Relative Stabilities of *trans*-Dichloro(olefin)(pyridine)platinum(II) Complexes. Re-examination of Hammett Equation for *para*-Substituted Styrene Complexes

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Relative solution stabilities of several olefin (L) complexes, *trans*-$[PtCl_2(py)L]$ (**1**) (py = pyridine) have been measured by means of ^1H n.m.r. spectroscopy by observing two separate methyl proton singlets of free $CH_2{=}CHC_6H_4Me$-*o* and (**1**; L = $CH_2{=}CHC_6H_4Me$-*o*). Data for (**1**; L = $CH_2{=}CHC_6H_4Y$-*p*, Y = NMe_2, OMe, Me, H, Cl, or NO_2) show the higher stability for the more electron-donating olefin complex, with the Hammett ρ^+ value being -0.82. This is consistent with previous ^{13}C n.m.r. and structural trends which suggest olefin-to-Pt σ donation to be much more important than π back-bonding in determining the stability of (**1**).

Zeise's salt and its analogues, $[PtCl_2L'L]$ (L = olefin; L′ = Cl, amine, *etc*.), have long been the subject of considerable theoretical and physicochemical investigation.[1] The relative stabilities of $[PtCl_3L]^-$ and $[PtCl_2L'L]$ (L = $CH_2{=}CHC_6H_4Y$-*p*, Y = OMe, Me, H, Cl, or NO_2; L′ = pyridine *N*-oxide) measured in very dilute solutions by u.v. spectroscopy showed no simple Hammett relationship.[2] This result has been interpreted [1] in terms of the energy level matching of the σ and π orbitals which are used in the Dewar–Chatt–Duncanson bonding model.[3] However, Powell and other workers presented a simpler bonding idea involving predominant olefin-to-metal σ donation, primarily on the basis of the rather regular variation of the ^{13}C n.m.r.[4] and *X*-ray structural[5] parameters with the Hammett σ^+ values in (**1**; L = $CH_2{=}CHC_6H_4Y$-*p*, Y = NMe_2, OEt, OPh, Me, H, Cl, MeCO, or NO_2). These authors then cast doubt about the accuracy of the stability data reported earlier.

We have found recently that the linear free-energy relationship exists in the stability of *para*-substituted styrene complexes of type (**2**).[6] The stability data were obtained by ^1H n.m.r. spectroscopy. We now report the relative stabilities of (**1**) (py = pyridine) containing substituted styrenes and several other olefins, as also measured by ^1H n.m.r. spectroscopy, which substantiate Powell's proposal.

Results and Discussion

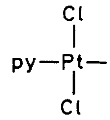
The rate of exchange of free and co-ordinated olefins in (**1**) is usually fast on the n.m.r. time-scale, making it difficult to analyse, by n.m.r. spectroscopy, quantities of species involved in a solution equilibrium. We found that the chemical shift of the methyl proton resonance of *o*-methylstyrene (2.34 p.p.m.) moves downfield considerably upon forming the complex (**1**; L = $CH_2{=}CHC_6H_4Me$-*o*) (2.87 p.p.m.). Moreover, the rate of ligand exchange is sufficiently slow at −15 °C to give two separate singlets for the methyl protons of free and co-ordinated *o*-methylstyrene (Figure 1), even though these signals are very broad at room temperature. Thus, these spectral features allowed us to estimate the equilibrium constant of equation (1) at −15 °C.

$$\textit{trans}\text{-}[PtCl_2(py)(CH_2{=}CHC_6H_4Me\text{-}o)] + L \overset{K}{\rightleftharpoons} \textit{trans}\text{-}[PtCl_2(py)L] + CH_2{=}CHC_6H_4Me\text{-}o \quad (1)$$

Table. Equilibrium constants (K)[a] for equation (1)

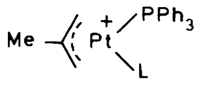
L	K
$CH_2{=}CHMe$	30 ± 10
Z-MeCH=CHMe	5.6 ± 0.9
E-MeCH=CHMe	2.9 ± 0.4
Z-MeCH=CHPh	0.027 ± 0.003
E-MeCH=CHPh	0.017 ± 0.002
$CH_2{=}CHC_6H_4Y$-*p*	
Y = NMe_2	7.0 ± 2.5
OMe	1.4 ± 0.2
Me	0.56 ± 0.15
H	0.32 ± 0.03 [b]
Cl	0.25 ± 0.03
NO_2	0.052 ± 0.006 [c]
$CH_2{=}CHC_6H_4Cl$-*o*	0.23 ± 0.03
$CH_2{=}CHCO(OMe)$	0.001 ± 0.0005 [d]

[a] In $CDCl_3$ at −15 °C. [b] $\Delta H^\circ = 0 \pm 1$ kJ mol^{-1}, $\Delta S^\circ = -9 \pm 4$ J K^{-1} mol^{-1}. [c] $\Delta H^\circ = 9 \pm 2$ kJ mol^{-1}, $\Delta S^\circ = 10 \pm 7$ J K^{-1} mol^{-1}. [d] At −30 °C.



$$py{-}\underset{\underset{Cl}{|}}{\overset{\overset{Cl}{|}}{Pt}}{-}L$$

(**1**)



(**2**)

Within the detection limit of the spectroscopy, no methyl resonances other than those of the free and co-ordinated [type (**1**)] *o*-methylstyrene could be observed (see Figure 1). Furthermore, several equilibrium runs for equation (1) (L = $CH_2{=}CHC_6H_5$) starting from either side of the equilibrium with different molar ratios of the reagents gave consistent K values. The results obtained for several olefins are summarized in the Table.

The stability data for (**1**; L = $CH_2{=}CHC_6H_4Y$-*p*, Y = NMe_2, OMe, Me, H, Cl, or NO_2) in the Table show the larger K value for the more electron-donating olefin complex. A plot of log K *vs*. the Hammett σ^+ parameter is shown in Figure 2 where $\rho^+ = -0.82$ and $r = 0.996$. The value of ΔH° for equation (2) estimated from the K values at 0, −15, −30, and −45 °C (9 ± 3 kJ mol^{-1}) can be well compared with those[7] obtained by a calorimetric investigation (5 kJ mol^{-1} in benzene, 2 kJ mol^{-1} in CH_2Cl_2). Thus, it is evident that the more electron-donating styrene gives the stronger Pt–olefin bond, in agreement with the ^{13}C n.m.r. and structural results.[4,5]

$$\textit{trans}\text{-}[PtCl_2(py)(CH_2{=}CHC_6H_5)] + CH_2{=}CHC_6H_4NO_2\text{-}p \rightleftharpoons \textit{trans}\text{-}[PtCl_2(py)(CH_2{=}CHC_6H_4NO_2\text{-}p)] + CH_2{=}CHC_6H_5 \quad (2)$$

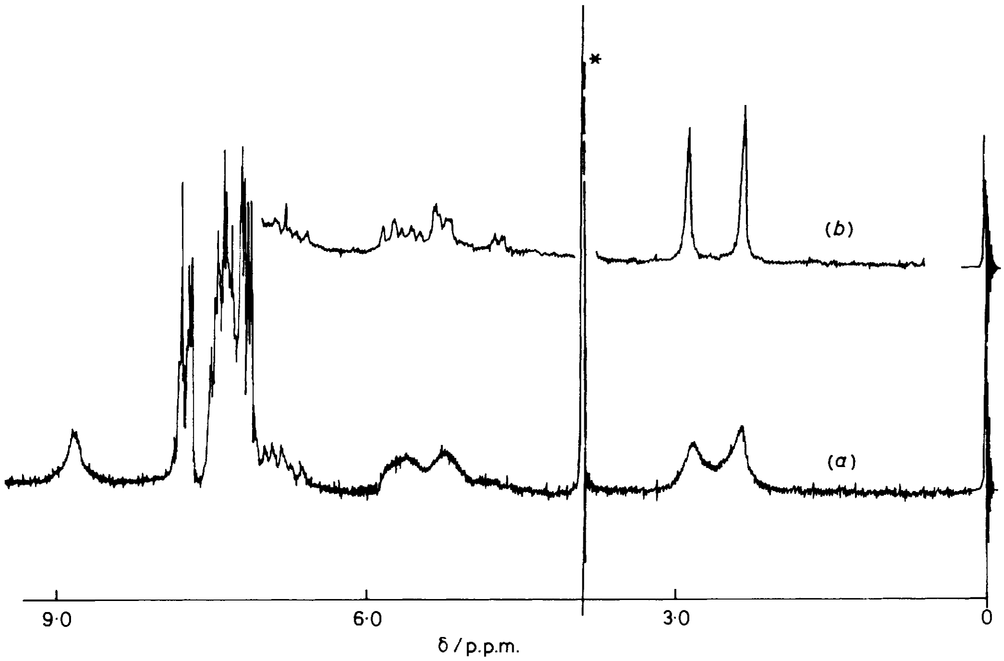


Figure 1. Hydrogen-1 n.m.r. spectra of an equilibrium mixture [equation (1)] starting from $CH_2{=}CHC_6H_4Me$-*o* (0.204 mol dm^{-3}) and *trans*-$[PtCl_2(py)(CH_2{=}CHC_6H_5)]$ (0.128 mol dm^{-3}) in $CDCl_3$. (*a*) At 25 °C, (*b*) at −15 °C. The asterisk denotes the OMe peak of the internal reference (methyl β-naphthyl ether)

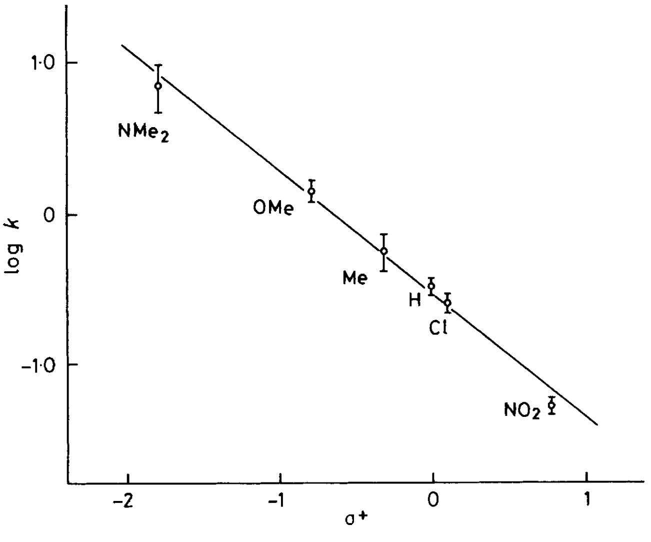


Figure 2. Hammett plot for equation (1) ($L = CH_2{=}CHC_6H_4Y$-*p*, Y indicated) in $CDCl_3$ at −15 °C ($\rho^+ = -0.82$, $r = 0.996$)

Another point of interest in the Table is that methyl acrylate, which is the most π-acidic among the olefins examined, gives the least stable complex. A previous i.r. study suggested that this olefin made a stronger bond with Pt than styrene, *Z*-but-2-ene, propene, and even ethylene.[8] It thus appears that there existed some ambiguity in deducing the olefin–Pt bond strength from the Pt–C stretching frequencies. Now it seems obvious that the olefin-to-metal σ donation plays a much more important role than the π back-bond in determining the solution stability of the Pt^{II} olefin complexes.

The stability trend in the other olefin complexes shown in the Table seems normal when compared to those of other square-planar d^8 metal–olefin complexes such as (**2**)[6,9] and [ML], where M = $Rh(acac)(C_2H_4)$ (acac = acetylacetonate),[10] $PdCl_3^-$,[11] Pd(acac)L′ (L′ = 5-acetoxytricyclo-[$2.2.1.0^{2,6}$]hept-3-yl),[12] or $PtCl_3^-$.[13] The stability constants are especially sensitive to the steric bulk of the co-ordinated olefin ligand; increasing methyl and/or phenyl substitution at the olefinic carbon(s) results in a great decrease in the stability. The stability constant *K* for equation (1) where $L = CH_2{=}CH_2$ was too large to be estimated by the present n.m.r. method.

Also common to all the d^8 metal complexes except for (**2**)[14] is the higher stability of the *Z*-olefin-metal bond than the *E*-olefin–metal bond. Finally, the *K* values for equation (1) where $L = CH_2{=}CHC_6H_4Me$-*p*, $CH_2{=}CHC_6H_4Cl$-*o* and -*p* suggest that the $PtCl_2(py)$ moiety has a much smaller steric demand on the *ortho*-substituent of the styrene ligand.

Experimental

Instruments and Materials.—Hydrogen-1 n.m.r. spectra were obtained on a JEOL PS-100 spectrometer in $CDCl_3$ with $SiMe_4$ as internal standard. The *o*-methylstyrene complex, *trans*-$[PtCl_2(py)(CH_2{=}CHC_6H_4Me$-*o*$)]$ was prepared as orange crystals in a manner similar to those for other complexes of type (**1**),[8] m.p. 133—135 °C (Found: C, 36.30; H, 3.30; N, 3.00. Calc. for $C_{14}H_{15}Cl_2NPt$: C, 36.30; H, 3.25; N, 3.00%). ^1H N.m.r. ($CDCl_3$): δ, 2.87 (s), 4.73 [d, *J*(HH) 8.3, *J*(PtH) 63 Hz], 5.41 [d, *J*(HH) 14.0, *J*(PtH) 58 Hz], 6.91 [dd, *J*(PtH) 68 Hz], 7.1—7.5 (m), 7.86 [t, *J*(HH) 7 Hz], 8.82 (br) p.p.m.

p-Nitro-, *p*-dimethylamino-, and *o*-methyl-styrene were prepared by the reported method.[15] The other styrenes were purchased from Nakarai Chemicals, Inc., and used without further purification.

Stability Measurements.—The methods of performing the low-temperature ^1H n.m.r. equilibrium measurements including the preparation of samples and instrumental manipulations for the temperature control are essentially the same as those already reported for the Pd^{II} complexes.[16] In all the systems of equation (1) examined, except for a few cases, the relative peak area of the methyl proton resonances of free and co-ordinated *o*-methylstyrene could be determined without difficulty (see below). The intensities of these peaks were also determined relative to that of an internal standard, namely the OMe peak of methyl β-naphthyl ether.

Each K in the Table is the mean of the values for three samples, except as noted below, containing different reagent ratios (concentration of the *o*-methylstyrene complex is 0.13 mol dm^{-3}), with the uncertainty being represented by twice the standard deviation of the mean. The reagent ratio was chosen as such that the relative peak area of the two methyl resonances was not very large (< 10:1) nor very small (> 1:10). The equilibrium constant of equation (1) where L = CH_2=CHC_6H_5 was determined from five samples containing varying concentrations (0.06—0.14 mol dm^{-3}) of the complex (three starting from the *o*-methylstyrene complex, and two from the styrene complex). There was no apparent concentration dependency of the K value. The ΔH° values were calculated from linear regression analysis using the data at 0, −15, −30, and −45 °C.

Where L = CH_2=CHC_6H_4Y-*p* (Y = NMe_2 or Me), the resonance of either free or co-ordinated *o*-methylstyrene overlapped with the methyl resonances of these *para*-substituted styrenes, resulting in somewhat larger errors. In the case where L = CH_2=CHMe, the K value is expected to be quite large. However, accurate determination of the K value was difficult for the following reasons. Addition of a large excess of *o*-methylstyrene to (**1**; L = CH_2=CHMe) resulted in the formation of comparable amounts of the two complexes, but determination of the co-ordinated *o*-methylstyrene peak contained considerable errors because of its somewhat broad nature and the appearance of the very strong signal of the free styrene near to it. Moreover, the methyl protons of both free and co-ordinated propene gave only a broad singlet even at −15 °C. In other trials from the different direction, addition of only a very small amount of free propene to (**1**; L = CH_2=CHC_6H_4Me-*o*) was needed to keep the concentrations of the free and co-ordinated *o*-methylstyrene comparable, but accurate determination of free propene in such a small quantity was very difficult.

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