Reactions of Acetylenes with Noble Metal Carbonyl Halides. Part 11.[1] Synthesis of $[Pt\{CMe{=}C(H)COOMe\}(CO)Cl]$ *via* Polynuclear Platinum Carbonyls. *X*-Ray Crystal Structure Determination of the σ-Alkenyl Platinum Complex $[N(PPh_3)_2][Pt\{CMe{=}C(H)CO_2Me\}(CO)Cl_2]$ †

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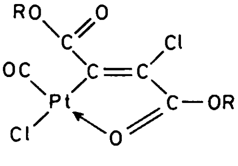
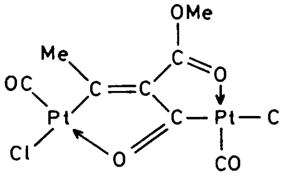
The polynuclear derivative $[\{Pt(CO)_2\}_n]$ reacts, in chloroform solution, with $H[Pt(CO)Cl_3]$ and $MeC{\equiv}CCO_2Me$ to give $[Cl(CO)Pt{-}CMe{=}C(COOMe){-}C({=}O){-}Pt(CO)Cl]$ (**2**) and $[Pt\{CMe{=}C(H)COOMe\}(CO)Cl]$ (**3**). Compound (**3**) reacts with PPh_3 to give $[Pt\{CMe{=}C(H)CO_2Me\}(PPh_3)_2Cl]$ (**7a**), while with chloride ions it is transformed into the anionic complex $[Pt\{CMe{=}C(H)CO_2Me\}(CO)Cl_2]^-$ (**4**). A multinuclear n.m.r. study on a series of derivatives is reported. The crystal and molecular structure of $[N(PPh_3)_2][Pt\{CMe{=}C(H)CO_2Me\}(CO)Cl_2]$ (**4a**) has been determined from three-dimensional *X*-ray data. The complex crystallizes in the monoclinic space group *Pc*, with two formula units in a unit cell of dimensions $a = 9.378(2)$, $b = 14.362(3)$, $c = 14.760(4)$ Å, and $\beta = 100.10(5)°$. The structure was determined by Patterson and Fourier methods and refined by least-squares methods to $R = 0.0268$ from 3 212 independent reflections with $I > 3\sigma(I)$. The platinum atom has the expected square-planar co-ordination; relevant bond lengths are Pt–C(sp^2) 2.016(7), Pt–C(sp) 1.836(9), Pt–Cl (*trans* to the alkene) 2.404(2), and Pt–Cl (*trans* to CO) 2.313(2), while the C=C bond distance is 1.32(1) Å. The plane of the olefinic moiety is rotated by 65.6(2)° with respect to the co-ordination plane of the metal atom giving a short intramolecular separation of 3.163(7) Å between Pt and the oxygen of the carboxylate carbonyl group.

We have reported that *cis*-$[Pt(CO)_2Cl_2]$ gives chlorometallation reactions with acetylenedicarboxylates, leading to the formation of $[Pt\{C(CO_2R)C{=}C(Cl)COOR\}(CO)Cl]$ (R = Me or Et) (**1**), showing a five-membered ring containing platinum.[2,3] On the other hand, phosphine hydride[4] and phosphine chlorohydride[5] platinum(II) complexes give, with disubstituted acetylenes, σ-alkenyl derivatives by hydrogen migration on the carbon of the alkyne triple bond.[4] Since neutral carbonyl hydride platinum(II) complexes are not known, the corresponding hydrometallation reaction has not been observed.



(**1**)



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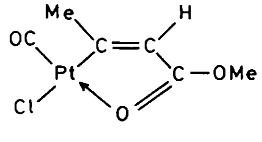

(**3**)

In a previous paper we described the preparation and the characterization of the cyclometallated species $[Cl(CO)Pt{-}CMe{=}C(COOMe){-}C({=}O){-}Pt(CO)Cl]$ (**2**).[1]

We now report the synthesis of $[Pt\{CMe{=}C(H)COOMe\}(CO)Cl]$ (**3**), obtained by treating *cis*-$[Pt(CO)_2Cl_2]$ with water and methyl but-2-ynoate under a carbon monoxide atmosphere, and the *X*-ray structural determination of the salt $[N(PPh_3)_2][Pt\{CMe{=}C(H)CO_2Me\}(CO)Cl_2]$ (**4a**).

Results and Discussion

In chloroform solution, at room temperature, *cis*-$[Pt(CO)_2Cl_2]$ reacts with water, under a carbon monoxide atmosphere, to give a dark precipitate of $[\{Pt(CO)_2\}_n]$ together with $H[Pt(CO)Cl_3]$ [reaction (1)].[6,7] We formulate platinum carbonyl as a neutral oligomer[6] even though, according to the literature,[7] it would be better described as the hydroxonium salt of the anion $[\{Pt_3(CO)_6\}_n]^{2-}$; however, this formulation would only

$$3[Pt(CO)_2Cl_2] + H_2O \longrightarrow \frac{1}{n}[\{Pt(CO)_2\}_n] + CO_2 + 2H[Pt(CO)Cl_3] + CO \quad (1)$$

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† Bis(triphenylphosphine)iminium carbonyldichloro[3-(methoxycarbonyl)prop-2-en-2-yl]platinate(II).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.

Non-S.I. unit employed: eV ≈ 1.60×10^{-19} J.

complicate the equations unnecessarily. In fact the cluster acts as a source of '$Pt(CO)_2$' units, therefore decreasing its nuclearity, but in the presence of $H[Pt(CO)Cl_3]$, which acts as an oxidizing agent, the starting cluster is regenerated, as soon as n decreases, in agreement with the formal stoicheiometry of equation (2). This is a common feature in the chemistry of platinum oligomers;[7] depending on the value of n, *e.g.* water displays an opposite effect on $[\{Pt_3(CO)_6\}_n]^{2-}$, reducing it when $n \geqslant 10$, oxidizing it when $n = 1$.[7]

$$(3n + 1)[\{Pt_3(CO)_6\}_{(n-1)}]^{2-} + 3[Pt(CO)Cl_3]^- + 3CO \longrightarrow (3n - 2)[\{Pt_3(CO)_6\}_n]^{2-} + 9Cl^- \quad (2)$$

In reaction (1) carbon monoxide is not required as a reagent, but it is necessary to prevent the reduction of $[Pt(CO)_2Cl_2]$ to platinum metal.

By addition of methyl but-2-ynoate to the products of reaction (1), $[\{Pt(CO)_2\}_n]$ and $H[Pt(CO)Cl_3]$ react according to equation (3) to yield the insoluble yellow compound (**2**) together with (**3**), as evidenced by i.r. spectroscopy, and the excess of $H[Pt(CO)Cl_3]$. From this solution, after extraction of the water-soluble $H[Pt(CO)Cl_3]$ with diluted aqueous HCl, $[Pt\{CMe{=}C(H)COOMe\}(CO)Cl]$ (**3**) was isolated by hexane addition. According to the overall stoicheiometry (4) compounds (**2**) and (**3**) were isolated in almost quantitative yield.

$$\frac{2}{n}[\{Pt(CO)_2\}_n] + H[Pt(CO)Cl_3] + 2MeC{\equiv}CCO_2Me \longrightarrow \underset{(\mathbf{3})}{[Pt\{CMe{=}C(H)COOMe\}(CO)Cl]} + \underset{(\mathbf{2})}{[Cl(CO)Pt{-}CMe{=}C(COOMe){-}C({=}O){-}Pt(CO)Cl]} + CO \quad (3)$$

$$6[Pt(CO)_2Cl_2] + 2H_2O + 2MeC{\equiv}CCO_2Me \longrightarrow \underset{(\mathbf{3})}{[Pt\{CMe{=}C(H)COOMe\}(CO)Cl]} + \underset{(\mathbf{2})}{[Cl(CO)Pt{-}CMe{=}C(COOMe){-}C({=}O){-}Pt(CO)Cl]} + 2CO_2 + 3H[Pt(CO)Cl_3] + 3CO \quad (4)$$

The i.r. spectrum of compound (**3**) shows stretchings due to a terminal carbonyl group and to an ester carbonyl group co-ordinated to platinum, whereas the ^1H n.m.r. spectrum (see Table 1) indicates the presence of a vinyl hydrogen. These data, together with the elemental analysis, mass spectrum, and other n.m.r. spectra (see the Experimental section and Table 1), suggest for compound (**3**) the structure displayed. This structure is also supported by the following observations: (*i*) *cis*-$[Pt(CO)_2Cl_2]$ reacts with acetylenedicarboxylates to give chlorometallation reactions, leading to an analogous metallacyclic derivative, where the four-co-ordination at the platinum atom is obtained through the intramolecular co-ordination of the alkoxycarbonyl group [compound (**1**)];[2] (*ii*) a similar five-membered-ring structure was established in compound (**2**).[1] In agreement with the proposed structure, the ^{13}C n.m.r. spectrum of (**3**) (see Table 1) showed the expected six signals. Discussion of the n.m.r. spectroscopic data is best deferred until the *X*-ray diffraction results have been presented.

Treatment of a solution of compound (**3**) with $[N(PPh_3)_2]Cl$ gives the white derivative $[N(PPh_3)_2][Pt\{CMe{=}C(H)CO_2Me\}(CO)Cl_2]$ (**4a**) identified by elemental analysis, i.r., ^1H, and ^{13}C n.m.r. spectroscopy (see Table 1), and *X*-ray analysis. The i.r. spectrum in the CO terminal region is similar to that of compound (**3**), but shows a new band at 1 700m cm^{-1}, in the CO ester region, with no band at 1 580 cm^{-1}; this indicates that the chelation of the carboxylate carbonyl is no longer present. The reactivity of compound (**3**) towards chloride ions is similar to that of compound (**1**),[2,3] where chloride ion replaces the oxygen of the carbonyl carboxylate group in the co-ordination sphere of platinum. The ^1H n.m.r. spectrum of (**4a**) is similar to that of (**3**) but with the signals of the methoxy group shifted to higher field. The formation of the anionic species from the neutral derivative (**3**) is evidenced in the ^{13}C n.m.r. spectrum, where the signal due to carbon C(2) is shifted to high field. The coupling constant J[Pt–C(4)] changes considerably from compound (**3**) to $[NBu^n_4][Pt\{CMe{=}C(H)CO_2Me\}(CO)Cl_2]$ (**4b**), confirming the different co-ordination around Pt (see the ^{13}C n.m.r. discussion).

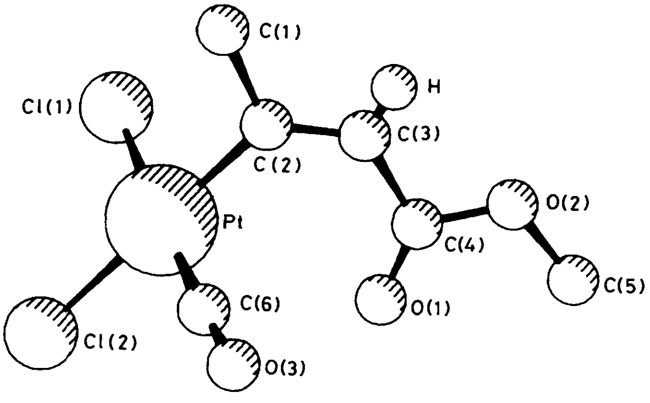


Figure 1. The molecular structure of the anion $[Pt\{CMe{=}C(H)CO_2Me\}(CO)Cl_2]^-$ showing the atom-numbering scheme

In order to establish the overall molecular structure of complex (**4a**), a single-crystal *X*-ray analysis was undertaken.

Molecular Structure of $[N(PPh_3)_2][Pt\{CMe{=}C(H)CO_2Me\}(CO)Cl_2]$ (**4a**).—A perspective view of the anion with the numbering scheme is given in Figure 1, relevant bond lengths and angles in Table 2.

The platinum(II) atom presents the expected square-planar co-ordination with Cl(1) *trans* to a terminal CO group and Cl(2) *trans* to the σ-alkenyl atom C(2). The olefinic moiety is planar to within ±0.016 Å [least-squares plane through atoms C(1), C(2), C(3), C(4), and Pt] and is rotated with respect to the platinum co-ordination plane by 65.6(2)°, while in other related compounds[8] this angle is very close to 90°.

The Pt–C(2) bond length, 2.016(7) Å, is typical for a Pt–C(sp^2) single bond[9] and may be compared with the separation of 1.97(2) Å found in the closely related anion[3] $[Pt\{C(CO_2Et){=}C(Cl)CO_2Pr^i\}(CO)Cl_2]^-$ (**5**) or of 2.022(8) Å in *trans*-$[PtBr($*trans*-$CH{=}CHPh)(PPh_3)_2]$.[8c] The two Pt–Cl distances are significantly different [Pt–Cl(2) 2.404(2) and Pt–Cl(1) 2.313(2) Å] and are consistent with a larger *trans* influence of the σ-alkenyl ligand compared to carbon monoxide.[3,9,10] The C(2)–C(3) bond length, 1.32(1) Å, is as usual for a double bond and indicates no back bonding from the metal atom. This is in keeping with the single-bond character of Pt–C(2) and with the rotation of the olefinic fragment with respect to the platinum co-ordination plane.

Only small deviations from ideality are present in the bond angles around Pt (see Table 2). On the other hand, the organic ligand shows large angular deformations from the ideal value of 120°, in particular Pt–C(2)–C(3) 126.7(6), C(2)–C(3)–C(4)

Table 1. Multinuclear n.m.r. data[a]

Compound	C^1	C^2	C^3	C^4	C^5	C^6	Pt	H	CH_3	OCH_3
(3)	32.3 ^2J(Pt–C) 122 ^1J(H–C) 128 ^3J(H–C) 5	182.9 ^1J(Pt–C) 786 ^2J(H–C) 8	122.5 ^2J(Pt–C) 28 ^1J(H–C) 170 ^3J(H–C) 7	191.3 ^2J(Pt–C) 91 ^3J(H–C)[d]	56.1 ^1J(H–C) 150	154.7 ^1J(Pt–C) 2 231	−3 762	6.31 ^3J(Pt–H) 73 ^4J(H–H) 1.5	2.5 ^3J(Pt–H) 63 ^4J(H–H) 1.5	4.06
(4a)							−3 582	6.36 ^3J(Pt–H) 100 ^4J(H–H) 1.4	2.42 ^3J(Pt–H) 39 ^4J(H–H) 1.4	3.67
(4b)	32.9 ^2J(Pt–C) 39	158.3 ^1J(Pt–C) 826	120.9 ^2J(Pt–C) 30	168.7 ^3J(Pt–C) 35	53.6	158.4 ^1J(Pt–C) 2 065				
(7a)[b]							−4 271 ^1J(P–Pt) 3 213	6.37 ^3J(Pt–H) 110 ^4J(H–H) 1	1.57 ^3J(Pt–H) 46 ^4J(H–H) 1	3.43
(7b)[c]	34.9 ^2J(Pt–C) 70	168.5 ^1J(Pt–C) 952 ^2J(P–C) 9.0	120.4 ^2J(Pt–C) 33 ^3J(P–C)[d]	169.2 ^3J(Pt–C) 39	50.3		−4 168 ^1J(P–Pt) 2 822			

[a] δ Values in p.p.m. from the standard; coupling constants in Hz; $CDCl_3$ solution. [b] ^{31}P N.m.r.: δ = 22.3 p.p.m., ^1J(Pt–P) = 3 213 Hz. [c] ^{31}P N.m.r.: δ = 5.6 p.p.m., ^1J(Pt–P) = 2 822 Hz. [d] Small coupling revealed by a broadening of the signal.

Table 2. Selected interatomic distances (Å) and angles (°) with estimated standard deviations (e.s.d.s) in parentheses for $[N(PPh_3)_2][Pt\{CMe{=}C(H)CO_2Me\}(CO)Cl_2]$ **(4a)**

Pt–Cl(1)	2.313(2)	O(2)–C(5)	1.45(1)
Pt–Cl(2)	2.404(2)	O(3)–C(6)	1.13(1)
Pt–C(2)	2.016(7)	C(1)–C(2)	1.52(1)
Pt–C(6)	1.836(9)	C(2)–C(3)	1.32(1)
P(1)–N	1.574(6)	C(3)–H	0.81(7)
P(2)–N	1.581(7)	C(3)–C(4)	1.51(1)
O(1)–C(4)	1.19(1)	P–C (av.)	1.804 ± 0.008
O(2)–C(4)	1.32(1)	C–C (av.)	1.385 ± 0.016
C(2)–Pt–C(6)	87.9(4)	Pt–C(2)–C(3)	126.7(6)
Cl(2)–Pt–C(2)	178.9(2)	C(2)–C(3)–C(4)	125.9(8)
Cl(2)–Pt–C(6)	92.3(3)	C(2)–C(3)–H	111(4)
Cl(1)–Pt–C(2)	89.4(3)	H–C(3)–C(4)	123(4)
Cl(1)–Pt–C(6)	117.3(3)	O(2)–C(4)–C(3)	108.8(7)
Cl(1)–Pt–Cl(2)	90.4(1)	O(1)–C(4)–C(3)	126.9(8)
P(1)–N–P(2)	139.6(4)	O(1)–C(4)–O(2)	124.3(9)
C(4)–O(2)–C(5)	116.4(7)	N–P–C (av.)	111 ± 3.2
Pt–C(6)–O(3)	177.9(9)	C–P–C (av.)	107.5 ± 1.2
Pt–C(2)–C(1)	113.6(5)	P–C–C (av.)	120 ± 1
C(1)–C(2)–C(3)	119.6(7)	C–C–C (av.)	120 ± 1

125.9(8), and C(3)–C(4)–O(1) 126.9(8)°. Furthermore, the carboxylate carbonyl group is slightly but significantly twisted with respect to the plane of the C=C bond, as shown by the torsion angles C(2)–C(3)–C(4)–O(1) −8.6(1.5)° and C(2)–C(3)–C(4)–O(2) 173.9(8)° or by the dihedral angle of 8.9(2)°, formed by the least-squares plane through atoms C(3), C(4), O(1), O(2) and the olefinic plane previously defined: strict coplanarity would be expected for an optimum conjugation. These distortions may relieve some steric interferences involving atom O(1) as indicated by the short intramolecular contacts O(1) ••• C(6) 2.87(1) Å and O(1) ••• Pt 3.163(7) Å. The former is much shorter than the sum of van der Waals radii (≈3.2 Å), while the latter is only somewhat less than expected (3.2—3.3 Å, using a radius of 1.7—1.8 Å for Pt as suggested by Bondi[11]), although larger separations are usually reported (about 3.4—3.5 Å).[3,12] This fact may indicate some favourable interaction between atoms O(1) and Pt, perhaps reminiscent of the chelation present in compound **(3)**.

The P–N and P–C distances [average 1.578(7) and 1.804(8) Å, respectively] as well as P–N–P 139.6(4)° (see Table 2) in the cation are similar to the values found in previous work.[3,10,13]

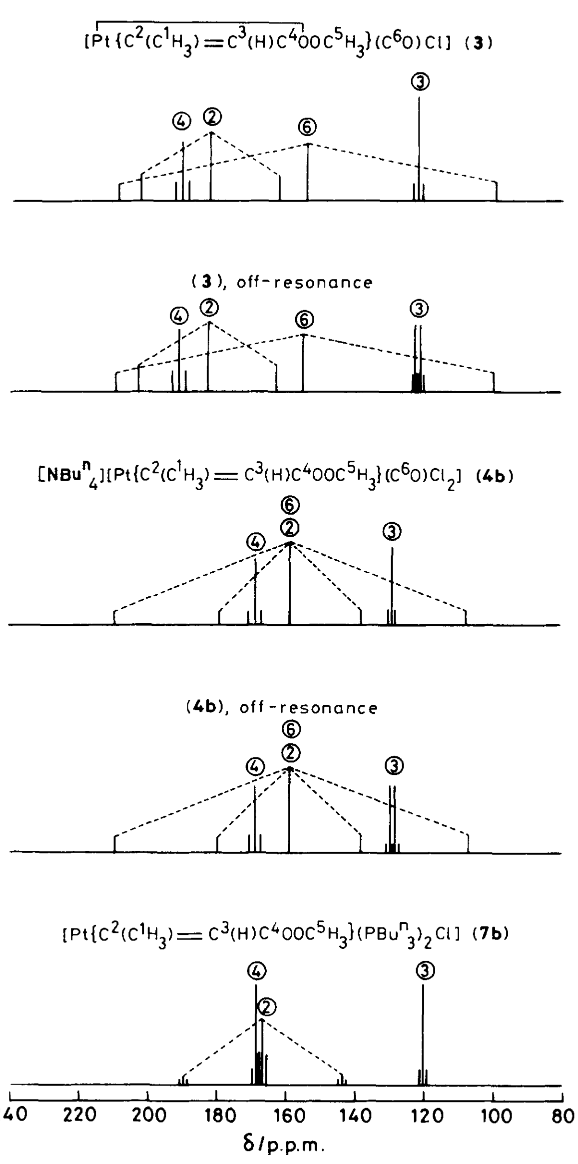
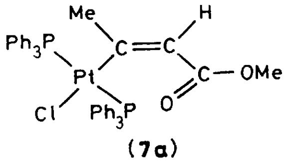


Figure 2. Schematic ^{13}C n.m.r. spectra in the region 80—240 p.p.m.



(7a)

The conformation of the phenyl rings is analogous to that found in refs. 3 and 13.

Chemical Characterization and ^{13}C *N.M.R. Studies*.—The *X*-ray structure of compound (**4a**) supports the structure proposed for compound (**3**). The former contains the same features found in the anionic derivative (**5**) but unexpectedly, their reactivities are quite different.[2,3] Thus we do not observe either specific alcoholysis[3] or the formation of the cyclic derivative $[Pt\{CMe=C(H)COO\}(CO)Cl]^-$ (**6**)[10] obtained by formal elimination of methyl chloride.

The neutral complex (**3**) reacts, in dichloromethane solution, with triphenylphosphine, in a 1:2 ratio, leading to the white derivative $[Pt\{CMe=C(H)CO_2Me\}(PPh_3)_2Cl]$ (**7a**). The i.r. spectrum shows the absence of terminal CO stretching and a strong band at 1 690 cm^{-1}, again arising from the ester group not co-ordinated to the metal. In keeping with the reactivity of compound (**1**), it is possible to propose for compound (**7a**) the structure shown. The ^{1}H n.m.r. spectrum is consistent with this structure and the ^{13}C, ^{31}P, and ^{195}Pt n.m.r. spectra confirm the presence of two phosphine ligands in *trans* position.

Table 1 summarizes the chemical shifts and the coupling constants of the complexes studied. The ^{13}C n.m.r. spectra were measured with different spectrometers operating at different fields, to overcome the difficulties due to accidental overlap of the signals with ^{195}Pt satellites. We chose a particular cation or ligand, with the two-fold purpose of increasing the solubility and of keeping clear the region between 80 and 240 p.p.m. in order to detect all the signals of significant carbon atoms which, in our case, are the atoms coupled to phosphorus and/or platinum, allowing an unambiguous structural characterization. When the isolation of a specific compound as a solid material was not possible, the n.m.r. data were measured on a sample obtained *in situ* by treating complex (**3**) with the stoicheiometric amount of ligand to give $[NBu^n_4][Pt\{CMe=C(H)CO_2Me\}(CO)Cl_2]$ (**4b**) and $[Pt\{CMe=C(H)CO_2Me\}(PBu^n_3)_2Cl]$ (**7b**).

Figure 2 gives a schematic view of all the ^{13}C-{^{1}H} n.m.r. spectra, in the range 80—240 p.p.m., for selected derivatives together with the numbering scheme. For clarity, the signals obtained with different spectrometers are scaled to a spectrometer operating at 20.14 MHz for carbon (80 MHz for proton). In order to assign the resonances to the different carbon atoms, we considered both the coupling constants and the chemical shifts, keeping in mind the values found for a series of similar compounds.[14,15] The assignment of the resonances of carbon atoms for compound (**4b**) was straightforward because the solid-state structure for this type of derivative was known. Carbon C(3) was assigned through off-resonance ^{13}C n.m.r. spectra, whereas the C(6) signal was attributed through labelling experiments. Carbon C(2) showed a large coupling constant with platinum, typical of a σ bond. [A further splitting to a triplet is present for (**7b**) because of the coupling with two phosphorus atoms in *trans* position.]

The most significant result obtained from ^{13}C n.m.r. spectra is the confirmation of the existence in complex (**3**) of the intramolecular interaction between platinum and the oxygen bonded to carbon C(4). The J[Pt–C(4)] value (91 Hz) is consistent with a two-bond interaction *via* the co-ordinated oxygen atom, while a value around 30 Hz for (**4b**) and (**7b**) is in agreement with a three-bond interaction *via* the carbon skeleton.

Reaction of $[Pt(CO)_2Cl_2]$ *with* $MeC\equiv CCO_2Me$ *in Anhydrous Solvents*.—The reaction between $[Pt(CO)_2Cl_2]$ and $MeC\equiv CCO_2Me$ in anhydrous solvents was studied in order to determine whether it is possible to obtain $[Pt\{CMe=C(Cl)COOMe\}(CO)Cl]$ (**8**), the same type of compound as isolated by treating $[Pt(CO)_2Cl_2]$ with acetylenedicarboxylates.[2,3] Despite several attempts only traces of (**8**) were obtained.

In anhydrous solvents such as toluene or chloroform the reaction leads to a violet solution and a black precipitate (**A**), which is completely insoluble in common organic solvents. Elemental analysis of this compound shows a variable platinum : acetylene ratio usually greater than one, suggesting a molar ratio of 2:1, and the same empirical formula as found for (**2**). The i.r. spectrum showed large and broad bands in the terminal carbonyl as well as in the carbonyl ester region, suggesting the presence of several non-equivalent groups. By adding hexane to the violet solution we obtained a dark violet compound (**B**). Several elemental analyses are consistent with the formulation $[\{Pt(CO)(MeC\equiv CCO_2Me)_2Cl_2\}_n]$, while molecular weight determinations suggest a value of n in the range 4—5. The ^{1}H n.m.r. spectrum exhibits unresolved signals around δ 2.4 (CH_3) and 3.8 p.p.m. (CO_2CH_3), in agreement with the presence of non-equivalent methyl and methoxy groups. The molecular weight in solution suggests an oligomeric system, but we cannot rule out a mixture of different organometallic complexes. The solution, from which compounds (**A**) and (**B**) had been isolated, was concentrated to dryness and with several treatments with hexane we obtained a mixture containing (**3**) (probably due to residual humidity present in the starting material) and only traces of (**8**). This compound was identified through n.m.r. and mass spectra. Compound (**B**) reacts with an excess of $MeC\equiv CCO_2Me$ to give a pale yellow compound which analyses as $[Pt(CO)(MeC\equiv CCO_2Me)_6Cl_2]$ (**C**).

To explain the formation of these oligomeric species we suggest the insertion of the activated acetylene molecule into a Pt–Cl bond, with a four-centre mechanism,[5] according to the polarity of the Pt–Cl bond and that of the asymmetric alkyne triple bond, to give a three-co-ordinate derivative with the electron-withdrawing group in α position on the alkenyl fragment, $[Pt\{C(CO_2Me)=C(Cl)Me\}(CO)Cl]$. In this structure there is no possibility of intramolecular co-ordination of the carboxylate carbonyl oxygen to platinum giving a stable four-co-ordinate complex and therefore the co-ordinatively unsaturated complex can react further with $MeC\equiv CCO_2Me$, in agreement with the formation of oligomers as the main reaction products.

Conclusions

The compound $[Pt(CO)_2Cl_2]$ reacts with carbon monoxide and water to give the not well characterized platinum oligomer $[\{Pt(CO)_2\}_n]$ and $H[Pt(CO)Cl_3]$;[6,7] $[\{Pt(CO)_2\}_n]$ and $[Pt(CO)_2Cl_2]$ react with $MeC\equiv CCO_2Me$ giving compound (**2**) quantitatively.[1] On the other hand, in the absence of $[Pt(CO)_2Cl_2]$, but in the presence of $H[Pt(CO)Cl_3]$, $[\{Pt(CO)_2\}_n]$ reacts, according to equation (3), to give compound (**3**) together with (**2**). The $[\{Pt(CO)_2\}_n]$ cluster reacts with nucleophiles such as I^- and PPh_3, leading to complicated mixtures, from which it is possible to isolate monomeric species such as $[Pt(CO)I_3]^-$ or $[Pt(CO)_2(PPh_3)_2]$:[7] therefore this compound can act as a source of the unsaturated '$Pt(CO)_2$' species.

Zerovalent platinum phosphine compounds react with disubstituted acetylenes to give stable π adducts,[16] which can undergo oxidative addition of HCl; also, phosphineplatinum chloro hydrides[5] undergo insertion of acetylene into the Pt–Cl bond. In both cases σ-alkenyl diphosphine chloro derivatives are obtained. For the formation of (**3**), we think that the vinylic hydrogen atom on the carbon atom originates by hydrogen migration from a platinum hydride complex of the type $[PtH(CO)Cl(MeC{\equiv}CCO_2Me)]$. This latter species could arise from the anion $[PtH(CO)Cl_2]^-$.[17] We have verified the presence of traces of $[PtH(CO)Cl_2]^-$, before adding methyl tetrolate (methyl but-2-ynoate) to the products of reaction (1), by the hydride peak in the n.m.r. spectrum [δ −15, ^1J(Pt–H) = 1 275 Hz]. We have also treated a suspension of $[\{Pt(CO)_2\}_n]$, free from $H[Pt(CO)Cl_3]$, with HCl and $MeC{\equiv}CCO_2Me$ and the reaction product does not contain compound (**3**). In agreement with reaction (3) to obtain compound (**3**), $[\{Pt(CO)_2\}_n]$ must react with $MeC{\equiv}CCO_2Me$ in the presence of $H[Pt(CO)Cl_3]$.

We have further verified that anionic polynuclear platinum compounds, such as $Na_2[\{Pt_3(CO)_6\}_n]$ (*n* = 10), do not react with $MeC{\equiv}CCO_2Me$, in the presence of HCl or $H[Pt(CO)Cl_3]$, to give (**3**), whereas other unidentified products are obtained; also $H[Pt(CO)Cl_3]$ does not react with $MeC{\equiv}CCO_2Me$, in presence of CO and water, to give (**3**). The binuclear compound (**2**), which contains as a part of the whole molecule complex (**3**), does not loose the $Pt(CO)_2Cl$ fragment upon reaction with HCl and water, but is degraded to several unidentified products among which it is possible to identify, by ^1H n.m.r. spectroscopy only traces of (**3**). This observation excludes (**2**) as the intermediate in the formation of (**3**). Finally, the nature of the solvent does not play an important role: we have carried out the reaction in toluene and water and obtained compound (**3**) in similar yields.

In hydrogen-transfer reactions specific formation of *cis* and/or *trans* isomers occurs depending on the acetylene, reaction conditions, solvent, and reaction temperature.[5] In our case we note the specific formation of the *trans* isomer, the formation of the five-membered ring being the 'driving force' for this reaction. On the basis of kinetic studies, several suggestions have been made to account for the formation of the *trans* isomer.[4] Our system is too complicated for kinetic studies and, therefore, it is impossible to obtain data which support an unambiguous mechanism. Otherwise, a four-centre mechanism, followed by isomerization,[18] is consistent with our results.

We note that $[Pt(CO)_2Cl_2]$ does not react with $MeC{\equiv}CCO_2Me$ in non-polar solvents such as toluene to give a compound of type (**2**), but gives oligomeric species in agreement with the polarity of the reagents. On the other hand, $[\{Pt(CO)_2\}_n]$ and $MeC{\equiv}CCO_2Me$ give quantitatively compound (**3**) in the presence of $H[Pt(CO)Cl_3]$, and this suggests that the Pt–H bond of the intermediate $[PtH(CO)(MeC{\equiv}CCO_2Me)Cl]$ has a polarization opposite to that of the Pt–Cl bond. This mechanism requires a subsequent isomerization of the alkenyl ligand and this is possible, in this case, because of the presence of a co-ordinatively unsaturated platinum atom.[18]

Experimental

Microanalyses and molecular weights were determined by Laboratorio Analisi Universita' di Milano and by Pascher Mikroanalytisches Laboratorium Bonn. Proton and $^{13}C-\{^1H\}$ n.m.r. spectra were recorded on a Bruker WP 80 spectrometer operating at 80 and 20.14 MHz respectively or on a Varian XL-200 spectrometer operating at 200 and 50.3 MHz respectively and are reported in p.p.m. downfield from the internal standard $SiMe_4$; ^{31}P n.m.r. spectra were recorded on a Bruker WP 80 spectrometer, operating at 32.4 MHz, and are reported downfield of the external standard (85% H_3PO_4 in D_2O); ^{195}Pt n.m.r. spectra were recorded on a Bruker WP 80 spectrometer, operating at 17.2 MHz (Na_2PtCl_6 external standard; pulse angle 60°, delay 0.5 s). For the ^{31}P and ^{195}Pt n.m.r. spectra the acquisition times were 0.4 and 0.5 s, respectively. Infrared spectra were recorded on a Perkin-Elmer 781 grating spectrophotometer calibrated with polystyrene film, or a Nicolet MX-1 FT-IR Fourier-transform interferometer using Nujol mull and NaCl or CsI plates. Electron-impact mass spectra were obtained on a Varian MAT 112 mass spectrometer, calibrated against known masses of perfluorokerosene, with a source voltage of 70 eV and probe temperature in the range 100—200 °C. Fast atom bombardment (f.a.b.) mass spectra were recorded on a V.G. 7070 EQ mass spectrometer equipped with an H.F. magnet and standard f.a.b. source with xenon gas at 8 keV (sulpholane and glycerine mull).

All the reactions were conducted under a carbon monoxide or nitrogen atmosphere using the Schlenk-tube technique and with anhydrous solvents. Solvents were purified and dried by standard methods. Chloroform (1% EtOH) was thoroughly deoxygenated before use by repeated evacuation followed by admission of nitrogen. Methyl but-2-ynoate was used as received from Fluka without further purification. The compound *cis*-$[Pt(CO)_2Cl_2]$ was prepared as described previously.[19]

Preparations.—$[Pt\{CMe{=}C(H)COOMe\}(CO)Cl]$ (**3**). The compound $[Pt(CO)_2Cl_2]$ (5.00 g, 15.52 mmol) was dissolved in $CHCl_3$ (200 cm^3) under a carbon monoxide atmosphere and water (0.4 cm^3, 22.2 mmol) was added under magnetic stirring for 2 h. When the i.r. spectrum of the solution did not reveal the bands of $[Pt(CO)_2Cl_2]$ (2 180vs and 2 140vs cm^{-1}), $MeC{\equiv}CCO_2Me$ (2.5 cm^3, 25.5 mmol) was added and the suspension stirred for 20 h. A yellow precipitate was formed, filtered off, dried, and identified as compound (**2**) (1.1 g, 23% on platinum). The solution was concentrated to half volume and further

Table 3. Crystal data and intensity collection parameters for $[N(PPh_3)_2][Pt\{CMe{=}C(H)CO_2Me\}(CO)Cl_2]$ (**4a**)

M	931.70
Crystal system	Monoclinic
Space group	*Pc*
a/Å	9.378(2)
b/Å	14.362(3)
c/Å	14.760(4)
β/°	100.10(5)
U/Å^3	1 957.2
Z	2
F(000)	924
D_c/g cm^{-3}	1.581
Radiation	Mo-K_α (graphite monochromated, λ = 0.710 69 Å)
μ/cm^{-1}	38.8
θ Range/°	$2.5 \leqslant \theta \leqslant 25$
Scan type	θ—2θ
Scan speed/° s^{-1}	0.03
Scan width/°	1.10
Total background time/s	20
Receiving aperture/°	
horizontal	1.0
vertical	1.0
No. of data collected	3 441 ($\pm h, +k, +l$)
No. of data 'observed' [$I_{net} > 3\sigma(I)$]	3 212
R^a	0.0268
R'^b	0.0283
Goodness of fit, S^c	1.20

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R' = \Sigma w||F_o| - |F_c||/\Sigma w|F_o|$. [c] $S = [\Sigma w(|F_o| - |F_c|)^2/(n - m)]^{\frac{1}{2}}$, where *n* is the number of observations and *m* the number of refined parameters.

Table 4. Positional parameters with e.s.d.s in parentheses for $[N(PPh_3)_2][Pt\{CMe{=}C(H)CO_2Me\}(CO)Cl_2]$ (**4a**)

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Pt	0.000 00	−0.142 97(2)	0.000 00	C(121)	0.772 3(9)	−0.174 2(6)	0.411 5(6)
Cl(1)	0.189 9(2)	−0.195 3(2)	0.109 8(2)	C(131)	0.560 3(8)	−0.236 2(5)	0.556 5(5)
Cl(2)	0.007 6(3)	−0.284 2(2)	−0.086 5(2)	C(141)	0.685 2(9)	−0.286 0(6)	0.591 8(6)
P(1)	0.498 8(2)	−0.234 5(1)	0.433 7(1)	C(151)	0.730 5(11)	−0.292 4(7)	0.687 0(7)
P(2)	0.317 1(2)	−0.403 8(1)	0.427 8(1)	C(161)	0.648 3(10)	−0.250 8(7)	0.745 6(7)
N	0.402 9(7)	−0.319 9(4)	0.393 4(4)	C(171)	0.524 2(10)	−0.202 4(6)	0.710 6(7)
O(1)	−0.297 2(7)	−0.117 4(5)	0.070 4(5)	C(181)	0.479 2(9)	−0.193 9(6)	0.615 2(6)
O(2)	−0.326 6(7)	−0.011 4(4)	0.174 5(4)	C(12)	0.163 1(7)	−0.426 9(5)	0.339 1(5)
O(3)	−0.245 8(9)	−0.066 8(6)	−0.132 8(5)	C(22)	0.165 1(8)	−0.394 5(6)	0.249 7(5)
C(1)	0.126 4(9)	0.034 0(6)	0.081 8(6)	C(32)	0.048 8(9)	−0.415 3(6)	0.180 4(6)
C(2)	−0.008 6(8)	−0.025 9(5)	0.074 2(5)	C(42)	−0.064 2(10)	−0.468 7(6)	0.199 1(7)
C(3)	−0.113 9(9)	−0.000 5(6)	0.117 3(5)	C(52)	−0.066 4(10)	−0.499 2(7)	0.286 5(6)
C(4)	−0.254 2(10)	−0.052 4(6)	0.116 7(6)	C(62)	0.046 5(9)	−0.479 4(6)	0.358 2(6)
C(5)	−0.463 7(10)	−0.053 6(8)	0.184 5(7)	C(72)	0.425 9(8)	−0.507 5(5)	0.446 8(5)
C(6)	−0.151 4(11)	−0.096 6(6)	−0.083 6(6)	C(82)	0.573 8(9)	−0.504 6(6)	0.438 7(6)
C(11)	0.403 2(7)	−0.125 9(5)	0.406 1(5)	C(92)	0.658 4(10)	−0.582 6(6)	0.458 0(6)
C(21)	0.464 7(9)	−0.043 6(5)	0.443 5(6)	C(102)	0.599 2(12)	−0.664 2(7)	0.484 9(7)
C(31)	0.394 8(10)	0.040 2(6)	0.420 7(6)	C(112)	0.456 5(9)	−0.668 3(7)	0.491 4(7)
C(41)	0.261 1(9)	0.041 7(6)	0.359 6(6)	C(122)	0.369 5(9)	−0.590 4(6)	0.471 5(6)
C(51)	0.206 3(9)	−0.040 7(6)	0.321 3(6)	C(132)	0.253 2(8)	−0.380 6(5)	0.534 8(5)
C(61)	0.273 7(8)	−0.124 0(5)	0.344 5(5)	C(142)	0.328 6(9)	−0.412 5(6)	0.617 3(6)
C(71)	0.654 8(7)	−0.229 8(5)	0.378 8(5)	C(152)	0.287 1(12)	−0.384 5(8)	0.697 8(8)
C(81)	0.650 2(9)	−0.277 1(6)	0.295 4(6)	C(162)	0.166 5(12)	−0.326 9(8)	0.695 6(8)
C(91)	0.766 6(10)	−0.266 7(7)	0.247 3(6)	C(172)	0.093 6(12)	−0.296 8(8)	0.614 6(7)
C(101)	0.881 8(10)	−0.211 7(7)	0.281 2(6)	C(182)	0.132 5(9)	−0.322 2(6)	0.531 0(6)
C(111)	0.885 0(11)	−0.165 9(7)	0.363 6(7)	H	−0.094 1(60)	0.047 6(51)	0.145 7(50)

compound (**2**) (0.3 g, 6.4% based on platinum) was isolated. The solution was concentrated to dryness and washed with hexane (2×30 cm^3) and $H[Pt(CO)Cl_3]$ was extracted with 2 mol dm^{-3} HCl (2×30 cm^3). The residue was dissolved in chloroform (20 cm^3) and the solution, dried over $MgSO_4$, upon hexane addition gave compound (**3**) (0.90 g, 16% based on initial platinum; calculated yield for a quantitative reaction 16.6%). I.r. (Nujol mull): 2 100s, 1 580m, and 1 560m cm^{-1} [Found: C, 19.5; H, 2.0; Cl, 10.0; O, 13.3; Pt, 54.3; M^+ (mass spectrum) 357. $C_6H_7ClO_3Pt$ requires C, 20.1; H, 1.3; Cl, 9.9; O, 13.4; Pt, 54.5%; *M*, 357 (^{195}Pt, ^{35}Cl)].

In toluene. A toluene (150 cm^3) solution of $[Pt(CO)_2Cl_2]$ (1.6 g, 5.0 mmol) was treated with water (1 cm^3, 50 mmol) and $MeC{\equiv}CCO_2Me$ (1.6 cm^3, 16 mmol) and left for 48 h under magnetic stirring. A dark unidentified precipitate was formed, filtered off, and the solution left over $MgSO_4$ for 48 h. Upon addition of hexane the yellow-orange compound (**3**) (0.180 g, 10.1%) was obtained.

$[N(PPh_3)_2][Pt\{CMe{=}C(H)CO_2Me\}(CO)Cl_2]$ (**4a**). To a stirred solution of $[N(PPh_3)_2]Cl$ (0.34 g, 0.59 mmol) in 2-propanol (10 cm^3) was added compound (**3**) (0.195 g, 0.55 mmol). The white precipitate was filtered off, washed, and crystallized from methanol–2-propanol (Found: C, 57.6; H, 4.2; N, 1.6. $C_{42}H_{37}O_3P_2Pt$ requires C, 58.2; H, 4.3; N, 1.6%). I.r. (Nujol mull): 2 060vs cm^{-1} [ν(CO)] and 1 700s cm^{-1} [ν(CO,CO_2Me)].

$[NBu^n{}_4][Pt\{CMe{=}C(H)CO_2Me\}(CO)Cl_2]$ (**4b**). A $CDCl_3$ (2 cm^3) solution of compound (**4b**) was obtained by treating pure compound (**3**) (0.367, 1.02 mmol) with $[NBu^n{}_4]Cl$ (0.305 g, 1.1 mmol).

$[Pt\{CMe{=}C(H)CO_2Me\}(PPh_3)_2Cl]$ (**7a**). To a stirred solution of compound (**3**) (0.195 g, 0.54 mmol) in $CHCl_3$ (10 cm^3) was added a sample of PPh_3 (0.314 g, 1.2 mmol) dissolved in $CHCl_3$ (5 cm^3). A white precipitate of (**7a**) was obtained by adding hexane, filtered off, and dried (yield 0.35 g, 80%) (Found: C, 56.1; H, 4.2. $C_{41}H_{37}ClO_2P_2Pt$ requires C, 57.6; H, 4.5%). I.r. (Nujol mull): 1 690s [ν(CO,CO_2Me)], 1 575m (C=C), and 289w cm^{-1} [ν(Pt–Cl)].

$[Pt\{CMe{=}C(H)CO_2Me\}(PBu^n{}_3)_2Cl]$ (**7b**). A $CDCl_3$ (2 cm^3) solution of compound (**7b**) was obtained by treating pure compound (**3**) (0.40 g, 1.11 mmol) with PBu_3 (0.50 g, 2.47 mmol).

Reaction of $[Pt(CO)_2Cl_2]$ *with* $MeC{\equiv}CCO_2Me$ *in Anhydrous Toluene*.—To a solution of $[Pt(CO)_2Cl_2]$ (5.47 g, 17.0 mmol) in toluene (80 cm^3) under nitrogen was added $MeC{\equiv}CCO_2Me$ (5.2 cm^3, 53.0 mmol) and the solution stirred at 80 °C. After 6 h all the $[Pt(CO)_2Cl_2]$ had reacted and a suspension was obtained. After cooling the dark precipitate was filtered off, washed with hexane (3×10 cm^3), and dried [compound (**A**)]. The violet solution was concentrated and treated with hexane to give the dark violet compound (**B**), $[\{Pt(CO)(MeC{\equiv}CCO_2Me)_2Cl_2\}_n]$ (3.2 g, 38.5%). The mother-liquor was concentrated to dryness and treated with hexane (5×30 cm^3) to obtain a dark yellow solid. Crystallization from toluene yielded a mixture (0.6 g) containing compounds (**3**) (70%) and (**8**) (30%), according to elemental analysis and integration of the signals in the ^{1}H n.m.r. spectra. Compound (**A**) (Found: C, 13.0; H, 0.8. $C_7H_6Cl_2O_4Pt_2$ requires C, 13.6; H, 1.0%). I.r. (Nujol mull): 2 100m,br [ν(CO)] and 1 730m,br cm^{-1} [ν(CO, CO_2Me)]. Compound (**B**) [Found: C, 27.6; H, 2.25; *M* (osmometric molecular weight in $CHCl_3$) 2 240. $C_{11}H_{12}Cl_2O_5Pt$ requires C, 26.9; H, 2.5%; *M*, 490)]. I.r. (Nujol mull): 2 120m,br [ν(CO)] and 1 740m,br cm^{-1} [ν(CO,CO_2Me)]. Compound (**8**): M^+, 391 (^{195}Pt, ^{35}Cl); ^{1}H n.m.r. ($CDCl_3$) δ 4.2 (OCH_3) and δ 2.54 (CH_3) [^3J(Pt–H) = 62 Hz].

Crystallography.—Prismatic, colourless crystals of compound (**4a**) suitable for *X*-ray diffraction were obtained by slow diffusion of hexane (40 cm^3) into a dichloromethane solution (20 cm^3) containing (**4a**) (0.4 g). A single crystal, of dimensions *ca*. $0.3 \times 0.2 \times 0.1$ mm, was mounted on a glass fibre on a Philips PW 1100 automated diffractometer and used for the analysis at room temperature. Cell constants were obtained by a least-squares fit of 32 accurately centred reflections having $22 \leqslant 2\theta \leqslant 46°$. From the systematic absences the space group could be *P*2/*c* or *Pc*. The latter was chosen because of the calculated density and from inspection of the Patterson map. Three standard reflections (1 3 −4, −1 −3 4, 1 −3 −4) were monitored every 2 h to check the stability of the crystal and the experimental set-up: no significant variation was detected. Cell constants and data collection conditions are in Table 3. Data were corrected for Lorentz and polarization factors and for absorption using azimuthal ψ scans of reflections 4 −3 −1, 7 −6 −2, and 7 −6 −1. The structure was solved by Patterson and Fourier methods and refined by blocked full-matrix least squares with anisotropic thermal factors for all the atoms, apart from the carbon atoms of the cation. Only a few H atoms could be located on a Fourier difference map, among which was the vinyl hydrogen atom. The latter was therefore refined isotropically, while the contributions of the other H atoms in the calculated positions (C–H 1.08 Å) were taken into account in the last stages of the refinement. Their isotropic thermal factors were refined in two groups: hydrogens of the methyl groups and hydrogens of the phenyl rings with optimized values of B = 8.5(5) and 6.3(5) Å^2, respectively. Upon convergence (largest shift/error = 0.11) the final Fourier difference map did not show any significant feature (the largest peaks, about 0.7 e Å^{-3}, were located around the Pt). The function minimized was $\Sigma w(|F_o| - |F_c|)^2$ with weights $w = k/[\sigma^2(F_o) + g|F_o|^2]$ (refined values: $k = 1.1504$, $g = 6.32 \times 10^{-4}$); atomic scattering factors, corrected for the real and the imaginary part of atomic dispersion, were taken from ref. 20. The absolute configuration was determined through Hamilton's test by refining the co-ordinates of the two enantiomers. Those giving the lower $R'' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$ (0.0341 *vs.* 0.0463) are reported in Table 4. The solution and refinement of the structure were carried out with the SHELX package of programs[21] and geometrical calculations with the program PARST.[22]

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond distances and angles.

Acknowledgements

We thank the Italian Consiglio Nazionale delle Ricerche for the opportunity to use the equipment and Ministero Pubblica Istruzione for financial support.

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Received 23rd *July* 1987; *Paper* 7/1335