Reactions of Acetylenes with Noble-metal Carbonyl Halides. Part 4.[1] The Formation of a Platinaoxacyclopentenone Ring

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The compound $[N(PPh_3)_2][\mathit{cis}\text{-}Pt\{C(CO_2R)=C(Cl)CO_2R\}(CO)Cl_2]$ (1; R = Me or Et) reacts with water in polar solvents to give $[N(PPh_3)_2][\overline{Pt\{C(CO_2R)=C(Cl)COO}\}(CO)Cl]$ (2), containing a platinaoxacyclopentenone ring. In anhydrous conditions $[Pt(CO)_2Cl_2]$ reacts with $RO_2CC{\equiv}CCO_2R$ to give the insoluble polymeric species $[\{\overline{Pt[C(CO_2R)=C(Cl)COO}](CO)\}_n]$ (7) which has been characterized both by conversion into (2) and by reaction with uni- and bi-dentate ligands to give $[\overline{Pt\{C(CO_2R)=C(Cl)COO}\}L_2]$ (L = PPh_3, $PMePh_2$, or $PEtPh_2$), $[\overline{Pt\{C(CO_2R)=C(Cl)COO}\}(L\text{–}L)]$ [L–L = 2,2′-bipyridine(bipy),4,4′-dimethyl-2,2′-bipyridine (dmbipy), or 1,2-bis(diphenylphosphino)ethane (dppe)], and $[\overline{Pt\{C(CO_2R)=C(Cl)COO}\}(CO)L]$ [L = pyridine (py), methylpyridine (mpy), or dimethylpyridine (dmpy)], where the metallo-organic ring is preserved. No breaking of the ring was observed on reaction with chlorine and hydrochloric acid; conversely alkyl iodide gave $[Pt\{C(CO_2R)=C(Cl)CO_2R'\}(CO)I]$ which is readily converted into salt-like compounds of type (1) by reaction with $[N(PPh_3)_2]Cl$. A cyclisation mechanism is proposed for both the reaction in anhydrous conditions and that in the presence of water. Crystals of $[N(PPh_3)_2][\overline{Pt\{C(CO_2Me)=C(Cl)COO}\}(CO)Cl]$ (2b) are triclinic, space group $P\bar{1}$, with a = 17.144(5), b = 11.975(4), c = 10.386(4) Å, α = 106.62(8), β = 77.07(7), γ = 95.94(7)°, and Z = 2. The crystal structure has been solved by the heavy-atom method from counter data and refined by least squares to a final R of 0.041 (for 3 055 observed reflections). The structure consists of discrete anionic molecules and cationic counter ions, $[N(PPh_3)_2]^+$.

THE reaction of transition-metal complexes containing carbonyl ligands with alkynes, leading to cyclobutadiene derivatives, as well as to metal–alkyl compounds, has been the subject of several investigations.[2,3] The interest in these reactions arises not only because of their potential synthetic value but also because they are useful models for the mechanism of the cyclization of alkynes and the formation of metal–carbon bonds.

During a study of the reaction of $[Pt(CO)_2Cl_2]$ with symmetrically disubstituted acetylenes we were able to show that different compounds can be obtained depending on the nature of the substituent present on the triple bond. Electron-donor groups favour the formation of the cyclobutadiene ring and the insertion of the carbonyl group into the organic moiety to form cyclopentadienone and quinone rings.[4,5] Strongly electron-withdrawing substituents, such as carboalkoxy-groups, however, lead to the insertion of the organic part into the platinum–chlorine bond to form σ-alkenyl compounds of platinum(II) with further stabilization achieved by chelation of the β-carboalkoxy-group on platinum.[6] This latter interaction has been found to play an important role in the labilization of the alkoxy-group on the γ-carbon atom so that specific alcoholysis may occur.[1]

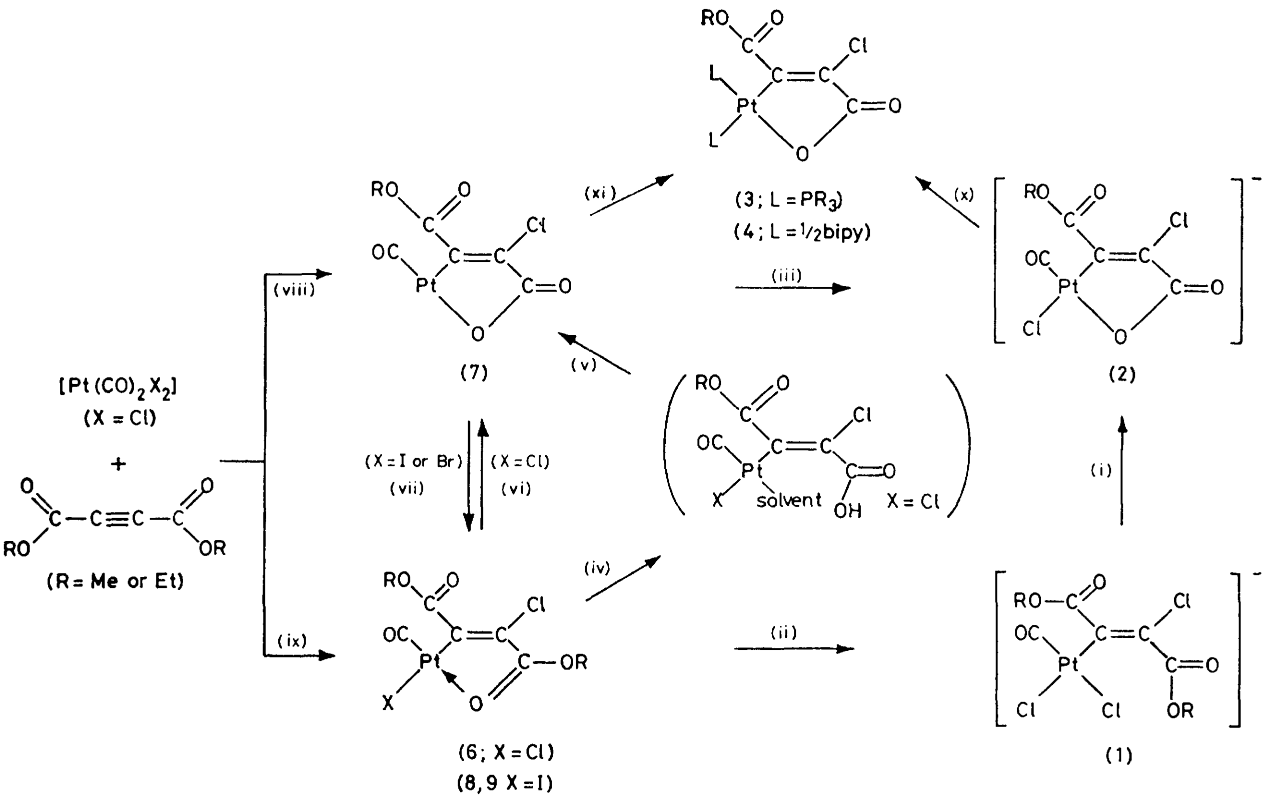
As part of our studies of the reactivity of $[Pt(CO)_2Cl_2]$ with alkynes we now report the preparation and properties of some new compounds of platinum(II) in which the metal is inserted into a five-membered ring.[7]

RESULTS AND DISCUSSION

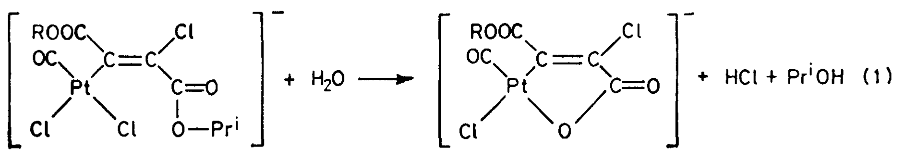
Anionic Species containing a Five-membered Ring.— σ-Alkenyl anions *cis*-$[Pt\{C(CO_2R)=C(Cl)CO_2R\}(CO)Cl_2]^-$ (1; R = Me or Et) react with dry primary and secondary alcohols to give specific alcoholysis of the γ-alkoxy-group. When this exchange reaction is carried out in wet alcohols the yield of the expected anion appears to be considerably lowered; moreover, both white and yellow crystals separate from the pale yellow solution, the former identified as those already reported,[1] the latter, much more soluble, containing a different type of anion. On the other hand, yellow crystals can be isolated as the only species from the mother-liquor of any alcoholysis reaction when solutions are left standing for several days at room temperature in a wet atmosphere [reaction (i) of Scheme].

A careful investigation of the reaction course by gas–liquid chromatography (g.l.c.) was carried out in order to clarify the nature and the mode of formation of this new anionic species. When the $[N(PPh_3)_2]^+$ salt of *cis*-(*trans*-1-alkoxycarbonyl-2-chloro-2-isopropoxycarbonylvinyl)carbonyldichloroplatinate(II) (1), the molecular structure of which has been previously determined,[1] is warmed in wet 1,2-dimethoxyethane the stoicheiometric amount of Pr^iOH detected corresponds to reaction (1). The same reaction was found to occur in wet acetone, chloroform, and dichloromethane and also with other σ-alkenyl anions containing different alkoxy-groups such as OMe, OEt, and OPr on the γ-carbon atom.

The nature of the bond giving rise to the formation of the ring was inferred from the chemical behaviour and i.r. and ^1H n.m.r. data (see Tables 1 and 2). The ^1H n.m.r. spectra of compounds (2b) and (2a) show only one set of signals, assignable to the methoxy- and to the ethoxy-group respectively, in the expected ratio for the



SCHEME (i) H_2O, $-HCl$, $-ROH$; (ii) Cl^-; (iii) Cl^-; (iv) H_2O, $-ROH$; (v) $-HX$; (vi) $-RX$; (vii) RX; (x) 2L, $-Cl^-$; (xi) 2L



(1a; R = Et)
(1b; R = Me)

(2a; R = Et)
(2b; R = Me)

bulky $[N(PPh_3)_2]^+$ cation, confirming that the cyclization reaction involves the β-carboalkoxy-group. The main feature of the i.r. spectrum of the $[N(PPh_3)_2]^+$ salt of the anions (2a) and (2b) is the three carbonyl-stretching bands at 2 080, 1 705, and 1 670 cm^{-1} and at 2 080, 1 715, and 1 680 cm^{-1} respectively; the first is assigned to the terminal CO group, the second to the carboalkoxy-carbonyl group, and the third to the β-carbonyl group inserted into the ring. Elemental analysis and conductivity data in acetone (Table 3) are consistent with the proposed formulation of these compounds as 1 : 1 electrolytes. The formation of a stable ring containing platinum is confirmed by the behaviour of the anion when modifications on the platinum atom are caused by the action of other ligands. Pyridine and 2-methylpyridine do not react with the ring, while phosphorus ligands and nitrogen-chelating ligands lead to neutral species according to reaction (x) of the Scheme.

Remarkable stability of both the Pt–C and Pt–O bonds was also observed in the reaction of (2) with chlorine: no cleavage of the vinyl moiety occurred while oxidative addition of the reagent on the platinum atom took place to give the new platinum(IV) anions $[\overline{\mathrm{Pt}\{\mathrm{C(CO_2R)=C(Cl)CO}}\mathrm{O}\}\mathrm{Cl_3}]^-$ (5a, R = Et; 5b, R = Me). Moreover, no cleavage of any bond or modifications in the ring were observed on reaction with hydrogen chloride in boiling benzene or toluene; in these conditions compounds (2) were recovered unchanged. Definitive support for the reaction path leading to the formation of the stable platinaoxacyclopentenone ring comes from an *X*-ray structural determination of $[N(PPh_3)_2][\overline{\mathrm{Pt}\{\mathrm{C(CO_2Me)=C(Cl)CO}}\mathrm{O}\}\mathrm{(CO)Cl}]$ (2b), confirming the formation of the Pt–O bond through the elimination of alkyl halide.

Description of the Structure of $[N(PPh_3)_2][\overline{\mathrm{Pt}\{\mathrm{C(CO_2Me)=C(Cl)CO}}\mathrm{O}\}\mathrm{(CO)Cl}]$ (2b).— A schematic view of the anion is given in the Figure. The most significant bond lengths and angles are reported in

TABLE 1

Infrared spectral data ($\mathrm{cm^{-1}}$)[a]

	Compound	$\nu(C{\equiv}O)$	Others
(2a)	$[\mathrm{N(PPh_3)_2}][\mathrm{Pt\{C(CO_2Et){=}C(Cl)COO\}(CO)Cl}]$[b]	2 080vs	1 705s, 1 670vs, 1 570w, 1 230vs
(2b)	$[\mathrm{N(PPh_3)_2}][\mathrm{Pt\{C(CO_2Me){=}C(Cl)COO\}(CO)Cl}]$[c]	2 080vs 2 055 (sh)	1 715s, 1 680vs, 1 565vw, 1 235s
(3a)	$[\mathrm{Pt\{C(CO_2Et){=}C(Cl)COO\}(PPh_3)_2}]$		1 720s, 1 670vs, 1 210s
(3b)	$[\mathrm{Pt\{C(CO_2Me){=}C(Cl)COO\}(PPh_3)_2}]$		1 700s, 1 675vs, 1 240s
(4a)	$[\mathrm{Pt\{C(CO_2Et){=}C(Cl)COO\}(bipy)}]$		1 700s, 1 670vs, 1 230vs
(4b)	$[\mathrm{Pt\{C(CO_2Me){=}C(Cl)COO\}(bipy)}]$		1 720vs, 1 560m, 1 220s
(5a)	$[\mathrm{N(PPh_3)_2}][\mathrm{Pt\{C(CO_2Et){=}C(Cl)COO\}Cl_3}]$[d]		1 730s, 1 670vs, 1 250s
(5b)	$[\mathrm{N(PPh_3)_2}][\mathrm{Pt\{C(CO_2Me){=}C(Cl)COO\}Cl_3}]$[e]		1 735s, 1 670vs, 1 250s
(7a)	$[\mathrm{Pt\{C(CO_2Et){=}C(Cl)COO\}(CO)}]$	2 130vs	1 720s, 1 700s, 1 600s, 1 550vs, 1 270s, 1 220m
(7b)	$[\mathrm{Pt\{C(CO_2Me){=}C(Cl)COO\}(CO)}]$	2 130vs	1 735s, 1 710s, 1 600s, 1 560vs, 1 280s, 1 235s
(8a)	$[\mathrm{Pt\{C(CO_2Et){=}C(Cl)CO_2Et\}(CO)I}]$	2 110vs 2 100vs	1 720 (sh), 1 700s, 1 570vs, 1 260s
(8b)	$[\mathrm{Pt\{C(CO_2Me){=}C(Cl)CO_2Et\}(CO)I}]$	2 100vs	1 720vs, 1 580s, 1 545m, 1 235s
(9a)	$[\mathrm{Pt\{C(CO_2Et){=}C(Cl)CO_2Me\}(CO)I}]$	2 115s 2 100vs	1 695s, 1 575s, 1 260s
(9b)	$[\mathrm{Pt\{C(CO_2Me){=}C(Cl)CO_2Me\}(CO)I}]$	2 120s 2 105vs	1 710vs, 1 570vs, 1 550m, 1 250s
(10a)	$[\mathrm{Pt\{C(CO_2Et){=}C(Cl)COO\}(CO)(py)}]$	2 095vs	1 720 (sh), 1 705vs, 1 695vs, 1 580w, 1 240s
(10b)	$[\mathrm{Pt\{C(CO_2Me){=}C(Cl)COO\}(CO)(py)}]$	2 100vs	1 730vs, 1 705 (sh), 1 700vs, 1 570w, 1 220s
(11a)	$[\mathrm{Pt\{C(CO_2Et){=}C(Cl)COO\}(CO)(mpy)}]$	2 100vs	1 720 (sh), 1 710s, 1 690vs, 1 680vs, 1 540w, 1 230s
(11b)	$[\mathrm{Pt\{C(CO_2Me){=}C(Cl)COO\}(CO)(mpy)}]$	2 100vs 2 050w	1 720s, 1 680vs, 1 530w, 1 225s
(12a)	$[\mathrm{Pt\{C(CO_2Et){=}C(Cl)COO\}(CO)(dmpy)}]$	2 095vs	1 718s, 1 685vs, 1 545w, 1 235s
(12b)	$[\mathrm{Pt\{C(CO_2Me){=}C(Cl)COO\}(CO)(dmpy)}]$	2 100vs 2 050w	1 720s, 1 680vs, 1 530w, 1 225s
(13a)	$[\mathrm{Pt\{C(CO_2Et){=}C(Cl)COO\}(PEtPh_2)_2}]$		1 710 (sh), 1 695s, 1 665vs, 1 240s
(13b)	$[\mathrm{Pt\{C(CO_2Me){=}C(Cl)COO\}(PEtPh_2)_2}]$		1 710 (sh), 1 705vs, 1 665vs, 1 235s
(14a)	$[\mathrm{Pt\{C(CO_2Et){=}C(Cl)COO\}(PMePh_2)_2}]$		1 690s, 1 675vs, 1 570w, 1 230s
(14b)	$[\mathrm{Pt\{C(CO_2Me){=}C(Cl)COO\}(PMePh_2)_2}]$		1 700s, 1 680s, 1 255s
(15a)	$[\mathrm{Pt\{C(CO_2Et){=}C(Cl)COO\}(dppe)}]$		1 705s, 1 660vs, 1 650s, 1 570w, 1 230m
(15b)	$[\mathrm{Pt\{C(CO_2Me){=}C(Cl)COO\}(dppe)}]$		1 720 (sh), 1 705s, 1 680, 1 645s, 1 580w, 1 240s
(16a)	$[\mathrm{Pt\{C(CO_2Et){=}C(Cl)COO\}(dmbipy)}]$		1 725w, 1 700w, 1 660s, 1 560w, 1 225s
(16b)	$[\mathrm{Pt\{C(CO_2Me){=}C(Cl)COO\}(dmbipy)}]$		1 718m, 1 670s, 1 625w, 1 560w, 1 240s

[a] As Nujol mulls. Relative intensities: w, weak; m, medium; s, strong; sh, shoulder. [b] Pt–Cl stretching frequency: 315s $\mathrm{cm^{-1}}$. [c] Pt–Cl stretch: 320s $\mathrm{cm^{-1}}$. [d] Pt–Cl stretch: 340s $\mathrm{cm^{-1}}$. [e] Pt–Cl stretch: 335s $\mathrm{cm^{-1}}$.

TABLE 2

Proton n.m.r. spectral data (δ/p.p.m.)*

Compound	OCH_3	OCH_2CH_3	OCH_2CH_3	Other signals
(2a)		4.66 (q)	1.26 (t)	7—8 (m) (C_6H_5)
(2b)	3.78 (s)			7—8 (m) (C_6H_5)
(3a)		3.08 (q)	0.95 (t)	6.5—8 (m) (C_6H_5)
(3b)	2.78 (s)			7—7.7 (m) (C_6H_5)
(8a)		4.36 (q), 4.71 (q)	1.35 (t), 1.52 (t)	
(8b)	3.86 (s)	4.7 (q)	1.5 (t)	
(9a)	4.27 (s)	4.39 (q)	1.35 (t)	
(9b)	3.92 (s) 4.28 (s)			
(10a)		4.33 (q)	1.36 (t)	8.5—9.5 (m) (C_6H_5)
(10b)	3.83 (s)			8.85—9.5 (m) (C_6H_5)
(11a)		4.35 (q)	1.35 (t)	2.45 (s) (CH_3-C_5H_4N); 7.5—9 (m)($CH_3C_5H_4N$)
(11b)	3.76 (s)			2.48 (s) (CH_3-C_5H_4N); 7.33—8.83(m)($CH_3C_5H_4N$)
(12a)		4.35 (q)	1.36 (t)	2.35 (s), 2.45 (s), 7—8.8 (m) $[(CH_3)_2C_5H_3N]$
(12b)	3.76 (s)			2.48 (s) $[(CH_3)_2C_5H_3N]$, 7.33—8.83 $[(CH_3)_2C_5H_3N]$
(13a)		3.26 (q)		0.6—1.6 (m) (OCH_2CH_3,PCH_2CH_3), 7—8 (m) (PC_6H_5), 2(m) (PCH_2CH_3)
(13b)	2.88 (s)			7—8 (m) (PC_6H_5), 0.6—1.2 (m) (PCH_2CH_3), *ca.* 2 (m) (PCH_2CH_3)
(14a)		3.33 (q)	0.98 (t)	1.76—1.97 (q) (PCH_3), 7—8 (m) (C_6H_5)
(14b)	2.85 (s)			1.4—2.2 (m) (PCH_3), 7.5—7.9 (m) (C_6H_5)

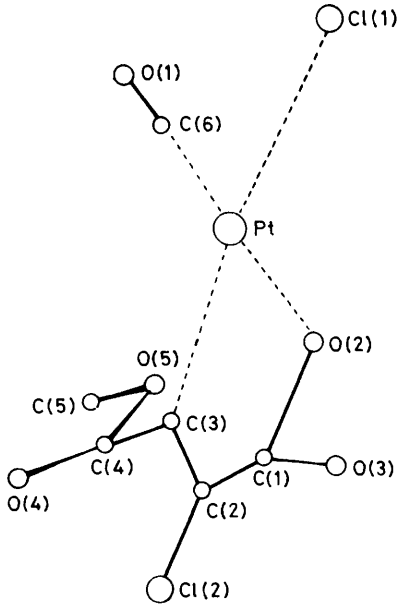
* Chloroform solution. Multiplicity: s, singlet; t, triplet; q, quartet; m, multiplet.

TABLE 3

Analyses, molecular weights, and conductivity

	Analyses[a] (%)						
Compound	C	H	N	Other	M[a]	M.p. (θ_c/°C)	Λ[b]/Ω^{-1} cm^2 mol^{-1}
(2a)	53.0	3.6	1.4	Cl 7.2		94	116 (1.3 × 10^{-3} mol dm^{-3})
	(53.0)	(3.6)	(1.4)	(7.3)	(973.7)		
(2b)	52.2	3.4	1.3	Cl 7.1		102	113 (1.02 × 10^{-3} mol dm^{-3})
	(52.7)	(3.5)	(1.4)	(7.4)	(959.7)		
(3a)	56.6	3.2			*c*	250	
	(56.3)	(3.9)			(896.2)	(decomp.)	
(3b)	55.8	3.8			*c*	*d*	
	(55.8)	(3.8)			(881.7)		
(4a)	36.2	2.4	5.3		*c*	*d*	
	(36.4)	(2.5)	(5.3)		(527.8)		
(4b)	35.8	2.2	5.2		*c*	*d*	
	(35.1)	(2.1)	(5.4)		(513.8)		
(5a)	49.2	3.2	1.2	Cl 14.1		108	
	(49.6)	(3.4)	(1.4)	(13.9)	(1 016.2)		
(5b)	49.1	3.7	1.3	Cl 13.8		125	109 (1.2 × 10^{-3} mol dm^{-3})
	(49.2)	(3.3)	(1.4)	(13.7)	(1 002.2)		
(7a)	21.3	1.3		Cl 8.5	*c*	*d*	
	(21.0)	(1.3)		(8.9)	(399.6)		
(7b)	18.7	0.8		Cl 9.1	*c*	*d*	
	(18.7)	(0.8)		(9.2)	(385.6)		
(8a)	20.5	1.7		Cl 6.3	550.4[e]	80	
	(19.4)	(1.8)		(6.4)	(555.6)	(decomp.)	
				I 23.0			
				(22.8)			
(8b)	16.8	1.2		Cl 6.3	480[e]		
	(17.2)	(1.5)		(6.5)	(541.6)		
				I 23.7			
				(23.5)			
(9a)	18.1	1.4		Cl 7.0	498[e]	150	
	(17.7)	(1.5)		(6.5)	(541.6)	(decomp.)	
				I 23.8			
				(23.5)			
(9b)	16.4	1.1		Cl 7.2	507[e]	180	
	(15.9)	(1.1)		(6.7)	(527.5)	(decomp.)	
				I 24.6			
				(24.0)			
(10a)	30.8	2.2	3.2		510[e]	102	
	(30.1)	(2.1)	(2.9)		(478.7)		
(10b)	28.5	1.8	3.1		*c*	196	
	(30.2)	(1.7)	(2.9)		(464.7)		
(11a)	32.9	2.6	3.1		*c*	165	
	(31.7)	(2.5)	(2.8)		(542)		
(11b)	29.9	2.0	2.9		528[e]	183	
	(30.1)	(2.1)	(2.9)		(478.7)	(decomp.)	
(12a)	33.6	2.9	2.7		508[e]	180	
	(33.2)	(2.8)	(2.8)		(506.8)	(decomp.)	
(12b)	31.5	2.5	2.8		505[e]	217	
	(31.7)	(2.4)	(2.8)		(492.8)		
(13a)	51.3	4.4			780	216	
	(51.0)	(4.4)			(809.1)		
(13b)	50.5	4.2			822	189	
	(50.4)	(4.2)			(789.1)		
(14a)	49.8	4.1			761	215	
	(49.8)	(4.2)			(772.1)	(decomp.)	
(14b)	49.2	3.6			739	218	
	(49.1)	(3.8)			(758.1)		
(15a)	49.0	3.5			*c*	*d*	
	(49.9)	(3.8)			(770.1)		
(15b)	50.5	3.5			*c*	*d*	
	(49.2)	(3.6)			(756.0)		
(16a)	38.5	2.9	5.1		*c*	*d*	
	(38.9)	(3.1)	(5.0)		(555.9)		
(16b)	37.4	2.7	5.2		*c*	*d*	
	(37.7)	(2.8)	(5.2)		(541.9)		

[a] Calculated values are given in parentheses. [b] Acetone solution at 25 °C. [c] Insoluble. [d] Melting point > 240 °C. [e] Chloroform solution.



Molecular geometry of the $[\overline{\mathrm{Pt}\{\mathrm{C(CO_2Me)=C(Cl)COO}}\}(\mathrm{CO})\mathrm{Cl}]^-$ anion

Tables 4 and 5 respectively, while relevant internal rotation angles are given in Table 6. The compound consists of discrete $[\overline{\mathrm{Pt}\{\mathrm{C(CO_2Me)=C(Cl)COO}}\}(\mathrm{CO})\mathrm{Cl}]^-$ and $[\mathrm{N(PPh_3)_2}]^+$ ions. The anion shows the expected square-planar co-ordination around the platinum(II) atom [the maximum deviation from the least-squares plane of the four co-ordinated atoms, Cl(1), O(2), C(3), C(6), being ±0.03 Å]. The carbonyl group is linearly co-ordinated to the Pt atom and lies in the co-ordination plane; the Pt–C(6) bond length [1.75 (1) Å] is in the expected range,[8] equal, within the estimated standard deviations (e.s.d.s) to that found in the related complex anion *cis*-$[\mathrm{Pt\{C(CO_2Et)=C(Cl)COOPr^i\}(CO)Cl_2}]^-$.[1] The Pt–C(3) length [2.035(9) Å] is the same as the corresponding bond length in the σ-alkenyl compound [1] [1.97(2) Å], although the somewhat higher e.s.d. of the latter may conceal possible differences in the σ-bond strength. It is of interest to compare the geometries of compound (1), in which the alkenyl moiety is bonded only through the carbon atom, with the present compound (2b) where the alkenyl ligand also bonds *via* an oxygen atom of the carboxylic group; in (2b) the L–Pt–L angles defining the square-planar co-ordination show significant angular deviations of ±5° from the ideal value of 90° whereas an average deviation of only ±0.6° was found in (1).[1] These distortions may be induced by steric factors caused by the formation of the five-membered ring containing the Pt, O(2), C(1), C(2), and C(3) atoms [C(3)–Pt–O(2) 83.3, O(2)–Pt–Cl(1) 87.9, C(3)–Pt–C(6) 95.6, and C(6)–Pt–Cl(1) 93.3°].

TABLE 4

Bond lengths (Å) in the anion of (2b) with estimated standard deviations in parentheses

Pt–Cl(1)	2.415(3)	O(2)–C(1)	1.33(1)
Pt–O(1)	2.907(11)	O(3)–C(1)	1.21(1)
Pt–O(2)	1.979(8)	O(4)–C(4)	1.23(1)
Pt–C(1)	2.780(13)	O(5)–C(4)	1.32(2)
Pt–C(2)	2.747(12)	O(5)–C(5)	1.49(1)
Pt–C(3)	2.035(9)	C(1)–C(2)	1.48(1)
Pt–C(6)	1.75(1)	C(2)–C(3)	1.28(2)
Cl(2)–C(2)	1.82(1)	C(3)–C(4)	1.51(3)
O(1)–C(6)	1.15(2)		

TABLE 5

Bond angles (°) in the anion of (2b) with estimated standard deviations in parentheses

Pt–O(2)–C(1)	112.7(6)	O(2)–Pt–C(6)	177.6(6)
Pt–C(3)–C(2)	109.9(6)	O(2)–C(1)–O(3)	121.3(5)
Pt–C(3)–C(4)	127.3(5)	O(2)–C(1)–C(2)	114.2(4)
Pt–C(6)–O(1)	178.8(4)	C(3)–C(1)–C(2)	124.5(3)
Cl(1)–Pt–O(1)	93.6(8)	O(4)–C(4)–O(5)	122.8(5)
Cl(1)–Pt–O(2)	87.9(8)	O(4)–C(4)–C(3)	126.5(6)
Cl(1)–Pt–C(3)	171.1(4)	O(5)–C(4)–C(3)	110.6(4)
Cl(1)–Pt–C(6)	93.3(2)	C(3)–Pt–C(6)	95.6(3)
Cl(2)–C(2)–C(1)	117.2(4)	C(4)–O(5)–C(5)	116.8(5)
Cl(2)–C(2)–C(3)	123.0(7)	C(1)–C(2)–C(3)	119.8(5)
O(1)–Pt–O(2)	177.1(4)	C(2)–C(3)–C(4)	122.9(4)
O(2)–Pt–C(3)	83.3(2)		

TABLE 6

Some relevant internal rotation angles (°) for the anion of (2b) with e.s.d.s in parentheses

Pt–C(3)–C(2)–C(1)	1.7(7)
Pt–C(3)–C(4)–C(2)	−178.3(9)
Pt–C(3)–O(2)–C(2)	−179.9(8)
Pt–C(3)–C(2)–Cl(2)	1.0(9)
Cl(1)–Pt–C(6)–O(1)	131.4(8)
Cl(1)–Pt–C(3)–C(2)	−8.7(9)
Cl(1)–Pt–C(2)–Cl(2)	179.9(9)
Cl(1)–Pt–C(3)–C(4)	169.7(8)
Cl(1)–Pt–O(2)–C(1)	176.9(8)
O(1)–C(6)–Pt–O(2)	13.2(8)
O(1)–C(6)–Pt–C(3)	49.6(9)
C(1)–O(2)–Pt–C(6)	−64.7(10)
C(4)–C(3)–Pt–C(6)	−3.8(9)
C(3)–Pt–C(2)–C(4)	−0.8(9)
Cl(2)–C(3)–C(2)–C(1)	−178.9(9)
Cl(2)–C(2)–C(1)–O(3)	−1.45(8)
Cl(2)–C(2)–C(1)–O(2)	177.7(8)
Cl(2)–C(2)–C(3)–C(4)	2.1(8)
C(1)–O(2)–O(3)–C(2)	0.5(8)
C(1)–C(2)–C(3)–C(4)	−176.8(8)
C(2)–C(3)–C(4)–O(4)	−55.8(8)
C(2)–C(3)–C(4)–O(5)	126.3(8)
C(3)–C(4)–O(4)–O(5)	−177.6(9)
O(4)–C(4)–C(5)–O(5)	−178.8(9)
C(5)–O(5)–C(4)–O(4)	1.4(8)
C(2)–C(1)–O(2)–O(3)	−179.2(8)
C(2)–C(1)–O(3)–O(2)	177.0(9)

The Pt–Cl(1) distance *trans* to C(3) [2.415(3) Å] is significantly longer than the value of 2.355(7) Å found for the similar Pt–Cl bond *trans* to the σ-bonded carbon in the σ-alkenyl species.[1] In this case it may be assumed that the lengthening is in part due to the *cis* influence exerted by the carboxylic group *cis* bonded through the oxygen atom. Note that a similar lengthening due to the *cis* influence, defined as the ability to weaken the *cis* metal–ligand bond, has already been reported for square-planar platinum(II) complexes containing tertiary phosphines as ligands,[9] although in the present case an electronic influence of the bonded oxygen atom may also contribute significantly to this lengthening. The C=O bonds in the two carboxylic groups of the co-ordinated olefin are in the expected range [average value 1.22(1) Å]. The carbon–carbon bond lengths, both single and double, are the same (within the standard deviations) as those found in σ-alkenyl derivatives.[1] This shows that no significant modification is introduced in the bonding of the skeleton of this ligand on changing from the uni- to the bi-dentate mode. Moreover, the conformation of the σ-alkenyl ligand is such that the double-bonded carbons and atoms O(3) and Cl(2) lie in the previously defined co-ordination plane (maximum deviation ±0.02 Å), while atom C(4) is pointing upward (at a distance of +0.1 Å from the least-squares plane). The ester group conformation (with respect to the C–C skeleton) can be judged from the values of the torsion angles C(2)–C(3)–C(4)–O(4) and C(2)–C(3)–C(4)–O(5) (−55.8 and 126.3° respectively).

The geometry of the cation is in agreement with that already found for $[N(PPh_3)_2]^+$ salts of other transition-metal anions. The average values for the bond lengths are P–N 1.596 (±0.011) and P–C 1.80 (±0.04) Å; P–N–P angle is 136.6(2)°. These values are comparable to those of the related σ-alkenyl compound [1.57(2), 1.79(2) Å, and 137.9(3)°][1] or those [1.60(2), 1.80(2) Å, and 133.92(3)°] found in the $[N(PPh_3)_2]^+$ salt of the anion $[PtRh_4(CO)_{15}]^-$.[10]

Neutral Species containing a Five-membered Ring.—The observed formation of a platinaoxacyclopentenone ring in the anion (2) prompted us to examine more carefully the neutral compounds obtained in the reaction of $[Pt(CO)_2Cl_2]$ with $RO_2CC{\equiv}CCO_2R$ (R = Me or Et).[6] These have been formulated as $[\{\overline{Pt[C(CO_2R){=}C(Cl)COO}](CO)\}_n]$ (7a, R = Et; 7b, R = Me), polymeric species derived from the elimination of the alkyl radical of the γ-alkoxy-group of the σ-alkenylplatinum moiety and of the chlorine atom bonded to platinum. These compounds were obtained in satisfactory yields when $[Pt(CO)_2Cl_2]$ was treated in boiling toluene with gradual addition of dimethyl or diethyl acetylenedicarboxylate up to the molar ratio 1 : 1. In spite of their insolubility in almost all the organic solvents, these pale green species can be dissolved by warming in *O*- and *N*-donor solvents such as tetrahydrofuran (thf) and CH_3CN. The i.r. spectra in these solvents appear to be very similar to that found for (2) suggesting that the solvated neutral and ionic species are related. The presence of an additional covalent Pt–O bond in the neutral pale green species is strongly supported by the fact that when the reaction was carried out in rigorously anhydrous toluene by adding the acetylene ligand drop by drop up to complete disappearance of the starting carbonyl [reaction (viii), Scheme], ethyl chloride or methyl chloride was formed in the stoicheiometric amount required by the yield of the insoluble species as demonstrated by g.l.c. Further support for the formation of a Pt–O bond in place of a Pt–Cl bond is given by the Nujol-mull spectra of these insoluble compounds where no Pt–Cl stretches were observed. On the other hand, neutral σ-alkenyl species $[Pt\{C(CO_2R){=}C(Cl)CO_2R\}(CO)Cl]$ (6; R = Me or Et) cannot be transformed into the compounds containing the five-membered ring by simply heating in anhydrous benzene or toluene for several hours. However, the addition of $[Pt(CO)_2Cl_2]$ and of dialkyl acetylenedicarboxylate allows the transformation to occur; this presumably means that some sort of activation is necessary in order to promote the elimination of alkyl chloride [reaction (vi), Scheme]. To clarify the reaction pathway, we have treated $[Pt\{C(CO_2Et){=}C(Cl)CO_2Et\}(CO)Cl]$ (6a) with $[Pt(CO)_2Cl_2]$ in the absence of acetylene; no formation of (7a) was observed. Adding $MeO_2CC{\equiv}CCO_2Me$ gradually to the reaction mixture until $[Pt(CO)_2Cl_2]$ had completely reacted produces both (7a) and (7b) which were characterized by n.m.r. after transformation into their soluble derivatives (2a) and (2b) [see reaction (iii), Scheme]. We then verified that to maximize the formation of (7) the best $[Pt(CO)_2Cl_2]$: (6) ratio is 1 : 1. On the other hand, the i.r. spectra, recorded during the course of reaction, do not show any formation of adduct between $[Pt(CO)_2Cl_2]$ and (6).

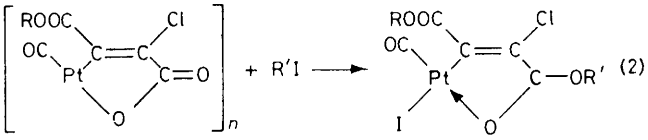
Two reaction mechanisms can reasonably be proposed. Behaving as a Lewis acid, $[Pt(CO)_2Cl_2]$ may extract chloride ion from (6), so that the acetylene ligand may enter the co-ordination sphere of platinum now carrying a positive charge, in order to stabilize it. The subsequent step may be the elimination of the positive charge through the release of Et^+, with formation of both EtCl and (7a). The formation of $[Pt(CO)Cl_3]^-$ and of a stable cationic species containing platinum has been observed by simply treating $[Pt(CO)_2Cl_2]$ with dialkylacetylenes.[11,12] However, the lack of any experimental evidence for the formation of $[Pt(CO)Cl_3]^-$ in this case, and the fact that this anion reacts only with difficulty with dialkyl acetylenedicarboxylate, make this mechanism unlikely.

We think it more reasonable to assume that the entering acetylene molecule simply displaces the co-ordinated β-carboalkoxy-group so that it may interact with $[Pt(CO)_2Cl_2]$ or better with some unstable cationic species {*e.g.* $[Pt(CO)_2Cl]^+$}, to eliminate the alkyl cation with formation of alkyl halide. The role of the entering activated acetylene in acting as a weak donor ligand able to displace the co-ordinated β-carboalkoxy-group is confirmed by the fact that both square-planar anions and neutral derivatives of the σ-alkenyl complexes (6) with nitrogen- and phosphorus-donor ligands,[6] where co-ordination of the β-carboalkoxy-group is removed, do not give rise, in anhydrous conditions, to the formation of a five-membered ring. Much less clear is the role of $[Pt(CO)_2Cl_2]$, which is effective in the ring closure only when free acetylene ligand is present. One can argue that the weak ligand favours the formation of a labile highly polarized intermediate which may interact with the neutral σ-alkenyl complex allowing the formation of alkyl halide through a concerted mechanism.

Compound (7) can also be obtained, in 30—40% yield, when (6) is refluxed in wet acetone or Bu^tOH; in this case the reaction is not producing any RCl, but g.l.c. showed that methanol or ethanol is released, although not in the stoicheiometric amount, probably owing to the limiting reaction (v) of the Scheme. It was not possible to isolate in a pure state the intermediate containing the free carboxylic group from the reaction mixture containing water. However, the formation of this intermediate by hydrolysis [see reaction (iv) in the Scheme] is supported by the i.r. [ν(OH) 3 500 cm^{-1}] and ^{1}H n.m.r. [δ(OH) 13 p.p.m.] spectra of the product isolated in wet alcohols, where the hydrolysis reactions are almost complete. The second step [see reaction (v), Scheme], corresponding to the elimination of HCl, could be achieved by operating in toluene at high temperature through a partial distillation of the solvent in order to remove HCl or, at room temperature, by extraction with water.

Owing to the poor quality of the crystals obtained, both in the direct synthesis and from hydrolysis of σ-alkenyl complexes, the molecular structure of (7) could not be determined by *X*-ray diffraction. Assuming that the same ring as in (2) is already present in compound (7), both the low solubility and the unusual co-ordination around platinum(II) suggest a polymeric character for (7) in the solid state: the units may be kept together through intermolecular co-ordination bonds between α-carboxy-groups or β-carbonyl groups and platinum atoms of a different molecule [6] or by metal–metal interactions. The formation of intermolecular covalent Pt–O bonds cannot be excluded. However, the chemical behaviour described below seems to suggest that this last situation is much less probable; the cleavage of intermolecular Pt–O bonds seems unlikely while a single-step intramolecular rearrangement occurs when (7) is treated with a weak nucleophile, such as chloride ion, to give (2) [see reaction (iii), Scheme].

Compounds (7a) and (7b) are very stable under an atmosphere of carbon monoxide and do not react with hydrogen or hydrogen chloride in boiling benzene, chloroform, or dry alcohols. Remarkable stability of both the Pt–C and Pt–O bonds was also observed in the reaction with chlorine, in which no change or breaking of the ring occurred. The most ready transformation concerns the intermolecular interactions which are immediately lost when (7) is stirred in dichloromethane in the presence of an excess of chloride ions to give (2) as shown in the Scheme [reaction (iii)]. The reaction can be performed with a stoicheiometric amount of any chloride soluble in dichloromethane: the addition of bulky cations such as $[NMe_4]^+$ or $[N(PPh_3)_2]^+$ permitted isolation of the corresponding salts of (2a) and (2b) as yellow plates in 60—70% yield. Elemental analysis and conductance data in acetone, as well as i.r. and ^{1}H n.m.r. spectra, confirmed that the salts are identical to the compounds obtained from the σ-alkenyl complexes through the closure of the ring. A comparison of the i.r. spectra of (2a) and (2b) with those of the parent compounds (7a) and (7b) showed that the very strong and broad band at *ca.* 1 550 cm^{-1}, due to CO of the carboalkoxy-group co-ordinated to platinum, was replaced by weak bands at *ca.* 1 550 cm^{-1} [ν(C=C)], while in the far-i.r. region a new strong absorption band was observed at *ca.* 315 cm^{-1}, which can be assigned to a terminal Pt–Cl bond. In both ^{1}H n.m.r. spectra the high-field resonance due to α-COOEt and α-COOMe shows coupling with ^{195}Pt [*J*(Pt–H) *ca.* 2 Hz]. This coupling is similar to that observed in other platinum compounds containing the α-carboalkoxy-group.[1,4] Cleavage of the intramolecular Pt–O bond in compound (7) was observed on heating (7) in toluene with alkyl iodide [reaction (2)]. A similar reaction also occurred with alkyl bromide, while alkyl chloride was completely ineffective. This behaviour indicates that the cleavage of the Pt–O bond is strongly dependent on the polarizability of the entering molecule which must interact with the acidic platinum atom. This last observation is confirmed by the fact that in both anionic and neutral derivatives of compound (7), where four-co-ordination around the central metal atom is achieved by means of strong nucleophiles, the five-membered ring is so stable that it cannot be opened unless the molecule is destroyed. Compounds (8) and (9) are closely related to the parent σ-alkenyl complexes (6) already described: [6] they can be separated from the yellow solution by cooling at −20 °C and fully characterized by i.r., ^{1}H n.m.r., and mass spectra. Compounds (8a) and (9b) are readily transformed by reaction with $[N(PPh_3)_2]Cl$ in alcohols into the salt-like species already described.[6]



(2)

(7) (8), (9)

R,R′ = Me or Et

Compound (7) reacts at room temperature with pyridine (py), 3-methylpyridine (mpy), or 3,4-dimethylpyridine (dmpy), the intermolecular interaction being removed to give monosubstituted soluble compounds $[Pt\{C(CO_2R){=}C(Cl)COO\}(CO)L]$ [L = py, R = Et (10a); L = py, R = Me (10b); L = mpy, R = Et (11a); L = mpy, R = Me (11b); L = dmpy R = Et (12a); L = dmpy, R = Me (12b)]. The reaction with other phosphorus and nitrogen ligands such as PPh_3, $PEtPh_2$, $PMePh_2$, 1,2-bis(diphenylphosphino)ethane (dppe), 2,2′-bipyridine (bipy), and 4,4′-dimethyl-2,2′-bipyridine (dmbipy) gives [reaction (xi), Scheme] disubstituted compounds, the carbon monoxide being replaced by the entering ligand without any change in the ring: $[Pt\{C(CO_2R){=}C(Cl)COO\}L_2]$ [L = PPh_3, R = Et (3a); L = PPh_3, R = Me (3b); L = $PEtPh_2$, R = Et (13a); L = $PEtPh_2$, R = Me (13b); L = $PMePh_2$, R = Et, (14a); L = $PMePh_2$, R = Me (14b); L_2 = dppe, R = Et (15a); L_2 = dppe, R = Me (15b); L_2 = bipy, R = Et (4a); L_2 = bipy, R = Me (4b); L_2 = dmbipy, R = Et (16a); L_2 = dmbipy, R = Me (16b)]. The same disubstituted derivatives can be obtained by reaction of (7) as well as by reaction of (2) with the appropriate ligands [see reactions (x) and (xi), Scheme]: they have been fully characterized by elemental analysis, i.r., and ^{1}H n.m.r. spectra. The *cis* arrangement of the phosphine around the platinum atom is confirmed in the case of the $PMePh_2$ complexes (14a) and (14b) by the observed resonance pattern made up of a clear central doublet [^2J(P–H) 10 Hz], further split by ^{195}Pt into two, incompletely resolved, doublets [J(Pt–H) 20 Hz].[13]

EXPERIMENTAL

Microanalyses, molecular weights, melting points, and conductivity data (determined by Laboratorio Analisi, Università di Milano) are collected in Table 3; ^{1}H n.m.r. data (60 MHz, Varian NV14 and EM 360A, internal $SiMe_4$) are collected in Table 2, i.r. data (Perkin-Elmer 457, Nujol mulls, NaCl, CsI plates) in Table 1.

Gas–liquid chromatography separations were carried out on a Perkin-Elmer F-20 using a 2-m stainless-steel column packed with Carbowax 20M (oven temperature, 50 °C; evaporator temperature, 110 °C) for determination of Pr^iOH and EtCl.

All the reactions were carried out under an atmosphere of nitrogen and with anhydrous solvents, although the products were rarely air sensitive. Solvents were purified and dried by standard methods.

The complexes $[Pt(CO)_2Cl_2]$, $[Pt\{C(CO_2R)=C(Cl)CO_2R\}(CO)Cl]$, and $[N(PPh_3)_2][Pt\{C(CO_2R)=C(Cl)CO_2R\}(CO)Cl_2]$ (R = Me or Et) were prepared as previously described.[1,6] Crystals of compound (2b) suitable for *X*-ray analysis were obtained as the $[N(PPh_3)_2]^+$ salt by slow evaporation from a methanol solution. The yellow crystals are stable in air and have an elongated prismatic habit.

Crystal Data.—$C_{42}H_{33}Cl_2NO_5P_2Pt$, $M = 959.68$, Triclinic, $a = 17.144(5)$, $b = 11.975(4)$, $c = 10.386(4)$ Å, $\alpha = 106.62(8)$, $\beta = 77.07(7)$, $\gamma = 95.94(7)°$, $U = 1\,989$ Å^3, $D_m = 1.61$ Mg m^{-3}, $Z = 2$, $D_c = 1.602$ Mg m^{-3}, $F(000) = 1\,452$, space group $P\bar{1}$, μ(Mo-K_α) = 22.4 cm^{-1}.

A reduced cell (type I, *cf.* ref. 14, ch. 5.1) with parameters $a = 10.386(3)$, $b = 11.975(4)$, $c = 17.144(5)$ Å, $\alpha = 84.06$, $\beta = 77.08$, and $\gamma = 77.39°$, may be obtained from that used applying the transformation matrix: $00\bar{1}$, 010, $\bar{1}00$.

Data Collection.—Unit-cell parameters were obtained by a least-squares fit of the 2θ values of 25 high-angle reflections. The data were collected with an automated four-circle diffractometer (graphite-monochromated Mo-K_α-radiation, $\lambda = 0.710\,69$ Å) using a ω scan. A scan speed of 0.04° s^{-1} was used with a scan width of 1.20°. Two background counts were measured at each side of the peak for 10 s and the counts subsequently averaged. During the data collection three standard reflections were measured every hour to check the stability of the experimental conditions and of the crystal: no significant variations were detected. Azimuthal (ψ) scans of four general reflections were measured to check the effect of absorption; no correction was found necessary. A total of 3 546 independent reflections was measured up to $(\sin\theta)/\lambda \leqslant 0.55$ and corrected for Lorentz and polarization factors; $\sigma(I)$ values were evaluated on counting statistics. 3 055 Reflections having $I \geqslant 3\sigma(I)$ were considered as observed and used in the structure analysis.

Structure Analysis.—The structure was solved by Patterson and Fourier methods and refined by block-matrix least squares. The function minimized was $\Sigma w|F_o - F_c|^2$; a Cruickshank weighting scheme [15] was used. Atomic scattering factors were taken from ref. 14, with correction for the real part of the anomalous dispersion for the Pt and Cl atoms.[14] No attempt was made to locate the hydrogen atoms and these were not included in the calculations. The refinement was carried out using anisotropic thermal factors for all the atoms (Pt, Cl, C, and O) of the anion and for the P and N atoms of the cation, while isotropic thermal factors were used for the others. The final conventional R factor [$R = \Sigma(k|F_o| - |F_c|)/\Sigma k|F_c|$] was 0.041 for the observed reflections (0.053 with the unobserved included). A final difference-Fourier map showed no significant features. The calculations were performed using a UNIVAC version of programs written by A. Immirzi.[16,17]

The final atomic co-ordinates of the anion are listed in Table 7, those of the cation are in Table 8. The observed and calculated structure factors, thermal parameters, bond distances and angles for the cation, and a schematic view of the latter are given in Supplementary Publication No. SUP 23112 (21 pp.).*

TABLE 7

Final positional co-ordinates for the anion of (2b) with e.s.d.s in parentheses

Atom	*x/a*	*y/b*	*z/c*
Pt	0.109 91(3)	0.108 69(4)	0.063 44(5)
Cl(1)	−0.006 5(2)	0.191 4(3)	0.037 7(4)
Cl(2)	0.375 0(2)	0.037 6(3)	−0.068(3)
C(1)	0.249 0(6)	0.140 6(8)	−0.122 2(10)
C(2)	0.271 0(6)	0.076 1(7)	−0.033 8(9)
C(3)	0.217 7(6)	0.051 5(8)	0.063 2(10)
C(4)	0.236 4(6)	−0.008 7(5)	0.162 4(11)
C(5)	0.224 5(8)	0.003 2(10)	0.400 1(13)
C(6)	0.056 2(7)	0.055 0(10)	0.199 5(14)
O(1)	0.021 4(5)	0.017 7(8)	0.287 9(10)
O(2)	0.171 6(4)	0.162 4(6)	−0.094 7(7)
O(3)	0.295 9(5)	0.171 0(7)	−0.213 4(8)
O(4)	0.268 3(5)	−0.102 9(6)	0.132 1(9)
O(5)	0.211 0(5)	0.052 2(6)	0.290 8(7)

$[N(PPh_3)_2][Pt\{C(CO_2Et)=C(Cl)COO\}(CO)Cl]$ (2a).—(*a*). To a solution of $[N(PPh_3)_2][cis\text{-}Pt\{C(CO_2Et)=C(Cl)CO_2Et\}(CO)Cl_2]$ (1.025 g, 0.99 mmol) in acetone (30 cm^3) was added water (0.5 cm^3, 27.7 mmol). After refluxing for 6 h the yellow solution was concentrated to dryness and the crude solid was recrystallized twice from ethanol (10 cm^3). The yellow crystalline precipitate of (2a) was dried under vacuum (0.625 g, 65%) (Found: C, 53.0; H, 3.6; Cl, 7.2; N, 1.4; Pt, 19.9. $C_{43}H_{35}Cl_2NO_5P_2Pt$ requires C, 53.0; H, 3.6; Cl, 7.3; N, 1.4; Pt, 20.0%).

(*b*). To a suspension of (7a) (0.28 g, 0.7 mmol) in dichloromethane (30 cm^3) was added $[N(PPh_3)_2]Cl$ (0.7 g, 1.21 mmol). After stirring for 30 min at room temperature, compound (7a) had dissolved and the pale yellow solution was filtered and concentrated to dryness. The crude solid was dissolved in ethanol (20 cm^3) and stirred at 60 °C. The solution, after filtration, was cooled (−20 °C) and yellow crystals of (2a) filtered off and dried under vacuum (0.305 g, 45%).

(*c*). A solution of $[N(PPh_3)_2][cis\text{-}Pt\{C(CO_2Et)=C(Cl)CO_2Pr^i\}(CO)Cl_2]$ (0.4 g, 0.38 mmol) in acetone (15 cm^3) containing water (1 cm^3, 55.5 mmol) was refluxed for 3 h. After cooling to −20 °C, a golden yellow precipitate was obtained which was filtered off, washed with cold ethanol (2 × 5 cm^3), and dried (0.38 g, 70%). From the mother-liquor, propan-2-ol was detected by g.l.c. in the correct

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* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1980, Index issue.

TABLE 8

Final positional co-ordinates for the cation $[\mathrm{N(PPh_3)_2}]^+$ with e.s.d.s in parentheses

Atom	x/a	y/b	z/c
P(1)	0.289 7(1)	0.400 3(2)	0.462 6(3)
P(2)	0.290 1(1)	0.544 7(2)	0.296 4(2)
N	0.296 5(4)	0.443 6(6)	0.329 5(7)
C(1P1)	0.358 8(7)	0.279 7(10)	0.425 4(12)
C(2P1)	0.382 8(7)	0.212 5(11)	0.289 4(14)
C(3P1)	0.434 2(8)	0.116 8(13)	0.260 0(16)
C(4P1)	0.461 0(9)	0.089 0(14)	0.368 2(16)
C(5P1)	0.436 8(9)	0.156 7(13)	0.501 6(16)
C(6P1)	0.384 3(8)	0.254 2(12)	0.533 6(14)
C(7P1)	0.316 5(7)	0.508 2(10)	0.603 1(13)
C(8P1)	0.395 3(8)	0.550 1(12)	0.581 9(14)
C(9P1)	0.418 7(8)	0.645 4(12)	0.683 9(15)
C(10P1)	0.364 7(9)	0.694 5(13)	0.800 4(16)
C(11P1)	0.286 8(9)	0.656 1(14)	0.821 3(17)
C(12P1)	0.261 5(8)	0.561 8(13)	0.722 4(15)
C(13P1)	0.190 5(7)	0.350 1(11)	0.516 7(13)
C(14P1)	0.174 1(8)	0.300 4(11)	0.625 7(14)
C(15P1)	0.097 2(9)	0.259 7(14)	0.664 2(17)
C(16P1)	0.038 0(10)	0.270 6(15)	0.593 1(18)
C(17P1)	0.055 5(10)	0.319 2(15)	0.482 4(18)
C(18P1)	0.132 9(8)	0.040 03(12)	0.462 6(15)
C(1P2)	0.255 0(7)	0.684 9(11)	0.445 2(13)
C(2P2)	0.175 3(8)	0.684 6(12)	0.510 4(14)
C(3P2)	0.855 0(10)	0.228 8(14)	0.368 5(17)
C(4P2)	0.800 9(10)	0.139 8(15)	0.319 4(17)
C(5P2)	0.723 0(9)	0.139 2(14)	0.384 3(16)
C(6P2)	0.308 0(8)	0.772 3(12)	0.495 7(15)
C(7P2)	0.219 5(7)	0.556 0(10)	0.187 8(13)
C(8P2)	0.204 3(8)	0.447 1(12)	0.102 3(15)
C(9P2)	0.147 4(10)	0.439 3(14)	0.015 7(17)
C(10P2)	0.109 6(9)	0.540 4(14)	0.016 7(16)
C(11P2)	0.125 8(8)	0.648 7(12)	0.099 3(15)
C(12P2)	0.182 0(8)	0.658 2(11)	0.184 8(14)
C(13P2)	0.386 6(7)	0.604 6(10)	0.213 0(13)
C(14P2)	0.454 9(8)	0.542 4(12)	0.209 1(14)
C(15P2)	0.530 8(9)	0.579 0(13)	0.154 0(16)
C(16P2)	0.537 8(9)	0.676 5(13)	0.104 2(16)
C(17P2)	0.469 1(9)	0.737 4(14)	0.107 1(16)
C(18P2)	0.392 1(8)	0.701 2(12)	0.163 1(15)

stoicheiometric amount (butan-2-ol was employed as internal standard).

The compound $[\mathrm{N(PPh_3)_2}][\mathit{cis}\text{-}\overline{\mathrm{Pt\{C(CO_2Me)=C(Cl)COO}}\mathrm{\}(CO)Cl}]$ (2b) was prepared *via* similar reactions.

Compounds (2a) and (2b) are soluble in dichloromethane, chloroform, acetone, methanol, and ethanol but insoluble in aliphatic and aromatic hydrocarbons.

$[\mathrm{N(PPh_3)_2}][\overline{\mathrm{Pt\{C(CO_2Et)=(Cl)COO}}\mathrm{\}Cl_3}]$ (5a).—Into a solution of (2a) (1.024 g, 1.0 mmol) in $\mathrm{CHCl_3}$ (50 cm^3) was bubbled chlorine for 30 min. After stirring for 3 h the yellow solution was concentrated to dryness and the residue recrystallized from ethanol (40 cm^3). At −20 °C a yellow crystalline precipitate of (5a) was obtained which was filtered off and washed with cold ethanol (0.79 g, 73%).

The compound $[\mathrm{N(PPh_3)_2}][\overline{\mathrm{Pt\{CO_2Me)=C(Cl)COO}}\mathrm{\}Cl_3}]$ (5b) was prepared *via* a similar reaction.

Compounds (5a) and (5b) are soluble in methanol, ethanol, acetone, and dichloromethane, but insoluble in hydrocarbons.

$[\overline{\mathrm{Pt\{C(CO_2Et)=C(Cl)COO}}\mathrm{\}(CO)}]$ (7a).—(*a*). To *a* hot solution (110 °C) of *cis*-dicarbonyldichloroplatinum (2.96 g, 9.21 mmol) in anhydrous toluene (80 cm^3) and under a nitrogen atmosphere was added diethyl acetylenedicarboxylate (1.46 cm^3, 9.15 mmol) over a period of 1 h and the reaction mixture kept at this temperature until the i.r. spectrum no longer showed the characteristic bands of *cis*-$[\mathrm{Pt(CO)_2Cl_2}]$. Usually the reaction was complete after 10 h. The precipitate was filtered off from the hot solution, washed with toluene (20 cm^3) and acetone (20 cm^3), and then dried (1.87 g, 47%). To confirm the formation of EtCl in the expected amount it was distilled out from the reaction flask, collected in a cold trap (−70 °C), and analysed by g.l.c.

(*b*). A solution of *cis*-carbonylchloro[2-chloro-1,2-bis-(ethoxycarbonyl)vinyl]platinum (6a) (0.37 g, 0.79 mmol) in wet ethanol (15 cm^3) was warmed (70 °C) to obtain a clear solution (30 min). After 30 min, the solution was concentrated to dryness and treated with toluene (30 cm^3). After 3 h at 110 °C in a nitrogen stream a pale yellow precipitate was formed which was then washed and dried (0.2 g, 65%).

The complex $[\overline{\mathrm{Pt\{C(CO_2Me)=C(Cl)COO}}\mathrm{\}(CO)}]$ (7b) was prepared in a similar way.

Compounds (7a) and (7b) are sparingly soluble in basic solvents such as thf and acetonitrile but insoluble in all other organic solvents.

$[\mathrm{Pt\{C(CO_2Et)=C(Cl)CO_2Et\}(CO)I}]$ (8a).—To a suspension of (7a) (0.34 g, 0.85 mmol) in toluene (40 cm^3) was added ethyl iodide (2 cm^3, 24.7 mmol). After stirring for 4 h at 70 °C the orange solution was filtered and concentrated to 15 cm^3. On adding hexane (60 cm^3) a golden yellow precipitate was obtained which was filtered off, washed with hexane (2 × 5 cm^3), and dried (0.29 g, 61%).

The compounds $[\mathrm{Pt\{C(CO_2Me)=C(Cl)CO_2Et\}(CO)I}]$ (8b), $[\mathrm{Pt\{C(CO_2Et)=C(Cl)CO_2Me\}(CO)I}]$ (9a), and $[\mathrm{Pt\{C(CO_2Me)=C(Cl)CO_2Me\}(CO)I}]$ (9b) were prepared *via* similar reactions.

Compounds (8a), (8b), (9a), and (9b) are soluble in chloroform, dichloromethane, benzene, and toluene, but insoluble in aliphatic hydrocarbons. For $[\mathrm{Pt\{C(CO_2Et)=C(Cl)CO_2Et\}(CO)I}]$ the parent ion occurs at $m/e = 555$.

Reactions of $[\{\overline{\mathrm{Pt[C(CO_2R)=C(Cl)COO}}\mathrm{](CO)\}_n}]$ (R = Et *or* Me).—(*a*). *With unidentate nitrogen ligands. Compound* $[\overline{\mathrm{Pt\{C(CO_2Me)=C(Cl)COO}}\mathrm{\}(CO)(py)}]$ (10b). Pyridine (0.5 cm^3, 6.2 mmol) was added to a suspension of (7b) (0.467 g, 1.21 mmol) in $\mathrm{CHCl_3}$ (35 cm^3). After stirring for 3 h at room temperature a pale yellow solution was obtained, filtered, and concentrated to 5 cm^3. On adding hexane (40 cm^3) a white microcrystalline precipitate of (10b) was obtained which was recrystallized from $\mathrm{CH_2Cl_2}$–heptane (1 : 3 v/v), washed with heptane, and dried (0.5 g, 88%).

In a similar way $[\overline{\mathrm{Pt\{C(CO_2Et)=C(Cl)COO}}\mathrm{\}(CO)(py)}]$ (10a), $[\overline{\mathrm{Pt\{C(CO_2R)=C(Cl)COO}}\mathrm{\}(CO)(MeC_5H_4N)}]$ [R = Et (11a) or Me (11b)], and $[\overline{\mathrm{Pt\{C(CO_2R)=C(Cl)COO}}\mathrm{\}(CO)(Me_2C_5H_3N)}]$ [R = Et (12a) or Me (12b)] were prepared by reaction of (7) with pyridine, 3-methylpyridine, and 3,4-dimethylpyridine respectively.

Compounds (10a,b), (11a,b), and (12a,b) are soluble in chloroform, dichloromethane, benzene, and toluene, but insoluble in aliphatic hydrocarbons.

(*b*). *With unidentate phosphorus ligands. Compound* $[\overline{\mathrm{Pt\{C(CO_2Et)=C(Cl)COO}}\mathrm{\}(PMePh_2)_2}]$ (14a). Methyldiphenylphosphine (0.9 g, 4.5 mmol) was added to a suspension of (7a) in $\mathrm{CHCl_3}$ (40 cm^3). After refluxing for 3 h the solution was filtered and concentrated to 20 cm^3. The white precipitate obtained on adding hexane (50 cm^3) was filtered off, washed with hexane, recrystallized twice from dichloromethane–heptane (1 : 5 v/v), and dried to give white microcrystalline (14a) (1.15 g, 84%).

Similarly, $[Pt\{C(CO_2Me){=}C(Cl)COO\}(PMePh_2)_2]$ (14b), $[Pt\{C(CO_2R){=}C(Cl)COO\}(PEtPh_2)_2]$ [R = Et (13a) or Me (13b)], and $[Pt\{C(CO_2R){=}C(Cl)COO\}(PPh_3)_2]$ [R = Et (3a) or Me (3b)] were prepared by treating (7) with methyldiphenylphosphine, ethyldiphenylphosphine, and triphenylphosphine respectively.

Compounds (3a,b), (13a,b), and (14a,b) are soluble in $CHCl_3$ and CH_2Cl_2, slightly soluble in toluene, but insoluble in alcohol and aliphatic hydrocarbons. The solubility in the above solvents increases in the order: (14) > (13) > (3).

(*c*). *With bidentate nitrogen and phosphorus ligands.* $[Pt\{C(CO_2Et){=}C(Cl)COO\}(bipy)]$ (4a). 2,2′-Bipyridine (0.324 g, 2 mmol) was added to a suspension of (7a) in $CHCl_3$ (30 cm^3). After refluxing for 3 h the suspension was concentrated to dryness and the crude product extracted in a Soxhlet apparatus with chloroform. After 24 h a yellow-green microcrystalline precipitate of (4a) was obtained which was filtered off, washed with $CHCl_3$ (2 × 5 cm^3) and with toluene (2 × 5 cm^3), and dried (0.427 g, 75%).

In a similar way $[Pt\{C(CO_2Me){=}C(Cl)COO\}(bipy)]$ (4b) and $[Pt\{C(CO_2R){=}C(Cl)COO\}(dmbipy)]$ [R = Et (16a) or Me (16b)] were prepared by reaction of (7) with 2,2′-bipyridine and 4,4′-dimethyl-2,2′-bipyridine respectively.

Compounds (4a), (4b), (16a), and (16b) are insoluble in all common organic solvents.

$[Pt\{C(CO_2Et){=}C(Cl)COO\}(dppe)]$ (15a). 1,2-Bis(diphenylphosphino)ethane (0.823 g, 1.38 mmol) was added to a suspension of (7a) (0.553 g, 1.38 mmol) in $CHCl_3$ (30 cm^3). After refluxing for 3 h the hot solution was filtered. On adding hexane (50 cm^3) and evaporating some of the solution, a solid was obtained, filtered off, and recrystallized twice from dichloromethane–hexane (1 : 1 v/v) to give white microcrystalline (15a) (0.72 g, 68%).

The complex $[Pt\{C(CO_2Me){=}C(Cl)COO\}(dppe)]$ (15b) was prepared by similar reaction of (5b) with dppe.

Compounds (15a) and (15b) are soluble in dichloromethane and chloroform, and insoluble in all other common organic solvents.

Reaction of (2a) *with Nitrogen Chelating Ligands and Phosphorus Ligands.*—To a solution of (2a) (0.16 g, 0.164 mmol) in $CHCl_3$ (10 cm^3) was added 2,2′-bipyridine (0.05 g, 0.32 mmol) and the solution refluxed for 3 h to give a green-yellow microcrystalline precipitate of (4a) (0.06 g, 71%).

Similarly, compound (3a) was prepared by reaction of (2a) with PPh_3.

Reaction of (8a) *with* $[N(PPh_3)_2]Cl$ *in Excess.*—Compound (8a) (0.45 g, 0.81 mmol) was added to a solution of $[N(PPh_3)_2]Cl$ (0.5 g, 9.28 mmol) in anhydrous methanol (30 cm^3). After refluxing for 3 h, reduction of the volume of the solution (10 cm^3), and cooling, a white precipitate of (1a) was obtained (0.4 g, 47.6%).

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