Reactions of Acetylenes with Noble-metal Carbonyl Halides. Part 6.[1] Carbonyl Insertion to give Cyclic Organo-carbene Complexes of Platinum(II): Synthesis and *X*-Ray Structure of the Complex *cis*-$[\mathrm{Pt\{CC(CO_2Et){=}C(Ph)C(CO_2Et){=}C(Ph)O\}(PPh_3)Cl_2}]$ †

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The complex $[\mathrm{Pt(CO)_2Cl_2}]$ reacts with ethyl phenylpropiolate, $\mathrm{PhC{\equiv}CCO_2Et}$, to give $[\mathrm{Pt\{CC(COOEt){=}C(Ph)C(CO_2Et){=}C(Ph)O\}(CO)Cl}][\mathrm{Pt(CO)Cl_3}]$ (1) which contains a six-membered carbenoid ring bonded to platinum. In acetonitrile, complex (1) gives *cis*-$[\mathrm{Pt\{CC(CO_2Et){=}C(Ph)C(CO_2Et){=}C(Ph)O\}(CO)Cl_2}]$ (2). The interconversion of complexes (1) and (2) with KCl and $[\mathrm{Pt(CO)_2Cl_2}]$ respectively are reported and a mechanism for the formation of (1) is proposed. Reaction of complex (1) with $\mathrm{PPh_3}$ results in displacement of CO to give *cis*-$[\mathrm{Pt\{CC(CO_2Et){=}C(Ph)C(CO_2Et){=}C(Ph)O\}(PPh_3)Cl_2}]$ (3). ^{13}C N.m.r. studies of complexes (2) and (3) with specific isotopic labelling are reported. The crystal structure of complex (3) has been solved by Patterson and Fourier methods from counter data and refined by block-matrix least squares to a final conventional *R* of 0.048 for 5 842 independent observed reflections. Crystals of (3) are triclinic, space group $P\bar{1}$, with unit-cell dimensions a = 11.523(3), b = 11.994(4), c = 14.512(6) Å, α = 106.2(1), β = 88.8(1), γ = 73.7(2)°, and Z = 2. The crystals contain discrete molecules in which the co-ordination of the platinum atom is slightly distorted square planar. Selected bond lengths (Å) are Pt–P 2.244(2), Pt–C 1.933(8), Pt–Cl (*trans* to carbenoid carbon atom) 2.350(3), and Pt–Cl (*trans* to $\mathrm{PPh_3}$) 2.347(2). On the basis of reactivities and spectroscopic data, an unambiguous relationship has been established between compound (3) and its precursors.

Several metal carbonyl complexes react with acetylenes through co-dimerisation of two acetylene molecules with one carbon monoxide group to form cyclopentadienone[2] derivatives or with two carbon monoxide groups to give quinone[3] compounds, or simple cyclodimerisation of the organic molecules leading to cyclobutadiene metal complexes.[2]

In the case of the reaction of $[\mathrm{Pt(CO)_2Cl_2}]$ (see Scheme 1) with disubstituted symmetric and asymmetric acetylenes ($\mathrm{RC{\equiv}CR'}$: R = R′ = $\mathrm{CH_3}$,[1,4] $\mathrm{C_2H_5}$,[1,4] or $\mathrm{C_3H_7}$; [1,5] R = $\mathrm{CH_3}$, R′ = Ph [5]), platinum compounds containing a C=O group inserted into the organic moiety have been isolated as by-products, while cationic cyclobutadiene derivatives were formed as the main products. Diphenylacetylene reacts with $[\mathrm{Pt(CO)_2Cl_2}]$ to give a neutral tetraphenylcyclobutadieneplatinum(II) derivative and a tetraphenylcyclopentadienone compound.[6] On the other hand, the reaction with symmetric activated acetylene molecules ($\mathrm{RO_2CC{\equiv}CCO_2R}$: R = $\mathrm{CH_3}$ or $\mathrm{C_2H_5}$) [7] did not give any product containing a carbonyl group inserted into the organic moiety: only σ-alkenyl derivatives $[\mathrm{Pt\{C(CO_2R){=}CCl(COOR)\}(CO)Cl}]$ and, in lower yield, $[\{\mathrm{Pt\{C(CO_2R){=}CCl(COO)\}(CO)\}_n}]$ were obtained.

We have now investigated the reactivity of $[\mathrm{Pt(CO)_2Cl_2}]$ with an asymmetric acetylene molecule, ethyl phenylpropiolate ($\mathrm{PhC{\equiv}CCO_2Et}$), which contains one strong electron-withdrawing group. This reaction results in the formation of a six-membered ring through dimerisation–insertion of two acetylene molecules and one carbonyl group originally bonded to platinum, so that new carbene platinum(II) compounds can be obtained. Both neutral[8] and cationic[9] alkoxy(organo)-platinum–carbene complexes have been reported and the chemical behaviour of both types of compound have been quite extensively investigated.[10] We now report a new synthesis which leads to the formation of cyclocarbeneplatinum(II) derivatives through the nucleophilic attack of the activated acetylene molecule on a carbon monoxide group co-ordinated to the metal.

Results and Discussion

The complex $[\mathrm{Pt(CO)_2Cl_2}]$ reacts with $\mathrm{PhC{\equiv}CCO_2Et}$ (when warmed in toluene under a nitrogen atmosphere at 80—100 °C, in the molar ratio 1 : 1.5) to give an orange solid which readily separated from the reaction medium. Elemental analyses of this material (yield 51%) are in agreement with the formula $\mathrm{Pt_2(PhCCCO_2Et)_2(CO)_3Cl_4}$ (1) (see Scheme 2). Treatment of the toluene mother-liquor with hexane yielded a yellow-brown solid, not yet fully characterised, whose elemental analysis appears to be in agreement with the formula $\mathrm{Pt(PhCCCO_2Et)_2(CO)Cl_2}$ (yield 19%), while the i.r. spectrum (Nujol mulls)

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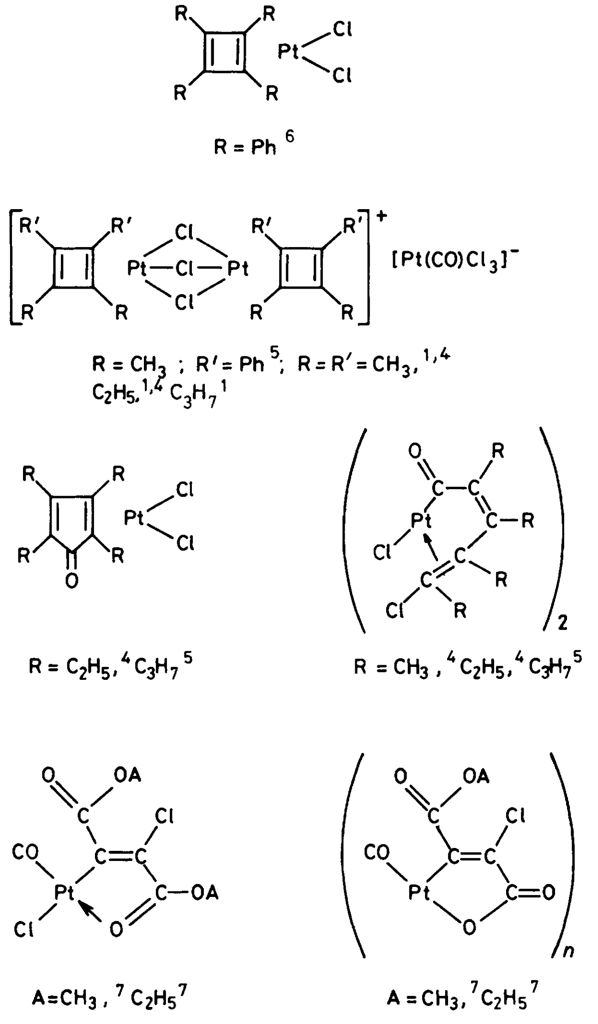
† *cis*-[3,5-Bis(ethoxycarbonyl)-4,6-diphenyl-2*H*-pyran-2-ylidene]dichloro(triphenylphosphine)platinum.

Supplementary data available (No. SUP 23499, 32 pp.): thermal parameters, least-squares planes, structure factors. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.



Scheme 1. Products of reaction of [Pt(CO)$_2$Cl$_2$] and acetylenes (RC≡CR′)

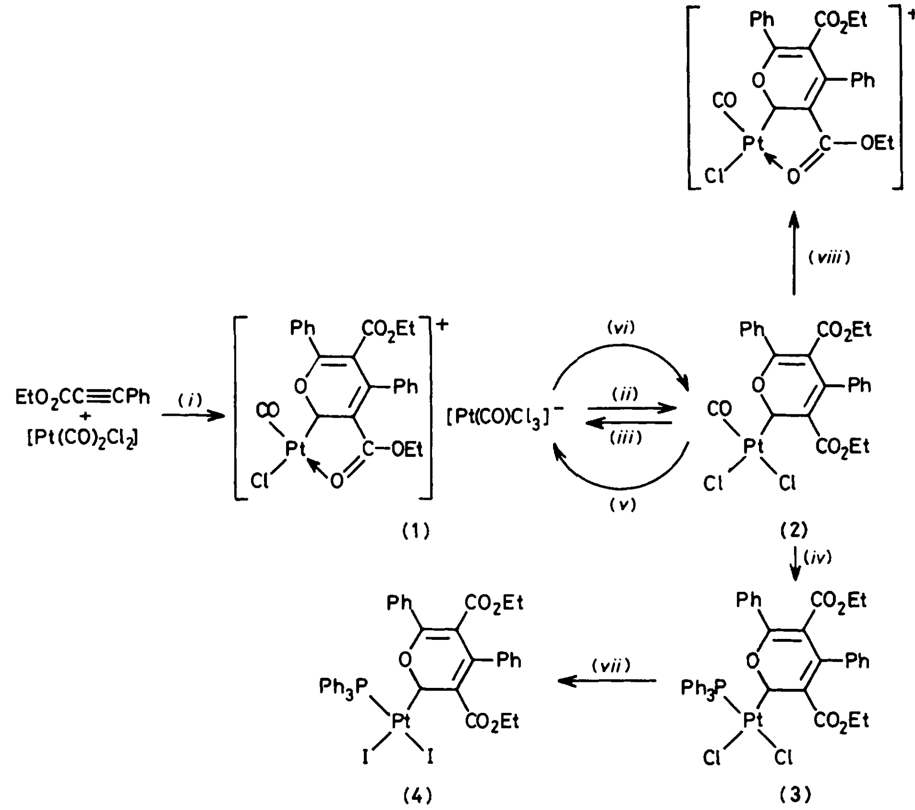
shows three strong broad bands at 2 100vs, 1 715s, and 1 560m cm^{-1}. The ^{1}H n.m.r. spectrum (CDCl$_3$) (see Experimental section) shows resonances for several non-equivalent ethyl groups with different intensities, suggesting the presence of isomers. Reaction with PPh$_3$ or 2,2′-bipyridine (bipy) leads to CO displacement and there is no modification of the organic ligand.

Compound (1) is stable in the solid state and is insoluble in non-polar solvents, whereas it quickly decomposes in polar solvents such as alcohols, chloroform, and dichloromethane. The i.r. spectrum (Nujol mulls) shows bands at 2 135vs and 2 120vs cm^{-1} due to the stretching of CO groups bonded to platinum, 1 740s and 1 610vs cm^{-1} due to the stretching of CO in the alkoxycarbonyl groups, 1 560m due to the C=C stretchings, and finally a broad band at 343m cm^{-1} due to the terminal Pt–Cl stretch. The band at 1 610 cm^{-1} is very significant, suggesting that one of the alkoxycarbonyl groups is co-ordinated to a platinum atom [7] and that the acetylene moieties are asymmetrically distributed between the two platinum atoms. The i.r. spectrum of compound (1) in acetonitrile shows two sharp bands at 2 135vs and 2 105s cm^{-1}, a broad band at 1 735s cm^{-1}, and a set of weak bands at 1 560 cm^{-1}. The absence of a strong band around 1 600 cm^{-1} suggests that a reaction occurs leading to a new compound (2) [see Scheme 2(*ii*)] which can easily be isolated as a white microcrystalline solid by toluene addition.

The elemental analysis of compound (2) is in agreement with a species containing two acetylene molecules per Pt atom; the compound is insoluble in aliphatic hydrocarbons, sparingly soluble in toluene and acetone, and soluble in anhydrous tetrahydrofuran (thf), and CH$_2$Cl$_2$. The i.r. spectrum (Nujol mulls) shows a band at 2 105vs cm^{-1} due to the stretching of a terminal CO group bonded to platinum and at 1 740m and 1 725s cm^{-1} due to the stretchings of two non-equivalent ethoxycarbonyl groups; the far-i.r. spectrum shows two bands at 349m and 318m cm^{-1} due to Pt–Cl stretchings, suggesting a *cis* geometry around the platinum atom. The ^{1}H n.m.r. spectrum (CD$_2$Cl$_2$) of compound (2) (see Experimental section) shows two sets of signals due to the resonances of two non-equivalent ethoxycarbonyl groups and a multiplet due to the resonance of the phenyl groups with the correct intensity ratio 1 : 1. Compound (2) reacts with an excess of PPh$_3$ in hot toluene to give quantitatively the known [Pt(PPh$_3$)$_2$Cl$_2$]. With the stoicheiometric amount of PPh$_3$ (1 mol per mol of complex), in thf at room temperature, quantitative displacement of CO occurs to give a yellow solid (3) [see Scheme 2(*iv*)] which has been recrystallised from dichloromethane–cyclohexane.

Compound (3) appears to be more stable both in solution and in the solid state than the parent compound (2). Whereas (2) decomposes in the presence of halides, complex (3) is more stable; a substitution reaction with NEt$_4$I gives complex (4) [see Scheme 2(*vii*)]. The i.r. spectrum (Nujol mulls) of (3) shows only a band at 1 730vs cm^{-1}, while in the far-i.r. spectrum two bands are present at 318m and 292m cm^{-1}. The ^{1}H n.m.r. spectrum (see Experimental section) shows a pattern very similar to that of compound (2), where two non-equivalent ethoxycarbonyl groups are present, in the correct intensity ratio with the phenyl groups. All the spectroscopic data suggest that the modification which occurs on going from compound (2) to (3) is merely the replacement by triphenylphosphine of a CO group bonded to platinum. The nature of compound (3) has been unambiguously determined by an *X*-ray structural analysis, allowing us to establish unique relationships (Scheme 2) between this compound and its precursors.

cis-[Pt{$\overline{\text{CC(CO}_2\text{Et)=C(Ph)(CO}_2\text{Et)=C(Ph)O}}$}(PPh$_3$)Cl$_2$] (3), *A Description of the Structure.* —A schematic view of compound (3) is shown in Figure 1; atomic co-ordinates are listed in Table 1, bond lengths and angles in Table 2. The compound shows a slightly distorted square planar co-ordination around the Pt atom with two chlorine atoms bonded *cis* to each other, a triphenylphosphine group, and a six-membered carbenoid ring which is rotated with respect to the co-ordination plane defined by PtCl(1)Cl(2)P, making a dihedral angle of 63.5°, a common feature in carbenoid complexes: this angle is smaller than those reported in the literature [11,12] which are usually in the range 77—90°. The Pt–C(1) bond distance [1.933(8) Å] suggests a bond order somewhat greater than one [13] and is in agreement with an estimated value of 2.02 Å for a Pt^{II}–C(*sp*^{2}) bond.[14] Moreover this bond length may be compared with the value found for similar carbenoid compounds, *e.g.* 1.96(2) Å in *cis*-[Pt{C(OEt)(NHPh)}(PEt$_3$)Cl$_2$] [11] and 1.920(9) Å in *cis*-[Pt{C(OEt)(CH$_2$Ph)}(PMe$_2$Ph)Cl$_2$].[8] A longer bond [2.086(8) Å] has been found in a molybdenum complex with a 2-oxacyclopentylidene ring.[15] The two Pt–Cl bond lengths [average 2.348(2) Å] are equal, indicating similar *trans* influences for the carbene ring and the triphenylphosphine ligand, and may be compared both with the value of 2.390(8) Å for a platinum–chlorine bond *trans* to PEt$_2$Ph [12] and to those found in



Scheme 2. (*i*) − CO; (*ii*) +CH$_3$CN, −[Pt(CH$_3$CN)(CO)Cl$_2$]; (*iii*) +[Pt(CH$_3$CN)(CO)Cl$_2$], −CH$_3$CN; (*iv*) +PPh$_3$, −CO; (*v*) + [Pt(CO)$_2$Cl$_2$], −CO; (*vi*) +KCl, −K[Pt(CO)Cl$_3$]; (*vii*) +NEt$_4$I, −NEt$_4$Cl; (*viii*) +AgPF$_6$, −AgCl

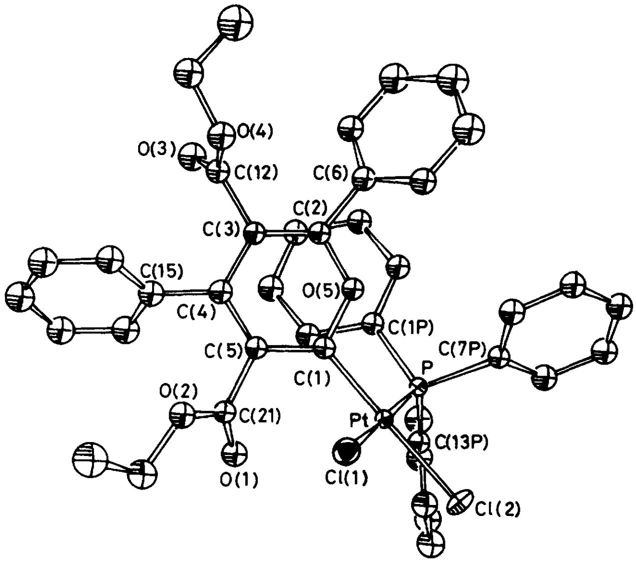


Figure 1. An ORTEP view of compound (3)

other non-cyclic carbenoid ligands (Pt–Cl 2.357—2.362 Å).[12,13]

The angles around the Pt atom are significantly different from the ideal value of 90.0°. The two Cl(2)–Pt–P and P–Pt–C(1) angles have larger values [average 91.7(2)°] possibly owing to the steric hindrance of bulky substituents, and the Cl(1)–Pt–C(1) angle [87.4(2)°] is smaller than that involving the other chlorine atoms [Cl(1)–Pt–Cl(2) 89.2(1)°]. There are two short intramolecular contacts between atoms Cl(1) and O(1) (3.55 Å) and atoms Cl(1) and C(21) (3.27 Å).

The Pt–P distance [2.244(2) Å] falls in the range expected for similar compounds when the *trans* ligand is a chlorine atom (*e.g.* 2.241 Å).[8,12] The six-membered carbenoid ring is planar [maximum deviations from least-squares plane, defined by C(1),O(5),C(2),C(3),C(4),C(5) atoms: ± 0.03 Å]; the values of bond angles in the ring (average 119.9 ± 2.9°) together with the shortening of the C–C [average 1.40(1) ± 0.02 Å (root mean square deviation from the mean)] and C–O [average 1.362(9) ± 0.01 Å] distances suggest an aromatic nature for this ligand. The co-ordination geometry around the carbenoid carbon atom is distorted trigonal planar: thus there are substantial differences in the angles subtended at C(1) [Pt–C(1)–C(5) 129.2(3) and Pt–C(1)–O(5) 114.6(4)°]. These values are unusual and compare with values such as 127.5(8) and 120.4(7)° found in the benzyl(ethoxy)carbene derivative of Pt^{II}.[8] Moreover, the significant deformation of the angles C(1)–C(5)–C(21) [117.9(5)°], C(3)–C(2)–C(6) [129.5(4)°], and C(6)–C(2)–O(5) [111.5(5)°] may be ascribed to steric hindrance due to the presence of bulky substituents. The overall conformation of the molecule may be described by the relevant internal rotation angles reported in Table 3. There are no short intermolecular contacts and the molecules are held together by van der Waals forces.

^{13}C *N.M.R. Studies on Compounds* (2) *and* (3).—The formation of a cyclocarbenoid ring induced by the insertion of a CO group displaced by triphenylphosphine in σ-alkenylcarbonyl compounds has been reported.[16]

In order to clarify the origin of the CO group inserted into the ring, a ^{13}C n.m.r. study on compounds (2) and (3) has been performed. The ^{13}C spectrum (CD$_2$Cl$_2$) of (2) prepared by direct exchange with ^{13}CO (the relevant numbering scheme is shown in Figure 2) shows one intense resonance {δ = 156.5

Table 1. Final positional parameters with estimated standard deviations (e.s.d.s) on the last figure in parentheses

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Pt	0.225 59(2)	0.218 53(2)	0.285 81(2)	C(17)	0.310 9(10)	0.256 0(10)	−0.240 1(8)
Cl(1)	0.092 9(2)	0.122 3(2)	0.199 5(1)	C(18)	0.429 3(10)	0.187 1(10)	−0.256 7(8)
Cl(2)	0.211 7(2)	0.121 8(2)	0.404 2(2)	C(19)	0.494 7(9)	0.161 1(9)	−0.182 9(7)
P	0.349 7(2)	0.314 4(2)	0.368 5(1)	C(20)	0.437 1(8)	0.206 8(8)	−0.087 3(6)
O(1)	0.387 1(5)	0.057 6(5)	0.079 8(4)	C(21)	0.309 1(7)	0.120 0(7)	0.048 3(5)
O(2)	0.252 4(5)	0.080 8(5)	−0.026 6(4)	C(22)	0.300 2(10)	−0.048 7(10)	−0.080 3(8)
O(3)	0.296 8(6)	0.560 4(6)	−0.011 8(5)	C(23)	0.237 0(12)	−0.065 8(13)	−0.170 4(10)
O(4)	0.093 9(6)	0.594 9(6)	−0.001 6(5)	C(1P)	0.405 5(7)	0.404 0(7)	0.304 8(5)
O(5)	0.170 4(4)	0.425 3(4)	0.223 1(4)	C(2P)	0.383 1(7)	0.528 0(7)	0.339 9(6)
C(1)	0.220 8(6)	0.302 5(6)	0.189 3(5)	C(3P)	0.425 9(8)	0.590 8(8)	0.285 3(6)
C(2)	0.162 6(6)	0.503 6(6)	0.169 6(5)	C(4P)	0.490 8(8)	0.528 3(8)	0.195 2(7)
C(3)	0.206 2(6)	0.457 4(7)	0.073 4(5)	C(5P)	0.515 3(8)	0.402 0(8)	0.158 6(6)
C(4)	0.258 6(7)	0.330 1(7)	0.032 0(5)	C(6P)	0.471 9(7)	0.339 9(7)	0.213 5(6)
C(5)	0.260 6(6)	0.253 9(6)	0.089 1(5)	C(7P)	0.270 9(6)	0.422 7(6)	0.483 0(5)
C(6)	0.111 3(7)	0.630 7(7)	0.229 0(6)	C(8P)	0.316 4(8)	0.427 7(8)	0.570 5(6)
C(7)	0.018 6(8)	0.658 9(8)	0.303 1(7)	C(9P)	0.251 9(9)	0.513 7(9)	0.655 0(7)
C(8)	−0.027 0(11)	0.779 8(11)	0.363 5(9)	C(10P)	0.142 2(8)	0.569 9(8)	0.651 7(7)
C(9)	0.023 8(11)	0.867 5(11)	0.348 3(9)	C(11P)	0.095 3(8)	0.592 8(8)	0.563 2(6)
C(10)	0.117 4(10)	0.838 3(10)	0.275 7(8)	C(12P)	0.159 5(8)	0.504 6(8)	0.479 2(6)
C(11)	0.160 3(8)	0.718 8(8)	0.215 6(6)	C(13P)	0.492 1(7)	0.226 3(7)	0.400 5(5)
C(12)	0.205 9(7)	0.542 7(7)	0.014 2(6)	C(14P)	0.587 3(8)	0.276 7(8)	0.417 6(7)
C(13)	0.081 8(10)	0.682 6(10)	−0.057 4(8)	C(15P)	0.695 3(9)	0.214 8(9)	0.447 2(7)
C(14)	0.065 5(12)	0.807 7(12)	0.011 9(10)	C(16P)	0.705 1(8)	0.105 2(8)	0.463 2(7)
C(15)	0.315 9(7)	0.280 5(7)	−0.069 7(6)	C(17P)	0.612 3(10)	0.053 0(10)	0.445 8(8)
C(16)	0.251 6(9)	0.304 8(9)	−0.145 4(7)	C(18P)	0.504 8(9)	0.114 0(9)	0.412 6(7)

Table 2. Some relevant bond distances (Å) and angles (°) with e.s.d.s on the last figure in parentheses

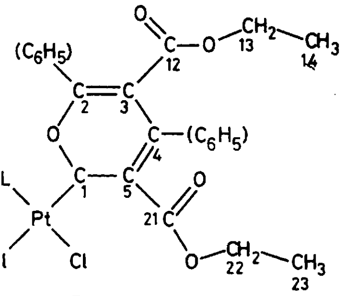
Pt–Cl(1)	2.347(2)	O(1)–C(21)	1.186(10)	O(5)–C(1)	1.361(8)	C(3)–C(12)	1.506(13)
Pt–Cl(2)	2.350(3)	O(2)–C(21)	1.322(10)	O(5)–C(2)	1.362(10)	C(4)–C(5)	1.391(12)
Pt–P	2.244(2)	O(2)–C(22)	1.465(11)	C(1)–C(5)	1.419(9)	C(4)–C(15)	1.489(10)
Pt–C(1)	1.933(8)	O(3)–C(12)	1.199(12)	C(2)–C(3)	1.375(10)	C(5)–C(21)	1.481(10)
P–C(1P)	1.828(9)	O(4)–C(12)	1.322(10)	C(2)–C(6)	1.468(9)	av. C–C(Ethyl)	1.50(1)
P–C(7P)	1.828(6)	O(4)–C(13)	1.475(15)	C(3)–C(4)	1.418(10)	av. C–C(Phenyl)	1.39(2)
P–C(13P)	1.831(8)						

Pt–P–C(1P)	113.1(2)	Cl(2)–Pt–C(1)	174.7(3)	O(5)–C(2)–C(3)	118.9(5)	C(3)–C(4)–C(15)	120.0(5)
Pt–P–C(7P)	111.1(2)	P–Pt–C(1)	92.0(2)	O(5)–C(2)–C(6)	111.5(5)	C(4)–C(3)–C(12)	120.3(5)
Pt–P–C(13P)	120.0(2)	O(1)–C(21)–O(2)	125.4(5)	C(1)–O(5)–C(2)	125.0(4)	C(4)–C(5)–C(21)	121.2(5)
Pt–C(1)–O(5)	114.6(4)	O(1)–C(21)–C(5)	124.1(5)	C(1)–C(5)–C(4)	120.9(5)	C(5)–C(4)–C(15)	121.0(5)
Pt–C(1)–C(5)	129.2(3)	O(2)–C(21)–C(5)	110.5(6)	C(1)–C(5)–C(21)	117.9(5)	C(1P)–P–C(7P)	105.4(3)
Cl(1)–Pt–Cl(2)	89.2(1)	O(3)–C(12)–O(4)	126.3(5)	C(2)–C(3)–C(4)	119.7(5)	C(1P)–P–C(13P)	101.0(3)
Cl(1)–Pt–P	178.8(1)	O(3)–C(12)–C(3)	122.8(5)	C(2)–C(3)–C(12)	119.9(5)	C(7P)–P–C(13P)	104.8(3)
Cl(1)–Pt–C(1)	87.4(2)	O(4)–C(12)–C(3)	110.9(6)	C(3)–C(2)–C(6)	129.5(4)		
Cl(2)–Pt–P	91.5(1)	O(5)–C(1)–C(5)	116.2(5)	C(3)–C(4)–C(5)	119.0(5)		

Table 3. Some relevant torsion angles (°) (e.s.d.s in the range 0.6—1.0)

Cl(1)–Pt–P–C(1P)	63.0	Cl(2)–Pt–C(1)–C(5)	112.2
Cl(1)–Pt–P–C(7P)	−55.3	O(1)–C(21)–C(5)–C(1)	52.3
Cl(1)–Pt–P–C(13P)	−177.9	O(2)–C(21)–C(5)–C(1)	−127.1
Cl(2)–Pt–P–C(1P)	−175.9	O(3)–C(12)–C(3)–C(4)	69.0
Cl(2)–Pt–P–C(7P)	65.8	O(4)–C(12)–C(3)–C(4)	−112.5
Cl(2)–Pt–P–C(13P)	−56.8	C(1)–C(5)–C(4)–C(15)	−171.5
Cl(1)–Pt–C(1)–O(5)	−115.8	C(3)–C(2)–C(6)–C(7)	−146.4
Cl(1)–Pt–C(1)–C(5)	63.3	C(5)–C(4)–C(15)–C(20)	52.7
Cl(2)–Pt–C(1)–O(5)	−67.0		

p.p.m.,[1] J[Pt–C(24)] = 1 831 Hz} due to the carbonyl bonded to platinum, whereas when prepared from [Pt(^{13}CO)$_2$Cl$_2$] an additional intense resonance is found at δ = 193 p.p.m. {^1J[Pt–C(1)] = 1 205 Hz}. This latter resonance shifts to higher frequency (lower field) on formation of compound (3): δ (CD$_2$Cl$_2$) = 207.8 p.p.m. {^1J[Pt–C(1)] = 1 350 Hz} and the rather low-field shift is consistent with the carbenoid character of the carbon atom.[17] The ^{31}P n.m.r. spectrum (CDCl$_3$) shows a non-binomial triplet at δ = 9.18 p.p.m. owing to coupling with ^{195}Pt [^1J(Pt–P) = 4 026 Hz] and additional coupling with the ^{13}C {^2J[C(1)–P] = 14 Hz}. On the basis of these ^{13}C n.m.r. spectra on selectively enriched samples, considering the chemical shifts of the resonances and the Pt–^{13}C coupling constant, a tentative assignment of the spectra of compounds (2) and (3) can be made. The ^{13}C-{^{1}H} n.m.r. spectrum of compound (2) in CDCl$_3$ shows signals at δ =



(2) L = CO [C(24)]; (3) L = $P(C_6H_5)_3$

Figure 2. Numbering scheme for ^{13}C n.m.r.

193.1 [C(1)], 172.8, 164.0 [C(12),C(21)], 162.2 [C(2)], 157.6 [C(5)] [^2J(Pt–C) = 31 Hz], 155.0 [C(24)], 140 p.p.m. [C(3)], several signals in the aromatic region (135—120 p.p.m.), 63.5, 63.4 [C(13),C(22)], and 13.5, 13.3 p.p.m. [C(14),C(23)]. The most probable assignment for the missing carbon atom [C(4)] is the relatively low-field resonance, in the aromatic region, which does not show ^1H coupling in the off-resonance ^{13}C n.m.r. spectrum: δ = 132.2 p.p.m. [C(4)]. The $^{13}C-\{^1H\}$ n.m.r. (natural-abundance) spectrum of compound (3) in $CDCl_3$ shows signals at δ = 207.0 [C(1)], 169.0, 164.1 [C(12), C(21)], 162.6 [C(2)], 157.3 [C(5)], 140.4 [C(3)], several bands between 135 and 120 p.p.m., 62.8, 62.3 [C(13),C(22)], and 13.5—13.3 p.p.m. [C(14),C(23)].

The similar ^{13}C n.m.r. spectra of compounds (2) and (3) together with elemental analysis, i.r., and ^1H n.m.r. spectra confirm that the carbenoid ring is present in compound (2) without any modification of the organic fragment in the reaction with PPh_3 [see Scheme 2(*iv*)].

Characterisation of Compound (1).—In order to clarify the nature of compound (1) the reaction with CH_3CN [see Scheme 2(*ii*)] has been carefully investigated. As already indicated, compound (2) has been isolated from a CH_3CN solution of (1), by addition of toluene. However, the i.r. spectrum of the mother-liquor shows bands at 2 320w and 2 130 cm^{-1} assignable to CH_3CN and a CO group co-ordinated to platinum. This i.r. evidence suggests that $[Pt(CH_3CN)(CO)Cl_2]$ [18] is present in the solution, but it was impossible to isolate this compound in a pure state owing to its very low stability. Further support for this formulation is given by the fact that when the acetonitrile–toluene solution was treated with PPh_3 the well known $[Pt(PPh_3)_2Cl_2]$ (yield 78%) separated with evolution of carbon monoxide. On the other hand, when the same solution was treated with an excess of Cl^- ions, *e.g.* by addition of $[N(PPh_3)_2]Cl$ the well known $[N(PPh_3)_2][Pt(CO)Cl_3]$ was isolated in the expected amount. The reaction of (1) with CH_3CN [equation (i)] is reversible: thus when the

$$Pt_2(PhCCCO_2Et)_2(CO)_3Cl_4\ (1) + CH_3CN \rightleftharpoons [Pt(CH_3CN)(CO)Cl_2] + [Pt\{CC(CO_2Et){=}C(Ph)C(CO_2Et){=}C(Ph)O\}(CO)Cl_2]\ (2) \quad \text{(i)}$$

white compound (2) isolated is treated with its mother-liquor, by evaporation of the solvents it is possible to isolate quantitatively (1) in the pure state. Alternatively, compound (1) has been obtained by treating (2) with the stoicheiometric amount of $[Pt(CO)_2Cl_2]$ [see Scheme 2(*v*)]. The easy interconversion of compounds (1) and (2) is in agreement with the presence of the same organic fragment in both species. The strong i.r. band at 1 610 cm^{-1} of compound (1) indicates an intramolecular interaction of carboxylic CO with platinum in a salt-like species [7] [see compound (1) of Scheme 2]; the square-planar co-ordination around the Pt^{II}, which is a common feature for this type of compound, is obtained through the co-ordination of the β-ethoxycarbonyl group to form the same five-membered ring found in the σ-alkenylplatinum(II) derivatives.[7]

Maitlis and co-workers [19] found an analogous interaction with the formation of a non-planar six-membered ring for some palladium(II) derivatives.

On the other hand, the easy formation of a salt-like compound with $[Pt(CO)Cl_3]^-$ as counter ion has been reported for cationic tetra-alkylcyclobutadieneplatinum(II) derivatives.[1] In the same way as compound (1) reacts with CH_3CN to give (2) and $[Pt(CH_3CN)(CO)Cl_2]$ [see Scheme 2(*ii*)], cyclobutadiene salt-like compounds dissolve in CH_3CN to give equilibrium (ii) (R = CH_3, C_2H_5, or C_3H_7) (as shown by i.r. spectroscopy).

$$[Pt_2(C_4R_4)_2Cl_3][Pt(CO)Cl_3] + CH_3CN \rightleftharpoons 2[Pt(C_4R_4)Cl_2] + [Pt(CH_3CN)(CO)Cl_2] \quad \text{(ii)}$$

In order to confirm the formulation of (1) and to exclude an alternative intermolecular [20] interaction between an alkoxycarbonyl group and a ' $Pt(CO)Cl_2$ ' unit, compound (2) was treated, in toluene, with the stoicheiometric amount of $AgPF_6$; $[Pt\{CC(COOEt){=}CPhC(CO_2Et){=}CPhO\}(CO)Cl]PF_6$ [see Scheme 2(*viii*)] was formed, as shown by i.r. spectroscopy (2 135vs, 1 740s, and 1 610vs cm^{-1}). In line with the reactivity of dicarboalkoxy σ-alkenyl derivatives, *e.g.* $[Pt\{C(CO_2R){=}CCl(COOR)\}(CO)Cl]$,[7] and cationic cyclobutadiene complexes,[1] when compound (1) was treated with KCl [see Scheme 2(*vi*)], $K[Pt(CO)Cl_3]$ and compound (2) were obtained quantitatively, as expected.

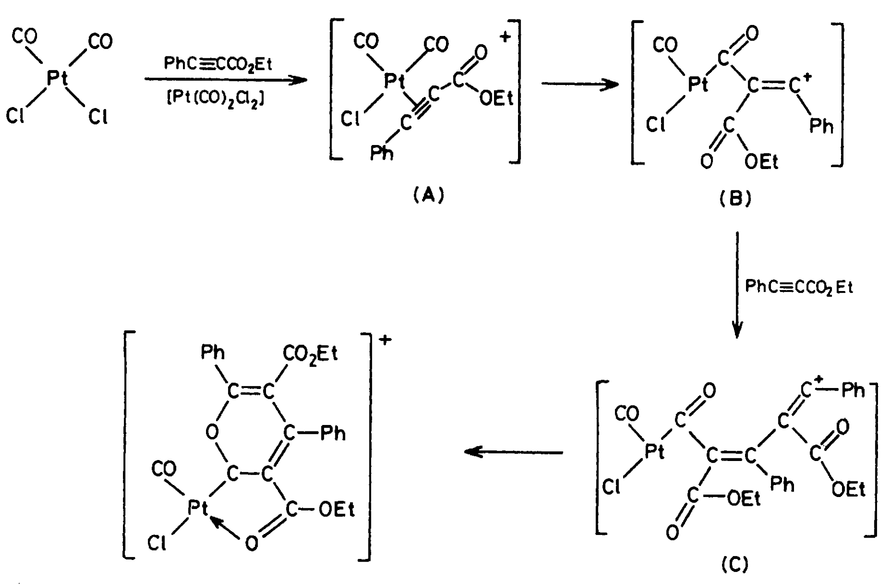
A reasonable mechanism for the reaction between $[Pt(CO)_2Cl_2]$ and $PhC{\equiv}CCO_2Et$ to give compound (1) can be proposed (see Scheme 3). The first step is the extraction of a chlorine atom to give $[Pt(CO)Cl_3]^-$ anion and the cation (A) containing the acetylene η-bonded to platinum. The highly polarised acetylene behaves as a nucleophile and attacks the positively charged C atom of a carbonyl group co-ordinated to platinum, giving intermediate (B). A second molecule of acetylene acts as a nucleophile and gives C which is sterically suitable for ring closure.

Experimental

Microanalyses were determined by Laboratorio Analisi, Università di Milano. The ^1H, ^{13}C (internal $SiMe_4$), and ^{31}P (external H_3PO_4, 85% in D_2O) n.m.r. spectra were recorded on Bruker WP 80 or Varian XL-200 spectrometers and are reported downfield of the standard. I.r. spectra were obtained on a Perkin-Elmer 457 grating spectrophotometer and the far-i.r. spectra with a Nicolet MX-1 FT-IR spectrometer using Nujol mulls and NaCl or CsI plates.

All the reactions were carried out under an atmosphere of nitrogen and with anhydrous solvents. Solvents were purified and dried by standard methods. The complex *cis*-$[Pt(CO)_2Cl_2]$ was prepared as described previously.[6] Crystals of compound (3) suitable for *X*-ray analysis were obtained by slow diffusion of cyclohexane (5 cm^3) into a dichloromethane (1 cm^3) solution of it. The yellow-red crystals are stable in air and have an elongated prismatic habit. A crystal of approximate dimensions 0.2 × 0.2 × 0.4 mm was used for data collection.

Crystal Data.—$C_{41}H_{35}Cl_2O_5PPt$, M = 904.70, Triclinic, space group $P\bar{1}$, a = 11.523(3), b = 11.994(4), c = 14.512(6)



Scheme 3. Mechanism of formation of compound (1)

Å, $\alpha = 106.2(1)$, $\beta = 88.8(1)$, $\gamma = 73.7(2)°$, $U = 1\,837.7(8)$ Å^3, $D_m = 1.64$ Mg m^{-3}, $Z = 2$, $D_c = 1.635$ Mg m^{-3}, $F(000) = 896$, μ(Mo-K_α) = 40.9 cm^{-1}.

Data Collection.—Unit-cell parameters were obtained by least-squares fit of the 2θ values of 25 high-angle reflections. The data were collected with an automated four-circle diffractometer (Philips PW 1 100, graphite-monochromated Mo-K_α radiation, $\lambda = 0.710\,69$ Å) using a ω—2θ scan. A scan speed of 0.07° s^{-1} was used with constant scan width of 1.20°. Two background counts were measured at each side of the peak for 4 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 three general reflections were made to check the effect of absorption; no correction was considered to be necessary. A total of 6 430 independent reflections was measured up to $(\sin\theta)/\lambda \leqslant 0.6058$ and corrected for Lorentz and polarisation factors; $\sigma(I)$ values were evaluated on counting statistics. 5 842 Reflections having $I \geqslant 3\sigma(I)$ were considered 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 minimised was $\Sigma w|F_o - (1/k)F_c|^2$; a Cruickshank weighting scheme [21] was used. Atomic scattering factors were taken from ref. 22, with correction for the real part of the anomalous dispersion for the Pt and Cl atoms.[22] It was not possible to locate all the hydrogen atoms which were placed in their calculated positions assuming a C–H bond length of 1.08 Å. Their contributions were taken into account but not refined. The refinement was carried out using anisotropic thermal parameters for Pt, Cl, and P and isotropic ones for the others. The final conventional R factor $[\Sigma(k|F_o| - |F_c|)/\Sigma k|F_c|)]$ was 0.048 for the observed reflections (0.053 with the unobserved included). A final difference-Fourier map showed no significant features. All calculations were carried out using local versions of programs written by Immirzi.[23]

Preparation of [Pt{CC(COOEt)=C(Ph)C(CO$_2$Et)=C(Ph)O}(CO)Cl][Pt(CO)Cl$_3$] (1).—(*a*) To a suspension of [Pt(CO)$_2$Cl$_2$] (8.26 g, 25.6 mmol) in hot anhydrous toluene (180 cm^3), ethyl phenylpropiolate (7 cm^3, 37.95 mmol) was gradually added (about 3 h). The solution was kept at 80 °C until all the [Pt(CO)$_2$Cl$_2$] had reacted (about 48 h). After cooling, the orange solid was filtered off, washed with toluene (5 × 30 cm^3), and dried; yield 6.32 g (51%). Compound (1) is insoluble in hydrocarbons, rapidly decomposes in dichloromethane, chloroform, alcohols, and acetone, and reacts with thf and CH$_3$CN (Found: C, 32.8; H, 2.1; Cl, 14.2; O, 12.3; Pt, 40.8. $C_{25}H_{20}Cl_4O_7Pt_2$ requires C, 31.1; H, 2.1; Cl, 14.7; O, 11.6; Pt, 40.5%).

The toluene mother-liquor was reduced in volume *in vacuo* (20 cm^3) and treated with hexane (100 cm^3). The crude yellow-brown product was stirred with hexane (3 × 50 cm^3) and crystallised from toluene–hexane (3.1 g, 19% yield) (Found: C, 43.1; H, 3.2; Cl, 10.9; O, 12.3; Pt, 30.1. $C_{23}H_{20}Cl_2O_5Pt$ requires C, 43.0; H, 3.1; Cl, 11.0; O, 12.4; Pt, 30.4%). ^{1}H N.m.r. (CDCl$_3$); δ = 0.8—2 (m, OCH$_2$CH_3), 3—5 (m, OCH_2CH$_3$), and 7—8 (m, C$_6$H$_5$).

(*b*) To a suspension of [Pt(CO)$_2$Cl$_2$] (0.21 g, 0.65 mmol) in anhydrous toluene (10 cm^3) was added compound (2) (0.426 g, 0.64 mmol) under stirring. The colour of the solution changed from white to yellow. After 48 h at room temperature the orange solid formed was filtered off, washed with toluene, and dried. It was identified as (1) (yield 90%).

(*c*) Compound (1) was also obtained when (2) reacts with its mother-liquor [see preparation (*a*) of (2)]. The solid can be isolated by evaporation of the solvent to dryness, followed by addition of fresh toluene (10 cm^3). It was fully characterised by elemental analysis and spectroscopic data.

Preparation of [Pt{CC(CO$_2$Et)=C(Ph)C(CO$_2$Et)=C(Ph)O}(CO)Cl$_2$] (2).—(*a*) *Reaction of* (1) *with* CH$_3$CN. Compound (1) (1.53 g, 1.58 mmol) was stirred with CH$_3$CN (20 cm^3) at room temperature (about 15 min). Toluene (40 cm^3) was added and the reaction mixture was reduced in volume *in vacuo* until the formation of a white microcrystalline solid was observed. This was filtered off, washed with toluene (5 × 3 cm^3), and dried; yield 0.946 g, (89%). Compound (2) is insoluble in aliphatic hydrocarbons, sparingly soluble in acetone or toluene, and soluble in dichloromethane, tetrahydrofuran, chloroform, and acetonitrile (Found: C, 43.0; H, 3.1; Cl, 10.6; O, 14.9; Pt, 28.4. $C_{24}H_{20}Cl_2O_6Pt$ requires C, 43.0;

H, 3.0; Cl, 10.6; O, 14.3; Pt, 29.1%). ^1H N.m.r. ($CDCl_3$): $\delta = 1.0$ (t), 1.1 (t) ($OCH_2C\mathit{H}_3$), 4.07 (q), 4.2 (q) ($OC\mathit{H}_2CH_3$), and 7.3—8.3 (m, C_6H_5). The mother-liquor was treated with PPh_3 (0.71 g, 2.71 mmol) and kept at 50 °C for 4 h. After carbon monoxide evolution, a white precipitate was formed; after cooling the compound was filtered off, dried, and identified as $[Pt(PPh_3)_2Cl_2]$ (0.91 g, 75%).

(*b*) *Reaction of* (1) *with* KCl. To a suspension of compound (1) (0.13 g, 0.143 mmol) in toluene (15 cm^3) was added KCl (0.425 g, 5.7 mmol); the mixture was stirred at room temperature for 24 h and the colour of the solid changed from yellow to white. The solid was filtered off and the crude product treated with CH_2Cl_2 (2 × 10 cm^3). After hexane (30 cm^3) addition the volume of the CH_2Cl_2–hexane mixture was reduced to 10 cm^3 and a white microcrystalline compound separated; yield 0.074 g (85%).

Preparation of $[Pt\{CC(CO_2Et)=C(Ph)C(CO_2Et)=C(Ph)O\}(PPh_3)Cl_2]$ (3).—To a solution of compound (2) (0.279 g, 0.42 mmol) in thf (15 cm^3) was added a solution of PPh_3 (0.11 g, 9.42 mmol; 10 cm^3 thf). The solution was stirred at room temperature for 2 h: a yellow solid was obtained, filtered off, washed with hexane, and dried; yield 0.27 g (71%). Compound (3) is insoluble in aliphatic hydrocarbons, sparingly soluble in toluene and thf, and soluble in CH_2Cl_2 and $CHCl_3$ (Found: C, 54.0; H, 4.0; Cl, 8.0; O, 9.1; Pt, 20.0. $C_{41}H_{35}Cl_2O_5PPt$ requires C, 54.4; H, 3.9; Cl, 7.85; O, 8.85; Pt, 21.6%). ^1H N.m.r. ($CDCl_3$): $\delta = 0.86$ (t), 0.95 (t) ($OCH_2C\mathit{H}_3$), 3.92 (q), 4.01 (q) ($OC\mathit{H}_2CH_3$) and 7—8 (m, C_6H_5).

Reaction of Compound (2) *with* PPh_3 *in Excess*.—To a solution of PPh_3 (0.49 g, 1.87 mmol) in toluene (20 cm^3) was added compound (2) (0.499 g, 0.67 mmol). After stirring for 24 h at 50 °C a white precipitate was filtered off, washed with toluene (3 × 10 cm^3), and dried; yield of $[Pt(PPh_3)_2Cl_2]$ 0.471 g (89%).

Preparation of $[Pt\{CC(CO_2Et)=C(Ph)C(CO_2Et)=C(Ph)O\}(PPh_3)I_2]$ (4).—To a solution of NEt_4I (1.2 g, 4.6 mmol) in CH_3OH (50 cm^3) was added compound (3) (0.2 g, 0.22 mmol). After stirring at room temperature for 24 h the orange-red microcrystalline solid was filtered off, washed with methanol (2 × 5 cm^3), and dried. Yield 0.195 g (83%) (Found: C, 45.3; H, 3.2. $C_{41}H_{35}I_2O_5PPt$ requires C, 45.3; H, 3.2%). ^1H N.m.r. ($CDCl_3$): $\delta = 0.89$ (t), 0.93 (t) ($OCH_2C\mathit{H}_3$), 3.94 (q), 4.04 (q) ($OC\mathit{H}_2CH_3$), and 7—8.2 (m, C_6H_5).

Preparation of ^{13}C*-Enriched Compounds*.—The complex $[Pt(^{13}CO)_2Cl_2]$ was prepared by direct exchange of $[Pt(CO)_2Cl_2]$ (1.6 g, 4.97 mmol) with ^{13}CO (^{13}CO, 70% enriched, 230 cm^3) in toluene (50 cm^3). After stirring for 24 h at room temperature the solution was cooled to −20 °C and the solid recovered by filtration (yield 85%). A sample of 35% ^{13}CO-enriched $[Pt(^{13}CO)_2Cl_2]$ was obtained. The complex $[Pt\{^{13}CC(CO_2Et)=C(Ph)C(CO_2Et)=C(Ph)O\}(^{13}CO)Cl_2]$ was prepared from $[Pt(^{13}CO)_2Cl_2]$ as described above and used to obtain $[Pt\{^{13}CC(CO_2Et)=C(Ph)C(CO_2Et)=C(Ph)O\}(PPh_3)Cl_2]$. The complex $[Pt\{CC(CO_2Et)=C(Ph)C(CO_2Et)=C(Ph)O\}(^{13}CO)Cl_2]$ was prepared by direct exchange of compound (2) with ^{13}CO (^{13}CO, 70% enriched); the final enrichment was about 30%. The compound was used after crystallisation from acetonitrile and toluene.

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