Thermochemistry of Platinum–Benzoyl and Platinum–Dibenzylideneacetone Complexes †

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The enthalpies of thermal decarbonylation of $(PPh_3)_2ClPt(RCO)$ complexes, where RCO = benzoyl or substituted benzoyl, have been measured by differential scanning calorimetry. A minimum value of 180 kJ mol^{-1} is calculated for the platinum–benzoyl bond dissociation energy. A value of 273 kJ mol^{-1} is calculated for the dissociation energy of the platinum–carbon π-bond in the complex bis(dibenzylideneacetone)platinum(0) from calorimetric measurements.

RECENT reviewers [1-3] of transition metal–carbon compounds have suggested, mainly from spectroscopic and bond-length data, that the long-held view of inherently weak bonding is unfounded. Thermochemical data for the strength of bonding between carbon and metals of the platinum group are particularly scarce, but strong bonds are indicated by the values

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† A preliminary account of this work was communicated by Dr. C. T. Mortimer to a meeting of the Société Chimique de France held at Bordeaux, 20–21 October, 1972.

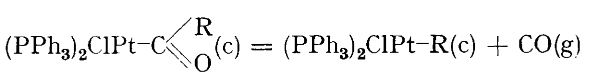
[1] P. S. Braterman and R. J. Cross, *J.C.S. Dalton*, 1972, 657.

[2] F. Calderazzo, *Pure and Appl. Chem.*, 1973, **33**, 453.

[3] S. J. Ashcroft and G. Beech, ' Inorganic Thermodynamics,' van Nostrand–Reinhold, London, 1973, ch. 5.

available[4,5] for the σ-bond in $(PEt_3)_2PtPh_2$ and the π-bond in $[(allyl)PdCl]_2$.

We report thermal and thermochemical studies on two types of platinum complex, both of which undergo quantitative breaking of metal–carbon bonds. The first type of complex is one in which a benzoyl (or substituted benzoyl) group attached to Pt^I is thermally converted into the corresponding phenyl complex by a decarbonylation (1). The second type of complex is bis(dibenzylideneacetone)platinum(0) in which platinum–carbon bonds are thermally broken according to reaction (2), where the ligand is represented by (dba).



$$(PPh_3)_2ClPt\text{–}C\overset{R}{\underset{O}{\lessgtr}}(c) = (PPh_3)_2ClPt\text{–}R(c) + CO(g) \quad (1)$$

$$Pt(dba)_2(c) = Pt(c) + 2(dba)(l) \qquad (2)$$

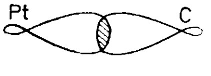
RESULTS AND DISCUSSION

The Table summarizes results for the temperatures of onset of thermal decomposition, enthalpies of thermal decarbonylation [reaction (1)], and the i.r. stretching ' frequencies ' for a number of benzoyl and substituted benzoyl complexes. The *o*-chlorobenzoyl, *m*-chlorobenzoyl, and the acetyl complexes, for which some results are given in the Table, decomposed to unidentified products. The decarbonylation processes for these complexes could not be separated clearly from further decomposition and no enthalpy changes could be measured.

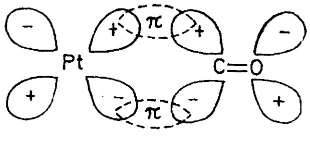
Results for the thermal decarbonylation (1)

RCO	Decarbonylation temperatures/K T_i	T_p	T_f	ΔH/kJ mol⁻¹ decarbonylation	ν(C=O)/cm⁻¹ of benzoyl group
PhCO	445	480	495	33·9 ± 1·4	1614
p-$Cl{\cdot}C_6H_4{\cdot}CO$	400	415	425	30·0 ± 1·0	1630
p-$Me{\cdot}C_6H_4{\cdot}CO$	425	443	450	20·0 ± 1·0	1615
p-$NO_2{\cdot}C_6H_4{\cdot}CO$	460	480	490	18·6 ± 0·5	1624
Ac	545			—	1644
o-$Cl{\cdot}C_6H_4{\cdot}CO$	413			—	1638
m-$Cl{\cdot}C_6H_4{\cdot}CO$	403			—	—

The bond between platinum and benzoyl in these complexes is probably, first an overlap of a carbon sp^2 orbital on the carbonyl group with a platinum σ-orbital (a), and secondly an overlap of a filled platinum d_π-orbital with empty antibonding π*-orbitals on the ligand (b). A significant involvement of the carbonyl antibonding π*-orbitals should weaken the C=O bond. In agreement with this, we observe a decrease in ν(C=O) from *ca.* 1700 cm⁻¹ in an uncomplexed aryl ketone to 1614 cm⁻¹ in the benzoyl complex. For the acetyl complex the carbonyl absorption occurs at 1644 cm⁻¹, close to the value[6] (1635 cm⁻¹) for the equivalent triethylphosphine complex.



(a)



(b)

Baird and Wilkinson have suggested[7] that the benzoyl complex has the *trans*-configuration. It seems likely that the substituted benzoyl complexes also have this configuration, but it is not certain that the *para*-position of the substituents is retained during decarbonylation (1). For the substituted benzoyl complexes, the values of ΔH decrease down the Table. It appears that substitution of either electron-withdrawing groups (Cl, NO_2) or electron-donating groups (Me) into the benzene ring causes a reduction in the enthalpy change when compared with the unsubstituted complex. The influence of benzene ring substituents is likely to be felt more by the direct platinum–phenyl bond of the reaction product than by the Pt–C bond of the initial benzoyl complex in which a CO group separates Pt and the ring. Relative strengthening of the former bond compared with the latter would lead to decreasing endothermicity of the decarbonylation (1). Such strengthening might occur by a σ–π mechanism. Platinum(I), with a $5d^9$ configuration, is able to donate π-electron density back to an antibonding orbital of the phenyl ring. The reverse mechanism, donation from the ring to the $5d^9$ shell of platinum(I), is less likely. Electron-withdrawing groups, such as NO_2 and Cl, should weaken the Pt–C σ-bond but this may be outweighed by the strengthening of the π-bond. Electron-donating groups, such as Me, should strengthen the Pt–C σ-bond and will leave the π-bond unaffected.

An estimate of the platinum–benzoyl bond dissociation energy may be obtained if the assumption is made that the enthalpy change for the gas-phase decarbonylation (3) is close to the value 33·9 kJ mol⁻¹ found for the crystalline species [reaction (1)]. This enthalpy change represents the difference [equation (4)] between the bond dissociation energies of the bonds broken (Pt–PhCO and Ph–CO) and those formed (Pt–Ph). The values of D(Ph–CO) = 126 kJ mol⁻¹ and D(Pt–Ph), recalculated from more recent subsidiary data to be 272 kJ mol⁻¹, are available.[4,8,9] These lead to D(Pt–PhCO) = 180 kJ mol⁻¹, indicating a moderately strong platinum–carbon bond, rather weaker than the direct platinum–phenyl bond.[4] The value may be compared

$$(PPh_3)_2ClPt(PhCO)(g) = (PPh_3)_2ClPt(Ph)(g) + CO(g) \quad (3)$$

$$\Delta H(3) = D(Pt\text{–}PhCO) + D(Ph\text{–}CO) - D(Pt\text{–}Ph) \quad (4)$$

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[4] S. J. Ashcroft and C. T. Mortimer, *J. Chem. Soc.* (*A*), 1967, 930.

[5] S. J. Ashcroft and C. T. Mortimer, *J. Chem. Soc.* (*A*), 1971, 781.

[6] D. M. Adams and G. Booth, *J. Chem. Soc.*, 1962, 1112.

[7] M. C. Baird and G. Wilkinson, *J. Chem. Soc.* (*A*), 1967, 865.

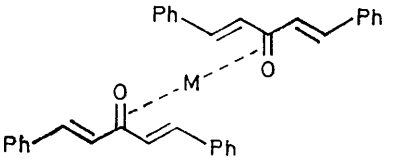
[8] J. A. Kerr, *Chem. Rev.*, 1966, **66**, 465.

[9] National Bureau of Standards, Technical Notes 270—3,4, Washington D.C., 1968, 1969.

with a mean nickel–carbonyl bond dissociation energy of 147 kJ mol^{-1} in nickel tetracarbonyl.[9,10] It should be noted that the value we have used for D(Pt–Ph) is actually a minimum value for the mean bond dissociation energy in the complex *trans*-$(PEt_3)_2PtPh_2$. The platinum–benzoyl bond energy is thus also a minimum value.

Qualitative confirmation of the increase in Pt–C bond strength from benzoyl to phenyl ligands is available from the far-i.r. spectra of the species. Although we have not positively identified the Pt–C absorption frequencies, the Pt–Cl stretching frequency decreases from 337 cm^{-1} in the benzoyl complex to 284 cm^{-1} in the phenyl complex. This weakening of the platinum–chlorine bond implies a strengthening of the platinum–carbon bond, in agreement with the thermochemical results.

Finally, we have studied the thermal properties of the complexes bis(dibenzylideneacetone)-platinum(0) and -palladium(0). The minor changes in the i.r. spectrum of dibenzylideneacetone on complex formation indicate [11,12] that a π-type of bond is involved. Quantitative thermal removal of dibenzylideneacetone occurs according to reaction (2) only for the platinum complex. At 438 K we find that $\Delta H(2) = 26{\cdot}2 \pm 0{\cdot}8$ kJ mol^{-1}. Decomposition of the palladium complex to unidentified products occurs at 430 K. We have measured the enthalpy of fusion of dibenzylideneacetone at its m.p. of 386 K, $\Delta H(5)$ $22{\cdot}6 \pm 0{\cdot}1$ kJ mol^{-1}. These



$$\mathrm{dba(c)} = \mathrm{dba(l)} \qquad (5)$$

lead to a value of $\Delta H(6) = -19{\cdot}0 \pm 1{\cdot}0$ kJ mol^{-1} for the decomposition (6) entirely in the solid phase. It is

$$\mathrm{Pt(dba)_2(c)} = \mathrm{Pt(c)} + 2\mathrm{dba(c)} \qquad (6)$$

expected that the major contribution to the conversion of this enthalpy value to that for the reaction completely in the gas phase will be the enthalpy of sublimation of platinum,[9] $\Delta_{\mathrm{c}}^{\mathrm{g}}H(\mathrm{Pt,c}) = 565$ kJ mol^{-1}. On this basis we calculate a mean Pt–(dba) bond dissociation energy of 273 kJ mol^{-1} indicating a strong π-type of bond. For comparison, the palladium–π-allyl mean bond dissociation energy in $[(\pi\text{-}C_3H_5)PdCl]_2$ is 237 kJ mol^{-1}. Stronger bonding is generally expected for platinum than palladium.

EXPERIMENTAL

Materials.—$(PPh_3)_3Pt$ was made [13] from K_2PtCl_4 and PPh_3. The benzoyl and substituted benzoyl complexes were made under an atmosphere of nitrogen, as described by Baird and Wilkinson [7] for the benzoyl species, from benzoyl chloride (AnalaR) or substituted benzoyl chlorides (Koch–Light). The solid *p*-nitrobenzoyl chloride was used as a solution in diethyl ether. The complexes were recrystallized from methanol–chloroform or methanol–dichloromethane.

$Pt(dba)_2$ and $Pd(dba)_2$ were made from K_2PtCl_4, Na_2PdCl_4, and dibenzylideneacetone (or 1,5-diphenylpentadien-3-one, Kodak) respectively, as described.[11,12]

All compounds showed satisfactory analyses for C, H, and N. The quantitative nature of reaction (1) was checked by measuring the change in mass associated with the loss of CO during the calorimetric experiments, and also by thermogravimetry. An attempt to make palladium–benzoyl complexes by reactions analogous to those used for the platinum complexes produced crystalline material which, whilst undergoing smooth thermal decomposition, did not show correct C, H, N analyses nor correct mass losses for decarbonylation.

Measurements.—Enthalpies of reactions were measured on a Perkin-Elmer Differential Scanning Calorimeter DSC 1B. The temperatures T_i, T_p, and T_f in the Table refer [14] to the initial, ' peak ', and final temperatures respectively of the decarbonylation. The uncertainties attached to ΔH values are twice the standard deviations of the means of at least four determinations of each quantity.

I.r. spectra were recorded on a Hilger and Watts Infrascan instrument as KBr discs, and on a Perkin-Elmer instrument as Nujol mulls between NaCl or Polythene plates.

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[14] G. Beech, C. T. Mortimer, and E. G. Tyler, *J. Chem. Soc.* (*A*), 1967, 925.