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Stability and reactivity of the *cis*-$Pt^{II}R$(alkyne) fragment (R = alkyl): an unprecedented rearrangement to form the $Pt^{II}(\eta^3$-allyl) moiety

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The complexes $[PtR(\eta^2$-*E*-$MeO_2CCH{=}CHCO_2Me)(phen)]^+BF_4^-$ (R = Me **1a** or Et **1b**; phen = 1,10-phenanthroline) reacted with alkynes yielding the corresponding products $[PtR(\eta^2$-alkyne)(phen)$]^+BF_4^-$ **2**. These can be isolated in the case of disubstituted electron-rich alkynes, while the electron-poor $MeO_2CC{\equiv}CCO_2Me$ inserted into the Pt−R bond leading to the corresponding σ-vinyl derivative. Type **2** complexes containing alk-1-ynes undergo an unprecedented rearrangement to form stable $[Pt(\eta^3$-allyl)(phen)$]^+BF_4^-$ products. Mechanistic aspects of the reaction are discussed.

Alkyne complexes of platinum(II) have been known since 1945.[1] A substantial upgrowth in the knowledge of their chemistry was prompted in the early 1970s by Clark and co-workers,[2] who found that the stability and reactivity of square-planar complexes *trans*-$[PtMeL_2(\eta^2$-alkyne)$]^+$ (L = phosphine) was markedly affected by the solvent and by the nature of the unsaturated ligand. Only with disubstituted electron-rich alkynes it was possible to isolate the complexes,[2h,i] while in all other cases further rearrangements occurred, *i.e.* (*i*) nucleophilic attack of the solvent,[2g,i] (*ii*) insertion reactions[2a,b,i] or (*iii*) acetylide formation.[2c,i]

Little attention has been devoted to the chemistry of square-planar platinum(II) complexes[3] having an alkyl group and an alkyne in mutual *cis* position, although this arrangement deserves particular attention due to its proposed occurrence in many reactive intermediates.[4] As a part of our research dealing with alkene and alkyne palladium(II) and platinum(II) derivatives,[5] we aimed to investigate the synthetic feasibility of cationic complexes of general formula $[PtR(N,N'$-chelate$)(\eta^2$-alkyne)$]^+$. In this paper we report the results, in comparison with what previously found for *trans*-$[PtMeL_2(\eta^2$-alkyne)$]^+$ complexes.[2] Also discussed is an unprecedented and remarkable rearrangement of the above N,N′-chelate species containing alk-1-ynes which leads to π-allyl products $[Pt(\eta^3$-allyl)(N,N′-chelate)$]^+$.

Results and Discussion

The chemistry developed in this work is depicted in Scheme 1. The starting compounds were the recently described[5d] square-planar complex $[PtMe(\eta^2$-*E*-$MeO_2CCH{=}CHCO_2Me)(phen)]^+$-$BF_4^-$ **1a** (phen = 1,10-phenanthroline) and its related ethyl derivative **1b**. They can be prepared *in situ* by adding a solution of the appropriate trialkyloxonium salt to the three-co-ordinate complex $[Pt(\eta^2$-*E*-$MeO_2CCH{=}CHCO_2Me)(phen)]$[6] [path (*i*)]. As generally found for an electron-poor olefin, dimethyl fumarate is weakly bound to the four-co-ordinate metal centre. Hence, it can be rapidly replaced by other ligands, *e.g.* alkynes. Reaction (*ii*) is very fast and the fate of the resulting type **2** product depends on the nature of the alkyne. Electron-rich disubstituted alkynes afford stable complexes, in analogy with the related *trans*-$[PtMeL_2(\eta^2$-alkyne)$]^+$ derivatives.[2h,i] The products can be isolated in high yield by adding diethyl ether to the reaction mixture and have been characterized through elemental analyses and NMR spectroscopy (Table 1). The most relevant NMR spectral features are: (*i*) ^{1}H NMR PtMe resonances fall in the range (δ 0.9–1.3) generally observed for square-planar complexes of type [PtMe(L)(N,N′-chelate)];[7] (*ii*) the two halves of phen are not equivalent, the H^2 and H^9 protons of phen coupling to ^{195}Pt to different extents [^2J(Pt−H) = *ca.* 50 and <15 Hz, respectively] with the smallest value attributed to the proton which is close to the N atom *trans* to Me; (*iii*) the alkyne signals also split due to coupling with ^{195}Pt which indicates that the exchange of the unsaturated ligand between different metal centres is slow on the NMR time-scale, in contrast with analogous olefin complexes which undergo fast exchange phenomena.[5d]

On the whole, the chemical behaviour of type **2** complexes which contain alkynes bearing electron-donor substituents resembles that of the analogous derivatives *trans*-$[PtMeL_2(\eta^2$-alkyne)$]^+$ described by Chisholm and Clark.[2h,i] In fact, no insertion of the unsaturated ligand into the platinum–alkyl bond occurs even after standing for several hours in nitromethane solution. We recall that examples of migratory insertion of aliphatic alkynes into the Pt−Me bond are known.[8] However, they concern cycloalkynes (*e.g.* cyclohexyne), and the main driving force of the reaction is probably the release of constraints which exist in the strained ligands.

Type **1** precursors have been also treated with terminal electron-rich alkynes (RC≡CH). After the attainment of a transient type **2** species [see below and path (*ii*)], stable η^3-allyl derivatives **3** rapidly form [path (*iii*)]. The NMR spectrum of the reacting mixture recorded within a few minutes from the addition of the alkyne to a solution of **1a** or **1b** discloses the quantitative formation of the final product. Thus, reaction of **1a** with PhC≡CH, $PhCH_2C{\equiv}CH$ or $Bu^nC{\equiv}CH$ affords respectively $[Pt(\eta^3$-$CH_2CHCHPh)(phen)]^+$ **3a**, $[Pt(\eta^3$-$CH_2CHCHCH_2Ph)$-$(phen)]^+$ **3b** and $[Pt(\eta^3$-$CH_2CHCHBu^n)(phen)]^+$ **3c**. Analogously, **1b** and phenylacetylene lead to $[Pt\{\eta^3$-CH(Me)CHCH-Ph$\}(phen)]^+$ **3d**. These new complexes belong to a known class of allyl derivatives.[9] Only **3a** exists in pure *syn* form, while in the other cases a mixture of the *syn* (70–80) and *anti* (20–30%) complexes is observed. The NMR spectral features as well as the factors which stabilize the *syn* or the *anti* form have been discussed thoroughly elsewhere.[9]

Aiming to gain information about the mechanism of the π-allyl formation, we have monitored the additions of Ph-$CH_2C{\equiv}CH$ and PhC≡CH to complex **1a** through NMR spectroscopy at 253 K. Under these conditions type **2** complexes (**2f** and **2g**, respectively) can clearly be detected in the early stage of the reaction. The reaction of **1a** and **1b** with deuteriophenyl-

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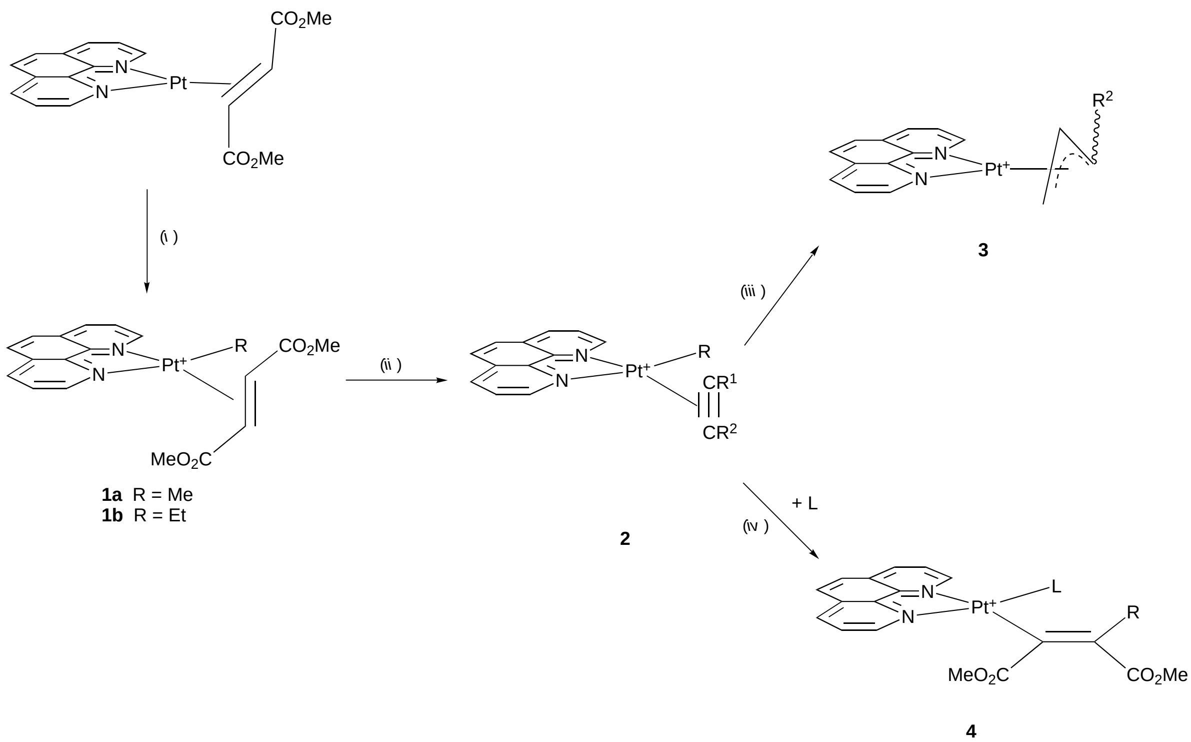


Scheme 1 (*i*) R_3OBF_4 (R = Me or Et); (*ii*) $R^1C{\equiv}CR^2$; (*iii*) R^1 = H, R^2 = Ph, CH_2Ph, Bu^n; (*iv*) R^1, R^2 = CO_2Me

Table 1 Selected NMR and analytical data for type **2** complexes

	$^1H^a$ [$^{13}C^b$] NMR (δ)				Analysis (%)^c		
Complex	H^2 of phen^{d,e}	C≡C^f	Pt–CH_x^{f,g}	Other signals^{e,h}	C	H	N
2a $[PtMe(\eta^2\text{-}MeC{\equiv}CMe)(phen)]BF_4$	9.36 (51, d)	[72.6 (162, 2 C)]	1.03 (76, 3 H) [−10.9 (1 C)]	2.35 (49, 6 H) [8.3 (2 C)]	38.6 (38.45)	3.2 (3.25)	5.45 (5.25)
2b $[PtMe(\eta^2\text{-}PhC{\equiv}CPh)(phen)]BF_4$	9.51 (53, d)	[82.4 (208, 2 C)]	1.23 (76, 3 H) [−8.8 (674, 1 C)]		49.1 (49.5)	3.35 (3.25)	4.35 (4.25)
2c $[PtMe(\eta^2\text{-}PhC{\equiv}CMe)(phen)]BF_4$	9.37 (52, d)	[82.1 (1 C)] [74.1 (1 C)]	1.13 (77, 3 H) [−9.8 (694, 1 C)]	2.69 (45, 3 H) [9.4 (1 C)]	44.3 (44.55)	3.3 (3.25)	4.75 (4.7)
2d $[PtEt(\eta^2\text{-}MeC{\equiv}CMe)(phen)]BF_4$	9.32 (52, d)	[71.2 (216, 2 C)]	1.73 (q, 83, 2 H) [4.0 (684, 1 C)]	2.38 (51, 6 H) 1.03 (36, t, 3 H) [16.5 (32, 1 C)] [7.9 (32, 2 C)]	39.75 (39.65)	3.45 (3.5)	4.95 (5.15)
2e $[PtEt(\eta^2\text{-}PhC{\equiv}CPh)(phen)]BF_4$	9.5 (br)	[83.2 (226, 2 C)]	1.94 (q, 81, 2 H) [6.9 (653, 1 C)]	0.94 (33, t, 3 H) [16.9 (33, 1 C)]	50.2 (50.25)	3.3 (3.45)	4.35 (4.2)
2f $[PtMe(\eta^2\text{-}PhCH_2C{\equiv}CH)(phen)]BF_4$^{i}	9.18 (d)		0.89 (73, 3 H)	3.75 (br, 2 H)			
2g $[PtMe(\eta^2\text{-}PhC{\equiv}CH)(phen)]BF_4$^{i}	9.28 (50, d)		1.04 (74, 3 H)				

^{a} At 270 or 200 MHz and 298 K; in CD_3NO_2, CHD_2NO_2 (δ 4.33) as internal standard. ^{b} At 67.9 or 50.3 MHz and 298 K; in CD_3NO_2, $^{13}CHD_2NO_2$ (δ 62.8) as internal standard. ^{c} Calculated values in parentheses. ^{d} Refers to the proton close to the N atom *trans* to the alkyne. The other phen protons resonate in the ranges 9.1–8.8 (H^4, H^7, H^9), 8.3–8.0 (H^3, H^5, H^6, H^8). ^{e} ^3J(Pt–H) Hz in parentheses (when measurable). ^{f} ^1J(Pt–C) Hz in parentheses (when measurable). ^{g} ^2J(Pt–H) Hz in parentheses. ^{h} ^2J(Pt–C) Hz in parentheses. ^{i} Recorded at 253 K, see text.

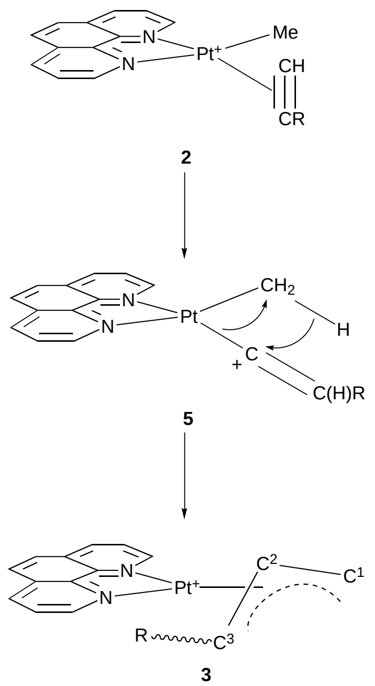
acetylene (PhC≡CD) proceeds in both cases with quantitative deuteriation at C^3 and subsequent formation of $[Pt(\eta^3\text{-}CH_2\text{-}CHCDPh)(phen)]^+$ and $[Pt\{\eta^3\text{-}CH(Me)CHCDPh\}(phen)]^+$, respectively. Furthermore, the addition of phenylacetylene to $[PtI(CD_3)(phen)]$ in the presence of $AgBF_4$ yields $[Pt(\eta^3\text{-}CD_2\text{-}CDCHPh)(phen)]^+$. The position of deuteriation was clearly deduced by comparing the ^1H NMR spectra of the non-deuteriated products with those of the corresponding labelled compounds.

With this in mind we propose the mechanism depicted in Scheme 2. It is suggested that a type **2** derivative is formed, which undergoes a hydride shift. A similar migration has been proposed by Chisholm and Clark [2i] and affords a Pt–C^+=C(H)R fragment. A further rearrangement prompted by the *cis* geometry of **5** would account for the formation of the final type **3** product. Other mechanisms may be formulated, *e.g.* insertion of the alkyne into the Pt–Me bond and rearrangement of the resulting σ-vinyl derivative. However, as far as we know, the insertion of terminal alkynes into platinum(II)–alkyl bonds has never been reported, although η^2-alk-1-yneplatinum(II) complexes are very reactive.‡

We wish to underline that rearrangement (*iii*) is novel and is of interest also because it affords a new route to π-allyl derivatives.

Complex **1a** has been also treated with an alkyne containing electron-withdrawing substituents, *i.e.* $MeO_2CC{\equiv}CCO_2Me$. The first NMR spectrum of the reaction mixture discloses that the

‡ When PhC≡CH was treated with *trans*-$[PtL_2L'(Me)]^+$ precursors, acetylide formation [2c,i] or nucleophilic attack [2g,i] of the solvent to the co-ordinated unsaturated ligand were observed. Although alk-1-ynes were known to give stable complexes in co-ordinatively saturated environments,[5b,10] only very recently a stable square-planar platinum(II) complex has been described.[11]



Scheme 2

reaction is poorly chemoselective. However, among unidentified products and free dimethyl fumarate, a complex showing asymmetric phen and a signal at δ 2.38 coupled to ^{195}Pt [^4J(Pt–H) = 14 Hz] is formed in yields higher than 60%. Its NMR features are compatible with a square-planar product [Pt{C(CO_2Me)=C(Me)CO_2Me}L(phen)]$^+$ (L = *e.g.* H_2O) **4a** possibly formed by *cis* insertion[2a,5b] of the alkyne into the Pt–Me bond of the elusive intermediate [PtMe(η^2-Me$_2$OCC≡CCO$_2$Me)(phen)]$^+$ **2h** [path (*iv*), Scheme 1]. The *cis* arrangement of the methoxycarbonyl groups in **4a** does not allow the formation of the five-membered cyclometallated ring Pt–C(CO_2Me)=C(Me)C(O)OMe, similar to those previously reported.[6] Therefore, the empty co-ordination site resulting from the insertion reaction must be occupied by some weak L (*e.g.* H_2O) donor present in solution. If MeCN is added to the reaction mixture **4a** transforms into the corresponding species [Pt{C(CO_2Me)=C(Me)CO_2Me}(MeCN)(phen)]$^+$ **4b**, which has been identified by comparison with related products.[5b] No attempts have been made to isolate it in the solid state.

When the addition of Me$_2$OCC≡CCO$_2$Me to complex **1a** is performed at 253 K the spectrum shows a fluxional product, which is accompanied by free dimethyl fumarate. A broad signal centred at δ 0.9 is attributed to Me on Pt. Thus, it appears that at this stage the insertion has not yet occurred, and that the product [PtMe(η^2-MeO$_2$CC≡CCO$_2$Me)(phen)]$^+$ **2h** is detectable by NMR spectroscopy. Its fluxionality is likely due to a fast alkyne exchange which may occur through association of another ligand, possibly H_2O. The ability of **2h** to add a fifth ligand has been also observed by adding acetonitrile to the cold reaction mixture. In this case the PtMe resonance sharpens and ^{195}Pt satellites become detectable [^2J(Pt–H) = 74 Hz]. Moreover, the signal shifts to δ 0.60. This high-field value is very close to that recently measured[5b] (δ 0.71) for the trigonal-bipyramidal complex [PtMe(η^2-MeO$_2$CC≡CCO$_2$Me)(MeCN)(dmphen)]$^+$ (dmphen = 2,9-dimethyl-1,10-phenanthroline), the stability of which is due to the presence of a crowded bidentate ligand.[12] Therefore, we may assume that acetonitrile participates in the dynamic process, which possibly occurs through the formation of the substitution-labile five-co-ordinate adduct [PtMe(η^2-MeO$_2$CC≡CCO$_2$Me)(MeCN)(phen)]$^+$. Finally, when the reaction mixture is allowed to stand at room temperature, insertion of MeO$_2$CC≡CCO$_2$Me into the Pt–Me bond occurs, and **4b** is formed.

Conclusion

This work has extended the scant knowledge[3] of alkylplatinum(II) complexes containing a *cis* η^2-bonded alkyne, through the study of novel species of general formula [PtR(η^2-alkyne)(phen)]$^+$ **2**. While in some cases the results have pointed out a behaviour analogous to that of *trans*-[PtMeL$_2$(η^2-alkyne)]$^+$ complexes,[2] the attainment of the *cis* geometry has allowed us to observe a remarkable and unprecedented reaction. More precisely, type **2** complexes containing terminal alkynes have been observed at 253 K. As the temperature rises they undergo a fast intramolecular rearrangement which affords π-allyl derivatives. According to the proposed mechanism (Scheme 2) this reaction appears to be prompted by the *cis* geometry of the alkyne and of the alkyl group.

On the other hand, type **2** species are stable in the presence of disubstituted electron-rich alkynes, which are not sufficiently electrophilic to undergo a migratory insertion reaction. Conversely, [PtMe(η^2-MeO$_2$CC≡CCO$_2$Me)(phen)]$^+$ **2h**, which contains an electron-poor alkyne, can be detected only at 253 K, while at room temperature the unsaturated ligand rapidly inserts into the Pt–Me bond. This is in agreement with previous studies concerning the insertion of electron-poor alkynes into Pt–Me bonds.[2j,3a,5b] In these cases, however, η^2 species similar to **2h** were only invoked as intermediates, but could never be detected.

Experimental

Proton and ^{13}C NMR spectra were recorded on a 270 MHz NMR (Bruker model AC-270) or a 200 MHz spectrometer (Varian model Gemini). The following abbreviations are used in description of NMR multiplicities: app, apparent; d, doublet; dd, double doublet; no attribute, singlet; m, multiplet; t, triplet. The complex [Pt(η^2-*E*-MeO$_2$CCH=CHCO$_2$Me)(phen)][6] and Et$_3$OBF$_4$[13] were prepared according to literature methods. Alkynes and Me$_3$OBF$_4$ are commercially available and were used without further purification. Nitromethane § was stored over A4 molecular sieves. Dichloromethane was distilled from $CaCl_2$ immediately before use.

Preparations

[PtMe(η^2-R^{1}C≡CR^2)(phen)]BF$_4$ (R^1 = R^2 = Me 2a or Ph 2b; R^1 = Me, R^2 = Ph 2c). A solution of Me$_3$OBF$_4$ (0.030 g, 0.20 mmol) in nitromethane (1 cm^3) was added to solid [Pt(η^2-*E*-MeO$_2$CCH=CHCO$_2$Me)(phen)] (0.10 g, 0.20 mmol). The appropriate alkyne (0.20 mmol) was added to the resulting red solution of complex **1a**. Careful addition of diethyl ether (5 cm^3) afforded the product as a beige glassy solid, which was washed with diethyl ether and dried under vacuum (yield 70–80%).

[PtEt(η^2-R^{1}C≡CR^2)(phen)]BF$_4$ (R^1 = R^2 = Me 2d or Ph 2e). A solution of Et$_3$OBF$_4$ (0.038 g, 0.20 mmol) in dichloromethane (1 cm^3) was added to solid [Pt(η^2-*E*-MeO$_2$CCH=CHCO$_2$Me)(phen)] (0.10 g, 0.20 mmol). The addition of the appropriate alkyne (0.20 mmol) to the resulting red solution of complex **1b** started the precipitation of the product. Diethyl ether (5 cm^3) was slowly added to complete the precipitation of a beige solid, which was washed with diethyl ether and dried under vacuum (yield 70–80%).

§ HPLC-grade nitromethane is required, since a less pure solvent was found to contain traces of acetonitrile or propionitrile, which prevent the attainment of complex **1a** and afford only the corresponding [PtMe(RCN)(phen)]$^+$ complexes.

[Pt(η³-CH$_2$CHCHR)(phen)]BF$_4$ (R = Ph 3a, CH$_2$Ph 3B or Bu^n 3c). A solution of Me_3OBF_4 (0.030 g, 0.20 mmol) in nitromethane (1 cm³) was added to solid [Pt(η²-*E*-MeO$_2$CCH=CHCO$_2$Me)(phen)] (0.10 g, 0.20 mmol). The appropriate alkyne RC≡CH (0.20 mmol) was added to the resulting red solution of complex **1a** and the product obtained in quantitative yield by removing the solvent under vacuum and by washing the beige glassy solid with diethyl ether. Selected ¹H NMR data (see Scheme 3) (200 MHz, solvent CD$_3$NO$_2$, standard CHD$_2$NO$_2$, δ 4.33): **3a** δ 5.73 [1 H, d, app t, ^2J(PtH²) 80, ^3J(H²H^{3a}) = ^3J(H²H^{1a}) 11.5, ^3J(H²H^{1s}) 7, H²], 4.45 (2 H, m, H^{1s} and H^{3a}) and 3.42 [1 H, d, ^2J(PtH²) 80, H^{1a}]; **3b** (*syn*) 5.15 [1 H, d app t, ^3J(H²H^{3a}) = ^3J(H²H^{1a}) 11, ^3J(H²H^{1s}) 7, H²], 4.4 (1 H, m, H^{1s}), 3.55 (2 H, m, PhC*H*$_2$), 3.25 (1 H, dd, H^{1a}) and 2.77 (1 H, m, H^{3a}); **3b** (*anti*), 5.35 [1 H, d app t, ^3J(H²H^{1a}) 13, ^3J(H²H^{3s}) = ^3J(H²H^{1s}) 7, H²] and 3.87 (2 H, m, PhC*H*$_2$); **3c** (*syn*); 5.01 [1 H, d app t, ^2J(PtH²) 81, ^3J(H²H^{3a}) = ^3J(H²H^{1a}) 11, ^3J(H²H^{1s}) 6.5, H²], 4.15 [1 H, dd, ^2J(H^{1a}H^{1s}) 2, H^{1s}], 3.55 (1 H, m, H^{3a}), 3.01 [1 H, dd, ^2J(PtH^{1a}) 72, H^{1a}] and 1.01 (3 H, t, Me); **3c** (*anti*), 5.30 [1 H, d app t, ^3J(H²H^{1a}) 13, ^3J(H²H^{3s}) = ^3J(H²H^{1s}) 7, H²], 4.25 [1 H, dd, ^2J(H^{1a}H^{1s}) 2.5 Hz, H^{1s}], 3.18 (1 H, dd, H^{1a}) and 0.85 (3 H, t, Me) (Found: C, 43.8; H, 3.0; N, 4.8. $C_{21}H_{17}BF_4N_2Pt$ **3a** requires C, 43.55; H, 2.95; N, 4.85. Found: C, 44.45; H, 3.1; N, 4.8. $C_{22}H_{19}BF_4N_2Pt$ **3b** requires C, 44.55; H, 3.25; N, 4.7. Found: C, 40.8; H, 3.7; N, 5.05. $C_{19}H_{21}BF_4N_2Pt$ **3c** requires C, 40.8; H, 3.8; N, 5.0%).

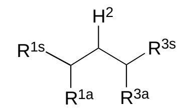
[Pt{η³-CH(Me)CHCHPh}(phen)]BF$_4$ 3d. A solution of Et_3OBF_4 (0.038 g, 0.20 mmol) in dichloromethane (1 cm³) was added to solid [Pt(η²-*E*-MeO$_2$CCH=CHCO$_2$Me)(phen)] (0.10 g, 0.20 mmol). Phenylacetylene (0.020 g, 0.20 mmol) was added to the resulting solution of complex **1b**. Diethyl ether (5 cm³) was slowly added to afford the product as a beige solid, which was washed with diethyl ether and dried under vacuum (0.090 g, 76%). Selected ¹H NMR data: *syn*, *syn*, δ 5.48 [1 H, app t, ^2J(PtH²) 80, ^3J(H²H^{3a}) = ^3J(H²H^{1a}) 11, H²], 4.40 [1 H, d, ^2J(PtH^{3a}) 75, H^{3a}], 3.92 [1 H, m, ^3J(H^{1a}H^{Me}) 6, H^{1a}] and 1.86 [3 H, d, ^3J(PtH) 12, Me^{1s}]; *syn*-Ph,, *anti*-Me, 5.78 [1 H, dd, ^3J(H²H^{3a}) 10, ^3J(H²H^{1s}) 6, H²], 4.73 (1 H, d, H^{3a}) and 1.52 [3 H, d, ^3J(PtH) 12 Hz, Me^{1a}] (Found: C, 44.35; H, 3.1; N, 4.65. $C_{22}H_{19}BF_4N_2Pt$ requires C, 44.55; H, 3.25; N, 4.7%).

Monitoring of the addition of MeO$_2$CC≡CCO$_2$Me and MeCN to complex 1a with formation of 4a and 4b

A solution of Me_3OBF_4 (0.006 g, 0.04 mmol) in deuterionitromethane (0.6 cm³) was added to solid [Pt(η²-*E*-MeO$_2$CCH=CHCO$_2$Me)(phen)] (0.020 g, 0.04 mmol). The red solution containing complex **1a** was transferred to an NMR tube and MeO$_2$CC≡CCO$_2$Me (0.006 g, 0.04 mmol) added with a microsyringe. The spectrum disclosed the presence of **4a** in higher than 60% yield. Addition of MeCN (0.002 g, 0.05 mmol) converted **4a** into **4b**. Selected ¹H NMR data: **4a**, δ 9.30 (1 H, d), 9.25 (1 H, d), 8.90 (2 H, app d), 8.2 (4 H, m) and 2.38 [3 H, ^4J(PtH) 14, C(*Me*)CO$_2$Me]; **4b**, 9.35 (1 H, d), 9.20 (1 H, d), 8.95 (2 H, app t), 8.22 (2 H, d), 8.20 (1 H, dd), 8.06 (1 H, dd), 2.83 [3 H, ^4J(PtH) 16, MeCN] and 2.32 [3 H, ^3J(PtH) 14 Hz, C(*Me*)CO$_2$Me].

Addition of PhC≡CH to [PtI(CD$_3$)(phen)] in the presence of AgBF$_4$: formation of [Pt(η³-CD$_2$CDCHPh)(phen)]$^+$

To a solution of [Pt(η²-*E*-MeO$_2$CCH=CHCO$_2$Me)(phen)] (0.10 g, 0.20 mmol) in chloroform (3 cm³) was added an excess of CD$_3$I (200 μl). The solution was dried under vacuum and the residue washed with diethyl ether affording [PtI(CD$_3$)(phen)] in quantitative yield. A solution of AgBF$_4$ (0.010 g, 0.05 mmol) and PhC≡CH (0.005 g, 0.05 mmol) in deuterionitromethane (1 cm³) was added to solid [PtI(CD$_3$)(phen)] (0.026 g, 0.05 mmol). After 1 h of stirring the suspension was filtered. The filtrate was transferred to an NMR tube and the spectrum revealed the quantitative formation of [Pt(η³-CD$_2$CDCHPh)(phen)]$^+$.



R¹ = H or Me

R³ = H or Ph, CH$_2$Ph, Bu

Scheme 3

Monitoring of the reactions through low-temperature ¹H NMR spectroscopy

A typical procedure was as follows: a solution of Me_3OBF_4 (0.006 g, 0.04 mmol) in deuterionitromethane (0.6 cm³) was added to solid [Pt(η²-*E*-MeO$_2$CCH=CHCO$_2$Me)(phen)] (0.020 g, 0.04 mmol). The red solution containing complex **1a** was transferred to an NMR tube, which was cooled at 253 K. The appropriate alkyne (0.04 mmol) was added with a microsyringe and the spectra were recorded at regular intervals of time.

Acknowledgements

We thank the Consiglio Nazionale delle Ricerche and the Ministero dell'Università e della Ricerca Scientifica e Tecnologica for financial support, the Centro Interdipartimentale di Metodologie Chimico-Fisiche, Università di Napoli 'Federico II', for NMR facilities, and Professor A. Panunzi for helpful discussion.

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Received 28*th October* 1996; *Paper* 6/07345J