Synthesis and Characterization of Five-co-ordinate Alkyne Complexes of Platinum(II). Crystal and Molecular Structure of [(dmphen)MePt(μ-Cl)(μ-MeC≡CMe)Pt(Cl)Me]·CH_2Cl_2 (dmphen = 2,9-dimethyl-1,10-phenanthroline)†

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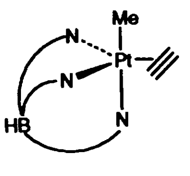
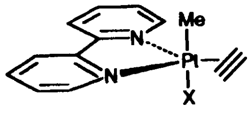
Alkynes with electron-withdrawing substituents add to square-planar platinum(II) complexes of general formula [Pt(Cl)R(N–N)] (R = Me or C_6H_4OMe-4, N–N = bidentate nitrogen ligand) affording the corresponding five-co-ordinate trigonal-bipyramidal (*TBPY*) compounds [Pt(Cl)R(alkyne)(N–N)]. The related five-co-ordinate cationic species $[PtMe(alkyne)(N–N)(MeCN)]^+$ have also been characterized in the presence of excess MeCN. Methyl insertion and formation of a β-methylvinyl derivative is instead observed by treating $[PtMe(N–N)(MeCN)]^+$ with $MeO_2CC≡CCO_2Me$ in the absence of free MeCN. Using a 1 : 2 alkyne:[Pt(Cl)Me(dmphen)] ratio (dmphen = 2,9-dimethyl-1,10-phenanthroline), binuclear species $[Pt_2Cl_2Me_2$(alkyne)(dmphen)] are isolated. An X-ray crystallographic study was carried out on the but-2-yne derivative. Crystals are monoclinic, space group $P2_1/c$, $Z = 4$, in a unit cell of dimensions $a = 15.719(4)$, $b = 12.307(3)$, $c = 25.048(7)$ Å, $\beta = 148.50(1)°$. The structure has been refined to R 0.054 (R' 0.064) for 3718 intensity data [$I \geqslant 3\sigma(I)$]. The two platinum atoms display different co-ordination numbers [a five- (*TBPY*) and a four-co-ordinate square-planar arrangement of the ligands] and are held together by the but-2-yne and one chlorine bridge. The MeC≡CMe ligand transversely bridges the Pt···Pt vector (3.079 Å) and the dihedral angle between the two planes formed by the two Pt–μ-C_2 units is 102.2(5)°.

The first[1,2] identified η^2 five-co-ordinate platinum(II) complexes involved co-ordination of alkynes. Subsequently, two classes of such compounds have been fully characterized: [PtMe(alkyne){HB$(pz)_3$}] **A** (pz = pyrazolyl)[3] and [Pt(X)Me(alkyne)(bipy)] **B** (X = Cl, Br or I; bipy = 2,2′-bipyridine).[4] Type **A** complexes are stable in solution, while alkyne release is observed for type **B** species. The presence of electron-withdrawing substituents, *e.g.* CF_3 or CO_2Me, on the triple bond is necessary in order to isolate the compounds in the solid state. No methyl migration to the alkyne was detected for these complexes. This process was instead observed by treating square-planar compounds *trans*-[Pt(X)MeL_2] (L = tertiary phosphine or arsine) with $CF_3C≡CCF_3$[5] or $MeO_2CC≡CCO_2Me$[6] and proposed to occur *via* the intermediacy of a five-co-ordinate species.

Following our previous studies on the stability[7] and reactivity[8] of five-co-ordinate alkene platinum(II) complexes [Pt(Cl)R(alkene)(N–N)] (R = hydrocarbyl group, L–L = bidentate nitrogen ligand), we undertook the synthesis and characterization of the corresponding alkyne derivatives in order to examine their reactivity toward a migratory insertion process.



A



B

Results and Discussion

Synthesis of the Complexes.—The synthesis of five-co-ordinate [Pt(Cl)Me(alkyne)(N–N)] complexes {N–N = 2,9-dimethyl-1,10-phenanthroline (dmphen), 2-methyl-6-[(phenylimino)methyl]pyridine (pimpy) or 2-methyl-6-[(methylimino)methyl]pyridine (mimpy)} was attempted by simply treating the starting [Pt(Cl)Me(N–N)] compounds with a slight excess of the appropriate alkyne ($CF_3C≡CCF_3$, $MeO_2CC≡CCO_2Me$, $CH_2ClC≡CCH_2Cl$, $HC≡CO_2Me$, MeC≡CMe or PhC≡CH) at room temperature in chloroform solution. The N–N ligands were selected on the basis of their different five-co-ordination stabilizing effect, as observed[7b] in the related five-co-ordinate alkene–platinum(II) complexes. Proposed structures of the products are given in Fig. 1.

For alkynes containing electron-withdrawing substituents 1 : 1 adducts were isolated in good yields, according to equation (1).

$$[Pt(Cl)Me(N–N)] + XC≡CY \longrightarrow [Pt(Cl)Me(XC≡CY)(N–N)] \quad (1)$$

1–8

The white microcrystalline complexes were only slightly soluble in chlorinated solvents and were characterized by usual procedures (elemental analysis, conductivity measurements, NMR and IR spectra). The previous assignment of a five-co-ordinate structure with a trigonal bipyramidal (*TBPY*) geometry to the related [Pt(Cl)Me(alkene)(N–N)] compounds[7a] was to a large extent based on the chemical shift of the bound alkene protons. This was found to be *ca.* 2 ppm upfield with respect to the values observed in four-co-ordinate compounds (or *ca.* 3 ppm upfield relative to the free alkene). In this instance such a comparison is impossible, however other spectral features can be of diagnostic value. If the ^1H NMR spectra of the

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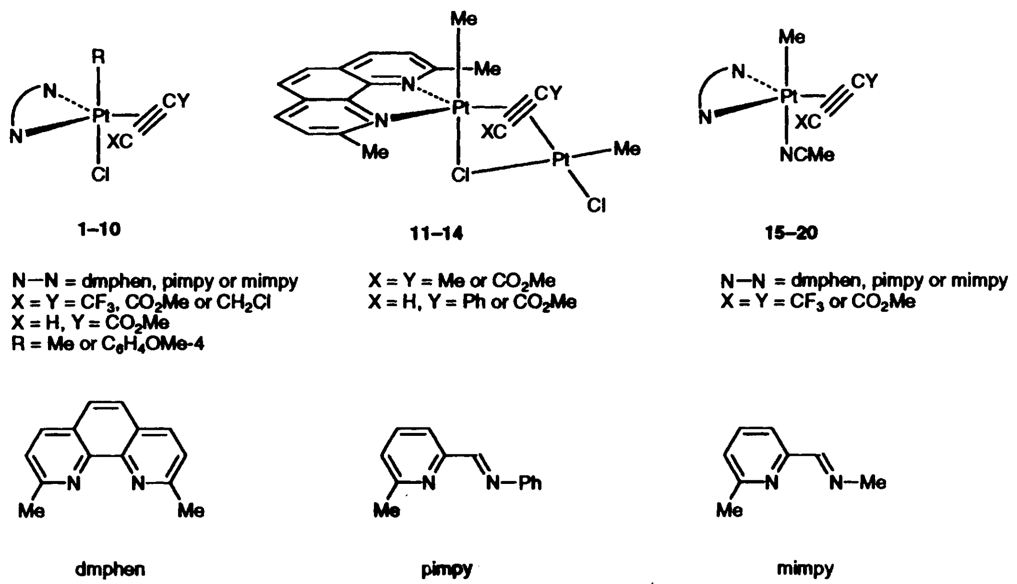
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.



1–10

N—N = dmphen, pimpy or mimpy
X = Y = CF$_3$, CO$_2$Me or CH$_2$Cl
X = H, Y = CO$_2$Me
R = Me or C$_6$H$_4$OMe-4

11–14

X = Y = Me or CO$_2$Me
X = H, Y = Ph or CO$_2$Me

15–20

N—N = dmphen, pimpy or mimpy
X = Y = CF$_3$ or CO$_2$Me

dmphen

pimpy

mimpy

Fig. 1 Proposed structures for the complexes

Table 1 Selected ^{1}H and ^{13}C (in square brackets) NMR data for five-co-ordinate [Pt(Cl)R(alkyne)(N–N)] complexes[a]

	δ(*J*/Hz)			
Complex	Pt–R	Me of N–N	N=CH	Alkyne
1 [Pt(Cl)Me(CF$_3$C≡CCF$_3$)(dmphen)]	0.55 (s, 70) [−8.5 (550)]	3.47 (s) [30.1]		[C≡C,[b] 112.8 {q, CF$_3$, *J*(CF) 262}]
2 [Pt(Cl)Me(MeO$_2$CC≡CCO$_2$Me)(dmphen)]	0.49 (s, 70) [−9.6 (595)]	3.52 (s) [29.8]		3.92 (s, OMe) [77.3 (C≡C, 478), 155.6 (CO), 53.1 (OMe)]
3 [Pt(Cl)Me(CH$_2$ClC≡CCH$_2$Cl)(dmphen)]	0.34 (s, 70)	3.51 (s)		4.73 (AB q, CH$_2$Cl,[c])
4 [Pt(Cl)Me(HC≡CCO$_2$Me)(dmphen)]	0.28 (s, 68) [−11.7 (580)]	3.50 (s), 3.65 (s) [30.2, 29.8]		4.79 (s, CH, 50), 3.88 (s, OMe) [84.0 (CH, 387), 68.8 (≡C, 497), 155.0 (CO), 52.6 (OMe)]
5 [Pt(Cl)Me(CF$_3$C≡CCF$_3$)(pimpy)]	0.56 (s, 68)	3.25 (s)	9.02 (s, 50)	
6 [Pt(Cl)Me(MeO$_2$CC≡CCO$_2$Me)(pimpy)]	0.52 (s, 70) [−9.5 (556)]	3.37 (s) [28.6]	9.02 (s, 48) [162.7]	3.64, 3.87 (2 s, OMe) [78.7 (437), 76.0 (476) (C≡C), 154.5, 154.0 (CO), 52.4, 52.0 (OMe)]
7 [Pt(Cl)Me(CF$_3$C≡CCF$_3$)(mimpy)]	0.50 (s, 70)	3.15 (s)	9.05 (s, 55)	
8 [Pt(Cl)Me(MeO$_2$CC≡CCO$_2$Me)(mimpy)]	0.56 (s, 71) [−10.3 (571)]	3.28 (s) [28.5]	8.97 (s, 57) [165.2]	3.83, 3.88 (2 s, OMe) [79.6 (C≡C, 440), 155.4, 153.2 (CO), 52.4 (2 OMe)]
9 [Pt(Cl)(C$_6$H$_4$OMe-4)(CF$_3$C≡CCF$_3$)(dmphen)]	6.38 (d, 2 H, 38), 61.5 (d, 2 H), 3.49 (s, OMe)	3.64 (s)		
10 [Pt(Cl)(C$_6$H$_4$OMe-4)(MeO$_2$CC≡CCO$_2$Me)-(dmphen)]	6.55 (d, 2 H, 38), 6.13 (d, 2 H), 3.48 (s, OMe)	3.76 (s)		3.89 (s, OMe)

[a] Spectra recorded in CDCl$_3$ or in C$_2$D$_2$Cl$_4$ {reference δ 7.26 (CHCl$_3$) or 5.96 (C$_2$H$_2$Cl$_4$) [δ 77.0 (^{13}CDCl$_3$) or 74.15 (^{13}C$_2$D$_2$Cl$_4$)]}; the coupling constants with ^{195}Pt (Hz) are reported in parentheses; abbreviations: s = singlet, d = doublet, q = quartet; the chemical shifts of the N–N ligands protons not listed in the table are centred at approximately δ 8.4–8.3 (d, 2 H), 7.9 (s, 2 H) and 7.9–7.8 (d, 2 H) [δ 162 (C^2,C^9, 30), 145 (2 quaternary C–N), 139 (C^4,C^7), 129 (2 C) and 126 (4 C)] for dmphen; δ 8.0–7.9 (t, 1 H), 7.9 (d, 1 H), 7.7 (d, 1 H), 7.85 (m, 3 H) and 7.5 (m, 2 H) [δ 162 (C^6, 32), 152 (C^2), 148 {N–C(phenyl), 30}, 139.5 (C^4) and 129–123 {C^3,C^5, 5 C(phenyl)}] for pimpy; δ 7.9 (t, 1 H), 7.75 (d, 1 H), 7.65 (d, 1 H) and 4.3–4.2 (s, NMe, 26) [δ 161.6 (C^6, 32), 151.9 (C^2), 139.4 (C^4), 128.1 and 125.4 (C^3 and C^5) and 50.1 (NMe, 92)] for mimpy. [b] Obscured by solvent signals. [c] The ^3J(PtH) coupling constants of the two magnetically non-equivalent CH$_2$Cl protons are different: a value of 58 Hz can be measured, the other undetermined value was significantly less.

already known five-co-ordinate [Pt(Cl)Me(alkene)(N–N)] species[7] and of the newly synthesized [Pt(Cl)Me(alkyne)-(N–N)] species (Table 1) are compared with those of the starting [Pt(Cl)Me(N–N)] complexes, some significant correlations can be found. (*i*) The chemical shift of the Pt–Me protons is shifted upfield by 0.5–1 ppm and a smaller (*ca.* 10 Hz) ^2J(PtH) coupling constant is observed on going from four- to -five-co-ordinate species. (*ii*) For complexes containing pimpy or mimpy the CH=N resonance is only slightly upfield shifted, but a markedly larger ^2J(PtH) coupling constant is observed (100 *vs.* 50 Hz).

In addition, in the IR spectra of the [Pt(Cl)Me(alkyne)(N–N)] adducts a medium to strong absorption band is found in the region 1850–1800 cm^{-1} which can be assigned to the C≡C stretching frequency of the co-ordinated alkyne and compares well with the values reported for the already known[3] [PtMe(alkyne){HB(pz)$_3$}] complexes, being *ca.* 400–450 cm^{-1} lower than that for the free alkynes.

On the basis of the above characterizing data, a *TBPY* arrangement of the ligands can be inferred for compounds **1–8**, with the alkyne lying in the equatorial plane and the Me and Cl groups in axial positions. Over a period of 24 h, the compounds

Table 2 Selected ^{1}H and ^{13}C (in square brackets) NMR data for [$Pt_2Cl_2Me_2$(alkyne)(dmphen)] complexes[a]

	δ(*J*/Hz)		
Compound	Pt–Me	2,9-Me_2	Alkyne
11 [$Pt_2Cl_2Me_2$(MeC≡CMe)(dmphen)]	−0.10 (s, 77), 0.86 (s, 88) [−11.0 (775), −12.9 (715)]	3.65 (s) [29.0]	2.23 (s, 56) [34.0 (C≡C, 292, 427), 10.1 (Me)]
12 [$Pt_2Cl_2Me_2$(HC≡CPh)(dmphen)]	0.13 (s, 78), 0.59 (s, 87)	3.18 (s), 3.72 (s)	1.81 (s, CH, 30, 48), 7.95 (d), 7.42 (t), 7.30 (d)
13 [$Pt_2Cl_2Me_2$($MeO_2CC≡CCO_2Me$)(dmphen)]	0.75 (s, 77), 1.03 (s, 88) [−6.2 (725), −6.5 (700)]	3.57 (s), [29.2]	3.92 (s, OMe) [18.5 (C≡C[b]), 156.7 (CO), 53.5 (OMe)]
14 [$Pt_2Cl_2Me_2$($HC≡CCO_2Me$)(dmphen)]	0.42 (s, 75), 0.91 (s, 88)	3.52 (s), 3.66 (s)	2.1 (s, CH[b]), 3.90 (s, OMe)

[a] Spectra recorded in $CDCl_3$ or in $C_2D_2Cl_4$ {reference δ 7.26 ($CHCl_3$) or 5.96 ($C_2H_2Cl_4$) [δ 77.0 ($^{13}CDCl_3$) or 74.15 ($^{13}C_2D_2Cl_4$)}; the coupling constants with ^{195}Pt (Hz) are reported in parentheses; abbreviations: s = singlet, d = doublet, t = triplet; the chemical shifts of the heteroaromatic dmphen protons are centred at approximately δ 8.4 (d, 2 H), 7.9 (s, 2 H) and 7.8 (d, 2 H) [^{13}C δ 161 (C^2,C^9, 30), 144 (2 quaternary C–N), 139 (C^4,C^7), 129 (2 C) and 127 (4 C)]. [b] Coupling constant with ^{195}Pt not evaluated.

do not release alkyne in chloroform solution. Hindered rotation of the unsaturated ligand around the Pt–alkyne bond is indicated by analysis of the NMR spectra, *e.g.* compounds **6** and **8**. The same procedure as represented by equation (1) was used to synthesise some similar five-co-ordinate arylalkyne–platinum(II) complexes (Table 1, compounds **9** and **10**) starting from [$PtCl(C_6H_4OMe\text{-}4)$(dmphen)].

Different behaviour was observed when but-2-yne or phenylacetylene were used. Upon treating [Pt(Cl)Me(dmphen)] with these ligands in chloroform solution a slow reaction ensued, the stoichiometry of which is given by equation (2). The pale yellow

$$2[\mathrm{Pt(Cl)Me(dmphen)}] + \text{alkyne} \longrightarrow \underset{\mathbf{11,\ 12}}{[\mathrm{Pt_2Cl_2Me_2(alkyne)(dmphen)}]} + \text{dmphen} \quad (2)$$

crystalline compounds crystallized from the reaction medium and in both cases elemental analysis agreed with the above formulation. In particular, for the but-2-yne derivative (**11**, Table 2), the ^{1}H NMR spectrum shows the equivalence of the two halves of the symmetric dmphen ligand while two distinct Pt–Me proton resonances [δ −0.10, ^2J(PtH) = 77 and δ 0.86, ^2J(PtH) = 88 Hz] are observed. The six methyl protons on the triple bond give rise to a singlet centred at δ 2.23 flanked by two sets of satellite peaks, leading to the observation of a pseudo-quintet with an intensity ratio of 1:8:18:8:1 and a line separation of 28 Hz. On these grounds co-ordination of the but-2-yne to two platinum atoms can be inferred and a molecular arrangement, as depicted in Fig. 1, is proposed in which the two metal atoms have different co-ordination numbers. The above spectral pattern of the co-ordinated but-2-yne is in accord with the platinum isotopic composition (33% ^{195}Pt), assuming that the two ^3J(PtH) coupling constants are nearly equal, being close to the measured value of 56 Hz. The ^{13}C NMR spectrum agrees with this hypothesis. Two distinct Pt–Me resonances are detected (δ −12.9 and −11.0, with ^{195}Pt coupling constants of 715 and 775 Hz, respectively). The acetylenic carbons give a signal at δ 34.0, flanked by two sets of satellite peaks from which two different ^{195}Pt coupling constants can be evaluated (292 and 427 Hz). This molecular arrangement for **11** was unequivocally confirmed by an X-ray crystal structure determination (see below).

A similar structure can be assigned to the phenylacetylene derivative **12**. The ^{1}H NMR spectrum shows, besides two distinct resonances for the Pt–Me groups, the non-equivalence of the two halves of the dmphen ligand owing to the presence of a monosubstituted alkyne. In addition, the ≡CH proton gives a singlet at δ 1.81, flanked by two sets of satellite peaks, leading to an intensity ratio of *ca.* 1:1:4:1:1. Thus, the two ^2J(PtH) coupling constants with the two different co-ordinating platinum atoms can be evaluated, and are found to have values of 30 and 48 Hz. The resonances due to the molecular units containing two ^{195}Pt atoms were of too low intensity to be detected.

The same type of complexes could also be obtained with alkyne ligands containing electron-withdrawing groups, by treating the five-co-ordinate adducts [Pt(Cl)Me(alkyne)(dmphen)] with an equimolar amount of [Pt(Cl)Me(dmphen)] [equation (3), alkyne = $HC≡CCO_2Me$ or $MeO_2CC≡CCO_2Me$].

$$\underset{\mathbf{2,\ 4}}{[\mathrm{Pt(Cl)Me(alkyne)(dmphen)}]} + [\mathrm{Pt(Cl)Me(dmphen)}] \longrightarrow \underset{\mathbf{13,\ 14}}{[\mathrm{Pt_2Cl_2Me_2(alkyne)(dmphen)}]} + \text{dmphen} \quad (3)$$

An alternative procedure to the synthesis of complexes **13** and **14** involves the addition of the corresponding alkyne to the [Pt(Cl)Me(dmphen)] substrate in 1:2 molar ratio. By comparing the NMR data listed in Tables 1 and 2 (see, for example, complexes **4** and **14**) as well as the reported[3] values for the ≡CH resonances in the known five-co-ordinate [PtMe(alkyne){$HB(pz)_3$}] complexes, a *ca.* 1.5–2 ppm downfield shift with respect to the free monosubstituted alkyne is observed when the acetylene co-ordinates to a single metal atom. An upfield shift of more than 1 ppm is instead observed for the binuclear derivatives. This is consistent with the change in the electronic density distribution that occurs when a C≡C bond co-ordinates to two rather than one metal centre. Similar conclusions can be reached if the ^{13}C NMR data are compared. A very slight downfield shift is observed for the acetylenic carbons in the five-co-ordinate adducts (compare the values reported for compounds **2** and **6** with the signal at δ 74.6 for free $MeO_2CC≡CCO_2Me$), while a marked upfield shift occurs for the binuclear complex **13**. The co-ordination of the triple bond to two metal atoms considerably affects the C≡C stretching frequency in the IR spectra. The C≡C absorption band, found at 1810 cm^{-1} in the mononuclear complex **2**, is lowered to *ca.* 1550 cm^{-1} in the corresponding binuclear species **13**.

When the N–N ligands pimpy or mimpy were used no binuclear complexes could be isolated. In addition, co-ordination of but-2-yne or phenylacetylene to the metal centre was only detected in solution at −40 °C, and raising the temperature and/or removing the solvent led only to recovery of [Pt(Cl)Me(N–N)]. Thus, the formation of the binuclear derivatives **11**–**14** seems to be attributable to the co-operative effects of at least three factors: the tendency of an alkyne to bind to two metal centres; the presence of steric constraints which prevents the two metals both having the same *TBPY* geometry; and the potential instability of structures containing dmphen in a square-planar co-ordination environment.[7]

Structure of [$Pt_2Cl_2Me_2$(MeC≡CMe)(dmphen)]·CH_2Cl_2 **11**·CH_2Cl_2.—The molecular structure of **11**·CH_2Cl_2 together

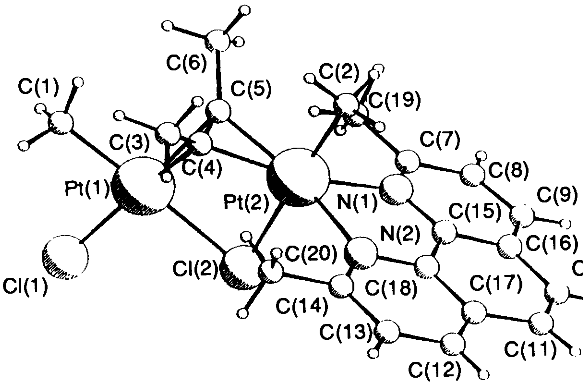


Fig. 2 View of the molecular structure of the complex $[Pt_2Cl_2Me_2(MeC{\equiv}CMe)(dmphen)]$ **11** showing the atom numbering

Table 3 Bond lengths (Å) and selected bond angles (°) for complex **11** with estimated standard deviations (e.s.d.s) in parentheses

(*a*) Co-ordination sphere of Pt(1)			
Pt(1)–Cl(1)	2.320(4)	Pt(1)–Cl(2)	2.524(3)
Pt(1)–C(4)	2.10(1)	Pt(1)–C(5)	2.13(1)
Pt(1)–C(1)	2.03(2)	C(4)–C(5)	1.35(2)
C(3)–C(4)	1.49(2)	C(5)–C(6)	1.48(2)
Cl(1)–Pt(1)–Cl(2)	89.6(1)	Cl(1)–Pt(1)–C(1)	88.4(5)
C(1)–Pt(1)–C(5)	91.9(6)	C(1)–Pt(1)–C(4)	91.0(6)
Cl(2)–Pt(1)–C(5)	89.8(4)	Cl(2)–Pt(1)–C(4)	91.0(4)
C(1)–Pt(1)–Cl(2)	178.0(4)	C(4)–Pt(1)–C(5)	37.1(5)
Cl(1)–Pt(1)–C(4)	158.2(4)	Cl(1)–Pt(1)–C(5)	164.7(4)
C(3)–C(4)–C(5)	143(1)	C(6)–C(5)–C(4)	139(1)
(*b*) Co-ordination sphere of Pt(2)			
Pt(2)–Cl(2)	2.514(3)	Pt(2)–C(2)	2.04(1)
Pt(2)–C(4)	2.07(1)	Pt(2)–C(5)	2.06(1)
Pt(2)–N(1)	2.21(1)	Pt(2)–N(2)	2.19(1)
N(1)–C(7)	1.35(2)	N(2)–C(14)	1.35(2)
N(1)–C(15)	1.35(2)	N(2)–C(18)	1.37(2)
C(7)–C(19)	1.46(2)	C(14)–C(20)	1.47(2)
C(7)–C(8)	1.43(2)	C(14)–C(13)	1.40(2)
C(8)–C(9)	1.37(2)	C(13)–C(12)	1.38(2)
C(9)–C(16)	1.36(2)	C(12)–C(17)	1.36(2)
C(16)–C(10)	1.43(2)	C(17)–C(11)	1.44(2)
C(16)–C(15)	1.41(2)	C(17)–C(18)	1.40(2)
C(15)–C(18)	1.45(2)	C(10)–C(11)	1.35(2)
C(4)–Pt(2)–C(5)	38.1(5)	N(1)–Pt(2)–N(2)	74.8(4)
C(5)–Pt(2)–N(1)	123.5(4)	C(4)–Pt(2)–N(2)	123.6(4)
Cl(2)–Pt(2)–C(2)	178.1(4)		

with the atom labelling scheme is shown in Fig. 2. Bond lengths and selected bond angles are given in Table 3. Fig. 3 shows the contents of the monoclinic unit cell. The binuclear complex displays near C_s symmetry, in which the approximate mirror passes through the Pt atoms, the chlorine atoms and the methyl ligands. If the but-2-yne group is regarded as a monodentate ligand, Pt(1) can be described as being in a square-planar co-ordination environment. Whereas Cl(1), Cl(2) and C(1) are strictly coplanar with Pt(1), the centre of the alkyne bond is slightly but significantly displaced [0.12(2) Å] out of this plane. The co-ordination geometry around Pt(2) is best described as trigonal bipyramidal with the dmphen ligand and the alkyne in equatorial positions and a methyl group and Cl(2) in axial positions. The dmphen ligand is planar within 0.10 Å and the atoms Pt(2), C(4) and C(5) lie out of this plane by 0.16(1), 0.28(2) and 0.32(2) Å respectively, towards the axial methyl group. This feature has been observed previously [9] and ascribed to non-bonding interactions between platinum and the methyl groups of the dmphen ligand.[9] The Pt(2)–N distances are virtually equal [average value 2.20(1) Å] and fall in the range characteristic for dmphen when bonded to Pt in five-co-ordinate complexes.[10] The two Pt atoms are bridged by Cl(2) and the but-2-yne molecule. The Pt(1)···Pt(2) distance of 3.079(2) Å lies outside the range found for Pt–Pt bonds. The bridging Cl(2) atom forms two bonds of nearly equal length with Pt (average value 2.52 Å), which are longer by 0.20 Å, than the bond formed by Pt(1) with the non-bridging Cl(1). The bond length Pt(1)–Cl(1) [2.320(4) Å] is comparable to values found in other complexes of Pt.[11] A major factor in the lengthening of the Pt–Cl distances involving Cl(2) can be ascribed to the strong *trans* influence exerted concomitantly by the two methyl ligands. The bridging alkyne ligand adopts a *cis*-bent configuration with the four non-hydrogen atoms strictly coplanar and with an average value of the bend-back angle of 39(1)°. The C≡C bond at 1.35(2) Å is slightly shorter than that found [1.38(2) Å] for the C≡C bonds of the bridging diphenylacetylene ligands in $[Pt_3(\mu\text{-}Ph_2C_2)_2(PEt_3)_4]$.[12] The distortions the bridging alkyne undergoes as a consequence of co-ordination to the two metal centres, *i.e.* the lengthening of the alkyne bond and bending of the molecule, appear to be larger than when the alkyne co-ordinates to a single metal atom.[13] These structural findings reflect well the spectral behaviour of the complex (see above). The alkyne ligand binds to the platinum atoms through its orthogonal π orbitals leading to a butterfly arrangement, in which the two wings are slightly inequivalent with the distances Pt(1)–C(4) and Pt(1)–C(5) [2.10(1) and 2.13(1) Å respectively] being slightly but significantly longer than Pt(2)–C(4) and Pt(2)–C(5) [2.07(1) and 2.06(1) respectively]. The Pt–C(methyl) distances, equivalent within experimental error, lie in the expected range.

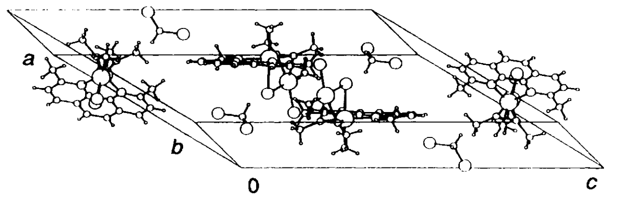


Fig. 3 Contents of the monoclinic unit cell of **11**·CH_2Cl_2

Stability and Reactivity of the Complexes.—As discussed above, the neutral five-co-ordinate alkyne complexes **1**–**10** are stable in the solid state as well as in solution. No significant alkyne release, *i.e.* the reverse of the reaction in equation (1), was observed when the complexes were kept over a period of days in chlorinated solvents at room temperature. This is in contrast to the behaviour of the similar [Pt(Cl)Me(alkyne)(bipy)] compounds for which a half-life of a few minutes is observed[4] for this process, which is solvent-dependent. The factors affecting the stability of the five-co-ordinate adducts towards the release of the unsaturated ligand have been already discussed[7] for the alkene–platinum(II) complexes. As well as the steric requirements of the N–N ligand, the presence of electron-withdrawing substituents on the double bond generally increases the stability of the complexes by enhancing the π-back donation. However, the bulkiness of these substituents acts as a destabilizing factor owing to unfavourable steric interactions with the axial ligands. In the present systems, however, in which the co-ordinated alkynes adopt a *cis*-bent configuration, such interactions should be of minor relevance. In fact, stable complexes can be obtained even with mimpy, which has only a moderate five-co-ordination stabilizing effect.

A simple reaction reported for five-co-ordinate alkene–platinum(II) complexes[14] is removal of the co-ordinated chlorine atom to give the corresponding cationic species. A similar reaction [equation (4)] was performed on the alkyne

$$[Pt(Cl)Me(alkyne)(N\text{–}N)] + AgBF_4 + MeCN \longrightarrow \underset{\textbf{15–20}}{[PtMe(alkyne)(N\text{–}N)(MeCN)]BF_4} + AgCl \quad (4)$$

Table 4 Proton NMR data for five-co-ordinate $[PtMe(alkyne)(N–N)(MeCN)]BF_4$ complexes*

	δ(*J*/Hz)			
Complex	Pt–Me	Me of N–N	N=CH	Alkyne
15 $[PtMe(CF_3C{\equiv}CCF_3)(dmphen)(MeCN)]BF_4$	1.00 (s, 74)	3.43 (s)		
16 $[PtMe(MeO_2CC{\equiv}CCO_2Me)(dmphen)(MeCN)]BF_4$	0.71 (s, 75)	3.42 (s)		3.96 (s, OMe)
17 $[PtMe(CF_3C{\equiv}CCF_3)(pimpy)(MeCN)]BF_4$	0.93 (s, 74)	3.23 (s)	9.47 (s, 57)	
18 $[PtMe(MeO_2CC{\equiv}CCO_2Me)(pimpy)(MeCN)]BF_4$	0.45 (s, 75)	2.95 (s)	9.17 (s, 52)	3.68, 3.45 (2 s, OMe)
19 $[PtMe(CF_3C{\equiv}CCF_3)(mimpy)(MeCN)]BF_4$	0.68 (s, 74)	3.06 (s)	9.36 (s, 61)	
20 $[PtMe(MeO_2CC{\equiv}CCO_2Me)(mimpy)(MeCN)]BF_4$	0.33 (s, 75)	2.89(s)	9.02 (s, 71)	3.72, 3.66 (2 s, OMe)

* Spectra recorded in $CDCl_3–CD_3NO_2$ [reference δ 7.26 ($CHCl_3$)]; the coupling constants with ^{195}Pt (Hz) are given in parentheses; abbreviations: s = singlet, d = doublet, t = triplet; the chemical shift of the co-ordinated MeCN is in the range δ 2.0–2.2; the chemical shifts of the N–N ligand protons not listed in the table are centred at approximately δ 8.8–8.7 (d, 2 H), 8.2 (s, 2 H) and 8.2–8.1 (d, 2 H) for dmphen; 8.2–8.0 (t, 1 H), 8.1–7.9 (d, 1 H), 8.0–7.8 (d, 1 H), 7.8 (m, 3 H) and 7.5 (m, 2 H) for pimpy; 8.1–7.9 (t, 1 H), 8.0–7.8 (d, 1 H), 7.8–7.6 (d, 1 H) and 4.2–4.0 (s, NMe, 27) for mimpy.

derivatives. The characterization data for complexes **15**–**20** are listed in Table 4. When N–N = dmphen or alkyne = $CF_3C{\equiv}CCF_3$, the cationic species could be isolated in the solid state and no alkyne release was observed in solution. However for N–N = pimpy or mimpy, alkyne = $MeO_2CC{\equiv}CCO_2Me$, the complexes were only identified in solution and slow alkyne release was detected by ^1H NMR spectroscopy. A chloroform solution of complex **20** showed the presence of **20** and of the corresponding four-co-ordinate species $[PtMe(N–N)(MeCN)]^+$ in a nearly 1:1 ratio after one week at room temperature. This dissociation is reversible (pK_d *ca.* 1.5), since **20** could be reformed by adding an excess of the alkyne. A similar lower stability, with respect to the corresponding neutral species, has already been observed[14] (at least when the neutral apical ligand is MeCN) for cationic five-co-ordinate alkene–platinum(II) complexes.

The above behaviour was also observed when an excess of MeCN was present in a chloroform solution of **20** (or **18**). In the absence of free MeCN a slow irreversible reaction ensued affording a σ-vinyl derivative by methyl insertion into the triple bond [equation (5)]. The insertion products were isolated as neutral compounds by adding LiCl to the reaction medium and were identified by usual procedures. The same compounds were also obtained when the alkyne was added to a solution of the four-co-ordinate species $[PtMe(N–N)(MeCN)]^+$ (N–N = pimpy or mimpy). In this respect, the reaction closely resembles the previously reported methyl insertion observed[6] when the cation *trans*-$[PtMe(Me_2CO)(PMe_2Ph)_2]^+$ was treated with $MeO_2CC{\equiv}CCO_2Me$. Concerning the stereochemistry of the σ Pt-bound vinyl, comparison of the ^1H NMR spectral data of the compounds obtained with those reported for *trans*-$[PtCl\{C(CO_2Me){=}CMe(CO_2Me)\}(PMe_2Ph)_2]$ suggests a similar configuration, *i.e.* a *cis* arrangement of the Me group and the Pt moiety. Protonolysis of the Pt–C bond, which should allow a correct stereochemical assignment, is reported[15] to cause *cis*–*trans* isomerization. However, in our case this procedure was not possible owing to the inertness of the Pt–C bond under acidic conditions.

$$[PtMe(MeO_2CC{\equiv}CCO_2Me)(N–N)(MeCN)]^+ \longrightarrow [Pt\{C(CO_2Me){=}CMe(CO_2Me)\}(N–N)(MeCN)]^+ \quad (5)$$

With respect to the insertion reaction mechanism, this reaction has only been observed with the two five-co-ordinate cationic substrates (**18** and **20**) which also show a moderate tendency towards alkyne release. In addition, the inhibitory effect of free MeCN was clearly detected. On these grounds, it seems that a five-co-ordinate adduct having a *TBPY* arrangement of the ligands with axial hydrocarbyl and equatorial alkyne cannot be considered as a viable intermediate for the insertion reaction. Were a five-co-ordinate species to be involved as the precursor, a different geometrical arrangement would be present in the early adduct between the alkyne and the $[PtMe(N–N)(MeCN)]^+$ substrate. This should therefore undergo two independent different fates: a fast *TBPY* five-co-ordinate complex formation and/or a slow migratory insertion. Thus, the stability of the *TBPY* species towards alkyne release, which is dependent primarily on the nature of the N–N ligand, is one of the factors influencing the observed reactivity.

Table 5 Microanalytical data (%) for five-co-ordinate [Pt(Cl)R-(alkyne)(N–N)] complexes*

	Analysis		
Complex	C	H	N
1	36.9 (37.1)	2.4 (2.5)	4.5 (4.6)
2	42.1 (42.3)	3.4 (3.5)	4.5 (4.7)
3	39.4 (39.6)	3.3 (3.3)	4.7 (4.9)
4	42.2 (42.4)	3.5 (3.6)	5.1 (5.2)
5	35.6 (35.8)	2.4 (2.5)	4.5 (4.6)
6	41.0 (41.0)	3.6 (3.6)	4.8 (4.8)
7	28.7 (28.8)	2.4 (2.4)	5.1 (5.2)
8	34.3 (34.5)	3.6 (3.7)	5.2 (5.4)
9	42.4 (42.4)	2.7 (2.7)	3.9 (4.0)
10	47.0 (47.1)	3.7 (3.8)	4.0 (4.1)

* Calculated values are given in parentheses. Most of the listed compounds contained $CHCl_3$ (or CH_2Cl_2) of crystallization. Satisfactory elemental analyses were obtained by dissolving the microcrystalline complexes in chloroform and reprecipitating with *n*-pentane.

Experimental

Physical Measurements.—The NMR spectra were recorded at 270 or 200 MHz on a Bruker AC-270 or a Varian XL-200 spectrometer, respectively, at the Centro Interdipartimentale di Metodologie Chimico-Fisiche of the University of Naples using $CDCl_3$, $C_2D_2Cl_4$ or CD_3NO_2 as solvent. IR spectra were obtained on a Perkin-Elmer 457 spectrophotometer in Nujol mulls. Elemental analyses are reported in Table 5.

Starting Materials.—Solvents and reagents were of AnalaR grade and, unless otherwise stated, were used without further purification. 2,9-Dimethyl-1,10-phenanthroline was obtained commercially while pimpy and mimpy were prepared according to a previously described general method.[16] The complexes [Pt(Cl)Me(N–N)] (N–N = dmphen, pimpy or mimpy), $[PtCl(C_6H_4OMe\text{-}4)(dmphen)]$ and $[PtMe(N–N)(MeCN)]BF_4$ (N–N = pimpy or mimpy) were synthesised by using known procedures.[7,8]

Preparations.—*Five-co-ordinate complexes* **1**–**10**. To a solution of the four-co-ordinate complex [Pt(Cl)R(N–N)] (0.5

Table 6 Summary of crystallographic data for complex **11**$\cdot CH_2Cl_2$

Formula	$C_{20}H_{24}Cl_2N_2Pt_2\cdot CH_2Cl_2$
M	838.4
Crystal system	Monoclinic
Space group	$P2_1/c$
a/Å	15.719(4)
b/Å	12.307(3)
c/Å	25.048(7)
β/°	148.50(1)
U/Å^3	2532(2)
Z	4
D_c/g cm^{-3}	2.20
D_m/g cm^{-3} (flotation)	2.20
Crystal size/mm	0.06 × 0.10 × 0.20
λ(Cu-Kα)/Å	1.5418
F(000)	1560
θ_{max}/°	74
μ/cm^{-1}	246.9
Number of independent reflections	5208
Number of reflections with $I > 3\sigma(I)$	3718
Number of refined parameters	137
Goodness of fit	1.22
R	0.054
R'	0.064

Table 7 Fractional atomic co-ordinates of non-hydrogen atoms of complex **11**$\cdot CH_2Cl_2$ with e.s.d.s in parentheses

Atom	x	y	z
Pt(1)	0.682 52(4)	0.300 48(5)	0.004 39(2)
Pt(2)	0.797 63(4)	0.068 07(5)	0.040 62(2)
Cl(1)	0.447 9(3)	0.404 3(3)	−0.113 7(2)
Cl(2)	0.513 4(2)	0.142 5(3)	−0.118 6(1)
C(1)	0.811(1)	0.431(2)	0.099 2(7)
C(2)	1.026(1)	0.004(1)	0.166 8(6)
C(3)	0.944(1)	0.199(1)	0.222 2(7)
C(4)	0.871(1)	0.195(1)	0.128 4(6)
C(5)	0.897(1)	0.222(1)	0.091 2(6)
C(6)	1.023(1)	0.276(2)	0.125 5(7)
N(1)	0.746 9(7)	−0.030(1)	−0.058 5(4)
N(2)	0.700 2(7)	−0.086(1)	0.018 6(5)
C(7)	0.759(1)	0.006(1)	−0.102 7(6)
C(8)	0.718(1)	−0.065(1)	−0.167 3(7)
C(9)	0.669(1)	−0.169(2)	−0.183 5(7)
C(10)	0.598(1)	−0.312(2)	−0.155 5(8)
C(11)	0.578(1)	−0.343(2)	−0.115 3(8)
C(12)	0.582(1)	−0.290(2)	−0.017 9(7)
C(13)	0.614(1)	−0.214(1)	0.038 1(7)
C(14)	0.672(1)	−0.111(1)	0.055 3(6)
C(15)	0.693(1)	−0.132(1)	−0.078 5(6)
C(16)	0.653(1)	−0.205(1)	−0.141 0(7)
C(17)	0.609(1)	−0.267(1)	−0.055 7(7)
C(18)	0.668(1)	−0.164(1)	−0.036 7(6)
C(19)	0.821(1)	0.116(2)	−0.080 0(7)
C(20)	0.708(1)	−0.028(1)	0.115 2(6)
C(21)	0.219(3)	0.571(4)	0.187(2)
Cl(3)	0.247 1(7)	0.574(1)	0.135 1(5)
Cl(4)	0.081(1)	0.650(1)	0.137 6(7)

mmol) (R = Me or C_6H_4OMe-4) in chloroform (50 cm^3), an equimolar amount of the appropriate alkyne was added. After 30 min at room temperature the precipitated product can be isolated as a white microcrystalline solid. Concentration of the mother-liquor afforded a second crop of crystals to give a total yield of 80–90%. Most of the complexes obtained contained $CHCl_3$ of crystallization.

Binuclear compounds **11** *and* **12**. To a solution of the four-co-ordinate complex [Pt(Cl)Me(dmphen)] (0.5 mmol) in dichloromethane (50 cm^3), a two-fold excess of but-2-yne was added. The mixture was kept overnight at room temperature and the solid product **11** was isolated as pale yellow microcrystals in 60% yield. Following a similar procedure **12** can be obtained in 50% yield.

Binuclear compounds **13** *and* **14**. *Method* (*a*). To a solution of the corresponding five-co-ordinate adduct **2** or **4** (0.5 mmol) in dichloromethane (50 cm^3) was added an equimolar amount of [Pt(Cl)Me(dmphen)]. The solution was kept at room temperature for 48 h and the product (**13** or **14**, respectively) isolated as pale-yellow microcrystals in 50% yield.

(*b*) To a solution of the four-co-ordinate complex [Pt(Cl)-Me(dmphen)] (0.5 mmol) in dichloromethane (50 cm^3) was added 0.25 mmol of the appropriate alkyne. Crystals of the product (**13** or **14**) were collected in yield comparable to that using method (*a*).

Cationic five-co-ordinate compounds **15**–**20**. To a solution of the corresponding five-co-ordinate neutral complex [Pt(Cl)-Me(alkyne)(N–N)] (0.5 mmol) in dichloromethane–methanol (5:1, 50 cm^3), an equimolar amount of $AgBF_4$ dissolved in acetonitrile (5 cm^3) was added dropwise at 0 °C. After 20 min of stirring the mixture was filtered through Celite and evaporated to dryness. White solids were obtained in 80–90% yield.

The preparation of complexes **18** and **20** was performed at −20 °C in deuteriated solvents. After 30 min stirring the cold mixture was quickly filtered through Celite. The compounds were not isolated and were identified in solution by ^1H NMR spectroscopy.

Reaction between $[PtMe(N\text{-}N)(MeCN)]BF_4$ *and* $MeO_2CC\equiv CCO_2Me$ (N–N = pimpy *or* mimpy).—To a solution of the cationic four-co-ordinate complex $[PtMe(N\text{-}N)(MeCN)]BF_4$ (0.5 mmol) in nitromethane–chloroform (2:1, 10 cm^3) an equimolar amount of alkyne was added at room temperature. After stirring for 2 d, a saturated aqueous solution of LiCl (10 cm^3) was added and the mixture vigorously shaken. The organic phase was separated and dried over Na_2SO_4. Evaporation of the solvent gave the crude product as a glassy oil which was purified by chromatography on Florisil eluting with dichloromethane (yield 60%). $[PtCl\{C(CO_2Me)=CMe(CO_2Me)\}(pimpy)]$ (Found: C, 41.2; H, 3.7; N, 4.7. $C_{20}H_{21}ClN_2O_4Pt$ requires C, 41.1; H, 3.6; N, 4.8%). Selected ^1H [^{13}C] NMR data ($CDCl_3$), δ 9.10 [168.3] [s, CH=N, ^3J(PtH) 90], 3.66–3.50 [51.4–51.1] (s, 2 OMe), 3.22 [26.5] (s, 6-Me) and 2.08 [21.5] [s, Me, ^4J(PtH) 15 Hz]. $[PtCl\{C(CO_2Me)=CMe(CO_2Me)\}(mimpy)]$ (Found: C, 34.6; H, 3.5; N, 5.2. $C_{15}H_{19}ClN_2O_4Pt$ requires C, 34.5; H, 3.7; N, 5.4%). Selected ^1H NMR data ($CDCl_3$), δ 8.97 [s, CH=N, ^3J(PtH) 98], 4.08 [s, =NMe, ^3J(PtH) 50], 3.78 (s, OMe), 3.66 (s, OMe), 3.14 (s, 6-Me) and 2.41 [s, Me, ^4J(PtH) 15 Hz].

Crystal Structure Determination of Compound **11**$\cdot CH_2Cl_2$.—Many of the details of the structure analysis are listed in Table 6. X-Ray data were collected at room temperature on an Enraf-Nonius CAD4-F automatic diffractometer using Cu-Kα graphite-monochromated radiation operated in the ω–θ scan mode. The unit-cell parameters were obtained by a least-squares fitting of the setting values of 25 strong reflections in the range $20 \leqslant \theta \leqslant 29°$. Three monitoring reflections, measured every 500, showed a slight crystal decay (about 7%), which was taken as negligible. In addition to usual corrections for Lorentz and polarization factors, a semiempirical correction for absorption[17] was applied (maximum and minimum values of the transmission factor were 1.00 and 0.30). The structure was solved by routine application of Patterson and Fourier techniques and refined by full-matrix least-squares procedures, minimizing the quantity $\Sigma w(\Delta F)^2$ with $w^{-1} = [\sigma^2(F_o) + (0.02F_o)^2 + 1]$ where σ is derived from counting statistics. Thermal vibrations were treated anisotropically only for the Pt and Cl atoms of the complex. The H atoms were added in calculated positions and included but not refined in the last refinement cycles with an isotropic thermal parameter 1.2 times larger than those of the carrier atoms. A molecule of

CH_2Cl_2 was located in a difference electron density map. Its non-hydrogen atoms were refined isotropically owing to the high values of the final thermal parameters. Atomic scattering factors were taken from ref. 18. All calculations, carried out on a Vax 750 at the Centro Interdipartimentale di Metodologie Chimico-Fisiche of the University of Naples, were performed with the Enraf-Nonius (SDP) set of programs.[19] Final atomic parameters are listed in Table 7.

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

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