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Models for Reactions of Acetylene on Platinum(111): A Vinyl(acetylene)triplatinum Complex and Evidence for an Ethylidyne Intermediate

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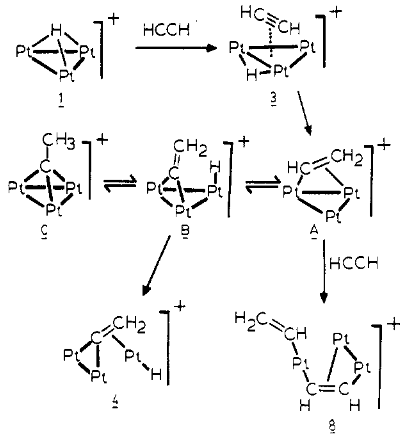
Reaction of $[Pt_3(\mu_3\text{-H})(\mu\text{-dppm})_3]^+$ (1) with excess acetylene gives $[Pt_3(CH{=}CH_2)(\mu_3\text{-}\eta^2(\|)\text{-HCCH})(\mu\text{-dppm})_3]^+$, where dppm = $Ph_2PCH_2PPh_2$. Deuterium-labeling studies indicate that H–D scrambling occurs within the vinyl group but not in the acetylene ligand. For example, $[Pt_3(\mu_3\text{-D})(\mu\text{-dppm})_3]^+$ with HCCH gave $[Pt_3(CH{=}CH_2\text{-}d_1)(\mu_3\text{-}\eta^2(\|)\text{-HCCH})(\mu\text{-dppm})_3]^+$, in which the deuterium label was distributed randomly in all three possible positions in the vinyl group. It is possible that this scrambling occurs by way of a short-lived ethylidyne intermediate. The complex is fluxional, due to rotation of the acetylene ligand, at room temperature. Similar reaction of 1 with excess propyne gives $[Pt_3(CH{=}CHMe)(\mu_3\text{-}\eta^2(\|)\text{-MeCCH})(\mu\text{-dppm})_3]^+$, but this complex is not fluxional at room temperature and is formed selectively by cis insertion of propyne into the Pt–H group. There is a strong resemblance to the chemistry resulting from chemisorption of acetylene on a Pt(111) surface, thus providing a clear example of the value of coordinatively unsaturated clusters as mimics of metal surfaces.

Introduction

A major effort has been made to determine the products of chemisorption of acetylene on a platinum(111) surface.[1] It is now thought that $Pt_3(\mu_3\text{-}\eta^2\text{-HCCH})$ groups are formed first and then rearrange to $Pt_3(\mu_3\text{-}\eta^2\text{-C}{=}CH_2)$ groups, which react with surface hydrogen to give $Pt_3(\mu_3\text{-CCH}_3)$ groups.[1,2] Hydrogen for deuterium exchange reactions in the ethylidyne unit can occur, and it is suggested that a necessary step in this process involves isomerization of $Pt_3(\mu_3\text{-CCH}_3)$ to $Pt_3(CH{=}CH_2)$ groups, which then undergo exchange of hydrogen for surface deuterium.[3,4] The interconversions of ethyne, vinyl, vinylidene, and ethylidyne groups on binuclear and trinuclear complexes have been studied before, especially using carbonyl clusters of the iron group as templates,[5] and these reactions can be said to model steps of the surface reaction. Since much of the surface science has been carried out by using the Pt(111) surface and since the coordinatively unsaturated clusters $[Pt_3(\mu_3\text{-H})(\mu\text{-dppm})_3]^+$ (1)[6] and $[Pt_3(\mu_3\text{-CO})(\mu\text{-dppm})_3]^{2+}$ (2)[7] can better mimic the coordinative unsaturation of surface metal (especially Pt) atoms than can the iron group clusters,[8] a study of the reactions of 1 and 2 with acetylene was initiated.

Scheme I[a]



[a] The structures of short-lived intermediates A, B, and C are speculative, and the sequence of reactions could also be A ⇌ C ⇌ B. Dppm ligands are omitted for clarity.

An unstable acetylene complex, $[Pt_3(\mu_2\text{-H})(HCCH)(\mu\text{-dppm})_3]^+$ (3), was formed by reaction of 1 with acetylene and was identified by low-temperature NMR spectroscopy. In the absence of excess acetylene, complex 3 rearranged to give a stable vinylidene complex, $[Pt_3H(\mu_3\text{-}\eta^2\text{-C}{=}CH_2)(\mu\text{-dppm})_3]^+$ (4).[9] In contrast, acetylene reacted with $[Pt_3(\mu_3\text{-CO})(\mu\text{-dppm})_3]^{2+}$ (2) to give $[Pt_3(CO)(\mu_3\text{-}\eta^2\text{-}$

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(8) In the 42e cluster complexes 1 and 2 all of the metal atoms are coordinatively unsaturated, whereas trinuclear iron group clusters either are coordinatively saturated (48e, e.g. $[Os_3(CO)_{12}]$) or have a single site of unsaturation (46e, e.g. $[Os_3H_2(CO)_{10}]$). For studies of the coordinative unsaturation of 2 see: (a) Jennings, M. C.; Payne, N. C.; Puddephatt, R. J. *J. Chem. Soc., Chem. Commun.* **1986**, 1809. (b) Lloyd, B. R.; Bradford, A.; Puddephatt, R. J. *Organometallics* **1987**, *6*, 424.

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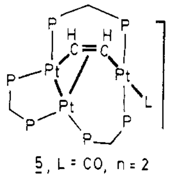
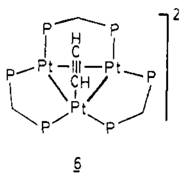
$HCCH)(\mu\text{-dppm})_3]^{2+}$ (**5**) and its derivatives $[Pt_3(\mu_3\text{-}\eta^2\text{-}HCCH)(\mu\text{-dppm})_3]^{2+}$ (**6**) and $[Pt_3Cl(\mu_3\text{-}\eta^2\text{-}HCCH)(\mu\text{-dppm})_3]^+$ (**7**) which were inert to rearrangement of the acetylene unit.[10] In this paper, the formation of a third product by reaction of **1** with excess acetylene is described. This product is characterized as $[Pt_3(CH{=}CH_2)(\mu_3\text{-}\eta^2\text{-}HCCH)(\mu\text{-dppm})_3]^+$ (**8**), a vinyl acetylene complex incorporating two of the functional groups proposed as intermediates in the chemisorption of acetylene on platinum(111). Multinuclear NMR studies, including studies of isotopically labeled derivatives, have allowed the structure and some aspects of the mechanism to be deduced. A similar derivative prepared from propyne is also described, and it is argued that there is a close analogy between the cluster and surface chemistry.



5, L = CO, n = 2
7, L = Cl, n = 1



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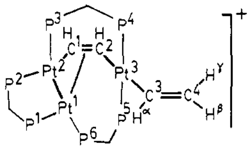

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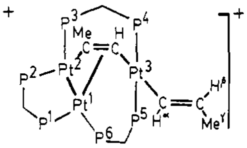

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Results

Synthesis of the Complexes. The synthetic work is summarized in Scheme I. Bubbling excess acetylene through a solution of **1** in dichloromethane at room temperature gave a transient dark color followed, within a few seconds, by formation of a lighter red-brown solution of the product **8**. If the reaction was carried out at -80 °C, the dark color, which is due to the intermediate **3**, persisted and further reaction to give **8** took place with a half-life of ~2 days. If excess acetylene was removed at -80 °C from the solution containing intermediate **3**, the vinylidene complex **4** was formed on warming. In a similar way, reaction of **1** with excess propyne gave complex **9**, but no intermediate was detected in this case. In addition, evaporation of excess propyne at -80 °C gave back complex **1** and no propylidene complex analogous to **4**.

The possibility that **4** may be an intermediate in the formation of **8** was considered but was eliminated by the observation that **4** failed to react with acetylene at room temperature. Reaction of complex **6** with $NaBH_4$ gave approximately equal amounts of complex **1**, by displacement of acetylene, and complex **4** but no vinyl derivative.

Complex **8** was air-stable and unreactive. It was not reduced by molecular hydrogen or by sodium borohydride at room temperature, and there was no exchange on attempted reaction with acetylene-d_2. The coordinated acetylene in **8** is therefore stable to dissociation or displacement.[11] Reaction of **8** with HCl led to cleavage of the vinylplatinum group and formation of the known complex **7**.

Characterization of Complex 8. Characterization of these complexes by NMR methods was complex, but an almost complete description of connectivities could be obtained by recording ^1H, ^{13}C, ^2H, ^{31}P, and ^{195}Pt NMR spectra of **8** and its derivatives **8*** and **8****, prepared from $H^{13}C^{13}CH$ and DCCD, respectively.

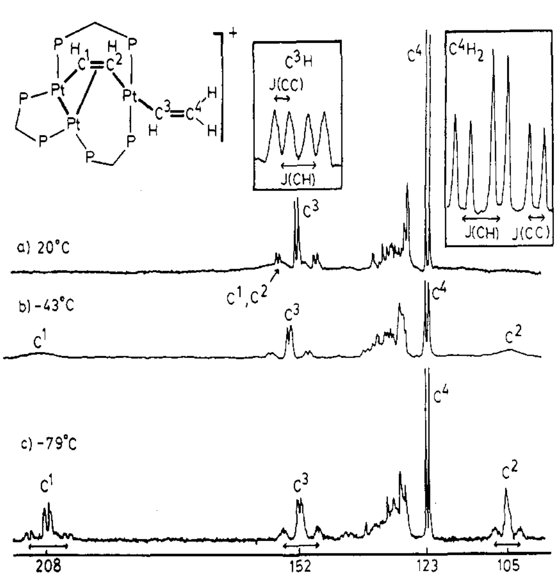

Figure 1. $^{13}C\{^1H\}$ NMR spectra (75 MHz) of complex **8*** in CD_2Cl_2: (a) at 20 °C, (b) at -43 °C, and (c) at -79 °C. The couplings due to $^1J(PtC)$ are shown below spectrum (c), and the insets above spectrum (a) show the signals due to C^3 and C^4 in the ^1H coupled ^{13}C NMR spectrum.

Complex **8** was fluxional at room temperature, and the static structure was deduced from the NMR spectra at -80 °C, by comparison with those at room temperature. The vinyl group remained bonded in a terminal fashion to Pt^3 at all temperatures as shown clearly by the ^1H and ^{13}C NMR spectra (Figure 1). The protons H^β and H^γ were clearly resolved in the ^1H NMR, but the signal due to H^α was obscured by the phenyl resonances of the dppm ligands. Its presence at δ 6.91 was confirmed from the ^2H NMR spectrum of **8**** (see later for further details) and by decoupling experiments in the ^1H NMR spectrum of **8**. Thus irradiation at δ 6.9 caused collapse of coupling to H^α in the multiplets due to H^β and H^γ. The $J(HH)$ coupling constants within the vinyl group were entirely consistent with those of other terminal vinyl groups,[12,13] and the magnitude of $^1J(C{=}C) = 62$ Hz is close to that in ethylene (69 Hz). The $\mu_2\text{-}\eta^2$-vinyl groups give lower values of $^1J(C{=}C)$. For example, $[Os_3H(\mu_2\text{-}\eta^2\text{-}CH{=}CH_2)(CO)_{10}]$ gives $^1J(C{=}C) = 33$ Hz, and a range of 27-36 Hz is found for W_2^- and $Rh_2(\mu_2\text{-}\eta^2\text{-}CH{=}CH_2)$ derivatives, close to $^1J(CC)$ for ethane of 35 Hz.[14-16] Similarly the ^{13}C chemical shifts for C^3 and C^4 fall in the range for terminal vinyl groups[12,16] but not for $\mu_2\text{-}\eta^2$-vinyl groups.[14-19] The magnitude of $^1J(Pt^3C^3)$ is lower than in most vinylplatinum(II) complexes,[12] but this is due to it being trans to a Pt–C σ-bond; similar values have been observed for some

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[11] The coordinatively unsaturated complex **6** does undergo alkyne exchange reactions.[10]

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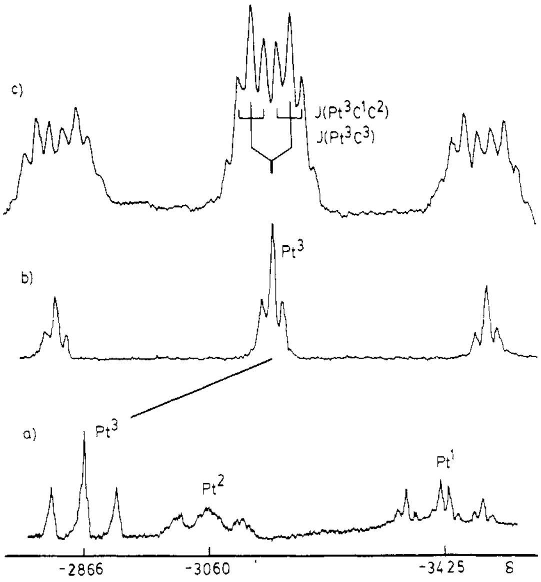
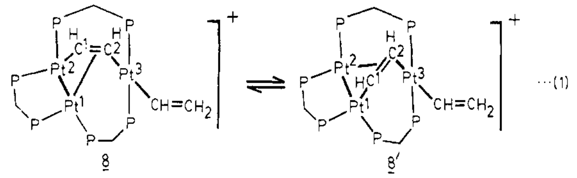


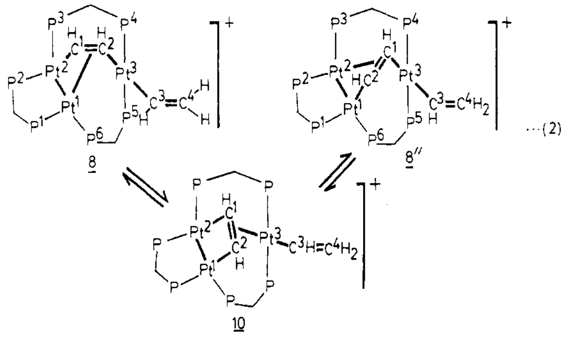
Figure 2. ^{195}Pt{^{1}H} NMR spectra (64.3 MHz): (a) spectrum of **8** at −80 °C; (b) expansion of the Pt^3 resonance of **8** at room temperature (the triplet is due to ^1J(PtP) coupling and the satellites are due to the "average" coupling between Pt^{3}Pt^1 and Pt^{3}Pt^2, which leads to a 1:8:18:8:1 pattern); (c) the Pt^3 resonance of **8*** at room temperature (the extra doublet of triplets is due to couplings ^1J(Pt^{3}C^3) and the "average" coupling between Pt^{3}C^1 and Pt^{3}C^2.

trans-divinylplatinum(II) complexes.[20]

The acetylene ligand in **8** was fluxional at room temperature, and only broad resonances were observed for the hydrogen (δ 9.93) and carbon (δ 156) atoms in the ^{1}H NMR of **8** or ^{13}C NMR of **8***, respectively (Figure 1). However, both signals split into two at low temperature. In the ^{1}H NMR, H^1 appeared at δ 11.61, and hence H^2 is expected at δ 8.25 where it is obscured by a phenyl resonance. In the ^{13}C NMR, C^2 was at δ 105 and C^1 at δ 208. The coupling constant ^1J(C^{1}C^2) was not resolved and was ≤30 Hz. Both C^1 and C^2 were doublets with ^1J(CH) ≈ 140 and 200 Hz, respectively, in the ^{1}H-coupled ^{13}C NMR spectrum at −80 °C, thus proving the HCCH groups was still present. The low value of ^1J(C^{1}C^2) indicates that the actylene is π-bonded to Pt^1, since otherwise a coupling constant closer to ethylene (69 Hz) than ethane (35 Hz) would be expected. The coupling of C^1 to Pt^1 observed in the ^{13}C NMR spectrum at −80 °C, ^1J(Pt^{1}C^1) = 150 Hz, supports this though ^1J(Pt^{1}C^2) was not resolved and must be less than 100 Hz. The bonding mode of the acetylene is the same as that found in complexes **5** and **7**[10] and is the most common bonding mode in cluster complexes.[21] The σ-bonds Pt^{3}C^2 and Pt^{2}C^1 are demonstrated by the coupling constants ^1J(Pt^{3}C^2) = 420 Hz and ^1J(Pt^{2}C^1) = 660 Hz in the −80 °C spectra.[22] At room temperature the Pt^3 resonance in the ^{195}Pt NMR of **8*** appeared as a triplet with ^1J(PtC) = 200 ± 10 Hz (Figure 2), i.e. half of the value of ^1J(Pt^{3}C^2) at −80 °C. The Pt^2 signal was too broad to observe at room temperature.

The above spectral data give a great deal of information about the fluxional process. The simplest form of fluxionality would interconvert the equivalent structures **8** and **8′** (eq 1). However, this process would interconvert Pt^1 and Pt^2 but not the C^{1}H^1 and C^{2}H^2 units. We suggest that the isomerization of **8** ⇌ **8′** occurs via a less stable species **10** (eq 2), in which the C^{1}H^1 and C^{2}H^2 units are equivalent.





Such a process is completely consistent with all the NMR data, so long as very little **10** is present in equilibrium with **8** and **8″**. The activation energy for the fluxionality, calculated from both the variable-temperature ^{13}C and ^{31}P NMR spectra, was $\Delta G^{\ddagger}$ = 44 ± 2 kJ mol^{-1}. It is, of course, possible that the mechanism of eq 1 also occurs and has a similar activation energy.[23] Why is **10** less stable than **8**? We note that the structure of **10** is analogous to that of the stable complex **4**, with a μ_3-η^2-HCCH unit in place of the μ_3-η^2-C=CH$_2$ unit of **4**. Geometrical constraints would require the olefin in **10** to lie in the coordination plane of Pt,^{3} whereas the configuration with the olefin perpendicular to the coordination plane of square-planar platinum(II) is always preferred and is required in complex **4**. We suggest that this feature destabilizes **10** with respect to **8**, though the NMR data indicate that the difference in energy is not great. The similar complexes **5** and **7** are not fluxional at room temperature.[10] This difference is probably due to the high trans influence of the vinyl group, which labilizes the Pt^{3}C^2 bond in **8** and lowers the activation energy for formation of the intermediate **10**.[22] We think it is probable that the vinylidene group would be more stable than the ethyne group in all complexes **5**, **7**, and **8** but that there is no facile route for the isomerization in the absence of a hydride ligand on platinum.

The ^{31}P NMR spectra lend support to the above conclusions on the fluxionality of **8**. At room temperature, three ^{31}P resonances were observed as expected for the fluxional system **8** ⇌ **8′** (eq 1 or 2). At −80 °C, the signal at δ +4.6 at room temperature had split into two signals due to P^3 and P^6 at δ 8.0 and 1.2 and that at −6.1 ppm had split into two signals due to P^1 and P^2 at δ −9.3, respectively, but the signal at δ 14.2 did not split at low temperature (Figure 3). Presumably the chemical shifts of P^4 and P^5 were degenerate.

Evidence about PtPt bonding was obtained from the ^{31}P and ^{195}Pt NMR spectra. First we note that **8** is a 46e complex and so, like **4**, is expected to contain just one metal–metal bond.[10] From the ^{195}Pt NMR spectrum at −80 °C, ^1J(Pt^{1}Pt^2) = 1700 Hz and this coupling indicates a Pt–Pt bond between these atoms. In contrast, no coupling

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(22) The corresponding coupling constants in complex **5** are ^1J(Pt^{3}C^2) = 530 and ^1J(Pt^{2}C^1) = 650 Hz. The lower value of ^1J(Pt^{3}C^2) for **8** is due to the high trans influence of the vinyl group.

(23) Similar fluxionality has been observed in other alkyne cluster complexes. See, for example, ref 5a and 21.

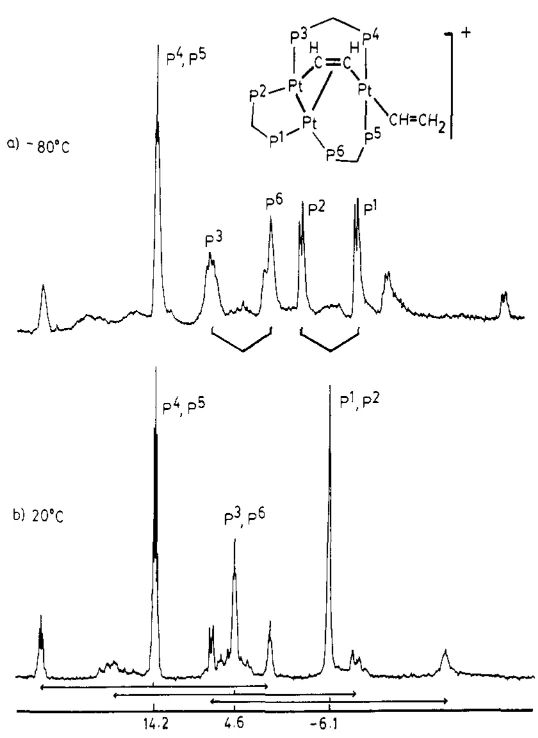


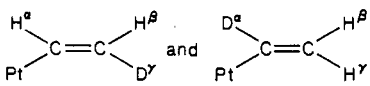
Figure 3. ^{31}P{^{1}H} NMR spectra (121 MHz) of complex 8: (a) at -80 °C and (b) at 20 °C. ^1J(PtP) couplings at 20 °C are shown below spectrum b and the ^{31}P signals that coalesce on warming are shown below spectrum a.

was resolved between Pt^{1}Pt^3 and the coupling J(Pt^{2}Pt^3) = 500 Hz. The latter value is low for a direct PtPt bond, and we suggest that the coupling operates through the bridging acetylene [^3J(Pt^{2}C^{1}C^{2}Pt^3)].[10] At room temperature the average value of J(Pt^{3}Pt^{1,2}) = 310 Hz, from which it can be deduced that J(Pt^{1}Pt^3) ≈ 120 Hz [note that $^1/_2$(500 + 120) = 310 Hz], a coupling which would not be resolved in the ^{195}Pt NMR spectrum at -80 °C. These couplings are fully consistent with the proposed structure for 8. In addition, the room-temperature ^{31}P spectra show a large coupling ^2J(Pt^{1}P^3) ≈ 300 Hz, typical of values through a Pt-Pt bond,[7,24,26,27] and again strongly suggest a bond between Pt^1 and Pt^2.

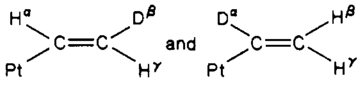
The NMR spectra described above are complex but very rich in structural information. Assignments of platinum resonances were aided by the observation of ^1J(PtC) coupling in the spectra of 8* and assignments of phosphorus resonances by correlation of J(PtP) values from the ^{195}Pt and ^{31}P NMR spectra (Figures 1-3). The presence of Pt-Pt bonds is partly based on the magnitudes of ^1J(PtPt) coupling constants (a not altogether reliable criterion)[25] but is confirmed by the characteristic long-range coupling to phosphorus atoms lying along the Pt-Pt axis.[26] Both criteria suggest only one Pt-Pt bond in 8, and this is also expected from the electron count of the cluster.[9,10,26,27] Finally we note that complex 8 is closely related to $[\mathrm{Pt_3Cl(\mu_3\text{-}\eta^2\text{-}HCCH)(\mu\text{-}dppm)_3}]^+$ (7) which has been characterized crystallographically.[10] Complexes 8 and 7 differ only in the terminal groups vinyl and chloro, respectively.

Studies with Deuterium-Labeled Reagents. Most insertion reactions of metal hydrides with alkynes occur selectively to give vinyl complexes by cis insertion although trans insertion may also be observed for cluster complexes.[28] Early experiments of 1 with C_2D_2, analyzed by ^{1}H NMR, suggested a less selective reaction, and so a detailed study was carried out. Because the signal due to H$^\alpha$ of 8 is obscured and that due to H$^\beta$ overlaps partly with a dppm resonance, the technique of ^{2}H NMR was used for quantitative analysis of deuterium label distribution.

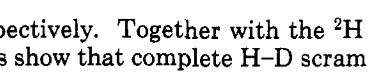
Reaction of $[\mathrm{Pt_3(\mu_3\text{-}D)(\mu\text{-}dppm)_3}]^+$ ($1^\dagger$) with C_2D_2 gave the fully deuteriated derivative $[\mathrm{Pt_3(CD{=}CD_2)(CDCD)(\mu\text{-}dppm)_3}]^+$ ($8^{\dagger\dagger}$), and the ^{2}H NMR spectrum was recorded at room temperature (low-temperature ^{2}H NMR spectra gave very broad resonances and were not useful). The four peaks due to the coordinated acetylene C_2D_2 (δ 9.9), and vinyl substituents D$^\alpha$ (δ 6.9), D$^\beta$ (δ 5.3), and D$^\gamma$ (δ 3.7) were all resolved. Next, reaction of $1^\dagger$ with C_2H_2 was carried out, and the product was identified as $[\mathrm{Pt_3(C_2H_2D)(C_2H_2)(\mu\text{-}dppm)_3}]^+$ ($8^\dagger$) with the deuterium label distributed equally among all the positions of the vinyl substituent (H$^\alpha$, H$^\beta$, and H$^\gamma$) but with no deuterium label in the coordinated acetylene. Finally reaction of 1 with C_2D_2 gave $[\mathrm{Pt_3(C_2HD_2)(C_2D_2)(\mu\text{-}dppm)_3}]^+$ (8**) with the deuterium label again randomly distributed in the vinyl group and with the coordinated acetylene fully deuteriated. These results were readily obtained by integration of the ^{2}H resonances. Further data were obtained from the ^{1}H NMR spectra. Thus the ^{1}H NMR spectrum of $8^\dagger$ gave a doublet at δ 5.24 due to H$^\beta$ with ^3J(H$^\alpha$H$^\beta$) = 12 Hz superimposed on an equal intensity singlet at δ 5.27. This clearly indicates the presence of



groups in equal amounts, the coupling ^2J(H$^\beta$H$^\gamma$) of 3.2 Hz not being resolved in the presence of the expected coupling ^3J(H$^\beta$D$^\alpha$) of ~2 Hz. Similarly, there was a doublet at δ 3.72 due to H$^\gamma$ with ^3J(H$^\alpha$H$^\gamma$) = 18 Hz with a superimposed equal intensity broad singlet at δ 3.74. These peaks indicate equal amounts of



respectively. The ^{1}H NMR spectrum of 4** gave a broad (width at half-height ~4 Hz) singlet at δ 5.24 due to H$^\beta$ and at δ 3.74 due to H$^\gamma$, indicating the presence of



groups, respectively. Together with the ^{2}H NMR data, these results show that complete H-D scrambling occurs within the vinyl groups and that this process is intramolecular and does not involve the coordinated acetylene ligand. Note that intermolecular processes would lead to vinyl groups $\mathrm{PtC_2H}_nD_{3-n}$ with all combinations of n = 0-3, a form of scrambling which is not consistent with the observed spectra.

We have observed previously that similar H-D scrambling occurs during the formation of complex 4.[9] The

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(24) Curiously, at low temperature, only the long-range coupling ^2J(Pt^{2}P^6) = 600 Hz was resolved in either the ^{31}P or ^{195}Pt NMR spectra. We presume that P^3 is distorted away from the Pt^{1}Pt^2 axis and so the expected long-range coupling ^2J(Pt^{3}Pt^1) is not resolved. For earlier references to long-range coupling through Pt-Pt bonds, see ref 6, 7, 9, and 10. Blau, R. J.; Espenson, J. H. *Inorg. Chem.* **1986**, *25*, 878.

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results are most readily interpreted in terms of the processes shown in Scheme I, in which rapid equilibration between intermediates having $Pt_3H(HC{\equiv}CH)$, $Pt_3(CH{=}CH_2)$, $Pt_3H(C{=}CH_2)$, and $Pt_3(CCH_3)$ groups occurs. Clearly, interconversion between vinyl and vinylidene hydride species[8] alone cannot lead to scrambling of H, D labels as observed above, but a short-lived species such as an ethylidyne, in which all hydrogens are equivalent, would naturally lead to such scrambling. If this mechanism is correct the intermediate vinylidene hydride species cannot be **4** since **4** fails to react with acetylene to give **8**. Since in **4** the vinylidene and hydride ligands are mutually trans, it is unlikely that rapid equilibration with vinyl or ethylidyne species would be possible. The proposed intermediate should therefore have the hydride and vinylidene ligands in a position allowing rapid reversible insertion. The scrambling reaction could equally well occur by the sequence $Pt_3(\mu\text{-}CH{=}CH_2) \rightleftharpoons Pt_3(CCH_3) \rightleftharpoons Pt_3H(C{=}CH_2)$. The vinyl to ethylidyne conversion is known.[5a,f]

A second possible mechanism involves rapid interconversion between complexes **3**, A, and B in Scheme I. Since the β-hydrogen atoms in the vinylidene species B are equivalent, this can lead to general scrambling within the vinyl group even though all hydrogens are not equivalent at any one time. The ethylidyne species C would not be necessary in this mechanism. Since none of intermediate A, B, or C is directly detectable, it is not possible to determine which sequence is followed.

The Characterization of Complex 9. Reaction of **1** with excess propyne at room temperature gave $[Pt_3(\mu_3\text{-}\eta^2\text{-}MeC{\equiv}CH)(CH{=}CHMe)(\mu\text{-dppm})_3][PF_6]$ (**9**). The complex was characterized by elemental analysis and by NMR spectroscopy. Complex **9** was not fluxional, and the room-temperature ^{31}P and ^{195}Pt NMR spectra contained six and three resonances, respectively, very similar to the low-temperature NMR spectra of the similar complex **8**. This lack of fluxionality is probably due to steric hindrance to rotation of the propyne ligand.

The connectivities of the propyne and propenyl groups were determined by ^1H NMR spectroscopy, including selective decoupling experiments.

For the $\mu_3\text{-}\eta^2\text{-}CH_3CCH$ ligand, the CH_3 resonance was at δ 2.31 and appeared as a doublet, $J(HH) = 5$ Hz, due to coupling to a proton at $\delta \sim 8.3$, which was obscured by phenyl resonances. There was no resonance in the region δ 9–14, which would be expected for the acetylenic proton if the connectivity were $Pt^2{-}CH{=}CMe{-}Pt^3$.[10] Well-resolved couplings $J(PtCH_3)$ of 11, 34, and 67 Hz were observed, indicating coupling of the CH_3 protons to all three platinum atoms.

For the propenyl group, the H^α, H^β, and $CH^\gamma{}_3$ resonances appeared at δ 6.10, 3.71, and 0.83, respectively, with $^3J(H^\alpha,H^\beta) = 17$ Hz and $^3J(H^\beta H^\gamma) = 7$ Hz. In addition, H^α was coupled to two ^{31}P atoms, $^3J(PH^\alpha) = 3$ Hz, and to Pt^a, $^2J(PtH^\alpha) = 18$ Hz. These data, particularly the magnitude of $^3J(H^\alpha H^\beta)$, clearly define the *trans*-propenyl geometry shown for **9**. The above assignments were confirmed by selective decoupling experiments.

Reaction of $Pt_3(\mu_3\text{-}D)(\mu\text{-dppm})_3]^+$ with propyne gave **9** with the deuterium label *selectively* situated in the H^β position. This was clearly demonstrated by both the ^1H (resonance at δ 3.7 ppm absent, resonance at δ 6.1 a broadened singlet) and the ^2H (broad resonance at δ 3.73, no resonance at δ 6.1) NMR spectra.

The propenyl group in **9** or **9*** is formed by the usual cis insertion of the alkyne into the PtH or PtD bond of **1** or **1***. The product **9** could be formed selectively only because it is the thermodynamically most stable product, but the absence of H–D scrambling in the formation of **9*** shows that a propylidyne intermediate is not formed in this system. It was noted earlier that no intermediate alkyne complex analogous to **3** and no propylidene complex analogous to **4** could be detected in the reactions with propyne, and it is possible that α-elimination cannot occur. However, in this case interconversion between species analogous to **3**, A, and B in Scheme I would not lead to H–D scrambling and, provided the *trans*-propenyl is thermodynamically favored over the the *cis*-propenylplatinum group, would give the observed product **9**. The result gives some support for this mechanism.

Discussion

This work was initiated in order to try to mimic some of the chemistry that occurs when acetylene reacts with a Pt(111) surface.[1] This has been successful in many respects although the simple model cluster complexes do not, and cannot be expected to, give identical chemistry.

In terms of the functional groups formed, complex **1** with acetylene has given $\mu_3\text{-}\eta^2\text{-}(\|)\text{-}HCCH$, $\mu_3\text{-}\eta^2\text{-}C{=}CH_2$, and $\eta^1\text{-}CH{=}CH_2$ groups as stable units, and there is some evidence for the intermediate ethylidyne group CCH_3. All of these groups are thought to play a part in the reaction of acetylene on the Pt(111) surface, but in this case the $Pt_3(\mu_3\text{-}CCH_3)$ group is the most stable species.[1] The possible ethylidyne intermediate $[Pt_3(\mu_3\text{-}CCH_3)(\mu\text{-dppm})_3]^+$ would be a 44e cluster and would be expected to have two Pt–Pt bonds.[29] Both stable complexes **4** and **8** are 46e complexes and, as expected, have only one Pt–Pt bond. The energy differences between these groups are probably small in both the model cluster compounds and the surface species.[1,2]

The structural[10] and spectroscopic data for the $Pt_3(HCCH)$ and $Pt_3(C{=}CH_2)$ groups may be of use in identifying similar groups on a platinum surface. For example, there is a strong resemblance between the CC distances in the $Pt_3(HCCH)$ groups on the Pt(111) surface [1.45 (3) Å][1e] and in complex **7** [1.40 (4) Å].[10] If CP-MAS solid-state spectra of the proposed HCCH and CCH_3 groups on a platinum surface can be obtained, the ^{13}C NMR data for the model compounds will be valuable for comparison. Unfortunately, the IR spectra of the model compounds are dominated by dppm absorptions and are not useful for comparison with the known vibrational spectra of the surface groups.[1,30]

Can the model system assist in understanding the mechanism of the HCCH to CCH_3 reaction on the Pt(111) surface? This is proposed to occur by rearrangement of $Pt_3(HCCH)$ to $Pt_3(C{=}CH_2)$ followed by reaction with surface hydrogen to give $Pt_3(CCH_3)$.[1] Acetylene to vinylidene rearrangements are known in a few binuclear and cluster complexes,[31] but, in the Pt_3 clusters, no rearrangement of the HCCH ligand occurs unless there is a hydride ligand present.[10] The possibility should therefore be considered that the surface reaction also requires surface hydrogen in the first step. The reaction sequences $Pt_3(HCCH) \rightleftharpoons Pt_3(CH{=}CH_2) \rightleftharpoons Pt_3(C{=}CH_2) \rightleftharpoons Pt_3(CCH_3)$ or $Pt_3(HCCH) \rightleftharpoons Pt_3(CH{=}CH_2) \rightleftharpoons Pt_3(CCH_3) \rightleftharpoons$

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[29] See, for example: Underwood, D. J.; Hoffman, R.; Tatsumi, K.; Nakamura, A.; Yamamoto, Y. *J. Am. Chem. Soc.* **1985**, *107*, 5968.

[30] Anson, C. E.; Keiller, B. T.; Oxton, I. A.; Powell, D. B.; Sheppard, N. *J. Chem. Soc., Chem. Commun.* **1983**, 470.

[31] See, for example, ref 5j, 5m, and Berry, D. G.; Eisenberg, R. *J. Am. Chem. Soc.* **1985**, *107*, 7181. It is not known if this rearrangement occurs by a single or a multistep mechanism. For a review, see: Bruce, M. I.; Swincer, A. G. *Adv. Organomet. Chem.* **1983**, *22*, 59. For reactions at a single Pt center, see: Chisholm, M. H.; Clark, H. C. *Acc. Chem. Res.* **1973**, *6*, 202.

$Pt_3(C{=}CH_2)$, both involving a vinyl intermediate, appear to be consistent with both the surface and the cluster chemistry though the stable species differ. The reaction of $[Pt_3(\mu_3\text{-}D)(\mu\text{-dppm})_3]^+$ with propyne proves that the first step in the cluster reaction, after alkyne coordination, involves cis insertion of the alkyne into the PtH bond to give an alkenyl derivative.

Experimental Section

^1H NMR spectra were recorded on a Varian XL-200 NMR spectrometer. ^{31}P, ^{195}Pt, ^{13}C, and ^2D NMR spectra were recorded on a Varian XL-300 NMR spectrometer. References were TMS (^1H), H_3PO_4 (^{31}P), aqueous $K_2[PtCl_4]$ (^{195}Pt), acetone (^2D), and TMS (^{13}C). C_2D_2 was prepared by reacting CaC_2 with D_2O and was dried by passing the evolved gas through a column of silica gel. C_2H_2 and $C_2H_2\text{-}^{13}C_2$ were commercial samples and were used without purification. $[Pt_3(\mu_3\text{-}CO)(\mu\text{-dppm})_3][PF_6]_2$ was prepared by the published method.[7] It was, however, purified as follows: crude $[Pt_3(\mu_3\text{-}CO)(\mu\text{-dppm})_3][PF_6]_2$ (0.5 g) was dissolved in acetone (7 mL) and layered carefully with methanol (20 mL). Slow diffusion of methanol at room temperature gave, after 4 days, large red crystals of the compound in good yield. $[Pt_3(\mu_3\text{-}H)(\mu\text{-dppm})_2][PF_6]$ was prepared by the literature method,[6] and $[Pt_3(\mu_3\text{-}D)(\mu\text{-dppm})_3][PF_6]$ was prepared similarly by using $NaBD_4$ and CH_3OD (as solvent).

$[Pt_3(CHCH_2)(HCCH)(\mu\text{-dppm})_3][PF_6]$. Acetylene was passed through a solution of $[Pt_3(\mu_3\text{-}H)(\mu\text{-dppm})_3][PF_6]$ (0.1 g) in CH_2Cl_2 (20 mL) for 2 min. The color immediately changed to a darker color and then, after a few seconds, to a lighter red-brown. This solution was stirred for 5 min at room temperature. The solvent was removed under reduced pressure and the residue dried under vacuum. A sample was purified by dissolving the compound in a minimum amount of acetone and leaving the solution for 4 days, after which yellow crystals were separated and washed with a few drops of acetone and dried under vacuum: yield 90%; mp 181–185 °C dec. Anal. Calcd for $[Pt_3(CHCH_2)(CHCH)(\mu\text{-dppm})_3][PF_6]$: C, 48.95; H, 3.66. Found: C, 48.43; H, 3.97. NMR in CD_2Cl_2 at −80 °C: ^1H, δ 6.91 [deduced by decoupling, H^{α}], 5.20 [m, $^3J(H^{\alpha}H^{\beta}) = 12$ Hz, $^2J(H^{\beta}H^{\gamma}) = 3$ Hz $^3J(PtH) = 86$ Hz, $J(PH) = 2$ Hz, H^{β}], 3.74 [m, $^3J(H^{\gamma}H^{\alpha}) = 18$ Hz, $^3J(PtH) = 40$ Hz, $J(PH) = 2$ Hz, H^{γ}], 11.61 [s, C^1H]; ^{13}C, δ 152 [m, $^1J(PtC) = 590$ Hz, $^1J(CC) = 62$ Hz, $^1J(CH) = 137$ Hz, C^3], 124 [m, $^1J(CH) = 150$ Hz, C^4], 105.4 [m, $^1J(Pt^3C) = 420$ Hz, $^1J(CH) = 200$ Hz, C^2], 208 [m, $^1J(Pt^2C) = 660$ Hz, $^1J(CH) = 140$ Hz, $^1J(Pt^1C) = 150$ Hz, $^2J(PC) = 95$ Hz, C^1]; ^{31}P, δ −9.3 [m, $^1J(PtP) = 4260$ Hz, P^1], −2.9 [m, $^1J(PtP) = 2440$ Hz, P^2], 8.0 [m, $^1J(PtP) = 3600$ Hz, P^3], 14.2 [m, $^1J(PtP) = 3280$ Hz, P^4, P^5], 1.2 [m, $^1J(PtP) = 3440$ Hz, $^2J(Pt^2P) = 600$ Hz, P^6]; ^{195}Pt, δ −3425 [m, $^1J(Pt^1Pt^2) = 1700$ Hz, Pt^1], −3060 [m, Pt^2], −2866 [m, $J(Pt^3Pt^2) = 500$ Hz, Pt^3]. Additional NMR data are given in the text and in Figures 1–3. Single crystals were grown as long yellow needles from acetone–pentane by slow diffusion, but they were all twinned and so not suitable for X-ray structure determination.

The corresponding deuteriated complexes were prepared similarly by using $[Pt_3(\mu_3\text{-}H)(\mu\text{-dppm})_3][PF_6]$ (or $[Pt_3(\mu_3\text{-}D)(\mu\text{-dppm})_3][PF_6]$ and C_2D_2 (or C_2H_2) in CH_2Cl_2.

The ^{13}C-labeled complex was synthesized by condensing excess acetylene-C^*_2 into a solution of $[Pt_3(\mu_3\text{-}H)(\mu\text{-dppm})_3][PF_6]$ in CH_2Cl_2 under vacuum. The solution was then allowed to warm up to room temperature. This was stirred for 5 minutes and worked up by the usual method.

$[Pt_3(CHCHMe)(CHCMe)(\mu\text{-dppm})_3][PF_6]$. Propyne was passed through a solution of $[Pt_3(\mu_3\text{-}H)(\mu\text{-dppm})_3][PF_6]$ (0.1 g) in CH_2Cl_2 (20 mL) for 2 min. This was stirred for 5 min at room temperature. The solvent was removed under reduced pressure and the residue dried under vacuum. This was purified by dissolving the compound in a minimum amount of acetone and leaving the solution for 4 days, after which yellow crystals were separated and washed with a few drops of acetone and dried under vacuum: yield 80%; mp 188 °C dec. Anal. Calcd for $[Pt_3(CHCHMe)(CHMe)(\mu\text{-dppm})_3][PF_6]$: C, 49.48; H, 3.81. Found: C, 50.03; H, 4.22. NMR in CD_2Cl_2: ^{31}P, δ 14.7 [m, $^1J(PtP) = 3260$ Hz, P^4, P^5], 7.02 [m, $^1J(PtP) = 3500$ Hz, $^3J(P^3P^6) = 100$ Hz, $^2J(P^5P^6) = 40$ Hz, P^6], 0.40 [m, $^1J(PtP) = 3275$ Hz, $^2J(Pt^1P^3) = 670$ Hz, P^3], −4.23 [m, $^1J(PtP) = 4040$ Hz, P^2], −5.50 [m, $^1J(PtP) = 2365$ Hz, $^2J(P^4P^5) = 55$ Hz, P^1]; ^{195}Pt, δ −2850 [m, $^1J(PtP) = 3260, 3260$ Hz, $J(Pt^3Pt^1) = 640$ Hz, Pt^3], −3003 [m, $^1J(PtP) = 3500, 2365$ Hz, $^1J(Pt^1Pt^2) = 1950$ Hz, $^2J(Pt^1P^3) = 670$ Hz, Pt^1], −3340 [m, $^1J(PtP) = 4040, 3275$ Hz, Pt^2]. ^1H NMR data are given in the text. Single crystals were grown as long yellow needles from acetone–pentane by slow diffusion but were unsuitable for X-ray structure determination.

$[Pt_3(CHCDMe)(CHCMe)(\mu\text{-dppm})_3][PF_6]$ was prepared similarly by using $[Pt_3(\mu_3\text{-}D)(\mu\text{-dppm})_3][PF_6]$.

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Registry No. **1**·PF_6, 104761-19-5; **1**†·PF_6, 114424-91-8; **7**, 110745-43-2; **8**·PF_6, 114424-83-8; **8***·PF_6, 114424-85-0; **8**†·PF_6, 114490-23-2; **9**, 114424-87-2; **9***, 114424-89-4; C_2H_2, 74-86-2; C_2D_2, 1070-74-2; ^{195}Pt, 14191-88-9; Pt, 7440-06-4; propyne, 74-99-7; acetylene-C^*_2, 35121-31-4.