The Role of Electronic Effects in Determining the Thermodynamic Stabilities of Olefin Complexes of Palladium(II) and Platinum(II)

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Summary The dominant factor in determining the thermodynamic stability of the metal–olefin bond in *p*-substituted styrene complexes of palladium(II) has been shown to be the olefin-π to metal-*d* component of the bond, rather than the metal-*d* to olefin-π^* component.

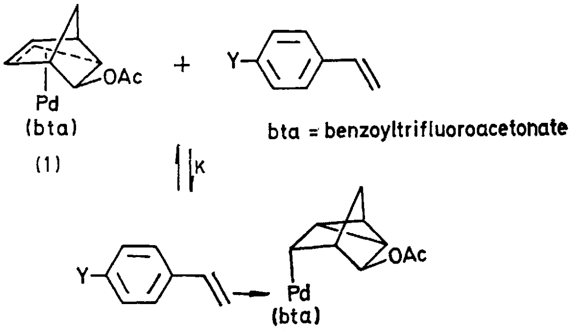
RECENT reviews[1] have concluded that the major factor determining the thermodynamic stabilities of olefin–Pt^{II} and –Pd^{II} bonds is the metal-*d*→olefin-π^* component of the Dewar–Chatt–Duncanson model. Studies of the effect of polar substituents on the enthalpy of formation of complexes $\{[CH_2{=}CH(CH_2)_nQ^+R^1R^2_2]PtX_3^-\}$ (R^1, R^2 = H, alkyl; Q = N, P, As; X = Cl, Br; n = 1, 2)[2] have been interpreted in these terms, even though variations in n, Q, R^1, and R^2 create a concomitant variation in steric factors close to the olefin–metal co-ordination site. A recent study of bond strengths[3] led to the conclusion that the Pd–N bond must have considerably more π-character than the Pd–olefin bond, a result that is unacceptable to the currently held view of metal ligand bonding in these compounds.[3] A reassessment of the thermodynamic significance of the metal-*d*→olefin-π^* component of Pd^{II}–olefin bonds is clearly indicated by the results presented below.

TABLE. *Thermodynamic parameters obtained for the equilibrium: complex* (**1**) + *p*-$YC_6H_4CH{=}CH_2 \rightleftharpoons$ *complex* (**2**) ($CDCl_3$ *solution;* 273—312 K).[a]

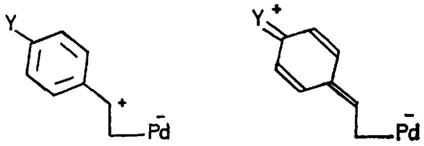
Y	ΔG° (kJ mol^{-1})	ΔH° (kJ mol^{-1})	ΔS° (J deg^{-1} mol^{-1})
NO_2	3·3 ± 0·4	−11·7 ± 2	50 ± 4
F	1·5 ± 0·4	−26·0 ± 2	92 ± 4
H	1·0 ± 0·4	−27·8 ± 2	96 ± 4
OMe	−1·0 ± 0·4	−33·0 ± 2	105 ± 4
NMe_2	−4·5 ± 0·4	−43·1 ± 2	126 ± 4

[a] $[(\mathbf{1})]_{initial}$ = [*p*-Y-$C_6H_4CH{=}CH_2]_{initial}$ = 0·82M; errors estimated from reproducibility of data for the equilibrium system with Y = H, varying the concentration range of the styrene from 0·40—1·00M.

^1H n.m.r. studies of the system (6-acetoxynorbornenyl)-Pd(benzoyltrifluoroacetonate) (**1**) + *p*-Y-$C_6H_4CH{=}CH_2 \rightleftharpoons$ (π-*p*-Y-$C_6H_4CH{=}CH_2$)(5-acetoxynortricyclenyl)Pd(benzoyltrifluoroacetonate) (**2**) provide an extremely simple route to values of the equilibrium constant (K).[4] For this system steric variations at the olefin–metal co-ordination site on changing the styrene substituent (Y) are expected to be negligible. $\log_{10}K$, at constant temperature (T), exhibits a linear dependence upon the σ_p^+ parameter of Y (ρ = − 0·54 at 34°). Plots of $\log_{10}K$ against $1/T$ are linear over the temperature range studied (273—312 K). Variations in ΔG°, ΔH°, and ΔS° as a function of Y are presented in the Table. There is a linear relationship between ΔH° and ΔS°.



(1) (2)



(3) (4)

The linear dependence of $\log_{10}K$ upon the σ_p^+ parameter of Y, rather than the Hammett σ_p value, indicates that resonance effects of Y are of importance in determining the value of K. The olefin-$\pi \rightarrow$metal-d σ-bonding component must be of predominant importance in determining the thermodynamic stability of the olefin–Pd bond in (**2**) since the reaction becomes more exothermic as the π-donor ability of Y increases. The observed changes in ΔS° on changing Y indicate an increased solvation requirement for (**2**) with increasing π-donor capability of Y. Increasing contributions from canonical forms (**3**) and (**4**) (*i.e.* Pd closer to the terminal olefinic C atom) as the donor properties of Y increases provides a reasonable rationalization of this feature. Similar proposals provide a rationalization of the ^{13}C n.m.r. and i.r. spectra of a series of styrene–Pt^{II} complexes.[5] Similar trends in ΔH° and ΔS° have long been known for substituted styrene complexes of Ag^{I}.[6] If metal-$d \rightarrow$ olefin-π^* back bonding was of prime importance in complexes (**2**) a reverse trend to that observed would have been anticipated for the ΔH° and ΔG° values.

These results indicate that the π-acceptor properties of olefins have been overemphasised in the interpretation of thermodynamic parameters. Supporting evidence for the dominance of the σ-donor properties of olefins has been recently obtained from ^{13}C n.m.r. data,[5,7] which indicate that the conclusions reached above should be equally applicable to olefin–Pt^{II} bonds since both Pd^{II} and Pt^{II} have comparable electronic requirements in their bonding to σ-carbon,[7] π-olefinic,[7,8] and π-allylic ligands.[7]

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[1] F. R. Hartley, *Chem. Rev.*, 1973, **73**, 163; *Angew. Chem. Internat. Edn.*, 1972, **11**, 569.
[2] R. G. Denning, F. R. Hartley, and L. M. Venanzi, *J. Chem. Soc.* (*A*), 1967, 324.
[3] W. Partenheimer, *Inorg. Chem.*, 1972, **11**, 743.
[4] R. P. Hughes and J. Powell, *J. Organometallic Chem.*, 1972, **34**, C51.
[5] D. G. Cooper, G. K. Hamer, J. Powell, and W. F. Reynolds, *J.C.S. Chem. Comm.*, 1973, 449.
[6] T. Fueno, T. Okuyama, T. Deguchi, and J. Furukawa, *J. Amer. Chem. Soc.*, 1965, **87**, 170.
[7] D. G. Cooper, R. P. Hughes, and J. Powell, *J. Amer. Chem. Soc.*, 1972, **94**, 9244.
[8] M. J. Grogan and K. Nakamoto, *J. Amer. Chem. Soc.*, 1968, **90**, 918.