

The rhodium-catalysed methanolysis of aryl acetates and of the hexafluorophosphate anion

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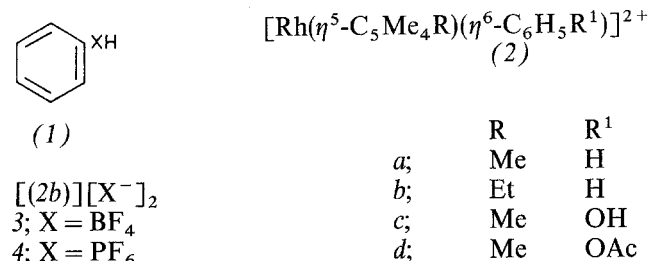
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Summary

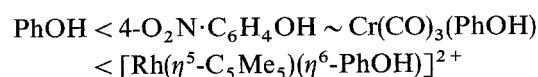
In nitromethane, the methanolysis of aryl acetates is catalysed by the tetrafluoroborate and hexafluorophosphate salts of the (η^5 -ethyltetramethylcyclopentadienyl)(η^6 -benzene)rhodium(III) cation. Under the conditions of the methanolysis, the anion of the latter salt reacts with methanol to give dimethyl phosphorofluoridate. The hydrogen fluoride formed also in this reaction is thought to be responsible for the greater efficiency of the hexafluorophosphate salt as a catalyst for the methanolysis.

Introduction

There are now many examples which illustrate that the acidity of the XH group in compounds of the general type (1) is increased by η^6 -coordination of the arene ring with zerovalent transition-metals such as chromium(0), iron(0) and molybdenum(0). For example, in 50% aqueous ethanol the phenol complex, $\text{Cr}(\text{CO})_3(\text{PhOH})$, has a pK_a value of 7.09⁽¹⁾ and is therefore comparable in acidity to 4-nitrophenol (pK_a 7.16, in water)⁽²⁾ rather than to phenol (pK_a 11.02)⁽¹⁾ itself. In the case of (1; $X = \text{CR}^1\text{R}^2$), the increase in acidity has been used widely to functionalise the benzylic position of benzenoid aromatics via chromium tricarbonyl complexes of the type $\text{Cr}(\text{CO})_3(\text{Ar}\cdot\text{CHR}^1\text{R}^2)$ ⁽³⁾. η^6 -Coordination with transition-metal cations appears to enhance the acidity of compounds of the type (1) even more dramatically, as indicated by the exceptionally high acidity⁽⁴⁾ of the thiophenol ligand in the iron(II) complex $[\text{Fe}(\text{C}_5\text{H}_5)(\eta^6\text{-Ph}\cdot\text{SH})]^+$, for example, and by the complete deprotonation of the cation (2c) to give $[\text{Rh}(\eta^5\text{-C}_5\text{Me}_5)(\eta^6\text{-PhO}^-)]^+$ by mild bases such as aqueous sodium carbonate⁽⁵⁾.

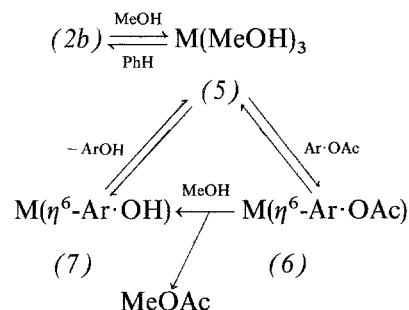


The specific examples given above are consistent with the acidity of the following four phenols being in the order:



From this, one can predict that the same order would probably also apply to the leaving-ability of the four corresponding phenoxide anions in nucleophilic substitutions at saturated and unsaturated carbons, and that

the cation (2d), for example, would undergo hydrolysis and alcoholysis at the acetate group far more rapidly than both phenyl acetate and 4-nitrophenyl acetate. This prediction is of synthetic interest in that, as the cation (2a) readily undergoes reversible arene-exchange reactions⁽⁶⁾, it should be possible to generate coordinated aryl esters, such as (2d), in solution by means of an arene-exchange reaction between the cation (2a) and the appropriate aryl ester. We have examined this possibility using the tetrafluoroborate and the hexafluorophosphate salts (3 and 4 respectively) of the analogous cation (2b)⁽⁷⁾, and in this paper we report that, in nitromethane, both these salts catalyse the methanolysis of aryl acetates. In accordance with the reasoning given above, we believe that this catalysis proceeds as shown in the scheme, and that the actual catalytic species is the solvated cation (5).



Scheme. $\text{M} = [\text{Rh}(\eta^5\text{-C}_5\text{Me}_4\text{Et})]^{2+}$

Experimental

¹H and ¹⁹F n.m.r. spectra were recorded on a Perkin-Elmer spectrometer. ³¹P n.m.r. spectra were recorded on a Bruker WM-360 spectrometer. The salts (3) and (4) were prepared as described by White and coworkers⁽⁷⁾. The aryl acetates (8a–f) were obtained from the parent phenols by acetylation with acetic anhydride in pyridine in the usual manner, and, in all cases, had the m.p. (or b.p.) reported in the literature.

Methanolysis of the aryl acetates (8a–f) in the presence of the salt (3 or 4). General procedure. Dry methanol (BDH, <0.02% water, 384 mg) was diluted to a volume of 10 ml with [²H₃]nitromethane, and a portion (0.50 ml) of the resultant solution was transferred to an n.m.r. sample tube (5 × 180 mm). The salt (3 or 4; 3 × 10⁻⁵ mol) and the aryl acetate (3 × 10⁻⁴ mol) were added, and the tube was stoppered and clamped in an electrically heated block at 80 ± 1°C so that only that portion of the tube which contained the reaction mixture was heated (under these conditions very little evaporation of solvent occurred, although it was observed that, in the subsequent methanolysis, the extent of reaction as deduced from the ¹H n.m.r. signals due to methyl acetate was consistently lower than the extent deduced from the signals due to the

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parent phenol). Periodically, the tube was removed from the heating-block, cooled, and spectra were recorded.

Rhodium-catalysed methanolysis of 4-nitrophenyl acetate: A solution of the acetate (1.09 g), methanol (384 mg), and the salt (3; 315 mg) in nitromethane (10 ml) was heated at 80° C for 48 h, and then the volatile material was removed under reduced pressure. The residue was extracted with ether (50 ml), and the extract was washed with aqueous sodium hydroxide (2 M, 4 × 25 ml). The washings were combined, acidified with 10 M-hydrochloric acid, and extracted with ether to give 4-nitrophenol (159 mg, 19%), m.p. 113° C (from ethanol) (lit.⁽⁸⁾, m.p. 114° C), whose infrared spectrum was indistinguishable from that of an authentic sample.

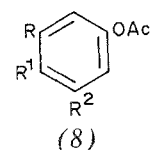
Results and discussion

The ¹H n.m.r. spectrum of the tetrafluoroborate salt (3) in [²H₃]nitromethane showed the expected^(7,9) signals at δ 7.46 and 2.33 due to the co-ordinated benzene and the four methyl groups respectively, while the ¹⁹F n.m.r. spectrum (CFCl₃ as internal standard) showed only a singlet at δ 156 due to the tetrafluoroborate anion (cf. Ref. 10). When a solution of the salt (0.06 M) and methanol (1.2 M) in [²H₃]nitromethane was heated at 80° C for 4 h, the last signal remained unchanged, but the first two signals were partly replaced by those at δ 7.34 and 1.65 due to uncoordinated benzene and the four methyl groups of the solvated cation (5), respectively^(7,9). A comparison of the intensities of the appropriate signals indicated that the ratio of the benzene complex (2b) to (5) was about 6:1; this ratio did not change when the solution was heated for a further 3 h. When a solution of methanol (1.2 M), 4-nitrophenyl acetate (0.6 M), and the salt (3; 0.06 M) in [²H₃]nitromethane was heated at 80° C, the initial changes in the ¹H n.m.r. spectrum due to the displacement of the benzene were slowly followed by the appearance of signals due to 4-nitrophenol (doublets at δ 6.94 and 8.1) and methyl acetate (singlets at δ 1.97 and 3.6). After 48 h of heating, the spectrum indicated that about 25% of the 4-nitrophenyl acetate had undergone methanolysis, and a 19% yield of 4-nitrophenol was isolated after the same reaction time when the experiment was repeated with unlabelled nitromethane as the solvent. In the absence of the salt (3), but with the same reaction time, no 4-nitrophenol or methyl acetate was detected (¹H n.m.r.).

The methanolysis of phenyl acetate and its 4-methyl derivative was examined in an identical manner, and it was found that after 48 h of heating the reaction had proceeded to the extent of about 35 and 80% respectively. The latter figure appeared to correspond to the equilibrium position between the four components, 4-methylphenyl acetate/methanol and 4-methylphenol/methyl acetate, for it showed no significant increase when the reaction time was extended by another 24 h.

The extent of methanolysis observed with phenyl acetate and with its 4-methyl and 4-nitro derivatives indicates that, with this rhodium-catalysed system, the rate of methanolysis is retarded by an electron-withdrawing nitro group in the *para* position of the aryl ester, but is increased by an electron-donating methyl group. This is, of course, the opposite to what is usually observed with nucleophilic substitutions of aryl esters (see, for example, Refs 10 and 11), and is presumably due to the effect of the

substituent on the π-electron density on the arene ring and, hence, on the rate of formation of the co-ordinated aryl ester (6) from the solvated species (5). The π-electron-withdrawing nitro group, for example, appears to decrease the rate of formation of the coordinated ester (6) to a much greater extent than it increases the rate at which this complex undergoes methanolysis.



	R	R ¹	R ²
a;	H	H	H
b;	H	NO ₂	H
c;	H	CO ₂ Et	H
d;	H	Me	H
e;	Me	H	Me
f;	Me	Me	Me

Table 1. Methanolysis of aryl acetates in the presence of (η⁵-ethyltetramethylcyclopentadienyl)(η⁶-benzene)rhodium(III) hexafluorophosphate.

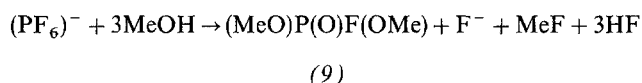
Aryl acetate	Extent of methanolysis (%) ^a
Phenyl acetate (8a)	30
4-Nitrophenyl acetate (8b)	15
4-(Ethoxycarbonyl)phenyl acetate (8c)	20
4-Methylphenyl acetate (8d)	65
3,5-Dimethylphenyl acetate (8e)	50
3,4,5-Trimethylphenyl acetate (8f)	50
2,3,5,6-Tetramethylphenyl acetate	10

^aCalculated (to the nearest 5%) from the ¹H n.m.r. spectrum obtained after a solution of the aryl acetate (0.6 M), the rhodium salt (0.06 M), and methanol (1.2 M) in [²H₃]nitromethane had been heated at 80° C for 4 h.

The methanolysis of the aryl esters (8; a–f) was then examined under the same conditions, but with the hexafluorophosphate salt (4) as the catalyst. As with the rhodium-catalysed cyclisation of 3-(2-fluorophenyl)propanols reported earlier⁽⁹⁾, the reaction proceeded far more rapidly than with the tetrafluoroborate salt, and, with the esters (8a, b, and d), the degree of methanolysis was about the same after 4 h with the hexafluorophosphate salt as after 24 h with the tetrafluoroborate salt (see Table 1). However, a nitro group (and CO₂Et) in the *para* position of the aryl ester still retarded the methanolysis, while a *p*-methyl group accelerated it. Interestingly, the extent of methanolysis with the di- and trimethyl derivatives (8e and f respectively) was lower than with the monomethyl derivative (8d), but, as expected, it was higher than with phenyl acetate (8a). The least reactive of the esters examined was 2,3,5,6-tetramethylphenyl acetate, presumably owing to the steric effect of the two *o*-methyl groups.

In order to establish why the hexafluorophosphate salt was more effective as a catalyst for the methanolysis than the tetrafluoroborate salt, the behaviour of the former in nitromethane was examined in both the presence and the absence of methanol. In nitromethane, the ¹⁹F and ³¹P n.m.r. spectra of the salt showed the expected^(12,13) signals due to the hexafluorophosphate anion, with a

doublet at δ 74.2 (J_{FP} 720 Hz) and a septet (J_{PF} 708 Hz) at δ 143 (with 85% phosphoric acid as external reference). Both spectra remained unchanged when the solution was heated at 80°C for 20 h, but, in contrast, when a solution of the salt (0.06 M) and methanol (0.12 M) in nitromethane was heated at 80°C, the spectra changed rapidly, and after 1 h of heating the signals due to the hexafluorophosphate anion had disappeared completely. The ^{19}F n.m.r. spectrum then showed a doublet at δ 88.8 (J_{FP} 1006 Hz), while the ^{31}P n.m.r. spectrum showed a doublet at δ 5.8 (J 966 and 11 Hz). These values are consistent with the hexafluorophosphate anion having undergone methanolysis to give dimethyl phosphorofluoridate (9):



Although spectral data for the ester (9) appear not to have been reported, the values obtained in the methanolysis experiment correspond well with those reported for the diethyl ester (as a neat liquid): ^{19}F , δ 82.05 (J_{FP} 971.1 Hz); ^{31}P , δ 9.1 (J_{PF} 970 Hz, J_{PH} 9 Hz)^(14,15). No attempt was made to isolate the dimethyl phosphorofluoridate on account of the toxicity reported for this compound⁽¹⁶⁾.

This rhodium-catalysed methanolysis of the hexafluorophosphate anion presumably involves a species (whose structure is not known) in which the anion is coordinated with the rhodium cation, and is directly analogous to the silver-catalysed⁽¹⁷⁾, cobalt-catalysed⁽¹⁸⁾, and rhodium-catalysed^(19,20) hydrolyses. The rhodium-catalysed hydrolysis, which afforded a rhodium complex of the difluorophosphate anion, occurred when the salt $[\text{Rh}(\eta^5\text{-C}_5\text{Me}_5)(\text{acetone})_3]^{2+}[\text{F}_6\text{P}^-]_2$ was heated in acetone for 12 h, and, presumably, was due to water formed by the rhodium-catalysed condensation of the acetone. Remarkably, the hydrolysis did not appear to be accelerated by the deliberate addition of water to the reaction mixture. This is probably because the addition of water resulted in the cation of the salt largely being converted into the aquo complex $[\text{Rh}(\eta^5\text{-C}_5\text{Me}_5(\text{H}_2\text{O})_3)]^{2+}$ (or related hydroxo species^(21,22)) in which the water molecules were firmly coordinated with the rhodium. This inhibited that degree of interaction of the hexafluorophosphate anion with the rhodium cation that was necessary for the catalysed hydrolysis to occur. A similar effect was noted in the present work when the hexafluorophosphate salt (4) was heated under reflux in methanol, i.e. in the absence of nitromethane. No methanolysis occurred after 4 h of heating.

No change occurred in the ^{19}F n.m.r. spectrum when a solution of the tetrafluoroborate salt (3; 0.06 M) and methanol (0.12 M) in nitromethane was heated at 80°C for 48 h, or when this experiment was repeated in the presence of 4-methylphenyl acetate (0.6 M). It can be assumed, therefore, that while both the tetrafluoroborate and the hexafluorophosphate salts catalyse the methanolysis of the aryl acetates by the mechanism shown in the scheme, the greater efficiency of the latter salt is probably due to the presence of hydrogen fluoride (see equation). This acid, whose presence was indicated by the

substantial etching of the glass reaction vessel, would be expected to catalyse both the methanolysis stage (6) \rightarrow (7) and the arene-exchange reaction (7) \rightarrow (5) \rightarrow (6), as well as promote the methanolysis of the aryl ester by the normal acid-catalysed route. No attempt was made, however, to determine the extent to which a solution of hydrogen fluoride in nitromethane will promote the methanolysis of aryl esters.

Acknowledgements

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