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RELATIVE OLEFIN–METAL BOND STRENGTHS IN SOME PLATINUM (0) COMPOUNDS. PART II[1]

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ABSTRACT

Measurements are reported for the enthalpies of solution of:

$$L_2Pt\cdot \text{olefin (c)} + n\ C_6H_6 \rightarrow L_2Pt\cdot \text{olefin (sol'n)}$$

where L is triphenylphosphine and the olefins used were *cis*- and *trans*-1,2-diphenylethene. These enthalpies, when combined with other data, lead to the conclusion that the difference in the relative strengths of the platinum–olefin bonds (*trans*-1,2-diphenylethene > *cis*-1,2-diphenylethene > phenylethene) found previously arises mainly from electronic rather than from steric effects of the olefins in the complexes.

INTRODUCTION

In our recent paper on some calorimetric investigations of bis-(triphenylphosphine) (un) platinum (0) complexes (un = olefin) no explanation was offered for the difference in enthalpy of reaction for the complexes where un = *trans*-1,2-diphenylethene and un = *cis*-1,2-diphenylethene. In light of recent evidence from Ibers et al.[2,3] concerning some nickel (0) complexes and further studies on our part, it would appear that the majority of the difference probably arises from electronic effects resulting from the geometry of the olefin and not from the packing of the molecules in the crystal.

EXPERIMENTAL

The enthalpies of solution were determined in a single vessel submarine calorimeter of conventional design. The temperature was measured by a 2000 Ω thermistor (Fenwal G.B. 32P28), with a temperature coefficient of −3.2% per degree at 25°C. This was contained in a Wheatstone bridge circuit with 2000 Ω resistors in each arm, any off-balance voltage being detected by a Model 895A (John Fluke Manufacturing Company) D.C. differential voltmeter. This voltmeter can be read reliably to 1 μV, which corresponded to 2×10^{-4} degree. In general between 1 and 4×10^{-4} mole of compound was used in each run and this was dissolved in a considerable volume of benzene (105 ml was used).

Materials and procedures

Bis-(triphenylphosphine)-1,2-diphenylethene. The *cis* and *trans* isomers of this compound, L_2Pt C_6H_5CH: CHC_6H_5, were prepared from bis-(triphenylphosphine) platinum(II) carbonate as described previously[1].

Benzene. A.C.S. grade benzene, supplied by the Fisher Scientific Company, was used. This material was refluxed for 6 h under a nitrogen flush and allowed to cool under nitrogen before use as the calorimetric solvent.

Nitrogen. The nitrogen used was obtained by scrubbing dry nitrogen supplied by Canadian Oxygen Limited with Fieser's solution followed by concentrated sulfuric acid (containing Ag_2SO_4) and passage through a column of silica gel.

General procedure

The following procedure was followed for assembling and using the calorimeter for an experimental determination:

(i) The sample was weighed into the open sample holder.

(ii) The benzene to be used was deoxygenated as described above.

(iii) The benzene solvent in a closed flask, the calorimeter, sample holder and ancillary equipment were placed in a dry-box (Labconco serial 2531).

(iv) A large rubber bladder was inflated (with N_2) in the dry-box to give a positive displacement of the air in the dry box.

(v) The bladder was deflated by a nitrogen flush.

(vi) Steps (iv) and (v) were repeated twice.

(vii) The system was left overnight under a slow positive flow of nitrogen. This was monitored by a bubbler on the output flow.

(viii) After 14 h an internal pumping system was turned on to recirculate the nitrogen atmosphere of the dry-box through a deoxygenating solution. The system consisted of a Crown W Super aquarium pump and a Fieser's solution scrubbing and drying train.

(ix) After 24–48 h the calorimeter was assembled in the dry-box. Just before assembling the inner calorimeter 10^{-4} moles of compound were dissolved in the benzene in order to react with any residual oxygen which might have been present in the benzene. (This step was considered necessary since calculations based on previous experiments[4] have shown that as little as 5% reaction with oxygen could have a significant effect on the measured enthalpy.)

(x) The enthalpy of solution was measured with the inner calorimeter under a slight positive pressure of nitrogen.

RESULTS

The results are given in Table 1. Each result is the average from three experiments, with the average deviation given after the result. These values plus data for the reaction:

$$L_2Pt(c) + \text{olefin}(g) \xrightarrow{\Delta H_1} L_2\,Pt \cdot \text{olefin}(c) \qquad (1)$$

allow us to consider the following explanation for the differences in enthalpy, noted previously, for reaction (1) for the olefins cited in Table 2.

TABLE 1

ENTHALPY OF SOLUTION IN BENZENE AT 298 K

Complex	$\Delta H_{\mathrm{sol'n}}$ (*kJ mol*$^{-1}$)	*Mean* ΔH (*kJ mol*$^{-1}$)
L_2Pt (*cis*-olefin)	12.6, 10.9, 15.9	13.1 ± 1.8
L_2Pt (*trans*-olefin)	10.9, 11.1, 10.6	10.9 ± 0.2

where olefin = 1,2-diphenylethene

(also 1 determination for $L_2PtC_2H_4$: $\Delta H_{\mathrm{sol'n}} = 3.36$ kJ mol^{-1})

The similarity in these values indicates that large differences in the crystal lattice forces in the two complexes are not responsible for the difference in the enthalpy observed in reaction (1) for these two complexes.

DISCUSSION

A simple Hückel molecular orbital treatment of the π-systems of the olefins leads to the experimentally verifiable conclusion that the lowest unfilled molecular orbital (LUMO) decreases in energy as more phenyl groups are introduced. Hence, presumably back-bonding from the platinum becomes increasingly important as more phenyl groups are introduced and this leads to more stable complexes as seen in Table 2.

TABLE 2

Olefin	$\pi \rightarrow \pi^*$ (*nm*)	$E(\pi \rightarrow \pi^*)$ (*kJ mol*$^{-1}$)	*Reaction (1)* ΔH_1 (*kJ mol*$^{-1}$)
(A) phenylethene	245	488.2	−29.7
(B) *cis*-1,2-diphenylethene	272	440.0	−78.6
(C) *trans*-1,2-diphenylethene	294	406.9	−96.9

The difference between the *cis*- and *trans*-1,2-diphenylethene complexes may arise from the difference in the electronic effects of the two ligands. It has been pointed out by Ibers et al.[2] that experimentally the lowest observed transition in the electronic spectrum is 294 nm for *trans*-1,2-diphenylethene and 272 nm for *cis*-1,2-diphenylethene in accord with the sophisticated molecular orbital calculations of Beveridge and Jaffé[5].

This transition, assigned to $\pi \rightarrow \pi^*$ in both cases, indicates that the LUMO is higher in energy in *cis*-1,2-diphenylethene than in *trans*-1,2-diphenylethene, resulting in a poorer π-background for the *cis*-olefin.

This is in agreement with the chemical and spectroscopic results Ibers[2,3] reported for complexes of the type $L_2Ni(un)$, where L is tertiary butylisocyanide and un is one of a variety of unsaturated molecules.

The frequencies $\lambda(N{\equiv}C) = 2168$, 2100 and 2080 cm^{-1} for un = azobenzene, *trans*-1,2-diphenylethene and *cis*-1,2-diphenylethene, respectively, indicate that the molecules accept progressively less electron density from the nickel. Azobenzene forms a better π-bond than *trans*-1,2-diphenylethene and this in turn is better than *cis*-1,2-diphenylethene. This trend is also observed in exchange reactions converting one complex into another. Azobenzene easily displaces *trans*-1,2-diphenylethene and both of these molecules displace *cis*-1,2-diphenylethene from the respective isocyanide complexes.

It is also interesting to note that the difference in $\pi \rightarrow \pi^*$ transitions for the *cis*- and *trans*-olefins is 33.1 kJ mol^{-1} (Table 3). This value is larger than the difference of 18.3 kJ mol^{-1} observed for the platinum–olefin interactions. This is not unexpected since the molecular geometry of the olefin in the L_2Pt olefin complex might have reduced the more favourable interaction of the metal with the π^* level in *trans*-1,2-diphenylethene relatively more than in the *cis*-1,2-diphenylethene case. Free *cis*-1,2-diphenylethene already exhibits a degree of non-planarity whereas *trans*-1,2-diphenylethene is planar both in the solid and in solution[6,7]. In the complexes though, both probably assume a geometry with the phenyl groups rotated out of the plane. Indirect evidence for this is supplied by the crystal structure of (tri-*p*-tolylphosphine) *trans*-1,2-diphenylethenenickel(0)[2].

TABLE 3

	I	*II*	*I–II*
Difference	$\Delta E(\pi \rightarrow \pi^*)$ *(kJ mol⁻¹)*	$\Delta(\Delta H_1)$ *(kJ mol⁻¹)*	*(kJ mol⁻¹)*
A–B	48.2	48.9	−0.7
A–C	81.3	67.2	14.1
B–C	33.1	18.3	14.8

In this complex the phenyl rings are rotated out of the plane of the olefin and this distortion will increase the energy of the π^* (the LUMO) level, making the interaction with the metal less favourable. This effect of the orientation of the phenyl rings on the energy levels in the free olefin has been demonstrated in the case of *cis*-1,2-diphenylethene by Jaffé et al.[5]. The only other complex of this type with a known crystal structure is 4,4′-dinitro-*trans*-1,2-diphenylethenebis(triphenylphosphine) platinum(0) in which the plane of each ring is perpendicular to the plane defined by platinum and the two olefinic carbon atoms. This geometry is considered to be the necessary result in order to obtain maximum overlap of the π-symmetry orbitals of the nitro-substituted substituents[8].

It must also be pointed out that any rotation of the phenyl groups out of the plane defined by the olefinic carbons and hydrogens means that there would be poorer angular overlap between the metal orbitals and the π-system of the ligand. This would also tend to reduce the metal–olefin interaction resulting in a weaker bond.

The differences, A−B, A−C, B−C and I−II, given in Table 3 could be interpreted as indicating that rotation of the phenyl groups has reduced the π-back-bonding interaction more in the *trans*-1,2-diphenylethene complex than in the *cis* complex. In effect the expected value of the difference in back-bonding interaction (Table 3, column 1) based on the free olefin relative to free phenylethene is greater than that actually observed (Table 3, column 2) in the case of *trans*-1,2-diphenylethene, whereas in the case of the *cis*-olefin it has the expected value. This may arise from the possibility that the change in orientation of the phenyl rings, on going from the free to the complexed olefin, is greater in the case of the *trans* isomer.

REFERENCES

1 William B. Kirkham, Maurice W. Lister and R. Barry Poyntz, *Thermochim. Acta*, 11 (1975) 89.
2 Steven D. Ittel and James A. Ibers, *J. Organomet. Chem.*, 74 (1974) 121.
3 Steven D. Ittel and James A. Ibers, *J. Organomet. Chem.*, 57 (1973) 389.
4 W. B. Kirkham and M. W. Lister, unpublished results.
5 David L. Beveridge and H. H. Jaffé, *J. Amer. Chem. Soc.*, 87 (1965) 5340.
6 J. Monteath Robinson and I. Woodward, *Proc. Roy. Soc. (London)*, A162 (1937) 493.
7 Hiroshi Suzuki, *Bull. Chem. Soc. Japan*, 33 (1960) 379.
8 Jay M. Baraban and John A. McGinnety, *Inorg. Chem.*, 13 (1974) 2864.