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Novel C–C and C–N Coupling Reactions on a Di-iron– α -Di-imine Complex in the Reaction of Fe₂(CO)₆{RN=C(H)C(H)=NR} with Methyl Propynoate; X-Ray Crystal Structures of Fe₂(CO)₅{(c-C₆H₁₁)N=CHCHN(c-C₆H₁₁)C(O)CH=CCO₂Me}, Fe₂(CO)₆-{PriNCHCH=N(Pri)CHCCO₂Me} and Fe₂(CO)₄{PriNCHCHN(Pri)CHCCO₂Me}

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The reaction of $Fe_2(CO)_6(Rdab)$ [Rdab = RN=CHCH=NR; R = Prⁱ or c-C₆H₁₁ (cyclohexyl)] with methyl propynoate at room temperature yields two products (*X*-ray): $Fe_2(CO)_5\{RN=CHCHN(R)C(O)CH=CCO_2Me\}$, where the Rdab ligand, a CO, and an alkyne are coupled to form an 8e donating ligand, and $Fe_2(CO)_6\{RNCHCH=N(R)CHCCO_2Me\}$, containing a 6e donating heterocyclic ligand, formed by coupling of the terminal alkyne C atom to both the Rdab N atoms in an unusual fashion; heating of the latter complex yields $Fe_2(CO)_4\{RNCHCHN(R)CHCCO_2Me\}$ (*X*-ray), with an unprecedented bis- η^3 -aza-allyl bonded ligand.

We have already shown that the α -diimine ligand Rdab (RN=CHCH=NR; dab = 1,4-diazabuta-1,3-diene), when co-ordinated as a σ -N, σ -N', η^2 -C=N 6e donor to transition metal atoms, may be involved in coupling reactions with unsaturated organic molecules, either *via* the C atom or *via* the N atom of the η^2 -C=N bonded part of the ligand. Examples of these reactions are those with Rdab itself, and with carbodiimines (RN=C=NR), sulphines (R₂C=S=O), alkynes, and ketene.^{1,2} An interesting aspect of the reactions of Ru₂(CO)₆(Rdab) with mono- and di-substituted alkynes is the ability of this complex to act as a cyclotrimerisation catalyst. Especially interesting was the selective formation of 1,3,5-trisubstituted benzene derivatives, when monosubstituted

alkynes were used. Recently Frühauf *et al.* showed that mononuclear iron–Rdab complexes react under CO pressure with activated alkynes to give also C–C and C–N coupled products.³ These and results for Ru-complexes stimulated us to study the reactivity of dinuclear $Fe_2(CO)_6(Rdab)$ complexes towards alkynes.⁴

We now report results for the reactions of $Fe_2(CO)_6(Rdab)$ complexes (R=Prⁱ or c-C₆H₁₁) (1) with methyl propynoate. Upon treating (1) with a threefold excess of HC=CCO₂Me at room temperature a mixture of complexes (2) and (3) was formed, which could be separated by column chromatography on silica. Heating of the dark yellow complex (3) for 2 h at 90 °C afforded in almost quantitative yield the brown complex



Scheme 1. Reaction of $Fe_2(CO)_6(Rdab)$ (1) [R = Prⁱ or c-C₆H₁₁ (cyclohexyl)] with methyl propynoate (alkyne).

(4). This complex was also formed when (1) was heated with an excess of HC=CCO₂Me in heptane for about 24 h. In that case, however, the yield was low (<10%) and the main product was the intensely purple coloured complex (5).† These reactions are summarized in Scheme 1.‡ The molecular structures of (2), (3) and (4) have been established by single-crystal X-ray diffraction.§

[‡] Important ¹H n.m.r. data (CDCl₃; proton numbering corresponds to C atom numbering in Figures 1––3): (**2**; R = Prⁱ), δ 7.86 (12-H), 2.84 (11-H), ${}^{3}J_{11,12}$ 2.2 Hz, and 4.21 (7-H); (**3**; R = Prⁱ), δ 6.71 (10-H), 3.75 (9-H), ${}^{3}J_{9,10}$ 5.2 Hz, and 6.6 (8-H, br. owing to quadrupole relaxation due to the N atoms), ${}^{4}J_{8,9}$ 1.1 Hz; (**4**; R = Prⁱ), δ 8.41 (13-H), 8.19 (5-H), and 7.73 (6-H), ${}^{3}J_{5,6}$ 8, ${}^{4}J_{5,13}$ 1.6 Hz.

§ Crystal Data (all structures were solved by the heavy atom method; refinement using anisotropic block-diagonal least-squares calculations): (2) M = 584.19, monoclinic, space group $P2_1/n$, $Z(C_{24}H_{28}N_2O_8Fe_2) = 4, a = 20.979(2), b = 8.9658(8), c = 14.693(1),$ $\beta = 107.393(9)^{\circ}$, $\mu(Cu-K_{\alpha}) = 97.2 \text{ cm}^{-1}$. H atoms were in calculated positions and not refined; R = 0.060, $R_w = 0.069$ for 1034 absorption-corrected reflections. (3) M = 504.06, monoclinic, space group $P2_1/n$, $Z(C_{18}H_{20}N_2O_8Fe_2) = 4$, a = 12.757(1), b = 18.247(1), c = 9.662(3) Å, $\beta = 107.35(1)^\circ$, $\mu(Mo-K_{\alpha}) = 14.61$ cm⁻¹, isotropic refinement for H, R = 0.045, $R_w = 0.085$ for 3717 absorption-corrected reflections. (4) M = 448.04, orthorhombic, space group *Pnca*, $Z(C_{16}H_{20}N_2O_6Fe_2) = 4$, a = 15.209(3), b = 17.685(3), c = 17.685(3)14.489(3) Å, μ (Mo- K_{α}) = 7.60 cm⁻¹, H-atoms were excluded, R = 0.076, $R_w = 0.142$ for 1320 absorption-corrected reflections. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemistry Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.



Figure 1. The molecular structure of complex $(2; R = c-C_6H_{11})$: bond lengths in Å: Fe(1)–Fe(2): 2.631(4), Fe(1)–C(8): 2.046(14), Fe(1)–C(7): 2.084(12), Fe(1)–C(11): 2.138(12), Fe(2)–C(8): 1.883(14), Fe(2)–N(1): 2.098(9), Fe(2)–N(2): 1.999(11), C(7)–C(8): 1.403(18), C(7)–C(6): 1.450(17), C(6)–O(6): 1.220(18), C(6)–N(1): 1.471(19), N(1)–C(11): 1.462(16), C(11)–C(12): 1.530(19), C(12)–N(2): 1.236(17).

The brown complex (2) consists of an $Fe_2(CO)_5$ unit [Fe(1)–Fe(2): 2.631(4) Å] bridged by a 8e donating dianionic organic ligand. This ligand is formed by coupling of the Rdab ligand with a CO and a HC=CCO₂Me unit. The triple bond of the alkyne fragment is reduced to a double bond, owing to the coupling of C(7) with a CO molecule, while C(8) is bridging between the two Fe atoms. The double bond is also asymmetrically η^2 -co-ordinated to one of the Fe atoms [C(7)–Fe(1): 2.084(12), C(8)–Fe(1): 2.046(14) Å], confirmed by the elongation of the C(7)-C(8) bond [1.403(18) Å]. The shortening of the bond lengths in the C(7)-C(6)-N(1)-C(11)part of the ligand indicates some delocalization of the negative charge over these three bonds [C(7)-C(6): 1.450(17); C(6)-N(1): 1.471(19); N(1)-C(11): 1.462(16) Å]. However, no delocalization occurs over the C(11)-C(12)-N(2) part of the original Rdab skeleton, as is clearly indicated by the C(11)-C(12) single bond length [1.530(19) Å] and the normal imine bond length [C(12)–N(2): 1.236(17) Å].

In complex (3) the $Fe_2(CO)_6$ unit [Fe-Fe: 2.563(4) Å] is bridged by a formally 6e donating ligand. An unusual feature is that in this ligand one of the alkyne C atoms is coupled to both the N atoms of the Rdab ligand, thus forming a five-membered heterocyclic ring. The other alkyne C atom symmetrically bridges the two Fe atoms [Fe(1)-C(13)]: 2.001(14), Fe(2)-C(13): 2.009(10) Å]. As can be seen from the C(8)-C(13) bond length of 1.523(5) Å, this former alkyne bond is reduced to a single bond with a change in hybridization of C(8) from sp to sp³. The imine bond N(2)–C(10) in the heterocyclic ring is slightly elongated [1.310(17) Å], while the C(9)-C(10) bond [1.425(11) Å] is somewhat short for a single bond. This indicates that the C(9)-C(10)-N(2) part of the ring has some allylic nature. This part of the ligand is probably best described as containing a positive charge on N(2) and a negative charge delocalized over the N(2)-C(10) and C(9)-C(10) bonds. The atoms C(9), C(10), N(2), and C(8) are

[†] In this complex the two alkyne atoms are tail-to-tail coupled and are σ , σ -bonded to one of the iron atoms to form a metallacyclopentadiene fragment. The latter fragment is η^2 , η^2 -co-ordinated to a second Fe atom, to which also the Rdab ligand is co-ordinated in the chelate bonding mode.





Figure 2. The molecular structure of complex (3; R = Pri): bond lengths in Å: Fe(1)–Fe(2): 2.563(4), Fe(1)–C(9): 2.122(8), Fe(1)–C(13): 2.001(14), Fe(2)–N(1): 2.062(4), Fe(2)–C(13): 2.009(10), N(1)–C(9): 1.493(9), C(9)–C(10): 1.425(11), C(10)–N(2): 1.310(17), N(2)–C(8): 1.477(5), C(8)–N(1): 1.503(15), C(8)–C(13): 1.523(5).

coplanar (r.m.s. deviation 0.062 Å), while N(1) is 0.55 Å above this plane.

The framework of (4) consists of an $Fe_2(CO)_4$ unit [Fe-Fe: 2.497(3) Å] with a 10e donating organic ligand bridging the two Fe atoms. This ligand can be seen as two coupled η^3 -bonded aza-allyl fragments, one of which consists of the N(2)-C(6)-C(5) part of the Rdab ligand and the other consisting of the originally bridging N atom, N(1), coupled with the terminal alkyne C atom, C(13), of the methyl propynoate. The η^3 -allylic nature of these two parts of the ligand is indicated by the bond lengths [Fe(2)-N(2): 2.011(10):Fe(2)-C(6): 2.056(14); Fe(2)-C(5): 2.047(12); N(2)-C(6):1.380(19); C(6)-C(5): 1.459(21) Å] for the aza-allyl fragment bonded to Fe(2) and those [Fe(1)-N(1): 1.997(11); Fe(1)-C(13): 2.038(12); Fe(1)–C(14): 2.057(12); N(1)–C(13): 1.427(16); C(13)-C(14): 1.357(16) Å] for the aza-allyl fragment bonded to Fe(1). This complex shows some structural resemblance to the complexes Co₂(CO)₄{(Bu^tC=CH)₂-(HC=CH)⁶ and $Mo_2(\eta^5-C_5H_5)_2\{(PhC=CH)_2(HC=CH)\}$,⁷ in which the three alkynes are coupled to form a ligand that co-ordinates via two η^3 -allyl functions to the Co₂(CO)₄ and the $Mo_2(\eta^5-C_5H_5)_2$ unit respectively, while the two metal atoms are bridged by both the terminal C-atoms of the ligand skeleton.

The thermally induced rearrangement of (3) to (4) probably involves, besides the elimination of two CO ligands, the fission of the N(2)–C(8) bond, followed by rotation of the N(2)– C(9)–C(10) part of the ligand along the N(1)–C(9) bond. We cannot, however, exclude the possibility of cleavage of the N(1)–C(8) bond, which would afford the same end product.

Figure 3. The molecular structure of complex $(4; R = Pr^i)$: bond lengths in Å: Fe(1)–Fe(2): 2.497(3): Fe(1)–N(1): 1.997(11), Fe(1)– C(13): 2.038(12), Fe(1)–C(14): 2.057(12), Fe(1)–N(2): 2.006(12), Fe(2)–N(2): 2.011(10), Fe(2)–C(6): 2.056(14), Fe(2)–C(5): 2.047(12), Fe(2)–C(14): 1.973(11), N(2)–C(6): 1.380(19), C(6)–C(5): 1.459(21), C(5)–N(1): 1.479(19), N(1)–C(13): 1.427(16), C(13)–C(14): 1.357(16). The terminal methyl C-atoms are drawn smaller for clarity.

Further delocalization of charge over the ligand then results in the formation of the bis-aza-allyl ligand in (4), which is the first example of its kind.

The present C-N and C-C coupling reactions take place with the dinuclear $Fe_2(CO)_6(Rdab)$ complexes, which strongly suggests that the activation of η^2 -C=N part of the Rdab ligand as well as the electronic activation of the alkyne bond by the methoxycarbonyl group are important factors. The small steric hindrance of the methyl propynoate CH group seems likewise to be important as is indicated by the fact that the disubstituted analogue (MeO₂CC=CCO₂Me) reacts with Fe₂(CO)₆(Rdab) in a quite different way.** Other workers,³ however, claim that η^2 -C=N co-ordination of the Rdab ligand is not necessary for the ligand to undergo C-N and C-C coupling reactions. This has been concluded from the observation that in the reaction of MeO₂CC=CCO₂Me with the mononuclear complex $Fe(CO)_3(Rdab)$, where the ligand is 4e σ -N, σ -N'-chelate bonded to the Fe atom, complexes with complicated organic ligands resulting from C-C and C-N coupling reactions are also obtained. It must be noted, however, that the latter reaction only takes place under CO pressure, which makes it difficult to conclude that the Rdab ligand is σ -N, σ -N'-co-ordinated when the coupling reaction with the alkyne molecule takes place. We are currently studying further reactions of alkynes with dinuclear Fe complexes containing either 4e σ -N, σ -N'-co-ordinated or 6e σ -N, σ -N', η^2 -C=N-co-ordinated Rdab ligands.

[¶] The distances in the aza-allyl fragments may be compared with similar bond lengths of 1.38(2) and 1.39(2) Å in $MnFe(CO)_{6^-}$ (PrⁱNCHCHNPrⁱ)⁵ and 1.396(7) and 1.405(8) Å in $Ru_2(CO)_{5^-}$ {PrⁱNCHCHNPrⁱC(:O)CH₂C(:O)CH₂}.²

^{**} In this reaction no coupling reaction with the Rdab ligand occurs, but one of the CO groups is substituted by an alkyne to form the complex $Fe_2(CO)_5(Rdab)(alkyne)$. At 69 °C this reaction is followed by the substitution of a second CO group by an alkyne, which is then coupled to the first alkyne, to form an RCCRCRCR fragment co-ordinated to an $Fe_2(CO)_4$ unit.

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