Acetylenes attached to Poly(pentafluorophenyl)platinum(II) Moieties. Syntheses and Molecular Structures of *cis*-$[Pt(C_6F_5)_2(PhC{\equiv}CPh)_2]$ and $[NBu^n_4][Pt(C_6F_5)_3(PhC{\equiv}CPh)]$ *

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The complexes *cis*-$[Pt(C_6F_5)_2(RC{\equiv}CR)_2]$ (R = Et **1a** or Ph **1b**) have been prepared by treating *cis*-$[Pt(C_6F_5)_2(thf)_2]$ (thf = tetrahydrofuran) with the appropriate alkyne. They undergo facile ligand exchange with either *cis*-$[Pt(C_6F_5)_2(thf)_2]$ or $[NBu^n_4]_2[Pt(C_6F_5)_4]$ giving rise respectively to neutral *cis*-$[Pt(C_6F_5)_2(thf)(RC{\equiv}CR)]$ **2** or anionic $[NBu^n_4][Pt(C_6F_5)_3(PhC{\equiv}CPh)]$ **7b** mono(η^2-alkyne) derivatives. A series of mono(η^2-alkyne) complexes of formulae *cis*-$[Pt(C_6F_5)_2L(RC{\equiv}CR)]$ (L = pyridine **3a**, **3b**; PPh_3 **4a**; $SbPh_3$ **5b**; or CO **6a**, **6b**) and $[N(PPh_3)_2][Pt(C_6F_5)_3(EtC{\equiv}CEt)]$ **7a** has also been prepared. None of these complexes except **7b** shows $\nu(C{\equiv}C)$ absorptions in their IR spectra. The molecular structures of complexes **1b** and **7b** have been established by X-ray diffraction studies: **1b**, monoclinic, space group $C2/c$, $a = 19.177(4)$, $b = 8.4971(4)$, $c = 19.790(3)$ Å, $\beta = 103.297(14)°$ and $Z = 4$ (C_2 symmetry imposed); **7b**, monoclinic, space group $P2_1/c$, $a = 10.5179(9)$, $b = 17.5834(20)$, $c = 25.369(5)$ Å, $\beta = 99.376(11)°$ and $Z = 4$. Parameters within the acetylene moiety of **1b** suggest that the platinum→alkyne π-back bonding is minimal.

Transition metal–acetylene complexes form a well defined area of study in organometallic chemistry, the interest in which can be ascribed to the wide variety of chemical processes undergone by alkynes when attached to mono- or poly-nuclear metal fragments[1] as well as to the richness of their co-ordination modes.[2]

In contrast to the plethora of olefin complexes of platinum(II) presently known, the number of simple platinum(II) mono(acetylene) derivatives is more limited.[3] This is primarily due to the activity shown by some platinum(II) complexes in effecting oligo- or poly-merization of acetylenes,[4] including cyclization processes,[5] and to the ability of alkynes to insert into Pt–E bonds (E = halide,[6] H[7] or alkyl[8]). Since $M{-}C_6F_5$ bonds are usually reluctant to undergo insertion reactions,[9] the choice of pentafluorophenyl derivatives as starting materials to prepare stable platinum(II) acetylene complexes seemed appropriate. Accordingly, we here report the synthesis of the first bis(η^2-alkyne)platinum(II) complexes and that of a number of mono(η^2-alkyne)platinum(II) complexes. Some of the results have been briefly communicated.[10]

Results and Discussion

The complex *cis*-$[Pt(C_6F_5)_2(thf)_2]$ (thf = tetrahydrofuran) reacts either with hex-3-yne or with diphenylacetylene in 1:2 molar ratio to give in high yields the bis(η^2-alkyne) complexes *cis*-$[Pt(C_6F_5)_2(RC{\equiv}CR)_2]$ (R = Et **1a** or Ph **1b**) as white, air-stable solids [equation (1)]. Analytical and relevant spectroscopic data are collected in Tables 1 and 2 respectively. Fluorine-19 NMR spectroscopy reveals that the two C_6F_5 groups in **1a** are equivalent ([^{2}H]chloroform, room temperature). No good-quality ^{19}F NMR spectrum of **1b** could be registered owing to its very low solubility in common non-co-ordinating solvents. The IR spectra of complexes **1a** and **1b** show the presence of two very strong, sharp absorptions at about 800 cm^{-1} assignable to the X-sensitive mode of the C_6F_5 group.[12] This observation suggests a *cis* geometry for **1a** and **1b**. Despite the fact that in symmetrically substituted alkynes $\nu(C{\equiv}C)$ becomes IR active on co-ordination,[13] no absorption attributable to this vibration mode has been observed for **1a** and **1b** in the typical 2050–1600 cm^{-1} region. Since $\nu(C{\equiv}C)$ usually provides valuable information about the metal–alkyne bonding mode, its absence in the IR spectra of **1a** and **1b** prompted us to establish the molecular structure of one of these complexes by X-ray diffraction.

$$cis\text{-}[Pt(C_6F_5)_2(thf)_2] + 2RC{\equiv}CR \longrightarrow \underset{\mathbf{1}}{cis\text{-}[Pt(C_6F_5)_2(RC{\equiv}CR)_2]} \quad (1)$$

An ORTEP diagram of complex **1b** is shown in Fig. 1, and bond lengths and angles are collected in Table 3. The molecule possesses a crystallographically imposed C_2 axis bisecting, and in the plane of, the C(1)–Pt–C(1′) angle. The Pt atom is in an almost square-planar environment formed by the C_{ipso} atoms of the C_6F_5 groups and the midpoints of the C(13)≡C(14) and C(13′)≡C(14′) triple bonds, the latter adopting orientations essentially perpendicular to the co-ordination plane. The most interesting structural features of **1b** are those concerned with the diphenylacetylene unit: first, the acetylenic C(13)≡C(14) bond distance [1.203(7) Å] is almost identical to that reported for the free ligand[14] (1.19 Å); and secondly the phenyl substituents scarcely deviate from linearity [C(12)–C(13)–C(14) 167.3(5), C(13)–C(14)–C(15) 165.5(5)°]. The small distortion suffered by the diphenylacetylene molecule on co-ordination to the '*cis*-$Pt(C_6F_5)_2$' moiety points to the existence of negligible platinum→alkyne π-back bonding in **1b**. The very high ν(CO) stretching frequencies (2173 and 2152 cm^{-1}) exhibited by the related complex *cis*-$[Pt(C_6F_5)_2(CO)_2]$[15] are also consistent with this hypothesis and further suggest that the Pt atom in the

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

Table 1 Analytical results and final yields obtained for complexes **1**–**7**

Compound	Analysis (%) N	C	H	Yield (%)
1a *cis*-$[Pt(C_6F_5)_2(EtC\equiv CEt)_2]$	—	41.7 (41.6)	2.8 (2.9)	84
1b *cis*-$[Pt(C_6F_5)_2(PhC\equiv CPh)_2]$	—	53.6 (54.2)	2.3 (2.3)	71
2a *cis*-$[Pt(C_6F_5)_2(thf)(EtC\equiv CEt)]$	—	38.3 (38.7)	2.5 (2.6)	65
2b *cis*-$[Pt(C_6F_5)_2(thf)(PhC\equiv CPh)]$	—	45.3 (46.2)	2.3 (2.3)	96
3a *cis*-$[Pt(C_6F_5)_2(py)(EtC\equiv CEt)]$	1.9 (2.0)	39.3 (40.0)	2.1 (2.2)	61
3b *cis*-$[Pt(C_6F_5)_2(py)(PhC\equiv CPh)]$	1.9 (1.8)	47.6 (47.3)	1.9 (1.9)	74
4a *cis*-$[Pt(C_6F_5)_2(PPh_3)(EtC\equiv CEt)]$	—	50.2 (49.5)	3.1 (2.9)	57
5b *cis*-$[Pt(C_6F_5)_2(SbPh_3)(PhC\equiv CPh)]$	—	49.4 (49.8)	2.4 (2.4)	65
6a *cis*-$[Pt(C_6F_5)_2(CO)(EtC\equiv CEt)]$	—	35.2 (35.7)	1.7 (1.6)	73
6b *cis*-$[Pt(C_6F_5)_2(CO)(PhC\equiv CPh)]$	—	44.1 (44.1)	1.4 (1.4)	61
7a $[N(PPh_3)_2][Pt(C_6F_5)_3(EtC\equiv CEt)]$	1.3 (1.0)	54.1 (54.7)	3.1 (3.1)	65

Table 2 Fluorine-19 NMR[a] and relevant IR[b] data for complexes **1**–**7**

	IR		^{19}F (δ)		
Compound	ν(CO)	X-Sensitive	*o*-F	*m*-F	*p*-F
1a	—	806, 795	−121.6 (385)	−164.6	−161.6
1b	—	805, 795	*c*	*c*	*c*
2a	—	814, 805, 802		−164.3, −165.6	−161.1, −162.8
2b	—	814, 798	−121.0 (418)[d]	−163.7, −165.5	−160.0, −162.2
3a	—	807, 795	−121.4 (440), −121.9 (397)	−164.7, −165.7	−162.0, −163.3
3b	—	807, 798	−120.1 (367), −121.3 (422)	−164.1, −165.7	−160.8, −162.7
4a	—	803, 785	−118.2 (397), −121.1 (301)	−164.4, −165.2	−162.2, −163.5
5b	—	798, 784	−116.4 (404), −119.2 (331)	−164.3[e]	−161.6[e]
6a	2110	807, 798	−119.2 (395), −121.8 (323)	−163.4, −163.6	−158.9, −159.1
6b	2129	809, 798	−118.7 (394), −120.3 (315)	−163.1, −164.1	−153.2, −159.0
7a	—	795, 781w, 770	−118.2 (513), −120.1 (322)[f]	−167.8, −167.6	−166.8[g]
7b	—	800, 783w, 758[h]	−118.5[d] (290, 480)[i]	−166.6, −167.2[i]	−165.8[g]

[a] δ values are referred to $CFCl_3$, $^3J(^{195}Pt–F)$, in parentheses, are given in Hz; solvent $[^2H]$chloroform. [b] Values in cm^{-1}. Unless stated otherwise the absorptions listed are strong in intensity. [c] Not soluble enough in $[^2H]$chloroform. [d] Every *o*-F is isochronous. [e] Superposition of the two signals expected for each of the *m*- and *p*-F respectively seems to occur. [f] Relative intensity 1:2. [g] Every *p*-F is isochronous. [h] Ref. 11. [i] Relative intensity 2:1.

'*cis*-$Pt(C_6F_5)_2$' fragment acts as a good σ-acceptor and a poor π-donor centre. In comparison, the geometries of diphenylacetylene in $[\{Mo^{IV}Cl_4(PhC\equiv CPh)\}_2]$ [d(C≡C) 1.331(5) Å, C–C≡C 146.2(4)°][16] and $[Re^{V}MeO_2(PhC\equiv CPh)]$ [d(C≡C) 1.280(9) Å; C–C≡C 141.8(7), 146.9(7)°][17] reveal extensive distortion even though in these complexes the metal centres are in rather high oxidation states.

Complexes **1a** and **1b** reacted with an equimolar amount of *cis*-$[Pt(C_6F_5)_2(thf)_2]$ to give *cis*-$[Pt(C_6F_5)_2(thf)(RC\equiv CR)]$ **2** as the result of a facile ligand-exchange process [equation (2)].

$$\underset{\mathbf{1}}{cis\text{-}[Pt(C_6F_5)_2(RC\equiv CR)_2]} + cis\text{-}[Pt(C_6F_5)_2(thf)_2] \longrightarrow \underset{\mathbf{2}}{2\,cis\text{-}[Pt(C_6F_5)_2(thf)(RC\equiv CR)]} \quad (2)$$

The reaction products, **2a** and **2b**, can be isolated in high yields as white, air-stable solids and proved to be suitable precursors in the synthesis of a number of mono(η^2-alkyne) complexes. Thus, addition of a stoichiometric amount of a typical monodentate ligand such as pyridine (py), PPh_3 or $SbPh_3$ (L) results in ready displacement of thf and formation of *cis*-$[Pt(C_6F_5)_2L(RC\equiv CR)]$ [equation (3): R = Et, L = py **3a** or

$$\mathbf{2} + L \longrightarrow cis\text{-}[Pt(C_6F_5)_2L(RC\equiv CR)] \quad (3)$$

PPh_3 **4a**; R = Ph, L = py **3b** or $SbPh_3$ **5b**]. Conversely, the analogous complexes *cis*-$[Pt(C_6F_5)_2(CO)(RC\equiv CR)]$ **6** can be prepared from the monocarbonyl complex *cis*-$[Pt(C_6F_5)_2(CO)(thf)]$[18] by reaction with the appropriate alkyne [equation (4)].

$$cis\text{-}[Pt(C_6F_5)_2(CO)(thf)] + RC\equiv CR \longrightarrow \underset{\mathbf{6}}{cis\text{-}[Pt(C_6F_5)_2(CO)(RC\equiv CR)]} \quad (4)$$

Analytical data for the neutral mono(η^2-alkyne) complexes **2**–**6** are listed in Table 1 and ^{19}F NMR and important IR spectroscopic features in Table 2. All these complexes show a double absorption in their IR spectra corresponding to the X-sensitive mode of the C_6F_5 group. It is in principle not possible to elucidate from this observation whether the complexes have a *cis* (C_s) or a *trans* (C_{2v}) geometry, as both of these should give rise to two IR-active X-sensitive vibration modes (C_s, 2A′; C_{2v}, A_1 + B_1). Nevertheless, the earlier synthesis of a series of related neutral or anionic monocarbonyl complexes $[Pt(C_6F_5)_2(CO)L]^{n-}$ (n = 0 or 1) as both their *cis* and *trans* isomers[19] led us to observe that the relative intensities of the two absorptions due to the X-sensitive modes of the C_6F_5 group greatly differ in each case; while for the *cis* isomers they are of almost equal intensity, for the *trans* isomers one appears as a very weak band if observable at all. The presence of two absorptions assignable to the X-sensitive modes of the C_6F_5 groups for **2**–**6** suggests, therefore, a *cis* structure; moreover, the ^{19}F NMR spectra show the presence of two inequivalent C_6F_5 groups, which unequivocally imply a *cis* geometry for all these compounds.

Attempts to displace the labile thf ligand in complex **2** by SC_4H_8 also result in alkyne substitution and formation of the known[20] tetrahydrothiophene-bridged binuclear complex $[\{Pt(\mu\text{-}SC_4H_8)(C_6F_5)_2\}_2]$ [equation (5)].

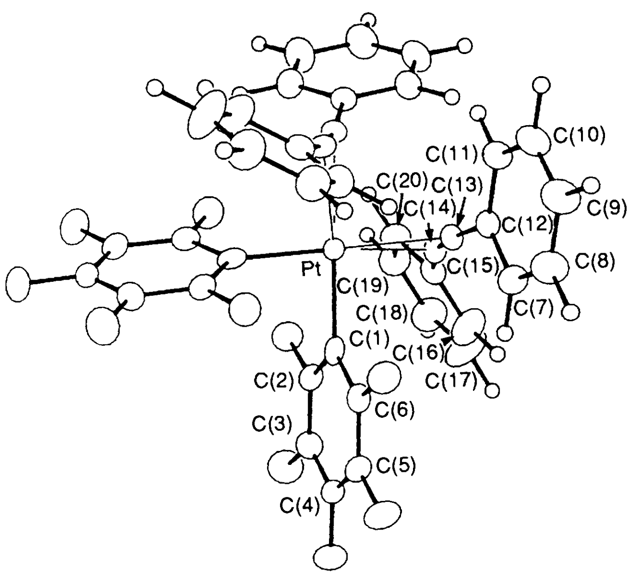

Fig. 1 Molecular structure of complex **1b** with the atom numbering scheme

Table 3 Selected interatomic distances (Å) and interbond angles (°) for complexes **1b** and **7b***

1b		**7b**	
Pt–C(1)	2.025(5)	Pt–C(11)	2.206(7)
Pt–C(13)	2.311(5)	Pt–C(12)	2.186(7)
Pt–C(14)	2.269(5)	Pt–C(21)	2.009(7)
C(12)–C(13)	1.451(6)	Pt–C(31)	2.074(8)
C(13)–C(14)	1.203(7)	Pt–C(41)	2.078(7)
C(14)–C(15)	1.440(7)	C(11)–C(111)	1.444(9)
		C(11)–C(12)	1.233(10)
		C(12)–C(121)	1.441(9)
C(1)–Pt–C(13)	96.01(19)	C(11)–Pt–C(12)	32.6(3)
C(1)–Pt–C(14)	85.04(20)	C(11)–Pt–C(21)	167.4(3)
C(1)–Pt–C(1′)	86.38(21)	C(11)–Pt–C(31)	90.4(3)
C(1)–Pt–C(13′)	168.68(19)	C(11)–Pt–C(41)	93.2(3)
C(1)–Pt–C(14′)	160.67(20)	C(12)–Pt–C(21)	159.9(3)
C(13)–Pt–C(14)	30.45(18)	C(12)–Pt–C(31)	98.0(3)
C(13)–Pt–C(13′)	83.82(18)	C(12)–Pt–C(41)	86.8(3)
C(13)–Pt–C(14′)	89.26(18)	C(21)–Pt–C(31)	87.4(3)
Pt–C(1)–C(2)	123.2(4)	C(21)–Pt–C(41)	88.4(3)
Pt–C(1)–C(6)	121.0(4)	C(31)–Pt–C(41)	175.2(3)
C(2)–C(1)–C(6)	115.8(5)	Pt–C(11)–C(111)	127.9(5)
Pt–C(13)–C(12)	119.6(3)	Pt–C(11)–C(12)	72.8(5)
Pt–C(13)–C(14)	72.9(3)	C(111)–C(11)–C(12)	159.3(7)
C(12)–C(13)–C(14)	167.3(5)	Pt–C(12)–C(11)	74.6(5)
Pt–C(14)–C(13)	76.7(4)	Pt–C(12)–C(121)	126.8(5)
Pt–C(14)–C(15)	116.3(3)	C(11)–C(12)–C(121)	158.6(7)
C(13)–C(14)–C(15)	165.5(5)		

* The dihedral angles formed by the phenyl rings of the acetylenes in complexes **1b** and **7b** are 34.3 and 21.6° respectively.

$$\underset{\mathbf{2}}{cis\text{-}[Pt(C_6F_5)_2(RC{\equiv}CR)(thf)]} + SC_4H_8 \longrightarrow 0.5[\{Pt(\mu\text{-}SC_4H_8)(C_6F_5)_2\}_2] \quad (5)$$

The reaction of complex **1b** with $[NBu^n_4]_2[Pt(C_6F_5)_4]$ to give $[NBu^n_4][Pt(C_6F_5)_3(PhC{\equiv}CPh)]$ **7b**[11] [equation (6)]

$$\underset{\mathbf{1b}}{cis\text{-}[Pt(C_6F_5)_2(PhC{\equiv}CPh)_2]} + [NBu^n_4]_2[Pt(C_6F_5)_4] \longrightarrow \underset{\mathbf{7b}}{2[NBu^n_4][Pt(C_6F_5)_3(PhC{\equiv}CPh)]} \quad (6)$$

provides a further example of the ability of **1** to undergo ligand-exchange processes. The capacity of $[NBu^n_4]_2[Pt(C_6F_5)_4]$ to act as an arylating agent in similar cases has already been documented.[21]

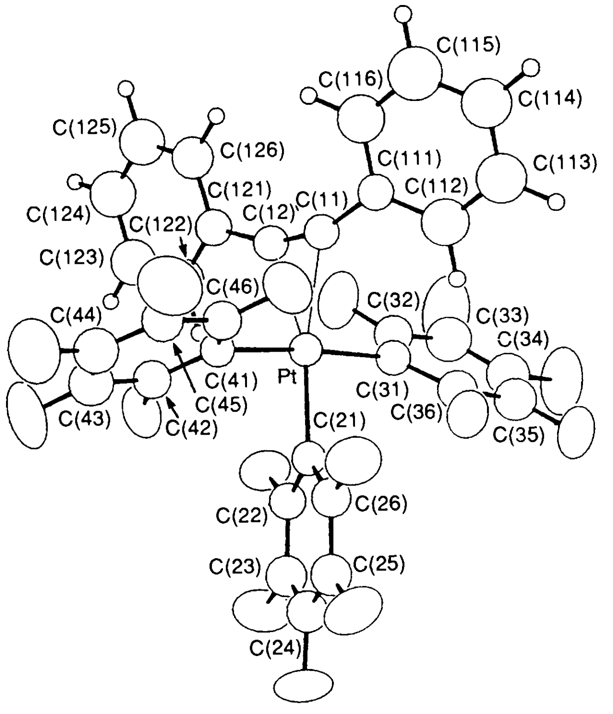

Fig. 2 Molecular structure of the anion in complex **7b** with the atom numbering scheme

Complexes **7a** and **7b** can best be obtained by simple halide substitution of $Q_2[Pt(C_6F_5)_3Cl]$ by the incoming alkyne, achieved in the presence of $NaClO_4$ [equation (7): R = Et,

$$Q_2[Pt(C_6F_5)_3Cl] + NaClO_4{\cdot}H_2O + RC{\equiv}CR \longrightarrow Q_2[Pt(C_6F_5)_3(RC{\equiv}CR)] \quad (7)$$

$Q = N(PPh_3)_2$ **7a**; R = Ph, $Q = NBu^n_4$ **7b**]. This method is similar to that first reported for the synthesis of **7b**.[11] Analytical results (**7a**) and relevant IR and NMR spectroscopic data (**7a**, **7b**) are collected in Tables 1 and 2 respectively. As reported for **7b**, the IR spectrum of **7a** shows three absorptions assignable to the X-sensitive modes of the C_6F_5 groups in agreement with the IR-active ν(M–C) vibration modes predicted by group theory (C_{2v}: $2A_1 + B_1$). No absorption assignable to the ν(C≡C) stretching mode was, nevertheless, observed. The ^{19}F NMR spectra of complexes **7a** and **7b** imply the presence of two inequivalent C_6F_5 groups in each compound. The resonances due to *o*-F are the most significant because at this position coupling to platinum can be observed. In this context, the much higher values of $^3J(^{195}Pt\text{–}F)$ associated with each C_6F_5 group *trans* to the alkyne ligand can be related to the notoriously low *trans* influence of η^2-co-ordinated alkynes.[22]

The molecular structure of complex **7b** has been determined by X-ray diffraction analysis. Fig. 2 shows an ORTEP view of the $[Pt(C_6F_5)_3(PhC{\equiv}CPh)]^-$ anion and the most important structural parameters are listed in Table 3. The Pt atom is located in an almost square-planar environment. The fact that the Pt–C(21) bond distance [2.009(7) Å] is considerably shorter than the corresponding Pt–C(31) and Pt–C(41) bond lengths [2.074(8) and 2.078(7) Å respectively] can be assigned to the low *trans* influence of diphenylacetylene, in agreement with our earlier spectroscopic observations. Again the C≡C vector is orientated essentially perpendicular to the local platinum square plane. The acetylenic C(11)–C(12) distance [1.233(10) Å] is longer than in the free ligand (1.19 Å)[14] and the phenyl substituents deviate appreciably from linearity [C(111)–C(11)–C(12) 159.3(7), C(11)–C(12)–C(121) 158.6(7)°],

Table 4 Crystal data and details of data collection and refinement

Complex	**1b**	**7b**
Formula	$C_{40}H_{20}F_{10}Pt$	$C_{48}H_{46}F_{15}NPt$
M	885.57	1116.81
System	Monoclinic	Monoclinic
Space group	C_2/c	$P2_1/c$
a/Å	19.177(4)	10.5179(9)
b/Å	8.4971(14)	17.5834(20)
c/Å	19.790(3)	25.369(5)
β/°	103.297(14)	99.376(11)
U/Å^3	3183.23	4628.9
T/K	185	273
Z	4 (C_2 symmetry imposed)	4 ion pairs
D_c/g cm^{-3}	1.874	1.602
μ(Mo-Kα)/cm^{-1}	46.04	31.53
F(000)	1712	2216
θ(orientation)/°	14–15	13–15
θ(data)/°	1–25	1–30
Scan speed/° min^{-1}	0.92–2.35	0.82–2.35
Data collection/h	43	140
Unique data	2763	7684
Observed data	2517 [$F > 6\sigma(F)$]	4799 [$F > 2\sigma(F)$]
U_H/Å^2	0.0677(8)	0.157(13) (Ph), 0.064(8) (α-CH_2), 0.082(9) (β-CH_2), 0.088(10) (γ-CH_2), 0.181(15) (Me)
g	0.002 027	0.000 337
R	0.0323	0.0414
R'	0.0442	0.0469
S	0.737	1.216
Maximum, minimum residue/e Å^{-3}	2.72, −1.75	0.99, −0.56

thus suggesting a higher degree of platinum→alkyne π-back bonding in **7b** in comparison with **1b**. This difference can be attributed to the anionic nature of the '$Pt(C_6F_5)_3$' moiety in **7b** which enhances the basic character of the platinum centre. On going to the limit in the range of basicity, L_nPt^0 fragments are known to effect much more extensive distortions to co-ordinated alkynes than L_nPt^{II} fragments.[3] According to the concept of synergism, an increase in the platinum→alkyne π-back bonding should lead to a reinforcement of the whole platinum–alkyne bond. This expectation finds support in the fact that the Pt–C(11) and Pt–C(12) bond distances in **7b** [2.206(7) and 2.186(7) Å respectively] are considerably shorter than the corresponding Pt–C(13) and Pt–C(14) bond lengths in **1b** [2.311(5) and 2.269(5) Å respectively].

Experimental

Infrared and ^{19}F NMR spectra were recorded, and C, H and N analyses, molecular weight and conductance measurements were performed as described elsewhere.[20] The complexes *cis*-$[Pt(C_6F_5)_2(thf)_2]$,[19] *cis*-$[Pt(C_6F_5)_2(CO)(thf)]$,[18] $[NBu^n_4]_2[Pt(C_6F_5)_4]$,[23] and $Q_2[Pt(C_6F_5)_3Cl]$ [Q = NBu^n_4 or $N(PPh_3)_2$][11] were prepared according to literature methods.

cis-*Bis*(η^2-*hex*-3-*yne*)*bis*(*pentafluorophenyl*)*platinum* **1a**.—A suspension of *cis*-$[Pt(C_6F_5)_2(thf)_2]$ (0.5 g, 0.74 mmol) in neat hex-3-yne (1 cm^3) was stirred at room temperature for 19 min and the product filtered off. The white solid was identified as complex **1a** (0.43 g).

cis-*Bis*(η^2-*diphenylacetylene*)*bis*(*pentafluorophenyl*)*platinum* **1b**.—To a solution of *cis*-$[Pt(C_6F_5)_2(thf)_2]$ (0.17 g, 0.25 mmol) in CH_2Cl_2 (20 cm^3) was added PhC≡CPh (0.1 g, 0.56 mmol) and the mixture stirred at room temperature for 10 min, after which time it was evaporated to dryness. Treatment of the residue with hexane gave a yellow solid, which was filtered off and identified as complex **1b** (0.16 g).

Suitable crystals for X-ray diffraction study were obtained by overlying an hexane solution of PhC≡CPh on a CH_2Cl_2 solution of *cis*-$[Pt(C_6F_5)_2(thf)_2]$ in molar ratio 2:1.

Table 5 Coordinates of non-hydrogen atoms for compound **1b**

Atom	x	y	z
Pt	0.500 00	0.456 61(3)	0.750 00
F(1)	0.458 49(17)	0.688 0(4)	0.619 75(16)
F(2)	0.363 17(21)	0.923 2(5)	0.590 36(20)
F(3)	0.279 59(20)	0.995 4(5)	0.679 49(22)
F(4)	0.290 29(19)	0.826 2(4)	0.797 00(20)
F(5)	0.386 50(19)	0.593 0(4)	0.828 64(17)
C(1)	0.426 3(3)	0.630 4(6)	0.724 93(25)
C(2)	0.417 5(3)	0.718 0(6)	0.665 5(3)
C(3)	0.369 1(3)	0.840 2(6)	0.649 7(3)
C(4)	0.325 8(3)	0.877 3(6)	0.693 7(3)
C(5)	0.332 0(3)	0.791 7(6)	0.753 4(3)
C(6)	0.382 1(3)	0.669 7(6)	0.768 92(25)
C(7)	0.359 64(18)	0.238 1(4)	0.843 07(19)
C(8)	0.352 29(18)	0.168 2(4)	0.904 83(19)
C(9)	0.395 33(18)	0.040 4(4)	0.932 07(19)
C(10)	0.445 71(18)	−0.017 5(4)	0.897 53(19)
C(11)	0.453 05(18)	0.052 4(4)	0.835 77(19)
C(12)	0.410 01(18)	0.180 2(4)	0.808 53(19)
C(13)	0.418 5(3)	0.254 2(6)	0.744 8(3)
C(14)	0.413 6(3)	0.299 6(6)	0.686 3(3)
C(15)	0.389 89(17)	0.338 1(6)	0.613 77(17)
C(16)	0.318 30(17)	0.380 6(6)	0.588 96(17)
C(17)	0.293 30(17)	0.422 2(6)	0.519 41(17)
C(18)	0.339 88(17)	0.421 4(6)	0.474 66(17)
C(19)	0.411 47(17)	0.378 9(6)	0.499 47(17)
C(20)	0.436 48(17)	0.337 3(6)	0.569 02(17)

cis-(η^2-*Hex*-3-*yne*)*bis*(*pentafluorophenyl*)(*tetrahydrofuran*)-*platinum* **2a**.—An equimolar mixture of complex **1a** (0.39 g, 0.57 mmol) and *cis*-$[Pt(C_6F_5)_2(thf)_2]$ (0.39 g, 0.52 mmol) was dissolved in $CHCl_3$ (20 cm^3). The resulting solution was immediately evaporated to dryness and the yellow residue extracted in hexane (60 cm^3). By concentrating the hexane solution (to 10 cm^3) and standing overnight at −30 °C a white solid separated which was identified as complex **2a** (0.5 g).

cis-(η^2-*Diphenylacetylene*)*bis*(*pentafluorophenyl*)(*tetrahydrofuran*)*platinum* **2b**.—Addition of *cis*-$[Pt(C_6F_5)_2(thf)_2]$ (0.2 g,

Table 6 Coordinates of non-hydrogen atoms of compound **7b**

Atom	*x*	*y*	*z*
Pt	0.268 93(3)	0.245 96(2)	0.037 03(1)
C(11)	0.071 9(7)	0.232 0(4)	−0.007 4(3)
C(111)	−0.031 1(4)	0.287 3(3)	−0.014 79(22)
C(112)	−0.008 9(4)	0.365 5(3)	−0.013 55(22)
C(113)	−0.112 2(4)	0.416 0(3)	−0.024 47(22)
C(114)	−0.237 7(4)	0.388 2(3)	−0.036 64(22)
C(115)	−0.260 0(4)	0.310 0(3)	−0.037 88(22)
C(116)	−0.156 7(4)	0.259 5(3)	−0.026 95(22)
C(12)	0.129 1(7)	0.171 6(4)	−0.011 1(3)
C(121)	0.149 6(5)	0.094 15(24)	−0.026 30(22)
C(122)	0.272 9(5)	0.062 65(24)	−0.019 97(22)
C(123)	0.290 0(5)	−0.011 44(24)	−0.037 19(22)
C(124)	0.184 0(5)	−0.054 02(24)	−0.060 75(22)
C(125)	0.060 7(5)	−0.022 52(24)	−0.067 10(22)
C(126)	0.043 5(5)	0.051 56(24)	−0.049 88(22)
C(21)	0.434 1(7)	0.281 1(4)	0.081 7(3)
C(22)	0.553 0(7)	0.254 5(4)	0.074 6(3)
C(23)	0.669 5(9)	0.275 8(5)	0.106 5(4)
C(24)	0.665 8(8)	0.325 6(5)	0.146 9(4)
C(25)	0.554 0(8)	0.355 8(5)	0.155 3(4)
C(26)	0.439 0(8)	0.332 8(4)	0.123 0(3)
F(22)	0.561 0(4)	0.202 3(3)	0.035 84(21)
F(23)	0.780 1(4)	0.243 8(3)	0.098 41(25)
F(24)	0.777 7(5)	0.344 4(4)	0.179 46(24)
F(25)	0.548 3(6)	0.405 5(3)	0.195 29(21)
F(26)	0.328 2(5)	0.363 1(3)	0.135 39(21)
C(31)	0.318 5(7)	0.311 3(4)	−0.024 6(3)
C(32)	0.334 7(8)	0.283 6(5)	−0.073 0(4)
C(33)	0.368 3(10)	0.325 2(6)	−0.114 4(4)
C(34)	0.397 9(9)	0.400 3(5)	−0.105 2(4)
C(35)	0.383 4(9)	0.433 0(5)	−0.059 2(4)
C(36)	0.341 2(8)	0.388 3(5)	−0.019 2(3)
F(32)	0.311 2(6)	0.208 5(3)	−0.085 30(20)
F(33)	0.376 7(8)	0.294 6(4)	−0.162 51(24)
F(34)	0.433 2(7)	0.443 7(4)	−0.145 4(3)
F(35)	0.404 6(6)	0.508 4(3)	−0.050 52(24)
F(36)	0.322 8(5)	0.424 60(25)	0.026 28(20)
C(41)	0.227 7(7)	0.187 1(4)	0.103 2(3)
C(42)	0.297 8(8)	0.127 4(4)	0.126 2(3)
C(43)	0.275 3(9)	0.089 8(5)	0.171 4(4)
C(44)	0.168 6(9)	0.113 3(5)	0.195 4(4)
C(45)	0.098 7(8)	0.172 2(5)	0.173 4(3)
C(46)	0.128 1(8)	0.208 5(4)	0.128 5(3)
F(42)	0.404 1(5)	0.101 6(3)	0.106 71(20)
F(43)	0.348 9(6)	0.031 8(3)	0.194 02(25)
F(44)	0.141 4(6)	0.076 2(4)	0.238 67(25)
F(45)	−0.004 9(5)	0.195 2(4)	0.195 47(22)
F(46)	0.051 3(5)	0.267 3(3)	0.109 35(20)
N	0.220 2(7)	0.443 7(4)	0.276 4(3)
C(51)	0.170 1(8)	0.432 2(5)	0.217 4(4)
C(52)	0.044 5(9)	0.466 8(5)	0.196 5(4)
C(53)	0.013 9(11)	0.458 0(6)	0.138 6(5)
C(54)	−0.112 2(11)	0.497 1(7)	0.113 7(5)
C(61)	0.231 3(8)	0.527 4(4)	0.289 4(3)
C(62)	0.315 3(9)	0.571 9(5)	0.258 1(4)
C(63)	0.340 5(10)	0.652 7(5)	0.280 3(4)
C(64)	0.422 4(11)	0.700 0(7)	0.247 6(5)
C(71)	0.350 4(8)	0.405 0(5)	0.289 8(4)
C(72)	0.425 3(8)	0.419 8(5)	0.344 2(4)
C(73)	0.552 2(9)	0.373 9(6)	0.350 3(4)
C(74)	0.634 3(12)	0.393 4(7)	0.404 3(5)
C(81)	0.126 1(8)	0.411 6(5)	0.310 6(4)
C(82)	0.090 7(10)	0.329 0(5)	0.301 3(4)
C(83)	−0.009 9(11)	0.304 1(6)	0.335 7(4)
C(84)	−0.037 7(14)	0.221 0(8)	0.331 3(6)

0.30 mmol) to a suspension of complex **1b** (0.27 g, 0.30 mmol) in $CHCl_3$ (20 cm^3) caused the white solid to dissolve. The solution was then evaporated to dryness and the residue treated with hexane. A white solid was afforded which was identified as complex **2b** (0.45 g).

cis-(η^2-*Hex*-3-*yne*)*bis*(*pentafluorophenyl*)(*pyridine*)*platinum* **3a**.—Addition of pyridine (23.5 µl, 0.29 mmol) to a solution of complex **2a** (0.2 g, 0.29 mmol) in $CHCl_3$ (20 cm^3) at −30 °C and subsequent evaporation to dryness gave a white solid which, on further recrystallization ($CHCl_3$–hexane, −30 °C), rendered yellow crystals of complex **3a** (0.12 g).

cis-(η^2-*Diphenylacetylene*)*bis*(*pentafluorophenyl*)(*pyridine*)*platinum* **3b**.—To a solution of complex **2b** (0.2 g, 0.25 mmol) in $CHCl_3$ (5 cm^3) was added pyridine (20.2 µl, 0.25 mmol). After 5 min of stirring the solvent was evaporated to dryness. On treating the residue with hexane a white solid formed which was recrystallized from $CHCl_3$–hexane at −30 °C. Eventually a white solid was obtained, identified as complex **3b** (0.15 g).

cis-(η^2-*Hex*-3-*yne*)*bis*(*pentafluorophenyl*)(*triphenylphosphine*)*platinum* **4a**.—The synthesis was performed as described for complex **3a** starting from **2a** (0.2 g, 0.29 mmol) and PPh_3 (77 mg, 0.29 mmol). After recrystallization, **4a** was obtained as a white solid.

cis-(η^2-*Diphenylacetylene*)*bis*(*pentafluorophenyl*)(*triphenylstibine*)*platinum* **5b**.—The synthesis was performed as described for complex **3b** starting from **2b** (0.2 g, 0.25 mmol) and $SbPh_3$ (90 mg, 0.25 mmol). After recrystallization, **5b** was isolated as a yellowish solid.

Reaction of Complex **2** *with* SC_4H_8.—To a solution of complex **2a** (0.15 g, 0.22 mmol) in $CHCl_3$ (20 cm^3) was added SC_4H_8 (19.4 µl, 0.22 mmol) and the mixture stirred at room temperature for 2 d. A white solid precipitated which was filtered off and identified[20] by elemental analyses and IR spectroscopy as $[\{Pt(\mu\text{-}SC_4H_8)(C_6F_5)_2\}_2]$ (0.1 g).

The reaction proceeds analogously starting from complex **2b** (0.2 g, 0.25 mmol) and SC_4H_8 (22.0 µl, 0.25 mmol). After recrystallization (CH_2Cl_2–$CHCl_3$) $[\{Pt(\mu\text{-}SC_4H_8)(C_6F_5)_2\}_2]$ was obtained (0.11 g).

cis-*Carbonyl*(η^2-*hex*-3-*yne*)*bis*(*pentafluorophenyl*)*platinum* **6a**.—To a $CHCl_3$ (10 cm^3) solution of *cis*-$[Pt(C_6F_5)_2(CO)(thf)]$ (0.2 g, 0.32 mmol) was added hex-3-yne (50 µl, 0.44 mmol) and after 5 min of stirring the solvent was evaporated to dryness. The residue was extracted in hexane (15 cm^3), the hexane solution concentrated (to 2 cm^3) and on standing overnight at −30 °C a white solid formed which was identified as complex **6a** (0.15 g).

cis-*Carbonyl*(η^2-*diphenylacetylene*)*bis*(*pentafluorophenyl*)*platinum* **6b**.—The synthesis was performed as described for complex **6a** starting from *cis*-$[Pt(C_6F_5)_2(CO)(thf)]$ (0.17 g, 0.27 mmol) and diphenylacetylene (47.8 mg, 0.27 mmol).

Bis(*triphenylphosphoranylidene*)*ammonium* (η^2-*Hex*-3-*yne*)*tris*(*pentafluorophenyl*)*platinate* **7a**.—To a $CHCl_3$ (20 cm^3) solution of $[N(PPh_3)_2]_2[Pt(C_6F_5)_3Cl]$ (0.5 g, 0.27 mmol) at 0 °C, stoichiometric amounts of $NaClO_4{\cdot}H_2O$ (40 mg, 0.27 mmol) and hex-3-yne (70 µl, 0.27 mmol) were added in order. After 6 h of stirring the solution was filtered and the filtrate evaporated to dryness. On treating the residue with Pr^iOH a white solid formed which, on recrystallization ($CHCl_3$–MeOH, −30 °C), rendered complex **7a** as a white, crystalline solid (0.23 g).

Tetra-n-butylammonium (η^2-*Diphenylacetylene*)*tris*(*pentafluorophenyl*)*platinate* **7b**.—(*a*) The synthesis was performed as described for complex **7a** starting from $[NBu^n_4]_2[Pt(C_6F_5)_3Cl]$ (0.3 g, 0.25 mmol), $NaClO_4{\cdot}H_2O$ (35 mg, 0.25 mmol) and diphenylacetylene (44 mg, 0.25 mmol). The reaction could, nonetheless, be carried out at room temperature and no recrystallization was needed.

(*b*) A CH_2Cl_2 (50 cm^3) solution of complex **1b** (0.2 g, 0.22 mmol) and $[NBu^n_4]_2[Pt(C_6F_5)_4]$ (0.3 g, 0.22 mmol) was stirred at room temperature for 2 d and then evaporated to dryness. By treating the resulting residue with Pr^iOH (10 cm^3) a white solid separated which was filtered off and identified as **7b** (0.31 g).

Crystals suitable for X-ray diffraction were obtained by the slow diffusion of hexane into a $CHCl_3$ solution of complex **7b** at room temperature.

Crystallographic Studies.—All measurements were made on an Enraf-Nonius CAD4 diffractometer fitted with a ULT1 low-temperature device (N_2 stream) and operating with graphite-monochromated Mo-Kα X-radiation ($\bar{\lambda}$ = 0.710 69 Å).

Crystal data and information on intensity data collection and structure refinement for both complexes **1b** and **7b** are given in Table 4. Lattice parameters and orientation matrices were calculated from the least-squares refinement of the setting angles of 25 reflections. Data collection was by ω–2θ scan in 96 steps with a ω scan width of $0.8 + 0.35 \tan\theta$. Structures were solved by Patterson and Fourier-difference methods, and refined by full-matrix least squares.[24] After isotropic convergence empirical absorption corrections[25] were applied. Phenyl rings were refined as regular planar hexagons (C–C 1.395 Å). Hydrogen atoms were introduced in calculated positions, riding on their respective C atoms. Single (**1b**) or multiple (**7b**) group isotropic thermal parameters were refined for H atoms. In the final stages of refinement anisotropic thermal parameters were refined for all non-H atoms (**1b**) or Pt and F atoms only (**7b**). Data were weighted according to $w^{-1} = \sigma^2(F) + gF^2$, with the parameter g as a variable. Atomic coordinates for non-H atoms are in Tables 5 (**1b**) and 6 (**7b**). Computer programs used in addition to those referenced above include CADABS,[26] CALC[27] and EASYORTEP.[28] Atomic scattering factors were taken from ref. 29 or were those inlaid in SHELX 76.

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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References

1 J. P. Collman, L. S. Hegedus, J. R. Norton and R. G. Finke, *Principles and Applications of Organotransition Metal Chemistry*, 2nd edn., University Science Books, Mill Valley, CA, 1987, p. 859; H. Bönnemann, *Angew. Chem., Int. Ed. Engl.*, 1985, **24**, 248; K. P. C. Vollhardt *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 539; S. Otsuka and A. Nakamura, *Adv. Organomet. Chem.*, 1976, **14**, 245.
2 Ch. Elschenbroich and A. Salzer, *Organometallics*, VCH, Weinheim, 1987, p. 272; P. R. Raithby and M. J. Rosales, *Adv. Inorg. Chem. Radiochem.*, 1985, **29**, 169; E. Sappa, A. Tiripicchio and P. Braunstein, *Coord. Chem. Rev.*, 1985, **65**, 219; *Chem. Rev.*, 1983, **83**, 203.
3 F. R. Hartley, in *Comprehensive Organometallic Chemistry*, eds. G. Wilkinson, F. G. A. Stone and E. W. Abel, Pergamon, Oxford, 1982, vol. 6, p. 704.
4 T. G. Appleton, H. C. Clark and R. J. Puddephatt, *Inorg. Chem.*, 1972, **11**, 2074; A. Furlani, I. Collamati and G. Sartori, *J. Organomet. Chem.*, 1969, **17**, 463.
5 F. Canziani, F. Galimberti, L. Garlaschelli, M. C. Malatesta and A. Albinati, *Gazz. Chim. Ital.*, 1982, **112**, 323; F. Canziani and M. C. Malatesta, *J. Organomet. Chem.*, 1975, **90**, 235; F. Canziani, P. Chini, A. Quarta and A. di Martino, *J. Organomet. Chem.*, 1971, **26**, 285.
6 L. Garlaschelli, M. C. Malatesta, S. Panzeri, A. Albinati and F. Ganazzoli, *Organometallics*, 1987, **6**, 63; F. Canziani, L. Garlaschelli, M. C. Malatesta and A. Albinati, *J. Chem. Soc., Dalton Trans.*, 1981, 2395; F. Canziani, L. Garlaschelli and M. C. Malatesta, *J. Organomet. Chem.*, 1978, **146**, 179.
7 A. C. Dema, X. Li, C. M. Lukehart and M. D. Owen, *Organometallics*, 1991, **10**, 1197; E. Baralt, C. M. Lukehart, A. T. McPhail and D. R. McPhail, *Organometallics*, 1991, **10**, 512; X. Li, C. M. Lukehart, A. T. McPhail and D. R. McPhail, *Organometallics*, 1991, **10**, 372; C. M. Lukehart, A. T. McPhail, D. R. McPhail and M. D. Owen, *J. Chem. Soc., Chem. Commun.*, 1990, 215; A. C. Dema, C. M. Lukehart, A. T. McPhail and D. R. McPhail, *J. Am. Chem. Soc.*, 1989, **111**, 7615; C. M. Lukehart, A. T. McPhail, D. R. McPhail, J. B. Myers, jun., and H. K. Soni, *Organometallics*, 1989, **8**, 1007; D. L. Packett, A. Syed and W. C. Trogler, *Organometallics*, 1988, **7**, 159.
8 H. C. Clark, C. R. C. Milne and C. S. Wong, *J. Organomet. Chem.*, 1977, **136**, 265.
9 J. Forniés, B. Menjón, N. Gómez and M. Tomás, *Organometallics*, 1992, **11**, 1187.
10 R. Usón, J. Forniés, M. Tomás, B. Menjón and A. J. Welch, *J. Organomet. Chem.*, 1986, **304**, C24.
11 R. Usón, J. Forniés, M. Tomás and R. Fandos, *J. Organomet. Chem.*, 1984, **263**, 253.
12 R. Usón and J. Forniés, *Adv. Organomet. Chem.*, 1988, **28**, 289 and refs. therein.
13 L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, 2nd edn., Chapman and Hall, London, 1980, vol. 2, p. 80; E. Maslowsky, jun., *Vibrational Spectra of Organometallic Compounds*, Wiley, New York, 1977, p. 260.
14 J. M. Robertson and I. Woodward, *Proc. R. Soc. London*, 1938, **164**, 436.
15 R. Usón, J. Forniés, M. Tomás and B. Menjón, *Organometallics*, 1985, **4**, 1912.
16 I. Pauls, K. Dehnicke and D. Fenske, *Chem. Ber.*, 1989, **122**, 481.
17 J. K. Felixberger, J. G. Kuchler, E. Herdtweck, R. A. Paciello and W. A. Herrmann, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 946.
18 R. Usón, J. Forniés, P. Espinet, C. Fortuño, M. Tomás and A. J. Welch, *J. Chem. Soc., Dalton Trans.*, 1988, 3005.
19 R. Usón, J. Forniés, M. Tomás and B. Menjón, *Organometallics*, 1986, **5**, 1581.
20 R. Usón, J. Forniés, M. Tomás, B. Menjón, R. Navarro and J. Carnicer, *Inorg. Chim. Acta*, 1989, **162**, 33.
21 J. Forniés, R. Navarro, V. Sicilia and M. Tomás, *Organometallics*, 1990, **9**, 2422; J. Forniés, R. Navarro, V. Sicilia, F. Martínez and A. J. Welch, *J. Organomet. Chem.*, 1991, **408**, 425.
22 See ref. 3, p. 706.
23 R. Usón, J. Forniés, F. Martínez and M. Tomás, *J. Chem. Soc., Dalton Trans.*, 1980, 888.
24 SHELX 76, G. M. Sheldrick, University of Cambridge, 1976.
25 DIFABS, N. G. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, 1983, **39**, 158.
26 CADABS, R. O. Gould and D. E. Smith, University of Edinburgh, 1986.
27 CALC, R. O. Gould and P. Taylor, University of Edinburgh, 1986.
28 EASYORTEP, P. D. Mallinson and K. W. Muir, *J. Appl. Crystallogr.*, 1985, **18**, 51.
29 *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4, p. 99.

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