Molecular Self Assembly: Temperature Controlled Reversible Formation of a Bicyclo[2.2.2]organoiron Complex *via* Consecutive Organometal 1,3-Dipolar Cycloaddition and Isocyanide Insertion Reactions

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In a unique temperature dependent reversible reaction, the bicyclo[2.2.2]organoiron complex **8** is assembled from three molecular components, *i.e.* the $Fe(CNR)_3(\alpha\text{-diimine})$ complex **1b**, dimethyl maleate and 2,6-xylyl isocyanide, and disassembled again *via* consecutive organometal 1,3-dipolar concerted cycloaddition–reversion and isocyanide insertion–deinsertion reactions.

Over the years, many examples have been found of C–C and C–N coupling reactions of 1,4-diazabuta-1,3-diene (dab) ligands in the coordination sphere of transition metals.[1] The (Pr^i-dab)tricarbonyl iron complex **1a** (see Scheme 1) reacts with electron-deficient alkynes. This reaction has been described as a [3 + 2] cycloaddition in which the C=N–Fe fragment of $Fe(CO)_3(dab)$ represents a 1,3-dipole.[2] The resulting bicyclo[2.2.1] intermediate **2** readily undergoes CO insertion into the Fe–N σ-bond followed by addition of an incoming two electron-donating ligand L′ to regain the 18-electron configuration. The bicyclo[2.2.2] structure **4** formed can isomerize *via* reductive elimination followed by recoordination of the double bond to give the 1,5-dihydropyrrol-2-one complex **5**.

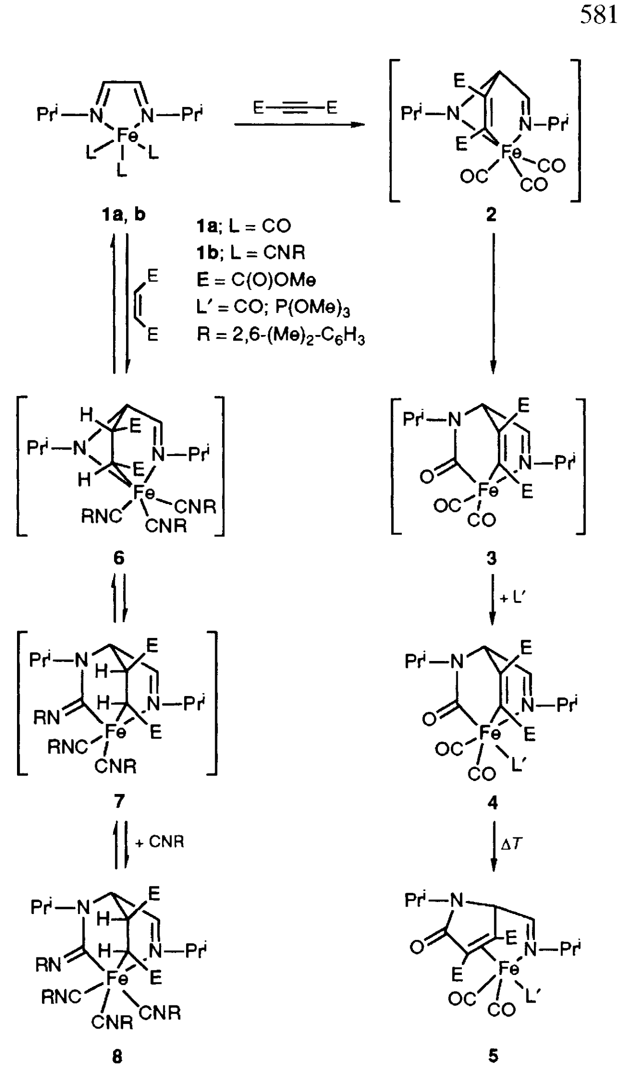
In order to expand the potential of this reaction we decided to employ CNR ligands. In the first place isocyanides are known to undergo insertion reactions, analogous to CO. Secondly, isocyanides are better σ-donating–less π-accepting ligands than CO[3] leading to an enhanced electron density on the metal. Since cycloaddition reactions are very sensitive to variations in the electron density at the reaction centres, the substitution of CO by CNR should lead to an enhanced 1,3-dipolar activity, as indeed was found.[4] Substitution of one CO ligand by CNR in the starting complex $Fe(CO)_3(Pr^i\text{-dab})$ gave rise to a double cycloaddition of dimethyl acetylenedicarboxylate (dmadc) to both of the C=N–Fe units, which resulted in the formation of $Fe(CO)_2(CNR)$(tetrahydropyrrolo[3,2-*b*]pyrrole).

Unfortunately, $Fe(CO)_2(CNR)(dab)$ did not react with less activated dipolarophiles, *e.g.* alkenes, indicating that a larger degree of substitution was needed. tom Dieck *et al.*[5] described the reaction of $Fe(dab)_2$ with CNR which resulted in formation of $Fe(CNR)_3(dab)$. By using this method we synthesized different $Fe(CNR)_3(dab)$ complexes[6] including the highly air-sensitive red coloured $Fe(2,6\text{-xylyl-NC})_3(Pr^i\text{-dab})$ complex **1b**.†

This highly activated complex indeed undergoes 1,3-dipolar [3 + 2] cycloaddition with dimethyl maleate which finally results in formation of the bicyclo[2.2.2] compound **8**. The existence of the bicyclo[2.2.1] intermediate **6**, which is not observed in the present case, has been demonstrated for the analogous reactions involving $M(CO)_3(dab)$ (M = Fe, Ru) and dmadc in which the initial cycloadduct, corresponding to **6**, has recently been isolated and fully characterized.[2c,7] The five-membered ring in **6** can expand by means of a CNR insertion into the Fe–N σ-bond to give the likewise unobserved coordinatively and electronically unsaturated intermediate **7** which accepts an incoming 2,6-xylyl isocyanide to regain the 18-electron configuration. This new bicyclo[2.2.2] product **8**‡ readily precipitates at room temperature from pentane solution.

The present results demonstrate that 1,3-dipolar [3 + 2] cycloaddition of the C=N–Fe fragment in $Fe(2,6\text{-xylyl-NC})_3(Pr^i\text{-dab})$ with an alkene containing two electron withdrawing ester functions gives rise to a similar type of reaction as does $Fe(CO)_3(dab)$ with an electron-deficient alkyne.[2ab,4] Both reactions yield a bicyclo[2.2.2] compound. On warming of the bicyclo[2.2.2] tricarbonyl complex **4** to above room temperature, isomerization *via* reductive elimination and recoordination *via* the C=C double bond affords complex **5**. The presently discovered bicyclo[2.2.2] trisisocyanide compound **8**, lacking the double bond in the two-carbon bridge, is found to behave differently.

The yellow iron complex **8** is stable as a solid but in solution it is easily converted back to the starting compounds when the solution is warmed above room temperature. This is accompanied by a spectacular colour change from yellow to dark red indicating the existence of a chelating α-diimine complex **1b**. Upon cooling down the red colour disappears again and returns to yellow. This process was followed by variable temperature ^1H NMR (C_6D_6, 300 MHz). After raising the temperature to 333 K the signals corresponding to the compounds $Fe(2,6\text{-xylyl-NC})_3(Pr^i\text{-dab})$,† dimethyl maleate§ and 2,6-xylyl isocyanide¶ increased, while at the same time the concentration of **8** decreased. At 293 K the bicyclo[2.2.2] complex was slowly formed back in about one day. Starting from pure **8**, the reaction can be followed back and forth for only a limited number of conversions because it is accompanied by some slow decomposition, probably due to the limited thermal stability of complex **1b**.



Scheme 1

This reversible process is quite unique since it involves the reversible insertion–deinsertion of CNR, and the reversible formation–rupture of C–C, C–N and Fe–C bonds when taking into account the microscopic reversibility of this reaction.

Not many examples are known of reversible cycloadditions under mild conditions.[8] Usually a mobile equilibrium in a cycloreversion is reached at more elevated temperatures.[9] In addition to the smooth reversible cycloaddition, the temperature controlled procedure gives rise to a unique isocyanide deinsertion which takes place between intermediates **6** and **7**. Evidence for a CNR deinsertion has never unambiguously been encountered before,[3b,d] and has only been claimed in two articles.[10] In the tricarbonyl system (right hand side of Scheme 1), CO-deinsertion has been found to compete to a small extent with isomerization towards **5**.[11] When selectively labelled **4** (L′ = ^{13}CO) was kept at a temperature where it just

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† *^1H NMR data* of **1b** (300.13 MHz, C_6D_6, 293 K): δ 7.67 (s, 2H, HC=N), 6.6–6.8 (m, 9H, aryl H), 5.39 [sp, J_{HH} 7 Hz, 2H, C*H*(Me)$_2$], 2.35 (s, 18H, aryl Me$_3$), 1.68 (d, J_{HH} 7Hz, 12H, CH*Me*$_2$).

‡ Synthesis of the [2.2.2]bicyclo **8**. To a solution of $Fe(2,6\text{-xylyl-NC})_3(Pr^i\text{-dab})$ **1b** (1.20 mmol) in 30 ml pentane with an excess of CNR (1 equiv.) was added a solution of 0.15 ml dimethyl maleate (1 equiv.) in 5 ml diethyl ether and 10 ml pentane at room temperature and stirred for 2 h. The resulting yellow precipitate was subsequently washed three times with 15 ml of pentane. The pure product was obtained by crystallization from a concentrated diethyl ether–dichloromethane (5:3) solution by slow diffusion of hexane at room temperature. The molecular structure and crystal structure data will be published in a forthcoming full paper.

^1H NMR data of **8** (300.13 MHz, C_6D_6, 293 K): δ 8.64 (d, J_{HH} 5 Hz, 2H, HC=N), 7.01 (d) and 6.92 (d) (J_{HH} 7 Hz, 2H, *m*-aryl H), 6.8–6.6 (m, 10H, aryl H), 4.72 (dd, J_{HH} 5 Hz, 1H, N=CCH), 4.41 (sept) and 4.21 (sept) [J_{HH} 7 Hz, 2H, C*H*(Me)$_2$], 3.60 (m, 2H, C*H*–C*H*–Fe), 3.58 (s) and 3.41 (s) (6H, ester OMe), 2.44 (s), 2.37 (s) and 2.36 (s) (18H, aryl Me) 2.30 (s) and 2.19 (s) (6H, inserted C=N aryl Me), 1.48 (d), 1.12 (d), 0.77 (d) and 0.72 (d) (J_{HH} 7 Hz, 12H, CH*Me*$_2$). $^{13}C\{^1H\}$ NMR data of **8** (75.47 MHz, $CDCl_3$, 243 K): δ 196.1 (inserted *C*=N aryl), 183.6, 183.0, 182.3 (*C*≡N aryl), 176.5, 153.6 (ester CO), 170.5 (N=CC), 134.7, 134.3, 134.0, 129.8, 129.1, 128.7, 127.7, 127.6, 127.2, 127.0, 126.6, 126.3, 126.2, 125.9, 125.0, 116.6 (aryl *C*), 63.5, 47.0 [*C*CH(Me)$_2$], 55.2 (N=C*C*), 51.5, 49.2 (ester O*Me*), 51.0 (Fe–C–*C*), 24.5, 23.6, 23.2, 19.5 (CH*Me*$_2$), 23.1 (Fe–*C*–C), 19.4, 19.2, 19.0, 18.9, 18.3 (aryl *Me*).

§ *^1H NMR data* of dimethyl maleate (300.13 MHz, C_6D_6, 293 K): δ 5.70 (s, 6H, ester OMe), 3.35 (s, 2H, alkene H).

¶ *^1H NMR data* of $2,6\text{-Me}_2\text{-C}_6H_3\text{-N}{\equiv}C$ (300.13 MHz, C_6D_6, 293 K): δ 6.8–6.5 (m, 3H, aryl H), 2.07 (s, 6H, aryl Me).

starts to isomerize, then, in both the resulting **5** and unaltered **4**, the ^{13}CO label was found to be non-statistically distributed over all possible positions, including the inserted positions.

This temperature controlled interconversion between $Fe(2,6\text{-xylyl-NC})_3)Pr^i$-dab), diethyl maleate and 2,6-xylyl isocyanide, and the bicyclo[2.2.2] complex on the other side is not only remarkable for its reversibility but the stereospecificity with respect to retention of *cis*-configuration of the alkene, as well in the forward as in the back reaction, also establishes the concertedness of the 1,3-dipolar cycloaddition and cycloreversion step.

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