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Photochemical head-to-head (R = H) *vs*. head-to-tail dimerization (R = Ph) of iron acetylide complexes (η^5-C_5Me_5)Fe(CO)$_2$–C≡C–R leading to a dimetallacyclopentenone and a μ-vinylidene complex *

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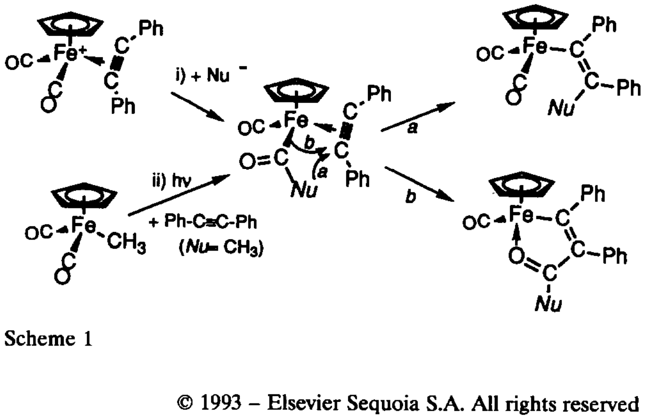
Abstract

Irradiation of a benzene solution of iron acetylides Fp*–C≡C–R (R = H, Ph) results in dimerization of the R–C≡C ligand to give dinuclear complexes with completely different structures, *i.e.* a dimetallacyclopentenone $Cp_2^*Fe_2(CO)(\mu\text{-}CO)[\mu\text{-}\eta^1:\eta^3\text{-}C(C{\equiv}CH){=}CHC({=}O)]$ (R = H) and a μ-vinylidene complex $Cp_2^*Fe_2(CO)_2(\mu\text{-}CO)[\mu\text{-}C{=}C(Ph)C{\equiv}C\text{–}Ph)]$ (R = Ph), depending on the substituent (R). The formation of the products has been interpreted in terms of head-to-head (R = H) and head-to-tail coupling (R = Ph) of the alkynyl ligands within the coordination sphere of the Cp*Fe(CO) fragment.

Metal acetylide complexes contain two reaction sites, that is, the C≡C part and the metal centre itself. Since the former works as an electron donating η^2-alkyne ligand and the latter possesses an ability to transform a ligand within its coordination sphere, combination of the two functions has been expected to effect unusual chemical reactivities. In previous papers we have demonstrated that, if an η^2-alkyne ligand and an η^1-organic group are introduced into a coordination sphere of the CpFe(CO) fragment, the C≡C part readily inserts into the Fe–C(η^1-ligand) bond to give *cis*-alkenic products [1,2**]. As summarized in Scheme 1, (i) nucleophilic addition to [Fp$^+$(η^2-Ph–C≡C–Ph)]BF$_4$ [1c] or (ii) photolysis of Fp–CH$_3$ [3] or Fp*–CH$_3$ [1b] in the presence of Ph–C≡C–Ph may generate the η^1-acyl-η^2-alkyne-intermediate, which undergoes intramolecular transfer of the acyl or Nu group to the alkyne ligand from the metal side to produce an alkenyl complex and/or a metallacycle with *cis*-configuration. These results prompted us to examine photolysis of iron acetylide complexes Fp*–C≡C–R [R = H(**1**), Ph(**2**)] which should serve as a substrate as well as a reactive metal centre. Here we report the first example of photochemical dimerization of metal acetylides [4*] and a clear-cut regiochemical dependence of C–C coupling processes on the substituent (R).

Irradiation of a benzene solution of iron acetylide complexes **1** and **2** [1a] with a high-pressure mercury lamp affords deep purple products **3** and **4** in moderate yields (38 and 19%) [5*], respectively, after chromato-



Scheme 1

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* Abbreviations: Fp = CpFe(CO)$_2$; Cp = η^5-C_5H_5, Fp* = Cp*Fe(CO)$_2$; Cp* = η^5-C_5Me_5.

** Reference number with an asterisk indicates a note in the list of references.

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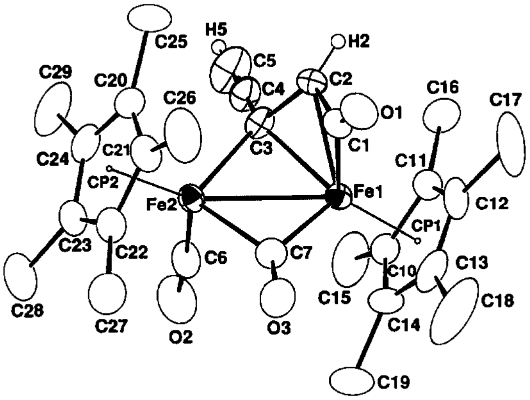
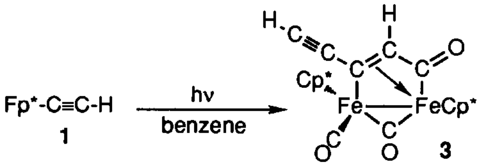
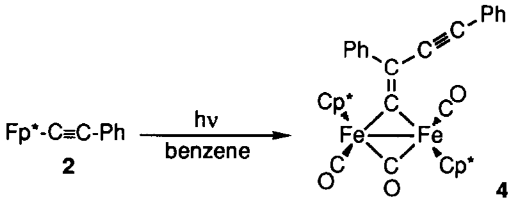


Fig. 1. An ORTEP view of **3** drawn at the 30% probability level. Important bond lengths (Å) and angles (°) are Fe1–Fe2: 2.582(1), Fe1–C1: 1.889(7), Fe1–C2: 2.058(7), Fe1–C3: 1.984(7), Fe1–C7: 1.940(6), Fe2–C3: 1.957(6), Fe2–C6: 1.746(9), Fe2–C7: 1.940(6), C1–C2: 1.44(1), C1–O1: 1.197(9), C2–C3: 1.439(9), C3–C4: 1.424(9), C4–C5: 1.18(1), C6–O2: 1.15(1), C7–O3: 1.161(8); Fe1–C3–Fe2: 81.9(3), Fe1–C3–C4: 129.4(6), Fe2–C3–C4: 121.2(5), Fe2–C1–O1: 143.9(6), O1–C1–C2: 139.2(7), C1–C2–C3: 115.3(5), C2–C3–C4: 119.1(6), C3–C4–C5: 178.2(9).

graphic separation (on alumina eluted with CH_2Cl_2-hexanes) followed by recrystallization from ether-hexanes. (eqs. (1) and (2)) The two distinct Cp* signals, the presence of a bridging carbonyl ligand, and the purple colour clearly indicate that both are dinuclear complexes with an Fe–Fe bond.

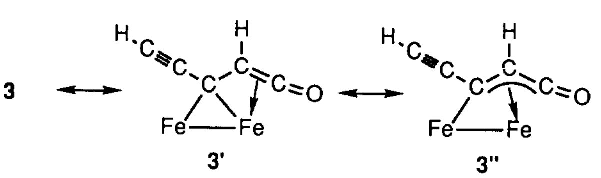


(1)



(2)

Spectroscopic analyses of the H derivative (**3**) [6*] merely reveal the presence of a non-coordinated ethynyl group, an acyl functional group, and only one η^1-CO ligand in addition to the above-mentioned structural informations. The structure has been determined unambiguously by crystallography (Fig. 1) [7*]. That C1, C2 and C3 lie within the range of bonding interaction of Fe1 and that C3 is almost equidistant from Fe1 and Fe2 may be interpreted in terms of the three possible resonance structures, *i.e.* the dimetallacyclopentenone structure (**3**), the ketene form (**3′**), and the η^3-allyl form (**3″**) (Scheme 2). Similar dimetallacyclopentenones (M = Fe, Ru) were prepared by a different method, *i.e.* addition of R–C≡C–R to a "$Cp_2M_2(CO)_3$" fragment, and their structures were characterized by Knox *et al.* [8]



Scheme 2

For the Ph derivative (**4**) [6], on the basis of the highly deshielded quarternary carbon signal diagnostic of a vinylidene ligand [δ 328.6 (Cα), 135.6 (Cβ); *cf.* $Cp^*_2Fe_2(\mu\text{-}C{=}CHR)(\mu\text{-}CO)(CO)_2$ (Cα, Cβ): R = H (295.5, 113.4), R = C(=O)^{t}Bu (334.9, 137.2) [1c]] [9], all the ^{13}C-NMR signals are readily assigned to the dinuclear μ-vinylidene structure, which has been confirmed by X-ray crystallography (Fig. 2) [7]. While most structural parameters fall in their normal ranges, the C1–C2 distance [1.41(2) Å] is the longest of the C=C lengths of the previously reported diiron μ-vinylidene complexes (1.30 to 1.38 Å) [9]. The elongation may result from twisting of the C=C bond as is evident from the torsion angles Fe2–C1–C2–C3 = 29.6° and Fe1–C1–C2–C11 = 41.4°, which suggest that the steric repulsion between the Cp* ring (C20 ~ 29) and the Ph group (C11 to ~ 16) is dominant.

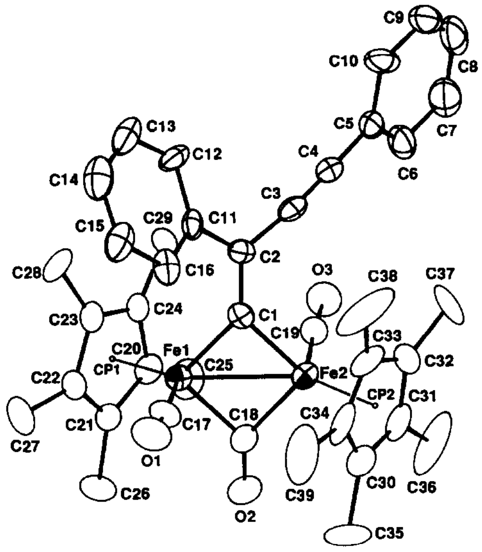
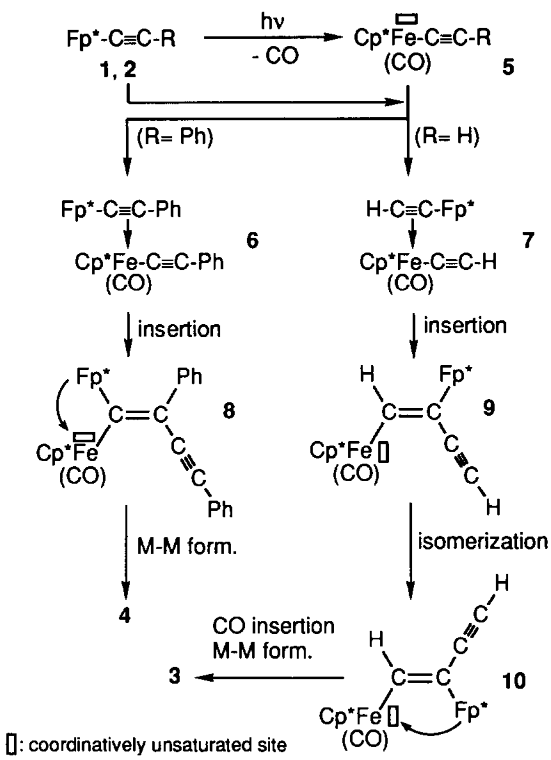


Fig. 2. An ORTEP view of **4** drawn at the 30% probability level. Important bond lengths (Å) and angles (°) are Fe1–Fe2: 2.565(3), Fe1–C1: 1.91(1), Fe1–C17: 1.72(1), Fe1–C18: 1.93(1), Fe2–C1: 1.90(1), Fe2–C18: 1.90(2), Fe2–C19: 1.75(2), C1–C2: 1.41(2), C2–C3: 1.43(2), C2–C11: 1.49(2), C3–C4: 1.20(2), C4–C5: 1.42(5), C17–O1: 1.16(2), C18–O2: 1.20(2), C19–O3: 1.15(2); Fe1–C1–C2: 138.5(9), Fe2–C1–C2: 136.2(9), Fe1–C1–Fe2; 84.7(5), C1–C2–C3: 117(1), C1–C2–C11: 125(1), C3–C2–C11: 119(1), C2–C3–C4: 172(1), C3–C4–C5: 176(1).



Scheme 3

Since no other isomeric product has ever been isolated from the reaction mixtures, the present photochemical dimerizations turn out to be regiospecific ones. In addition, it should be noted that the regiochemistries of the C–C coupling observed for **3** and **4** are completely different. In **3** the two ethynyl groups are bonded to each other at the α-carbon of the acetylide (head-to-head dimerization), whereas in **4** the C–C bond formation has taken place between the α-carbon of one Ph–C≡C ligand and the β-carbon of the other ligand (head-to-tail dimerization).

Taking into account our previous results, a plausible mechanism for the formation of **3** and **4** is shown in Scheme 3. Photochemical decarbonylation of **1** and **2** generates a coordinatively unsaturated species **5**, which incorporates another molecule of **1** and **2** to give a dinuclear intermediate, **6** and **7**, respectively. In the next insertion step two orientations may be possible depending on the substituent of the acetylide ligand. When R = Ph, head-to-tail insertion leads to the formation of **8**, which is subsequently transformed to **4** *via* metal–metal bond formation. On the other hand, an insertion reaction of **7** may take place in the opposite direction (head-to-head) to give **9**. Isomerization giving **10** followed by CO insertion and Fe–Fe bond formation finally produces **3**. Since rationalization of the observed regiochemistry by preliminary EHMO calculations has been unsuccessful, we now assume that the difference may partly result from steric reasons. When R = H, the steric repulsion between the two Fp* groups should stabilize **7** [10*]. However, in the case of **6** the bulky Ph groups may destabilize the orientation like **7** or, more likely, some attractive interaction between the two Fe atoms, which finally results in the formation of the Fe–Fe bond, may favour **6**.

Thus quite regioselective dimerization of metal acetylides has been realized by the C–C coupling reaction of the acetylide ligands in the coordination sphere of the Cp*Fe(CO) fragment.

References and notes

1 (a) M. Akita, S. Oyama, M. Terada and Y. Moro-oka, *Organometallics, 9* (1990), 816; (b) M. Akita, S. Oyama, M. Terada and Y. Moro-oka, *Organometallics, 10* (1991) 1561; (c) M. Akita, M. Terada and Y. Moro-oka, *Organometallics, 10* (1991) 2961; (d) M. Akita, S. Kakuta, S. Sugimoto, M. Terada and Y. Moro-oka, *J. Chem. Soc., Chem. Commun.*, (1992) 451.

2 Coupling between η^2-alkyne and η^1-acyl ligands is precedented. See, for example, E. B. Brookhardt, J. J. Doney, R. G. Bergman and C. H. Heathcock, *J. Am. Chem. Soc., 109* (1987) 2022, and references cited therein.

3 H. G. Alt, M. Herberhold, M. D. Rausch and B. H. Edwards, *Z. Naturforsch., Teil B, 34* (1979) 1070.

4 Dehydrogenative coupling of ethynyl complexes giving 1,3-butadiyne-1,4-diyl complexes [M–C≡C–C≡C–M] was reported by P. J. Kim, H. Masai, K. Sonogashira and N. Hagihara, *Inorg. Nucl. Chem. Lett., 6* (1970) 181.

5 Fp_2^* is formed as a major byproduct.

6 Spectroscopic data. **3**: ^1H NMR ($CDCl_3$): δ 1.48 (15H, s, Cp*), 1.57 (15H, s, Cp*), 1.60 (1H, s, ≡CH), 4.26 (1H, s, =CH). ^{13}C NMR ($CDCl_3$): δ 7.8 (q, $J = 127.4$ C_5Me_5), 9.2 (q, $J = 127.4$, C_5Me_5), 23.6 (d, $J = 156.0$, =CH), 90.3 (d, $J = 248.6$, ≡CH), 95.0 (dd, $J = 48.0$, 5.2, *C*≡CH), 97.0, 97.9 (s, C_5Me_5), 166.5 (s, *C*=CH), 212.6 (s, C≡O), 232.0 (s, C=O), 262.5 (s, μ-CO). IR (KBr): ν(≡C–H) 3227, ν(C≡O) 1937, 1780, ν(C=O) 1734 cm^{-1}. **4**: ^1H NMR ($CDCl_3$): δ 1.33 (15H, s, Cp*), 1.67 (15H, s, Cp*), 7.04–7.92 (10H, m, Ph_2). ^{13}C NMR ($CDCl_3$): δ 9.0 (q, $J = 128.0$, C_5Me_5), 9.6 (q, $J = 127.9$, C_5Me_5), 89.9, 93.9 (s, C≡C), 100.1, 100.2 (s, C_5Me_5), 124.9 (dt, $J = 160.3$, 7.0 *p*-Ph), 126.1 (dt, $J = 160.1$, 7.8, *p*-Ph), 126.2 (t, $J = 8.5$, *ipso*-Ph), 128.1 (dd, $J = 158.7$, 8.0, *m*-Ph), 128.2 (dd, $J = 160.3$, 8.0, *m*-Ph), 130.7 (dt, $J = 161.8$, 6.7, *o*-Ph), 135.6 (t, $J = 3.5$, =*C*-Ph), 142.4 (t, $J = 7.0$, *ipso*-Ph), 215.1, 216.8 (s, C≡O), 275.8 (s, μ-CO). 328.6 (s, μ-C=). (One of the *o*-Ph carbon signals could not be located, presumably owing to overlapping with another signal.) IR (KBr): ν(C≡C) 2168, ν(C≡O) 1945, 1924, 1769 cm^{-1}.

7 Crystal data. **3**: $C_{27}H_{32}O_3Fe_2$, M = 516.22, monoclinic, space group $P2_1/a$, $a = 19.600(7)$, $b = 8.790(4)$, $c = 14.796(2)$ Å, $\beta = 105.74(2)°$; V = 2453(2) $Å^3$; $Z = 4$; $d_{calc.} = 1.398$ g cm^{-3}; $\mu = 12.07$ cm^{-1}; $2 < 2\theta < 55°$; $R(R_w) = 0.0780$ (0.0850) for 3621 data (385 variables) with $F > 3\sigma(F)$ (measured reflections: 6253; unique data: 5641; $R_{int} = 0.046$). **4**: $C_{39}H_{40}O_3Fe_2$, M = 668.40, monoclinic, space group $P2_1/a$, $a = 17.262(2)$, $b = 13.318(1)$, $c = 14.359(2)$ Å, $\beta = 93.88(1)°$; $V = 3293.7(7)$ $Å^3$; $Z = 4$; $d_{calc.} = 1.348$ g cm^{-3}; $\mu = 9.15$ cm^{-1}; $2 < 2\theta < 50°$, $R(R_w) = 0.0870$ (0.0737) for 2505 data (396 variables) with $F > 3\sigma(F)$ (measured reflections: 6537; unique data: 5941; $R_{int} = 0.051$). Diffraction measurements were made on a Rigaku AFC-5 automated four-circle diffractometer by using graphite-monochromated Mo Kα radia-

tion ($\lambda = 0.71069$ Å). All the data processing was performed on a Facom A-70 computer by using the R-CRYSTAN structure solving system. In reducing data Lorentz and polarization corrections were made and no absorption correction was made. The positions of the metal atoms were located by the direct method (SAPI 85). Subsequent difference Fourier mapping revealed the positions of all the non-hydrogen atoms. Full-matrix refinements minimized the function $[\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|_2]^{1/2}$ where $w = 1/[\sigma(F_o)^2 + (pF_o)^2]$, the parameter p being automatically optimized. For **3** all the non-hydrogen atoms were refined anisotropically, and all the hydrogen atoms were refined by using isotropic thermal parameters with $B(\mathrm{H}) = B(\mathrm{C})$. For **4** all the non-hydrogen atoms were refined anisotropically. Detailed crystallographic results are available from the authors.

8 A. F. Dyke, S. A. R. Knox, P. J. Naish and G. E. Taylor, *J. Chem. Soc., Dalton Trans.*, (1982) 1297.

9 M. I. Bruce, *Chem. Rev.*, *91* (1991) 197.

10 For formation of **3**, a mechanism involving an η^1-vinylidene intermediate may also be possible. In order to check its validity photochemical reactions of **1** and **2** with 1-alkynes are now under investigation, and the results will be reported elsewhere.