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ALKYL SUBSTITUENT EFFECTS ON C-13 NMR PARAMETERS FOR TRICHLORO-PLATINUM(II)-OLEFIN COMPLEXES AND β-METHOXYALKYLMERCURIC CHLORIDES

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C-13 nmr parameters for a series of Pt(II)-olefin complexes and β-methoxyalkylmercuric chlorides are reported and discussed in terms of alkyl substituent effects on the direct metal-carbon couplings and others in order to clarify the property of Pt-C bonding by comparing with Hg-C bonding.

Introduction

Recently, C-13 nmr spectroscopy has been widely used for organometallic compounds by its potential in the elucidation of the nature of metal-carbon bondings.1) With regard to transition metal olefin complexes, several reports of C-13 chemical shifts have appeared.1,2) However, the investigations regarding the metal-carbon nuclear spin-spin couplings, which should give unique information upon metal-carbon bonding properties, are not systematic and still limited.3,4)

In the present paper, both platinum-carbon couplings and C-13 chemical shifts for a series of Zeise's type salts are studied to clarify the bonding property between platinum and the coordinated olefinic carbon. In order to support the interpretation the platinum-carbon couplings are contrasted with mercury-carbon couplings of β-methoxyalkylmercuric chlorides, since they are representative organometallic compounds having metal-carbon σ-bonds.

Experimental

Potassium olefin trichloroplatinites and β-methoxyalkylmercuric chlorides were prepared and purified according to the usual method,5,6) by introducing olefins into platinous potassium chloride aqueous solutions and mercuric acetate methanol solutions, respectively. Completely proton-decoupled C-13 nmr spectra at room temperatures were obtained at 25.15 MHz on a JEOL PS-100 spectrometer equipped with an IS-100 proton irradiation unit and an SD-HC hetero spin decoupler. Samples were made in 40 mol % acetone solutions for the Hg(II) compounds and in 5 mol % acetone solutions for the Pt(II) complexes. Spectra were scanned 100∿200 times using a JEOL JRA-5 spectrum computer to obtain enhanced S/N values.

Results and Discussion

(I) Metal-carbon coupling constants of β-methoxyalkylmercuirc chlorides.

The mercury-carbon coupling constants of the Hg(II) compounds are summarized

Table 1. $^{199}Hg-^{13}C$ Coupling Constants of β-Methoxyalkylmercuric chlorides, $[CR_1R_2(OCH_3)CR_3R_4HgCl]$.$^{a)}$

Compound					Hg-C Coupling Constant		
R_1	R_2	R_3	R_4		$^1J_{HgC}$	$^2J_{HgC}$	$^3J_{HgC}$
H	H	H	H	(1)	1607	91	
CH_3	H	H	H	(2)	1630	108	132
C_2H_5	H	H	H	$(3)^{b)}$	1635	106	118
CH_3	CH_3	H	H	(4)	1645	100	143
CH_3	H	CH_3	H	$(5)^{c)}$	1705	98, $76^{e)}$	107
CH_3	H	CH_3	H	$(6)^{d)}$	1705	117, $68^{e)}$	106
CH_3	CH_3	CH_3	H	(7)	1724	113, $53^{e)}$	98
CH_3	CH_3	CH_3	CH_3	(8)	1814	97, $76^{e)}$	143

a) Hz. The accuracy is within 1 Hz. b) $^4J_{HgC}$ is 0 Hz.
c) erythro isomer d) threo isomer e) $^2J_{HgC}$ (R_3)

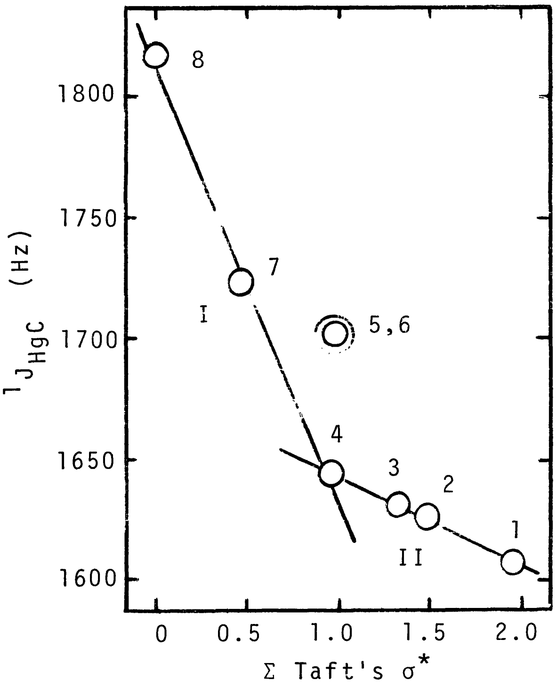

Figure 1. Correlation of $^1J_{HgC}$ with the summation of Taft's σ^* of the substituents for $CR_1R_2(OCH_3)CR_3R_4HgCl$. The points are designated by their numbers given in Table 1.

in Table 1. It is to be noted that the vicinal Hg-C couplings ($^3J_{HgC}$) are generally larger than the geminal ones ($^2J_{HgC}$). Remarkable alkyl substituent effects were observed with regard to the direct Hg-C couplings ($^1J_{HgC}$). As shown in Fig. 1, two kinds of straight lines are drawn by the plots of $^1J_{HgC}$ vs. the summation of Taft's σ^* of the substituents.$^{7)}$ The line (I) is obtained when R_3 and/or R_4 in Table 1 are changed from hydrogens to methyl groups, and the line (II) is obtained with regard to R_1 and/or R_2. It is very plausible that the slope with respect to the Taft's σ^* axis, 172.2 Hz of the line (I), is larger than that of the line (II), 38.5 Hz, since the alkyl substitution at the α-carbon attached directly to HgCl group is more effective than the β-carbon. Based on these values of the slopes, $^1J_{HgC}$ of methoxymercurated trans- and cis-2-butenes are calculated to be 1706 Hz, while the observed values are 1705 Hz for both compounds. This perfect agreement, together with the excellent linear relation between $^1J_{HgC}$ and Taft's σ^*, indicates that $^1J_{HgC}$ varies in proportion to the increase in the electron densities at the mercury-carbon bonding. It is conceivable, therefore, that the more the alkyl groups are substituted, the stronger the Hg-C σ-bonding.

(II) C-13 nmr parameters of the Zeise's type salts.

The platinum-carbon coupling constants of K[(olefin)PtCl$_3$] are listed in Table 2. The vicinal and geminal couplings between ^{195}Pt and ^{13}C nuclei ($^3J_{PtC}$ and $^2J_{PtC}$) are reported here for the first time. It is worthwhile to mention that $^3J_{PtC}$ is larger than $^2J_{PtC}$ in 1-butene-Pt(II) complex, since similar tendency was found for the Hg-C couplings. However, the alkyl substituent effects on the direct Pt-C couplings ($^1J_{PtC}$) are different from those on $^1J_{HgC}$ of the Hg(II) compounds. As shown in Table 2, the order in the magnitude of $^1J_{PtC}$ is ethylene > propylene for the methylene carbon, and propylene > trans-2-butene > cis-2-butene

Table 2. ^{195}Pt-^{13}C Coupling Constants of K[(olefin)PtCl$_3$].[a]

Olefin	$^1J_{PtC}$	$^2J_{PtC}$	$^3J_{PtC}$
CH_2=CH_2	196[b]		
CH_3CH=CH_2	190,[c] 186[d]	26.4	
CH_3CH_2CH=CH_2	192,[c] 195[d]	23.6	37.6
trans-CH_3CH=$CHCH_3$	182	30.2	
cis-CH_3CH=$CHCH_3$	180	23.6	

a) Hz. The accuracy is within 1 Hz. b) This value agrees well with the literature one.[3] c) $^1J_{PtC}(\underline{C}H_2)$ d) $^1J_{PtC}(\underline{C}H)$

Table 3. C-13 Chemical Shifts of Olefin Carbons in K[(olefin)PtCl$_3$].[a]

Olefin	C($\underline{C}$H=)	C($\underline{C}H_2$=)	C($\underline{C}H_3$)
CH_2=CH_2		66.9 (+56.4)	
CH_3CH=CH_2	87.5 (+48.2)	64.3 (+54.3)	19.7 (-1.0)
CH_3CH_2CH=CH_2[b]	91.8 (+48.4)	63.9 (+48.9)	13.6 (-0.7)
trans-CH_3CH=$CHCH_3$	82.4 (+40.9)		14.5 (+2.8)
cis-CH_3CH=$CHCH_3$	85.5 (+39.0)		19.4 (-8.8)

a) C-13 shifts are given relative to TMS (± 0.1 ppm), increasing positive values toward lower field. The difference in shifts between coordinated and free olefin carbons are given in parentheses., (+)= upfield shift and (-)= downfield shift. b) The aliphatic methylene carbon resonance decreased 0.7 ppm upon coordination.

for the methyne carbon.

The alkyl substituent effects on $^1J_{PtC}$ are just opposite to those observed in the organomercuric compounds. As suggested by Stothers,[3,8] $^1J_{PtC}$ reflects the magnitude of σ-donation from olefin to platinum, or σ-bonding between platinum and carbon. Therefore the present results indicate that Pt(II) π-complexes are different from Hg(II) σ-compounds in σ-bonding property.

The C-13 chemical shifts of these complexes are also informative for the Pt-C bonding property.[3] These values relative to TMS are shown in Table 3, and the difference in shifts between the coordinated and free olefins is also given in parentheses.

It is apparent that the olefinic carbon resonances are markedly shifted upfield upon coordination, whereas the saturated carbon ones are shifted slightly downfield. The order in the magnitude of the upfield shifts is ethylene > propylene for the methylene carbon, and propylene > trans-2-butene ≥ cis-2-butene for the methyne carbon. These substantial upfield shifts of the olefinic carbons are mainly ascribed to large π-back donation from platinum to olefin,[3] the magnitude of which is decreased by methyl groups.

From the alkyl substituent effects on $^1J_{PtC}$ and C-13 chemical shifts, it is concluded that both σ-donation and π-back donation of the bonding between platinum and carbon in Zeise's type salts are weakened by alkyl substitution at the olefinic carbons in contrast with the σ-bonding in the organomercuric compounds.

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