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RING CONTRACTION AND OTHER REACTIONS OF AZIDOBENZENE- AND AZIDOTOLUENE-TRICARBONYLMANGANESE CATIONS *

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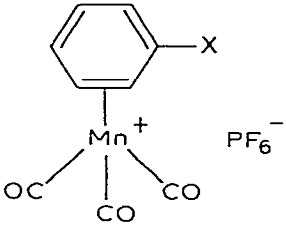
Summary

Azidobenzene- and azidotoluene-tricarbonylmanganese cations are reduced to the corresponding aniline and toluidine complexes not only by lithium aluminium hydride but also by azide ion in polar solvents. Direct substitution of the azido group by methoxy occurs with sodium methoxide in methanol. Above 130°C nitrogen is lost from the azido compounds and ring contraction occurs yielding the corresponding (cyanocyclopentadienyl)tricarbonylmanganese complexes.

We have previously [1] described the facile formation of azidobenzenetricarbonylmanganese hexafluorophosphate (I, X = N_3) by stirring chlorobenzenetricarbonylmanganese hexafluorophosphate (I, X = Cl) with sodium azide in acetone solution. Attempts to repeat and extend this reaction showed that the product was frequently contaminated by a different arenetricarbonylmanganese salt. On closer investigation it became apparent that the initially formed azido complex undergoes further reaction and is reduced to the corresponding aniline



(I)

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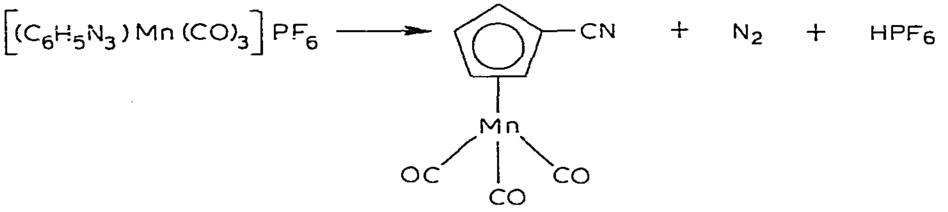
* Dedicated to Professor Ernst Otto Fischer on the occasion of his 60th birthday on November 10, 1978.

complex. Although this can be minimised by careful control of reaction conditions, acetonitrile proved preferable as solvent for the formation of the pure azido complexes.

Stirring in acetone alone did not affect the azidobenzenetricarbonylmanganese salt (I, X = N_3) but in the presence of sodium azide reduction to the aniline complex (I, X = NH_2) occurred. As expected the same reduction could be effected with lithium aluminium hydride. The IR spectra of the two samples were identical with each other and with those of the sample described previously. The reduction with azide occurs so smoothly that stirring the chloroarene complexes with excess azide in acetone constitutes an effective and convenient preparative method for the aniline and toluidine complexes.

Although cold solvents do not affect the azido complexes hot acetonitrile displaces the arene nucleus yielding tris(acetonitrile)tricarbonylmanganese hexafluorophosphate and refluxing butanone or methanol again caused at least partial reduction of the azidoarene to the aniline and toluidine complexes. In the case of methanol, spectroscopic examination of the product suggested the presence of the anisoletricarbonylmanganese salt (I, X = OMe). The azido complex I (X = N_3) was therefore stirred with methanol containing sodium methoxide. After only 30 seconds the complex had dissolved and reacted completely yielding chiefly the anisole complex I (X = OMe). Nucleophilic substitution of azido groups by e.g. methoxide has been studied in nitroazidobenzenes by Miller et al. [2] who found the azide ion to be closely similar to chloride as a leaving group.

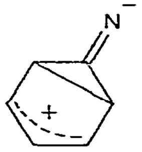
Finally we were interested in ascertaining the fate of the nitrene complex I (X = N) which is the presumed initial product formed on thermolysis of the azidobenzene complex by loss of dinitrogen. This was best effected by heating the dry salt and was found to give cyanocyclopentadienyltricarbonylmanganese (II). The overall reaction can be written as shown in eq. 1.



(1)

(II)

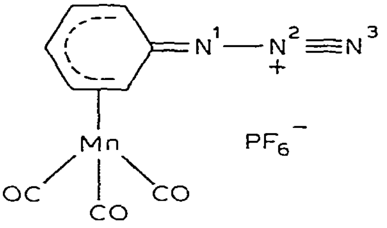
It involves a ring contraction previously only observed at very much higher temperature in the pyrolysis of aryl azides. Thus in solution, pyrolysis of phenyl azide yields azobenzene from dimerisation of phenylnitrene together with aniline from hydrogen abstraction and other products of nitrene—solvent reaction [3].



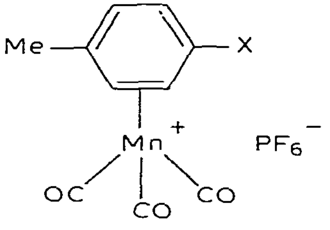
(III)

Even at 350°C in the vapour phase [4] azobenzene is formed in high yield (72%). Cyanocyclopentadiene is found [5,6] above 500°C, its yield increasing sharply with temperature [5] from 9% at 600°C to 46% at 700°C. It is therefore believed to arise from vibrationally excited singlet nitrene possibly via an intermediate of the type III [5,6]. The behaviour of the manganese complex may thus be compared with that of an excited state of the free ligand.

The loss of nitrogen occurs at relatively low temperature and it is notable that we can write an additional resonance structure IV for the azido complex which has no counterpart for the free ligand and which implies a lowering of the N(1)—N(2) bond order. A further difference from the free ligand is the proton loss which leads to the cyclopentadienyl complex. If not actually concerted with ring contraction this must follow too rapidly to permit sigmatropic cyanide migration. Hence the *p*-azidotoluene complex V (X = N_3) rearranges smoothly to yield as the single product the expected (1-cyano-3-methylcyclopentadienyl)tricarbonylmanganese (VI) whereas all three metal-free azidotoluenes yield [5] the same mixture of 2- and 4-methyl-1-cyanocyclopentadienes.



(IV)



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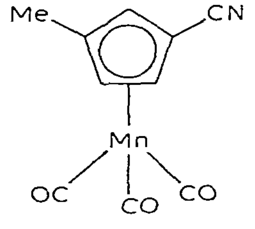

(VI)

Experimental

(Azidobenzene)tricarbonylmanganese hexafluorophosphate (I, X = N_3)

Sodium azide (0.42 g) was stirred with acetonitrile (30 ml) for 5 min. (Chlorobenzene)tricarbonylmanganese hexafluorophosphate [1] (I, X = Cl) (0.5 g) was then added and vigorous stirring continued for 20 min. The solution was filtered, the solvent removed using a rotary evaporator and the residue washed with dichloromethane (3 × 5 ml) and collected by filtration. Recrystallisation from acetone/ether gave the pure azido complex [1] I (X = N_3) (0.39 g, 77%).

(4-Azidotoluene)tricarbonylmanganese hexafluorophosphate (V, X = N_3)

Repetition of the above procedure with (4-chlorotoluene)tricarbonylmanganese hexafluorophosphate [1] (2.7 g) yielded the corresponding azidotoluene complex (2.1 g, 77%). (Found: C, 28.9; H, 1.7; N, 10.1. $C_{10}H_7F_6MnN_3O_3P$ calcd.: C, 28.8; H, 1.7; N, 10.1%.)

Formation of anilinetricarbonylmanganese hexafluorophosphate (I, X = NH_2) via the azido complex I (X = N_3)

(a) (Chlorobenzene)tricarbonylmanganese hexafluorophosphate (I, X = Cl) (0.2 g) was added to a vigorously stirred suspension of powdered sodium azide

(0.17 g) in acetone (10 ml). After stirring for 3 h the solution was filtered and evaporated under reduced pressure. The residue was stirred with dichloromethane (15 ml) for 2 h and the solution then concentrated. The product was collected, washed with dichloromethane (2 × 5 ml) and recrystallised from acetone/ether yielding anilinetricarbonylmanganese hexafluorophosphate [7] (I, X = NH_2) (0.1 g, 53%). The same result was obtained starting with the azidobenzene complex I (X = N_3) in place of the chlorobenzene complex, but not when the azidobenzene complex was stirred in acetone (or acetonitrile or dichloromethane) without added azide.

(b) Azidobenzene complex I (X = N_3) (0.3 g) was refluxed in methanol (20 ml) for 30 min. The yellow solution was filtered, concentrated and ether (20 ml) added. The precipitated product (70 mg) was collected, washed with ether (10 ml) and dried in vacuo. IR comparison showed this to be the anilino complex I (X = NH_2) containing a small proportion of the anisole complex I (X = OMe).

(c) Azidobenzene complex I (X = N_3) (0.9 g) was suspended in tetrahydrofuran (30 ml) and lithium aluminium hydride (60 mg) added with vigorous stirring. After 1 min water (1 ml) was added, the solvent removed and the residue extracted with acetone (2 × 30 ml). The combined extracts were concentrated and ether (30 ml) was added; the precipitated product was washed with ether (10 ml) and dried in vacuo. IR comparison established the identity of this product with an authentic sample of the anilino complex [1] I (X = NH_2) and with the sample prepared in (a) above.

Formation of (p-toluidine)tricarbonylmanganese hexafluorophosphate (V, X = NH_2)

(a) Following the procedure (a) above for the aniline complex, the *p*-toluidine complex V (X = NH_2) (0.11 g, 58%) was obtained from the 4-chlorotoluene complex V (X = Cl) (0.25 g) or from the 4-azidotoluene complex V (X = N_3) by stirring with sodium azide in acetone.

(b) The 4-azidotoluene complex V (X = N_3) (0.3 g) was refluxed in butanone (20 ml) for 1.5 h. The cooled solution was filtered, concentrated and ether (20 ml) was then added. The precipitate was collected, washed with ether (10 ml) and dried in vacuo; IR comparison showed this to be a mixture of the toluidine complex V (X = NH_2) and the unchanged azido complex V (X = N_3).

Decomposition of the azidobenzene complex I (X = N_3) by acetonitrile

The complex I (X = N_3) (0.4 g) was refluxed in acetonitrile (25 ml) for 1 h. The solution was cooled, evaporated and the residue extracted with acetone (2 × 10 ml). The extracts were concentrated and ether (20 ml) was added. The precipitated solid was shown to be tris(acetonitrile)tricarbonylmanganese hexafluorophosphate [7] by IR and NMR comparison with an authentic sample.

Reaction of azidobenzenetricarbonylmanganese hexafluorophosphate with sodium methoxide

Sodium (0.24 g) was dissolved in methanol (25 ml) and the complex I (X = N_3) (0.3 g) was added with vigorous stirring. After 30 sec water (1 ml) was added, the solvent removed using a rotary evaporator and the residue extracted with acetone (2 × 15 ml). The extracts were concentrated and ether (30 ml) was added. The precipitate was collected, washed with water (10 ml) and then ether (20 ml) and dried in vacuo. IR comparison showed that this was the anisole complex [1] I (X = OMe) containing a small amount of the aniline complex I (X = NH_2).

Thermolysis of the azidoarene complexes

(a) Azidobenzene complex I (X = N_3). This complex (0.5 g) was heated at 132°C/0.5 Torr for 45 min, allowing the product to sublime out. After dissolution in dichloromethane and clarification with charcoal, light petroleum (b.p. 40—60°C) was added and the solution left to crystallise by slow evaporation. Yellow (cyanocyclopentadienyl)tricarbonylmanganese (II) (65 mg, 22%), m.p. 74°C (lit. [8] m.p. 70—71.5°C) separated. (Found: C, 47.2; H, 1.9; N, 6.1; *M*, 228.9565. $C_9H_4MnNO_3$ calcd.: C, 47.2; H, 1.8; N, 6.1%; *M*, 228.9572.)

The same product was obtained by conducting the pyrolysis under nitrogen at atmospheric pressure and extracting the residue with light petroleum.

(b) 4-Azidotoluene complex V (X = N_3). This complex (0.5 g) was pyrolysed in the same manner as the azidobenzene complex I (X = N_3) yielding (1-cyano-3-methylcyclopentadienyl)tricarbonylmanganese (VI) (65 mg, 21%), m.p. 82°C. (Found: C, 49.5; H, 2.6; *M*, 242.9735. $C_{10}H_6MnNO_3$ calcd.: C, 49.3; H, 5.8%; *M*, 242.9729.)

Acknowledgements

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