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ELECTRONIC EFFECT OF η^5-CYCLOPENTADIENYL AND η^3-ALLYL LIGANDS ON THE NATURE OF THE METAL–OLEFIN BOND: REVERSAL OF THE RELATIVE OLEFIN AFFINITY OF PALLADIUM(II) AND PLATINUM(II) IONS *

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Summary

The barrier to olefin rotation in $[Pt(\eta^3\text{-}CH_2CMeCH_2)(olefin)(PPh_3)]PF_6$ (**3**) (olefin = $CH_2{=}CH_2$, *E*-MeCH=CHMe) has been found to be extremely low compared to those in the other known, 4-coordinate olefin complexes of Pt^{II}. This can be ascribed to the smaller steric congestion around the olefin in **3**. The corresponding barrier in $[Pt(\eta^5\text{-}C_5H_5)(CH_2{=}CH_2)(PPh_3)]ClO_4$ (**2**), possessing likewise small steric congestion, was substantially higher than that in **3** (olefin = $CH_2{=}CH_2$). The ^{13}C and ^{31}P NMR measurements have revealed much larger $J(Pt\text{–}C(olefin))$ in **2** than that in **3** (olefin = $CH_2{=}CH_2$), while $J(Pt\text{–}P)$ are comparable in these two. Stability constant data suggested that Pd^{II} ion in the $Pd(\eta^5\text{-}C_5H_5)(PPh_3)^+$ moiety is a better π-donor to olefins than Pt^{II} ion in the $Pt(\eta^3\text{-}CH_2CMeCH_2)(PPh_3)^+$ moiety, a reversal of the normal trend in the relative olefin affinity of these metal ions. The above spectral and stability features have been related to the electronic effect of the Cp ligand in enhancing the π back-bond interaction in one particular orientation of the C=C bond.

Introduction

The olefin complexes of Pd^{II} and Pt^{II} with the η^5-cyclopentadienyl (Cp) and η^3-allyl ligands, **1–3** are suited for the better understanding of the nature of the metal–olefin bond owing to ease of preparation and characterization of complexes containing a variety of olefins [1, 2]. Thus, for example, we were able to demonstrate, for the first time for a Pt^{II} series, the linear free energy relationship for the substituted styrene complexes using **3** (olefin = $CH_2{=}CHC_6H_4Y\text{-}p$) [2]. Particularly

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[*] Dedicated to Prof. S. Otsuka on the occasion of his 65th birthday.

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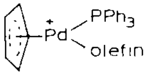
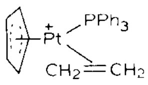
intriguing was the first structural elucidation, through the X-ray study of **3a**, of the simple mono-olefin ligand lying parallel to the coordination plane of d^8 square-planar complexes [3]. It was also interesting to compare this structure with that of **1a** in which styrene is located perpendicular to the plane of Pd, P and the center of Cp [4], for both **1a** and **3a** appear to possess similar steric congestion for the olefin coordination. Significant difference lies in their electronic configuration; **1** is an 18-electron complex, while **3** a 16-electron one.


(**1**)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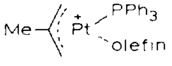
(**3**)

(**1a**, olefin = $CH_2=CHC_6H_5$,
1b, olefin = $CH_2=CH_2$)

(**3a**, olefin = $CH_2=CHC_6H_5$,
3b, olefin = $CH_2=CH_2$,
3c, olefin = E-$MeCH=CHMe$)

Both the Cp and the η^3-allyl groups are very common as ancillary ligands in organometallic chemistry, but few studies have focused on the comparison of the properties of those complexes that have the identical composition except for the ancillary hydrocarbon parts *. In order to further elucidate the role of such hydrocarbon ligands in affecting the nature of the metal–olefin bond *, we have compared the NMR spectral aspects and stability trend in various olefin complexes of types **1**–**3**. We have found that the electronic requirement is very significant for the olefin coordination in these complexes, and the general metal trend in terms of the relative olefin affinity (Pd < Pt) can be reversed by the choice of the ancillary ligands.

Results and discussion

NMR spectral aspects of η^5-cyclopentadienyl and η^3-allylplatinum(II) olefin complexes

The ethylene ligand in **2** was previously shown to undergo the restricted rotation about the Pt–ethylene bond ($\Delta G^{\neq}_{rot}$ 13.0 kcal mol^{-1} at 0 °C) [1]. We have prepared the ethylene complex with the η^3-allyl ligand, **3b**, and now find that the rotation in **3b** is too rapid to cause separation of the intrinsically non-equivalent olefin carbon and proton resonances at lower temperatures. Thus, the ^{13}C NMR spectra of **3b** showed only one resonance due to the ethylene carbons at down to -90 °C (see Experimental). Furthermore, the ^1H NMR spectra of the deuterio analog of **3b** (olefin = E-CHD=CHD) in CD_2Cl_2 showed, at 23– -90 °C, two sets of the olefin proton signals, each in equal intensity and flanked by the ^{195}Pt satellites (Experimental). Each set is clearly due to the averaged resonance of the two non-equivalent protons of E-CHD=CHD in a different diastereomer; coordination of a pro-chiral olefin to the $Pt(\eta^3\text{-}CH_2CMeCH_2)(PPh_3)^+$ moiety produces a diastereomeric pair [2].

If we assume a chemical shift difference ($\Delta\nu$) of the two protons interchanging

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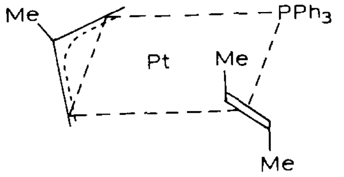
* Guggenberger and Cramer made a brief comparison of the nature of the Rh–olefin bonds in $Rh(\eta^5\text{-}C_5H_5)(C_2H_4)(C_2F_4)$ and $Rh(acac)(C_2H_4)(C_2F_4)$, primarily on the basis of the difference in the *trans* influence of the Cp and the acac ligands [5].

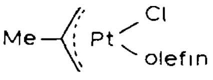
their positions as 0.5 ppm, then we calculate * $\Delta G^{\neq}_{\mathrm{rot}}$ for ethylene in **3b** at $-90\,^{\circ}\mathrm{C}$ as ≤ 8.8 kcal mol^{-1}. Such estimate of the shift difference (0.5 ppm) would be rather a lower limit value for a complex bearing PPh_3, which exerts a large magnetic anisotropy effect to nearby olefin protons [6a] as in **1a** and **2** [1] (see also the data for the *E*-2-butene complex below). Therefore, the value of 8.8 kcal mol^{-1} may correspond to a higher limit estimate, and clearly is much smaller than those of **2** and the other known, 4-coordinate ethylene complexes of $\mathrm{Pt^{II}}$ [6].

Whatever configuration the ethylene ligand of **3b** may take, one of the reasons for the lower ethylene rotation barrier compared to the other 4-coordinate complexes would be a smaller steric congestion around the olefin in the former. The theoretical calculations suggested that the steric factor dominates the olefin rotation barrier in the d^8 square-planar complexes [7]. A more definite example of the low barrier in **3** is found in a comparison between the *E*-2-butene complexes **3c** and PtCl(*E*-MeCH=CHMe)(acac) (**4**) [6b]. Thus, the variable temperature ^{1}H NMR spectral feature of the major diastereomer of **3c** (Fig. 1) is quite reminiscent of that of **4**, but $\Delta G^{\neq}_{\mathrm{rot}}$ of the former at $-55\,^{\circ}\mathrm{C}$ (coalesc. temp.), 11.0 kcal mol^{-1} is much smaller than that of the latter (15.8 kcal mol^{-1}). A preliminary X-ray structural study of **3c** showed a considerably distorted orientation of the C=C bond (see **A**; the angle between the C=C axis and the coordination plane is ca. 67°) [8]. The extent of such rotational distortion is less in the other 4-coordinate, sterically more demanding complexes [9], possibly owing to considerable repulsion between the olefinic hydrogens and the *cis* ligands [7].



(**A**)

There have been found still lower rotational barriers in the neutral complexes **5a** and **5b**, which have been generated in solution from $[\mathrm{Pt}(\eta^3\text{-}\mathrm{CH_2CMeCH_2})\mathrm{Cl}]_2$ [10] and characterized spectroscopically for the confirmation of the ^{13}C assignments in **3b** and **3c**. Thus, the ^{1}H and ^{13}C NMR spectra of not only **5a** but **5b** were totally temperature independent down to $-90\,^{\circ}\mathrm{C}$. These findings are presumably associated with the extremely small steric congestion around the olefin in **5**.



(**5**)

(**5a**, olefin = $CH_2{=}CH_2$,
5b, olefin = *E*-MeCH=CHMe)

Now the relative rotation barrier in **2** and **3b** discussed earlier seems to deserve special comment, for the molecular geometries determined in **1a** and **3a** [3,4] lead to

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* Approximate value by $\Delta G^{\neq}_{\mathrm{rot}} = -RT\ln[\pi(\Delta\nu)h/2kT]$.

TABLE 1

NMR DATA OF THE ETHYLENE-PLATINUM(II) COMPLEXES

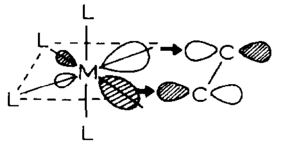
	Complex	
	2 [a]	**3b**
$\Delta\delta(C_2H_4)$ [b]	3.38 [c], 1.65 [c]	1.82 [d], 1.57 [d]
J(Pt–H(olefin)) (Hz)	64 [c], 76 [c]	54 [d], 54 [d]
$\Delta\delta$(C=C) [b]	79.9	53.4
J(Pt–C(olefin)) (Hz)	223.4	81.8
J(Pt–P) (Hz)	4343	3818

[a] Mostly from Ref. 1. [b] $\Delta\delta = \delta(\text{free}) - \delta(\text{complex})$. [c] Non-equivalent pair in one isomer. [d] Two diastereomers containing *E*-CHD=CHD.

an estimation that the steric congestion around the ethylene during rotation is not very different in **2** * and **3b**. A closer examination of the NMR spectral parameters in these complexes appears of particular help for the comparison of the nature of the Pt–ethylene bond in them.

The relevant ^{1}H, ^{13}C and ^{31}P NMR data are compared in Table 1. For the ethylene proton signals, **2** has the larger coordination shift (to the higher field) and J(Pt) value than **3b**. A similar, yet more prominent trend is seen in the coordination shifts and the J(Pt) values of the olefin carbon resonances. The dramatic increase of the J(Pt–C) value on going from **3b** to **2** cannot be related to the change of any isotropic factors of the platinum nucleus which affect the spin coupling constants (e.g. effective nuclear charge) [12], since the J(Pt–P) values for the coordinated PPh_3 are not so different between the two complexes as are the J(Pt–C) values. These spectral results are all suggesting the stronger Pt–ethylene bond strength in **2** than in **3b**, while the Pt–P bond strengths are comparable in these. Behind the difference in the Pt-ethylene bond strength would be a different π back-bond trend as discussed below.

1 and **2** are among a class of d^8 ML_4(olefin) complexes (Cp ≡ L_3) that exert quite an effective π back-bond interaction in one particular orientation of the C=C bond (see **B**) [7], as was shown crystallographically for **1a** [4] and ^{1}H NMR spectroscopically for **2** [1]. More important, the stabilization energy gained by the π interaction is larger in ML_4(olefin) than in square-planar complexes ML_3(olefin) to which **3** belongs, resulting in the stronger Pt–ethylene bond in **2** than in **3b**. Also compare the ν(CO) values between $[Pt(\eta^5\text{-}C_5H_5)(CO)(PPh_3)]ClO_4$ (2081 cm^{-1}) and $[Pt(\eta^3\text{-}$



(B)

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* The molecular geometry of the $Pt(\eta^5\text{-}C_5H_5)(PPh_3)^+$ moiety may be very close to that of $Pd(\eta^5\text{-}C_5H_5)(PPh_3)^+$ in view of the similar covalent radii of Pt and Pd in the complexes bearing analogous compositions [11].

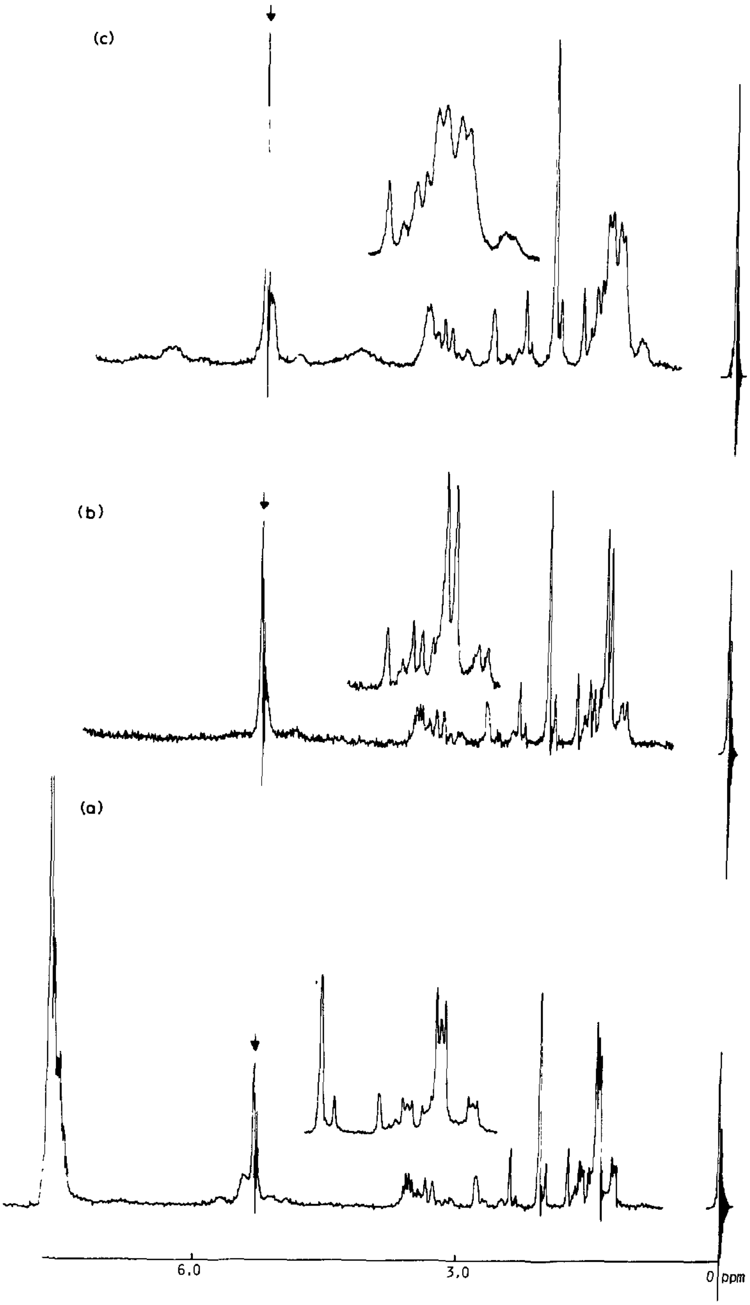


Fig. 1. Temperature dependent ^1H NMR spectra of $[Pt(\eta^3\text{-}CH_2CMeCH_2)(E\text{-}MeCH{=}CHMe)(PPh_3)]PF_6$ (**3c**) in CD_2Cl_2. (a) At 25 °C, (b) at −20 °C, (c) at −67 °C. The methyl signal regions are expanded at twice the width. Arrows denote CH_2Cl_2 signal.

$CH_2CMeCH_2)(CO)(PPh_3)]PF_6$ (2120 cm^{-1}) [1,2]. The ^{31}P NMR data shown in Table 1 are consistent with the weaker π-acceptor property of PPh_3 than ethylene.

In **2** the configurational restriction on the effective π interaction would make some contribution, in addition to that of steric origin, to the olefin rotation barrier. On the other hand, in **3b** the configurational restriction on the π interaction would be much weaker, with the in-plane component only slightly larger than the out-of-plane one [7]. This notion may further be supported by the largely distorted configuration of the C=C bond in **3c**. Thus, such weaker configurational demand, together with the intrinsically smaller π interaction energy, may be responsible for the lower rotational barrier in **3b** than in **2**.

Relative olefin affinity in η^5-cyclopentadienylpalladium(II) and η^3-allylplatinum(II) complexes

A systematic comparison of the stability data on the relative olefin affinity is desirable for the better access to the electronic effects of Cp and the η^3-allyl ligands on the metal–olefin bond. We have previously found the well-behaved equilibrium systems of the type eq. 1 for M = $Pd(\eta^5\text{-}C_5H_5)(PPh_3)^+$ and $Pt(\eta^3\text{-}CH_2CMeCH_2)(PPh_3)^+$ [1,2]. Since metal–PhCN linkages are expected to have a very narrow variation of the π interaction energy in various types of complexes bearing similar steric requirements, the relative olefin affinity in terms of the K_1 value would be a good measure of the π-donor property of the metal moiety.

$$\text{M-NCPh} + \text{olefin} \overset{K_1}{\rightleftharpoons} \text{M(olefin)} + \text{PhCN} \qquad (1)$$

Unfortunately, **2** is too inert toward ligand substitution to obtain quantitative estimation of the relative olefin affinity of the $Pt(\eta^5\text{-}C_5H_5)(PPh_3)^+$ moiety. We were also unable to determine K_1 values for M = $Pd(\eta^3\text{-}CH_2CMeCH_2)(PPh_3)^+$ by the reaction of $[Pd(\eta^3\text{-}CH_2CMeCH_2)(PhCN)(PPh_3)]PF_6$ and several olefins in $CDCl_3$ because of the gradual decomposition of the palladium species. Any stable olefin complexes could not be formed from this system, too, nor confirmed spectroscopically. We estimate the following order of the olefin affinity of the metal moiety:

$$Pd(\eta^3\text{-}CH_2CMeCH_2)(PPh_3)^+ < Pd(\eta^5\text{-}C_5H_5)(PPh_3)^+$$

$$Pd(\eta^3\text{-}CH_2CMeCH_2)(PPh_3)^+ < Pt(\eta^3\text{-}CH_2CMeCH_2)(PPh_3)^+$$

The latter order is in agreement with the general metal trend (Pd < Pt) in terms of the π-donor property if the Pd and the Pt complexes in question have electronically and sterically similar ligands [13]. The relative ethylene rotation barriers in **1b** and **2** were explained by this order of the π-donor property [1]. An interesting question then is: which is the better π-donor, $Pd(\eta^5\text{-}C_5H_5)(PPh_3)^+$ or $Pt(\eta^3\text{-}CH_2CMeCH_2)(PPh_3)^+$.

Table 2 compares several stability data for eq. 1 involving **1** and **3**. The remarkable feature in Table 2 is that the $Pd(\eta^5\text{-}C_5H_5)(PPh_3)^+$ moiety gives the K_1 value for a given olefin approximately 10 times as large as that of the $Pt(\eta^3\text{-}CH_2CMeCH_2)(PPh_3)^+$ moiety except for *E*-2-butene complexes. These data may be contrasted to the K_2 values determined for eq. 2 where the stability constants of the Pd-olefin complexes are about a factor of 10^2 less than those of the Pt analogs [13].

$$MCl_4{}^{2-} + \text{olefin} \overset{K_2}{\rightleftharpoons} MCl_3(\text{olefin})^- + Cl^- \qquad (2)$$

Also, somewhat smaller $\Delta H°$ values for the Pd system than those for the Pt system in Table 2 may be compared with the $\Delta H°$ values for the Pd series in eq. 2 which

TABLE 2

EQUILIBRIUM CONSTANTS (K_1) FOR eq. 1 [a]

Olefin	M	
	$Pd(\eta^5-C_5H_5)(PPh_3)^+ PF_6^-$	$Pt(\eta^3-CH_2CMeCH_2)(PPh_3)^+ PF_6^-$
$CH_2=CH_2$	15 ± 3 [b]	1.3 ± 0.3 [c]
$CH_2=CHMe$	0.81 ± 0.09	0.12 ± 0.05
$CH_2=CHEt$	0.87 ± 0.09	0.10 ± 0.05
E-MeCH=CHMe	0.03 ± 0.01	0.020 ± 0.005
$CH_2=CHPh$	0.26 ± 0.05 [d]	0.035 ± 0.006 [e]

[a] In $CDCl_3$ at 25 °C. [b] $\Delta H°$ -5.6 ± 0.5 kcal mol^{-1}. [c] $\Delta H°$ -5.2 ± 0.5 kcal mol^{-1}. [d] $\Delta H°$ -3.3 ± 0.7 kcal mol^{-1}. [e] $\Delta H°$ -2.0 ± 0.5 kcal mol^{-1}.

are more than 3 kcal mol^{-1} larger than those for the Pt series [13].

It is interesting in Table 2 that the difference in the K_1 values of the two metal moieties for olefin = *E*-MeCH=CHMe is smaller than those for the other olefins. This fact possibly has some relation with the strong configurational restriction in **1** on one hand, and the distorted structure of **3c** on the other. However, more detailed structural studies are clearly needed for the more satisfactory explanation.

In agreement with the data in Table 2, the Pd–C(olefin) distances in **1a** (2.182(5) and 2.255(5) Å) are somewhat shorter than the Pt–C(olefin) distances in **3a** (2.203(12) and 2.301(12) Å) [3,4]. Also, the $\nu(CO)$ of $[Pd(\eta^5-C_5H_5)(CO)(PPh_3)]ClO_4$ (2113 cm^{-1}) [1] is smaller than that of $[Pt(\eta^3-CH_2CMeCH_2)(CO)(PPh_3)]PF_6$ (2120 cm^{-1}), though the difference is small. In conclusion, we have demonstrated that the introduction of Cp to Pd^{II} ion is capable of providing this ion with the greater π-donor ability than that of Pt^{II} ion bearing the η^3-allyl ligand.

Experimental

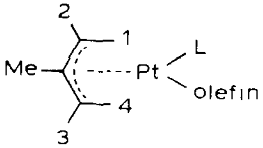
NMR spectra

^1H, ^{13}C and ^{31}P NMR spectra were measured on a JEOL PS-100, a JEOL FX-60 and a JEOL FX-90Q spectrometers, respectively, with tetramethylsilane as internal standard for ^1H and ^{13}C, and 10% H_3PO_4 as external standard for ^{31}P data. The carbon spectra were determined with noise-modulated proton decoupling. Temperature stability for lower temperature measurements was believed to be ±0.5 °C, and accuracy would be ±1 °C.

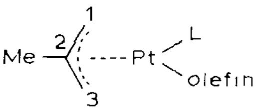
Preparation of platinum(II) complexes

The complex **2** was prepared by the reported method [1]. ^{31}P NMR ($CDCl_3$): 8.2 ppm *J*(Pt) 4343 Hz. **3b** and **3c** were prepared in a manner identical with those for the other complexes of type **3** containing gaseous olefins [10].

3b $[Pt(CH_2CMeCH_2)(CH_2=CH_2)(PPh_3)]PF_6$, colorless microcrystals, had decomposition point at 135 °C. Found: C, 42.11; H, 3.87. $C_{24}H_{26}F_6P_2Pt$ calcd.: C, 42.05; H, 3.82%. ^1H NMR (CD_2Cl_2; for proton numbering, see **C**): 1.91 ppm (s) *J*(Pt) 65 Hz (Me); 2.93(d) *J*(H(2)) 2.5, *J*(Pt) 60 Hz (H(1)); 3.65(br) (H(2)); 5.35(br) (H(3)); 3.28(d) *J*(P) 8, *J*(Pt) 29 Hz (H(4)); the olefinic proton resonances appeared at ca. 3.7 and 4.0 as complex multiplets. However, these multiplets became two doublets with equal intensity over the range of 23– – 90 °C if *E*-CHD=CHD was introduced instead of $CH_2=CH_2$; at −50 °C, 3.58 ppm(d) *J*(P) 2, *J*(Pt) 54 Hz and 3.83(d) *J*(P) 2, *J*(Pt) 54 Hz. ^{13}C NMR (CD_2Cl_2; for carbon numbering, see **D**): 23.0 ppm(s) *J*(Pt) 34.2 Hz (Me); 69.1(s) *J*(Pt) 152.6 (C(1)); 69.7(d) *J*(P) ca. 20, *J*(Pt) not defined (C(3)); 69.1(s) *J*(Pt) 81.8 Hz (C=C); the C(2) resonance overlapped with the Ph carbon resonances at 126–135 ppm. ^{31}P NMR ($CDCl_3$): 13.6 ppm *J*(Pt) 3818 Hz.



(C)



(D)

3c $[Pt(CH_2CMeCH_2)(E\text{-}MeCH=CHMe)(PPh_3)]PF_6$, colorless needles, had decomposition point at 145–150 °C. Found: C, 43.85; H, 4.47. $C_{26}H_{30}F_6P_2Pt$ calcd.: C, 43.77; H, 4.24%.

^1H NMR (CD_2Cl_2 at −67 °C): *major isomer* 2.06 ppm(s) *J*(Pt) 68 Hz (Me); 2.78 (br s) *J*(Pt) 56 (H(1)); 3.56(m) (H(2)); 5.3(br) (H(3)); 3.32(d) *J*(P) 8, *J*(Pt) 31 (H(4)); 1.30(d) *J*(H) 5, *J*(Pt) 51 (MeC=); 1.45(d) *J*(H) 5, *J*(Pt) 25 (=CMe); 4.27(v br) (–CH=); 6.42(br) *J*(Pt) 72 (=CH–); *minor isomer* 1.98(s) *J*(Pt) 69 (Me); 2.70(br) (H(1)); 4.97(br) (H(3)); the other proton resonances of the minor isomer could not be well resolved. The isomer ratio at 23 °C was 6.5/1.

^{13}C NMR (CD_2Cl_2 at −50 °C): *major isomer* 23.7 ppm(s) *J*(Pt) 35.4 Hz (Me); 63.6(s) *J*(Pt) 155.1 (C(1)); 72.5(d) *J*(P) 23.0, *J*(Pt) not defined C(3)); 19.5(s) *J*(Pt) 37.8 (*Me*C=); 21.3(s) *J*(Pt) 36.6 (=C*Me*); 86.5(s) *J*(Pt) 87.9 (–C=); 93.8(s) *J*(Pt) 103.8 (=C–). The C(2) resonance overlapped with the Ph resonances. No clear resonances due to the minor isomer could be resolved.

5a and **5b** were formed from $[Pt(\eta^3\text{-}CH_2CMeCH_2)Cl]_2$ and excess of the corresponding olefin as reported previously [10].

5a $Pt(CH_2CMeCH_2)(CH_2=CH_2)Cl$. ^1H NMR (CD_2Cl_2 at −28 °C): 1.95 ppm(s) *J*(Pt) 81 Hz (Me); 2.82(d) *J*(H(2)) 2, *J*(Pt) 40 (H(1)); 3.73(br) *J*(Pt) 18 H(3)); 2.36(br) *J*(Pt) 68 (H(4)); 4.1 ~ 4.65(m) ($CH_2=CH_2$); the H(2) resonance overlapped with the olefin protons. ^{13}C NMR (CD_2Cl_2 at −10 °C); 23.4 ppm(s) *J*(Pt) 46.4 Hz (Me); 68.2(s) *J*(Pt) 144.0 (C(1)); 123.4(s) *J*(Pt) 57 (C(2)); 51.7(s) *J*(Pt) 190.4 (C(3)); 78.0(s) *J*(Pt) 106.8 (C=C).

5b $Pt(CH_2CMeCH_2)(E\text{-}MeCH=CHMe)Cl$. ^1H NMR ($CDCl_3$ at −10 °C): *major isomer* 2.01 ppm(s) *J*(Pt) 86 Hz (Me); 2.70(d) *J*(H(2)) 2.5, *J*(Pt) 38 (H(1)); 4.32(dd) *J*(H(3)) 2.5, *J*(Pt) 19 (H(2)); 3.75(s) *J*(Pt) 24 (H(3)); the other resonances overlapped with the free olefin protons; *minor isomer* 4.05 ppm(br) (H(2)); 3.44(br) (H(3)); the other resonances could not be resolved. The isomer ratio was ca. 5/1. ^{13}C NMR (CD_2Cl_2 at −50 °C): *major isomer* 23.5 ppm(s) *J*(Pt) 47.6 Hz (Me); 61.5(s) *J*(Pt) 152.6 (C(1)); 122.1(s) *J*(Pt) 68.4 (C(2)); 51.2(s) *J*(Pt) 223.4 (C(3)); 21.2(s) *J*(Pt) 37.8 (*Me*C=C*Me*); 95.8(s) *J*(Pt) 112.9 (–C=C–); *minor isomer* 23.9(s) *J*(Pt) 50.0 (Me); 60.6(s) C(1)); 123.4(s) (C(2)); 99.3(s) *J*(Pt) 109.9 (C=C); the other resonances could not be observed.

Stability data

Essentially similar methods to those reported before [1,2] were employed in measuring the stability constants of eq. 1 through ^{1}H NMR spectroscopy. Mixtures of $[Pd(\eta^5\text{-}C_5H_5)(PhCN)(PPh_3)]PF_6$ or $[Pt(\eta^3\text{-}CH_2CMeCH_2)(PhCN)(PPh_3)]PF_6$ and the relevant olefin in several molar ratios in $CDCl_3$ were put in a constant temperature NMR probe, and examined for integrations of the appropriate signals. The ΔH° values for certain systems were determined from plots of $1/T$ vs. log K_1 at 25, 5 and $-10\,^\circ$C.

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