

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

Gabriele Albertin, Stefano Antoniutti, and Emilio Bordignon*

Dipartimento di Chimica dell'Università di Venezia, Calle Larga S. Marta 2137, 30123 Venezia, Italy

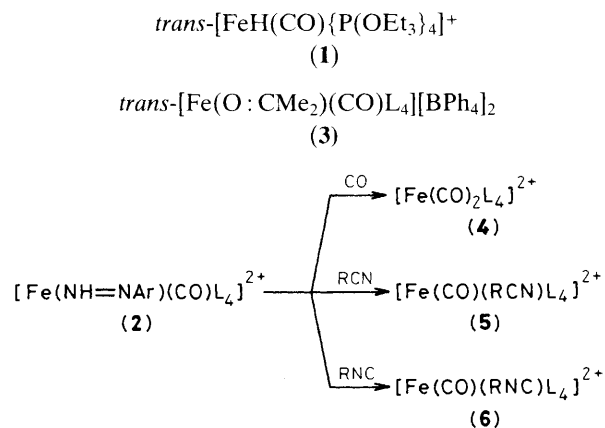
The hydride $trans\text{-}[\text{FeH}(\text{CO})\text{L}_4]\text{BPh}_4$ [L = P(OEt)₃] reacts with aryldiazonium cations to give aryldi-imine $[\text{Fe}(\text{NH}=\text{NAr})(\text{CO})\text{L}_4]^{2+}$ derivatives, which undergo substitution reactions with ketones, CO, RCN, and isocyanides to produce hexaco-ordinate cations $[\text{Fe}\{\text{OC}(\text{RR}')\}(\text{CO})\text{L}_4]^{2+}$, $[\text{Fe}(\text{CO})_2\text{L}_4]^{2+}$, $[\text{Fe}(\text{CO})(\text{RCN})\text{L}_4]^{2+}$, and $[\text{Fe}(\text{CO})(\text{RNC})\text{L}_4]^{2+}$ respectively, while in the reaction with gaseous NO the pentaco-ordinate complex $[\text{FeL}_4\text{NO}]^+$ 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(II) together with studies on its reactivity, allowing new cationic Fe^{II} compounds to be obtained.

The new monohydride² (1) slowly reacts with ArN₂⁺BF₄⁻ (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 [$\Lambda_M(\text{MeNO}_2$ at 25 °C) 131.6 S cm² mol⁻¹], i.r., and n.m.r. data support its formulation. The i.r. spectrum of (2) shows a strong $\nu(\text{CO})$ absorption at 2002 cm⁻¹ (CH₂Cl₂), no bands attributable to $\nu(\text{N}=\text{NAr})$, and an absorption at 3330 cm⁻¹, of medium intensity, tentatively attributed to $\nu(\text{NH})$ 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 (CD₃)₂SO shows a singlet at δ



Scheme 1. (4): $\nu(\text{CO})$ (CH₂Cl₂) 2053 s and 2090 s cm⁻¹; (5, R = 4-MeC₆H₄): $\nu(\text{CO})$ (ClCH₂CH₂Cl) 2023 s, $\nu(\text{CN})$ 2268 m cm⁻¹; (6, R = 4-MeC₆H₄): $\nu(\text{CO})$ (ClCH₂CH₂Cl) 2048 s, $\nu(\text{CN})$ 2175 s cm⁻¹.

† 4-ClC₆H₄ and 4-FC₆H₄ derivatives were also obtained by a similar procedure.

2.26 (3H, 4-MeC₆H₄N=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 [$J(^{15}\text{NH})$ 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 ³¹P{¹H} 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 ArN₂⁺BF₄⁻ gave a yellow compound which was shown to be the acetone complex *trans*-[Fe(OCMe₂)(CO)L₄][BPh₄]₂ (3) { $\Lambda_M(\text{MeNO}_2$ at 25 °C)126.4 S cm² mol⁻¹; $\nu(\text{CO})$ (CH₂Cl₂) 2002 s; $\nu(\text{OC})$ (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 $\nu(\text{OC})$ in the complexes] and ¹H 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 [FeL₄(NO)]⁺ is obtained [$\nu(\text{NO})$ (CH₂Cl₂) 1734 s cm⁻¹].

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