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A Remarkable Accidental Degeneracy in the ^{1}H-n.m.r. Spectrum of a (Cyanoethene)platinum(II) Complex

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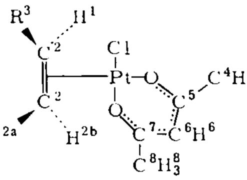
Summary

In the ^{1}H-n.m.r. spectra of (acetylacetonato)chloro-(η^2-cyanoethene)platinum(II), the three protons of the ligand appear to be equivalent. ^{13}C-n.m.r., i.r. and further ^{1}H-n.m.r. studies indicate that the metal-ligand bonding is of orthodox π-olefin type (as formulated in the name of the compound above). The two 2-hydrogens are made equivalent by fluxion, but there is an accidental degeneracy with 1-hydrogen atom.

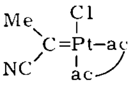
Introduction and Discussion

In the ^{1}H-n.m.r. spectra of many π-bonded olefin complexes related to (*1*), H^1, H^{2a} and H^{2b} are, as expected, inequivalent$^{(1)}$.



(*1*)

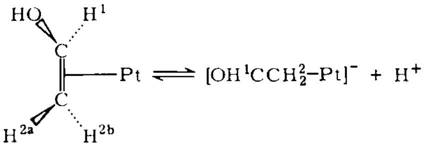
An attempt to prepare the analogous cyanoethene derivative (*1*, R = CN) gave a compound in which the corresponding protons produce at 25° one sharp singlet at δ 4.75 with ^{195}Pt satellites, J(Pt-H) 65 Hz. As the ^{1}H-n.m.r. spectra due to the three protons in various cyanoethene complexes are often complicated and certainly inequivalent$^{(2-4)}$, we wondered whether we had in fact prepared a carbene, perhaps of structure (*2*).



(*2*)

(acac = acetylacetonato)

Alternatively, the new compound could be as in (*1*) with R = CN in the solid, and fluxional in solution due to formation of (*2*). The corresponding vinyl alcohol compound$^{(5)}$ (*1*, R = OH) is fluxional, reaction (1) scrambling



(1)

H^{2a} and H^{2b}, though not H^1 as would have to occur with our cyanoethene complex. However the evidence below leads us to the conclusion that we have in fact prepared an orthodox π-bonded olefin complex as in (*1*), that it is not fluxional from the point of view of H^1 *vis-a-vis* the two H^2s, and that the degeneracy is partly accidental.

The new compound is readily prepared from cyanoethene and $H[Pt(acac)_2Cl]$. Treatment of the product in $CDCl_3$ with pyridine displaces cyanoethene (which can be identified by its characteristic AMX ^{1}H-n.m.r. spectrum).

In the ^{1}H-n.m.r. spectrum of the new compound (Table 1) the resonance due to the protons derived from the cyanoethene group is much closer in δ value to those shown by other π-bonded $C\underline{H}=C\underline{H}_2$ than to those of σ-bonded $C\underline{H}_2$ or $C\underline{H}_3$ either in α or β positions relative to the platinum atom where $\delta < 2.5^{(6,7)}$. The Pt-H coupling constants in the cyanoethene, ethene and propene complexes are close enough to suggest very similar structures, but the evidence is slightly weakened by the fact that some σ-bonded $\underline{Pt}-CH_2-C\underline{H}_3$ and $\underline{Pt}-C\underline{H}_2$ systems show somewhat similar

Table 1. ^{1}H-n.m.r. data for cyanoethene- and propeneplatinum(II) complexes$^{a)}$

Complex (*1*)	H^1		$H^{2a,\,2b}$		H^4		H^8		H^6	
	δ (ppm)	J(Pt-H) (Hz)	δ (ppm)	J(Pt-H) (Hz)	δ (ppm)	J(Pt-H) (Hz)	δ (ppm)	J(Pt-H) (Hz)	δ (ppm)	J(Pt-H) (Hz)
R = CN; $H^1 = {}^1H$	4.75	65	4.75	65	2.15	5	2.25	5.5	5.72	9
R = CN; H^1 = D			4.75	65	2.15	5	2.25	5	5.72	9
R = H; $H^1 = H^{b)}$	4.55	66	4.55	66						
R = Me; $H^1 = {}^1H^{b)}$	5.4	68	4.62 4.57	66 70						

a) In $CDCl_3$ at 25°; b) Ref. 1.

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Table 2. ^{13}C-n.m.r. data for free ligands and platinum(II) complexes$^{a)}$

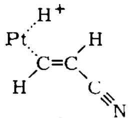
Compound	C^2 δ (ppm)	J(Pt-C) (Hz)	C^1 δ (ppm)	J(Pt-C) (Hz)	C^3 δ (ppm)	C^4 δ (ppm)	J(Pt-C) (Hz)	C^8 δ (ppm)	J(Pt-C) (Hz)	C^5 δ (ppm)	J(Pt-C) (Hz)	C^7 δ (ppm)	J(Pt-C) (Hz)	C^8 δ (ppm)	J(Pt-C) (Hz)
1, R = CN; H^1 = ^{1}H	65.7	217.3	47.7	254.9	116.1	26.1	40.3	26.8	36.6	186.2	21.9	187.9	30.5	101.8	70.8
1, R = CN; H^1 = D	65.6	217.3	*ca.* 48$^{b)}$		116.1	26.1	40.3	26.8	36.6	186.2		187.9	30.5	101.8	70.8
CH_2 = CHCN	137.5		108.1		117.5										
1, R = H; H^1 = ^{1}H		214.8	67.4	214.8		26.3	26.9	26.5		186.2		186.3		101.4	70.8
acacH$^{c)}$						24.3		24.3		191.4		191.4		100.3	

a) In $CDCl_3$ at 25°; b) Broad due to Pt-D coupling; c) Ref. 1.

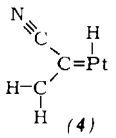
values[(6–8)]. The relative area of the resonance at δ 4.75 compared to those from the protons in the acac ligand confirms that all three hydrogen atoms from the cyanoethene are still present.

The corresponding complex derived from CH_2=CDCN also absorbs at δ 4.75 at 25° as a narrow singlet, peak areas showing that the resonance is due to two protons. Treatment with pyridine liberates deuteriated cyanoethene; what is striking is that its ^{1}H-n.m.r. spectrum gives no evidence of rearrangement of the original CH_2=CDCN.

On cooling the sample below 8° the peak at δ 4.75 and its ^{195}Pt-satellites in the ^{1}H-complex broaden but in the deuteriated compound they split into two. Comparison of spectra run at 60 and 100 MHz indicate that this should be interpreted not as a doublet, but as two separate resonances whose difference in δ is *ca.* 0.03. These must be due to H^{2a} and H^{2b}, J(H^{2b}–H^{2c}) being negligible as in other similar olefin complexes[(1)]. As traces of D_2O in neutral, mildly acidic and mildly alkaline environments have no effect on the two lines, the fluxional process interchanging the two H^2 seems to be intramolecular, perhaps involving hydrogen transfer as in (*3*) or (*4*), and different from that involved in the corresponding vinyl alcohol complex (*1*, R = OH), see reaction (1)[(5)].



(*3*)



(*4*)

ν(C≡N) occurs at 2230 cm^{-1} in free cyanoethene and at 2205 cm^{-1} and at 2195 cm^{-1} in $C_5H_5Mn(CO)_2(\pi\text{-}CH_2{=}CHCN)$[(2)] and $Pt(PPh_3)_2(\pi\text{-}CH_2{=}CHCN)$[(3)] where bonding is thought not to involve the CN group. When MeCN coordinates, ν(C≡N) is lowered by *ca.* 200 cm^{-1} if the π-system is involved, and raised by *ca.* 80 cm^{-1} if bonding occurs through the N atom[(9, 10)]. Here absorptions occur at 2240 and 2220 cm^{-1} (in KBr) which imply considerable retention in the complex of the character of the original C≡N group.

^{13}C-n.m.r. data, given in Table 2, indicate that, in the new compound, CH_2=CH$\underline{C}$N is very similar to that in uncomplexed cyanoethene. They also show that the other two carbon atoms of the ligand are fairly similar to those in the truly-π, ethene analogue (*1*, R = H). δ(^{13}C) tend to lie[(10, 11)] in the regions: M–$\underline{C}$ and M–C–$\underline{C}$, < 16; M=$\underline{C}$, > 250; M–$\underline{C}$=C and M–C=$\underline{C}$, 120–180; M-π($\underline{C}$=C), 30–120. Incidentally, the intensities of the ^{13}C resonances from coordinated cyanoethene decrease with respect to those from the acac ligand from −45° to 25° suggesting a relaxation process such as fluxion. There are greater differences in δ(^{13}C) and J(^{195}Pt-^{13}C) for C^1 than C^2 between free and complexed cyanoethene which suggests that the Pt-C^1 bond length may be shorter than Pt-C^2. In the analogous vinyl alcohol complex[(5)] the reverse is true and the fluxional process involves formation of a σ-Pt-C link with C^2. If the C atom closer to the platinum is involved more significantly in the fluxional process, then (*4*) is more likely than (*3*) as an intermediate.

To summarize, i.r. data, ^{13}C-n.m.r., δ values from ^{1}H-n.m.r. and J(Pt-H) coupling constants all indicate that the new compound is the cyanoethene complex (*1*, R = CN),

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that the bonding is of ordinary π-olefin type and that there is no interaction between platinum and the CN group. The recovery of unisomerized CH_2=CDCN from the deuterio complex excludes a fluxional effect which scrambles all three hydrogen atoms. Therefore, while there appears to be a means of interchanging the 2-hydrogen atoms, we conclude that the equivalence of these with the 1-hydrogen atom in the ^{1}H-n.m.r. spectrum of the new compounds is accidental and as such rather extraordinary.

Accidental degeneracy has also been observed(12) between the $C\underline{H}_2$ and $C\underline{H}_3$ protons in the ethyl group of Ni(acac)(CH_2CH_3)(PPh_3). However our example seems to be the first involving olefinic protons.

Experimental

Pt(acac)Cl(η^2-cyanoethene)

This compound was prepared by stirring together for 30 min H[Pt(acac)$_2$Cl](14) (0.40 g) in $CHCl_3$ (20 cm^3) and CH_2=CHCN (*ca.* 0.075 cm^3) at room temperature, followed by evaporation under reduced pressure. The yellow powder so obtained was washed with hexane and dried under vacuum (Found: C, 25.2; H, 2.65; N, 3.4; Cl, 9.4; $C_8H_{10}ClNO_2Pt$ calcd.: C, 25.1; H, 2.6; N, 3.7; Cl, 9.3%). CH_2=CDCN was prepared following Leitch's method(15) with the small modification of using D_2O and CaO directly in place of $Ca(OD)_2$.

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Palladium(II) Complexes with Primary Thioamides

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Summary

Palladium(II) complexes of thioacetamide, thiooxamide, N°, N°-dimethylthiooxamide and ethyl thiooxamidate have been prepared and investigated by electronic and i.r. spectroscopy. It is concluded that the ligands always act as monodentate sulphur donors, and that planar $[PdL_4]X_2$ (X = Cl, Br or ClO_4) compounds are formed. The ν(PdS) frequencies and the ligand field strengths are enhanced by electron donor groups and lowered by electron withdrawing groups.

Introduction

During the course of investigating the spectroscopic properties of thioamides and their complexes in our laboratory, Pd^{II} complexes containing primary thioamides [$RC(S)NH_2$ with R = Me, thioacetamide (TA); R = $CONH_2$, thiooxamide (TO); R = $CONMe_2$, N°, N°-dimethylthiooxamide (DMTO); and R = CO_2Et, ethyl thiooxamidate (ETO)] have been prepared. Their electronic and vibrational spectra are reported and discussed. Some Pd^{II} complexes of TA(1) and thiourea [R = NH_2, (TU)](2, 3) have already been studied.

In these compounds, ν(M–S) frequencies have been assigned in the 280–250 cm^{-1} region. As the substituents in both TA and TU are electron donors, extension to electron

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