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Coordination, fluxionality and fragmentation in reactions of platinum cluster complexes with alkynes [1]

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Abstract

The activated alkyne $MeO_2CC\equiv CCO_2Me$ reacts at low temperature with the cluster complexes $[Pt_3(\mu\text{-}CO)_3L_3]$, L = PCy_3, and $[Pt_6(\mu\text{-}CO)_6(\mu\text{-}dppm)_3]$, **4**, to give 1:1 complexes $[Pt_3(CO)_3L_3(MeO_2CC\equiv CCO_2Me)]$, L = PCy_3, and $[Pt_6(\mu\text{-}CO)_6(\mu\text{-}dppm)_3(MeO_2CC\equiv CCO_2Me)]$, which undergo cluster fragmentation on warming to room temperature to yield the binuclear complexes $[Pt_2(CO)_2L_2(\mu\text{-}MeO_2CC\equiv CCO_2Me)]$ and $[Pt_2(CO)_2(\mu\text{-}dppm)(\mu\text{-}MeO_2CC\equiv CCO_2Me)]$, respectively. © 1998 Elsevier Science S.A.

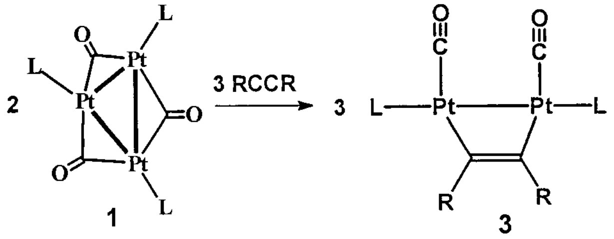
Keywords: Platinum cluster; Alkyne complexes; Fluxionality

1. Introduction

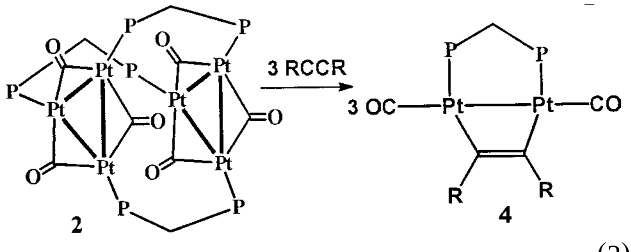
There is a rich chemistry of alkynes with palladium and platinum compounds, and there is current interest in comparing the chemistry of alkynes with a platinum surface and with well-defined, coordinatively unsaturated platinum cluster complexes [1–8]. The reactions of alkynes with the clusters $[Pt_3(\mu_3\text{-}CO)(\mu\text{-}dppm)_3]^{2+}$ and $[Pt_3(\mu_3\text{-}H)(\mu\text{-}dppm)_3]^{+}$, dppm = $Ph_2PCH_2PPh_2$, in which the presence of the $Pt_3(\mu\text{-}dppm)_3$ unit limits reactivity to the positions above or below the Pt_3 plane and prevents fragmentation of the Pt_3 cluster, have been reported [4–8], and it was of interest to compare the reactions of alkynes with the clusters $[Pt_3(\mu\text{-}CO)_3L_3]$, **1**, L = PCy_3, and $[Pt_6(\mu\text{-}CO)_6(\mu\text{-}dppm)_3]$, **2**, which either contain no bridging diphosphine ligands (**1**) or only one bridging diphosphine for each two platinum atoms (**2**) and so are less stabilized with respect to fragmentation [9,10]. In reactions with the activated alkyne $MeO_2CC\equiv CCO_2Me$ it will be shown that both **1** and **2** react at low temperature to give fluxional 1:1 adducts, but that fragmentation occurs at higher temperatures to give stable diplatinum complexes containing $Pt_2(\mu\text{-}RCCR)$ units. Alkynes are already known to form interesting complexes with both mononuclear and binuclear platinum reagents [11–22].

2. Results and discussion

The reactions of $RC\equiv CR$, R = CO_2Me, with **1** and **2** at room temperature occur very cleanly to give the products **3** and **4** according to Eqs. (1) and (2). Less activated alkynes, such as $PhC\equiv CPh$, $PhC\equiv CH$ or $HC\equiv CH$ either did not react ($PhC\equiv CPh$) or gave mixtures of products which could not be characterized ($PhC\equiv CH$, $HC\equiv CH$).



(1)



(2)

The new compounds **3** and **4** contain the same $Pt_2(\mu\text{-}RCCR)$ unit but differ in terms of the relative

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[1] Dedicated to Professor Peter Maitlis in recognition of his distinguished contributions to organometallic chemistry.

positions of the carbonyl and phosphine ligands. Complex **3** is isostructural with the known complex $[Pt_2(\mu\text{-}RCCR)(CO)_2(PPh_3)_2]$, **3b**, which has been prepared from two different mononuclear platinum complexes [19,20]. Thus reaction of either $[Pt(CO)_2L_2]$ with RC≡CR or of $[Pt(RCCR)L_2]$ with CO gives **3b** and, since it is now shown that the analogous complex **3**, $L = PCy_3$, is formed from a trinuclear precursor, it seems that this binuclear structure is the 'thermodynamic sink' when sources of Pt(0), CO, monodentate phosphine and alkyne are present. The alternative arrangement of CO and phosphine donors in **4** is clearly due to the need to accommodate the $Pt_2(\mu\text{-dppm})$ group.

The compounds **3** and **4** were readily characterized by analytical and spectroscopic methods, especially by comparison with data for **3b** [19,20], and the data are summarized in Table 1. Perhaps the clearest evidence for the structures comes from the observation of long range couplings $^{2}J(PtP)$ or $^{2}J(PtC)$ for the linear P–Pt–Pt–P or C–Pt–Pt–C units in **3** and **4**, respectively (Table 1), an indication of strong coupling through the metal–metal bond [23] (note that **3b** has d(PtPt) = 2.6354(8) Å as determined by X-ray structure determination [19,20]). For example, $^{2}J(PtPtCO) = 324$ Hz in **4**, Fig. 1, but was too small to observe in **3**.

The low temperature intermediates were characterized by carrying out the reactions at −78°C in CD_2Cl_2 in an NMR tube and recording ^{1}H, ^{13}C (using ^{13}CO enriched samples) and ^{31}P NMR spectra at −90°C, −50°C, −30°C, 0°C and 23°C. By 0°C the reactions to give **3** or **4** were complete and so useful additional data were obtained only at low temperature. Fortunately, the intermediates **5** and **6** were formed very easily even at −78°C; note that the same intermediates were formed if the stoichiometry was cluster:alkyne = 1–3 and free alkyne was detected if this ratio was > 1, thus defining the 1:1 stoichiometry.

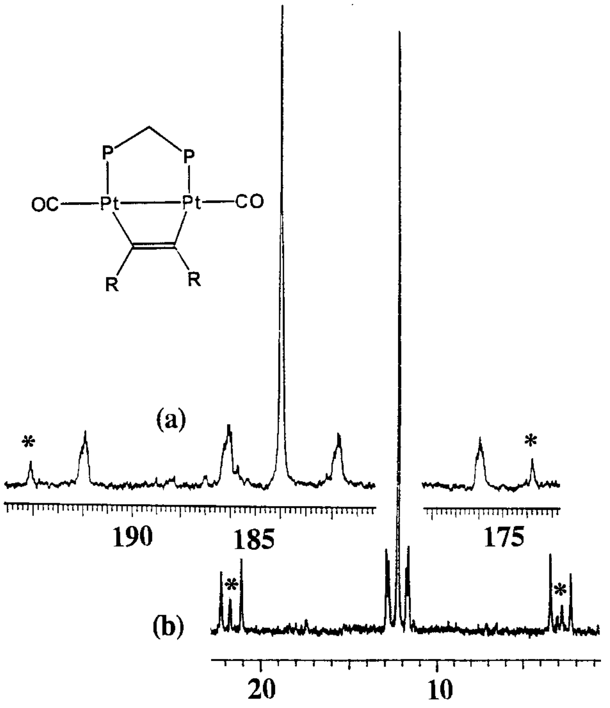
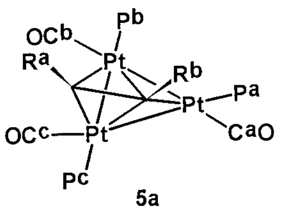
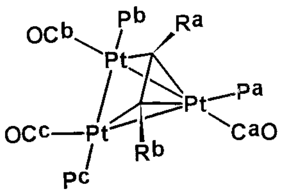


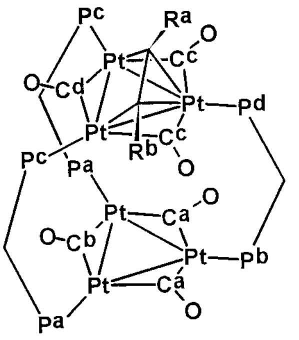
Fig. 1. NMR spectra of complex **4**: (a) ^{13}C NMR spectrum; (b) ^{31}P NMR spectrum. The peaks labelled * are due to the $^{195}Pt_2$ isotopomer and are separated by $^{1}J(PtC) + ^{2}J(PtC)$ or $^{1}J(PtP) + ^{2}J(PtP)$ in (a) and (b), respectively.



5a



5b



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Proposed structures of intermediates
R = CO2Me

Table 1
Selected NMR and IR Data for **3** and **4**[a]

	3	4
$\delta(^{31}P)$	30.0	13.5
$^{1}J(PtP)$	3076	2259
$^{2}J(PtP)$	55	14
$^{3}J(PP)$	27	140
$\delta(^{1}H)$[b]	3.56	3.77[c]
$\delta(^{13}C)$	188.7	183.9
$^{1}J(PtC)$	1610	1205
$^{2}J(PtC)$	[d]	324
IR (υ_{CO}, cm^{-1})	2051 (s) 2018 (s) 1690	2018 (s) 1980 (sh) 1691 (s)

[a] In $(CD_3)_2CO$, 23°C, J values in Hz.
[b] MeO protons.
[c] $\delta(CH_2P_2) = 5.31$ [m, $^{2}J(PH) = 11$ Hz, $^{3}J(PtH) = 70$ Hz].
[d] Not resolved.

Consider first the case of **1** with $MeO_2CC{\equiv}CCO_2Me$ to give **5**. In the ^{31}P NMR spectrum at −90°C, there were three broad, equal intensity resonances at $\delta = 31.0$ [$^{1}J(PtP^{a}) = 3640$ Hz], 29.1 [$^{1}J(PtP^{b}) = 3810$ Hz] and

24.0 [$^1J(\mathrm{PtP^c}) = 3830$ Hz]. At -50°C, the resonance at $\delta = 31.0$ [$^1J(\mathrm{PtP^a}) = 3640$ Hz, $^2J(\mathrm{PtP^a}) = 260$ Hz, $^3J(\mathrm{P^{b,c}P^a}) = 60$ Hz] had sharpened and appeared as a triplet due to ^3J(PP) coupling, with satellites due to both ^1J(PtP) and ^2J(PtP) couplings also resolved, while the other two resonances had coalesced to give a broad resonance at $\delta = 28.5$ [$^1J(\mathrm{PtP^{b,c}}) = 3820$ Hz]. At -30°C, the spectrum was similar but the resonance at $\delta = 28.5$ was less broad. These data show clearly that the cluster is still intact at this stage and that, at -30°C, there is an effective plane of symmetry perpendicular to the Pt_3 plane, passing through P^a and bisecting P^b and P^c. The PtP coupling constants are smaller than in the parent cluster **1**, which has $\delta(\mathrm{P}) = 73.2$ [$^1J(\mathrm{PtP}) = 4410$ Hz, $^2J(\mathrm{PtP}) = 430$ Hz, $^3J(\mathrm{PP}) = 60$ Hz]. In the ^{13}C NMR spectrum at -90°C there were three very broad resonances in the carbonyl region at $\delta = 186$ [C^b], 195 [C^a] and 204 [C^c] and no satellites were resolved. On warming to -50°C, the two outer peaks coalesced to give a broad resonance at $\delta = 192$ [C^b, C^c], while the center peak became sharper. At -30°C, these peaks were sharper and were at $\delta = 195.8$ [$^1J(\mathrm{PtC^a}) = 1370$ Hz] and $\delta = 192.2$ [$^1J(\mathrm{PtC^{b,c}}) = 1660$]. These data show that three carbonyl ligands are still present and that at -30°C the cluster contains an effective plane of symmetry passing through C^a and bisecting C^b and C^c. It is instructive to compare the ^{13}CO NMR parameters with those for **1**, which has $\delta(^{13}\mathrm{CO}) = 259.0$ [$^1J(\mathrm{PtC}) = 705$ Hz], values typical of bridging carbonyls. In contrast, the chemical shift values of < 200 ppm and the ^1J(PtC) couplings of > 1300 Hz for **5** provide clear evidence that **5** has three *terminal* carbonyl ligands. The ^{1}H NMR spectrum of **5** contained two equal singlet resonances due to MeO protons at $\delta = 3.58$ and 3.62 at -90°C and at -30°C. Together these data suggest an effective structure **5a** at -30°C with a less symmetrical structure as the ground state. We suggest that a twisting of the structure is likely, simply to minimize steric effects between the bulky PCy_3 ligands, and that this removes the mirror symmetry, but the evidence does not exclude less symmetrical but fluxional ground state structures. Note that the alkyne must lie in the mirror plane rather than perpendicular to it as in **5b**, which would give only one MeO resonance at -30°C.

Consider next the reaction of **2** with $MeO_2CC{\equiv}CCO_2Me$ at -78°C to give **6**. In the ^{31}P NMR spectrum at -90°C, three resonances are resolved in a 3:1:2 ratio at $\delta = 39.9$ [$^1J(\mathrm{PtP}) = 5240$ Hz, $^2J(\mathrm{PtP}) = 420$ Hz, P^b; $^1J(\mathrm{PtP}) = 4130$ Hz, $^2J(\mathrm{PtP}) = 420$ Hz, P^a], 53.9 [$^1J(\mathrm{PtP}) =$ ca. 5070 Hz, $^2J(\mathrm{PtP}) = 440$ Hz, P^d] and 71.8 [$^1J(\mathrm{PtP}) = 4370$ Hz, $^2J(\mathrm{PtP}) = 440$ Hz, P^c], respectively. These data indicate that there is a mirror plane containing P^b and P^d and their attached platinum atoms. Note that the chemical shifts of P^a and P^b are accidentally degenerate, but the nonequivalence is demonstrated by very different values of ^1J(PtP). On warming, the resonances due to P^c and P^d coalesce and that due to P^a and P^b sharpens. At -30°C, there are thus two equal intensity resonances at $\delta = 38.8$ [$^1J(\mathrm{PtP}) = 4470$, $^2J(\mathrm{PtP}) = 420$ Hz, P^a,P^b] and 64.3 [$^1J(\mathrm{PtP}) = 4780$ Hz, $^2J(\mathrm{PtP}) = 440$ Hz, P^c,P^d], and this is readily interpreted in terms of rapid rotation of the alkyne ligand about the upper Pt_3 face of the cluster, leading to equivalence of the atoms P^a,P^b and P^c,P^d. The ^{13}CO NMR data support this picture. Thus, at -90°C there are 4 resonances in a 1:1:2:2 ratio at $\delta = 202.7$ [$^1J(\mathrm{PtC}) = 785$ Hz, C^b], 213.8 [$^1J(\mathrm{PtC}) = 595$ Hz, C^d], 221.7 [$^1J(\mathrm{PtC}) = 1009$, 495 Hz, C^c] and 232.2 [$^1J(\mathrm{PtC}) = 900$, 825 Hz, C^a], respectively. At -30°C, the resonances due to C^c and C^d had coalesced to give a resonance at $\delta = 217.3$ [$^1J(\mathrm{PtC}) = 700$ Hz, C^c,C^d], while those due to C^a and C^b gave an extremely broad signal at $\delta =$ ca. 220 ppm, whose satellites were not resolved. For comparison, the parent cluster **2** has $\delta(^{13}\mathrm{CO}) = 240.5$ [$^1J(\mathrm{PtC}) = 757$ Hz] [9,10]. The data indicate that the carbonyl ligands in **6** are still bridging but, in some cases, the bridges may be asymmetrical, based on the different values of ^1J(PtC). The ^{1}H NMR spectrum at -90°C and at -30°C contained a single resonance due to the MeO protons of the alkyne at $\delta = 3.55$, so in this case the alkyne appears to lie perpendicular to the mirror plane.

3. Conclusions

In summary, this work shows clearly that the alkyne $MeO_2CC{\equiv}CCO_2Me$ reacts with **1** or **2** at low temperature to give the corresponding 1:1 adduct **5** or **6**, which can then undergo fragmentation on warming to give the similar binuclear complex **3** or **4**, respectively. However, although the nature of the alkyne-cluster binding in the intermediates **5** and **6** is not rigorously defined, there are clearly major differences between them. Thus, **5** appears to contain the μ_3–η^2-$\perp$ -alkyne and has terminal carbonyl ligands, whereas **6** probably has the μ_3–η^2-$\|$-alkyne, has bridging carbonyl ligands and exhibits a greater degree of fluxionality. Nevertheless, it is clear that, in both cases, alkyne coordination leads easily to cluster fragmentation.

4. Experimental

NMR spectra were recorded by using a Varian Gemini-300 spectrometer. Chemical shifts are quoted with positive shifts for ^{1}H and ^{13}C downfield of the signal of $Si(CH_3)_4$, for ^{19}F downfield of the signal of $CFCl_3$, and for ^{31}P downfield of the signal of external 85% H_3PO_4. IR spectra were recorded using a Bruker IFS-66 FTIR spectrometer as Nujol mulls between NaCl plates, or in solution cells with NaCl windows. The complexes

$[Pt_3(\mu\text{-}CO)_3(PCy_3)_3]$ and $[Pt_6(\mu\text{-}CO)_6(\mu\text{-dppm})_3]$ were prepared according to published procedures [9,10]. All syntheses were performed using standard Schlenk or drybox techniques using an atmosphere of dry nitrogen.

4.1. $[Pt_2(CO)_2(\mu\text{-}MeO_2CCCCO_2Me)(PCy_3)_2]$

To a solution of $[Pt_3(\mu\text{-}CO)_3(PCy_3)_3]$ (0.043 g) in benzene (3 ml) was added $MeO_2CC{\equiv}CCO_2Me$ (6 μl). The solution was stirred for 5 min, the solution was evaporated and the product was crystallized from benzene/pentane. Yield 63%. Analysis: Calcd. for $C_{44}H_{72}O_6P_2Pt_2$: C, 46.0; H, 6.3. Found: C, 45.6; H, 6.1%. Spectroscopic data are in Table 1.

4.2. $[Pt_2(CO)_2(\mu_2\text{-}MeO_2CCCCO_2Me)(\mu\text{-dppm})]$

To a solution of $[Pt_6(\mu\text{-}CO)_6(\mu\text{-dppm})_3]$ (0.047 g) in dry THF (25 ml) was added $MeO_2CC{\equiv}CCO_2Me$ (6.9 μl). The color of the reaction solution immediately changed from dark purple to brown. The solution was allowed to stir for 24 h and then was concentrated down to dryness under reduced pressure. The brown residue was redissolved in acetone (2 ml) and excess hexane (100 ml) was added to precipitate the product as a light brown solid. The solid was recovered, washed with pentane (15 ml) and dried under reduced pressure for 24 h. Yield: 81%. Analysis: Calcd. for $C_{31}H_{28}O_4P_2Pt_2$: C, 40.6; H, 3.1. Found: C, 40.7; H, 2.9%. Spectroscopic data are in Table 1.

4.3. $[Pt_2(CO)_2(\mu\text{-}CF_3CCCF_3)(\mu\text{-dppm})]$

This was prepared similarly from **2** (0.028 g) in dry THF (20 ml) with excess $CF_3C{\equiv}CCF_3$. IR (Nujol): $\nu(CO) = 2032$ (s), 2000 (sh) cm^{-1}. NMR in $(CD_3)_2CO$ (23°C): $\delta(^1H) = 5.47$ [m, $^3J(PtH) = 72$ Hz, $^2J(PH) = 12$ Hz, CH_2 of dppm]; $\delta(^{19}F) = -56.9$ [m, $^3J(PtF) = 102$ Hz, CF_3 of CF_3CCCF_3]; $\delta(^{31}P) = 10.6$ [m, $^1J(PtP) = 2291$ Hz, $^2J(PtP) = 28$ Hz, $^3J(PP) = 126$ Hz, dppm].

4.4. Reactions with $MeO_2CC{\equiv}CCO_2Me$ at −78°C

An NMR tube charged with cluster **2** (0.046 g, 0.018 mmol) was dissolved in CD_2Cl_2 (~0.5 ml) giving a purple solution. The solution was cooled to −78°C and then $MeO_2CC{\equiv}CCO_2Me$ (0.0076 g, 0.054 mmol) was added. The tube was shaken and placed in the probe of the spectrometer at −90°C. Variable temperature NMR spectra were then recorded as described in the text. The experiments with **1** were carried out in a similar way.

Acknowledgements

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