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Preparation and Reactivity of Iron(1) Aryldi-imine Derivatives

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The hydride *trans*-[FeH(CO)L₄]BPh₄ [L = P(OEt)₃] reacts with aryldiazonium cations to give aryldi-imine [Fe(NH=NAr)-(CO)L₄]²⁺ derivatives, which undergo substitution reactions with ketones, CO, RCN, and isonitriles to produce hexaco-ordinate cations [Fe{OC(RR')}(CO)L₄]²⁺, [Fe(CO)₂L₄]²⁺, [Fe(CO)(RCN)L₄]²⁺, and [Fe(CO)(RNC)L₄]²⁺ respectively, while in the reaction with gaseous NO the pentaco-ordinate complex [FeL₄NO]⁺ is obtained.

Current interest in the chemistry of arylazo and aryldi-imine complexes¹ prompts us to report the synthesis and characterization of the first example of an aryldi-imine derivative of iron(π) together with studies on its reactivity, allowing new cationic Fe^{II} compounds to be obtained.

The new monohydride² (1) slowly reacts with $ArN_2^+BF_4^-$ (Ar = 4-MeC₆H₄) in CH₂Cl₂ to give the aryldi-imine derivative (2) whose BPh₄⁻ salt was isolated as a white solid moderately stable both in the solid state and in solution.[†]

Good elemental analyses, conductivity $[\Lambda_M(MeNO_2 \text{ at } 25 \text{ °C}) 131.6 \text{ S cm}^2 \text{ mol}^{-1}]$, i.r., and n.m.r. data support its formulation. The i.r. spectrum of (2) shows a strong v(CO) absorption at 2002 cm}^{-1} (CH_2Cl_2), no bands attributable to v(N=NAr), and an absorption at 3330 cm⁻¹, of medium intensity, tentatively attributed to v(NH) of the aryldi-imine.

Besides signals due to the $P(OEt)_3$ moiety and to the phenyl rings, the ¹H n.m.r. spectrum in $(CD_3)_2SO$ shows a singlet at δ

 $[\]pm$ 4-ClC₆H₄ and 4-FC₆H₄ derivatives were also obtained by a similar procedure.



Scheme 1. (4): v (CO) (CH₂Cl₂) 2053 s and 2090 s cm⁻¹; (5, R = 4-MeC₆H₄): v(CO) (CICH₂CH₂Cl) 2023 s, v(CN) 2268 m cm⁻¹; (6, R = 4-MeC₆H₄): v(CO) (CICH₂CH₂Cl) 2048 s, v(CN) 2175 s cm⁻¹.

2.26 (3H, 4-*Me*C₆H₄N=NH) and a broad singlet at δ 13.3 attributable to the NH group. Moreover in the labelled [Fe(¹⁵NH=NAr)(CO)L₄]²⁺ cation the broad signal at δ 13.3 is replaced by a doublet [*J*(¹⁵NH) 67 Hz], which strongly supports the presence of the diazene ligand in the complex.

Finally, a *trans*-geometry for (2) may be deduced from the ${}^{31}P{}^{1}H{}$ n.m.r. spectrum in (CD₃)₂SO (135.17 p.p.m. to high frequency of H₃PO₄, s). While aryldi-imine complexes of Rh, Ru, and Os are reported to react with triethylamine to give arylazo compounds,¹ deprotonation of (2) with NEt₃ was not observed.

Surprisingly, by using acetone instead of CH₂Cl₂ as solvent, the reaction of (1) with $ArN_2^+BF_4^-$ gave a yellow compound which was shown to be the acetone complex trans- $[Fe(OCMe_2)(CO)L_4][BPh_4]_2$ (3) { $\Lambda_M(MeNO_2 \text{ at } 25 \ ^\circ\text{C})126.4$ $S cm^2 mol^{-1}$; v(CO) (CH₂Cl₂) 2002 s; v(OC) (CH₂Cl₂) 1685 m cm^{-1} ; ¹H n.m.r. [(CD₃)₂SO] δ 2.31 (6H, s, Me₂CO); ³¹P{¹H} n.m.r. 130.8 (s) p.p.m.}. An authentic sample of (3) was also obtained by the reaction of (2) with acetone (1:1) in CH₂Cl₂. Since the hydride (1) does not react with acetone, the formation of (3) presumably proceeds via the intermediate (2). Several ketone complexes [ketone = Me(C:O)Ph, Me(C:O)Et, or cyclohexanone] were prepared; their σ -bonded O-co-ordination³ can be deduced from i.r. [lowering of 30-35 cm⁻¹ of v(OC) in the complexes] and ^{1}H n.m.r. data (Me singlet shifted downfield by ~0.25 p.p.m.). Ketone co-ordination to a transition metal is generally uncommon and, in the case of iron complexes, the only example reported⁴ involves a cyclopentadienyl co-ligand.

The easy substitution of the aryldi-imine ligand was also observed in the presence of carbon monoxide, nitriles, and isocyanides, leading to the formation of the hexaco-ordinate cations (4), (5), (6), respectively (Scheme 1).‡

However, with gaseous NO, the reaction does not appear to be a simple substitution, since the pentaco-ordinate complex $[FeL_4(NO)]^+$ is obtained $[v(NO) (CH_2Cl_2) 1734 \text{ s cm}^{-1}]$.

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 \ddagger The aryldi-imine moiety decomposes to form N₂ and toluene, as determined by gas chromatography.