Effect of Organic Groups on the Carbonyl-insertion Reaction of Platinum(II)

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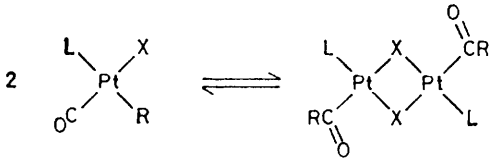
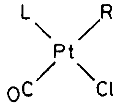
The equilibria between the isomers of [PtCl(R)(CO)(PMePh$_2$)] which undergo CO insertion and their halide-bridged insertion products [Pt$_2$Cl$_2$(COR)$_2$(PMePh$_2$)$_2$] have been examined for 12 *ortho*-, *meta*-, and *para*-substituted aryl groups, R. Values of the equilibrium constants, enthalpy, and entropy of the reactions are presented. The electronic effects of the aryl groups on this R migration reaction are found to be at least as critical as any previously reported factors influencing this process. Electron-donating substituents in *meta*- or *para*-positions promote the insertions, whereas electron-withdrawing groups inhibit them. A correlation with Hammett σ values is found. *Ortho*-substituents tend to prevent the reaction for steric reasons. Enthalpies of the reactions become less negative with electron-withdrawing groups, and this may reflect strengthening Pt–aryl bonds.

ISOMER (I) of [PtX(R)(CO)L] (X is halide; L is tertiary phosphine or arsine) undergoes R migration to form the halide-bridged acyl or aroyl complex, (IV), with which it equilibrates in solution, equation (1).[1,2] In the presence of added ligand, L, the equilibrium is usually displaced to produce *trans*-[PtX(COR)L$_2$], although in some cases when the equilibrium position is well to the left, L displaces CO from (I) to form *trans*-[PtX(R)L$_2$] instead. The other two isomers of [PtX(R)(CO)L], (II) and (III), resist attempts to promote CO insertion, although they equilibrate with each other in solution, and are slowly converted into (I) and (IV).[1-3]

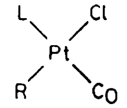


(I) (IV)

(1)



(II)



(III)

The bis(phosphine) compounds *trans*-[PtX(R)L$_2$] react with CO to produce *trans*-[PtX(COR)L$_2$] *via* two pathways.[3,4] In one, migration-insertion to form the aroyl product occurs at a five-co-ordinate intermediate [PtX(R)(CO)L$_2$] of unknown geometry; the other route is *via* loss of L to form (II) and/or (III), which isomerises to (I) before R migration occurs.[3] Which of the two pathways dominates depends on the nature of the substituents.

The ready observation of the (I) $\rightleftharpoons$ (IV) equilibria makes the system ideal for examining the effects of varying reaction conditions and substituent groups at the metal. Thus acyl or aroyl formation is favoured by neutral ligands, L, of strong *trans* influence, and by halides, X, which form strong bridge bonds.[2] A steric effect also operates, however. Bulky L block the migration of R. The nature of the organic group itself has a profound effect on the (I) $\rightleftharpoons$ (IV) equilibrium position, with (IV) being favoured by R = Et (*ca.* 90% in a 0.02 mol dm^{-3} solution) > Ph > Me > CH$_2$Ph [where (IV) could not be detected]. We report here a systematic investigation into the effects of the organic group on this R migration reaction.

RESULTS AND DISCUSSION

Isomers (I) and/or complexes (IV) were prepared in good yield from the reactions of *cis*-[PtCl$_2$(CO)(PMePh$_2$)] and HgR$_2$ in chloroform (R = C$_6$H$_4$NMe$_2$-*p*, C$_6$H$_4$OMe-*p*, C$_6$H$_5$,[1] C$_6$H$_4$Cl-*p*, C$_6$H$_4$OCOMe-*p*, C$_6$H$_4$CN-*p*, C$_6$H$_4$-Me-*p*, C$_6$H$_4$Cl-*m*, C$_6$H$_4$Me-*m*, C$_6$H$_4$OMe-*m*, C$_6$H$_4$-OMe-*o*, and C$_6$H$_4$Me-*o*). Most reactions were complete after *ca.* 30 min at ambient temperatures, but those of the *ortho*-substituted aryls required considerably longer to reach completion (*ca.* 24 h). In most cases, complex (IV) was isolated as a crystalline solid after the arylmercury(II) halide by-product had been removed by vacuum sublimation, chromatography on silica gel, or fractional crystallisation. The solid materials appeared to be indefinitely stable in air at ambient temperatures, although in solution the platinum complexes decomposed in a matter of days, the rate being accelerated by contact with air. The sparingly soluble complex [Pt$_2$(μ-Cl)$_2$(COC$_6$H$_4$NMe$_2$-*p*)$_2$(PMePh$_2$)$_2$] resisted recrystallisation attempts. It was produced along with a red solution which yielded a green solid, believed to be Mischler's ketone. Addition of PMePh$_2$ to solutions of [Pt$_2$(μ-Cl)$_2$(COC$_6$H$_4$NMe$_2$-*p*)$_2$(PMePh$_2$)$_2$] yielded *trans*-[PtCl(COC$_6$H$_4$NMe$_2$-*p*)(PMePh$_2$)$_2$]. The platinum complexes with R = C$_6$H$_4$OMe-*o*, C$_6$H$_4$Me-*o*, and C$_6$H$_4$CN-*p* also resisted attempts at purification and proved to be viscous liquids at room temperature [only isomers (I) were detectable for these R groups]. Addition of PMePh$_2$ to these complexes displaced CO to produce *trans*-[PtCl(R)(PMePh$_2$)$_2$]. Analytical data, ^{31}P n.m.r. spectroscopic parameters, and values of ν(CO) from their i.r. spectra are presented in Table 1.

The equilibria positions for the (I) $\rightleftharpoons$ (IV) migration reactions were calculated from the integrations of the ^{31}P n.m.r. spectra of the compounds isolated. Values of the equilibrium constants calculated at two dilutions

TABLE 1

Analytical and spectroscopic data

Compound ($L = PMePh_2$)	Analysis (%) [a]		^{31}P N.m.r. [b] (δ/p.p.m.) [d]	$\nu(CO)$ [c]/cm^{-1}
	C	H		
$[PtCl(C_6H_4OMe\text{-}p)(CO)L]$			7.06 (1 417)	2 084
$[Pt_2Cl_2(COC_6H_4OMe\text{-}p)_2L_2]$	44.6 (44.6)	3.4 (3.5)	−3.32 (5 362)	1 626
$[PtCl(C_6H_4Me\text{-}p)(CO)L]$			7.00 (1 402)	2 087
$[Pt_2Cl_2(COC_6H_4Me\text{-}p)_2L_2]$	45.85 (45.85)	3.5 (3.6)	−3.33 (5 355)	1 628
$[PtCl(C_6H_4Cl\text{-}p)(CO)L]$			6.44 (1 440)	2 086
$[Pt_2Cl_2(COC_6H_4Cl\text{-}p)_2L_2]$	42.1 (42.1)	2.8 (3.0)	−3.40 (5 268)	1 639
$[PtCl(C_6H_4CO_2Me\text{-}p)(CO)L]$			6.16 (1 430)	2 093
$[Pt_2Cl_2(COC_6H_4CO_2Me\text{-}p)_2L_2]$	44.3 (44.5)	3.4 (3.4)	−3.10 (5 232)	1 635
$[PtCl(C_6H_4CN\text{-}p)(CO)L]$			5.67 (1 463) [e]	2 090
$[Pt_2Cl_2(COC_6H_4NMe_2\text{-}p)_2L_2]$			−3.20 (5 443)	1 615
$[PtCl(C_6H_4OMe\text{-}m)(CO)L]$			6.50 (1 409)	2 090
$[Pt_2Cl_2(COC_6H_4OMe\text{-}m)_2L_2]$	44.7 (44.6)	3.7 (3.5)	−3.49 (5 315)	1 635
$[PtCl(C_6H_4Me\text{-}m)(CO)L]$			6.86 (1 395)	2 086
$[Pt_2Cl_2(COC_6H_4Me\text{-}m)_2L_2]$	45.7 (45.85)	3.5 (3.6)	−3.36 (5 342)	1 631
$[PtCl(C_6H_4Cl\text{-}m)(CO)L]$			5.99 (1 450)	2 085
$[Pt_2Cl_2(COC_6H_4Cl\text{-}m)_2L_2]$	42.3 (42.1)	3.0 (3.0)	−3.24 (5 203)	1 640 [f]
$[PtCl(C_6H_4OMe\text{-}o)(CO)L]$			6.56 (1 517) [e]	2 090
$[PtCl(C_6H_4Me\text{-}o)(CO)L]$			7.05 (1 442) [e]	2 084
trans-$[PtCl(C_6H_4OMe\text{-}o)L_2]$	53.5 (53.7)	4.7 (4.5)	8.2 (2 992)	
trans-$[PtCl(C_6H_4Me\text{-}o)L_2]$	54.8 (54.9)	4.7 (4.6)	7.5 (3 016)	
trans-$[PtCl(C_6H_4CN\text{-}p)L_2]$	54.1 (54.1)	3.7 (4.1) [g]	8.6 (2 912)	
trans-$[PtCl(COC_6H_4NMe_2\text{-}p)L_2]$			5.4 (3 282)	1 615

[a] Calculated values are given in parentheses. [b] In $CDCl_3$ at 38 °C, δ is positive downfield of external H_3PO_4. [c] In $CHCl_3$ at ambient temperatures. [d] J(PPt)/Hz in parentheses. [e] In $CDCl_3$ at ambient temperatures. [f] KBr disc. [g] N, 2.2 (1.9)%.

agreed well. Errors arising from the integration are calculated at *ca.* 15%. Values of K_c, the equilibrium constant, are presented in Table 2 for two temperatures, along with the percentage of each component found in *ca.* 0.06 mol dm^{-3} solutions at 38 °C. The K_c values allow calculation of K_p [$= K_c(RT)^{-1}$], from which estimates can be made for $\Delta H^\ominus$ and $\Delta S^\ominus$ for the insertion reaction, and these are also presented in Table 2.

TABLE 2

Thermodynamic data on the equilibrium
$2[PtCl(R)(CO)(PMePh_2)] \rightleftharpoons [Pt_2Cl_2(COR)_2(PMePh_2)_2]$

R	% (IV) [a]	% (I) [a]	K_c/dm^3 mol^{-1} at 38 °C	K_c/dm^3 mol^{-1} at −11 °C	$\Delta H^\ominus$/kJ mol^{-1}	$\Delta S^\ominus$/J K^{-1} mol^{-1}
$C_6H_4NMe_2\text{-}p$	100	0	∞			
$C_6H_4OMe\text{-}p$	88	12	2 170	→∞	−60	−200
$C_6H_4Me\text{-}p$	76	24	360	14 400	−55	−190
$C_6H_4Me\text{-}m$	64	36	140	7 080	−56	−200
C_6H_5 [b]	54	46	100	2 160	−44	−170
$C_6H_4OMe\text{-}m$	45	55	70	990	−38	−150
$C_6H_4Cl\text{-}p$	27	73	20	375	−45	−190
$C_6H_4Cl\text{-}m$	12	88	3.3	13	−20	−120
$C_6H_4OCOMe\text{-}p$	12	88	3.3	11	−20	−120
$C_6H_4CN\text{-}p$	0	100	0	0		
$C_6H_4Me\text{-}o$	0	100	0	0		
$C_6H_4OMe\text{-}o$	0	100	0	0		

[a] *ca.* 0.06 mol dm^{-3} in $CDCl_3$ at 38 °C. [b] Errors in K_c are calculated at ±20% for this compound. Values agree well with published data from other methods.

The K_c values for the *para*- and *meta*-substituted aryls span the entire range from near 0 to approaching ∞, indicating that electronic effects at the aryl groups exert at least as big an effect on the R migration process at platinum as varying the neutral or anionic ligands,[2] or changing alkyl substituents from ethyl to benzyl.[1] The *ortho*-substituted aryls don't fit the sequence, indicating that steric crowding blocks the migration of the organic group. Bulky phosphine ligands have a similar effect.[2] Electron-donating substituents in *m* or *p* positions promote the carbonyl-insertion reaction, and the order follows the sequence of Hammett σ constants, but not Taft σ_I or σ_R values (Table 3). Thus, it is the *overall* electron-donating or -withdrawing properties which influence these reactions.

TABLE 3

Hammett and Taft σ values *

R	Hammett σ	Taft σ_I	Taft σ_R
$C_6H_4NMe_2\text{-}p$	−0.60		
$C_6H_4OMe\text{-}p$	−0.27	+0.23	−0.50
$C_6H_4Me\text{-}p$	−0.17	−0.05	−0.13
$C_6H_4Me\text{-}m$	−0.07	−0.05	−0.02
C_6H_5	0	0	0
$C_6H_4OMe\text{-}m$	+0.12	+0.23	−0.11
$C_6H_4Cl\text{-}p$	+0.23	+0.47	−0.24
$C_6H_4Cl\text{-}m$	+0.37	+0.47	−0.10
$C_6H_4OCOMe\text{-}p$	+0.45	+0.31	+0.14
$C_6H_4CN\text{-}p$	+0.66	+0.59	+0.07

* L. P. Hammett, 'Physical Organic Chemistry,' 2nd edn., McGraw-Hill, New York, 1970; M. S. Newman, 'Steric Effects in Organic Chemistry,' Wiley, New York, 1963; A. W. Neuse, *J. Organomet. Chem.*, 1975, **99**, 287.

The magnitude of the changes in the K_c values reported is comparable to that for the sequence R = Et, Ph, Me, CH_2Ph.[1] This sequence in turn closely resembles that reported for the equilibria (2) for manganese complexes

$$[MnR(CO)_5] + CO \rightleftharpoons [Mn(COR)(CO)_5] \qquad (2)$$

for which K_c values of 3 300 (Et), 366 (Me), 66 (Ph), and 0 dm^3 mol^{-1} (CH_2Ph) have been published.[5] The relative rates of the forward reactions also reflect this order, with R = Et (13) > Ph (1.7) > Me (1.0) > CH_2Ph (0).[6] It seems reasonable, therefore, to conclude that these equilibrium-constant variations for manganese and platinum complexes largely reflect changes in the ease of the forward (R migration) reaction.

Whilst no other work on the CO insertion reaction involves so extensive an array of organic groups, a number of kinetic studies on substituted benzyls and related alkyls show similar variations at several metals.[7] The effects are not as pronounced, since the site of the electronic variation is further removed from the metal atom. In all these studies also, electron-donating groups enhance the CO insertion step and electron-withdrawing substituents inhibit it. The reverse is frequently (although not exclusively) true for a number of examples of the reverse step: CO elimination from an acyl to form an alkyl group.[7]

Heck and co-workers[4,8] examined the effect of a limited series of *para*-substituted aryls on the rate of CO insertion at *trans*-[PtX(R)L$_2$]. The reaction-rate sequence for the organic groups examined followed the same order as our K_c values, but the magnitude of the observed variation from C$_6$H$_4$Cl-*p* to C$_6$H$_4$Me-*p* changed from a factor of only two for L = P(C$_6$H$_4$Me-*p*)$_3$[4] to a factor of 20 when L = PPh$_3$[8] {the last values assume a constant value for the equilibrium constants for [PtX(R)L$_2$] + CO $\rightleftharpoons$ [PtX(R)(CO)L$_2$]}. The magnitude of the variation in our results for the four-co-ordinate migration route falls close to Heck's values for the PPh$_3$ complexes, and implies a similar effect of the R groups on the two pathways. Nevertheless, it is clear that the nature of the tertiary phosphine has a profound effect on the five-co-ordinate route also. Since Heck found much less significance in the variations of R for his dissociative pathway, the R migration step cannot be rate determining in that reaction sequence.[3,4,8] Kubota *et al.*[9] also found little dependence on R for the reverse reaction, decarbonylation, by this route.

Thermodynamic data for CO insertion sequences are still scarce.[7] It has been suggested that a large contribution to the enthalpy of the process simply reflects the difference between the M–R and M–COR bond energies. Thus weaker M–R bonds favour formation of acyl or aroyl complexes. In the present work, the energy terms derived encompass two processes, the migration reaction to form the aroyl complex and halide-bridge formation to complete the dimers, (IV). The large negative entropy values (Table 2) reflect the dimer formation.* The enthalpy values cannot be equated directly to the aryl ⟶ aroyl process, but by making the reasonable assumption that the strengths of the chloride bridges of (IV) will not vary greatly from compound to compound, the differences in ΔH will relate to differences in the enthalpy of the R migration step. It is tempting to suggest that the observed trend towards less negative ΔH values with increasing electron-withdrawing power of the aryl groups may reflect strengthening Pt–R bonds, with the Pt–COR and PtC(O)–R bond-energy terms of the aroyls remaining fairly constant. This is probably not the case with the *ortho*-substituted aryls, however, where steric crowding of the aroyl may mean reduction of bond energies at that side of the equilibria.

These thermodynamic results are somewhat at variance with calorimetric studies by Ashcroft *et al.*[10] on the decarbonylation of *trans*-[PtCl(COR)(PPh$_3$)$_2$] (R = Ph, C$_6$H$_4$Me-*p*, C$_6$H$_4$Cl-*p*, or C$_6$H$_4$NO$_2$-*p*). There, both electron-withdrawing and -donating substituents were found to reduce the enthalpy change and thus favour CO elimination. Although the error margins (*ca.* 20%) in our values of $\Delta H^\ominus$ could mask any minor variations, the overall trend is clear and would lead us to expect that the electron-donating 4-methyl substituent would disfavour CO elimination. It should be noted that Heck and co-workers,[8] who measured the kinetics of the reverse reaction to Ashcroft's process, found a rate progression of C$_6$H$_4$NO$_2$-*p* < C$_6$H$_4$Cl-*p* < C$_6$H$_5$ < C$_6$H$_4$Me-*p*, in complete agreement with our results.

Finally, it can be noted that even slow addition of solutions of PMePh$_2$ to solutions of [PtCl(R)(CO)(PMePh$_2$)] [isomers (I)] failed to promote insertion in the cases where R = C$_6$H$_4$CN-*p*, C$_6$H$_4$Me-*o*, and C$_6$H$_4$OMe-*o*. Carbon monoxide was eliminated instead. This indicates that the immeasurably small (I) $\rightleftharpoons$ (IV) equilibrium constants for these complexes are less than that when R = CH$_2$Ph, since in that case careful addition of PMePh$_2$ trapped the inserted material to yield *trans*-[PtCl(COCH$_2$Ph)(PMePh$_2$)$_2$].[1]

EXPERIMENTAL

Phosphorus-31 n.m.r. spectra were recorded on a Varian XL-100 spectrometer operating in the Fourier-transform mode, with CDCl$_3$ locking signal, and integrated to determine the equilibrium constants. The accuracy of the integrations was confirmed by calibration experiments with mixtures of pure compounds which did not equilibrate in solution. Infrared spectra were recorded on a Perkin-Elmer 577 spectrophotometer (0.02 mol dm^{-3} solutions in CHCl$_3$) or a Perkin-Elmer 580 spectrophotometer (KBr discs).

The mercurials were prepared by standard methods,[11] forming first the arylmercury(II) salt by mercuriation of the arene or *via* the arenediazonium salt, then symmetrising the mercurials to form bis(aryl)mercury. All are known compounds.[11]

The platinum complexes were prepared according to published procedures.[1-3] Spectroscopic and analytical data for the new compounds are presented in Table 1.

We thank Dr. D. S. Rycroft of this Department for help and advice in obtaining the n.m.r. spectra.

[1/519 *Received, 1st April,* 1981]

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* The variations in $\Delta S^\ominus$ presumably reflect changes in solvation or internal degrees of freedom. We cannot explain the trend observed.

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