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A ^{13}C NMR INVESTIGATION OF SOME VINYL ETHER COMPLEXES OF PLATINUM(II)

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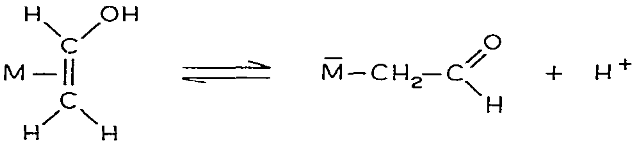
Summary

The ^{13}C NMR spectra, including $J(^{13}C,^{1}H)$ and $^{1}J(^{195}Pt,^{13}C)$, of (η^2-CH_2=CHOR)$PtCl_2$(Py), (R = Me, i-Pr, t-Bu, CHMeEt, CHMeBu-t, Py = pyridine) have been recorded and used to reinterpret the bonding in these compounds.

Introduction

Vinyl alcohol complexes of transition metals are of particular interest on account of eq. 1, which has been demonstrated for PtCl(acac)(η^2-H_2C=CHOH)



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[1]. The ^{1}H NMR spectra of *trans*-(η^2-CH_2=CHOR)$PtCl_2$(C_5H_5N), (R = Me, i-Pr, t-Bu) have been investigated previously [2], but unfortunately the chemical shifts proved to be dominated by near neighbour anisotropy, and $^{2}J(^{195}Pt,^{1}H)$ was not significantly different from that observed for the analogous *trans*-(η^2-CH_2=CHR')$PtCl_2$(C_5H_5N) complexes. Subsequently, in an extensive ^{13}C NMR study of a wide variety of complexes of the type *trans*-(η^2-olefin)$PtCl_2$-(C_5H_4MeN), it was found that the data for *trans*-(η^2-CH_2=CHOMe)$PtCl_2$(NC_5H_4Me) were anomalous with marked differences in both $^{1}J(^{195}Pt,^{13}C)$ and the coordination shifts for the two different coordinated olefin carbon atoms [3]. This behaviour is consistent with the X-ray structures of (η^2-CH_2=CHOH)PtCl(acac) [4] and *cis*-(η^2-CH_2=CHOCHMeBu-t)$PtCl_2$(NH_2CHMePh) [5], which have shown

TABLE 1

^{13}C CHEMICAL SHIFTS ($^{1}J(^{195}Pt,^{13}C)$, in parentheses) AND COORDINATION SHIFTS (in square brackets, high frequency positive) FOR *trans*-(η^2-CH_2=CHOR)$PtCl_2$(Py) IN $CDCl_3$ (numbering as CH_2=CH—O—C_α—C_β—C_γ)

R		CH_2	CH	C_α	C_β	C_γ
Me [a]		44.1	139.7	48.0		
		(194.6)	(87.0)			
		[—44.3]	[—13.1]	[6.6]		
i-Pr		42.3	140.2	79.4	21.9; 22.4	
		(202.6)	(75.7)			
		[—45.8]	[—10.3]	[7.6]	[—0.1; 0.4]	
t-Bu		41.5	138.3	83.1	28.2	
		(207.5)	(70.2)			
		[—49.1]	[—7.9]	[7.1]	[0.2]	
CHMeEt	A [b]	42.0	141.7	85.3	20.1 [c]; 29.1 [d]	9.6
		(203)	(72)			
		[—45.8]	[—9.3]	[8.2]	[0.7; —0.1]	[0.1]
	B [b]	41.7	141.4	84.5	19.2 [c]; 28.9 [d]	9.6
		(201)	(75)			
		[—46.0]	[—9.6]	[7.5]	[—0.2; —0.3]	[0.1]
CHMeBu-t	A [b]	41.1	143.1	92.0	15.7 [c]; 34.8 [e]	25.5
		(206)	(70)			
		[—45.9]	[—8.9]	[8.5]	[1.2; —0.1]	[—0.3]
	B [b]	40.0	143.9	91.3	15.4 [c]; 34.8 [e]	26.1
		(197)	(74)			
		[—47.0]	[—8.1]	[7.8]	[0.9; —0.1]	[0.3]

[a] For the free ligand, $^{1}J(^{13}C,^{1}H)$ (methyl) 143.4 Hz; $^{3}J(^{13}C,^{1}H)$ (methyl carbon) 6.9 Hz; $^{1}J(^{13}C,^{1}H)$(CH) 181.6 Hz; $^{3}J(^{13}C,^{1}H)$(vinyl CH carbon atom) 5.0 Hz; $^{1}J(^{13}C,^{1}H)(CH_2)$ 156.3 and 161.3 Hz; $^{2}J(^{13}CH_2,^{1}H)$ 9.8 Hz. For the complexed ligand, $^{1}J(^{13}C,^{1}H)$(methyl) 146.3 Hz; $^{3}J(^{13}C,^{1}H)$ (methyl carbon atom) 5.5 Hz; $^{1}J(^{13}C,^{1}H)$(CH) 167.2 Hz; $^{2}J(^{13}CH,^{1}H)$ 6.4 Hz; $^{1}J(^{13}C,^{1}H)(CH_2)$ 161.6 and 163.7 Hz; $^{2}J(^{13}CH_2,^{1}H)$ 10.7 Hz. [b] Two diastereoisomers, form A predominating. [c] Methyl group. [d] CH_2 group. [e] Quaternary carbon atom.

that the Pt—CHOR bond length is significantly greater than the Pt—CH_2 bond length. It is therefore apparent that ^{13}C NMR spectroscopy is more sensitive than ^{1}H NMR spectroscopy to changes in the bonding and a detailed study of the ^{13}C NMR spectra of *trans*-(η^2-CH_2=CHOR)$PtCl_2$(Py), (R = Me, i-Pr, t-Bu, CHMeEt, CHMeBu-t; Py = pyridine) has been carried out.

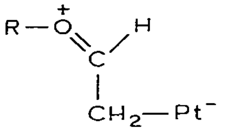
Experimental

The compounds were prepared as previously described [2]. The ^{13}C NMR spectra were measured in $CDCl_3$ using a JEOL PS-100 NMR spectrometer at 25.15 MHz. Tetramethylsilane was used as an internal reference and the chemical shifts are reported with reference to TMS, high frequency being taken as being positive. The ^{1}H coupled ^{13}C NMR spectra were recorded with nuclear Overhauser enhancement. The ^{13}C NMR chemical shifts, coupling constants, and coordination shifts are given in Table 1.

Discussion

It is known that there are many factors contributing to the change in chemical shift of a π-system when coordinated to a metal [6]. However, fewer factors contribute to the chemical shift of a methyl group, the main ones being the charge on the substituent and steric effects [7]. When a vinyl ether is coordinated to platinum, the α-carbon atom is moved to high frequency by ca. 7 ppm. On coordination, it would be expected that both the alkoxy group and the vinylic hydrogen atom would move away from the metal, thus increasing any mutual steric compression. However, such a steric compression would produce a low frequency shift rather than the observed high frequency shift. The high frequency shift of ca. 7 ppm can be readily explained by assuming that the shift arises predominantly from an increase in positive charge on the oxygen atom on coordination [8]. This observation is consistent with $pK_a = 3.5$ observed previously for (η^2-$CH_2{=}CHOH$)Pt(acac)Cl [1].

The data for the olefinic carbon atoms are far more difficult to interpret. The coordination shifts of the $^{13}CH_2$ group and the slight increases in $^1J(^{13}C,^1H)$ are very similar to that observed for simple olefin complexes, yet $^1J(^{195}Pt,^{13}CH_2)$ increases markedly from 160 Hz normally observed for olefin complexes to 200 Hz. The ^{13}CH group is even stranger, with very small coordination shifts and $^1J(^{195}Pt,^{13}C)$, suggesting a weak platinum—carbon interaction, but $^1J(^{13}C,^1H)$ decreases significantly. It is clear that no single factor of the many possible ones is dominant in causing these changes. The explanation of Cooper and Powell [3], in terms of increased contributions from the cannonical form, I, does not



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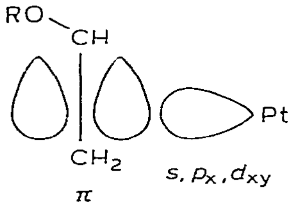
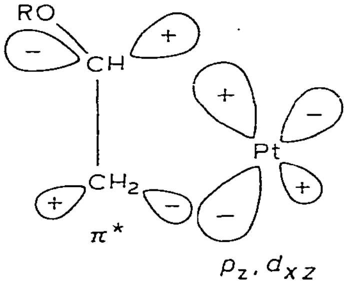
explain why the coordination shift and $^1J(^{13}C,^1H)$ for the CH_2 group are approximately the same for coordinated olefins and vinyl ethers. A far more plausible explanation comes from examining the expected shape of the π and π^* orbitals. The π donation from the oxygen to the vinyl group will cause the polarisation of the vinyl π-bonding orbital towards the CH_2 group with the consequential partial negative charge. The π^* orbital will be polarised towards the CH(OR) group. Consequently, the vinyl group will move to optimise both σ donation from the π orbital to a suitable platinum s, p_x, d_{xy} hybrid orbital and π donation from a suitable p_z, d_{xz} hybrid orbital to the π^* orbital of the vinyl group. This model has the advantage that it allows the explanation of all the observations





and is consistent with the X-ray structures. Both the CH_2 and CH groups remain essentially sp^2 hybridised. The removal of negative charge from the CH_2 group permits more to be given by the oxygen, with the consequential increase in positive charge on the oxygen atom. There is little nett change at the CH_2 group compared with an alkene. The CH group receives negative charge from the platinum, causing $^1J(^{13}C,^1H)$ to decrease. The ^{13}CH chemical shift should then move to lower frequency, but as we remove negative charge from the CH_2 group, we get a further contribution from I causing a high frequency shift, ($\delta(^{13}C)$ for $[HO{-}CHMe]^+$ is 237.2) [9], but there is still an overall nett low frequency shift. $^1J(^{195}Pt,^{13}CH)$ is small as the principal is via a platinum *d*-orbital while it is the *s*-orbital which produces the greatest coupling effect via the Fermi contact mechanism.

Comparison of the ^1H and ^{13}C NMR spectra of these compounds shows that there is little or no correlation between the data. It has been previously reported for methyl-platinum derivatives that there is a rough correlation between $^2J(^{195}Pt,^1H)$ and $^1J(^{195}Pt,^{13}C)$. On this basis, $^2J(^{195}Pt,^1H)$ for the CH group would be ca. 10 Hz and for the CH_2 group would be ca. 20 Hz rather than the observed ca. 65 Hz. It is clear that for these complexes, $^2J(^{195}Pt, ^1H)$ is made more complicated by such factors as angular dependence and through space coupling. Consequently, it is dangerous to relate $^2J(^{195}Pt,^1H)$ simply to the bonding mode of the vinyl ether. There is also no correlation between the ^1H and ^{13}C chemical shifts, but this is due to chlorine anisotropy as described previously [2].

In order to investigate the possible use of ^{13}C NMR spectroscopy in investigating diastereoisomers of these complexes, the ^{13}C NMR spectra of $(\eta^2\text{-}CH_2{=}CHOR)\text{-}PtCl_2(Py)$, (R = CHMeEt, CHMeBu-t) [10] were also examined. In both cases, there are two diastereoisomers present which give rise to two sets of signals in approximately the same ratio as found in the ^1H NMR spectra. Only small shift differences were found between the two diastereoisomers and there appeared to be little or no correlation between stability and chemical shift differences.

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