Abstraction of an Acetyl Group from *NN*-Dimethylacetamide by a Rhodium–Porphyrin Complex

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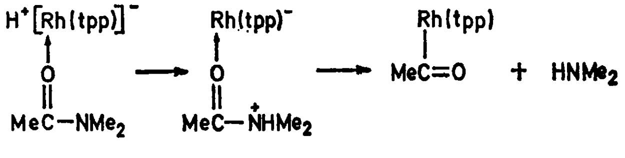
Summary Acetylrhodium(III) tetraphenylporphyrin is formed on warming *NN*-dimethylacetamide solutions containing the rhodium(I) tetraphenylporphyrin anion, [Rh(tpp)]⁻.

During the course of our investigations[1] of the reduction of rhodium(II) tetraphenylporphyrin [Rh(tpp), (**1**)] with molecular hydrogen, we have observed an unusual reaction with *NN*-dimethylacetamide solvent (DMA); abstraction of an acetyl group occurs with production of a rhodium(III) acetyl complex. To our knowledge this represents the first example of acyl abstraction from an amide under mild conditions at a metal centre.

At 25°, the reduction of (**1**) with H_2 proceeds to completion in a few hours in DMA, dimethylformamide, or propanol, to give the monovalent rhodium complex[1] H[Rh(tpp)], (**2**); this complex is air-sensitive, rapidly reverting to (**1**).

If the reduction with hydrogen is carried out in DMA at 60° for *ca.* 24 h, an air-stable, diamagnetic compound (**3**) is obtained. Compound (**3**) has an intense i.r. band at 1730 cm^{-1} (KBr disc), which is not consistent with the presence of a Rh carbonyl complex,[2,3] nor can it be attributed to co-ordinated or protonated DMA.[4] Elemental analysis and its n.m.r. spectrum [τ ($CDCl_3$) 1·2 (8H, sharp s, pyrrole-H), 2·0 (20H, m, Ph), and 12·8 (3H, sharp s, Me above porphyrin plane)] rule out the presence of DMA. The methyl n.m.r. resonance, and the C=O i.r. stretch are similar to those reported for acetylcobalt(III) aetioporphyrin I.[5] The spectroscopic evidence, and satisfactory elemental analysis for MeCORh(tpp), are consistent with (**3**) being acetylrhodium (III) tetraphenylporphyrin.



The visible spectrum of (**3**) in $CHCl_3$ shows peaks at 413 (ϵ 1·3 × 10^5), 521 (1·05 × 10^4), and 601 (3·8 × 10^3) nm, and is quite different from those reported for (**1**), (**2**), and RhCl(tpp).[1] On addition of pyridine the maxima shift to 420, 532, and 602 nm, and a new peak appears at 567 nm. These changes are attributed to a rapid equilibrium (1). The

$$(\text{MeCO})\text{Rh(tpp)} + \text{py} \rightleftharpoons (\text{MeCO})\text{Rh(tpp) (py)} \qquad (1)$$

change in spectrum on going from 5- to 6-co-ordination is similar to that observed with RhCl(tpp)[6] and cobalt(III) tetraphenylporphyrins.[7] The existence of the 5-co-ordinate Rh^{III} compound provides another example of the increased lability of d^6 metal ions when complexed with porphyrins.[8]

A possible mechanism for the formation of (**3**) from (**2**) could involve *N*-protonation of a co-ordinated DMA followed by a two-electron transfer with resulting cleavage of the amide bond.

The formation of cobalt–carbon bonds using a reduced form of the metal is well documented in vitamin B_{12} chemistry[9] and in simpler model systems.[5,10] Studies on the formation of rhodium–carbon bonds in corresponding model systems involving rhodium have been limited.[3,11]

We thank the National Research Douncil of Canada for financial support and Johnson, Matthey Ltd., for loan of the rhodium.

(*Received*, *27th July* 1972; *Com.* 1304.)

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† The possibility that the acetyl group is attached to a ring nitrogen atom (*cf.* R. Grigg, A. W. Johnson, and G. Shelton, ***Annalen***, 1971, **746**, 32) cannot be completely excluded, but the spectral data appear much more consistent with metal acylation.

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