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Vibrational and NMR Spectroscopic Studies on PtCl(acac)(olefin)

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Spectroscopic studies (IR, Raman, ^{1}H- and ^{13}C-NMR) on the complexes $PtCl(acac)(olefin)$ (olefin = ethylene, propene, vinyl chloride, vinyl acetate, methyl acrylate and styrene) have been carried out. Comparison of the data with previously reported results for $(acac)M(olefin)_2$ ($M = Rh(I), Ir(I)$), and for trans-*$PtCl_2(L)(olefin)$ reveals that σ- and π back-bonding are of about equal importance in the Pt(II)–olefin bond, while π back-bonding appears to be stronger than σ-bonding in the Ir–olefin bond. The σ-bonding of the Pt(II)–olefin bond is stronger for $PtCl(acac)(olefin)$ than for* trans-*$PtCl_2(4CH_3$-PyN-oxide)(olefin).*

Introduction

The spectroscopic (vibrational, ^{1}H- and ^{13}C-NMR) and some thermochemical properties of the complexes *trans*-$PtCl_2(L)$(olefin) and (acac)M(olefin)$_2$ (M = Rh(I), Ir(I)) have been studied in our laboratory in some detail [1–5]. The spectroscopic results show that the substituent R of the olefin $CH_2{=}CHR$ influences the Rh(I)– and Ir(I)–olefin bond in the same way. The Ir–olefin bond is, however, stronger than the Rh–olefin bond. In order to compare these results with those of the Pt(II)–olefin bond, the complexes PtCl(acac)(olefin) (acac = acetylacetonate; olefin = ethylene (ET), propene (PR), vinyl chloride (VCl), vinyl acetate (VA), methyl acrylate (MA) and styrene (ST)) have been investigated. Extensive ^{1}H-NMR studies on the orientation, the distortion and the rotational barriers of the olefin in Pt(X)(acac)(olefin) (X = Cl, Br, olefin, *e.g.* ET, PR, VCl) have been carried out by Lewis *et al.* [6–8]. We report in this paper more specifically vibrational and NMR data which shed some more light on the factors influencing the platinum–olefin bond strength.

TABLE I. Analytical Data for PtCl(acac)(olefin).

Olefin	%C		%H	
	Calc.	Found	Calc.	Found
ET	23.50	23.81	3.10	3.18
PR	25.85	26.13	3.53	3.65
VCl	21.44	21.51	2.57	2.66
VA	26.00	24.39	3.15	3.07
MA	26.00	26.31	3.15	3.25
ST	35.99	36.17	3.49	3.60

Experimental

Preparation of the Complexes

$HPtCl(acac)_2$ was prepared by acidifying a solution of $KPtCl(acac)_2$ [9, 10]. The complexes PtCl(acac)(olefin) where olefin is ET, PR, MA and ST were prepared according to the method of Holloway *et al.* [7] by reaction of $HPtCl(acac)_2$ with the olefin in benzene. The complexes PtCl(acac)(VCl) and PtCl(acac)(VA), however, were contaminated with red impurities. Better results were obtained when PtCl(acac)(ET) was dissolved in the liquid olefin (for VCl at –20 °C). All complexes were purified by forcing a solution of the complex in dichloromethane over a layer of silicagel (Merck 0.063–0.200 mm). Addition of n-hexane to the filtrate afforded yellow crystals after cooling to –40 °C. Elemental analyses (Table I) were carried out at the Institute for Organic Chemistry TNO, Utrecht, The Netherlands.

Spectroscopic Measurements

Infrared spectra of the solid compounds (KBr pellets) were recorded on a Beckman 4250 spectrophotometer. Raman spectra of the solid compounds were obtained using a Coderg PH 1 spectrophotometer with dc detection. The 6471 Å line of a CRL 52 Kr^+ laser was used as the exciting line. ^{1}H-NMR spectra were obtained in $CDCl_3$ on a Varian T60

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TABLE II. The Frequencies of Modes of the Complexes PtCl(acac)(olefin)[a].

	ν_s(Pt–C$_2$)	ν_{as}(Pt–C$_2$)	$\bar{\nu}$(Pt–C$_2$)[b]	ν(Pt–Cl)	ν(Pt–O)[c]		
ST	392	501	447	*346*	470	*650*	*691*[d]
PR	398	498	448	*346*	474	*652*	*700*
ET	*402*	*498*	*450*	*340*	*474*	*647*	*696*
MA	396	505	451	*340*	476	*652*	*696*
VA	394	534	464	*345*	474	*654*	*698*
VCl	425	514	472	*345*	475	*646*	*700*

[a] Raman data for the solid compounds; infrared data (KBr pellets) are in italics. [b] $\bar{\nu}$(Pt–C$_2$) = ½(ν_s(Pt–C$_2$) + ν_{as}(Pt–C$_2$)). [c] The couplings between ν(Pt–O) and acac ring modes give rise to these three bands [11]. [d] Coincides with ST-vibration.

TABLE III. Frequencies and Percentage Lowerings (PL) of the Vibrational Bands I, II and III for the Complexes PtCl(acac)(olefin)[a,b,c,d].

Olefin	Band I			Band II			Band III			
	free	coord.	PL	free	coord.	PL	free	coord.	PL	SPL.
VCL	1612	1470	*8.81*	1374	1361	*.95*	1281	1231	*3.90*	*13.7*
ET	1623	1516	*6.59*	1342	1251	*6.78*				*13.4*
MA	1633	1506	*7.78*	1402	1384	*1.28*	1283	1230	*4.13*	*13.2*
VA	1647	1500	*8.93*	1386	1377	*.65*	1295	1249	*3.55*	*13.1*
PR	1648	1512	*8.25*	1415	1395	*1.41*	1297	1254	*3.32*	*13.0*
ST	1632	1521	*7.30*	1414	1410	*.28*	1305	1265	*3.07*	*10.7*

[a] Raman data for the solid compounds. [b] Bands I, II and III represent the coupled modes ν(C=C), δ(CH$_2$)$_{scis}$ and δ(CH)$_{bend}$. [c] The percentage lowerings are in italics, SPL = summed percentage lowering. [d] Data for the free olefins are from ref. 2, 15 and ref. therein.

spectrometer and the ^{13}C-NMR spectra were measured in CDCl$_3$ at 20 MHz on a Varain CFT 20 spectrometer with proton decoupling.

Results and Discussion

The structure of the complexes PtCl(acac)(olefin) has been proposed to be square planar [6]. The most stable orientation of the olefin, which rotates about the Pt–olefin axis at room temperature, is perpendicular to the square plane [6–8]. Isolation of the complexes PtCl(acac)(VCl) and PtCl(acac)(VA) in the pure state appeared to be difficult. Although repeated crystallisation improved the analytical results (Table I), no satisfactory data were obtained for PtCl(acac)(VA). Nevertheless the ^{1}H- and ^{13}C-NMR spectra of the latter compounds did not show resonances which could be attributed to impurities (Tables V, VI).

Vibrational Spectra

IR and Raman spectroscopy were used as complementary methods. In this way it was possible to assign olefinic bands between 1200 and 1600 cm^{-1} which coincide with bands of the acac ring.

In Table II the frequencies of the platinum–olefin, platinum–oxygen and platinum–chlorine vibrations are given. The assignment was carried out by comparison with the complexes *trans*-PtCl$_2$(L)(olefin) [2] and with the complex PtCl(acac)(ET) [11]. In contrast to the results of Behnke *et al.* [11] we found a band at about 500 cm^{-1} for all olefin complexes which we assigned to ν_{as}(Pt–C$_2$) in accordance with previous results for *trans*-PtCl$_2$(L)(olefin) [2].

The results show that variation of the olefin has a small irregular influence on ν(Pt–Cl) and ν(Pt–O). The values of $\bar{\nu}$(Pt–C$_2$), which is the mean of ν_s(Pt–C$_2$) and ν_{as}(Pt–C$_2$), are of the same order as for K[PtCl$_3$(olefin)] and smaller than for *trans*-PtCl$_2$(4CH$_3$-PyN-oxide)(olefin) [2]. This means that the *trans* influence of the acac-group resembles that of Cl$^-$ and differs from that of 4CH$_3$-PyN-oxide. The values of $\bar{\nu}$(Pt–C$_2$) also show that for VA and VCl the Pt–olefin bond is stronger than for the other olefins.

Coordination of an olefin to a metal decreases the double bond character [12] and accordingly the frequency of ν(C=C) will also decrease. This vibration, however, is coupled to δ(CH$_2$)$_{scis}$ and/or δ(CH)$_{bend}$ depending on the type of olefin [13]. It has been shown that the summed percentage lowering (SPL) of the olefinic frequencies ν(C=C) and δ(CH$_2$)$_{scis}$ in metal–ethylene d^8 complexes is a measure of the decrease in double bond character

TABLE IV. Summed Percentage Lowerings (SPL) for Complexes of Pt(II), Rh(I) and Ir(I).

	PtCl(acac)(olefin)^a	(acac)Rh(olefin)$_2$^{b}	(acac)Ir(olefin)$_2$^{b}
VCl	13.7	16.4	18.1
ET	13.4	15.1	16.1
MA	13.2	11.7	13.9
VA	13.1	14.0	15.2
PR	13.0	14.1	16.1
ST	10.7	12.1	13.2

^{a}This work. ^{b}From ref. 3.

TABLE V. ^{1}H and ^{13}C-NMR of the (acac) Moiety in PtCl(acac)(olefin) in $CDCl_3$.^{a,b}

Olefin	e-value^c	^{1}H-NMR			^{13}C-NMR				
		CH	*tr*CH$_3$	*cis*CH$_3$	CH	CO		*tr*CH$_3$	*cis*CH$_3$
MA	0.60	5.59	1.98	2.18	101.2(71)	185.7	186.6	25.8(39)	26.3(37)
VCl	0.20	5.55	2.02	2.17	101.2(70)	185.8	186.5	25.9(36)	26.4(40)
ET	−0.20	5.53	1.95	2.15	101.1(70)	185.7	186.0		26.1 (35 and 40)
VA	−0.22	5.52	1.95	2.19	101.1(69)	185.9	186.0	26.0(35)	26.1(39)
PR	−0.78	5.52	1.93	2.12	101.0(69)	185.4		26.2(34)	26.3(40)
ST	−0.80	5.33	1.68	2.05	100.7(69)	185.2	185.4		25.9 (38 and 40)

^{a}The chemical shifts were measured at room temperature relative to TMS (for ^{13}C using $\delta_{TMS} = \delta_{CDCl_3} - 76.9$ ppm) and are reported in ppm in the δ scale. ^{b}Platinum–carbon couplings are given in brackets. ^{c}Data from ref. 19.

[14]. In Table III bands I, II and III belonging to the coupled modes ν(C=C), $\delta(CH_2)_{scis}$ and $\delta(CH)_{bend}$ for PtCl(acac)(olefin) are presented. The assignment is based on comparison of these spectra with those for (acac)Rh(olefin)$_2$, (acac)Ir(olefin)$_2$ and *trans*-PtCl$_2$(L)(olefin) [2, 3].

For ET band I and II shift by about the same percentage indicating that both bands have about the same contribution from ν(C=C), while for the other olefins ν(C=C) contributes most to band I, than to band III and only to a small extent to band II. The SPL for the complexes PtCl(acac)(olefin) are of the same order of magnitude as for the complexes K[PtCl$_3$(olefin)] [2]. Except for MA, the order in SPL is Ir(I) > Rh(I) > Pt(II) (Table IV), in agreement with the order of decreasing metal–olefin bond strength [14].

The sensitivity of the SPL to variation of R in the olefin CH$_2$CHR also decreases from Ir(I) > Rh(I) > Pt(II). This could indicate that (i) variation in π back-bonding, which is larger for Ir(I) than for Rh(I) [16], mostly influences ν(C=C) and accordingly the SPL; or (ii) that in the Pt–olefin bond the contributions from σ- and π back-bonding are of about equal importance. It has been found, however, that σ-bonding causes a greater weakening of the C=C bond than π back-bonding [17] so (ii) seems to be a more likely explanation.

NMR Spectra

The ^{1}H and ^{13}C shifts of the acac ring in PtCl(acac)(olefin) (Table V) are little affected by variation of the olefin. Just as has been observed for the complexes (β-diket)Rh(olefin)$_2$, δ^1H_{CH} increases linearly with increasing e-value of the olefin (Table V) although ST again deviates from this relation [18]. This e-value is a measure of the polarisation of the olefin [19]. The influence of variation of the substituent R on δ^1H_{CH} is less than for the complexes (acac)Rh(olefin)$_2$, probably because only one olefin is coordinated to Pt. In contrast to (β-diket)Rh(olefin)$_2$ also $\delta^{13}C_{CH}$ and $\delta^{13}C_{CO}$ decrease with decreasing e-value, while this is not observed for the other ^{1}H and ^{13}C shifts. In the ^{1}H-NMR spectra the high field methyl resonance belongs to the methyl group *trans* to the olefin, the low field resonance to the methyl group *trans* to chlorine [6]. The same assignment has been used for the interpretation of the ^{13}C-NMR spectra. $^3J(^{195}Pt–^{13}C)$ for C_{CH} is nearly constant and $^3J(^{195}Pt–^{13}C)$ for the methyl group *trans* to the olefin shows a stronger dependence on the olefin than $^3J(^{195}Pt–^{13}C)$ for the methyl *trans* to chlorine. This effect has also been observed for $J(^{195}Pt–^1H)$ [6].

In Table VI the ^{13}C chemical shifts and platinum–carbon coupling constants for the olefinic carbon atoms are given.

TABLE VI. ${}^{13}C$ Chemical Shifts (in ppm) for the Olefinic Carbon Atoms in PtCl(acac)(olefin). The values for $J({}^{195}Pt-{}^{13}C)$ (in Hz) are given in brackets.[a]

Olefin	δC_1	δC_2	δC_{mean}		
			free	Pt	Δ
VA	47.2(214)	102.6(229)	119.0	74.9(222)	44.1
PR	64.9(210)	88.8(200)	124.0	76.9(205)	47.1
VCl	61.6(206)	85.2(268)	121.8	73.2(237)	48.6
ST	55.7(221)	87.7(179)	124.0	71.7(200)	52.3
ET	67.0(214)	67.0(214)	122.8	67.0(214)	55.8
MA	64.4(205)	68.2(235)	129.3	66.3(220)	63.0

[a] The chemical shifts were measured at room temperature relative to TMS using $\delta_{TMS} = \delta_{CDCl_3} - 76.9$.

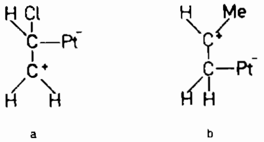

Figure 1. Valence Bond representations of the Pt–VCl and Pt–PR bond. a) ${}^1J({}^{195}Pt-{}^{13}C_2) > {}^1J({}^{195}Pt-{}^{13}C_1)$. b) ${}^1J({}^{195}Pt-{}^{13}C_1) > {}^1J({}^{195}Pt-{}^{13}C_2)$.

The resonance at lower field is assigned to the substituted olefinic carbon atom C_2 and the resonance at higher field to C_1 [2]. The mean upfield shift upon coordination ($\Delta\delta{}^{13}C_{mean}$) corresponds to that for the complexes $K[PtCl_3(olefin)]$ and it is smaller than for $(acac)Rh(olefin)_2$ and $(acac)Ir(olefin)_2$ [2, 3]. The upfield shift upon coordination decreases in the order Ir(I) > Rh(I) > Pt(II). Although the factors which determine ${}^{13}C$ shifts differ from those which influence the SPL [20], the sequence is the same.

The mean coupling constant ${}^1J({}^{195}Pt-{}^{13}C)_{mean}$ increases with increasing $\bar{\nu}(Pt-C_2)$. This increase will be caused by an increasing Fermi contact (s-orbital overlap) when the Pt–olefin bond is strengthened (increasing $\bar{\nu}(Pt-C_2)$). $\bar{\nu}(Pt-C_2)$ has about the same magnitude as for other complexes of the type *trans*-$PtCl_2(L)$ (olefin) (*e.g.* $K[PtCl_3(olefin)]$) but ${}^1J({}^{195}Pt-{}^{13}C)$ is much higher presumably because of a larger degree of σ-bonding [21].

${}^1J({}^{195}Pt-{}^{13}C_1)$ and ${}^1J({}^{195}Pt-{}^{13}C_2)$ show the asymmetry in the platinum–olefin bond. For the olefins with electron donating substituents (*i.e.* PR and ST) ${}^1J({}^{195}Pt-{}^{13}C_1) > {}^1J({}^{195}Pt-{}^{13}C_2)$ while for the olefins with electron withdrawing substituents (*i.e.* VCl and MA) ${}^1J({}^{195}Pt-{}^{13}C_2) > {}^1J({}^{195}Pt-{}^{13}C_1)$. This can be rationalized by the Valence Bond representations in Fig. 1 [22], which also indicate that the asymmetry is electronic and not steric in origin.

Conclusions

The weakening of the olefinic C=C bond upon coordination, as indicated by vibrational data, decreases according to Ir(I) > Rh(I) > Pt(II). The variation in the SPL depending on the olefin decreases from Ir(I) > Rh(I) > Pt(II) which is probably caused by the about equal importance of σ-bonding and π back-bonding in the Pt(II)–olefin bond and the larger importance of π back-bonding in the Ir(I)–olefin bond. The spectroscopic parameters SPL, $\Delta\delta{}^{13}C$ and $\bar{\nu}(Pt-C_2)$ for PtCl(acac)(olefin) are about the same as for $K[PtCl_3(olefin)]$, but the much higher coupling constants ${}^1J({}^{195}Pt-{}^{13}C)$ indicate that σ-bonding is relatively strong.

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