds of type III, formed when the reaction was carried out at relatively high temperature with low platinum/acetylene ratio, have been isolated as pale-green powders, insoluble in all the common organic solvents. Repeated elemental analysis confirmed that C/H/Cl ratios were very close to 6/3/1 in IIIA and to 7/5/1 in IIIB, indicating that one of the two chlorine atoms initially present on platinum has been eliminated. Owing to their insolubility no spectroscopic data were available for elucidating the structure. However the IR spectrum of the solid showed that terminal carbonyl groups were still present (2100 cm^{-1}) as well as carbonyl ester groups (1720 cm^{-1}), while major changes were observed both in the $1550\text{--}1600\text{ cm}^{-1}$ region and in the far IR region. In the former, two strong absorption bands at 1600 and 1560 cm^{-1} appeared, while in the latter no band assignable to the Pt—Cl stretching was found. We are presently studying the chemical behaviour of these compounds [8], which are also formed when compounds I are refluxed in wet benzene or toluene for several hours. Preliminary data indicate that Pt—O bonds are formed, probably through the elimination of the alkyl group from the β -carboalkoxy moiety and of the chlorine atom attached to platinum so that a polymeric species should arise both from the formation of covalent bonds between platinum and oxygen atoms located in different units and from the intermolecular interaction of the remaining carboalkoxy groups with the coordinatively unsaturated platinum atoms.

Chemical reactions of I

The compounds of type I are stable under a carbon monoxide atmosphere in dry non polar solvents, and do not react with hydrogen or hydrogen chloride in boiling benzene, chloroform, or in dry alcohols. Remarkable stability of the Pt—C bond was also observed in the reaction with chlorine, in which no cleavage of the vinyl moiety occurred. The stability of these compounds in acidic conditions and the complexity of the decomposition reaction in alkaline medium owing to the formation of platinum carbonyls, did not allow cleavage

of the platinum—vinyl bond as means of confirming the stereochemistry of the Pt—C=C—Cl double bond. However confirmation that such stereochemistry is *trans*, and consequently that the two carboalkoxy groups are *trans* on the double bond, is based on the NMR spectra of the related β -chlorovinyl compounds obtained from IA and IB with a large variety of ligands. The more facile transformation concerns the interaction between the chelate carboalkoxy group and platinum which is immediately removed when IA and IB are dissolved in anhydrous polar solvents in the presence of an excess of chloride ions:



The reaction could be carried out with the stoichiometric amount of lithium chloride or other chloride soluble in CHCl_3 and in THF: the addition of bulky cations such as PPh_4^+ or PPN^+ ($\text{PPN} = [\mu\text{-nitridobis(triphenylphosphorous)}]$) permitted isolation of the corresponding salts of IVA and IVB as colourless needles in 60–70% yield. Elemental analysis, reported in Table 1, and conductivity data in acetone (Λ_M , 103.8 ohm^{-1} for IVA and 106.7 ohm^{-1} for IVB) are fully consistent with the proposed formulations. The more significant IR absorption bands and the ^1H NMR chemical shifts are reported in Tables 2 and 3.

The comparison of the IR spectra of IVA and IVB with those of the parent compounds IA and IB showed that the strong band at ca. 1570 cm^{-1} was replaced by weak bands at ca. 1550 cm^{-1} ($\nu(\text{C}=\text{C})$), partially obscured by the presence of the bands due to the PPN cation, while in the far IR region two strong absorption bands were observed (300 and 340 cm^{-1}), which can be assigned to terminal Pt—Cl bonds with a *cis* configuration [9]. The ^1H NMR spectrum of IVA shows two equally intense signals at δ 3.76s and 3.715 ppm, due to the two inequivalent methoxycarbonyl groups, in agreement with the asymmetry of the ligand. Similarly the ^1H NMR spectrum of IVB shows two clearly distinct sets of quartets (at δ 4.26 and 4.23 ppm) and triplets (at δ 1.40 and 1.27 ppm), confirming that the two carboethoxy groups are still inequivalent. In both compounds the higher field resonance attributable to $\alpha\text{-COOCH}_3$ and $\alpha\text{-COOC}_2\text{H}_5$ show coupling with ^{195}Pt ($J(\text{Pt}-\text{H})$ ca. 2 Hz). This coupling is similar to that observed in other platinum compounds containing α,β -dicarboalkoxy groups [4], as well as to that found for the $\alpha\text{-CF}_3$ group vicinal to platinum in the ^{19}F spectra of the related trifluorovinylplatinum complexes [10].

The chelation by the carboalkoxy group can also be described by reaction with π -donor ligands. Nitrogen donor ligands, such as pyridine and β -picoline, react smoothly giving white adducts in which platinum displays the usual planar tetracoordination, the Pt \leftarrow OCOR bond being replaced by the stronger Pt \leftarrow N bond:

TABLE 1
 ANALYTICAL DATA

Compound	Analysis (found (calcd.)) (%)				M.p. (°C)	Mol. wt.
	C	H	Cl	N		
IA	Pt(CO)Cl(CH ₃ OCCO=C(Cl)COOCH ₃)	19.38 (19.28)	1.13 (1.39)	16.15 (16.26)	44.20 (Pt) (44.73)	436 ^a (436.15)
IB	Pt(CO)Cl(C ₂ H ₅ OCCO=C(Cl)COOC ₂ H ₅)	24.70 (23.25)	2.32 (2.17)	14.81 (15.28)	43.15 (Pt) (42.03)	414 ^b (464.2)
IIA	[Pt(CO)Cl(CH ₃ OCCO=C(O)OCH ₃) ₂ Cl] ₃	27.30 (27.00)	2.00 (2.09)	12.08 (12.26)		1720 ^a (1734)
IIB	[Pt(CO)Cl(C ₂ H ₅ OCCO=C(O)OC ₂ H ₅) ₂ Cl] ₃	32.41 (32.19)	3.29 (3.18)	11.35 (11.18)		>240 >240
IIIA	[Pt(CO)(CH ₃ OCCO=C(Cl)COO)] _n	18.73 (18.65)	0.82 (0.78)	9.07 (9.19)		>240
IIIB	[Pt(CO)(C ₂ H ₅ OCCO=C(Cl)COO)] _n	20.53 (21.04)	1.13 (1.23)	8.20 (8.87)		>240
IVA	PPN[<i>cis</i> -Pt(CO)Cl ₂ (CH ₃ OCCO=C(Cl)COOCH ₃)]	51.83 (51.13)	3.68 (3.39)	10.46 (10.53)	1.44 (1.39)	131
IVB	PPN[<i>cis</i> -Pt(CO)Cl ₂ (C ₂ H ₅ OCCO=C(Cl)COOC ₂ H ₅)]	52.42 (52.06)	3.75 (3.88)	10.26 (10.25)	1.40 (1.35)	128
VA	Pt(CO)Cl(C ₅ H ₅ N)(CH ₃ OCCO=C(Cl)COOCH ₃)	28.84 (27.87)	2.24 (2.15)	2.84 (2.73)	2.84 (2.73)	88
VB	Pt(CO)Cl(C ₅ H ₅ N)(C ₂ H ₅ OCCO=C(Cl)COOC ₂ H ₅)	30.57 (30.95)	2.65 (2.78)	2.32 (2.58)	2.32 (2.58)	536 ^d (515)
VIA	Pt(CO)Cl(CH ₃ C ₅ H ₄ N)(CH ₃ OCCO=C(Cl)COOCH ₃)	29.38 (29.50)	2.32 (2.47)	2.63 (2.65)	2.63 (2.65)	610 ^a (543)
VIB	Pt(CO)Cl(CH ₃ C ₅ H ₄ N)(C ₂ H ₅ OCCO=C(Cl)COOC ₂ H ₅)	31.87 (32.32)	2.95 (3.07)	2.30 (2.51)	2.30 (2.51)	582 ^a (529) 596 ^a (557.4)

VIIA	<i>trans</i> -PtCl(PPh ₃) ₂ (CH ₃ OCCC=C(Cl)COOCH ₃)	54.00 (54.09)	3.83 (3.89)	>240	1107 ^b (932)
VIIIB	<i>trans</i> -PtCl(PPh ₃) ₂ (C ₂ H ₅ OCC=C(Cl)COOC ₂ H ₅)	55.80 (55.02)	4.12 (4.17)	218	1020 ^b (960.5)
VIIIA	<i>trans</i> -PtCl(PMePh ₂) ₂ (CH ₃ OCC=C(Cl)COOCH ₃)	48.44 (47.54)	3.90 (3.99)		860 ^a (808.6)
VIIIB	<i>trans</i> -PtCl(PMePh ₂) ₂ (C ₂ H ₅ OCC=C(Cl)COOC ₂ H ₅)	49.22 (48.81)	4.12 (4.34)	103	882 ^a (838.6)
IXA	PtCl(DPE)(CH ₃ OCC=C(Cl)COOCH ₃)	47.90 (47.65)	3.84 (3.75)	177	
IXB	PtCl(DPE)(C ₂ H ₅ OCC=C(Cl)COOC ₂ H ₅)	49.20 (48.93)	4.27 (4.10)	183	
XA	PtCl(öipy)(CH ₃ OCC=C(Cl)COOCH ₃)	34.60 (34.06)	2.32 (2.50)	>240	4.93 (4.96)
XB	PtCl(öipy)(C ₂ H ₅ OCC=C(Cl)COOC ₂ H ₅)	36.75 (36.50)	3.05 (3.04)	215	4.72 (4.74)
XIA	PtCl(Me ₂ bipy)(CH ₃ OCC=C(Cl)COOCH ₃)	36.28 (36.50)	2.91 (3.04)	>240	4.77 (4.74)
XIB	PtCl(Me ₂ bipy)(C ₂ H ₅ OCC=C(Cl)COOC ₂ H ₅)	39.12 (38.78)	3.43 (3.57)	>240	4.54 (4.61)
XIIA	PPN[<i>cis</i> -Pt(CO)(SCN) ₂ (CH ₃ OCC=C(Cl)COOCH ₃)]	50.10 (51.21)	3.61 (3.44)	131	3.98 (3.98)
XIIB	PPN[<i>cis</i> -Pt(CO)(SCN) ₂ (C ₂ H ₅ OCC=C(Cl)COOC ₂ H ₅)]	52.00 (52.10)	3.51 (3.72)	166	3.94 (3.88)
XIIIA	PPN[<i>cis</i> -Pt(CO) ₂ (CH ₃ OCC=C(Cl)COOCH ₃)]	43.32 (43.29)	3.08 (3.04)	158	1.21 (1.17)
XIIIB	PPN[<i>cis</i> -Pt(CO) ₂ (C ₂ H ₅ OCC=C(Cl)COOC ₂ H ₅)]	44.32 (44.26)	3.35 (3.30)	124	1.17 (1.14)
XIVA	<i>trans</i> -Pt(PPh ₃) ₂ (CH ₃ OCC=C(Cl)COOCH ₃)	49.10 (49.26)	3.50 (3.54)	>240	
XIVB	<i>trans</i> -Pt(PPh ₃) ₂ (C ₂ H ₅ OCC=C(Cl)COOC ₂ H ₅)	50.74 (50.73)	3.90 (3.83)	245	

^a In chloroform. ^b In acetone.

TABLE 2

INFRARED DATA (relative intensities: w = weak; m = medium; s = strong; vs = very strong; (br) = broad; (sh) = shoulder)

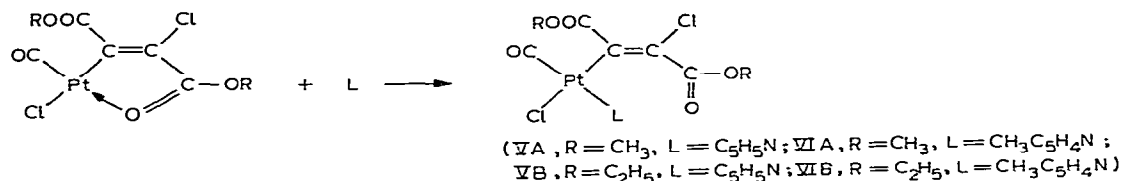
Compound	$\nu(\text{C}\equiv\text{O})$	$\nu(\text{C}=\text{O})$	$\nu(\text{C}-\text{OC})$	$\nu(\text{C}=\text{C})$	$\nu(\text{Pt}-\text{X})$
IA	2120vs	1728m 1710s 1575s	1230m 1275s	1550m	320m
α	2128vs	1725m(br) 1578s			
IB	2120vs	1710m 1695s 1570vs	1260vs 1285(sh)	1545m(sh)	320m
α	2118vs	1720m(br) 1570s			
IIA	2100m	1720vs(br) 1560s(br)	1250vs(br)		328w
IIB	2110m	1720vs(br) 1565m(br)	1240vs(br)		328w
IIIA	2120vs	1735s 1710s 1600m(sh) 1560vs(br)	1280s 1240s	1540m(sh)	
IIIB	2125vs	1725s 1705s 1605m(sh) 1560vs(br)	1270s 1240s	1545m(sh)	
IVA	2075vs	1712(sh) 1704s	1245vs	1555w	340s 300s
IVB	2080vs	1720s 1698s	1230vs	1550w	338s 305s
VA	2100vs	1715s 1685s	1275s 1240vs	1585w	315m
VB	2120vs	1705s 1690m	1260s 1240s	1580w	320m
VIA	2120vs	1715s 1705s	1265s 1245s	1580w	312m
VIB	2120vs	1720vs 1700s	1260vs 1230s	1585w	310m
VIIA		1710vs	1210s	1560w	302m
VIIIB		1705vs 1695(sh)	1208s	1565w	305m
VIIIA		1705s	1225s 1260vs	1560w	300m
VIIIB		1705vs	1245s 1220s	1555w	298m
IXA		1700vs	1255s 1230s	1560w	303m
IXB		1705vs	1240m 1205vs	1565w	298m
XA		1710vs 1700vs	1250vs 1215m	1545w	335m
XB		1715s 1705vs	1240s 1200m	1545w	330m
XIA		1715vs 1692vs	1265m 1225vs	1550w	345m
XIB		1708vs 1690vs	1260(sh) 1225vs	1550w	344m
XIIA	2080s	1720(sh) 1710vs	1245vs		2120s ($\nu(\text{SCN})$) 2060(sh) ($\nu(\text{SCN})$) 2140s ($\nu(\text{SCN})$) 2080(sh) ($\nu(\text{SCN})$)
XIIB	2095s	1718(sh) 1705vs	1240vs		

(Table continued)

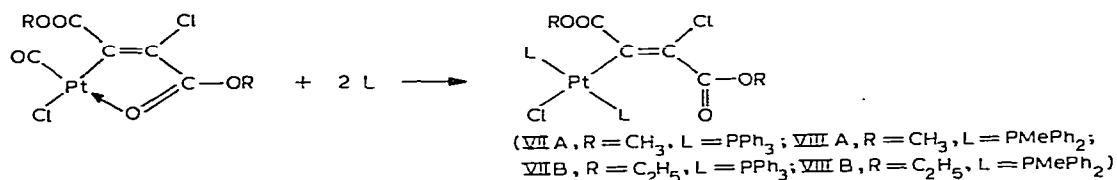
TABLE 2 (continued)

Compound	$\nu(\text{C}\equiv\text{O})$	$\nu(\text{C}=\text{O})$	$\nu(\text{C}-\text{OC})$	$\nu(\text{C}=\text{C})$	$\nu(\text{Pt}-\text{X})$
XIIIA	2070vs	1723s	1240vs	1575w	
XIIIB	2060vs	1700vs 1714vs 1704s	1230vs	1570w	
XIVA		1705vs	1255vs 1220vs	1570w	
XIVB		1705vs	1245s 1213s	1570w	

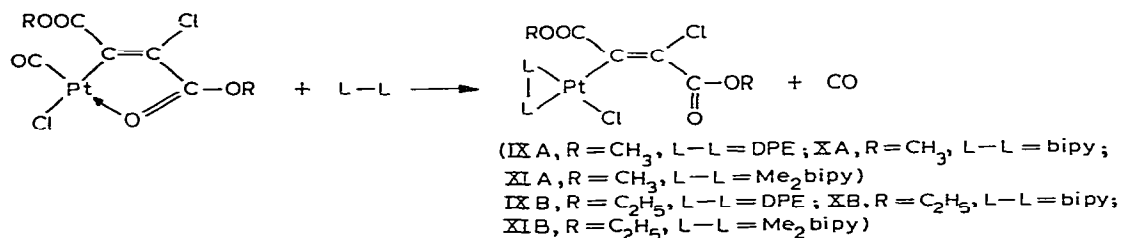
^a In chloroform.



The reaction with phosphorous donor ligands such as triphenylphosphine and methyldiphenylphosphine gives bis(tertiary phosphine) adducts, the carbon monoxide being replaced by a second molecule of the new ligand:



The stereochemical arrangement of the phosphines around the platinum atom has been defined in the case of the methyldiphenyl complexes VIIIA and VIIIB through the ⁴J(P-H) coupling constants, the value found (4 Hz) indicating that the phosphine ligands have a *trans* disposition [4,10]. Reaction with chelating donor ligands such as 1,2-bis(diphenylphosphino)ethane (DPE), 2,2'-bipyridine (bipy) and 4,4'-dimethyl-2,2'-bipyridine (Me₂bipy), gives substitution compounds in which the chloro atom is *cis* to the β-chlorovinyl moiety:



Further support for the view that two types of chlorine atoms are present in the molecules of compounds I, one still bonded to platinum, the other shifted to the β-carbon owing to the insertion of the activated acetylenes, came from

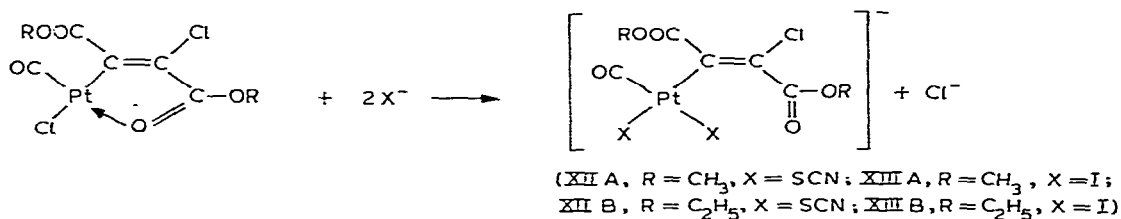
TABLE 3
 NMR DATA (Multiplicity: s = singlet; t = triplet; q = quartet; m = multiplet)

Compound	$\delta(\text{COOCH}_3)$	$\delta(\text{COOCH}_2\text{CH}_3)$	$\delta(\text{COOCH}_2\text{CH}_3)$	Other signals	$J(\text{P}-\text{H})$	Solvent
IA	3.86(s)				2	CDCl_3
	4.27(s)					
	3.87(s)				2	$\text{C}_3\text{D}_6\text{O}$
	4.32(s)					
IB		4.34(q)	1.28(t)		2.4	$\text{C}_3\text{D}_6\text{O}$
		4.77(q)	1.50(t)			
		4.37(q)	1.35(t)		2.4	CDCl_3
		4.72(q)	1.51(t)		—	$\text{C}_3\text{D}_6\text{O}$
IIA	3.80(m)				—	$\text{C}_3\text{D}_6\text{O}$
IIB	4.32(m)		1.3(m-broad)		—	$\text{C}_3\text{D}_6\text{O}$
		4.20(m) 3.75(m)				
IVA	3.76(s)			7-8(m) (C_6H_5)	2	CDCl_3
IVB	3.71(s)					
		4.26(q) 4.23(q)	1.40(t) 1.27(t)	7-8(m) (C_6H_5)	2.3	CDCl_3
VA	3.78(s)			7.6-9(m) ($\text{C}_5\text{H}_5\text{N}$)	2	$\text{C}_3\text{D}_6\text{O}$
	3.82(s)			7.6-9(m) ($\text{C}_5\text{H}_5\text{N}$)	2	$\text{C}_3\text{D}_6\text{O}$
VIB	3.76(s)		1.26(t)	2.4(s) ($\text{CH}_3\text{C}_5\text{H}_4\text{N}$)	2	CDCl_3
	3.83(s)		1.29(t)	7.2-9(m) ($\text{CH}_3\text{C}_5\text{H}_4\text{N}$) 2.54(s) ($\text{CH}_3\text{C}_5\text{H}_4\text{N}$)	2	$\text{C}_3\text{D}_6\text{O}$
VIA		4.27(q)	1.28(t)	7.2-9(m) ($\text{CH}_3\text{C}_5\text{H}_4\text{N}$)	2	$\text{C}_3\text{D}_6\text{O}$
		4.28(q)	1.30(t)	7.5(m) (C_6H_5)	2.4	CDCl_3
VIIA	3.23(s)					
	3.37(s)					

VIII		3.77(q) 3.82(q)	0.80(t) 1.05(t)	7.5(m) (C ₆ H ₅)	—	CDCl ₃
VIIIA	3.22(s) 3.56(s)			2.08(t) (P-CH ₃) ^a 7.5(m) (P-C ₆ H ₅) 2.07(t) (P-CH ₃) ^a 7.5(m) (P-C ₆ H ₅) 2.27(m) (CH ₂ -CH ₂) 7.5(m) (P-C ₆ H ₅) 2.37(m) (CH ₂ -CH ₂) 7.5(m) (P-C ₆ H ₅) 2.64(s) ((CH ₃) ₂ C ₁₀ H ₈ N ₂) 2.45(s) ((CH ₃) ₂ C ₁₀ H ₈ N ₂) 7.8-9.5(m) ((CH ₃) ₂ C ₁₀ H ₈ N ₂) 2.34(s) (CH ₂) ₂ C ₁₀ H ₈ N ₂) 2.46(s) ((CH ₃) ₂ C ₁₀ H ₈ N ₂) 7.8-9.5(m) ((CH ₃) ₂ C ₁₀ H ₈ N ₂) 7-8(m) (C ₆ H ₅)	4	CDCl ₃ ^b
VIIIB	3.76(q) 4.06(q)	0.82(t) 1.20(t)			3.5	CDCl ₃ ^b
IXA	3.37(s) 3.67(s)					CDCl ₃
IXB	3.76(q) 3.81(q)	0.76(t) 1.00(t)			2.5	CDCl ₃
XIA	3.78(s) 3.87(s)					CDCl ₃
XIB	4.16(q) 4.36(q)	1.14(t) 1.36(t)			—	CDCl ₃
XIIA	3.78(s) 3.82(s)					CDCl ₃
XIIB	4.07(q) 4.23(q)	1.20(t) 1.43(t)		7.5-8.5(m) (P-C ₆ H ₅)		C ₃ D ₆ O
XIIIA	3.67(s) 3.70(s)			7.2-7.8(m) (P-C ₆ H ₅)	1.5	C ₃ D ₆ O
XIIIB	4.17(q)	1.36(t) 1.25(t)		7.4-8.2(m) (P-C ₆ H ₅) 7.5(m) (P-C ₆ H ₅)	—	C ₃ D ₆ O
XIVA	3.36(s) 3.31(s)					CDCl ₃
XIVB	3.78(q) 3.90(q)	0.80(t) 1.03(t)		7.2-7.8(m) (P-C ₆ H ₅)	—	CDCl ₃

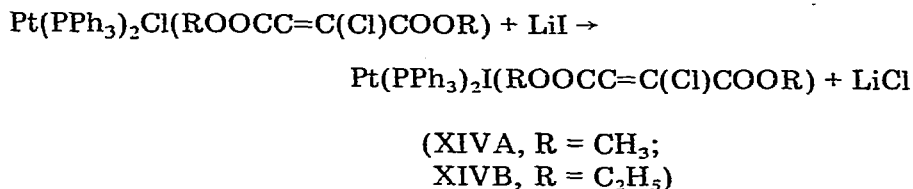
^a J(H-3|P) 4 Hz. ^b J(P-P-CH₃) 31 Hz.

the metathesis reaction with SCN^- and I^- , in which only one of the two chlorine atoms is replaced by the entering ion. The lability of the $\text{Pt}-\text{OCOR}$ bond favours the formation of an anion which could be isolated and fully characterized as salts of NEt_4^+ or PPN^+ :



The stereochemistry of these anions is closely related to the parent compounds I, as far as the geometry around the double bond is concerned: in fact the ^1H NMR spectrum of XIIA shows two almost equivalent singlets at δ 3.78 and 3.82 ppm, the higher resonance being coupled with platinum.

Finally the presence of a much less reactive chlorine atom located in the vinylic part of the molecule is confirmed by the reaction of the chlorobis(triphenylphosphine) derivatives VIIA and VIIB with LiI in acetone, which led to iodobis(triphenylphosphine)(1,2-*trans*-dicarboalkoxy-2-chloroethenyl)platinum (XIV) by exchange of the chlorine bonded to platinum:



Conclusions

The reaction of dichlorodicarbonylplatinum with dialkylacetylene dicarboxylate to give β -chlorovinyl derivatives requires that an intermediate complex is first formed by replacement of one of the carbonyl groups, and this followed by the *trans* insertion of the coordinated acetylene into the $\text{Pt}-\text{Cl}$ bond. This insertion does not seem to proceed through the formation of chlorine atoms, contrary to the scheme proposed for the reaction of dimethylacetylene dicarboxylate with methylplatinum(II) compounds [4]. We did not observe any change in the type of compounds formed and in the rate of formation of I when the reaction was carried out in chloroform. Moreover the addition of HCl gas prevented the reaction, owing to the formation of inactive $[\text{Pt}(\text{CO})\text{Cl}_3]^-$, and the addition of free radical initiator (benzoyl peroxide) did not affect the rate of reaction. The lack of any evidence of radical formation or induction makes more probable an alternative path involving formation of the *cis* isomer, as observed in reaction of acetylenes with halopalladium [10], hydridoplatinum(II) [11], and methylplatinum complexes [3]. This *cis* isomer is unstable and

undergoes rapid isomerisation to the *trans* form. This type of facile isomerisation mechanism has been proposed for the cyclopentadienyl complexes of ruthenium [12], implying the formation of a dipolar intermediate with localisation of a negative charge on the carbonyl oxygen rather than on the β -carbon atom. This second scheme could require some degree of stabilisation of the intermediate carbonium ion by the metal, perhaps involving some donation of electron density from the electron rich metal centre or by delocalisation of the negative charge through the conjugate system. On the other hand, formation of the much more thermodynamically stable chelate complex may provide the driving force of the isomerisation. The formation of a relatively stable carbocation as intermediate is also in agreement with the reactions of the organic moiety of these complexes with nucleophiles [13]. As for the influence of the substituents present on the acetylene molecule on the reactivity towards dichlorodicarbonylplatinum, it seems that electron-withdrawing groups are important in stabilizing an ionic intermediate which may undergo nucleophilic attack by the chloride anions arising from dissociation of the Pt—Cl bond. On the other hand the (1,2-*trans*-dicarboalkoxy-2-chlorovinyl) derivative, being stabilized by the interaction of the carbonyl ester group with platinum, inhibits the insertion of the second mole of disubstituted acetylene, at least in the conditions in which the synthesis was carried out, and prevents any formation of cyclobutadiene compounds, such as occurs in the case of 2-butyne and 3-hexyne [1].

Experimental

Solvents were purified and dried by standard methods. Infrared spectra were recorded on a Perkin—Elmer 457 grating spectrophotometer, the samples being examined as Nujol mulls between NaCl and CsI plates; the spectra of the solutions were recorded with 0.1 mm CaF₂ cells. The spectra were calibrated with polystyrene. Molecular weights were determined with a Mechrolab Osmometer Mod. 301. Mass spectra were recorded on a Varian Mar CH-7 spectrometer.

Nuclear magnetic resonance spectra were recorded on a Varian Nera NV 14 spectrometer at 60 MHz or on a Varian XL-100 A using chloroform or acetone-d solutions. Chemical shifts (δ) are reported in ppm, down-field from internal TMS, and coupling constants (J) are given in Hz.

Reaction of dicarbonyldichloroplatinum with dimethylacetylene dicarboxylate

(a) 70 ml of a benzene solution containing 3.5 g (0.0168 mol) of Pt(CO)₂Cl₂ and 2.04 g (0.0144 mol) of dimethylacetylene dicarboxylate was refluxed under nitrogen for 12 h. The solution was filtered at 80°C; a pale green solid was collected on the filter, washed with hot benzene (50 ml) and dried (yield 3.170 g, 4.8%). It is insoluble in all the common organic solvents, and was identified as the polymeric species IIIA. Cooling of the benzene solution gave a yellow solid, which was filtered off and recrystallized by extraction with hexane in a Soxhlet apparatus (2.52 g). It was identified as carbonylchloro (1,2-*trans*-dicarboalkoxy-2-chloroethyl) platinum (IA). Concentration of the benzene solution (50 ml) followed by hexane addition (50 ml) gave more IA, which was recrystallized by hexane extraction (1.5 g). Total yield of IA 84.15%

(b) The same reaction was carried out with a different $\text{Pt}(\text{CO})_2\text{Cl}_2$ /acetylene ratio ($\text{Pt}(\text{CO})_2\text{Cl}_2$ 6.62 g, 0.02 mol; $\text{CH}_3\text{OOC}=\text{C}=\text{COOCH}_3$ 5.54 g, 0.044 mmol; benzene 90 ml). No green product was obtained. Cooling the solution gave thin yellow needles of IA which were purified by extraction with hexane in a Soxhlet apparatus: 5.6 g of pure IA were obtained (yield 56%). Addition of hexane to the benzene mother liquor gave a pale-yellow solid, which was purified by crystallization from toluene/hexane and identified as IIA (1.85 g yield 15.5%).

Reaction of IA with dimethylacetylene dicarboxylate

IA (0.240 g, 0.55 mmol) was refluxed in benzene (20 ml) with dimethylacetylene dicarboxylate (0.25 g, 1.76 mmol) for 12 h. Addition of hexane (50 ml) gave the pale-yellow compound IIIA, which was filtered off, washed with hexane, and dried. It was recrystallized from toluene/hexane (0.170 g, yield 53%).

Reaction of dicarbonyldichloroplatinum with diethylacetylene dicarboxylate

(a) $\text{Pt}(\text{CO})_2\text{Cl}_2$ (8 g, 24.8 mmol) was refluxed under nitrogen with acetylenedicarboxylate diethyl ester (5.7 g, 31.5 mmol) in toluene (100 ml) for 3 h. Filtration at 80°C gave a pale-green solid, which was washed with hot toluene (50 ml), and dried (0.346 g, 3.5%). This compound, insoluble in all the organic solvents, was identified as the polymeric species IIIB. On cooling the toluene solution gave golden-yellow needles, which were filtered off, washed with cold toluene, dried, and recrystallized by extraction in a Soxhlet apparatus with hexane (10.3 g, 89.3%). They were identified as carbonylchloro(1,2-*trans*-dicarboethoxy-2-chloroethenyl)platinum (IB).

(b) $\text{Pt}(\text{CO})_2\text{Cl}_2$ (2.045 g, 10.5 mmol) dissolved in toluene (100 ml) was treated with acetylenedicarboxylate diethyl ester at 100°C (1.79 g, 10.5 mmol): the organic reagent was added to the solution gradually (0.2 ml, 2 h) with vigorous stirring. After 8 h the suspension obtained was filtered at 80°C and a pale-green powder was collected on the filter, washed with hot toluene (60 ml) and hexane (50 ml), and dried. It was identified as IIIB (yield 1.76 g, 47.37%).

The toluene solution was evaporated in vacuum to a volume of 40 ml: cooling at -10°C gave golden-yellow needles of IB (yield 1.78 g, 31.6%).

*(PPN)[carbonyl-cis-dichloro(1,2-*trans*-dicarbomethoxy-2-chloroethenyl)platinum] (IVA)*

IA (0.445 g, 1.02 mmol) in CHCl_3 (20 ml) were treated with PPNCl (1.17 g, 2.04 mmol). The solution was evaporated to dryness and the solid residue redissolved in methanol (10 ml). Cooling at -10°C gave a white crystalline solid which was filtered off, washed with methanol (15 ml) and dried. (0.722 g, yield 70%). Λ_M 103.8 $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$ ($\sim 10^{-3} M$ acetone).

*(PPN)[carbonyl-cis-dichloro(1,2-*trans*-dicarboethoxy-2-chloroethenyl)platinum] (IVB)*

IB (0.422 g, 0.91 mmol) in CHCl_3 (10 ml) was treated with PPNCl (1.043 g, 1.82 mmol) in CHCl_3 (5 ml). The solution was evaporated to dryness in vacuum and the solid residue was stirred with ethanol (10 ml) at 50°C for 1 h. Cooling at -10°C , gave a white crystalline solid, which was filtered off, washed with

cold ethanol (5 ml), and dried (0.640 g, yield 68%). Λ_M 106.7 ohm⁻¹ cm² mol⁻¹ ($\sim 10^{-3}$ M acetone).

[Carbonylchloropyridine(1,2-trans-dicarbomethoxy-2-chloroethenyl)platinum] (VA)

IA (0.120 g, 0.275 mmol) was treated in CH₂Cl₂ (10 ml) with pyridine (0.110 g, 1.39 mmol). The solution immediately went colourless. After filtration the solvent was evaporated to a volume of 2 ml, and hexane (20 ml) was added. The white solid which separated was filtered off, washed, and dried (0.07 g, yield 48%).

[Carbonylchloropyridine(1,2-trans-dicarboethoxy-2-chloroethenyl)platinum] (VB)

IB (0.47 g, 1.01 mmol) was treated with pyridine (0.4 g, 5.06 mmol) in benzene (10 ml). Addition of hexane (30 ml) to the colourless solution gave a white crystalline solid, which was washed with hexane (20 ml) and dried (430 mg, yield 78%).

[Carbonylchloro-3-methylpyridine(1,2-trans-dicarbomethoxy-2-chloroethenyl)platinum] (VIA)

IA (0.26 g, 0.59 mmol) was treated in CHCl₃ (10 ml) with 3-methylpyridine (172 mg, 1.85 mmol). The solution immediately went colourless. It was filtered, and the volume reduced to 2 ml: addition of hexane (40 ml) gave a white powder, which was filtered off, washed with hexane and dried (0.178 g, yield 60%).

[Carbonylchloro-3-methylpyridine(1,2-trans-dicarboethoxy-2-chloroethenyl)platinum] (VIB)

To a suspension of IB (0.4 g, 0.862 mmol) in hexane (10 ml) was added 3-methylpyridine (0.2 g, 2.15 mmol). After stirring for 1 h a cream solid was filtered off, washed with hexane, and dried (0.302 g, yield 63%).

[Bis(triphenylphosphine)chloro(1,2-trans-dicarbomethoxy-2-chloroethenyl)platinum] (VIIA)

IA (0.270 g, 0.62 mmol) was treated in CHCl₃ (30 ml) with 3 ml of CHCl₃ solution of PPh₃ (0.40 g, 1.52 mmol). As soon as the solution became colourless, it was filtered and the volume was reduced to 5 ml. Addition of hexane (20 ml) gave a white powder, which was filtered off, washed with toluene (5 ml), and dried (0.407 g, yield 70.5%).

[Bis(triphenylphosphine)chloro(1,2-trans-dicarboethoxy-2-chloroethenyl)platinum] (VIIB)

IB (0.494 g, 1.06 mmol) was stirred at 60°C under nitrogen with PPh₃ (0.559 g, 2.13 mmol) in toluene (15 ml) for 20 min. The white precipitate was washed and dried (0.7 g, yield 68.5%).

[trans-Bis(methyldiphenylphosphine)chloro(1,2-trans-dicarbomethoxy-2-chloroethenyl)platinum] (VIIIA)

IA (0.607 g, 1.39 mmol) was treated with methyldiphenylphosphine (0.606 g,

3.03 mmol) in toluene (20 ml) under nitrogen. After 20 min warming the colourless solution was filtered and the solvent evaporated to dryness. The oily residue was treated with hexane (50 ml) and shaken until a white solid was obtained. This was filtered off, dried, and recrystallized from CHCl_3 /hexane (0.808 g, yield 72%).

[trans-Bis(methyldiphenylphosphino)chloro(1,2-trans-dicarboethoxy-2-chloroethenyl)platinum] (VIII B)

IB (0.455 g, 0.93 mmol) and PMePh_2 (0.616 g, 3.08 mmol) were dissolved in toluene (20 ml) under nitrogen and heated at 80°C for 4 h. The colourless solution was filtered and evaporated to dryness. The solid residue was treated twice with 30 ml hexane, and stirred to give a white solid which was filtered off, washed with 30 ml hexane, and dried (0.568 g, yield 73%).

[1,2-Bis(diphenylphosphino)ethanechloro(1,2-trans-dicarbomethoxy-2-chloroethenyl)platinum] (IX A)

IA (1.08 g, 2.47 mmol) was treated with 1,2-bis(diphenylphosphino)ethane (1.058 g, 2.65 mmol) in toluene (15 ml) and heated for 10 min at 60°C . Cooling at -20°C gave a white solid, which was filtered off and crystallized from CHCl_3 (1.39 g, yield 70%).

[1,2-Bis(diphenylphosphino)ethanechloro(1,2-trans-dicarboethoxy-2-chloroethenyl)platinum] (IX B)

IB (0.503 g, 1.08 mmol) in toluene (20 ml) was treated with DPE (0.483 g, 1.21 mmol) and heated at 80°C for 3 h. The white solid was filtered off, washed with toluene, and dried (0.586 g, yield 65%).

[2,2'-Bipyridinechloro(1,2-trans-dicarbomethoxy-2-chloroethenyl)platinum] (XA)

IA (0.2 g, 0.458 mmol) was added to a toluene solution (15 ml) containing 2,2'-bipyridine (0.074 g, 0.474 mmol). After 2 h stirring the volume of the solution was reduced to 5 ml by evaporation in vacuum. Addition of hexane (30 ml) gave a yellow-green solid, which was filtered off and washed with hexane (0.240 g, yield 92%).

[2,2'-Bipyridinechloro(1,2-trans-dicarboethoxy-2-chloroethenyl)platinum] (XB)

IB (0.340 g, 0.732 mmol) dissolved in benzene (20 ml) was treated with 2,2'-bipyridine (0.150 g, 0.96 mmol) with vigorous stirring. After 1 h the yellow-green solid was filtered off, washed with benzene (20 ml), and dried (0.368 g, yield 85%).

[(4,4'-Dimethyl-2,2'-bipyridine)chloro(1,2-trans-dicarbomethoxy-2-chloroethenyl)platinum] (XIA)

IA (0.695 g, 1.59 mmol) and 4,4'-dimethyl-2,2'-bipyridine (0.322 g, 1.75 mmol) were dissolved in chloroform (15 ml) with stirring. After warming at 85°C for 4 h a yellowish crystalline solid separated; this was filtered off, washed with toluene (20 ml) and chloroform (20 ml), and dried (0.753 g, yield 80%).

[4,4'-Dimethyl-2,2'-bipyridine]chloro(1,2-trans-dicarboethoxy-2-chloroethenyl)-platinum] (XIB)

IB (0.514 g, 1.1 mmol) was dissolved in toluene (20 ml) containing 4,4'-dimethyl-2,2'-bipyridine (0.264 g, 1.43 mmol). After warming up at 80°C for 3 h, the solution was evaporated to dryness, and the solid residue treated with hexane (20 ml) and stirred. The yellow solid was filtered off, washed with hexane (20 ml), and dried (0.614 g, yield 90%).

(PPN)[carbonylbis(thiocyanide)(1,2-trans-dicarbomethoxy-2-chloroethenyl)-platinum] (XIIA)

IA (0.210 g, 0.48 mmol) was added with stirring to an anhydrous methanol (30 ml) solution of LiSCN (0.290 g, 4.46 mmol). The colourless solution was refluxed for 4 h, then cooled, and a solution of PPNSCN (0.298 g, 0.5 mmol) in MeOH (5 ml) was added. After reducing the volume of the solution to 5 ml by evaporation of the methanol in vacuum, and cooling at -20°C, a white crystalline solid was obtained, which was washed with cold methanol and dried (0.120 g, yield 24%).

(PPN)[carbonylbis(thiocyanide)(1,2-trans-dicarboethoxy-2-chloroethenyl)-platinum] (XIIB)

IB (0.142 g, 0.3 mmol) and PPNSCN (0.3874 g, 0.65 mmol) were dissolved in anhydrous ethanol (30 ml). The solution was refluxed for 3 h. Standing at -10°C gave a white crystalline solid, which was washed with ethanol (10 ml) and dried (0.140 g, yield 43%).

(PPN)[carbonyldiiodo(1,2-trans-dicarbomethoxy-2-chloroethenyl)platinum] (XIIIA)

IA (0.444 g, 1.02 mmol) was dissolved in anhydrous methanol (20 ml) containing NaI (3.1 g, 19.3 mmol). The pale-yellow solution was heated at 60°C for 4 h. PPNI (1.35 g, 2.04 mmol) was added. On cooling at -10°C a pale yellow crystalline solid separated, and this was filtered off and washed with cold methanol (5 ml) (0.535 g, 44% yield).

(PPN)[carbonyldiiodo(1,2-trans-dicarboethoxy-2-chloroethenyl)platinum] (XIIIB)

IB (0.402 g, 0.87 mmol) was dissolved in anhydrous ethanol (15 ml) containing LiI (1.16 g, 8.7 mmol). The pale-yellow solution was heated at 70°C for 3 h. Addition of PPNI (1.16 g, 1.74 mmol) gave, after cooling at -10°C, a pale-yellow crystalline solid, which was filtered off and washed with cold ethanol (5 ml) (0.393 g, yield 37%).

[Bis(triphenylphosphine)iodo(1,2-trans-dicarbomethoxy-2-chloroethenyl)-platinum] (XIVA)

VIIA (0.3085 g, 0.33 mmol) was added to acetone (20 ml) containing NaI (0.5 g, 3.3 mmol). After 4 h refluxing the suspension was evaporated to dryness and the solid residue treated with 20 ml methanol. The pale-yellow solid was filtered off, washed with methanol, and dried in vacuum (0.253 g, yield 75%).

[Bis(triphenylphosphine)iodo(1,2-trans-dicarboethoxy-2-chloroethenyl)-platinum] (XIVB)

VIIB (0.430 g, 0.448 mmol) and LiI (0.210 g, 1.56 mmol) were refluxed in acetone (20 ml) for 3 h. The solution was evaporated to dryness and the solid residue was treated with ethanol (30 ml) and stirred. The pale-yellow solid was filtered off, washed with ethanol (10 ml), and dried (0.245 g, yield 52%).

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