[3+2+1] cycloaddition involving alkynes, CO and bridging vinyliminium ligands in diiron complexes: a dinuclear version of the Dötz reaction?†

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The vinyliminium complex [Fe₂{μ-η¹:η³-C(SiMe₃)=CHC= $N(Me)_2$ {(μ -CO)(CO)(Cp)_2[SO₃CF₃] reacts with HC \equiv CR $(R = CPh_2OH)$, affording a mixture of the 2,4,6-trisubstituted oxo-n⁵-cyclohexadienyl complex [Fe{n⁵-C₆H₂O(NMe₂)(SiMe₃)-(R) $\{(Cp)\}\$, the 2,6-disubstituted phenol $C_6H_3R'(NMe_2)OH$ $(\mathbf{R}' = \mathbf{CHPh}_2)$ and 1,2,4-trisubstituted ferrocene [1-NMe₂-2-R-4-SiMe₃-Fc]. The corresponding reaction with HC=CR (R = CMe₂OH) yields analogous products: $[Fe{\eta^{5}-C_{6}H_{2}O (NMe_2)(SiMe_3)(R')$ (Cp)] (R' = CMe=CH₂), the phenol C₆H₃R'(NMe₂)OH together with [1-NMe₂-2-R-4-SiMe₃-Fc].

In the expanding field of transition-metal mediated transformations of organic molecules, dinuclear complexes might have a special role in consideration of the cooperative effects associated with the presence of adjacent metal centres, and of the activation modes offered by multisite coordination.¹ These possibilities have been, so far, under-exploited.

We have been interested in the assembly, functionalization and transformation of bridging organic frames in diiron complexes which offer, as further advantage, the use of a non-toxic, readily available and inexpensive transition metal, better responding to the growing need for a "sustainable metal catalysis".² Recently, we reported that bridging vinylalkylidene ligands in diiron complexes can be involved in a [3+2]cycloaddition with alkynes resulting in the formation of new polysubstituted ferrocenyl products.³ One example is reported in Scheme 1.

A mixture of different ferrocenes is formed since, in the cyclization reaction, the bridging vinylalkylidene ligand loses one of the two substituents: H or NMe2, generating the triand di-substituted ferrocenes, respectively (i.e. 2 and 3 in Scheme 1). Nevertheless, the reaction shows that is possible to involve bridging C₃ frames in cycloaddition with alkynes, reminiscent of the well known cycloaddition reactions of mononuclear Fischer-type vinylcarbene complexes.⁴

Then, we became interested in extending these studies to other related diiron complexes containing different bridging C₃ ligands. In particular we investigated vinyliminium

complexes of the type $[Fe_2\{\mu-\eta^1:\eta^3-C(R)=CHC=NMe_2\}$ - $(\mu$ -CO)(CO)(Cp)₂][SO₃CF₃] (4) (R = alkyl, aryl, SiMe₃),⁵ mostly because the less saturated bridging C₃ chain, has the appropriate number of substituents to give cyclopentadienyls, by reaction with alkynes, without requiring any C-N or C-H bond cleavage, as for 1. Unfortunately, vinyliminium complexes were rather unreactive toward alkynes, with a relevant exception concerning propargyl alcohols, as shown in Scheme 2. We have found that complex 4 reacts with $HC \equiv CPh_2OH$ and $HC \equiv CMe_2OH$ to give a mixture of products that include the trisubstituted $0x0-\eta^5$ -cyclohexadienyl complexes 6 and 9, the phenols 7, 10, and the trisubstituted ferrocenyl complexes 5 and 8, respectively (Scheme 2).‡

Complex 5 was identified by comparison of its spectroscopic properties with those reported in the literature,³ whereas the other products have been characterized by spectroscopy, elemental analysis and high-resolution mass spectrometry.[‡] Moreover, the molecular structure of 6 has been determined by X-ray diffraction studies.⁶ In the structure of **6** (Fig. 1), the iron center is n⁵-coordinated to a Cp ligand [average Fe-C distances 2.041(7) Å] and also η^5 -coordinated to a trisubstituted oxo-cyclohexadienyl ligand n⁵-C₆H₂O(NMe₂)(SiMe₃)-(CPh₂OH). The Fe–C interactions with this η^5 -ligand are sensibly spread [range 2.049(3)-2.116(3) Å, average 2.098(7) Å] whereas Fe(1)-C(1) [2.275(3) Å] is rather long (sum of the covalent bonds for Fe and C 2.02 Å). The η^5 -coordination of the ligand is also in agreement with the fact that the C(3)–C(2)[1.413(4) Å], C(3)–C(4) [1.419(4) Å], C(6)–C(5) [1.414(3) Å] and C(5)-C(4) [1.413(4) Å] interactions all display a considerably delocalised π -character, whereas C(2)–C(1) [1.457(4) Å] and C(1)–C(6) [1.446(4) Å] are essentially single bonds. Moreover, the C(1)–O(1) distance [1.227(3) Å] is indicative of a ketonic nature of this group. A significant hydrogen bond is, then, found between the hydroxy O(2)-H(40) group and O(1) $[O(2)-H(40) 0.862(17) \text{ Å}; H(40) \cdots O(1) 1.78(2) \text{ Å}; O(2) \cdots O(1)$ 2.578(3) Å; O(2)–H(40)···O(1) 153(3)°].

The differences between the two series of products, obtained $HC \equiv CPh_2OH$ and $HC \equiv CMe_2OH$, respectively from





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Scheme 2



Fig. 1 ORTEP drawing of 6. Thermal ellipsoids are at the 30% probability level. Selected bond lengths (Å): Fe(1)-C(1) 2.275(3), Fe(1)-C(2) 2.166(3), Fe(1)-C(3) 2.078(3), Fe(1)-C(4) 2.073(3), Fe(1)-C(5) 2.049(3), Fe(1)-C(6) 2.126(3), Fe(1)-Cp(av.) 2.041(7).C(1) - C(2)1.457(4), C(2)-C(3) = 1.413(4),C(3) - C(4)1.419(4), C(5)–C(6) 1.414(3), 1.446(4), C(4) - C(5)1.413(4), C(1)-C(6)C(2)-N(1) 1.408(3), C(1)-O(1) 1.277(3), C(6)-C(17)1.542(4), C(4)-Si(1) 1.883(3), C(17)-O(2) 1.427(3).

(*i.e.* 5, 6, 7 *vs.* 8, 9, 10) is not limited to the presence of Ph groups in the place of Me. A further difference between 8, 10 and 5, 7 is that the cyclopentadienyl substituent CMe₂OH undergoes H₂O elimination to form the -C(Me)=CH₂ group. This additional transformation is reasonable in consideration of the reaction conditions: prolonged heating and subsequent workup by chromatography on deactivated alumina.

The cycloaddition reactions reported in Scheme 2 deserve further comments. First, the expected ferrocenes **5** and **8** are obtained only in low yields. Conversely, other products are formed: the $0x0-\eta^5$ -cyclohexadienyl complex **6** and **9**, and the phenols **7** and **10**. In these compounds a six-membered ring (*i.e* the $0x0-\eta^5$ -cyclohexadienyl ligand and the phenol) is most likely originated by a [3+2+1] cycloaddition that involves the bridging C₃ ligand of the parent complex **4**, the alkyne and a CO. The incorporation of CO makes the cycloaddition substantially different from that shown in Scheme 1, and closer to the classic Dötz benzannulation, that consists in the assembly of a α,β -unsaturated carbene ligand, an alkyne and a carbonyl, and is one of the most powerful protocols for the synthesis of phenols and other organic products.⁷ These include cyclohexadienones, which in addition, are also indicated as possible reaction intermediates.⁸

On the other hand, cyclization reactions analogous to the benzannulation, but involving bridging vinylalkylidenes, are almost unknown. This is believed to be the consequence of the higher stability and inertness associated with vinylalkylidenes in the bridging η^1 : η^3 -coordination. To the best of our knowledge, there is only one example of cyclohexadienone formation at a dinuclear centre, by assembling of a bridging vinylalkylidene, an alkyne and a CO, that is the reaction of the dimolvbdenum complex [Mo₂(u-CHCHCMe₂)(CO)₄(Cp)₂] with $HC \equiv CBu^{t,9}$ In this case, the cyclohexadienone remains coordinated as bridging ligand, which is a remarkable difference with respect to our results. Indeed, the reaction of 4 with alkynes leads to fragmentation of the diiron species and formation of mononuclear complexes. Therefore, it will be of great interest understanding to what extent the cyclizations shown in Schemes 1 and 2, result from dinuclear activation, or are simply associated to processes occurring at mononuclear centres.

The formation of phenols 7 and 10 takes place in too low yields to be useful as a synthetic approach. Moreover, it should be noted that 7 and 10 are not simply the result of a [3+2+1] cycloaddition, but also involve the replacement of a C-SiMe₃ bond with a C-H bond, and the replacement of OH with H, in the case of 7. Thus, the reaction sequence leading to the observed products must include a number of rearrangements and transformations that, at this stage, can be hardly formulated in a reliable mechanism. Beside these limitations, it is worth noting that the phenols 7 and 10 exhibit an unusual substitution pattern, and neither 7 nor 10 have been described previously.

As concluding remark, our results evidence that bridging vinyliminium ligands in diiron complexes can undergo a [3+2+1] cycloaddition which resembles the classic Dötz benzannulation. Therefore, this type of cyclization is not necessarily restricted to vinylalkylidene ligands, but can be extended to other bridging unsaturated C₃ fragments.¹⁰ A further interesting aspect is that iron complexes are involved, whereas the classic benzannulation mostly concern Group 6 metals, with a limited extension to Mn and Ru.¹¹ Our findings add a new piece of evidence that bridging ligands in diiron complexes offer

potential for new transformations and C-C bond forming reactions, unattainable in mononuclear species.

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Notes and references

‡ Synthesis of **5**, **6** and **7**: Complex **4** (0.610 g, 1.01 mmol), in toluene (15 ml), was treated with HC \equiv CCPh₂OH (457 mg, 2.19 mmol) and the resulting mixture was heated at reflux temperature for 10 h. Removal of the solvent and chromatography of the residue on a alumina column, with petroleum ether (bp 40–60 °C) as eluent, gave a first yellow fraction containing ferrocene [FeCp₂] (2.4%), **5** (4.2%) and 7 (19.8%; yields calculated by ¹H NMR integration). Elution with Et₂O gave a second orange fraction containing **6** (33.0% yield). Crystals of **6** suitable for X-ray analysis were obtained from a MeOH–H₂O solution.

6. Anal. Calc. for C₂₉H₃₃FeNSiO₂: C, 68.10; H, 6.46; N, 2.74. Found: C, 67.95; H, 6.48; N, 2.70%. IR (CH₂Cl₂) ν (CO) 1512 (s) cm⁻¹. ¹H NMR (CDCl₃) δ 9.12 (s, 1 H, OH); 7.58–7.10 (m, 10 H, Ph); 5.25 (d, ⁴J_{HH} = 1.2 Hz, 1 H, C³H); 4.92 (d, ⁴J_{HH} = 1.2 Hz, 1 H, C⁵H); 4.45 (s, 5 H, Cp); 3.00 (s, 6 H, NMe₂); 0.24 (s, 9 H, SiMe₃). ¹³C{¹H} NMR (HSQC, HMBC) (CDCl₃) δ 148.2 (C¹); 143.9, 143.5 (*ipso-Ph*); 128.4–126.3 (Ph); 115.35 (C²); 97.47 (C⁶); 84.07 (C⁵); 80.93 (CPh₂OH); 77.11 (C³) 72.52 (C⁴); 71.37 (Cp); 41.91 (NMe₂); -1.10 (SiMe₃). ESI-MS(+) *m*/*z*: [M]⁺ + H = 512; [M]⁺ + Na = 534.

7. ¹H NMR (CDCl₃) δ 7.29–7.13 (m, 10 H, Ph); 7.08 (dd, ³J_{HH} = 7.6 Hz, ⁴J_{HH} = 2 Hz, 1 H, C⁵H); (6.76, t, ³J_{HH} = 7.6 Hz, 1 H, C⁴H); 6.65 (dd, ³J_{HH} = 7.6 Hz, ⁴J_{HH} = 2 Hz, 1 H, C³H); 5.90 (s, 1 H, CHPh₂); 2.63 (s, 6 H, NMe₂). ¹³C{¹H} NMR (HSQC, HMBC) (CDCl₃) δ 149.4 (C¹); 143.6 (*ipso*-Ph); 140.3 (C²); 129.4–126.1 (Ph); (126.9) (C³); 118.92 (C⁴), 118.70 (C⁵); 50.17 (CHPh₂); 45.3 (NMe₂). ESI-MS: [M]⁺ + H = 304 *m*/*z*; [M]⁺ + Na = 326 *m*/*z*. HRMS *m*/*z* Calc. for [M]⁺ C₂₁H₂₁N₁O₁ 303,1623, found 303,1623.

Compounds 8, 9 and 10 were obtained by an analogous procedure, upon reaction of 4 (490 mg, 0.80 mmol) and $HC \equiv CCMe_2OH$ (0,30 mL, 3.1 mmol)

8 (12%). Anal. Calc. for C₁₈H₂₇FeNSi: C, 63.34; H, 7.97; N, 4.10. Found: C, 63.51; H, 7.90; N, 4.15%. ¹H NMR (CDCl₃) δ 5.36, 5.07 (m, 2 H, ==CH₂); 4.16 (s, 5 H, Cp); 3.95 (m, 2 H, C⁵H and C³H); 2.60 (s, 6 H, NMe₂); 2.11 (s, 3 H, Me); 0.21 (s, 9 H, SiMe₃). ¹³C{¹H} NMR (HSQC, HMBC) (CDCl₃) δ 141.8 (*C*=CH₂); 114.8 (C¹); 112.8 (=CH₂); 81.2 (C²); 70.6 (C³). **9** (30%). Anal. Calc. for C₁₉H₂₉Fe₂NO₂-Si: C, 58.91; H, 7.55; N, 3.62. Found: C, 58.84; H, 7.60; N, 3.54%. IR (CH₂Cl₂) ν (CO) 1519 (s) cm⁻¹. ¹H NMR (CDCl₃) δ 5.23 (d, 1 H, CH, ⁴J_{HH} = 1.2 Hz); 5.08 (d, 1 H, CH, ⁴J_{HH} = 1.2 Hz); 4.55 (s, 5 H, Cp); 2.98 (s, 6H, NMe₂); 1.57 (s, 3H, Me); 1.54 (s, 3H, Me); 0.36 (s, 9H, SiMe₃); OH not observed. ¹³C{¹H} NMR (HSQC, HMBC) (CDCl₃) δ 148.4 (C¹); 114.8 (C²); 99.0 (C⁶); 81.3 (CMe₂); 78.4 (CH); 73.8 (C⁴); 72.5 (CH); 71.5 (Cp); 42.2 (NMe₂); 31.2, 27.8 (Me); 1.3 (SiMe₃). ESI-MS m/z: 389 [M]⁺ + H; 411 [M]⁺ + Na 10 (17%).¹H NMR (CDCl₃, 400 MHz) δ 7.09 (dd, 1 H, ³J_{HH} = 7.8 Hz, ⁴J_{HH} = 1.5 Hz, C⁵H); 7.03 (dd, 1H, ³J_{HH} = 7.8 Hz, ⁴J_{HH} = 1.5 Hz, C³H); 6.81 (t, 1 H, ³J_{HH} = 7.8 Hz, C⁴H); 5.32–5.20 (m, 2 H, =CH₂); 2.66 (s, 6 H, NMe₂); 2.17 (s, 3 H, CH₃); OH not observed. ¹³C{¹H} NMR (HSQC, HMBC) (CDCl₃) δ 148.5 (C¹); 143.4 (C⁶); 140.2 (C²); 128.3 (C=CH₂); 125.7 (C³), 119.8, (C4), 119.4 (C⁵); 115.6 (=CH₂); 45.3 (NMe₂); 23.1 (CH₃).

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