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Carbon-13 Nuclear Magnetic Resonance Spectra of Some Five-Coordinate Platinum(II)–Olefin Complexes

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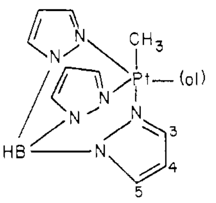
^{13}C nuclear magnetic resonance spectra for the five-coordinate platinum(II) complexes $Pt(CH_3)[HB(pz)_3](ol)$ (where pz = $N_2C_3H_3$; ol = tetrafluoroethylene, maleic anhydride, fumaronitrile, ethylene, diethyl fumarate, acrylonitrile, and methyl acrylate) are reported. The olefinic carbon resonances are substantially shifted upfield from those of the free olefin and the magnitude of this shift is related to metal to olefin π back-bonding.

Introduction

Recently we described[1-3] the preparation of a series of five-coordinate olefin complexes of platinum(II) which were stabilized by the strongly electron-donating hydrotris(1-pyrazolyl)borate ($HB(pz)_3$) ligand. Because these compounds represent the first extensive series of stable five-coordinate olefin complexes of platinum(II), a ^{13}C NMR study was undertaken to investigate the nature of the platinum–olefin bond. We report here ^{13}C chemical shifts and coupling constants for the series of compounds of type **1** where ol =



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tetrafluoroethylene (TFE), maleic anhydride (MA), fumaronitrile (FN), ethylene (E), diethyl fumarate (DEF), acrylonitrile (AN), and methyl acrylate (MAC).

Experimental Section

The complexes were prepared as previously described[2] by reacting $Pt(CH_3)[HB(pz)_3]$ with the appropriate olefin in dichloromethane. The preparations of the two new complexes are outlined below.

Microanalyses were performed in this department.

^1H NMR spectra were recorded on a Varian HR-220 spectrometer operating at 220 MHz using CD_2Cl_2 solutions. The ^{13}C spectra were recorded on a Bruker WH-90 spectrometer operating at 22.63 MHz. Chemical shifts were measured relative to the solvent and then adjusted to a tetramethylsilane (TMS) scale using $\delta_{CD_2Cl_2}$ 53.6 ppm.

I. Preparation of $Pt(CH_3)[HB(pz)_3](C_2H_4)$. A suspension of $Pt(CH_3)[HB(pz)_3]$ (0.60 g) in CH_2Cl_2 was stirred under 30 psig of ethylene for 1 h. The solid dissolved to give a clear solution. The solution was then filtered through a fine frit and the solvent removed by rotary evaporation to give a clear colorless oil. The oil was triturated with pentane to give white crystals; yield 0.55 g; mp 153–160°C. Anal. Calcd for $C_{12}H_{17}BN_6Pt$: C, 31.94; H, 3.80; N, 18.63. Found: C, 32.21; H, 4.14; N, 18.49. ^1H NMR: $\delta(Pt-CH_3)$ 0.55, $J(Pt-H)$ = 65.2 Hz; $\delta(=CH_2)$ 2.14, 2.27, $J(Pt-H)$ = 69, 80 Hz; 4-H_{ax} δ 6.12, $J(Pt-H)$ = 4.8 Hz, $J(H-H)$ = 2.0 Hz; 4-H_{eq} δ 6.19, $J(Pt-H)$ = 7.4 Hz, $J(H-H)$ = 2.0 Hz; 3-H_{ax} δ 7.10, $J(Pt-H)$ = 8.0 Hz; 3-H_{eq} δ 7.66; 5-H_{ax} δ 7.64; 5-H_{eq} δ 7.69.

II. Preparation of $Pt(CH_3)[HB(pz)_3]$(*trans*-NCCH=CHCN). To a stirred suspension of $Pt(CH_3)[HB(pz)_3]$ (0.50 g, 1.18 mmol) in CH_2Cl_2 was added 0.092 g of fumaronitrile. When all of the solid had dissolved, the solution was filtered and the solvent was removed by rotary evaporation to give a solid that was recrystallized from dichloromethane and ether to give white crystals; yield 0.45 g; mp >200 °C. Anal. Calcd for $C_{14}H_{15}BN_8Pt$: C, 33.54; H, 3.02; N, 22.36. Found: C, 33.87; H, 2.73, N, 22.49. ^1H NMR: $\delta(Pt-CH_3)$ 1.17, $J(Pt-H)$ = 63.0 Hz; $\delta(=CH)$ 3.42, 3.03, $J(Pt-H)$ = 78.5, 65.0 Hz, $J(H-H)$ = 8.5 Hz; 4-H_{ax} δ 6.47, $J(Pt-H)$ = 5.0 Hz, $J(H-H)$ = 2.4 Hz; 4-H_{eq} δ 6.67, $J(Pt-H)$ = 10.8 Hz, $J(H-H)$ = 2.2 Hz; 4-H_{eq} δ 6.62, $J(Pt-H)$ = 10.5 Hz, $J(H-H)$ = 2.2 Hz; 3-H_{ax} δ 7.06, $J(Pt-H)$ = 10.7 Hz; 3-H_{eq} not resolved; 5-H_{eq} δ 7.61, 7.58; 5-H_{ax} not resolved.

Results

Complexes of **1**, where ol = TFE, MA, DEF, AN, and MAC, except for the fumaronitrile and ethylene complexes, were prepared as previously described.[3]. The fumaronitrile and ethylene complexes were prepared analogously and were isolated as air-stable white crystalline solids.

I. ^{13}C NMR Data. The ^{13}C NMR spectra of the complexes were recorded and the various coupling constants and chemical shifts are given in Table I. The $^{13}C\{^1H\}$ spectrum of the ethylene complex is shown in Figure 1. The platinum methyl resonances absorb *upfield* from TMS in the range −4 to −17 ppm and are flanked by ^{195}Pt satellites ($I = {}^1/_2$, 33.8% natural abundance). The magnitude of $^1J(Pt-C)$ is in the range 570–630 Hz. In the proton-coupled ^{13}C spectrum the central $Pt-CH_3$ resonance appears as a quartet and $^1J(C-H)$ is in the range 130–135 Hz. For the symmetrically substituted olefins TFE, MA, and E the olefinic carbons appear as singlets, flanked by ^{195}Pt satellites ($J(Pt-C)$ = 340–420 Hz). These resonances occur to higher magnetic field from those of the uncoordinated olefins by about 95–120 ppm. The pyrazolyl carbon resonances generally appear in the ratio of 2:1 for the two equatorial rings and one axial ring. The 4-C resonance (for numbering see **1**) falls in the narrow range 105–107 ppm while the 3-C and 5-C resonances are further downfield at 135–145 ppm. The Pt–C coupling constant is larger to the equatorial ring than to the axial ring and decreases in the order 3-C > 4-C > 5-C. This trend has been observed previously for fluxional five-coordinate molecules $Pt(CH_3)(L)[HB(pz)_3]$.[4] Direct assignment of the 3-C and 5-C resonances is not possible; however, indirect evidence is obtained from the spectrum of the TFE complex shown in Figure 2. The 4-C resonances are at 106.3 and 105.6 ppm and because of the 2:1 ratio are assigned to equatorial and axial ring resonances. Two sets of resonances are observed at ~136 and 141 ppm. Each set contains two resonances in the ratio of 2:1 arising from the equatorial and axial carbons. The high-field set does not show appreciable Pt coupling, while the low-field set shows appreciable coupling. The axial resonance appears as a triplet with Pt satellites resulting from coupling with two fluorine atoms on the TFE molecule. Such interaction was observed previously[5] in the ^1H NMR spectrum and was attributed to a through-space coupling. An x-ray crystal structure of the TFE complex does in fact show a close interaction between the axial 3 position and the two fluorine atoms directed below the plane defined by the two equatorial nitrogens and olefinic carbons. Therefore, the resonances of the various 3-C and 5-C carbons can be assigned on the basis of their $J(Pt-C)$ values. The FN, AN, and MAC compounds give more complicated ^{13}C NMR spectra. Because of the absence of a mirror plane perpendicular to the C=C bond in the complexes, the olefinic carbons are magnetically nonequivalent and give rise to distinct

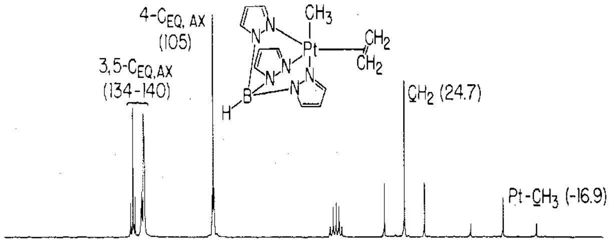


Figure 1. ^{13}C NMR spectrum of $Pt(CH_3)[HB(pz)_3](C_2H_4)$ in CD_2Cl_2 solution.

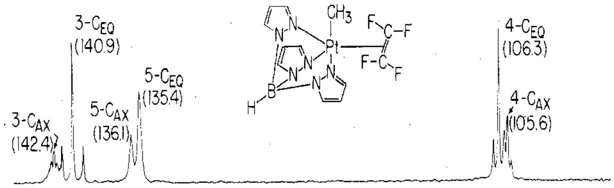


Figure 2. ^{13}C NMR spectrum of $Pt(CH_3)[HB(pz)_3](C_2F_4)$ in CD_2Cl_2 solution showing only the pyrazolyl carbons.

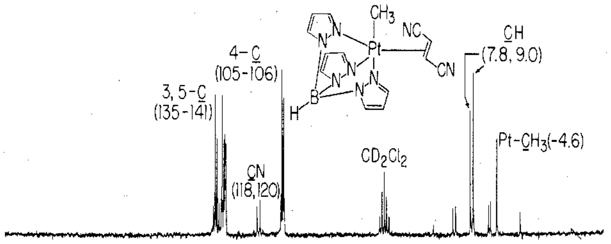
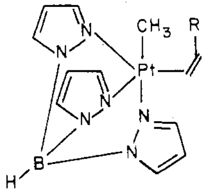


Figure 3. ^{13}C NMR spectrum of $Pt(CH_3)[HB(pz)_3]$(*trans*-NCCH=CHCN) in CD_2Cl_2 solution.

resonances. This is illustrated in Figure 3 which shows the ^{13}C NMR spectrum of the fumaronitrile complex. Two olefinic carbon resonances are observed at 7.8 and 9.0 ppm, each flanked by ^{195}Pt satellites. Three separate 3-C, 4-C, and 5-C pyrazolyl resonances are observed in the ratio of 1:1:1 which on the basis of their Pt–C coupling constants may be assigned to two equatorial carbons and one axial carbon. With acrylonitrile and methyl acrylate two isomers are obtained, **2** and **3**, and in the case of AN it was possible to assign resonances to each isomer.



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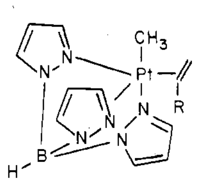

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The cyano and carboxyl carbons are also observed and are shifted downfield about 5 Hz from the resonance of the free olefin.

The TFE C=C carbon resonances are observed in the ^{19}F decoupled ^{13}C spectrum at 79.6 ppm downfield from TMS. The Pt–C coupling constant of 606 Hz is substantially larger than for the other complexes.

Discussion

During the past several years there have been numerous reports on the ^{13}C NMR spectra of coordinated olefins. In general, for systems other than d^{10}, *upfield* shifts of the olefinic carbons are observed when coordinated to a metal.[7-17] However, the nature of this shift has been the subject of some controversy. We initially examined a series of platinum(II)–olefin complexes,[7] observed the largest upfield shifts for the more electron-rich complexes, and suggested that there was a relationship between π back-bonding from the metal to the olefin and $\Delta\delta$(C), the upfield shift on coordination. Powell and co-workers[8] questioned this interpretation on the basis of a study in which they found a correlation between π-bonded (C_2 and C_3) and σ-bonded (C_1) carbons in the series of complexes **4**. This and the similarity of changes in $\delta(C_1)$ and δ(H) in *trans*-$PtHX(P(C_2H_5)_3)_2$ complexes led these authors to suggest that changes in chemical shifts are due primarily to a change in a nonbonding shielding term associated with partly filled d orbitals rather than changes in π back-bonding. Subsequently, we found[9] a close relationship between σ- and π-bonded carbons in a series of complexes $[(CH_3)Pt(1,5\text{-}C_8H_{12})L]^+$ (where L is Cl$^-$ or a variety of neutral ligands) and concluded that any π-bonding component that was reflected in the shielding either remains fairly constant or parallels changes in the σ-bonding components. Finally, a series of olefin complexes of the type L_2Ni(ol) (where L = P(O-*o*-tol)) were examined[10] and a clear relationship was found between π back-bonding (*measured independently by alternate techniques*) and $\Delta\delta$(C) of the coordinated olefin carbons. It was concluded that the factors which contribute to good π back-bonding also give increased shielding of π-bonding carbons. Figure 4 shows a plot of $\Delta\delta$(C) for the olefinic carbons in the nickel(0) complexes (ol)Ni[P(O-*o*-tol)$_3$]$_2$ vs. the $\Delta\delta$(C) for the platinum complexes in this study. There is a clear trend in the olefinic chemical shifts for Ni(0) and Pt(II). This correlation suggests that the same factors which govern olefinic chemical shifts for Ni(0) also operate for Pt(II) and the most important factor is metal d to olefin π^* back-bonding. It should be noted that there is no correlation between the chemical shifts of σ-bonded (Pt–CH$_3$) and π-bonded (C=C) carbons in these molecules. The difference in $\Delta\delta$(C) from one complex to another (~17 ppm) is relatively small compared to the magnitude of $\Delta\delta$(C) (~100 ppm). This suggests that the amount of π back-bonding does not vary substantially. However the small variations are possibly due to substituent effects on the olefins.

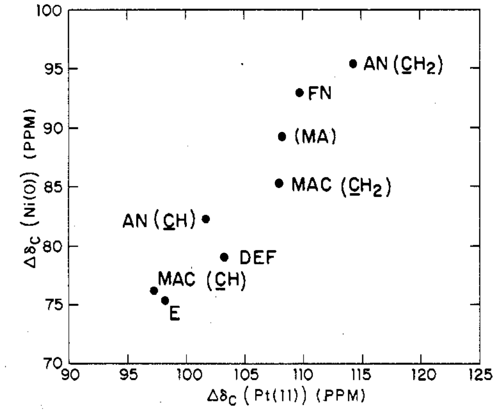
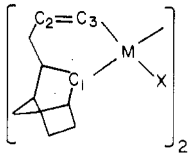


Figure 4. Plot of $\Delta\delta$(C) of the olefinic carbons in (ol)NiP(*O*-*o*-tol)$_3$ vs. $Pt(CH_3)[HB(pz)_3]$(ol).



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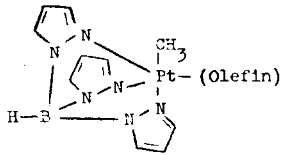
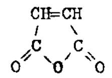
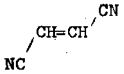
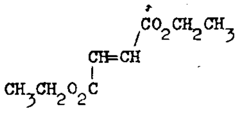
Conclusions

1. The large upfield ^{13}C chemical shifts of the coordinated olefinic carbons in $Pt(CH_3)[HB(pz)_3]$(ol) may be attributed to a substantial amount of π back-bonding.

Table I. ^{13}C NMR Data^{a} for Five-Coordinate Platinum(II)-Poly(pyrazolyl)borate-Olefin Complexes



Olefin	Platinum-Methyl δC	^1J(Pt-C)	^1J(C-H)		3-C δC	^2J(Pt-C)		4-C δC	^3J(Pt-C)		5-C δC	^3J(Pt-C)	Olefin Carbons δ(=C)	ΔδC	J(Pt-C)	J(C-H)	Other
$CF_2=CF_2$	-5.7	615	b	eq ax	140.9 142.4	38^c 19^c	eq ax	106.3 105.6	21 12	eq ax	135.4 136.4	- -	79.6	-	606	-	
	-6.8	571	134	eq ax	140.4 135.0	46 12	eq ax	106.5 106.1	28 10	eq ax	135.9 136.7	10 -	28.8	108.3	390	177	δ(CO)=171.1; J(Pt-C)=33
	-4.6	550	135	eq eq ax	141.1 140.2 137.6	48 46 14	eq eq ax	106.6 106.5 105.8	27 27 14	eq eq ax	136.0 135.7 136.6	10 10 -	7.8 9.0	110.0 108.8	406 416	168	δ(CN)=118,120 J(Pt-C)=28,35
$CH_2=CH_2$	-16.9	628	131	eq ax	139.6 135.1	43 18	eq ax	105.4 105.4	22 13	eq ax	134.9 135.9	- -	24.7	98.1	384	156	
	-8.6	572	134	eq eq ax	140.9 139.8 139.6	44 47 12	eq ax	106.1 105.0	28 13	eq eq ax	135.4 135.2 136.2	- - -	31.0 30.9	103.1 103.2	347 354	160	δ(CO)=172.2,171.1 δ(CH_2)=60.4; J(C-H)=146 δ(CH_3)=14.7; J(CH)=126 13.9
CH_2=CH-CN(major)	-9.2	596	132		NR			NR			NR		23.4 8.0	114.4 100.2	396 412	160^t 165^d	δ(CN)=121.0
(minor)	-12.2	576	134		NR			NR			NR		23.8 7.4	114.0 100.8	397 403	160^t 169^d	δ(CN)=122.3
$CH_2=CH-CO_2(CH_3)$	-13.1	607	132		NR			NR			NR		31.3 21.6	97.2 108.3	356 377	147^d 156^t	δ(CO)=172.6 δ(OCH_3)=51.2 J(CH)=146

(a) Chemical shifts are given in ppm relative to tetramethyl silane. Positive values are downfield of TMS. Coupling constants are given in hertz.

(b) Resonance appears as a triplet, J(C-F) = 22 Hz.

(c) Resonance appears as a triplet, J(C-F) = 10 Hz.

2. The stability of these five-coordinate platinum(II)–olefin complexes may be due to extensive π back-bonding by the anionic tridentate hydrotris(1-pyrazolyl)borate ligand.

Acknowledgment. The author thanks Mr. F. Davidson for running the ^{13}C spectra and Dr. D. W. Ovenall for obtaining the ^{19}F-decoupled ^{13}C spectrum.

Registry No. $Pt(CH_3)[HB(pz)_3](TFE)$, 51548-82-4; $Pt(CH_3)[HB(pz)_3](MA)$, 51607-50-2; $Pt(CH_3)[HB(pz)_3](FN)$, 59983-08-3; $Pt(CH_3)[HB(pz)_3](E)$, 59983-09-4; $Pt(CH_3)[HB(pz)_3](DEF)$, 51607-52-4; $Pt(CH_3)[HB(pz)_3](AN)$, 51607-38-6; $Pt(CH_3)[HB(pz)_3](MAC)$, 41982-15-4; $Pt(CH_3)[HB(pz)_3]$, 39395-33-0; ^{13}C, 14762-74-4.

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Intermolecular Back-Bonding. 1. Stabilization of the Highly Conducting One-Dimensional Bis(oxalato)platinates

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In order to rationalize the structure of the highly conducting one-dimensional bis(oxalato)platinates an *intermolecular back-bonding* model was formulated. The model involves overlap of a higher occupied molecular orbital (HOMO) on a molecular plane with a lower unoccupied molecular orbital (LUMO) on an adjacent molecular plane. Evaluation of the b_{3g} HOMO–b_{2g} LUMO interactions derived from the symmetric and antisymmetric molecular orbital combinations for the oxalato ligand for the bis(oxalato)platinate molecular planes results in eight ligand-centered intermolecular back-bonding overlaps when adjacent molecules are rotated by 60°. Rotation of a molecular plane will increase four back-bonding overlaps while breaking the remaining four overlaps. Thus a 60° relative rotation maximizes overlap. Similarly b_{1u} HOMO–a_u LUMO overlap gives rise to an additional net four back-bonding situations when adjacent molecular planes are rotated by 60°. These observations are in accord with the previously published structure of $Mg_{0.86}Pt(ox)_2 \cdot 5.3H_2O$. Thus, the intermolecular back-bonding contributes to the stabilization of the short intermolecular spacings ($\sim$2.85 Å) and provides an additional back-bonding mechanism to reduce the Coulomb repulsion of electrons in an a_g band.

In recent years there has been considerable interest in the chemical[1-7] and physical properties[1,3-5,9,10] of highly and poorly conducting one-dimensional (1-D) inorganic complexes comprised of equivalent molecules within a chain.[11] All of these chains are formed from d^8 square-planar complexes with small planar ligands which permit close approach of adjacent molecular planes. For the highly conducting partially oxidized materials close approach is an acute problem as strong overlap of the a_g (d_{z^2} like) orbitals is important in the stabilization of the system via band formation and subsequent partial oxidation.[1] In order to achieve the necessary strong overlap of the a_g metal orbitals several design criteria surface: (1) use of third-row d^8 complexes as the $5d_{z^2}$ orbital has the largest spatial extension; (2) use of transition metals with smaller nuclear charge as the larger nuclear charge will contract the spatial extension of the $5d_{z^2}$ orbital; (3) formation of a one-dimensional chain of negatively charged square-planar ions since net positive charges will contract the $5d_{z^2}$ orbital; (4) utilization of small nonbulky ligands in order to permit close approach of these ions; (5) use of strong-field ligands which are able to reduce the Coulomb repulsion of electrons on the metal through intramolecular d–π^* back-bonding (in order to achieve high conductivity); (6) optionally, hydrogen bonding between chains knitting together and stabilizing the one-dimensional strands. These general criteria for designing new highly conducting systems have been empirically extracted from evaluation of the known highly conducting one-dimensional complexes based on Ir^I, Pt^{II}, CO, CN^-, $O_2C_2O_2^{2-}$, and H_2O moieties.[1,2]

In the midst of the typical 1-D complexes[1,2,7] containing small monodentate ligands which presumably minimize steric interaction, e.g., $K_2Pt(CN)_4X_{0.3} \cdot 3H_2O$ (X = Cl, Br), $K_{1.75}Pt(CN)_4 \cdot 1.5H_2O$, "$Ir(CO)_3Cl$", and (cation)$_{\sim 0.5}Ir(CO)_2Cl_2$, lies a series of partially oxidized complexes based upon the bis(oxalato)platinates,[7,12-17] e.g., (alkali$^+$)$_{\sim 1.64}Pt(ox)_2 \cdot xH_2O$ [ox = oxalato = $O_2C_2O_2^{2-}$]. Although these complexes have not been characterized in detail, powder x-ray data indicate that all of these materials have short intermolecular spacings of $\sim$2.85 Å.[7,14,16] The room-temperature single-crystal conductivity of $K_{1.64}Pt(ox)_2 \cdot xH_2O$ has been reported to be high,[13] i.e., 42 Ω^{-1} cm^{-1}, suggesting the possibility of a metallic state.[1] The single-crystal x-ray determination of $Mg_{0.86}Pt(ox)_2 \cdot 5.3H_2O$ reveals[12] that adjacent molecules are rotated by $\sim$60° and alternating molecules are eclipsed, Figure 1. The metal atoms form equivalently spaced 1-D chains with an interplanar separation of $\sim$2.85 Å. Thus, the bis(oxalato)platinates form a highly conducting 1-D chain with weak-field bidentate ligands,[18] which by virtue of the weak-field character does not remove electron density (reducing Coulomb repulsion between electrons on the metal[1]) from the metal to the same extent as of strong-field π-acceptor ligands.