

Facile Synthesis of (1,2-Dihydrobenzoxazol-2-ylidene)tetracarbonyliron Complexes from 2-Trimethylsiloxyphenyl Isocyanide

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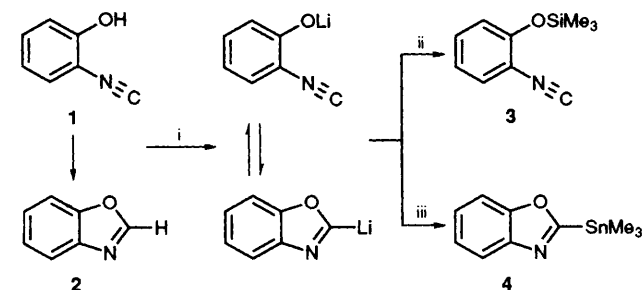
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Reaction of 2-trimethylsiloxyphenyl isocyanide **3** with $\text{Fe}(\text{CO})_5$ and subsequent cleavage of the Si–O bond gives (1,2-dihydrobenzoxazol-2-ylidene)tetracarbonyliron **6**, the structure of which has been determined by X-ray crystallography; complex **6** can be alkylated at the ring nitrogen yielding (*N*-methyl-1,2-dihydrobenzoxazol-2-ylidene)tetracarbonyliron **7**.

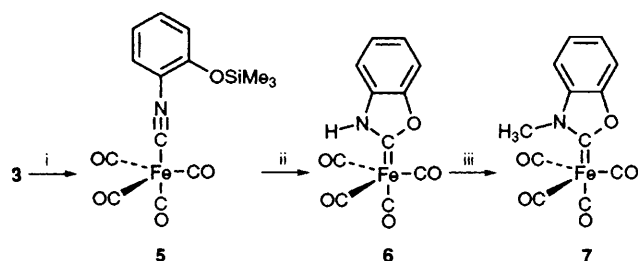
The reaction of coordinated isocyanides with nucleophiles such as alcohols or amines is the oldest procedure for the formation of carbene complexes¹ and numerous examples have been studied.² However, this method is only applicable to isocyanides coordinated to late transition metals or metals in a higher oxidation state where the isocyanide is activated towards nucleophilic attack due to the lack of (d–p) π backbonding from the metal centre. Therefore, 2-hydroxyalkyl isocyanides coordinated at $\text{M}(\text{CO})_5$ fragments ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) do not cyclize to form complexes with oxazolidin-2-

ylidene ligands,³ whereas with Pd^{2+} or Co^{3+} even homoleptic carbene complexes can be synthesized.⁴

We became interested in stabilizing 2-hydroxyphenyl isocyanide **1** in group 6 transition metal complexes, in order to evaluate reactions at the hydroxy group, possibly leading to a template synthesis for aromatic tripodal triisocyanides.⁵ In coordinated **1**, backbonding is even stronger than in aliphatic 2-hydroxyalkyl isocyanides. Free **1** is not stable and cyclizes to benzoxazole **2**.⁶ Lithiation of **2** leads to an equilibrium between lithiated **1** and **2**. Reaction of this mixture with



Scheme 1 Reagents and conditions: i, Bu^nLi , Et_2O , -78°C ; ii, Me_3SiCl ; iii, Me_3SnCl



Scheme 2 Reagents and conditions: i, $\text{Fe}(\text{CO})_5$, 80°C , in *vacuo*, 12 h; ii, MeOH , KF (catalytic amount), room temp., 2 days; iii, DMF , NaH , MeI , -60°C

Me_3SiCl yields regiospecifically 2-trimethylsiloxyphenyl isocyanide 3, while reaction with Me_3SnCl gives the C-metallated 2-trimethylstannylbenzoxazole 4[†] (Scheme 1).

Compound 3 is a suitable source for the generation of coordinated and thereby stabilized 1. It reacts with an excess of $\text{Fe}(\text{CO})_5$ in an evacuated autoclave at 80°C according to the method of Hieber and von Pigenot⁸ to give complex 5 in 90% yield.[†] Cleavage of the Si–O bond in 5 was achieved by stirring in methanol with a catalytic amount of KF for two days. The product can be crystallized from CH_2Cl_2 giving yellow crystals. The ^{13}C NMR spectrum ($[\text{D}_6]\text{acetone}$, 20.15 MHz) showed a resonance at δ 223.5 indicating that the expected complex with the 2-hydroxyphenyl isocyanide ligand was surprisingly not stable and formed exclusively the carbene complex (1,2-dihydrobenzoxazol-2-ylidene)tetracarbonyliron 6 by intramolecular nucleophilic attack (Scheme 2).[†] In the ^1H NMR spectra ($[\text{D}_6]\text{acetone}$, 80 MHz) the NH resonance appeared as a broad singlet at δ 10.95. None of the expected (2-hydroxyphenyl isocyanide) $\text{Fe}(\text{CO})_4$ could be detected.

We believe that thermodynamic reasons are responsible for the strong tendency of the intermediately formed (2-hydroxyphenyl isocyanide)tetracarbonyliron to cyclize and form carbene complex 6. As shown in Fig. 1, the aromaticity of the ligand C contributes significantly to the carbene stabilization, besides metal to ligand (d–p) π backbonding A and (p–p) π bonding from the heteroatoms to the carbene

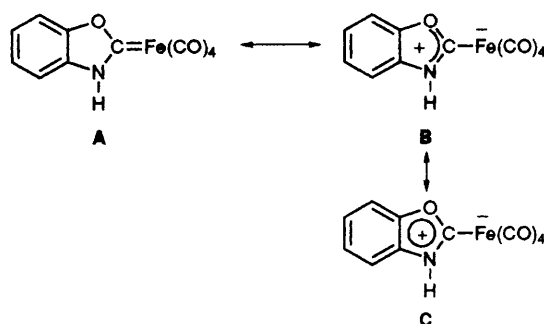


Fig. 1 Mesomeric structures for (1,2-dihydrobenzoxazol-2-ylidene)tetracarbonyliron 6

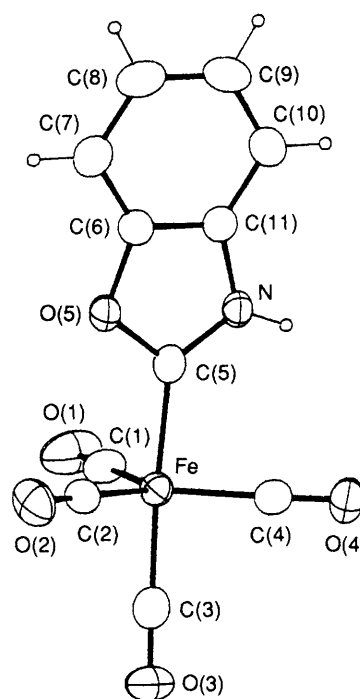


Fig. 2 ORTEP drawing of 6. Selected bond length (Å) and angles ($^\circ$): Fe–C(1) 1.795(3), Fe–C(2) 1.778(3), Fe–C(3) 1.793(3), Fe–C(4) 1.783(3), Fe–C(5) 1.927(2), C(5)–O(5) 1.362(3), C(5)–N 1.333(3), O(5)–C(6) 1.391(3), N–C(11) 1.395(3), C(6)–C(11) 1.360(3); C(3)–Fe–C(5) 174.95(10), Fe–C(5)–O(5) 122.9(2), Fe–C(5)–N 131.1(2), O(5)–C(5)–N 106.0(2), C(5)–O(5)–C(6) 109.0(2), C(5)–N–C(11) 111.9(2).

carbon B. No aromatic system can form from coordinated 2-hydroxyalkyl isocyanides and therefore carbene formation is only observed if the isocyanide carbon is previously activated by coordination to an electron deficient metal centre.

These suggestions are supported by an X-ray structure analysis[‡] of 6 shown in Fig. 2. As expected the carbene ligand is axially coordinated to the $\text{Fe}(\text{CO})_4$ fragment. The Fe–C_{carbene} distance [1.927(2) Å] falls in the range observed for

[†] All new compounds gave satisfactory elemental analyses. Compound 3 was synthesized according to the method in ref. 7.

Spectral data: 5, IR (KBr): ν/cm^{-1} 2169 (νCN), 2058, 1995, 1957 (νCO); ^1H NMR (CDCl_3 , 80 MHz): δ 0.59 (s, 9H, CH_3), 7.07–7.65 (m, 4H, aryl-H); ^{13}C NMR (CDCl_3 , 20.15 MHz): δ –0.4 (CH_3), 120.1 (aryl-C), 120.5 (aryl-C–NC), 121.4, 126.2, 130.1, 151.0 (aryl-C), 169.3 (NC), 212.5 (CO); 6, IR (KBr): ν/cm^{-1} 3413 (νNH), 2052, 1975, 1910 (νCO); ^1H NMR ($[\text{D}_6]\text{acetone}$, 80 MHz): δ 7.22–7.83 (m, 4H, aryl-H), 10.95 (s, 1H, NH); ^{13}C NMR ($[\text{D}_6]\text{acetone}$, 20.15 MHz): δ 111.6, 112.4, 125.6, 126.2, 132.0, 153.7 (aryl-C), 216.2 (CO), 223.5 (NCO); m/z : 287 (M^+); 7, IR (KBr): ν/cm^{-1} 2052, 2048, 1994, 1966, 1940, 1916 (νCO); ^1H NMR (CD_2Cl_2 , 80 MHz): δ 4.05 (s, 3H, CH_3), 7.31–7.70 (m, 4H, aryl-H); ^{13}C NMR (CD_2Cl_2 , 20.15 MHz): δ 34.7 (CH_3), 110.6, 111.3, 125.47, 125.48, 133.0, 152.9 (aryl-C), 215.1 (CO), 225.1 (NCO); m/z : 301 (M^+).

Crystal data: 6, $\text{C}_{11}\text{H}_5\text{NO}_5\text{Fe}$, $M = 287.0$, triclinic, space group $P\bar{1}$ (No. 2), $a = 7.3492(15)$, $b = 8.945(2)$, $c = 9.212(2)$ Å, $\alpha = 94.831(14)$, $\beta = 107.170(14)$, $\gamma = 77.11(2)^\circ$, $U = 563.9(3)$ Å³, $D_m = 1.70$, $D_c = 1.69$ g cm^{–3}, Mo–K α radiation ($\lambda = 0.71073$ Å), $\mu(\text{Mo–K}\alpha) = 13.4$ cm^{–1}. 1460 unique reflections collection at $-100(5)^\circ\text{C}$ on a four-circle diffractometer in the 2θ -range between 2 and 45° . Structure solution by Patterson method, refined (Fe, O, N, C anisotropic thermal parameters, H positions calculated, not refined, $B_{\text{eq,H}} = 1.3B_{\text{eq,C}}$) to $R = 0.025$, $R_w = 0.037$ for 1375 reflections [$F_o^2 \geq 3\sigma(F_o^2)$] and 163 variables. Atomic coordinates, bond length and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

similar complexes.² Comparison with bond lengths in oxazolidin-2-ylidene ligands⁹ shows that in **6** the C_{carbene}–heteroatom distances are longer, whereas the distances O(5)–C(6) and N–C(11) are shorter than the corresponding distances in the aliphatic carbene ligand. This indicated the strong contribution of the mesomeric structure **C** in **6**.

Complex **6** is an extremely stable species which can easily be alkylated at the ring nitrogen atom (Scheme 2). Reaction with NaH and MeI in dimethylformamide (DMF) gives (*N*-methyl-1,2-dihydrobenzoxazol-2-ylidene)tetracarbonyliron **7** in 65% yield. This compound was identified by NMR and mass spectroscopy.[†]

2-Trimethylsiloxyphenyl isocyanide **3** thus proved to be a useful starting material for the synthesis of early transition metal carbene complexes *via* Si–O cleavage followed by intramolecular nucleophilic attack of the hydroxy group at the isocyanide carbon atom. Backbonding from the metal centre does not prevent carbene formation which is driven by the formation of an aromatic system in the resulting dihydrobenzoxazol-2-ylidene ring. Work is in progress to evaluate the potential of this reaction to produce polycarbene complexes.

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