Journal of Organometallic Chemistry, 217 (1981) 259—266
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

LINEAR FREE ENERGY RELATIONSHIP IN SUBSTITUTED STYRENE COMPLEXES OF PLATINUM(II) CONTAINING THE η^3-METHYLALLYL LIGAND

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(Received February 20th, 1981)

Summary

Stability studies of a series of complexes, $[Pt(\eta^3\text{-}CH_2CMeCH_2)(PPh_3)(CH_2{=}CHC_6H_4Y\text{-}p)]PF_6$ in $CDCl_3$ revealed a linear free energy relationship for substituted styrene complexes of Pt^{II}. ^1H and ^{13}C NMR spectral data have been examined in terms of the structure and bonding of these complexes.

Introduction

Studies of bonding and stabilities of substituted styrene complexes of transition metals have received much attention. The stability trend observed in a series of *para*-substituted styrene complexes of Ag^I [1] and Pd^{II} [2,3] indicated the electrophilic nature of these metals toward the olefinic ligand. ^{13}C NMR studies [4], as well as other related spectroscopic [4] and structural [5] studies, of substituted styrene complexes of Pt^{II} of the type, *trans*-$PtCl_2(L)(CH_2{=}CHC_6H_4Y\text{-}p)$ **1** ($L = Cl^-$, py) and *trans*-$[PtCl(NH_3)_2(CH_2{=}CHC_6H_4Y\text{-}p)]^+$ **2** also suggested the important role of olefin to platinum σ-donation. Nevertheless, the only available stability data for Pt^{II} complexes, namely those of **1** ($L = Cl^-$, pyridine-*N*-oxide), exhibited no simple linear free energy relationship [6]. This result has long been interpreted in terms of the energy level matching of the orbitals which are used in the Dewar-Chatt-Duncanson bonding scheme. Later on, Cooper and Powell presented a criticism [4] that there may have existed solution equilibria other than the reference ligand-styrene exchange equilibrium (eq. 1) which was used for the relative stability measurements of **1** by UV spectroscopy [6].

$$PtCl_2(L)\,(\text{dodecene}) + CH_2{=}CHC_6H_4Y\text{-}p \rightleftharpoons PtCl_2(L)\,(CH_2{=}CH_6H_4Y\text{-}p) + \text{dodecene} \quad (1)$$

(1)

We sought a better behaved equilibrium system involving another type of styrene complexes of Pt^{II} which, at the same time, could readily be analyzed by NMR spectroscopy. By this method we could avoid using very dilute solutions which may enhance a chance for the complex to undergo undesirable, additional solution equilibria. By making use of one such suitable system involving $[Pt(\eta^3\text{-}CH_2CMeCH_2)(PPh_3)L]PF_6$ where L = C_6H_5CN **3** and $CH_2{=}CHC_6H_4Y\text{-}p$ **4** (eq. 2), we have found the first linear free energy relationship for styrene complexes of Pt^{II}.

$$[Pt(\eta^3\text{-}CH_2CMeCH_2)(PPh_3)(C_6H_5CN)]^+ + CH_2{=}CHC_6H_4Y\text{-}p \overset{K}{\rightleftharpoons}$$

(3)

$$[Pt(\eta^3\text{-}CH_2CMeCH_2)(PPh_3)(CH_2{=}CHC_6H_4Y\text{-}p)]^+ + C_6H_5CN \qquad (2)$$

(4)

Experimental

Preparation of styrene complexes

An acetone solution (2 ml) of $AgPF_6$ (126 mg; 0.5 mmol) was added to a CH_2Cl_2 solution (10 ml) kept at 0°C containing $Pt(\eta^3\text{-}CH_2CMeCH_2)Cl(PPh_3)$ (274 mg; 0.5 mmol) and styrene (104 mg; 1 mmol). After AgCl was filtered, the solution was concentrated to a volume of ca. 4 ml. To this was added n-hexane (4 ml), and this solution was kept in a refrigerator overnight to give fine crystals of 4d (see Table 1) (80%). The complexes 4a—4c and 4e were prepared similarly except that the recrystallization solvents were CH_2Cl_2-benzene. Crystals of these complexes contained benzene of crystallization the presence of which was confirmed by analyses and ^1H NMR spectra. The *p*-nitro analogue gave no crystalline material but was isolated as a fluffy, powdery solid.

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TABLE 1

PROPERTIES OF STYRENE COMPLEXES $[Pt(CH_2CMeCH_2)(PPh_3)(CH_2{=}CHC_6H_4Y\text{-}p)]PF_6$

No.	Complex Y =	m.p. (°C)	Analysis Found (calcd.) (%)		
			C	H	N
4a	NMe_2 [a]	93—95	54.70	4.96	1.41
			(55.00)	(4.93)	(1.46)
4b	OMe [b]	105—107	51.02	4.48	
		(dec.)	(51.10)	(4.41)	
4c	Me [b]	102—104	51.96	4.47	
		(dec.)	(52.05)	(4.49)	
4d	H	140—143	47.27	3.98	
		(dec.)	(47.31)	(3.97)	
4e	Cl [b]	113—116	49.38	4.14	
		(dec.)	(49.47)	(4.04)	
4f	NO_2	[c]	45.27	3.94	1.71
			(44.67)	(3.62)	(1.74)

[a] Two molecules of benzene of crystallization. [b] One molecule of benzene of crystallization. [c] No definite m.p.

TABLE 2

^{1}H NMR SPECTRAL DATA [a] OF STYRENE COMPLEXES 4

No.	H(1)	H(2)	H(3)		H(4)		H(5)	H(6)	H(7)	Me	
4a	4.37 J(H(3)) = 13.8 J(P) = 4.8 J(Pt) = 62	3.60 J(H(3)) = 9.0 J(P) $\leqslant$ 2 J(Pt) = 60	b		2.69 J(Pt) = 60	(2.51)	3.42	4.87	3.28 J(P) = 7.8	1.65 J(Pt) = 66	(1.63) (J(Pt) = 70)
4b	4.26 J(H(3)) = 13.5 J(P) = 6.3 J(Pt) = 59	b	b	(6.27)	2.79 J(Pt) = 60	(2.63) (J(Pt) = 60)	3.48	4.92(4.62)	3.60 J(P) = 8.5	1.58 J(Pt) = 63	(1.70) (J(Pt) = 68)
4c	4.20 J(H(3)) = 14.3 J(P) = 6.4 J(Pt) = 56	3.71 J(H(3)) = 9.8 J(P) $\leqslant$ 2	6.74 J(Pt) = 53	(6.20)	2.79 J(Pt) = 58	(2.64)	3.46	4.92(4.71)	3.58 J(P) = 8.3	1.52 J(Pt) = 62	(1.76) (J(Pt) = 68)
4d	4.22 J(H(3) = 13.5 J(P) = 7.2 J(Pt) = 57	3.80 J(H(3)) = 9.3 J(P) = 3	6.55 J(Pt) = 51	(6.02)	2.85 J(Pt) = 60	(2.73)	3.54	4.96	3.67 J(P) = 7.5	1.52 J(Pt) = 63	(1.81) (J(Pt) = 66)
4e	4.16 J(H(3)) = 14.3 J(P) = 6.3 J(Pt) = 57	3.78 J(H(3)) = 9.5 J(P) = 3	6.61 J(Pt) = 54	(6.11)	2.84 J(Pt) = 60	(2.73) (J(Pt) = 60)	3.52	4.95	3.64 J(P) = 8.3	1.57 J(Pt) = 63	(1.85) (J(Pt) = 66)
4f	4.18 J(H(3)) = 13.5 J(P) = 6.0 J(Pt) = 52	3.92 J(H(3)) = 9.0 J(P) $\leqslant$ 3	6.46 J(Pt) = 54	(6.00)	2.95 J(Pt) = 59	(2.62)	3.60	5.01	3.77 J(P) = 7.9	1.59 J(Pt) = 64	(1.90) (J(Pt) = 65)

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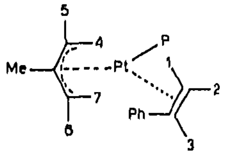
[a] In CD_2Cl_2 at 26°C. Chemical shift in ppm and coupling constant in Hz. The resonances due to the minor isomers well resolved are shown in parentheses. Proton numbering is:



[b] Obscured by the phenyl or the O-methyl proton resonances.

TABLE 3

^{13}C NMR SPECTRAL DATA [a] OF STYRENE COMPLEXES 4

No.	C(1)		C(2)		C(3)		C(5)		Me	
4a	100.4 J(Pt) = 32.9	(111.5)	61.2 J(Pt) = 126.1	(60.8)	62.5 J(Pt) = 170.0	(61.7)	76.4 J(P) = 26.1 J(Pt) = 60.0		22.5 J(Pt) = 35.6	(23.1)
4b	93.7 J(Pt) = 50.7	(101.6)	64.7 J(Pt) = 111.1	(65.4)	64.0 J(Pt) = 168.6		78.5 J(P) = 23.3 J(Pt) = 54.8	(77.4)	22.4 J(Pt) = 35.6	(23.0)
4c	91.9 J(Pt) = 55.5	(98.5) (J(Pt) = 58.8)	65.9 J(Pt) = 108.3	(66.7)	64.4 J(Pt) = 167.3	(65.0)	79.2 J(P) = 23.3 J(Pt) = 52.1		22.2 J(Pt) = 38.4	(23.0)
4d	90.6 J(Pt) = 61.1	(96.7)	66.8 J(Pt) = 107.4	(67.7)	64.9 J(Pt) = 163.6	(65.6)	79.6 J(P) = 23.2 J(Pt) = 51.3		22.2 J(Pt) = 36.6	(23.0)
4e	88.7 J(Pt) = 60.3	(93.2) (J(Pt) = 64.6)	66.7 J(Pt) = 102.8	(67.7)	65.4 J(Pt) = 164.5		79.4 J(P) = 21.9 J(Pt) = 49.4		22.4 J(Pt) = 35.7	(22.9)
4f	84.5 J(Pt) = 77.8	(86.5)	68.1 J(Pt) = 98.7	(69.2)	67.0 J(Pt) = 159.0	(68.5)	79.8 J(P) = 21.9 J(Pt) = 46.6		22.4 J(Pt) = 35.7	(22.7)

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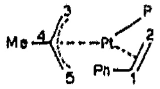
[a] In CD_2Cl_2 at 26°C. Chemical shift in ppm and coupling constant in Hz. The resonances due to the minor isomers well resolved are shown in parentheses. Carbon numbering is:



The resonances due to C(4) may have been obscured by the phenyl carbon resonances.

TABLE 4

EQUILIBRIUM CONSTANT OF eq. 2 [a]

No.	Y	K
4a	NMe_2	0.44 ± 0.08
4b	OMe	$(9.0 \pm 1.6) \times 10^{-2}$
4c	Me	$(5.7 \pm 0.9) \times 10^{-2}$
4d	H	$(3.5 \pm 0.6) \times 10^{-2}$
4e	Cl	$(1.7 \pm 0.4) \times 10^{-2}$
4f	NO_2	$(3.5 \pm 0.7) \times 10^{-3}$

[a] In $CDCl_3$ at 26°C.

Melting points and analytical data are summarized in Table 1. Relevant ^1H and ^{13}C NMR spectral data are shown in Tables 2 and 3.

Preparation of benzonitrile and carbonyl complexes

The complex 3 was prepared in a manner similar to that for the styrene complex; colorless microcrystals decomposed above 150°C. Found: C, 45.80; H, 3.58; N, 1.82. $C_{29}H_{27}NF_6P_2Pt$ calcd.: C, 45.80; H, 3.58; N, 1.84%. ^1H NMR ($CDCl_3$): 2.20 ppm (s), $J(Pt) = 77$ Hz (Me); 2.63 (d), $J(H(5)) = 3.5$, $J(Pt) = 75$ (H(4)); 3.17 (d), $J(Pt) = 15$ (H(5)); 4.93 (s, br) (H(6)); 3.59 (d), $J(P) = 8.2$, $J(Pt) = 26$ (H(7)) (for proton numbering, see Table 2). The carbonyl complex, $[Pt(\eta^3\text{-}CH_2CMeCH_2)(PPh_3)(CO)]PF_6$ 5 was prepared similarly by using a CH_2Cl_2 solution of $Pt(\eta^3\text{-}CH_2CMeCH_2)Cl(PPh_3)$ saturated with carbon monoxide; colorless microcrystals decomposed above 170°C. Found: C, 40.53; H, 3.40. $C_{23}H_{22}OF_6P_2Pt$ calcd.: C, 40.30; H, 3.24%. ^1H NMR($CDCl_3$): 2.09 ppm (s) $J(Pt) = 74$ Hz (Me); 3.13 (d), $J(H(5)) = 3.5$, $J(Pt) = 38$ (H(4)); 3.7—3.9 (br) (H(5) and H(7)); 5.22 (br) H(6)). IR (Nujol): 2120 cm^{-1}.

Relative stability measurements

The equilibrium constants of eq. 2 were measured by the ^1H NMR method in $CDCl_3$ at 26°C primarily on the basis of the peak area ratios for the methyl pro-

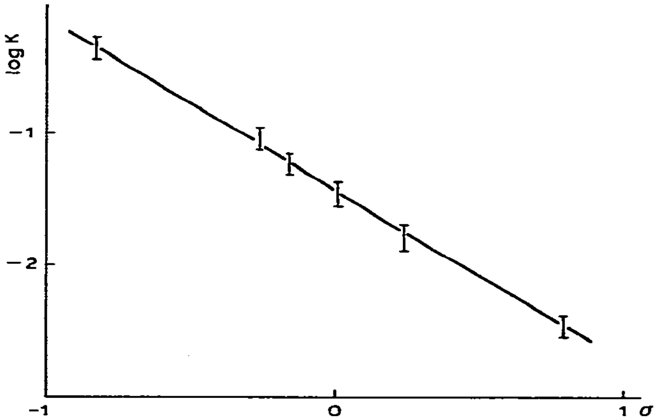


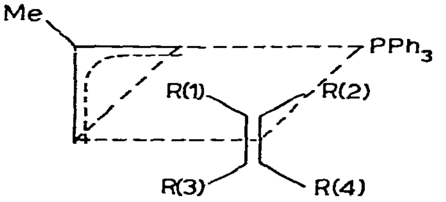
Fig. 1. Hammett plot for eq. 2 ($\rho = -1.32$, $r = 0.999$).

ton resonances (see above and Table 2). The procedure employed is essentially the same as that described previously [3] for the system containing $[Pd(\eta^5\text{-}C_5H_5)(PR_3)L]^+$ where L = C_6H_5CN and substituted styrenes. The equilibrium is attained rapidly within the time of mixing of the reactants. The equilibrium constants of eq. 2 were counterchecked by analyzing an equilibrium mixture consisting of **4d**, a substituted styrene complex, styrene and the respective substituted styrene. The relative stabilities (K_Y/K_H) obtained from the two equilibrium systems agreed within experimental error. The results are summarized in Table 4 and a Hammett plot is given in Fig. 1.

^1H and ^{13}C NMR spectra were measured on a JEOL PS-100 and a JEOL FX-60 spectrometers, both with tetramethylsilane as internal reference. The carbon spectra were determined with noise-modulated proton decoupling, but proton-coupled spectra were also obtained for some samples to ensure spectral assignments.

Discussion

The ^1H and ^{13}C NMR spectra of the styrene complexes **4** in $CDCl_3$ and CD_2Cl_2 showed the existence of two stereoisomers with the isomer ratio (3.6/1 ~ 3.9/1) being almost independent of the *para* substituent. Due to limited solubility of the complexes and overlapping with more intense absorptions, not all of the resonances due to the minor isomers could be detected. The proton spectral features for **4d** did not change over the temperature range —90 ~ 50°C. In principle, there can be four isomers depending on the relative disposition of the C-phenyl and the methyl or the phosphine group (see **A**). At present it is difficult to assign unambiguously the structures of the spectroscopically detectable isomers. We tentatively propose that this isomerism arises from the *enantio*-face discrimination of the styrene molecule upon its coordination to a chiral platinum center; this produces a diastereomeric pair. If the two isomers detected correspond to a rotameric pair having the same diastereomeric configuration, namely the isomers with R(1) = Ph and R(4) = Ph in one diastereomer or those with R(2) = Ph and R(3) = Ph in the other (see **A**), they would have converted to each other more rapidly than the NMR time scale at higher temperatures. This assumption is based on the fact that the rate of olefin rotation about the olefin—metal bond axis, but not the C=C axis, is usually very fast at room or higher temperatures in square-planar Pt^{II} complexes [7]. Furthermore, we observed [8] even more facile olefin rotation in complexes quite analogous to **4**, namely $[Pt(\eta^3\text{-}CH_2CMeCH_2)(PPh_3)(olefin)]^+$ (olefin = CH_2=CH_2 and *trans*-MeCH=CHMe). Judging from the temperature-independent spectral aspects, it may well be that in each diastereomer one rotamer predominates or almost excludes the other.



(A)

For the purpose of examining a linear free energy relationship, it may reasonably be assumed that the structures of both the major and minor isomers do not change to any significant extent when the *para* substituent changes. This may be supported by the fact that the ^{13}C chemical shift of the olefinic carbons shows a good correlation with the Hammett σ^+ constants within the major or minor isomer series (see later), and that other ^1H and ^{13}C shifts also show almost regular variation within each isomeric series as the *para* substituent changes.

The complexes 3 and 4 used in eq. 2 contain the η^3-methylallyl and PPh_3 ligands which are completely inert with respect to solvolysis or any other ligand substitution under the equilibrium conditions. The ^1H NMR spectra of the equilibrium mixtures are straightforward in that no resonances other than those of the four components in eq. 2 are observed, and that the resonances of each component are the same as those of the respective species measured separately. The latter fact indicates that the rate of ligand exchange in eq. 2 is slower than the NMR time scale.

In calculating the *K* values of eq. 2, we used as the concentration of the styrene complex the combined concentration of the two isomers. This poses no problem for comparing the relative stability, for the isomer ratio is almost constant irrespective of the *para* substituent. The high reliability of the solution equilibria in the present system was checked by obtaining the consistent equilibrium constant data for an equilibrium mixture containing **4d** and a substituted styrene complex (see Experimental).

A plot of log *K* against the Hammett σ gave a straight line with $\rho = -1.32$ and $r = 0.999$ (Fig. 1). The negative sign of ρ implies the important role of olefin to platinum σ-donation, i.e., the electrophilic nature of the platinum atom. In order to make a rough evaluation of the electronic demand of the platinum atom in olefin complexes, it may be appropriate to compare chemical shifts of the coordinated olefin carbons and ν(CO) values of those complexes in which carbon monoxide is replacing the olefin ligand. We find nothing unusual in those values of 4 or $[Pt(\eta^3\text{-}CH_2CMeCH_2)(PPh_3)(CO)]PF_6$, 5, particularly in comparison with those [4,9] of the type 1 complexes, *trans*-$PtCl_2(L)$ (un) ($L = Cl^-$, py, pyridine-*N*-oxide; un = olefin, CO). Thus, the good correlation shown in Fig. 1, together with the above consideration, may cast doubt about the likelihood of the reported unusual stability trend in 1 [6].

The correlation of log *K* with σ^+ is worse ($r = 0.976$), while the ^{13}C NMR data for the olefinic carbons correlate better with σ^+ (Table 5), in exactly the

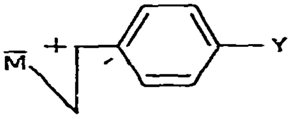
TABLE 5

CORRELATION ($X = a\sigma^+ + b$) BETWEEEN ^{13}C NMR DATA AND HAMMETT σ^+ CONSTANTS [a]

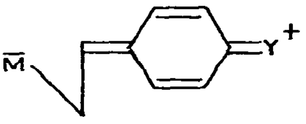
X [b]	a (ppm/Hz)	b (ppm/Hz)	r
δ(C(1))-A	−6.04	89.6	0.994
δ(C(1))-B	−9.51	94.9	0.992
δ(C(2))-A	2.72	66.5	0.987
δ(C(2))-B	3.31	67.3	0.981
J(PtC(1))-A	16.58	61.9	0.988
J(PtC(2))-A	−10.54	105.6	0.979

[a] By linear regression analysis using data in Table 3. [b] A refers ro the major isomers, B to the minor isomers.

same way as those of the complexes of the type **1** [4]. A similarly different Hammett parameter dependency of the stability and ^{13}C NMR data has also been observed in a series of Pd^{II} complexes of the type, $[Pd(\eta^5\text{-}C_5H_5)(PBu_3)(styrene)]^+$ [3]. It may well be that the variation of the olefinic carbon NMR parameters is particularly sensitive to even a small change in the degree of contribution of the canonical forms [4] such as **B** and **C** to the overall bonding.



(B)



(C)

In Table 3 the increase of *J*(PtC(3)) for the allylic carbon *trans* to the styrene with the increasing electron-donating ability of the *para* substituent is noteworthy. The ^3J(PtC) value of the coordinated picoline in the complexes of the type **1** (L = γ-picoline) showed an opposite substituent dependency (^3J(PtC): Y = NO_2 > NMe_2), which is consistent with the expected order of *trans* influence of the substituted styrene ligand [4]. It is possible that the mechanism of Pt—C(3) spin-spin coupling in the allylic system is more complex. A more detailed study such as determination of the sign of the coupling is necessary before any reasonable explanation is given for the observed change of the *J*(PtC(3)) value.

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