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Nature of Metal-Olefin Bond in Neutral η^3-Allyl(olefin)platinum(II) Complexes. In-plane Olefin Coordination and Stability Trend Unusually Weakly Dependent on Electronic Effect of Olefin-substituent

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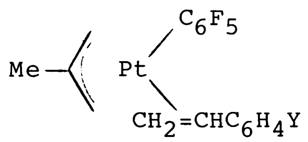
Relative olefin coordination ability in Pt(η^3-CH_2CMeCH_2)-(CH_2=CHC_6H_4Y)(C_6F_5)(**2**)was determined to show the stability trend unusually weakly dependent on the electronic property of the substituent Y. The crystal structure of the styrene complex **2** (Y= H) revealed the C=C bond oriented parallel to the coordination plane. The nature of Pt-olefin bond in **2** has been discussed in terms of these stability and structural trends.

The studies on the cationic olefin complexes of the type [Pt(η^3-CH_2CMeCH_2)-(olefin)(PPh_3)]$^+$(**1**)have revealed[1,2] that these are somewhat unique in terms of the nature of metal-olefin bond when compared to the classic, more ordinary olefin complexes of Pt(II) such as Zeise's salt. That is, the former class complexes contain the C=C bond oriented parallel to the coordination plane (in-plane geometry) in contrast to that oriented perpendicular (upright geometry) in the latter class,[1] while the metal atom in both classes is very electrophilic in nature toward the coordinated olefin ligand.[2,3] In order to gain more insight into the nature of metal-olefin bond in complexes containing the η^3-allyl ligand, we undertook synthetic, stability and structural studies of neutral analogs, Pt(η^3-CH_2CMeCH_2)(CH_2=CHC_6H_4Y)(C_6F_5)(**2**).

The substituted styrene complexes **2b** and **2c** were prepared[4] from [Pt(η^3-CH_2CMeCH_2)Cl]$_2$ and C_6F_5Li in the presence of appropriate styrenes, in the manner similar to that described for the unsubstituted analog **2a**.[5] The other



2

(Y= H **a**; 3-NO_2 **b**; 4-Cl **c**;
4-Me **d**; 4-OMe **e**)

Table 1. Equilibrium Constants of Eq. 1 [a)]

Y=	K
H	1.0
3-NO_2	0.59 ± 0.10
4-Cl	0.89 ± 0.09
4-Me	1.3 ± 0.2
4-OMe	1.4 ± 0.2

a) In $CDCl_3$ at 25 °C.

derivatives **2d** and **2e** were generated in solutions by quite a slow ligand exchange (see later) between **2b** and the appropriate olefin, and characterized by ^1H NMR spectra. The relative stability of **2a-e**, as expressed by the equilibrium constant of Eq. 1, was determined by ^1H NMR spectroscopy in the manner analogous to that for **1**.[2a)] The K values thus determined are summarized in Table 1.

$$Pt(\eta^3\text{-}C_4H_7)(CH_2{=}CHC_6H_5)(C_6F_5) + CH_2{=}CHC_6H_4Y \overset{K}{\rightleftarrows} Pt(\eta^3\text{-}C_4H_7)(CH_2{=}CHC_6H_4Y)(C_6F_5) + CH_2{=}CHC_6H_5 \quad (1)$$

Of particular note in Table 1 is that the K values do not deviate much from unity (Hammett ρ= -0.38), which is quite different from the trend in **1** (ρ= -1.32)[2a)] and trans-$PtCl_2(CH_2{=}CHC_6H_4Y)$(pyridine) (Hammett ρ^+= -0.82)[3a)] showing the strongly electrophilic nature of the platinum atom to the olefin. Such a novel stability trend as observed in **2** showing very small sensitivity to the electronic effect of the olefin-substituent has been found before only in the closely related palladium complexes, $Pd(\eta^3\text{-}CH_2CMeCH_2)(CH_2{=}CHC_6H_4Y)(C_6HCl_4\text{-}2,3,5,6)$ (ρ= -0.25) which, however, were characterized only in solutions at low temperatures without isolation.[5)]

The structure of **2a** was determined by X-ray crystallography. Crystal data: $C_{18}H_{15}F_5Pt$, F.W.= 521.40, triclinic, space group $P\bar{1}$, a= 6.292(2) Å, b= 11.874(4) Å, c= 12.736(4) Å, α= 117.39(2)°, β= 82.07(3)°, γ= 97.50(4)°, V= 834.3(5) Å^3, Z= 2, D_c= 2.075 g cm^{-3}, R= 0.074 for 3410 reflections ($|F_o|>3\sigma(|F_o|)$).[6)] The molecular structure is shown in Figure 1 and the relevant bond lengths and angles in Table 2.

It seems of interest to note that the C=C bond in **2a** makes an angle of 10.2° with the coordination plane defined by Pt, CAL, and C(21). This feature is the same as that in the cationic complex **1** (olefin= $CH_2{=}CHC_6H_5$).[1a)] However, the Pt-

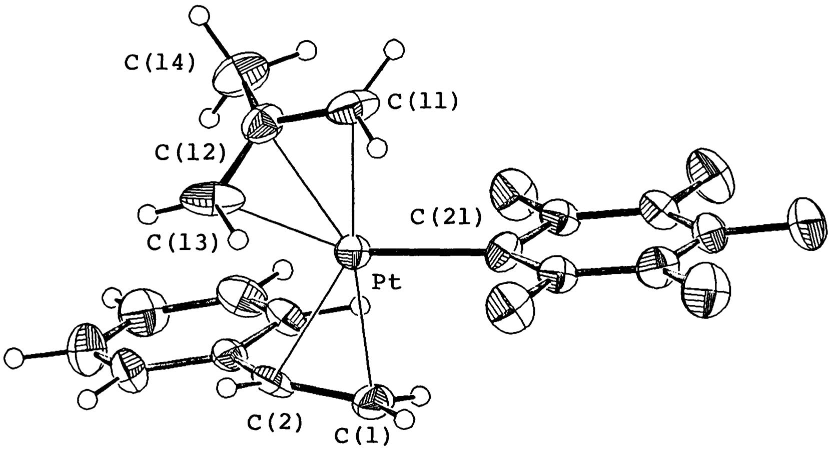


Fig. 1. Molecular Structure of **2a**.

C(olefin) bond lengths in **2a** are considerably shorter than those in the cationic complex (2.203(12) and 2.301(12) Å),[1a] suggesting the stronger Pt-olefin bond strength in **2** than in **1**. Consistent with this is the observation that the olefin ligand exchange in **2** (e.g. Eq. 1) is very slow (e.g. half-life of ca. 10 min for the equilibrium stage to be attained from **2a** (0.19 M) and 3-nitrostyrene (0.48 M) at 25 °C), while the corresponding process in **1** occurred almost instantaneously under the similar conditions.

Preliminary extended Hückel MO calculations on a model, $Pt(\eta^3-CH_2CHCH_2)(CH_2=CH_2)(CH_3)$ indicated that the in-plane C=C geometry is electronically favored[7] over the upright one, as was the case in the cationic model, $[Pt(\eta^3-CH_2CHCH_2)(CH_2=CH_2)(PH_3)]^+$.[8] This is attributed primarily to the larger π back bonding in the in-plane than the upright geometries, since the dπ orbital of the fragment, $Pt(\eta^3-CH_2CHCH_2)(CH_3)$ suited for π interaction[9] with π^* of the in-plane oriented ethylene lies ca. 0.6 eV higher than that for the π interaction with the upright ethylene. Another MO aspect shown below is also consistent with a notion

Table 2. Relevant Bond Lengths (Å) and Angles (°) of **2a**

Pt-C(1)	2.17(3)	Pt-C(2)	2.23(2)
Pt-C(11)	2.12(3)	Pt-C(12)	2.15(2)
Pt-C(13)	2.10(3)	Pt-C(21)	2.05(2)
C(1)-C(2)	1.41(3)	C(11)-C(12)	1.42(4)
C(12)-C(13)	1.31(4)	C(12)-C(14)	1.50(4)
CET-Pt-CAL	134.8	CET-Pt-C(21)	101.0
CAL-Pt-C(21)	124.1		

CET: the midpoint of the C(1)-C(2) bond.
CAL: the center of gravity of the allyl triangle.

implicated by the present experimental results that metal-to-olefin π back bonding in **2** is larger than in **1** and Zeise's salt's class (electrophilic metal center), but smaller than in the zerovalent complexes of the type, M(olefin)L_2 where M= Ni, Pd, Pt, and L= PR_3 or L_2= bipy (nucleophilic metal center).$^{10)}$ That is, the relevant dπ orbital of the Pt(η^3-CH_2CHCH_2)(CH_3) fragment lies higher in energy than those of the fragments, $[PtCl_3]^-$ (by ca. 0.5 eV) and $[Pt(\eta^3\text{-}CH_2CHCH_2)(PH_3)]^+$ (0.25 eV), but lower than that of the $Pt(PH_3)_2$ fragment (0.3 eV).

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6) Computations were done on an ACOS 850 computer, at the Crystallographic Research Center, Institute for Protein Research, Osaka University.
7) The in-plane geometry gave the larger Pt-C(olefin) overlap populations (Pt-C(1)= 0.257, Pt-C(2)= 0.240; Pt-C= 2.20 Å) than the upright one (0.230, 0.228), even though the total energy was almost the same in the two geometries possibly due to overestimation of steric factors in the in-plane geometry.
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