DALTON
FULL PAPER

Preparation and characterisation of neutral double- and mono-alkynyl bridged diplatinum complexes†

Jesús R. Berenguer,[a] Juan Forniés,*[b] Elena Lalinde,*[a] Antonio Martín[b] and Blanca Serrano[a]

[a] *Departamento de Química-Grupo de Síntesis Química de La Rioja, UA-CSIC Universidad de La Rioja, 26001 Logroño, Spain*

[b] *Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza-Consejo Superior de Investigaciones Científicas, 50009 Zaragoza, Spain*

Received 31st May 2001, Accepted 25th July 2001
First published as an Advance Article on the web 5th September 2001

The novel acetylide complexes [*trans*-Pt(C≡CR)$_2$(PPh$_3$)$_2$] [R = (*Z*)-CMe=CHMe **2a** and C(OMe)EtMe **3**] have been prepared starting from [*trans*-Pt{C≡CC(OH)EtMe}$_2$(PPh$_3$)$_2$] **1** by dehydration (**2a**) and etherification (**3**) reactions, respectively. The analogous α-hydroxyacetylide, R = C(OH)Ph$_2$ **4**, has been obtained by reaction of [*cis*-PtCl$_2$(PPh$_3$)$_2$] with HC≡CC(OH)Ph$_2$ in NEt$_2$H, in presence of CuI. These bis(acetylide) complexes react with [*cis*-Pt(C$_6$F$_5$)$_2$(THF)$_2$] leading to symmetrical diplatinum species [*trans*,*trans*-(PPh$_3$)(C$_6$F$_5$)Pt(μ-1κC^{α}:η^2-C≡CR)(μ-2κC^{α}:η^2-C=CR)Pt(C$_6$F$_5$)-(PPh$_3$)] [R = C(OH)EtMe **5**, (*Z*)-CMe=CHMe **6**, C(OMe)EtMe **7**, C(OH)Ph$_2$ **8**] containing a double alkynyl bridging system. Complexes **5** and **7** have been obtained as mixtures of the corresponding *RR*/*SS* and *RS*/*SR* diastereomers (1 : 1 molar ratio). Treatment of **4**–**8** with 2 equivalents of PPh$_3$ produces bridge splitting to yield the corresponding mixed mononuclear derivatives [*trans*-Pt(C≡CR)(C$_6$F$_5$)(PPh$_3$)$_2$] [R = C(OH)EtMe **9**, (*Z*)-CMe=CHMe **10**, C(OMe)-EtMe **11**, C(OH)Ph$_2$ **12**]. Treatment of the hydroxyalkynyl complex **9** with HBF$_4$ in Et$_2$O also produces the dehydrated enynyl derivative **10**. The mononuclear complexes [*trans*-Pt(C≡CR)$_2$(PPh$_3$)$_2$] (**1**, **3**, **4**) react with [*cis*-Pt(C$_6$F$_5$)$_2$(CO)-(THF)] to afford, under alkynylation of the carbonyl fragment "Pt(C$_6$F$_5$)$_2$(CO)", the μ-η^2-acetylide-bridged zwitterionic derivatives [*cis*,*trans*-(CO)(C$_6$F$_5$)$_2$Pt(μ-1κC^{α}:η^2-C≡CR)Pt(C≡CR)(PPh$_3$)$_2$] [R = C(OH)EtMe **13**, C(OMe)EtMe **14**, C(OH)Ph$_2$ **15**]. On the other hand, while the analogous reaction with the bis-enynyl complex **2a** is not clean, the related mixed pentafluorophenyl enynyl complex **10** produces the simple displacement of THF from [*cis*-Pt(C$_6$F$_5$)$_2$(CO)(THF)] by the alkynyl fragment and formation of the adduct [*trans*,*cis*-(PPh$_3$)$_2$(C$_6$F$_5$){μ-1κC^{α}:η^2-C^{3,4}-C≡C-(*Z*)-CMe=CHMe}Pt(C$_6$F$_5$)$_2$(CO)] **16**. The crystal structures of **7**, **8** and **13** have also been determined. For complex **8**, the dimer units are linked *via* unusual intermolecular hydrogen bonds (O–H · · · F–C) leading to an extended polymeric chain along the crystallographic *c* axis.

The chemistry of alkynyl platinum derivatives has been the subject of longstanding interest mainly focused on structure, reactivity and physical properties.[1] In recent years, considerable efforts have been directed towards the preparation of specialty materials including non-linear optical,[2] liquid crystalline[3] or luminescent materials.[4] Platinum σ-acetylide (including diynyl and functionalised ligands) fragments have been employed as building blocks in the synthesis of macrocycles or branched materials (dendrimers)[5] and conjugated metal-containing polymers,[6] which are particularly attractive due to their potentially useful photophysical properties. The additional η^2-coordinating capability of these ligands has also been widely used to construct heteropolymetallic systems[1a,b] which are attractive, not only for their structural richness,[7] but also for their interesting emissive properties.[4b,c,8] As part of our work in this area, we have investigated the factors that govern the final structural disposition of the alkynyl ligands on complexes stabilised by double alkynide-bridging systems (μ-C≡CR)$_2$.[1b,9] We have found that the preferred σ/η^2 coordination sites, obviously related to ligand exchange processes, as well as the final planar or hinged geometries found, are governed by a tuned balance of electronic and steric effects, which can be seen from a distinct influence of metals, coligands and alkynyl substituents. It should be noted that these types of complexes have also been found as intermediates in the reaction pathway of carbon–carbon coupling processes leading to free or complexed diynes.[10]

The most general synthetic approach to these types of complexes employs a preformed bis- (usually *cis*) or tetra-alkynide platinum derivative as starting building block,[8,11,12] and a second, coordinatively unsaturated, substrate or a solvento complex, thus leading to heterometallic and unsymmetrical final systems. Symmetrical diplatinum complexes stabilized by a double alkynide bridging system are scarce, probably due to the lack of adequate precursors. The only examples known (reported by us) are: the anionic derivatives [(C$_6$F$_5$)$_2$Pt-(μ-C≡CR)]$_2^{2-}$ (R = Ph, Bu^t)[13] prepared from the dianionic mixed species [*cis*-Pt(C$_6$F$_5$)$_2$(C≡CR)$_2$]$^{2-}$ and the solvate complex [*cis*-Pt(C$_6$F$_5$)$_2$(THF)$_2$] *via* migration of one σ-alkynyl group between the two platinum metal centres; and the neutral compounds [*trans*-Pt(μ-C≡CR)(C$_6$F$_5$)(PPh$_3$)]$_2$ (R = Ph, Bu^t, SiMe$_3$),[14] generated by a redistribution of ligands between [*trans*-Pt(C≡CR)$_2$(PPh$_3$)$_2$] and the corresponding synthon "Pt(C$_6$F$_5$)$_2$". In contrast to this behaviour, we have observed that [*trans*-Pt(C≡CR)$_2$L$_2$] (L = PPh$_3$, PEt$_3$) reacts with [*cis*-Pt(C$_6$F$_5$)$_2$(CO)(THF)], which contains only one labile coordination site, yielding, through alkynylation of the carbonyl platinum fragment, formally zwitterionic complexes [*cis*,*trans*-Pt$^-$(C$_6$F$_5$)$_2$(CO)(μ-κC^{α}:η^2-C≡CR)Pt$^+$(C≡CR)L$_2$] (R = Ph, Bu^t, SiMe$_3$)[15] with only one alkynyl group connecting the platinum centres. The alkynyl substituent seems to have an influence on

---

† Electronic supplementary information (ESI) available: tables of NMR data for **1**–**16**; variable temperature ^{1}H and ^{19}F NMR spectra for **7**; molecular structure diagrams for **8**·CH$_2$Cl$_2$ and the *SS* isomer of **13**. See http://www.rsc.org/suppdata/dt/b1/b104783n/

DOI: 10.1039/b104783n

the final geometry and stability of these dimers. Thus, while the neutral complex [Pt(μ-σ:η^2-C≡CPh)(C$_6$F$_5$)(PPh$_3$)]$_2$ shows a planar PtC$_4$Pt core, the analogous *tert*-butyl derivative exhibits a non-planar structure, as is suggested by variable ^{19}F NMR data.[14] On the other hand, while the η^2-acetylenic interaction is quite stable in the bimetallic zwitterionic derivatives with R = Ph, Bu^t, being inert towards Ph$_2$C$_2$, CO, Py, PPh$_3$ or HBF$_4$, the analogous [*cis*,*trans*-Pt$^-$(C$_6$F$_5$)$_2$(CO)(μ-κ*C*^{α}:η^2-C≡CSiMe$_3$)-Pt$^+$(C≡CSiMe$_3$)L$_2$] readily interact with alcohols (EtOH, MeOH) yielding (μ-ethynediyl)(methylalkoxycarbene)diplatinum species [*cis*,*trans*-(CO)(C$_6$F$_5$)$_2$Pt(–C≡C–)Pt{C(Me)OR}L$_2$].[16]

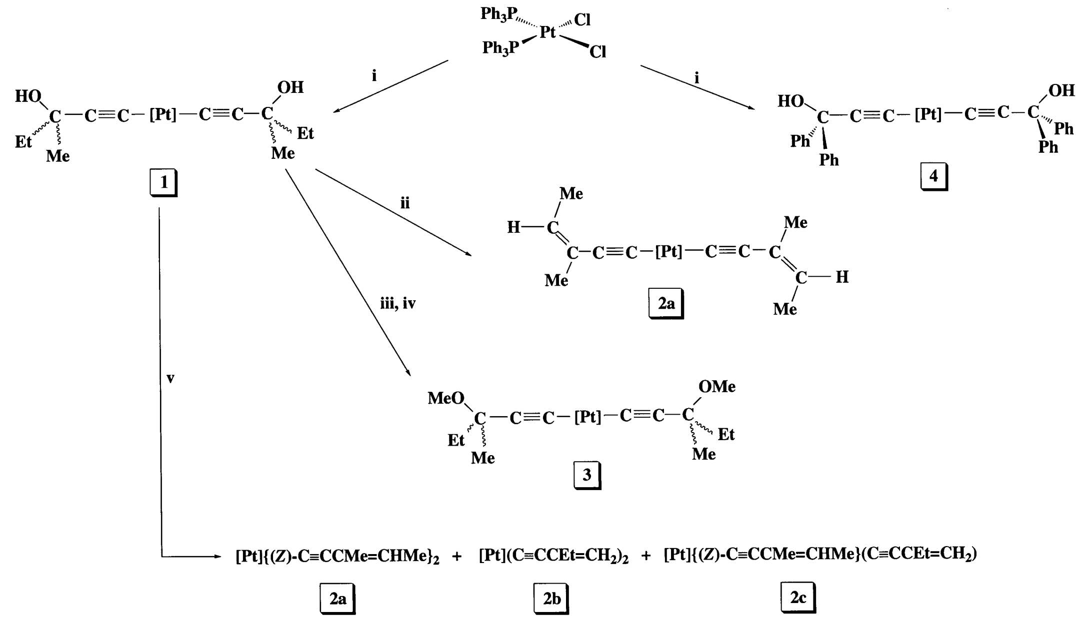
All these results prompted us to investigate the effect of the alkynyl substituents on the course of these reactions and initially we focused our interest on the α-hydroxyalkynide complexes [*trans*-Pt(C≡CR)$_2$(PPh$_3$)$_2$] [R = C(OH)EtMe **1**; C(OH)Ph$_2$ **4**], and on the enyne and methyl-ether analogous derivatives [R = (*Z*)-CMe=CHMe **2a** and C(OMe)EtMe **3**, respectively], which were formed from **1**. Thus, in this paper we report the synthesis and characterisation of [*trans*-Pt(C≡CR)$_2$-(PPh$_3$)$_2$] (**2**–**4**), and describe their reactions towards the solvate complexes [*cis*-Pt(C$_6$F$_5$)$_2$(THF)$_2$] and [*cis*-Pt(C$_6$F$_5$)$_2$(CO)-(THF)], respectively. Several mixed mononuclear complexes [*trans*-Pt(C≡CR)(C$_6$F$_5$)(PPh$_3$)$_2$] (**9**–**12**), obtained from the symmetrical dimers [*trans*,*trans*-(PPh$_3$)(C$_6$F$_5$)Pt(μ-1κ*C*^{α}:η^2-C≡CR)(μ-2κ*C*^{α}:η^2-C≡CR)Pt(C$_6$F$_5$)(PPh$_3$)] (**5**–**8**) by bridge splitting reactions with PPh$_3$, and some reactivity studies are also presented. The crystal structures of complexes [*trans*,*trans*-(PPh$_3$)(C$_6$F$_5$)Pt(μ-1κ*C*^{α}:η^2-C≡CR)(μ-2κ*C*^{α}:η^2-C≡CR)Pt(C$_6$F$_5$)-(PPh$_3$)] [R = C(OMe)EtMe **7**, C(OH)Ph$_2$ **8**] have also been included. The preparation of [*trans*,*trans*-(PPh$_3$)(C$_6$F$_5$)Pt{μ-1κ*C*^{α}:η^2-C≡CC(OH)EtMe}{μ-2κ*C*^{α}:η^2-C≡CC(OH)EtMe}Pt-(C$_6$F$_5$)(PPh$_3$)] **5**, which reacted with PhSH yielding a very unusual thiolate cyclobutenediylidene heterobridged diplatinum complex {*cis*-(PPh$_3$)(C$_6$F$_5$)Pt[μ$\overset{\cdots}{-}$C$\overset{\cdots}{-}$C(CEtMeOH)$\overset{\cdots}{-}$C(C=CEtMe)](μ-SPh)Pt(C$_6$F$_5$)(PPh$_3$)} has been included in a preliminary report.[17]

Results and discussion

Synthesis of [*trans*-Pt(C≡CR)$_2$(PPh$_3$)$_2$]

The preparation of the precursors (**1**–**4**) is summarized in Scheme 1. The synthesis of the bis(alkoxyalkynyl) complexes [*trans*-Pt{C≡CC(OH)EtMe}$_2$(PPh$_3$)$_2$] **1**, which was reported previously,[18] and [*trans*-Pt{C≡CC(OH)Ph$_2$}$_2$(PPh$_3$)$_2$] **4** was based on a slight modification of the method reported by Furlani *et al.*, by refluxing [*cis*-PtCl$_2$(PPh$_3$)$_2$] for 20 minutes with an excess of the corresponding propargyl alcohol (Pt/HC≡CR 1 : 14 for **1** and 1 : 2.3 for **4**) in NEt$_2$H (≈15 cm^3) and in the presence of catalytic amounts of CuI (Scheme 1, i). The resulting white suspensions were evaporated to dryness and treated with EtOH, affording the final complexes in very high yield (90% **1**, 75% **4**). The spontaneous, or induced, dehydration process of unsaturated hydroxyhydrocarbon ligands is a very common feature in organometallic chemistry.[18*b*,19] Initial attempts[18*b*] to induce the dehydration process by refluxing complex **1** in toluene for 1 hour were unsuccessful. However, if the complex is refluxed in the presence of acidic alumina (Scheme 1, v), a yellow microcrystalline solid is obtained. This was identified by NMR spectroscopy (^{1}H, ^{13}C and ^{31}P, see Experimental and Table S4 in the ESI) as a mixture of [*trans*-Pt{C≡C-(*Z*)-CMe=CHMe}$_2$(PPh$_3$)$_2$] **2a**, [*trans*-Pt(C≡C-CEt=CH$_2$)$_2$(PPh$_3$)$_2$] **2b** and [*trans*-Pt{C≡C-(*Z*)-CMe=CH-Me}(C≡CCEt=CH$_2$)(PPh$_3$)$_2$] **2c** in a *ca.* molar ratio of 2 : 1 : 1 (**2a** : **2b** : **2c**). Under these conditions, the two most plausible forms of H$_2$O elimination within the acetylenic moieties (Me and Et) seem to be greatly facilitated. In our hands, further attempts to separate this mixture were unsuccessful. The regioselectivity of the water elimination is notably increased using milder conditions. Thus, the Saytzeff product **2a** (in which the double bond goes mainly towards the most highly substituted carbon) can be obtained in 73% yield by room temperature stirring of a solution of **1** in chloroform with HBF$_4$ (two drops of a 0.1 M solution in Et$_2$O) for only 5 minutes (Scheme 1, ii). The use of higher amounts of HBF$_4$ or longer reaction times lead again to mixtures of **2a**, **2b** and **2c**.

Although the Saytzeff process could lead to several isomers for **2** (*ZZ*, *EE*, *ZE*), only one set of signals was observed by NMR spectroscopy. The corresponding methoxy derivative [*trans*-Pt{C≡CC(OMe)EtMe}$_2$(PPh$_3$)$_2$] **3** is easily obtained, as a white solid, in moderate yield (68%) by refluxing complex **1** in MeOH for 36 hours (Scheme 1, iii); but, again, the etherification process is accelerated in the presence of HBF$_4$ (97% yield, Scheme 1, iv, see Experimental). The characterisation of complex **1** has been reported previously.[17] The remaining complexes **2**–**4** have been characterised by microanalysis, mass spectra



Scheme 1 [Pt] = *trans*-Pt(PPh$_3$)$_2$. Reagents and conditions: (i) HC≡CR + CuI (cat), NEt$_2$H, 20 min, reflux; (ii) HBF$_4$ (cat), CHCl$_3$, rt, immediately; (iii) MeOH, 36 hours, reflux; (iv) HBF$_4$ (cat), MeOH, 30 min, reflux; (v) Al$_2$O$_3$, toluene, 1 hour.

[FAB$^+$] and IR and NMR (^{1}H, ^{13}C{^{1}H} and ^{31}P{^{1}H}) spectroscopy (details are given in the Experimental and Tables S1 and S2 of the ESI). It should be noted that complex **3** (and also **1**), with two stereogenic centres, should be a mixture of *dl* and *meso* diastereomers, but the NMR data show no evidence for this. The presence of alkynyl ligands is confirmed by the presence, in the IR spectra, of a $\tilde{\nu}$(C≡C) absorption in the range 2122–2088 cm^{-1}. Complex **4** also shows the expected IR absorption band due to $\tilde{\nu}$(O–H) (3558 cm^{-1}), and displays a broad singlet at δ 1.17 in its ^{1}H NMR spectrum. This signal disappears upon addition of a drop of D_2O and, therefore, is assigned tentatively to the OH group.

The *trans* geometry in all complexes is suggested by the magnitude of the ^1J(PtP) coupling constant (2654–2699 Hz, δ_P 18.6–19.4); and it is confirmed unambiguously by ^{13}C NMR spectroscopy.[20] In particular, the resonance of the acetylenic carbons [δ C_α/C_β 112.8/112.9 **2a**; 111.8/112.8 **3**; (**4** is not sufficiently soluble), which are easily identified due to the presence of platinum satellites [^1J(PtC$_\alpha$)/^2J(PtC$_\beta$) 946/244 **2a**; 939/244 Hz **3**], are seen as typical AX_2 (X = P) systems. In this regard, it should be noted that although there are reported examples of stereospecific syntheses of platinum diacetylide complexes starting from *cis*-platinum dichlorides,[21a,b] or even *cis*/*trans* mixtures,[21c] usually the presence of metal salts, including CuI, catalyses the isomerization of the less stable *cis*-platinum diacetylides to the corresponding *trans*-derivatives.[5i,22] In the proton spectrum of complex **2a** a quartet at δ 4.88 and a doublet at δ 0.96 [J(HH) = 6 Hz], together with a singlet at δ 1.04 is consistent with the presence of the vinyl fragment (*Z*)-CMe=CHMe. The *ZZ* stereoisomer is confirmed by a ^{1}H phase-sensitive NOESY spectrum at room temperature, which shows cross positive peaks correlating the vinyl proton at δ 4.88 with both of the methyl signals. The data for the mixture of **2a**, **2b** and **2c** are included as ESI, the most characteristic being the presence of a multiplet at δ 4.87 due to vinyl protons in **2a** and **2c**, and two broad singlets at δ 4.41 and 4.02 due to the non-equivalent protons of the terminal =CH(a)H(b) unit of the C(Et)=CH$_2$ fragment in **2b** and **2c**.

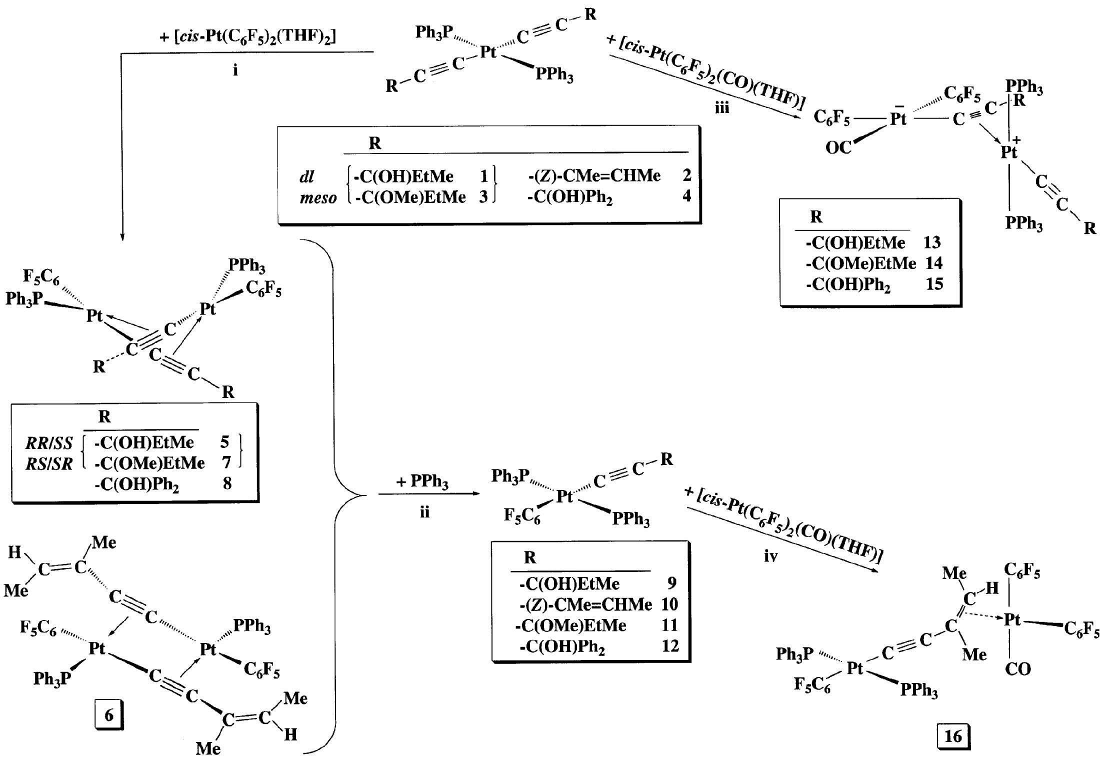
Reactions with [*cis*-Pt(C_6F_5)$_2$(THF)$_2$]

In spite of the presence of a vinyl fragment in **2a** or oxygen atoms in **1**, **3** or **4**, which could act as donor centres, the reactions of these complexes with [*cis*-Pt(C_6F_5)$_2$(THF)$_2$]$_2$ in CH_2Cl_2 take place with rearrangement of the ligands yielding the symmetrical dimers [*trans*,*trans*-(PPh$_3$)(C_6F_5)Pt(μ-1κC^α:η^2-C≡CR)(μ-2κC^α:η^2-C≡CR)Pt(C_6F_5)(PPh$_3$)], stabilised by a double alkynyl bridging system, in high yields (71–90%) (Scheme 2, i). Spectroscopic data of **5**–**8** [mass spectra, IR, ^{31}P NMR (Experimental); ^{1}H, ^{13}C and ^{19}F NMR (Tables S1–S3 in the ESI)] are in accordance with the proposed formulations shown in Scheme 2. Complexes **5** and **7** crystallise with CH_2Cl_2 (**5**·CH_2Cl_2 and **7**·½CH_2Cl_2) as confirmed by the analytical data, NMR spectroscopy (^{1}H and ^{13}C) and, in the case of complex **7**, even by X-ray crystallography (see below). For complexes **5**, **7** and **8** the $\tilde{\nu}$(C≡C) absorptions (in cm^{-1} 1975 **5**, 1986 **7**, 1995 **8**) and, particularly, the notable $\Delta\tilde{\nu}$(C≡C) shift relative to the corresponding monomers (in cm^{-1} 139 **5**, 124 **7**, 127 **8**) are in agreement with the presence of a σ/π double alkynyl bridging system.[9a–c,13,14] Complex **6** [$\tilde{\nu}$(C≡C) 2019 cm^{-1}] exhibits a lower shift (69 cm^{-1}), suggesting a weaker η^2-platinum acetylenic interaction. The planar formulation for this complex is suggested by ^{19}F NMR, which displays, even at low temperature (−50 °C in CDCl$_3$), the typical sharp pattern of three signals in 2 : 1 : 2 ratio due to two equivalent C_6F_5 groups for which the plane of coordination is a mirror plane. As expected, due to the presence of two stereogenic centres, complexes **5** and **7** have been obtained as non-separable mixtures of diastereomers in a *ca.* 1 : 1 molar ratio, for which the non-planar structural disposition is inferred mainly by ^{19}F NMR spectroscopy and confirmed by X-ray crystallography on complex **7**. These dimers have both equivalent metal centres on the *RR*/*SS* pair due to the presence of a C_2 axis, but they are inequivalent on the *RS*/*SR* pair. Therefore, three sets of resonances in a 2 : 1 : 1 molar ratio should be expected for both complexes **5** and **7** which are 1 : 1 diastereomeric mixtures. Furthermore, the five fluorine resonances due to each C_6F_5 ring (*endo* and *exo* on *ortho*-F, *meta*-F and *para*-F) are non-equivalent for a bent conformation of the central dimetallacycle. Only for complex **7** (δ_P 12.9 **5**, 13.0 **7**) is the singlet observed in the ^{31}P{^{1}H} NMR spectrum split at low temperature (−50 °C) into two different signals of equal intensity [δ 13.5, 13.4 J(PtP) ≈ 3900 Hz], suggesting that the expected two different resonances for the *RS*/*SR* pair are isochronous. A similar pattern is observed for complex **5** in its ^{1}H NMR spectrum, which exhibits only two different sharp hydroxyl (δ 1.40, 1.38 at 16 °C; 1.35, 1.36 at 40 °C) and methyl (δ 0.54, 0.49 at 16 °C; 0.56, 0.51 at 40 °C) resonances due to the alkynyl C(O*H*)(C*H*$_3$)Et groups, even at high temperature. On cooling, the line shapes of all signals broaden but at −50 °C only coalescence of the hydroxyl resonances has been detected.

In contrast, for complex **7** (see Fig. S1 in the ESI) the sharp OMe resonance observed at high temperature (δ 2.79) broadens as the temperature is lowered, and coalesces between −5 and −10 °C, finally giving, in the low exchange region, the expected three singlets at δ 3.15 (two CH$_3$ due to the *RR*/*SS* isomer) and at δ 2.63 (CH$_3$) and 2.56 (CH$_3$) (*RS*/*SR*), respectively. The σ/π pairwise intramolecular exchange and fast inversion of the central ring (for bent systems) are common features for this type of complex. For both complexes (**5** and **7**) only broad resonances are observed in the *ortho*- and *meta*-fluorine regions in their ^{19}F NMR spectra at room temperature. At low temperature (−50 °C, see Fig. S2 for complex **7**, ESI) both derivatives show patterns confirming the presence of at least two non-equivalent and rigid C_6F_5 rings. It should be noted that for complex **7**, even at high temperature (40 °C), two different *para*-F resonances are clearly seen, suggesting that the diastereomers do not interconvert. The observed equivalence, seen as broad signals (40 °C for **7** or 16 °C for **5**), for the resonances due to *ortho*-F and *meta*-F seems to be casual and the exchange between *endo* and *exo* fluorine resonances could be due to an induced free rotation of the C_6F_5 rings, because a simple fast inversion of the central metallacycle, which can not be excluded, does not reach the C_{2h} symmetry.

For complex **8**, a set of five fluorine signals is observed at −50 °C in accordance with a non-planar formulation, which is also confirmed by X-ray crystallography. A similar rigid pattern is found at room temperature, suggesting that the energy barrier to the free rotation of C_6F_5 rings and/or to the inversion of the central dimetallacycle is unusually high. It is noteworthy that the highest frequency *ortho*-F resonance displays a somewhat broad appearance. These ^{19}F NMR patterns and the fact that the hydroxyl protons have the appearance of a doublet (J = 15 Hz) could suggest the existence in solution of a H···*ortho*-F interaction between the OH and the C_6F_5 groups, stabilizing the bridging system. In support of this, the reaction of complex **8** and PPh$_3$ to give the mononuclear complex **12** (see Scheme 2) requires the use of an excess of ligand (4 equivalents) for completion.

The X-ray diffraction studies on **7** and **8** clearly establish the presence of binuclear structures bridged by two σ/π alkynyl ligands. Complex **7** (Fig. 1, Table 1) contains two stereocentres [C(27) and C(27′)] on the molecule giving rise to two pairs of enantiomers (*RR*/*SS* and *RS*/*SR*), that crystallise together in the unit cell. The molecule is solved generating half of its atoms by a C_2 axis, thus leading to a disorder on the C(OMe)EtMe groups. The structure displayed in Fig. 1 corresponds to the idealised situation for one isomer (*SS*) and details of the X-ray crystal structure analyses are also given in Table 2. A view of the molecular geometry of **8** is shown in Fig. 2 and selected



Scheme 2

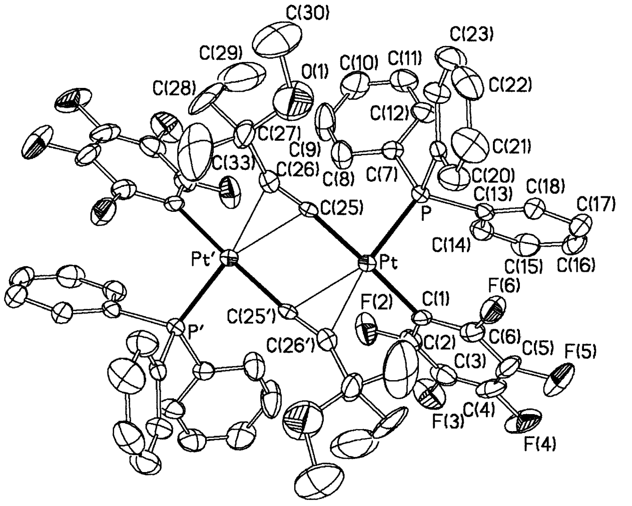


Fig. 1 Molecular structure of [*trans*-Pt{μ-C≡CC(OMe)EtMe}$(C_6F_5)(PPh_3)]_2·½CH_2Cl_2$ ($\mathbf{7}·½CH_2Cl_2$). Ellipsoids are drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity.

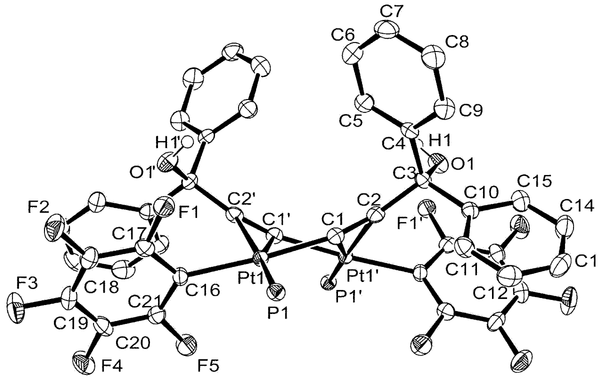


Fig. 2 Molecular structure of [*trans*-Pt{μ-C≡CC(OH)Ph$_2$}$(C_6F_5)(PPh_3)]_2·CH_2Cl_2$ ($\mathbf{8}·CH_2Cl_2$). Ellipsoids are drawn at the 50% probability level. Hydrogen atoms and phenyl groups of the PPh_3 ligands have been omitted for clarity.

bond distances and angles are given in Table 1. The most remarkable features of both structures are: i) the bent structural disposition of the central PtC_4Pt dimetallacycle, which contrasts with the planar structure previously found for [*trans*-Pt(C≡CPh)$(C_6F_5)(PPh_3)]_2$.[14] Both planar[23] and non-planar[9a,b,13,24] C_4M_2 cores have been found previously. The dihedral angle formed by the corresponding best platinum coordination planes (47.5 **7**; 49.26° **8**) resembles values of related complexes. ii) In complex **7** the platinum η^2-linkages are clearly symmetric [Pt–C(25′) 2.328(6) and Pt–C(26′) 2.317(7) Å], while in complex **8** they are slightly asymmetric [Pt(1)–C(1′) 2.339(3) and Pt–C(2′) 2.289(3) Å]. This structural feature contrasts with the asymmetric η^2 interactions previously found in [*trans*-Pt(C≡CPh)$(C_6F_5)(PPh_3)]_2$, with the platinum–C_β distance being perceptibly shorter than the corresponding Pt–C_α [2.261(6) *vs.* 2.362(6) Å] and, accordingly, iii) the Pt···Pt separation in these compounds [3.359 **7**, 3.4066(1) Å **8**] is considerably shorter than that found in the bis(phenylethynyl) planar dimer [3.653(1) Å]. The deviations of the Pt–C_α≡C_β–C skeletons from linearity [at C_α 171.8(6) **7**, 166.0(3) **8**; at C_β 152.1(6) **7**, 154.9(3)° **8**] and the C≡C distances [1.223(9) **7**, 1.237(4) Å **8**] are within the usual range found for related σ/π alkynyl bridged compounds.

The main purpose of the X-ray study on complex **8** was to check for the presence of hydrogen bond interactions, in particular with the *ortho*-fluorine atoms, aiming to understand the unusual stability of this [μ-C≡CC(OH)Ph$_2$]$_2$ bridging system. Hydrogen bonds combine the most favourable aspects of directionality and strength amongst intermolecular interactions and, for this reason, are being widely employed in supramolecular chemistry and crystal engineering.[25,26] Our interest was also attracted by recent studies[27] on the participation of organic fluorine in hydrogen bonding (X–H···F–C where X = O, N, C), which indicate that fluorine, when covalently bound to carbon, does not frequently form hydrogen bonds with conventional hydrogen bond donors. Although this

Table 1 Selected bond lengths (Å) and angles (°) for complexes **7**·½CH_2Cl_2 and **8**·CH_2Cl_2[a]

$[$*trans*,*trans*-Pt{μ-C≡CC(OMe)MeEt}(C_6F_5)(PPh_3)$]_2$·½CH_2Cl_2 (**7**·½CH_2Cl_2)

Pt–C(25)	2.015(6)	Pt–C(25′)	2.328(6)
Pt–C(26′)	2.317(7)	Pt–Pt′	3.359
C(26)–C(27)	1.489(10)	Pt–P	2.241(2)
Pt–C(1)	2.063(6)	C(25)–C(26)	1.223(9)
C(25)–Pt–C(1)	176.2(3)	C(25)–Pt–P	89.6(2)
C(1)–Pt–P	91.6(2)	C(1)–Pt–C(25′)	108.0(2)
C(1)–Pt–C(26′)	85.4(2)	C(26′)–Pt–C(25′)	30.5(2)
C(25)–Pt–C(25′)	70.5(3)	C(25)–Pt–C(26′)	94.4(2)
C(26)–C(25)–Pt	171.8(6)	C(25)–C(26)–C(27)	152.1(6)

$[$*trans*,*trans*-Pt{μ-C≡CC(OH)Ph_2}(C_6F_5)(PPh_3)$]_2$·CH_2Cl_2 (**8**·CH_2Cl_2)

Pt(1)–C(1)	2.015(3)	Pt(1)–C(2′)	2.289(3)
Pt(1)–C(1′)	2.339(3)	Pt(1)–Pt(1′)	3.4066(1)
C(2)–C(3)	1.500(4)	Pt(1)–P(1)	2.2578(7)
Pt(1)–C(16)	2.072(3)	C(1)–C(2)	1.237(4)
C(1)–Pt(1)–C(16)	175.12(11)	C(1)–Pt(1)–P(1)	93.91(8)
C(16)–Pt(1)–P(1)	90.44(8)	C(1)–Pt(1)–C(1′)	69.42(12)
C(1)–Pt(1)–C(2′)	91.88(10)	C(1′)–Pt(1)–C(2′)	30.98(9)
C(16)–Pt(1)–C(1′)	106.68(10)	C(16)–Pt(1)–C(2′)	83.42(10)
C(2)–C(1)–Pt(1)	166.0(3)	C(1)–C(2)–C(3)	154.9(3)

[a] Symmetry transformation used to generate equivalent primed atoms is $-x, y, -z + ½$ in **7**·½CH_2Cl_2 and $-x + 1, y, -z + ½$ in **8**·CH_2Cl_2.

is supported by database analysis and theoretical calculations,[27] some evidence of weak X–H · · · F–C interactions, both in solution and the solid state, have been reported.[27,28] In complex **8**, the hydroxyl hydrogen atom [H(1)] has been located, using the Fourier difference maps, at a distance of 0.84(3) Å from the oxygen atom. In spite of the presence of OH donors and O acceptors, no hydrogen bond contacts of the type O–H · · · O have been detected and, contrary to our expectations, the shortest separation between H(1) and a fluorine atom on a pentafluorophenyl ring within the molecule [H(1)–*ortho*-F(1′) 2.796(5) Å] is quite long, excluding any intramolecular bonding interaction.[29] However, it is interesting to note that, in the solid, the OH group acts as a donor towards a *meta*-fluorine atom of a C_6F_5 group from the neighbouring molecule. The dimers are thus linked by two hydrogen bonds [H(1) · · · F(2′a) 2.325(7) Å, O(1)–H(1) · · · F(2′a) 158.81°] giving an extending chain along the *c* axis. The hydrogen · · · fluorine separation [2.325(7) Å] is within the usual range for this type of contact.[27–30] A perspective view of the resulting pattern, showing that each binuclear entity [*trans*,*trans*-(PPh_3)(C_6F_5)Pt{μ-C≡CC(OH)Ph_2}$_2$Pt(C_6F_5)(PPh_3)] is involved in a total of four (O–H · · · *meta*-F) interactions is shown in Fig. 3. We tentatively suggest that these interactions probably do not survive in solution, and this fact allows the hydroxyl proton a stronger intramolecular interaction with the *ortho*-fluorine [O(1)–H(1) · · · F(1′)] atom, which could be responsible for the observed stability of the bridging system. A similar proposal has been recently suggested to explain the hydrolysis reaction of CF_2 groups in perfluoroalkyl aqua coordinated complexes, which is extremely facile *via* intramolecular O–H · · · F–C bonding, if the counterion [BF_4^-, $B(Ar_F)_4^-$] is unable to participate in hydrogen bonding.[30b]

Reactivity of 5–8 towards PPh_3

We have examined the reactivity of the dimers **5**–**8** towards PPh_3. As shown in Scheme 2, treatment of the bridged complexes **5**–**7** with PPh_3 (2 equivalents) results in bridge splitting to give the mononuclear complexes [*trans*-Pt(C_6F_5)(C≡CR)$(PPh_3)_2$] [R = C(OH)EtMe **9**, (*Z*)-CMe=CHMe **10**, C(OMe)EtMe **11**] as white solids. For **6** and **7** the reactions are slower than those previously observed for related dimers [*trans*-Pt(C≡CR)(C_6F_5)(PPh_3)$]_2$ (R = Ph or $SiMe_3$) requiring 4.5 h (for **6**) and 48 h (for **7**), respectively to go to completion. For complex **8**, the reaction is so slow that it requires the use of an excess of PPh_3 ligand. In this case, the initial orange solution was stirred with 4 equivalents of PPh_3 until a colourless solution was finally obtained (*ca.* 12 h). In an alternative synthetic procedure complex **10** could be prepared by controlled dehydration of compound **9**. Thus, the treatment of a solution of **9** in CH_2Cl_2 with four drops of HBF_4 (0.1 M in Et_2O) at room temperature for 5 min gives rise to an orange solution from which the vinylacetylide derivative **10** is isolated in a 77% yield. The terminal coordination of the alkynyl ligand in all complexes **9**–**12** is confirmed by their IR spectra in which the $\tilde{\nu}$(C≡C) is found shifted to higher wavenumbers (2131–2102 cm^{-1}) in comparison with the C≡C stretching frequency in the corresponding dimers. Their $^{31}P\{^1H\}$ spectra exhibit the expected singlet resonance (δ 19.7–20.1) with a ^1J(PtP) coupling constant (2710–2740 Hz) characteristic of mutually *trans* phosphines.[20] In the ^{13}C NMR spectra, the C_α resonances occur as a broad multiplet [δ $C_\alpha/J(PtC_\alpha)$ Hz 94.0 **9**; 106.0 **10**; 94.7/942 **11**; 99.9/948 **12**] probably due to unresolved coupling to *ortho*-fluorine nuclei [$^4J(C_\alpha F)$] whereas the C_β resonances appear, as in complexes **1**–**4**, at higher frequencies [δ $C_\beta/J(PtC_\beta)$ Hz 117.2/240 **9**; 114.4/285 **10**; 114.3/247 **11**; 115.5/250 **12**] as a broad singlet.

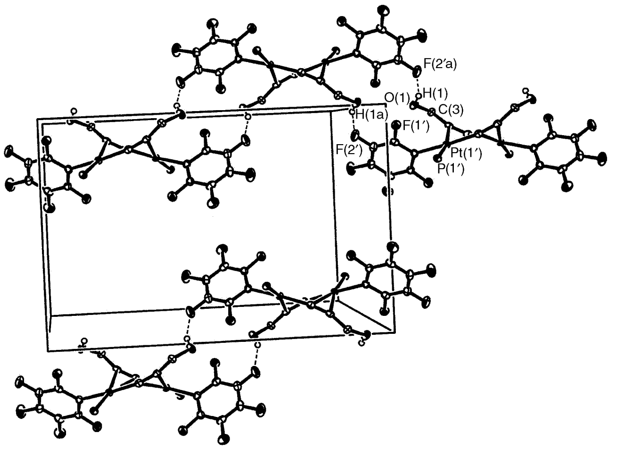


Fig. 3 Perspective view along the *c* axis of ¼ of the unit cell (0 < *x* < 0.25, 0 < *y* < 1, 0 < *z* < 1), showing the pattern of O–H · · · F–C interactions in compound **8**·CH_2Cl_2 [O(1)–H(1) 0.84(3) Å, H(1)–F(2′a) 2.325(7) Å, H(1)–F(1′) 2.796(5) Å, O(1)–H(1)–F(2′a) 158.81°, O(1)–H(1)–F(1′) 85.84°]. Hydrogen atoms, all the phenyl groups and CH_2Cl_2 molecules have been omitted for clarity.

Reactions with [*cis*-Pt$(C_6F_5)_2$(CO)(THF)]

There has been growing interest in binuclear transition metal complexes containing unsaturated hydrocarbon bridges linking the metal fragments and without metal–metal bonds, due to their unique chemical and physical properties.[31] In this area, although σ,σ alkynediyl compounds are well known,[5a,b,32] binuclear complexes stabilised solely by a μ-η^1:η^2-C≡CR bridging group are rare, particularly those containing platinum.[1a,b] In this context, we have recently shown that the solvento complex [*cis*-Pt$(C_6F_5)_2$(CO)(THF)] ≡ [{Pt}(THF)] containing only a labile tetrahydrofuran solvent molecule is an excellent precursor to a diverse variety of this type of complex. Thus, whereas the reaction between metallaalkynyl compounds $ML_nC{\equiv}CR$ of type *cis* or *trans* [Pt$(C{\equiv}CR)_2L_2$], [Pt(dppe)$(C{\equiv}CR)_2$] or [Au(C≡CR)L] (R = Ph, Bu^t; L = PPh_3, PEt_3) and [{Pt}(THF)] takes place with stereo retention but with formal alkynylation of the "Pt$(C_6F_5)_2$(CO)" ≡ {Pt} fragment yielding $[\{Pt^-\}(\mu\text{-}{}^1\kappa C^\alpha{:}\eta^2\text{-}C{\equiv}CR)M^+L_n]$ zwitterionic species,[15] the analogous reactions with [*trans*-Pt$(C{\equiv}CSiMe_3)_2L_2$] results in an unexpected rearrangement chemistry, giving rise to a (μ-ethynediyl)(methylalkoxycarbene)-

diplatinum species of the type [{Pt}(C≡C)Pt{C(Me)OR}L$_2$].[16] Interestingly, the reaction of [{Pt}(THF)] with the hydride alkynyl complex [*trans*-Pt(H)(C≡CPh)(PPh$_3$)$_2$] affords a μ-phenylethenylidene diplatinum derivative [{Pt}(μ-C=CPhH)Pt(PPh$_3$)$_2$] containing a platinum–platinum bond.[33] In this case, it was suggested that the initial zwitterionic species [{Pt$^-$}(μ-^{1}κ*C*^{α}:η^2-C≡CPh)Pt$^+$H(PPh$_3$)$_2$] probably evolves, *via cis,cis* isomerisation and *cis* H-1,2 addition, to yield the final μ-phenylethenylidene complex.

As one of our main objectives in the present work was to understand the influence of functionalised alkynyl substituents on the course of these reactions, we decided to explore the reactivity of this electrophilic metal building block “*cis*-Pt(C$_6$F$_5$)$_2$(CO)” with the bis-alkynyl complexes **1**–**4** and the mixed derivatives **9**–**12**. In keeping with previous results,[15] complexes **1**, **3** and **4** react with [*cis*-Pt(C$_6$F$_5$)$_2$(CO)(THF)] in CH$_2$Cl$_2$ at room temperature, affording the zwitterionic derivatives [*cis*,*trans*-{Pt$^-$}(μ-1κ*C*^{α}:η^2-C≡CR)Pt$^+$(C≡CR)(PPh$_3$)$_2$] [R = C(OH)EtMe **13**, C(OMe)EtMe **14**, C(OH)Ph$_2$ **15**], which are formed *via* the expected alkynylation of the carbonyl platinum fragment “*cis*-Pt(C$_6$F$_5$)$_2$(CO)” (Scheme 2, iii). It is interesting to note that the zwitterionic nature of organometallic complexes (zwitterionic metallates) has recently become an influential factor in the design of cationic metal catalysts, and may become a fundamental consideration in the design of mixed valence (donor–acceptor) complexes for applications in materials science (non-linear optics, molecular electronics).[34] The reactions are immediate and complexes are isolated as yellow (**13**) or beige (**14**, **15**) solids in moderate (55% **14**) or high yields (86% **13**, 81% **15**). Spectroscopic data are in agreement with the formulation shown in Scheme 2 (details are given in the Experimental section and in Tables S1–S3 in the ESI). It should be noted that again the NMR spectra of complexes **13** and **14** reveal the presence of two diastereomers in *ca.* 1 : 1 ratio, in agreement with the presence of two chiral carbon atoms (C$_γ$). This fact is also confirmed by a single-crystal X-ray study on complex **13**. However, due to the poor data quality, the structure analysis is not of a high accuracy. Nevertheless, the connectivity, shown in Scheme 2, can be established, with the four expected diastereomers (two pairs of enantiomers) crystallising together in the unit cell, which causes a disorder located on the C(OH)EtMe group of the terminal C≡C–R ligand. An idealised view of the molecular geometry corresponding to the *SS* isomer is given in Fig. S4 in the ESI.

The most remarkable spectroscopic feature appears on their IR spectra, which show the strong ṽ(CO) absorption (2083–2096 cm^{-1}), along with the two expected and weaker additional ṽ(C≡C) bands corresponding to terminal (2133 cm^{-1} **13**, 2130 cm^{-1} **14**, not observed for **15**) and bridging (1972 cm^{-1} **13**, 1988 cm^{-1} **14**, 2005 cm^{-1} **15**) alkynyl ligands. In agreement with previous observations,[15,16] the simultaneous increase and decrease of electron density at the platinum centres caused by alkynyl ligand migration is reflected in the ṽ(CO) and terminal ṽ(C≡C) bands, which are perceptibly shifted to lower and higher wavenumbers, respectively, in relation to the precursors {ṽ(CO) 2124 cm^{-1} for [*cis*-Pt(C$_6$F$_5$)$_2$(CO)(THF)]; ṽ(C≡C) 2114 cm^{-1} **1**, 2110 cm^{-1} **3**}. In the ^{31}P NMR spectra the magnitude of ^1J(PtP) is still typical of mutually *trans* phosphine groups, but its value (≈2510 **13**, 2563 **14**, 2547 Hz **15**) is slightly smaller when compared to the corresponding precursors in accordance with the formal positive charge developed on this platinum fragment.[20a] The acetylenic carbon resonances are assigned unequivocally only in complex **13**. Modest but perceptible upfield shifts are observed for the bridged C$_α$≡C$_β$ carbon resonances in relation to the precursor **1** {δ C$_α$/[^1J(PtC$_α$)]{^2J(PC$_α$)} Hz 94.0(br)/[950] C≡C$_{\mathbf{bridge}}$, 86.5/{16} C≡C$_{\mathbf{term}}$; C$_β$/^2J(PtC$_β$) 119.1, 119.0/300 C≡C$_{\mathbf{term}}$, 94.8/234 C≡C$_{\mathbf{bridge}}$ *vs.* δ C$_α$/[^1J(PtC$_α$)]{^2J(PC$_α$)} Hz 98.7/[955]{15}; C$_β$/[^2J(PtC$_β$)]{^3J(PC$_β$)} 115.2/[245]{2}]. The ^{19}F NMR spectrum of **15** displays the expected two sets of C$_6$F$_5$ signals (2 : 1 : 2). For **13** and **14**, although two *para*-F resonances are seen, the complex pattern in the *ortho*-fluorine region (2 : 2 : 4 **13** or 1 : 1 : 2 : 4 **14**) is in accordance with the presence of two diastereomers for which the coordination plane of the anionic fragment “*cis*-Pt$^-$(C$_6$F$_5$)$_2$(CO)(μ-C≡CR)” is not a symmetry plane.

Under different reaction conditions, low (−30 °C) or room temperature, the analogous reaction between the enynyl derivative **2a** and [*cis*-Pt(C$_6$F$_5$)$_2$(CO)(THF)] affords a mixture of compounds containing the expected [*cis*,*trans*-{Pt$^-$}{μ-1κ*C*^{α}:η^2-C≡C-(*Z*)-CMe=CHMe}Pt$^+${C≡C-(*Z*)-CMe=CHMe}(PPh$_3$)$_2$] as the main component [δ$_P$ 16.1, ^1J(PtP) 2519 Hz, ^{19}F and ^{1}H NMR data are collected in the Experimental section]. However, all attempts to separate this dimer from the mixture were fruitless. Dehydration reactions of complex **13** were also attempted using HBF$_4$ or Me$_3$OBF$_4$, but these reactions usually led to a similar mixture of products and, again, we were not able to separate the expected pure dimer.

In contrast to this result, only the analogous reaction between the mixed derivative [*trans*-Pt{C≡C-(*Z*)-CMe=CHMe}(C$_6$F$_5$)(PPh$_3$)$_2$] **10** with [*cis*-Pt(C$_6$F$_5$)$_2$(CO)(THF)] (Scheme 2, iv) gives a pure product. In this case, the presence of the vinyl fragment causes a simple displacement of the tetrahydrofuran molecule affording the adduct [*trans*,*cis*-(PPh$_3$)$_2$(C$_6$F$_5$)Pt{μ-1κ*C*^{α}:η^{2}C^{3,4}-C≡C-(*Z*)-CMe=CHMe}Pt(C$_6$F$_5$)$_2$(CO)] **16**. Complex **16** was isolated as a yellow solid in 61% yield. The IR spectrum of **16** shows the characteristic ṽ(CO) (2117 cm^{-1}) stretching frequency in a similar position to that seen in the precursor [ṽ(CO) 2124 cm^{-1}], in agreement with the small changes in the electron density on the platinum centres during the reaction. The coordination of the vinyl entity causes a small shift of the ṽ(C≡C) (2083 cm^{-1} in **16** *vs.* 2102 cm^{-1} in **10**), and is inferred from NMR spectroscopy. Thus, the vinyl proton (=CHMe) is observed as a quartet by coupling to geminal methyl protons [δ 1.38, d, *J*(HH) = 6 Hz] at lower frequencies (δ 4.46) in relation to **10** (δ 4.86), and displays a platinum proton coupling [^2J(PtH) = 50 Hz] similar to those observed for other μ-vinyl or η^2-alkenyl platinum complexes.[35] In the ^{13}C NMR spectrum the C$_γ$ (δ 123.2) and C$_δ$ (δ 95.52) vinyl resonances are observed as singlets and also exhibit the expected ^{195}Pt satellites. The low field signal shows a platinum–carbon coupling (23 Hz) similar to that seen in **2a** and is, therefore, suggested to be a ^3J(PtC) coupling. The low frequency resonance displays a greater coupling [^1J(PtC) = 60 Hz] confirming that this fragment is involved in η^2 coordination. The chemical shift of the phosphorus resonance, as well as the *J*(PtP) coupling constant, in **16** are very similar to those observed in **10** [δ/^1J(PtP) Hz 19.6/2676 **16** *vs.* 19.7/2710 Hz **10**] confirming again that a small structural rearrangement has taken place. The ^{19}F NMR spectrum confirms the presence of three inequivalent C$_6$F$_5$ rings (see Table S3 in the ESI for details). Furthermore, as is usual for other compounds[15,16,33,35a] in which the “*cis*-Pt(C$_6$F$_5$)$_2$” fragment is stabilised by different ligands *trans* to the C$_6$F$_5$ rings, which induces different energy barriers to the rotation of C$_6$F$_5$ groups, one set of signals displays a marked dependence upon temperature (see Table S3 in the ESI). It is worth mentioning that the vinyl fragment on the precursor complex **10** is prochiral and complex **16** should therefore be obtained as a mixture of two enantiomers.

It was previously shown that the reactions of monoalkynyl platinum complexes [*trans*-PtX(C≡CR)(PPh$_3$)$_2$] (R = Ph, Bu^t or SiMe$_3$; X = Cl or C$_6$F$_5$)[15] with [*cis*-Pt(C$_6$F$_5$)$_2$(CO)(THF)] yielded complicated mixtures of products, probably due to the presence of electron withdrawing groups (Cl or C$_6$F$_5$), which enhance the acidity of the platinum centres and reduce its alkynylation power. Similarly, the reactions between the alkoxy (**9**, **12**) and methoxy (**11**) derivatives with [*cis*-Pt(C$_6$F$_5$)$_2$(CO)(THF)] evolved affording very complex mixtures, which were not investigated further. However, it should be noted that complex **16** is clearly detected in the final reaction mixtures starting from **9** and **11** (in this case **16** is isolated in 37% yield), thus suggesting that spontaneous dehydration processes also play a decisive role in the course of these reactions.

Concluding remarks

In conclusion, the presence of functionalised (vinyl, OH or OMe) alkynyl substituents on bis-alkynyl platinum precursors seems to have little influence on the course of the reactions with [*cis*-$Pt(C_6F_5)_2(THF)_2$] (redistribution of ligands with final formation of symmetrical dimers) or [*cis*-$Pt(C_6F_5)_2(CO)(THF)$] (formal alkynylation and final stereo retention around Pt centres). In contrast to this in the analogous reactions of mixed [*trans*-$Pt(C_6F_5)(C{\equiv}CR)(PPh_3)_2$] (**9**–**12**) with [*cis*-$Pt(C_6F_5)_2(CO)(THF)$] only the presence of a good coordination entity [(*Z*)-CMe=CHMe] on the alkynyl ligand allows the formation of a stable binuclear complex (**16**).

Experimental

General

All manipulations were carried out under a nitrogen atmosphere, except for the synthesis of complexes **1**–**4** and **9**–**12**. Solvents (hexane, alkanes) were dried by standard procedures and distilled under dry N_2 before use. NEt_2H, HC≡CC(OH)EtMe and $HC{\equiv}CC(OH)Ph_2$ were used as received. NMR spectra were recorded on a Bruker ARX-300 spectrometer and the ^1H phase-sensitive NOESY spectrum was recorded following the literature methods.[36] Chemical shifts are reported in ppm relative to external standards ($SiMe_4$, $CFCl_3$ and 85% H_3PO_4) and all coupling constants are given in Hz. IR spectra were obtained on Perkin-Elmer 883 or Perkin-Elmer FT-IR Spectrum 1000 spectrometers using Nujol mulls between polyethylene sheets. Elemental analyses were carried out with a Perkin-Elmer 2400 CHNS/O or Carlo Erba EA1110 CHNS-O microanalyzers. Mass spectra were recorded on a VG Autospec double-focusing mass spectrometer operating in the FAB^+ mode, except for complex **12** (HP-5989B mass spectrometer using the ES^+ technique). [*cis*-$Pt(C_6F_5)_2(THF)_2$][37a] and [*cis*-$Pt(C_6F_5)_2(CO)(THF)$][37b] were prepared by published methods. ^1H, ^{19}F and $^{13}C\{^1H\}$ NMR data for all the complexes reported in this paper have been provided as ESI.

Preparations

[*trans*-Pt{C≡CC(OH)EtMe}$_2$(PPh$_3$)$_2$] 1. The synthesis of this complex has been carried out as described previously by Furlani *et al.*[18] with slight modifications. 0.02 g (0.1 mmol) of CuI and 2 cm^3 of HC≡CC(OH)EtMe (17.6 mmol) were added to a white suspension of [*cis*-$PtCl_2(PPh_3)_2$] (1.00 g, 1.26 mmol) in 15 cm^3 of NEt_2H, and the mixture was stirred at reflux for 20 min. The resulting white suspension was evaporated to dryness and the solid residue treated with ≈5 cm^3 of EtOH to yield **1** as a white solid (1.04 g, 90%) (Found: C, 63.02; H, 5.56%. $C_{48}H_{48}O_2P_2Pt$ requires C, 63.08; H, 5.29%); $\tilde{\nu}_{max}/cm^{-1}$ (OH) 3601m, (C≡C) 2114m; $\delta_P(CDCl_3)$ 19.1 [s, *J*(PPt) 2685 Hz]; *m*/*z* (% intensity) 913 (M^+, 5), 896 ($M^+ - H_2O + H$, 23).

[*trans*-Pt{C≡C-(*Z*)-CMe=CHMe}$_2$(PPh$_3$)$_2$] 2a. A colourless solution of [*trans*-Pt{C≡CC(OH)EtMe}$_2$(PPh$_3$)$_2$] **1** (0.20 g, 0.22 mmol) in 5 cm^3 of $CHCl_3$ was treated, at room temperature, with two drops of a 0.1 M solution of HBF_4 in Et_2O (0.10 cm^3, 0.01 mmol). The mixture was stirred for 5 min, evaporated to dryness and treated with 2 cm^3 of EtOH to afford **2a** as a yellow solid (0.14 g, 73%) (Found: C, 65.59; H, 4.46%. $C_{48}H_{44}P_2Pt$ requires C, 65.67; H, 5.05%); $\tilde{\nu}_{max}/cm^{-1}$ (C≡C) 2088m; $\delta_P(CDCl_3)$ 18.6 [s, *J*(PPt) 2689 Hz]; *m*/*z* (% intensity) 878 ($M^+ + H$, 25).

Complex **2a** was also obtained, as a yellow solid, by treatment of 15 cm^3 of a white toluene suspension of **1** (0.19 g, 0.21 mmol) with one drop of a 54% solution of HBF_4 in Et_2O (0.05 cm^3, 0.36 mmol) at room temperature. The resulting red solution was filtered through Celites and evaporated to dryness. Addition of ≈5 cm^3 of Et_2O caused the precipitation of **2a** (0.07 g, 36%).

Other reactions of [*trans*-Pt{C≡CC(OH)EtMe}$_2$(PPh$_3$)$_2$] 1 in toluene. A white suspension of [*trans*-Pt{C≡CC(OH)EtMe}$_2$(PPh$_3$)$_2$] **1** (0.20 g, 0.22 mmol) in 20 cm^3 of toluene was refluxed for 1 h. The resulting solution was evaporated to *ca.* 5 cm^3, recovering 0.14 g (71%) of unaltered starting material **1**. A mixture of 0.45 g (0.49 mmol) of [*trans*-Pt{C≡CC(OH)EtMe}$_2$(PPh$_3$)$_2$] **1** and 0.1 g (0.98 mmol) of Al_2O_3 was refluxed for 1 h and the resulting yellow solution was evaporated to dryness. Addition of Et_2O (*ca.* 5 cm^3) afforded 0.32 g of a yellow solid which was identified by NMR (^1H, ^{13}C, and ^{31}P) as a mixture of **2a**, [*trans*-Pt(C≡CCEt=CH$_2$)$_2$(PPh$_3$)$_2$] **2b** and [*trans*-Pt{C≡C-(*Z*)-CMe=CHMe}(C≡CCEt=CH$_2$)(PPh$_3$)$_2$] **2c** (74%). Further attempts to separate this mixture by standard recrystallization methods were unsuccessful (Found: C, 65.89; H, 5.14%. $C_{48}H_{44}P_2Pt$ requires M^+ 877; C, 65.67; H, 5.05%); $\delta_P(CDCl_3)$ 18.6 [s, *J*(PPt) 2689], 18.7 [s, *J*(PPt) 2674 Hz]; *m*/*z* (% intensity) 877 (M^+, 9), 719 ($[Pt(PPh_3)_2]^+$, 68).

[*trans*-Pt{C≡CC(OMe)EtMe}$_2$(PPh$_3$)$_2$] 3. 0.10 g (0.11 mmol) of [*trans*-Pt{C≡CC(OH)EtMe}$_2$(PPh$_3$)$_2$] **1** were refluxed for 36 h in 15 cm^3 of MeOH. Evaporation of the resulting yellow solution to *ca.* 5 cm^3 caused the precipitation of complex **3** as a white solid (0.07 g, 68%) (Found: C, 63.37; H, 5.23%. $C_{50}H_{52}O_2P_2Pt$ requires C, 63.75; H, 5.56%); $\tilde{\nu}_{max}/cm^{-1}$ (C≡C) 2110m; $\delta_P(CDCl_3)$ 19.2 [s, *J*(PPt) 2699 Hz]; *m*/*z* (% intensity) 941 (M^+, 5), 912 ($M^+ - CH_3OH + 3H$, 23). Complex **3** was also obtained, as a white solid, by addition of two drops of a 0.1 M solution of HBF_4 in Et_2O (0.10 cm^3, 0.01 mmol) to a suspension of **1** (0.3 g, 0.33 mmol) in 25 cm^3 of MeOH, and refluxing the mixture for 30 min. Evaporation of the resulting colourless solution to *ca.* 5 cm^3 caused the precipitation of **3** (0.3 g, 97%).

[*trans*-Pt{C≡CC(OH)Ph$_2$}$_2$(PPh$_3$)$_2$] 4. Complex **4** was obtained following the same method described for complex **1**, but starting with 0.5 g (0.63 mmol) of [*cis*-$PtCl_2(PPh_3)_2$], 0.02 g (0.1 mmol) of CuI and 0.29 g (1.47 mmol) of HC≡C(OH)Ph$_2$ (0.54 g, 75%), (Found: C, 69.76; H, 4.78%. $C_{66}H_{52}O_2P_2Pt$ requires C, 69.89; H, 4.62%); $\tilde{\nu}_{max}/cm^{-1}$ (OH), 3558s, (C≡C) 2122s; $\delta_P(CDCl_3)$ 19.4 [s, *J*(PPt) 2654 Hz]; *m*/*z* (% intensity) 1117 ($M^+ - OH$, 27).

[*trans*-Pt(μ-C≡CR)(C$_6$F$_5$)(PPh$_3$)]$_2$ [R = C(OH)EtMe 5, (*Z*)-CMe=CHMe 6, C(OMe)EtMe 7, C(OH)Ph$_2$ 8]. A colourless solution of [*trans*-Pt{C≡CC(OH)EtMe}$_2$(PPh$_3$)$_2$] **1** (0.4 g, 0.44 mmol) in 20 cm^3 of CH_2Cl_2 was treated with 0.295 g (0.44 mmol) of [*cis*-$Pt(C_6F_5)_2(THF)_2$] at room temperature. The mixture was stirred for 20 min and the resulting orange solution was evaporated to dryness. Treatment of the residue with *ca.* 5 cm^3 of EtOH caused the precipitation of **5** as a white solid. Complexes **6**–**8** were prepared similarly as white (**7**) or beige (**6**, **8**) solids, except for complex **8**. For complex **8** the initial stirring of the mixture was for only 2 min and the final residue was treated with hexane: 0.15 g (0.17 mmol) of [*trans*-Pt{C≡C-(*Z*)-CMe=CHMe}$_2$(PPh$_3$)$_2$] **2a** and 0.115 g (0.17 mmol) of [*cis*-$Pt(C_6F_5)_2(THF)_2$] for **6**; 0.18 g (0.19 mmol) of [*trans*-Pt{C≡CC(OMe)EtMe}$_2$(PPh$_3$)$_2$] **3** and 0.13 g (0.19 mmol) of [*cis*-$Pt(C_6F_5)_2(THF)_2$] for **7**; 0.15 g (0.13 mmol) of [*trans*-Pt{C≡CC(OH)Ph$_2$}$_2$(PPh$_3$)$_2$] **4** and 0.09 g (0.13 mmol) of [*cis*-$Pt(C_6F_5)_2(THF)_2$] for **8**. Complexes **5** and **7** crystallise with one or half a molecule of CH_2Cl_2, respectively, as observed by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy in $CDCl_3$.

Complex 5. Yield 0.67 g, 90%; (Found: C, 48.30; H, 3.33%. $C_{60}F_{10}H_{48}O_2P_2Pt_2{\cdot}CH_2Cl_2$ requires C, 47.95; H, 3.30%. CH_2Cl_2 observed in the ^1H and $^{13}C\{^1H\}$ NMR spectra in $CDCl_3$);

$\tilde{\nu}_{max}$/cm^{-1} (OH) 3579m, ($C\equiv C$) 1975m, $(C_6F_5)_{X\text{-sensitive}}$ 792s; δ_P($CDCl_3$) 12.9 [s, *J*(PPt) 3895 Hz]; *m*/*z* (% intensity) 1345 ($M^+ - C_2R$, 9).

Complex 6. Yield 0.17 g, 71%; (Found: C, 50.82; H, 3.67%. $C_{60}F_{10}H_{44}P_2Pt_2$ requires C, 51.22; H, 3.15%); $\tilde{\nu}_{max}$/cm^{-1} ($C\equiv C$) 2019m, $(C_6F_5)_{X\text{-sensitive}}$ 793s; δ_P($CDCl_3$) 13.4 [s, *J*(PPt) 4047 Hz]; *m*/*z* (% intensity) 1405 ($M^+ - H$, 2).

Complex 7. Yield 0.22 g, 75%; (Found: C, 50.01; H, 3.60%. $C_{62}F_{10}H_{52}O_2P_2Pt_2 \cdot \frac{1}{2}CH_2Cl_2$ requires C, 49.63; H, 3.53%. CH_2Cl_2 observed in the ^1H and $^{13}C\{^1H\}$ NMR spectra in $CDCl_3$); $\tilde{\nu}_{max}$/cm^{-1} ($C\equiv C$) 1986m, $(C_6F_5)_{X\text{-sensitive}}$ 788s; δ_P($CDCl_3$) 13.0 [s, *J*(PPt) 3954]; at −50 °C 13.5, 13.4 [s, *J*(PPt) ≈ 3900 Hz]; *m*/*z* (% intensity) 1470 (M^+, 2); 1439 ($M^+ - MeOH + H$, 3).

Complex 8. Yield 0.15 g, 71%; (Found: C, 55.88; H, 2.79%. $C_{78}F_{10}H_{52}O_2P_2Pt_2$ requires C, 56.32; H, 3.15%); $\tilde{\nu}_{max}$/cm^{-1} (OH) 3577s,br, ($C\equiv C$) 1995m,br, $(C_6F_5)_{X\text{-sensitive}}$ 789s; δ_P($CDCl_3$) 10.6 [s, *J*(PPt) 4040 Hz]; *m*/*z* (% intensity) 1644 ($M^+ - OH - H$, 2).

[*trans*-Pt{C≡CC(OH)EtMe}(C_6F_5)(PPh_3)$_2$] 9. An orange solution of [*trans*-Pt{μ-C≡CC(OH)EtMe}(C_6F_5)(PPh_3)]$_2$ **5** (0.20 g, 0.13 mmol) in 15 cm^3 of CH_2Cl_2 was treated with 0.07 g (0.28 mmol) of PPh_3 to immediately give a colourless solution. The mixture was stirred for 1 h at room temperature, evaporated to dryness and the residue was treated with *ca.* 5 cm^3 of hexane to give **9** as a white solid (0.21 g, 83%) (Found: C, 58.42; H, 3.66%. $C_{48}F_5H_{39}OP_2Pt$ requires C, 58.59; H, 3.99%); $\tilde{\nu}_{max}$/cm^{-1} (OH), 3596m, ($C\equiv C$) 2131m, $(C_6F_5)_{X\text{-sensitive}}$ 790m; δ_P($CDCl_3$) 20.1 [s, *J*(PPt) 2729 Hz]; *m*/*z* (% intensity) 983 (M^+, 3), 965 ($M^+ - H_2O$, 17).

[*trans*-Pt{C≡C-(*Z*)-CMe=CHMe}(C_6F_5)(PPh_3)$_2$] 10. The addition, at room temperature, of four drops of a 0.1 M solution of HBF_4 in Et_2O (0.2 cm^3, 0.02 mmol) to a colourless solution of [*trans*-Pt{C≡CC(OH)EtMe}(C_6F_5)(PPh_3)]$_2$ **9** (0.13 g, 0.13 mmol) in 5 cm^3 of $CHCl_3$ immediately gave an orange solution that was stirred for 5 min. Evaporation of the mixture to dryness and treatment of the residue with hexane (*ca.* 5 cm^3) yielded **10** as a white solid (0.10 g, 77%) (Found: C, 59.42; H, 3.27%. $C_{48}F_5H_{37}P_2Pt$ requires C, 59.69; H, 3.86%); $\tilde{\nu}_{max}$/cm^{-1} ($C\equiv C$) 2102m, $(C_6F_5)_{X\text{-sensitive}}$ 796m; δ_P($CDCl_3$) 19.7 [s, *J*(PPt) 2710 Hz]; *m*/*z* 967 ($M^+ + 2H$, 18). Complex **10** was also obtained by addition, at room temperature, of 0.07 g (0.28 mmol) of PPh_3 over an orange solution of [*trans*-Pt{μ-C≡C-(*Z*)-CMe=CHMe}(C_6F_5)(PPh_3)]$_2$ **6** (0.2 g, 0.14 mmol) in 10 cm^3 of CH_2Cl_2. The mixture was stirred for 4.5 h to give a colourless solution which was evaporated to dryness. Addition of Et_2O (*ca.* 3 cm^3) to the solid residue yielded **10** as a white solid (0.12 g, 44%).

[*trans*-Pt(C≡CR)(C_6F_5)(PPh_3)$_2$] {R = C(OMe)EtMe 11, C(OH)Ph$_2$ 12}. A pale-yellow solution of [*trans*-Pt{μ-C≡CC(OMe)EtMe}(C_6F_5)(PPh_3)]$_2$ **7** (0.15 g, 0.10 mmol) in 15 cm^3 of CH_2Cl_2 was treated with 0.05 g (0.20 mmol) of PPh_3 and the mixture was stirred at room temperature for 2 days. Evaporation of the resulting solution to dryness and addition of 5 cm^3 of MeOH to the residue afforded **11** as a white solid. Complex **12** was obtained (white solid) in a similar way starting from 0.13 g (0.08 mmol) of [*trans*-Pt{μ-C≡CC(OH)Ph$_2$}(C_6F_5)(PPh_3)]$_2$ **8** and 0.08 g (0.32 mmol) of PPh_3, with 12 h of stirring and 5 cm^3 of cold absolute EtOH for the treatment of the final solid residue.

Complex 11. Yield 0.17 g, 85%; (Found: C, 58.67; H, 3.68%. $C_{49}F_5H_{41}OP_2Pt$ requires C, 58.98; H, 4.14%); $\tilde{\nu}_{max}$/cm^{-1} ($C\equiv C$) 2124m, $(C_6F_5)_{X\text{-sensitive}}$ 790m; δ_P($CDCl_3$) 20.0 [s, *J*(PPt) 2740 Hz]; *m*/*z* (% intensity) 997 (M^+, 3).

Complex 12. Yield 0.14 g, 81%; (Found: C, 62.30; H, 4.02%. $C_{57}F_5H_{41}OP_2Pt$ requires C, 62.58; H, 3.78%); $\tilde{\nu}_{max}$/cm^{-1} (OH) 3551s, ($C\equiv C$) 2122m, $(C_6F_5)_{X\text{-sensitive}}$ 790m; δ_P($CDCl_3$) 19.7 [s, *J*(PPt) 2710 Hz]; *m*/*z* (% intensity) 1077 ($M^+ - OH + H$, 40).

[*cis*,*trans*-(OC)(C_6F_5)$_2$Pt{μ-C≡CC(OH)EtMe}Pt{C≡CC(OH)EtMe}(PPh_3)$_2$] 13. A colourless solution of [*trans*-Pt{C≡CC(OH)EtMe}$_2$(PPh_3)$_2$] **1** (0.17 g, 0.19 mmol) in 20 cm^3 of CH_2Cl_2 was treated with 0.12 g (0.19 mmol) of [*cis*-Pt(C_6F_5)$_2$(CO)(THF)] at room temperature. The mixture was stirred for 10 min and the resulting yellow solution evaporated to a small volume (*ca.* 1 cm^3). Treatment of the residue with *ca.* 5 cm^3 of EtOH caused the precipitation of **13** as a pale-yellow solid (0.24 g, 86%) (Found: C, 49.45; H, 3.20%. $C_{61}F_{10}H_{48}O_3P_2Pt_2$ requires C, 49.80; H, 3.29%); $\tilde{\nu}_{max}$/cm^{-1} (OH) 3565m,br, (CO) 2093s, ($C\equiv C$) 2133w, 1972w, $(C_6F_5)_{X\text{-sensitive}}$ 799s, 785m; δ_P($CDCl_3$) 17.31 (s), 17.22 (s), 17.19 (s) (2 : 1 : 1) [*J*(PPt) ≈ 2510 Hz]; *m*/*z* (% intensity) 1081 ([$Pt_2(PPh_3)_2(C_6F_5)$]$^+$, 6); 897 ([$Pt(C_2R)_2(PPh_3)_2$]$^+$ − OH + H, 35); 816 ([$Pt(C_2R)(PPh_3)_2$]$^+$, 16); 719 ([$Pt(PPh_3)_2$]$^+$, 100).

[*cis*,*trans*-(OC)(C_6F_5)$_2$Pt(μ-C≡CR)Pt(C≡CR)(PPh_3)$_2$] [R = C(OMe)EtMe 14, C(OH)Ph$_2$ 15]. A pale-yellow solution of [*trans*-Pt{C≡CC(OMe)EtMe}$_2$(PPh_3)$_2$] **3** (0.15 g, 0.16 mmol) in 20 cm^3 of CH_2Cl_2 was treated with 0.10 g (0.16 mmol) of [*cis*-Pt(C_6F_5)$_2$(CO)(THF)] and the mixture stirred for 1 min. Evaporation of the resulting orange solution to dryness and addition of 5 cm^3 of MeOH to the solid residue afforded **14** as a beige solid. Complex **15** was obtained, as a beige solid, in a similar way starting from 0.20 g (0.18 mmol) of [*trans*-Pt{C≡CC(OH)Ph$_2$}$_2$(PPh_3)$_2$] **4** and 0.11 g (0.18 mmol) of [*cis*-Pt(C_6F_5)$_2$(CO)(THF)], with 5 min stirring and 5 cm^3 of hexane for the treatment of the final solid residue.

Complex 14. Yield 0.13 g, 55%; (Found: C, 50.37; H, 3.18%. $C_{63}F_{10}H_{52}O_3P_2Pt_2$ requires C, 50.47; H, 3.50%); $\tilde{\nu}_{max}$/cm^{-1} (CO) 2083s, ($C\equiv C$) 2130w, 1988w, $(C_6F_5)_{X\text{-sensitive}}$ 799s, 790s; δ_P($CDCl_3$) 18.0 [s, *J*(PPt) 2563 Hz]; *m*/*z* (% intensity) 912 ([$Pt(C_2R)_2(PPh_3)_2$]$^+$ − OMe + 2H, 40); 831 ([$Pt(C_2R)(PPh_3)_2$]$^+$ + H, 9); 719 ([$Pt(PPh_3)_2$]$^+$, 70).

Complex 15. Yield 0.25 g, 81%; (Found: C, 55.89; H, 2.79%. $C_{79}F_{10}H_{52}O_3P_2Pt_2$ requires C, 56.10; H, 3.10%); $\tilde{\nu}_{max}$/cm^{-1} (OH) 3562s,br, (CO) 2096s, ($C\equiv C$) 2005m, $(C_6F_5)_{X\text{-sensitive}}$ 800s,br; δ_P($CDCl_3$) 17.3 [s, *J*(PPt) 2547 Hz]; *m*/*z* (% intensity) 1117 ([$Pt(C_2R)_2(PPh_3)_2$]$^+$ − OH, 18); 926 ([$Pt(C_2R)(PPh_3)_2$]$^+$, 16); 719 ([$Pt(PPh_3)_2$]$^+$, 69).

Reaction of [*trans*-Pt{C≡C-(*Z*)-CMe=CHMe}$_2$(PPh_3)$_2$] 2a with [*cis*-Pt(C_6F_5)$_2$(CO)(THF)]. 0.11 g (0.17 mmol) of [*cis*-Pt(C_6F_5)$_2$(CO)(THF)] were added at room temperature to a solution of [*trans*-Pt{C≡C-(*Z*)-CMe=CHMe}$_2$(PPh_3)$_2$] **2a** (0.15 g, 0.17 mmol) in 20 cm^3 of CH_2Cl_2. The mixture was stirred for 5 minutes and the resulting red solution evaporated to *ca.* 1 cm^3. Addition of *ca.* 5 cm^3 of hexane afforded a pale-orange solid (0.13 g), which was identified by NMR (^1H, ^{19}F and ^{31}P) as a mixture of complexes containing [*cis*,*trans*-(OC)(C_6F_5)$_2$Pt{μ-C≡C-(*Z*)-CMe=CHMe}Pt{C≡C-(*Z*)-CMe=CHMe}(PPh_3)]$_2$ as the main species. Further attempts to separate this product pure from the mixture by standard recrystallization methods were unsuccessful and the complex was tentatively characterised by multinuclear NMR (^1H, ^{19}F and ^{31}P) δ_H($CDCl_3$) 5.05 (q, –CMe=C*H*Me), 4.84 (q, –CMe=C*H*Me); δ_F($CDCl_3$) −117.3 [dd, ^3J(Pt–*ortho*-F) = 382, 2 *ortho*-F], −118.2 [dd, ^3J(Pt–*ortho*-F) = 382, 2 *ortho*-F], −161.3 (t, 1 *para*-F), −161.9 (t, 1 *para*-F), −164.3 (m, 2 *meta*-F), −165.0 (m, 2 *meta*-F); δ_P($CDCl_3$) 16.1 [s, *J*(PPt) 2519 Hz].

[*trans*,*cis*-(PPh_3)$_2$(C_6F_5)Pt{μ-C≡C-(*Z*)-CMe=CHMe}Pt(C_6F_5)$_2$(CO)] 16. 0.06 g (0.10 mmol) of [*cis*-Pt(C_6F_5)$_2$(CO)(THF)] were added at room temperature to an orange solution of [*trans*-Pt{C≡C-(*Z*)-CMe=CHMe}(C_6F_5)(PPh_3)$_2$] **10** (0.10 g, 0.10 mmol) in 20 cm^3 of CH_2Cl_2. The mixture was stirred for 5 minutes and the resulting deep orange solution evaporated to dryness. Addition of *ca.* 5 cm^3 of a Et_2O–hexane mixture (1 : 5) afforded **16** as a yellow solid (0.09 g, 61%), (Found: C, 47.84; H, 2.48%. $C_{61}F_{15}H_{37}OP_2Pt_2$ requires C, 48.10; H, 2.45%); $\tilde{\nu}_{max}$/cm^{-1}

Table 2 Crystal data and structure refinement parameters for $\mathbf{7}\cdot\frac{1}{2}CH_2Cl_2$ and $\mathbf{8}\cdot CH_2Cl_2$

	$\mathbf{7}\cdot\frac{1}{2}CH_2Cl_2$	$\mathbf{8}\cdot CH_2Cl_2$
Empirical formula	$C_{62}H_{58}F_{10}O_2P_2Pt_2\cdot\frac{1}{2}CH_2Cl_2$	$C_{78}H_{52}F_{10}O_2P_2Pt_2\cdot CH_2Cl_2$
Molecular mass	1519.60	1748.24
Temperature/K	173(1)	173(2)
Wavelength/Å	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	$C2/c$	$C2/c$
a/Å	27.468(6)	24.0550(4)
b/Å	10.055(2)	13.5280(2)
c/Å	23.037(5)	20.3500(3)
β/°	115.56(3)	91.303(1)
Volume/Å^3	5740(2)	6620.5(2)
Z	4	4
Absorption coefficient/mm^{-1}	5.047	4.429
Reflections collected	5178	7849
Independent reflections	5037 [R(int) = 0.053]	7849 [R(int) = 0.0000]
Data/restraints/parameters	5029/6/375	7849/0/442
Goodness-of-fit on F^2	1.094	1.355
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0326$, $wR2 = 0.0763$	$R1 = 0.0273$, $wR2 = 0.0594$
R indices (all data)[a]	$R1 = 0.0543$, $wR2 = 0.0988$	$R1 = 0.0363$, $wR2 = 0.0620$

[a] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{0.5}$; $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.

(CO) 2117vs, (C≡C) 2083s, $(C_6F_5)_{\text{X-sensitive}}$ 796s,br; $\delta_P(CDCl_3)$ 19.6 [s, J(PPt) 2676 Hz]; m/z (% intensity) 965 ($[Pt(C_2R)(C_6F_5)(PPh_3)_2]^+$, 5); 886 ($[Pt(C_6F_5)(PPh_3)_2]^+$, 7); 718 ($[Pt(PPh_3)_2]^+$ − H, 25).

Reaction of [*trans*-Pt{C≡CC(OH)EtMe}(C_6F_5)(PPh_3)$_2$] 9 with [*cis*-Pt(C_6F_5)$_2$(CO)(THF)]. A colourless solution of [*trans*-Pt{C≡CC(OH)EtMe}(C_6F_5)(PPh_3)$_2$] **9** (0.15 g, 0.15 mmol) in 20 cm^3 of CH_2Cl_2 was treated with an equimolar amount of [*cis*-Pt(C_6F_5)$_2$(CO)(THF)] (0.09 g, 0.15 mmol) and the mixture was stirred for 30 min. NMR spectra of the resulting yellow solution showed a complex mixture of products also containing complex **16**. No pure product could be isolated from this mixture by standard work-up.

Reaction of [*trans*-Pt{C≡CC(OMe)EtMe}(C_6F_5)(PPh_3)$_2$] 11 with [*cis*-Pt(C_6F_5)$_2$(CO)(THF)]. 0.10 g (0.16 mmol) of [*cis*-Pt(C_6F_5)$_2$(CO)(THF)] were added to a yellow solution of [*trans*-Pt{C≡CC(OMe)EtMe}(C_6F_5)(PPh_3)$_2$] **11** (0.16 g, 0.16 mmol) in 20 cm^3 of CH_2Cl_2. The mixture was stirred for 30 min and the resulting orange solution evaporated to *ca.* 1 cm^3. Addition of *ca.* 5 cm^3 of a Et_2O–hexane mixture (1 : 5) afforded **16** as a yellow solid (0.09 g, 37%).

Reaction of [*trans*-Pt{C≡CC(OH)Ph$_2$}(C_6F_5)(PPh_3)$_2$] 12 with [*cis*-Pt(C_6F_5)$_2$(CO)(THF)]. A suspension of [*trans*-Pt{C≡CC(OH)Ph$_2$}(C_6F_5)(PPh_3)$_2$] **12** (0.09 g, 0.08 mmol) in 20 cm^3 of CH_2Cl_2 was treated with 0.11 g (0.17 mmol) of [*cis*-Pt(C_6F_5)$_2$(CO)(THF)] to immediately give a dark green solution. Its ^{31}P NMR spectrum showed that it was a mixture containing mainly a product with a singlet at δ 18.3. The solution was evaporated to dryness and the residue thus obtained was treated with a mixture of Et_2O–hexane (1 : 5) to yield the starting substrate **12** as a brown solid in a 18% yield (16 mg). Evaporation of the filtrate and subsequent treatment of the solid residue with hexane and Pr^{i}OH rendered two new fractions (12 and 7 mg), which were identified by ^{31}P NMR as mixtures of the mononuclear complex **12** and the product with the signal at δ 18.3, which we were not able to isolate and identify.

X-Ray crystallography

Crystal data and other details of the structure analyses are presented in Table 2. Suitable crystals of $\mathbf{7}\cdot\frac{1}{2}CH_2Cl_2$ and $\mathbf{8}\cdot CH_2Cl_2$, obtained by slow diffusion of hexane into CH_2Cl_2 solutions of the complexes at room temperature, were mounted on the end of a quartz fiber and held in place with fluorinated oil. X-Ray intensity data were collected, at 173 K, using Siemens STOE/AED2 four circle and Nonius Kappa CCD diffractometers for $\mathbf{7}\cdot\frac{1}{2}CH_2Cl_2$ and **8**, respectively. In both cases no decay of the crystal was observed over the period of data collection. For complex $\mathbf{7}\cdot\frac{1}{2}CH_2Cl_2$ an absorption correction was applied based on 504 azimuthal scan data and the structure was solved by Patterson and Fourier methods and refined by full-matrix least squares on F^2 using the SHELXL-93 program.[38] For complex **8**, images were processed using the DENZO and SCALEPACK suite of programs.[39] The structure was solved by Patterson and Fourier methods using the DIRDIF92 program[40] and refined by full-matrix least squares on F^2 using the SHELXL-97 program.[41] In both cases, all non-hydrogen atoms were assigned anisotropic displacement parameters and, for $\mathbf{8}\cdot CH_2Cl_2$, refined without positional constraints. The methyl and methoxy fragments of the acetylide ligands in $\mathbf{7}\cdot\frac{1}{2}CH_2Cl_2$ are disordered over two sets of positions with populations 0.55/0.45 in such a way that their positions are interchanged. The interatomic distances of the –C(OMe)EtMe fragment were constrained. The hydrogen atoms were constrained to idealised geometries and assigned anisotropic displacement parameters 1.2 times the U_{iso} value of their attached carbon atoms (1.5 times for the methyl hydrogen atoms), except for H(1) in $\mathbf{8}\cdot CH_2Cl_2$, which was located from Fourier difference maps and refined isotropically without any restraints.

CCDC reference numbers 165089 and 165090.

See http://www.rsc.org/suppdata/dt/b1/b104783n/ for crystallographic data in CIF or other electronic format.

Acknowledgements

Financial support was provided by the Dirección General de Investigación Científica y Técnica, (Spain, Projects PB98-1595-C02-01,02) and the University of La Rioja (Project API-00/B17). We also thank Dr E. Urriolabeitia of the University of Zaragoza (Spain) for the recording of the ^{1}H phase-sensitive NOESY spectrum.

References

1 For recent reviews see: (*a*) U. Belluco, R. Bertani, R. A. Michelin and M. Mozzon, *J. Organomet. Chem.*, 2000, **600**, 37; (*b*) J. Forniés and E. Lalinde, *J. Chem. Soc., Dalton Trans.*, 1996, 2587; (*c*) J. Manna, K. D. John and H. D. Hopkins,, *Adv. Organomet.*

Chem., 1995, **38**, 79; (*d*) R. Nast, *Coord. Chem. Rev.*, 1982, **47**, 89; (*e*) *Comprehensive Organometallic Chemistry II*, ed. G. Wilkinson, F. G. A. Stone and E. W. Abel, vol. ed. R. J. Puddephat, Pergamon Press, Oxford, 1995, vol. 9, ch. 8 and 9; (*f*) A. Vojcicki and C. E. Shuchart, *Coord. Chem. Rev.*, 1990, **105**, 35; (*g*) A. Sebald, C. Stader, B. Wrackmeyer and W. Bensch, *J. Organomet. Chem.*, 1986, **311**, 233.

2 (*a*) K. L. Myers, D. M. Ho, M. E. Thompson and C. Langhoff, *Polyhedron*, 1995, **14**, 57; (*b*) N. J. Long, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 826; (*c*) P. Nguyen, G. Lesley, T. B. Marder, I. Ledoux and J. Zyss, *Chem. Mater.*, 1997, **9**, 406; see also; (*d*) I. R. Whittall, A. M. McDonagh and M. G. Humphrey, *Adv. Organomet. Chem.*, 1998, **42**, 291.

3 (*a*) S. Takahashi, H. Takati, K. Morimoto, K. Sonogashira and N. Hagihara, *Mol. Cryst. Liq. Cryst.*, 1982, **32**, 139; (*b*) T. Kahara, H. Matsubara and S. Takahashi, *J. Mater. Chem.*, 1992, **2**, 43.

4 (*a*) W. W. W. Yam, C. H. Tao, L. Zhang, K. M. C. Wong and K. K. Cheung, *Organometallics*, 2001, **20**, 453; (*b*) W. W. W. Yam, K. K. W. Lo and K. M. C. Wong, *J. Organomet. Chem.*, 1999, **587**, 3; (*c*) J. P. H. Chartman, J. Forniés, J. Gómez, E. Lalinde, R. I. Merino, M. T. Moreno and A. G. Orpen, *Organometallics*, 1999, **18**, 3353; (*d*) I. Ara, J. R. Berenguer, E. Eguizábal, J. Forniés, J. Gómez, E. Lalinde and J. M. Saez-Rocher, *Organometallics*, 2000, **19**, 4385; (*e*) W. Y. Wong, K. H. Choi and K. W. Cheah, *J. Chem. Soc., Dalton Trans.*, 2000, 113; (*f*) N. J. Long, A. J. Martín, R. Vilar, A. J. P. White, D. J. Williams and M. Younus, *Organometallics*, 1999, **18**, 4261; (*g*) N. Chawdhury, A. Köhler, R. H. Friend, M. Younus, N. J. Long, P. R. Raithby and J. Lewis, *Macromolecules*, 1998, **31**, 722; (*h*) C. W. Chan, L. K. Cheng and C. M. Che, *Coord. Chem. Rev.*, 1994, **132**, 87; (*i*) M. Hissler, W. B. Connick, D. K. Geiger, J. E. McGarrah, D. Lipa, R. J. Lachicotte and R. Eisenber, *Inorg. Chem.*, 2000, **39**, 448.

5 (*a*) M. Oshiro, F. Takei, K. Onitsuka and S. Takahashi, *J. Organomet. Chem.*, 1998, **569**, 195; (*b*) K. Onitsuka, M. Ohsiro and S. Takahashi, *Angew. Chem., Int. Ed.*, 1999, **38**, 689; (*c*) S. Leininger and P. Stang, *Organometallics*, 1998, **17**, 3981; (*d*) J. A. Whiteford, C. V. Lu and J. P. Stang, *J. Am. Chem. Soc.*, 1997, **119**, 2524; (*e*) J. Manna, J. A. Whiteford, P. J. Stang, D. C. Muddiman and R. D. Smith, *J. Am. Chem. Soc.*, 1996, **118**, 8731; (*f*) S. M. AlQuaisi, K. J. Galat, M. Chai, D. G. Ray, P. L. Rinaldi, C. A. Tessier and W. J. Young, *J. Am. Chem. Soc.*, 1998, **120**, 12149; (*g*) A. Harriman, M. Hissler, R. Ziessel, A. De Cian and J. Fischer, *J. Chem. Soc., Dalton Trans.*, 1995, 4067; (*h*) A. Harriman and Z. Ziessel, *Coord. Chem. Rev.*, 1998, **171**, 331; (*i*) E. Bosch and C. L. Barnes, *Organometallics*, 2000, **19**, 5522.

6 (*a*) J. Lewis, P. R. Raithby and W. Y. Wong, *J. Organomet. Chem.*, 1998, **556**, 219; (*b*) N. Chawdhury, A. Köhler, R. H. Friend, W. Y. Wong, J. Lewis, M. Younus, P. R. Raithby, T. C. Corcoran, M. R. A. Al-Mandhary and S. M. Khan, *J. Chem. Phys.*, 1999, **110**, 4963; (*c*) C. J. Adams, S. L. James and P. R. Raithby, *Chem. Commun.*, 1997, 2155; (*d*) K. Onitsuka, N. Ose, F. Ozawa and S. Takahashi, *J. Organomet. Chem.*, 1999, **578**, 169; see also; (*e*) R. P. Kingsborough and T. M. Swager, *Prog. Inorg. Chem.*, 1999, **48**, 123.

7 For some recent examples see: (*a*) A. J. Deeming, G. Hogart, M. Lee, M. Saha, S. P. Redmond, H. Phetmung and A. G. Orpen, *Inorg. Chim. Acta*, 2000, **309**, 109; (*b*) S. Back, R. A. Gossage, M. Luzt, I. Del Río, A. L. Spek, H. Lang and G. van Koten, *Organometallics*, 2000, **19**, 3296; (*c*) M. I. Bruce, B. C. Hall, P. J. Law, M. F. Smith, B. W. Skelton and A. H. White, *Inorg. Chim. Acta*, 2000, **300**, 633.

8 (*a*) I. Ara, J. R. Berenguer, J. Forniés, J. Gómez, E. Lalinde and R. I. Merino, *Inorg. Chem.*, 1997, **36**, 6461; (*b*) I. Ara, J. Forniés, J. Gómez, E. Lalinde, R. I. Merino and M. T. Moreno, *Inorg. Chem. Commun.*, 1999, **2**, 62; (*c*) I. Ara, J. Forniés, J. Gómez, E. Lalinde and M. T. Moreno, *Organometallics*, 2000, **19**, 3137; (*d*) J. P. H. Chartmant, L. R. Falvello, J. Forniés, J. Gómez, E. Lalinde, M. T. Moreno, A. G. Orpen and A. Rueda, *Chem. Commun.*, 1999, 2045; (*e*) C. J. Adams and P. R. Raithby, *J. Organomet. Chem.*, 1999, **578**, 178; (*f*) W. W. W. Yam, K. L. Yu, K. M. C. Wong and K. K. Cheung, *Organometallics*, 2001, **20**, 721.

9 (*a*) J. R. Berenguer, E. Eguizábal, L. R. Falvello, J. Forniés, E. Lalinde and A. Martín, *Organometallics*, 2000, **19**, 490; (*b*) I. Ara, J. R. Berenguer, E. Eguizábal, J. Forniés, E. Lalinde and F. Martínez, *Organometallics*, 1999, **18**, 4344; (*c*) I. Ara, J. R. Berenguer, E. Eguizábal, J. Forniés, E. Lalinde, A. Martín and F. Martínez, *Organometallics*, 1998, **17**, 4578; (*d*) I. Ara, L. R. Falvello, S. Fernández, J. Forniés, E. Lalinde, A. Martin and M. T. Moreno, *Organometallics*, 1997, **16**, 5923; (*e*) I. Ara, J. R. Berenguer, J. Forniés and E. Lalinde, *Inorg. Chim. Acta*, 1997, **264**, 199.

10 For reviews see: (*a*) U. Rosenthal, P. M. Pellny, F. G. Kirchbauer and V. V. Burlakov, *Acc. Chem. Res.*, 2000, **33**, 119; (*b*) P. Siemsen, R. C. Livingston and F. Diederich, *Angew. Chem., Int. Ed.*, 2000, **39**, 2632; (*c*) E. D. Jemmis and K. T. Giju, *J. Am. Chem. Soc.*, 1998, **120**, 6952; for recent examples; (*d*) Y. Hayashi, M. Osawa and Y. Wakatsuki, *J. Organomet. Chem.*, 1997, **542**, 241; (*e*) S. Back, H. Pritzkow and H. Lang, *Organometallics*, 1998, **17**, 41; (*f*) W. Baumann, P. M. Pellny and U. Rosenthal, *Magn. Reson. Chem.*, 2000, **38**, 515 and references therein; (*g*) C. V. Ursini, G. H. M. Dias, M. Horner, A. J. Bortoluzzi and M. K. Morigaki, *Polyhedron*, 2000, **19**, 2261; (*h*) R. Choukroun, B. Donnadieu, J. S. Zhao, P. Cassoux, C. Lepetit and B. Silvi, *Organometallics*, 2000, **19**, 1901.

11 (*a*) J. Forniés, E. Lalinde, A. Martín and M. T. Moreno, *J. Chem. Soc., Dalton Trans.*, 1994, 135; (*b*) J. R. Berenguer, J. Forniés, E. Lalinde, A. Martín and M. T. Moreno, *J. Chem. Soc., Dalton Trans.*, 1994, 3343; (*c*) J. Forniés, E. Lalinde, A. Martín and M. T. Moreno, *J. Organomet. Chem.*, 1995, **490**, 179; (*d*) I. Ara, J. R. Berenguer, J. Forniés, E. Lalinde and M. T. Moreno, *J. Organomet. Chem.*, 1996, **510**, 63; (*e*) J. R. Berenguer, J. Forniés, E. Lalinde and F. Martínez, *Organometallics*, 1996, **15**, 4537; (*f*) I. Ara, J. R. Berenguer, J. Forniés and E. Lalinde, *Organometallics*, 1997, **16**, 3921.

12 (*a*) D. Zhang, D. B. McConville, C. A. Tessier and W. Youngs, *Organometallics*, 1997, **16**, 824; (*b*) S. Yamazaki and A. J. Deeming, *J. Chem. Soc., Dalton Trans.*, 1993, 3051; (*c*) H. Lang, A. del Villar and G. Rheinwald, *J. Organomet. Chem.*, 1999, **587**, 284; (*d*) J. A. Whiteford, P. J. Stang and S. D. Huang, *Inorg. Chem.*, 1998, **37**, 5595; (*e*) C. Müller, J. A. Whiteford and P. J. Stang, *J. Am. Chem. Soc.*, 1998, **120**, 9827.

13 J. Forniés, M. A. Gómez-Saso, E. Lalinde, F. Martínez and M. T. Moreno, *Organometallics*, 1992, **11**, 2873.

14 J. R. Berenguer, J. Forniés, F. Martínez, J. C. Cubero, E. Lalinde, M. T. Moreno and A. J. Welch, *Polyhedron*, 1993, **12**, 1797.

15 J. R. Berenguer, J. Forniés, E. Lalinde, F. Martínez, E. Urriolabeitia and A. J. Welch, *J. Chem. Soc., Dalton Trans.*, 1994, 1291.

16 J. R. Berenguer, J. Forniés, E. Lalinde and F. Martínez, *Organometallics*, 1995, **14**, 2532.

17 J. R. Berenguer, J. Forniés, E. Lalinde, F. Martínez, L. Sánchez and B. Serrano, *Organometallics*, 1998, **17**, 1640.

18 (*a*) M. V. Russo and A. Furlani, *J. Organomet. Chem.*, 1979, **165**, 101; (*b*) A. Furlani, P. Carussi and M. V. Russo, *J. Organomet. Chem.*, 1976, **116**, 113.

19 (*a*) C. Gauss, D. Veghini, O. Orama and H. Berke, *J. Organomet. Chem.*, 1997, **541**, 19 and references therein; (*b*) M. A. Jiménez Tenorio, M. J. Tenorio, M. C. Puerta and P. Valerga, *Organometallics*, 1997, **16**, 5528; (*c*) G. Jia, W. F. Wu, R. Y. Yeung and H. Xia, *J. Organomet. Chem.*, 1997, **538**, 31 and references therein; (*d*) S. Brait, G. Gervasio, D. Marabello and E. Sappa, *J. Chem. Soc., Dalton Trans.*, 2000, 989; (*e*) P. Crochet, M. A. Esteruelas, A. M. López, N. Ruiz and J. I. Tolosa, *Organometallics*, 1998, **17**, 3479; (*f*) M. P. Gamasa, J. Gimeno and B. M. Martin-Vaca, *Organometallics*, 1998, **17**, 3707; (*g*) N. Ruiz, D. Peron, S. Sinbandith, P. H. Dixneuf, C. Baldoli and S. Maiorana, *J. Organomet. Chem.*, 1997, **533**, 213; (*h*) D. Empsall, B. L. Shaw and A. J. Stringer, *J. Organomet. Chem.*, 1975, **94**, 131; (*i*) A. Furlani, S. Licoccia and M. V. Russo, *J. Chem. Soc., Dalton Trans.*, 1980, 1958.

20 (*a*) P. S. Pregosin and R. W. Kunz, *^{31}P and ^{13}C NMR of Transition Metal Phosphine Complexes*, Springer, New York, 1997; (*b*) A. Sebald, B. Wrackmeyer and W. Beck, *Z. Naturforsch, Teil B*, 1983, **38**, 45.

21 (*a*) A. Furlani, S. Licoccia, M. V. Russo, A. Ch. Villa and C. Guastini, *J. Chem. Soc., Dalton Trans.*, 1984, 2197; (*b*) K. Sonogashira, Y. Fujikura, T. Yatake, N. Toyoshima, S. Takahashi and N. Haghihara, *J. Organomet. Chem.*, 1978, **145**, 101; (*c*) I. Collamati and A. Furlani, *J. Organomet. Chem.*, 1969, **17**, 457.

22 (*a*) R. J. Cross and M. F. Davidson, *Inorg. Chim. Acta*, 1985, **97**, L35; (*b*) R. J. Cross and M. F. Davidson, *J. Chem. Soc., Dalton Trans.*, 1986, 1987.

23 (*a*) G. L. Wood, C. B. Knobler and M. F. Hawthorne, *Inorg. Chem.*, 1989, **28**, 382; (*b*) G. Erker, W. Frömberg, R. Benn, R. Mynott, K. Angermund and C. Krüger, *Organometallics*, 1989, **8**, 911; (*c*) P. M. Pellny, N. Peulecke, V. V. Burlakov, A. Tillack, W. Baumann, A. Spannenberg, R. Kempe and U. Rosenthal, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 2615; (*d*) P. M. Pellny, V. V. Burlakov, W. Baumann, A. Spannenberg, R. Kempe and U. Rosenthal, *Organometallics*, 1999, **18**, 2906.

24 J. Muller, M. Tschampel and J. Pickardt, *J. Organomet. Chem.*, 1988, **355**, 513.

25 (*a*) G. R. Desiraju, *Crystal Engineering: The design of organic solids*, Elsevier, New York, 1989; (*b*) M. C. Etter, *Acc. Chem. Res.*, 1990, **23**, 120; (*c*) F. H. Allen, W. D. S. Motherwell, P. R. Raithby, G. P. Shields

and R. Taylor, *New J. Chem.*, 1999, **23**, 25; (*d*) G. A. Jeffrey and W. Saenger, *Hydrogen bonding in biological structures*, Springer-Verlag, Berlin, 1991.

26 For some recent reviews see: (*a*) T. B. Aakeröy and K. R. Seddon, *Chem. Soc. Rev.*, 1993, 397; (*b*) D. Braga and F. Grepioni, *Coord. Chem. Rev.*, 1999, **183**, 19; (*c*) T. Steiner, *J. Phys. Chem. A*, 1998, **102**, 7041; (*d*) M. J. Calhorda, *Chem. Commun.*, 2000, 801; see also the special volume dedicated to this topic in: *J. Chem. Soc., Dalton Trans.*, 2000, issue 21; (*e*) A. D. Burrows, C. W. Chan, M. M. Chowdry, J. E. McGrady and D. M. P Mingos, *Chem. Soc. Rev.*, 1995, 331; (*f*) R. H. Crabtree, P. E. M. Siegbhan, O. Eisenstein, A. L. Reingold and T. F. Koetzle, *Acc. Chem. Res.*, 1996, **29**, 348.

27 (*a*) J. D. Dunitz and R. Taylor, *Chem. Eur. J.*, 1997, **3**, 89; (*b*) J. A. K. Howard, V. J. Hoy, D. O'Hagan and G. T. Smith, *Tetrahedron*, 1996, **52**, 12613; (*c*) M. Pham, M. Gdaniec and T. Polonski, *J. Org. Chem.*, 1998, **63**, 3731; (*d*) M. P. Thornberry, C. Slebodnick, P. A. Deck and F. R. Fronczek, *Organometallics*, 2000, **19**, 5352.

28 (*a*) L. Shimoni and J. P. Glusker, *Struct. Chem.*, 1994, **5**, 583; (*b*) D. J. Teff, J. C. Hoffmann and K. G. Coulton, *Inorg. Chem.*, 1997, **36**, 4372; (*c*) U. Fekl, R. van Eldik, S. Lovell and K. I. Golberg, *Organometallics*, 2000, **19**, 3535.

29 This distance is even larger than the sum of the van der Waals radii of H and F ($r_{\mathrm{H}} + r_{\mathrm{F}} = 2.5$–2.7 Å). L. Pauling, *The Nature of the Chemical Bond*, 3rd edn., Cornell University Press, Ithaca, New York, 1960.

30 (*a*) F. Crepioni, G. Cojazzi, S. M. Draper, N. Scully and D. Braga, *Organometallics*, 1998, **17**, 296; (*b*) R. P. Hughes, D. C. Lindner, A. L. Rheingold and L. M. Liable-Sands, *J. Am. Chem. Soc.*, 1997, **119**, 11544.

31 For recent reviews see: (*a*) W. Beck, B. Niemer and M. Weiser, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 923; (*b*) S. Lotz, P. H. Van Rooyen and R. Meyer, *Adv. Organomet. Chem.*, 1995, **37**, 219; (*c*) U. Bunz, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 969; (*d*) F. Paul and C. Lapinte, *Coord. Chem. Rev.*, 1998, **178–180**, 431; (*e*) V. Cadierno, S. Conejero, M. P. Gamasa and J. Gimeno, *J. Chem. Soc., Dalton Trans.*, 2000, 451; (*f*) G. Jia and C. P. Lau, *J. Organomet. Chem.*, 1998, **565**, 37; (*g*) T. Bartik, W. Weng, J. A. Ramsden, S. Szafert, S. B. Falloon, A. M. Arif and J. A. Gladysz, *J. Am. Chem. Soc.*, 1998, **120**, 11071 and references therein; (*h*) M. Laubender and H. Werner, *Chem. Eur. J.*, 1999, **5**, 2937 and references therein; (*i*) C. Bianchini, G. Purches, F. Zanobini and M. Peruzzini, *Inorg. Chim. Acta*, 1998, **272**, 1.

32 (*a*) K. Onitsuka, N. Ose, F. Ozawa and S. Takahashi, *J. Organomet. Chem.*, 1999, **578**, 169; (*b*) H. Lang, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 547.

33 I. Ara, J. R. Berenguer, J. Forniés, E. Lalinde and M. Tomás, *Organometallics*, 1996, **15**, 1014.

34 For a review see: R. Chauvin, *Eur. J. Inorg. Chem.*, 2000, 577.

35 (*a*) J. R. Berenguer, E. Eguizábal, L. R. Falvello, J. Forniés, E. Lalinde and A. Martín, *Organometallics*, 1999, **18**, 1653; (*b*) F. R. Hartley, *The chemistry of platinum and palladium*, Applied Science Publishers Ltd., London, 1973, p. 370.

36 S. Braun, H.-O. Kalinonowski and S. Berger, *100 and More Basic NMR Experiments*, VCH, Weinheim, Germany, 1996.

37 (*a*) R. Usón, J. Forniés, M. Tomás and B. Menjón, *Organometallics*, 1985, **4**, 1912; (*b*) R. Usón, J. Forniés, P. Espinet, C. Fortuño, M. Tomás and A. J. Welch, *J. Chem. Soc., Dalton Trans.*, 1988, 3005.

38 G. M. Sheldrick, SHELXL-93, a program for crystal structure determination, University of Göttingen, Germany, 1993.

39 Z. Otwinowski and W. Minor, in *Methods in Enzymology*, ed. C. W. Carter, Jr. and R. M. Sweet, Academic Press, New York, 1997, p. 307.

40 P. T. Beursken, G. Admiraal, G. Beursken, W. P. Bosman, S. García-Granda, R. O. Gould, J. M. M. Smits and C. Smykalla, The DIRDIF92 program system, Technical report of the Crystallography laboratory, University of Nijmegen, The Netherlands, 1992.

41 G. M. Sheldrick, SHELXL-97, a program for the refinement of crystal structures, University of Göttingen, Germany, 1997.