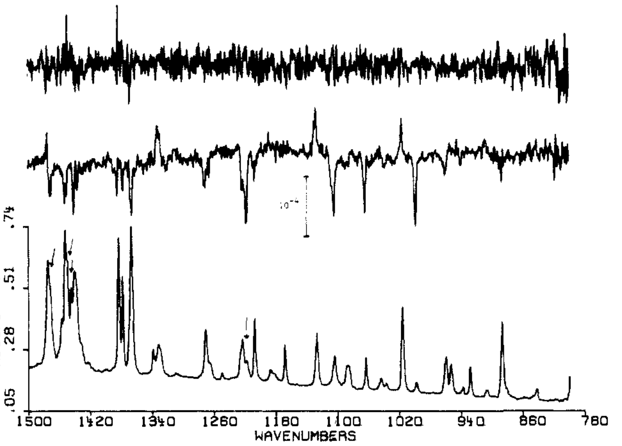

Figure 1. FTIR absorption (bottom) and VCD (middle) spectra of (+)-α-pinene in N_2 matrix at 1-cm^{-1} resolution. VCD is presented as, $\Delta A = A_L - A_R$, the difference in absorbance and its scale is displayed below the middle trace. The top most trace is the difference between the VCD obtained from the first and latter halves of the collected data and reflects spectral reproducibility and matrix stability. Matrix to sample ratio is estimated to be in the range 200:1–300:1, with the uncertainty resulting from the very low vapor pressure of α-pinene.

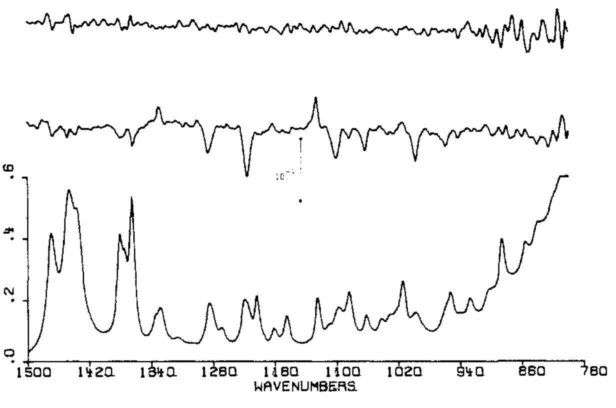

Figure 2. FTIR absorption (bottom) and VCD (middle) spectra of (+)-α-pinene as neat liquid at 4-cm^{-1} resolution. The top trace has same meaning as that in Figure 1. Samples were held in a variable-path-length cell with BaF_2 windows.

at every fourth zero crossing of the He–Ne laser interferometer signal, so that the Fourier transformation gave spectra at 1-cm^{-1} resolution. Since the VCD spectra of individual enantiomers contain significant artifacts, which make the determination of zero line difficult, these artifacts were eliminated by taking one-half of the difference in the raw VCD of enantiomers with identical absorption intensities and base lines. Matrix stability and spectral reproducibility were verified by comparing the VCD obtained from the first and latter halves of the collected data. Total time involved in obtaining the final VCD spectra, including the time for evacuating the cryostat during sample changeover from one enantiomer to the other, was about 12 h. Since the amount of sample used for VCD measurements on matrix-isolated α-pinene (Figure 1) is much less than that used for those on neat liquid (Figure 2) and the spectral resolution in the former is 1 cm^{-1} while that in the latter is 4 cm^{-1}, slightly higher noise is apparent in the VCD of matrix-isolated α-pinene. However, the significant points are the following: (a) Signs of VCD bands in the neat liquid VCD spectrum match with those in the VCD spectrum of matrix-isolated α-pinene, as would be expected for rigid molecules and for good quality matrices; this suggests that in the matrix, aggregates were either absent or, if present, did not influence VCD. (b) Some closely spaced bands, for which there is no indication in the neat liquid spectrum, are nicely resolved (marked by arrows in Figure 1) in the spectrum of matrix-isolated α-pinene; although we do not expect the fine spectral features to be originating from aggregates (see above), further experiments would be needed to verify this. (c) For closely spaced bands associated with bisignate VCD, the dissymmetry factors and hence signal quality in the VCD spectrum of matrix-isolated α-pinene are clearly superior. Similar observations are noted for (+)-3(*R*)-methylcyclohenanone and (+)-3(*R*)-methylcyclopentanone in nitrogen matrices.

Further improvements to these FTIR–VCD measurements on matrix-isolated molecules can be incorporated. For example, by inclusion of two remotely rotatable and mutually orthogonal deposition windows with shutters[7] to prevent gas movement to adjacent window and deposition of one enantiomer on each window, the dead time in evacuating the cryostat can be eliminated. This time savings can inturn be used to further improve the FTIR-VCD spectral resolution.

Acknowledgment. This work is supported by a grant from NIH (GM 29375).

Registry No. (+)-α-Pinene, 7785-70-8.

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(7) For example, see: Hauge, H. R.; Fredin, L.; Kafafi, Z. H.; Margrave, J. L. *Appl. Spectrosc.* **1986**, *40*, 588–595.

Models for Reactions of Acetylene on Platinum(111): The Vinylidene Intermediate

Mehdi Rashidi and Richard J. Puddephatt*

Department of Chemistry, University of Western Ontario
London, Canada N6A 5B7

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One of the most studied surface reactions is that of acetylene on platinum(111). A μ_3-η^2-acetylene complex is formed at low temperature but this rearranges on warming to a μ_3-η^2-vinylidene, $Pt_3(\mu_3\text{-}\eta^2\text{-}C{=}CH_2)$, which then reacts with surface-bound hydrogen to give a μ_3-ethylidyne, $Pt_3(\mu_3\text{-}CMe)$.[1,2] Since the cluster $[Pt_3(\mu_3\text{-}H)(\mu\text{-}dppm)_3]^+$ (**1**, dppm = $Ph_2PCH_2PPh_2$) acts as a useful model for the triply bridging sites on a Pt(111) surface,[3] a study of its reaction with acetylene was initiated with the aim of isolating complexes having the above functional groups, none of which appears to be known. This article reports the formation of a stable μ_3-η^2-$C{=}CH_2$ complex.

Reaction of acetylene with **1**, as the PF_6^- salt, at −80 °C gave an unstable acetylene complex, characterized as $[Pt_3(\mu_2\text{-}H)(HCCH)(\mu\text{-}dppm)_3]^+$ (**2**). The hydride was clearly characterized as μ_2 rather than μ_3 by the ^1H and ^{195}Pt NMR spectra[4] but the

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(1) Kesmodel, L. L.; Dubois, L. H.; Somorjai, G. A. *J. Chem. Phys.* **1979**, *70*, 2180. (b) Steininger, H.; Ibach, H.; Lehwald, S. *Surf. Sci.* **1982**, *117*, 685. (c) Megiris, C. E.; Berlowitz, P.; Butt, J. B.; Kung, H. H. *Surf. Sci.* **1985**, *159*, 184. (d) Bertolini, J. C.; Massardier, J. *The Chemical Physics of Solid Surfaces and Heterogeneous Catalysis*; King, D. A., Woodruff, D. P., Eds.; Elsevier: Amsterdam, 1984; Vol. 3, Chapter 3. (e) Ogle, K. M.; White, J. M. *Surf. Sci.* **1986**, *165*, 234. (f) Wang, P.-K.; Slichter, C. P.; Sinfelt, J. H. *Phys. Rev. Lett.* **1984**, *53*, 82.

(2) (a) Simonetta, M.; Gavezzotti, A. *Theochem* **1984**, *107*, 75. (b) Kang, D. B.; Anderson, A. B. *Surf. Sci.* **1985**, *155*, 639. (c) Silvestre, J.; Hoffmann, R., unpublished results.

(3) Lloyd, B. R.; Puddephatt, R. J. *J. Am. Chem. Soc.* **1985**, *107*, 7785.

(4) NMR for at −80 °C in CD_2Cl_2: ^1H δ −8.2 [*m*, $^1J(Pt(B)H) = 625$, $^2J(PH) = 14$ Hz, $Pt_2(\mu\text{-}H)$]; ^{31}P 21.21 [m, $^1J(Pt(A)P) = 4200$, $^2J(Pt(B)P) = 210$, $^3J(P(A)P(C) = 80$ Hz, P(A)], 34.76 [m, $^1J(Pt(B)P) = 1970$, $^3J(P\cdot(B)P(B) = 135$ Hz, p(B)], 27.29 ppm [m, $^1J(Pt(B)P) = 4440$, $^2J(Pt(B)P) = 640$, $^3J(P(A)p(C) = 80$ Hz, Pt(C)]; ^{195}Pt −3138 [m, Pt(A)], −3394 ppm [*m* $^1J(Pt(B)H) = 625$ Hz, Pt(B)]. Note the coupling of the hydride to Pt(B) but not Pt (A). No ^{195}Pt couplings to the coordinated acetylene was resolved in the $^{13}C\{^1H\}$ or $^{195}Pt\{^1H\}$ NMR spectra of **2***, but the ^{13}C atoms and P(B) atoms gave rise to an AA′XX′ spin system for which the inner four lines were resolved in the ^{31}P NMR spectrum and gave $J(P(B)C) + J(P(B)C') = 92$ Hz. This shows that the acetylene is aligned parallel to the P(B)Pt(B)Pt(B)P(B) axis, but it could lie along the Pt(B)Pt(B) bond or lie above one Pt(B) atom but flip rapidly between Pt(B) atoms. If the acetylene were freely rotating, a triplet resonance for P(B) due to ^{13}C coupling would be observed. The $^{13}C\{^1H\}$ NMR spectrum of 2* at −90 °C gave only a broad singlet at 256.5.

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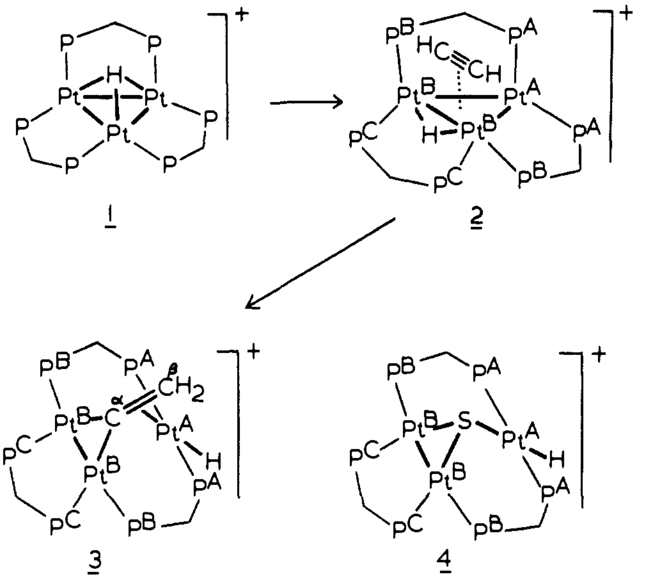
bonding mode of the acetylene was less clearly defined. The proton-coupled ^{13}C NMR spectrum of a sample, **2***, prepared from $H^{13}C^{13}CH$ could be simulated in terms of an AA′XX′ spin system, with $\delta(C) = 256.5$ and $^1J(CC) = 195 \pm 20$, $^1J(CH) = 262 \pm 5$, and $^2J(CH) = 40 \pm 5$ Hz; the chemical shift is dramatically changed but the coupling constants are not significantly perturbed from those of free acetylene which has $\delta(C) = 72.5$ and $^1J(CC) = 172$, $^1J(CH) = 249$, and $^2J(CH) = 50$ Hz and clearly indicates a very weakly bound and probably fluxional HCCH molecule.[5]



If excess acetylene is removed at −80 °C and the sample then isolated by solvent evaporation, the vinylidene complex $[Pt_3H(\mu_3\text{-}\eta^2\text{-}C{=}CH_2)(\mu\text{-dppm})_3]^+$ (**3**) can be isolated in analytically pure form. Crystals of **3** suitable for X-ray diffraction have not yet been obtained, but characterization was possible by NMR.[6] Complex **3** is a 46e cluster and is isoelectronic with **4**, in which a 4e sulfide ligand replaces the 4e vinylidene ligand of **3** and which has been characterized crystallographically.[7] The ^{195}Pt and ^{31}P NMR parameters of **3** and **4** are similar and characteristic of the skeleton with only one Pt–Pt bond.[6,7] The terminal hydride bound to Pt^A was characterized by the ^{1}H, ^{195}Pt{^{1}H}, and ^{195}Pt NMR spectra.[6] Finally the vinylidene ligand in **3** was characterized by ^{1}H, ^{13}C{^{1}H}, ^{13}C, and ^{195}Pt{^{1}H} NMR studies of complexes prepared from HC≡CH(**3**), $H^{13}C{\equiv}^{13}CH$(**3***), DC≡CD(**3****), and **1**.[6] In particular, the presence of a $C{=}CH_2$ group was shown by comparison of the ^{13}C{^{1}H} and ^{1}H coupled ^{13}C NMR spectra of **3*** (Figure 1). The pattern of $^{195}Pt^{13}C$ couplings was diagnostic of the bonding mode in **3*** (for example, the Cα signal appeared as a 1:8:18:8:1 quintet due to coupling to Pt(B)) and the coupling $^1J(C\alpha C\beta) = 36$ Hz is considerably less than in ethylene and similar to the value for ethane[4] as expected for a $\mu_3\text{-}\eta^2\text{-}C{=}CH_2$ group. The $Pt_2(\mu\text{-}C{=}CH_2)$ unit in **3** is similar to that found in binuclear complexes[8] but differs significantly in being bonded to Pt(A) through the π-bond.

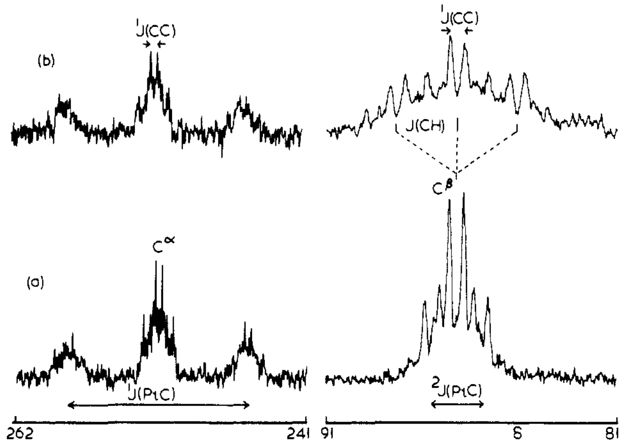


Figure 1. ^{13}C NMR spectra (75.5 MHz) of complex **3***. (a) ^{1}H decoupled, only the inner three lines of the 1:8:18:8:1 quintet due to Pt(B)C coupling are clearly resolved, but the intensity ratios are as expected. The J(Pt(B)C) couplings are shown below. (b) ^{1}H coupled, the centers of the triplet due to $^1J(C\beta H)$ coupling are shown below and the couplings $^1J(C\alpha C\beta)$ above. Note that the Cα and Cβ resonances are shown at different sweep widths.

The ^{1}H and ^{2}H NMR spectra of **3**** and of **3$^+$**, prepared by reaction of $[Pt_3(\mu_3\text{-}D)(\mu\text{-dppm})_3]^+$ with HCCH, showed that scrambling of the isotopic label had occurred within the $Pt_3H(CCH_2)$ groups. The data[9] could be interpreted in terms of the equilibria below, with an equilibrium isotope effect $K = 1.6 \pm 0.2$, close to values found for a related system.[10]

$$Pt_3D(C{=}CHD) \xrightleftharpoons{0.5K} Pt_3H(C{=}CD_2)$$

$$Pt_3D(C{=}CH_2) \xrightleftharpoons{2K} Pt_3H(C{=}CHD)$$

The data do not define a mechanism but are consistent with an equilibration of $Pt_3(CH{=}CH_2) \rightleftharpoons Pt_3H(C{=}CH_2) \rightleftharpoons Pt_3(CCH_3)$ groups which has been proposed to account for H–D exchange between surface-bound deuterium and $Pt_3(CCH_3)$ groups on Pt(111).[1e]

The loss of two Pt–Pt bonds in the transformation of the 42e cluster **1** to the 46e cluster **3** can be understood in terms of cluster bonding theories[11] and models the weakening of Pt–Pt bonding predicted when a $\mu_3\text{-}\eta^2\text{-}C{=}CH_2$ unit binds to the platinum(111) surface.[2c] The system developed here thus models several features of the chemistry of acetylene on platinum(111).[1,2] It differs in that complex **3** does *not* rearrange to the expected ethylidyne $[Pt_3(\mu_3\text{-}CCH_3)(\mu\text{-dppm})_3]^+$. Further studies of this system are in progress.

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(5) Compare, for example, a very strongly bonded acetylene complex, $[W_2Cl_3(NMe_2)_3(PMe_2Ph)_2(\mu_2\text{-}\eta^2\text{-}HCCH)]$, which has $^1J(CC) = 18$ Hz. Ahmed, K. J.; Chisholm, M. H.; Folting, K.; Huffman, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 989. $[Co_2(CO)_6(\mu_2\text{-}\eta^2\text{-}HCCH)]$ has $^1J(CC) = 56$ Hz. Aime, S.; Osella, D.; Giamello, E.; Granozzi, G. *J. Organomet. Chem.* **1984**, *262*, C1. The apparent higher value of $^1J(CC)$ in **2*** than in free HCCH is not statistically significant.

(6) NMR data for **3*** in acetone-d_6 (references Me_4Si, $(MeO)_3PO$, or K_2PtCl_4): ^{1}H δ -6.29 [m, 1 H, $^1J(Pt(A)H) = 1150$, $^2J(P(A)H) = 12$ Hz, Pt*H*], 5.54 [m, 2 H, $^1J(CH) = 156$, $J(PH) = 19$ Hz, $=CH_2$]; ^{13}C δ 252.1 [m, $^1J(Pt(B)C) = 990$, $^1J(Pt(A)C) = 48$, $^1J(CC) = 36$, $^2J(P(C)C) = 64$, $^2J(P(B)C) = 11$ Hz, Cα]; 86.8 [m, $^2J(Pt(B)C) = 125$, $^1J(Pt(A)C) = 90$, $^1J(CH) = 156$ Hz, $C\beta H_2$]; ^{31}P δ 24.8 [m, $^1J(Pt(A)P) = 2935$, $^2J(P(A)P(B)) = 35$, $^3J(Pt(B)P) = 100$ Hz, *P*(A]; 8.95 [m, $^1J(Pt(B)P) = 3450$, $^2J(Pt(B)P) = 470$, $^3J(P(B)P(B)) = 140$ Hz, *P*(B)], 5.17 [*m*, $^1J(Pt(B)P) = 2655$, $^2J(P(C)P(C)) = 90$ Hz, *P*(C)]; ^{195}Pt −3290 [m, $^1J(Pt(A)H) = 1150$, $^1J(Pt(A)P(A)) = 2935$ Hz, Pt(A)], −3082 [m, $^1J(Pt(B)P(B)) = 3450$, $^1J(Pt(B)P(C)) = 2655$, $^2J(Pt(B)P(B)) = 470$, $^1J(Pt(B)C\alpha) = 990$, $^2J(Pt(B)C\beta) = 125$ Hz, Pt(B)].

(7) The atoms $Pt(B)_2$ in **3** are regarded as Pt_2(I) and the cationic center Pt(A) as square-planar Pt(II) with hydride trans to vinylidene. In **4** hydride is trans to sulfide, and approximate distances are $d(Pt(B)Pt(B)) = 2.6$ and $d(Pt(B)Pt(A)) = 3.6$ Å. Jennings, M.; Payne, N. C.; Puddephatt, R. J., *J. Chem. Soc., Chem. Commun.*, in press.

(8) (a) Afzal, D.; Lenhert, P. G.; Lukehart, C. M. *J. Am. Chem. Soc.* **1984**, *106*, 3050. (b) Awang, M. R.; Jeffery, J. C.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1983**, 2091.

(9) Integration of the ^{1}H and ^{2}H NMR spectra gave for **3****, PtH/C=CH = 0.75 and PtD/C=CD = 0.41, and for **3$^+$**, PtH/C=CH = 0.65 and PtD/C=CD = 0.33. The total integral for the PtH and C=CH resonances of **3****, by comparison with the CH_2P_2 peaks, corresponded to a single proton. These NMR spectra were recorded in CD_2Cl_2 (^{1}H) or CH_2Cl_2 (^{2}H) since partial H–D exchange appeared to occur slowly in acetone. ^{2}H NMR data for **3**** or **3$^+$**: -6.30 [s, $^1J(PtD) = 177$ Hz, Pt*D*], 5.66 (s, C=C*D*).

(10) Calvert, R. B.; Shapley, J. R.; Schulz, A. J.; Williams, J. M.; Suib, S. L.; Stucky, G. D. *J. Am. Chem. Soc.* **1978**, *100*, 6240.

(11) Underwood, D. J.; Hoffmann, R.; Tatsumi, K.; Nakamura, A.; Yamamoto, Y. *J. Am. Chem. Soc.* **1985**, *107*, 5968.