Synthesis and Molecular Structure of a Complex Containing all three Intermediates of the Carbene Synthesis from Coordinated Isocyanides

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Reaction of 3 equiv. of 2-trimethylsiloxyphenyl isocyanide **1** with $(\eta^5\text{-}C_5H_5)Fe(CO)_2Cl$ yields the triisocyanide complex $[(\eta^5\text{-}C_5H_5)Fe(\mathbf{1})_3]Cl$ **5**; hydrolysis of the Si–O bonds in **5** leads to intramolecular nucleophilic attack of the hydroxy oxygen atoms at the isocyanide carbon atoms and formation of $\{(\eta^5\text{-}C_5H_5)Fe[\overline{CN(H)(C_4H_4\text{-}2\text{-}O)}][\overline{CN(C_4H_4\text{-}2\text{-}O)}](CN\text{-}C_6H_4\text{-}2\text{-}OH)\}$ **6**, a complex which was shown by X-ray crystallography to contain a 2-hydroxyphenyl isocyanide, a benzoxazol-2-yl and a 1,2-dihydrobenzoxazol-2-ylidene ligand.

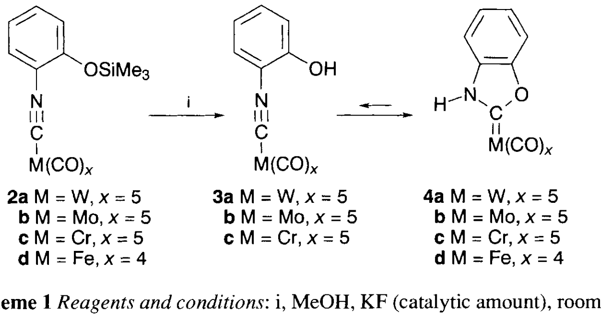
Coordinated isocyanides react with nucleophiles to give heteroatom-stabilized carbene complexes and very old examples[1] for this reaction can be found in the literature.[2] Carbene formation is particularly favoured for isocyanides which contain an additional nucleophilic group and thus can react in an intramolecular fashion. Such a situation exists in complexes **2** with a 2-trimethylsiloxyphenyl isocyanide ligand (**1**) after hydrolysis of the Si–O bond (Scheme 1). Complexes of type **3** react *via* an intramolecular nucleophilic attack of the hydroxy oxygen at the isocyanide carbon to give mostly complexes of type **4** with the 1,2-dihydrobenzoxazol-2-ylidene ligand.[3,4]

Recently we have shown,[5] that the intramolecular ylidene formation can be suppressed if the transition metal fragment maintains strong backbonding to the coordinated isocyanide carbon. For example, if one good π-acceptor (CO) in **2a** is substituted for a good σ-donor (PPh_3), hydrolysis of the Si–O bond leads again to an isocyanide complex of type **3**. However, no further reaction to give the ylidene complex of type **4** occurs. The enhanced (d→p)π backbonding from the electron richer transition metal fragment now deactivates the isocyanide carbon for nucleophilic attack and thus stabilizes the isocyanide complex. Here we show, that not only the substitution of σ-donors for π-acceptors on a transition metal fragment changes the reactivity of coordinated 2-hydroxyphenyl isocyanide. In the presence of three 2-hydroxyphenyl isocyanide ligands, the stepwise conversion of these π-accepting isocyanides into σ-donating ylidenes does also influence the reactivity of the remaining 2-hydroxyphenyl isocyanide ligands.

Treatment of the triisocyanide complex **5** with KF in methanol (Scheme 2) leads to the complex **6**.† The identity of **6** was established by means of an X-ray structure analysis‡ and the results are shown in Fig. 1. The Si–O bonds in all three ligands have been cleaved and the liberated 2-hydroxyphenyl isocyanide ligands have reacted and now coordinate in 3 different forms (as 2-hydroxyphenyl isocyanide, benzoxazol-2-yl and 1,2-dihydrobenzoxazol-2-ylidene) to the C_5H_5Fe-fragment. Thus complex **6** contains all three possible intermediates for the conversion of coordinated isocyanides into ylidenes.

The formation of the unusual complex **6** can be rationalized if the σ-donor/π-acceptor properties of the ligands in complexes **5** and **6** are compared. Phenyl isocyanides like **1** are considered to be moderate π-acceptors. Intramolecular conversion of a 2-hydroxyphenyl isocyanide into a 1,2-dihydrobenzoxazol-2-ylidene ligand converts a moderate π-acceptor into a σ-donor, since heteroatom substituted ylidenes have been shown to act as good σ-donors with little or no π-acceptor properties.[9] If the isocyanide ligands in a poly(2-hydroxyphenyl) isocyanide complex are converted stepwise into ylidene ligands, the electron density at the metal centre will increase with each conversion, since π-acceptors are converted into σ-donors. The (d → p)π backbonding to the remaining isocyanides will increase and the nucleophilic attack of the hydroxy oxygen atom at the isocyanide carbon becomes more and more hampered. Eventually, the backbonding becomes so strong, that the reaction comes to a standstill before all isocyanides are converted into ylidenes. This situation is found in complex **6**.

The reactivity of coordinated carbonyl or isocyanide ligands towards nucleophilic attack can be related to the wavenumbers of the IR absorptions or the calculated force constants for the CO or NC bonds.[10] For the coordinated 2-hydroxyphenyl isocyanide ligand N≡C force constants[11] above 1710 N m^{-1} are typical for enhanced intramolecular ylidene formation[5] while lower values indicate the presence of an isocyanide which is stabilized against intramolecular nucleophilic attack by (d → p)π backbonding. For the N≡C bond in the remaining isocyanides of **6** a force constant of 1659 N m^{-1} was calculated. This value is typical for a coordinated 2-hydroxyphenyl isocyanide, which is completely deactivated for intramolecular nucleophilic attack. As expected, the double intramolecular

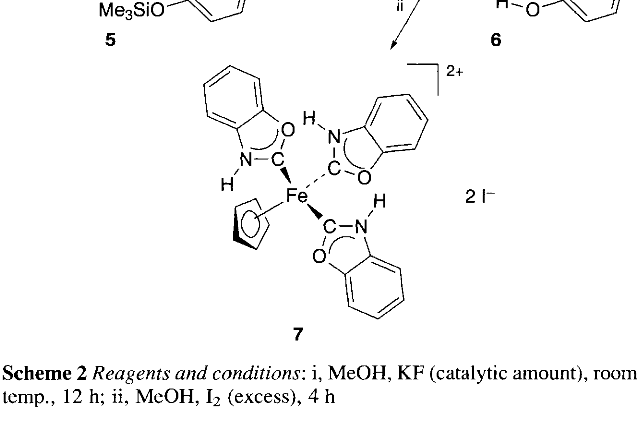


2a M = W, *x* = 5
b M = Mo, *x* = 5
c M = Cr, *x* = 5
d M = Fe, *x* = 4

3a M = W, *x* = 5
b M = Mo, *x* = 5
c M = Cr, *x* = 5

4a M = W, *x* = 5
b M = Mo, *x* = 5
c M = Cr, *x* = 5
d M = Fe, *x* = 4

Scheme 1 *Reagents and conditions*: i, MeOH, KF (catalytic amount), room temp., 12 h



Scheme 2 *Reagents and conditions*: i, MeOH, KF (catalytic amount), room temp., 12 h; ii, MeOH, I_2 (excess), 4 h

ylidene formation leads to enhanced backbonding and prevents the formation of a third ylidene in complex **6**.

To allow intramolecular ylidene formation for the third ligand in **6** the (d → p)π backbonding to the remaining 2-hydroxyphenyl isocyanide ligand must be reduced. This is best achieved by oxidizing the Fe^{II} in **6** to Fe^{III}. Preliminary electrochemical investigations of **6** show two irreversible oxidations at +0.72 and +1.31 V (cyclic voltammography in acetonitrile, *vs.* ferrocene). Chemical oxidation of **6** with I_2 yields a red solid, which shows no absorptions for isocyanides in the IR spectrum. Based on a satisfactory elemental analysis and mass spectral data we assume, that the tri(ylidene)-complex $\{(\eta^5\text{-}C_5H_5)Fe[\overline{CN(H)(C_4H_4\text{-}2\text{-}O})]_3\}I_2$ **7** was formed (Scheme 2).

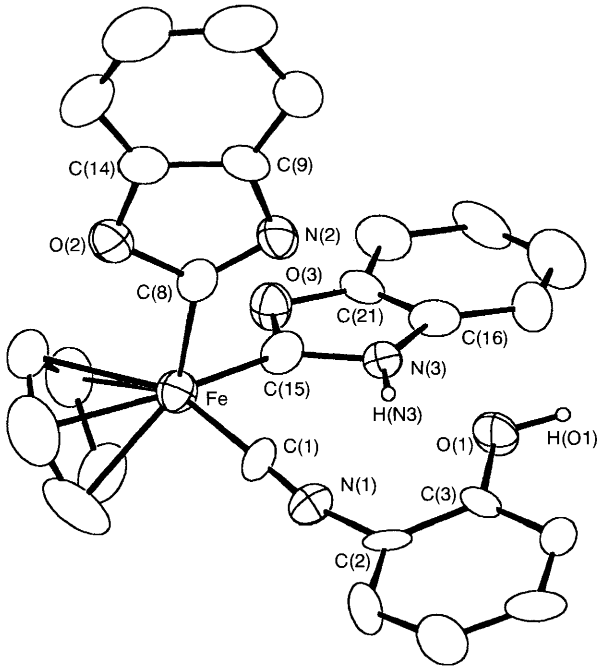


Fig. 1 ORTEP drawing of **6**. Selected bond lengths (Å) and angles (°): Fe–C(1) 1.798(10), Fe–C(8) 1.931(9), Fe–C(15) 1.843(9), O(1)–C(3) 1.372(11), O(1)–H(O1) 0.80(8), O(2)–C(8) 1.399(9), O(2)–C(14) 1.376(10), O(3)–C(15) 1.393(9), O(3)–C(21) 1.387(10), N(1)–C(1) 1.164(10), N(1)–C(2) 1.393(11), N(2)–C(8) 1.327(10), N(2)–C(9) 1.408(11), N(3)–C(15) 1.368(11), N(3)–C(16) 1.398(11), N(3)–H(N3) 0.93(11), C(1)–Fe–C(8) 87.4(4), C(1)–Fe–C(15) 90.5(4), C(8)–Fe–C(15) 90.6(4), C(8)–O(2)–C(14) 106.2(7), C(15)–O(3)–C(21) 110.0(7), C(1)–N(1)–C(2) 165.8(10), C(8)–N(2)–C(9) 106.6(8), C(15)–N(3)–C(16) 112.4(8), Fe–C(1)–N(1) 178.3(8), Fe–C(8)–O(2) 117.0(6), Fe–C(8)–N(2) 132.0(7), O(2)–C(8)–N(2) 111.0(8), Fe–C(15)–O(3) 122.9(6), Fe–C(15)–N(3) 133.0(7), O(3)–C(15)–N(3) 104.1(7).

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Footnotes

† All new compounds gave satisfactory elemental analyses. **5** was prepared as a red powder in 50% yield from $(\eta^5\text{-}C_5H_5)Fe(CO)_2Cl$[6] and 3 equiv. of 2-trimethylsiloxyphenyl isocyanide **1**[7] in toluene according to the method of Pauson.[8] IR (KBr): ν/cm^{-1} 2130, 2083 (ν CN). Hydrolysis of the Si–O bonds in methanol–KF[3,4] gives deep red **6**, which was recrystallized from CH_2Cl_2–hexane. ^1H NMR ($CDCl_3$, 250 MHz): δ 12.23 (s br, 2H, O*H* + N*H*), 7.44–6.73 (m br, 12H, Ar–*H*), 5.10 (s, 5H, C_5H_5); IR (KBr): ν/cm^{-1} 2087 (ν CN); MS (FAB, positive ions): *m/z*, rel. intens. 478 (MH^+, 30.1%), 412 [$(M - C_5H_5)^+$, 4.4%], 359 [(M − benzoxazol-2-yl)$^+$, 28.3%], 240 [$(C_5H_5FeL)^+$ (L = isocyanide or ylidene), 100%].

‡ *Crystal data* for $C_{26}H_{19}FeN_3O_3$ **6**: M = 477.31, monoclinic, space group $P2_1/c$ (No. 14), a = 10.259(2), b = 20.001(5), c = 11.074(5) Å, β = 110.76(2)°, U = 2125(2) Å^3, D_m = 1.50, D_c = 1.492 g cm^{-3}, Z = 4, Mo-Kα-radiation (λ = 0.71073 Å), μ(Mo-Kα) = 7.41 cm^{-1}. 2760 unique diffraction data collected on a CAD-4 four-circle diffractometer at 20(3) °C in the 2θ-range between 2 and 45°. Structure solution with Patterson and Fourier methods, refined [non-hydrogen atoms with anisotropic thermal parameters, C–H positions calculated, not refined $B_{eq,H} = 1.3\,B_{eq,C}$, H(O1), H(N3) positions identified in Difference-Fourier map and refined in least-squares] to R = 4.61, R_w = 5.38 for 1240 absorption corrected structure factors [$F_o^2 \geqslant 3\sigma(F_o)^2$] and 307 variables. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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