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Electrocatalytic dimerisation of non-heteroatom-substituted manganese alkynylcarbene complexes[†]

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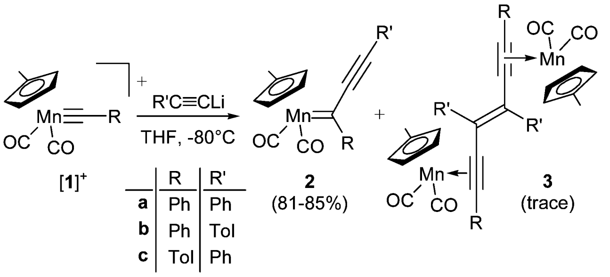
Upon controlled potential electrolysis (−1.30 V *vs.* SCE), the alkynylcarbene complexes $\mathbf{MeCp(CO)_2Mn{=}C(R)C{\equiv}CR'}$ are seen to undergo an electrocatalytic dimerisation by coupling of the remote alkynyl carbon atoms to afford the ene-diyne dimanganese complexes $\mathbf{[MeCp(CO)_2Mn]_2[\eta^4\text{-}(\mathit{E})\text{-}RC{\equiv}C(R')C{=}C(R')C{\equiv}CR]}$.

Heteroatom-substituted alkynylcarbene complexes have become valuable building blocks in organic synthesis within the past ten years,[1] whereas only recently has the reactivity of non-heteroatom-substituted alkynylcarbene been investigated.[2,3] Notably, Casey *et al.* have reported that the alkynyl complexes $Cp(CO)_2Re{=}C(R)C{\equiv}CR'$, (**A**) undergo dimerisation *via* a coupling involving *the remote carbon atoms* to afford the bis-rhenium ene-diyne complexes $[Cp(CO)_2Re]_2[\eta^4\text{-}RC{\equiv}C(R')C{=}C(R')C{\equiv}CR]$ (**C**).[2] This unprecedented reactivity pattern was interpreted in terms of an equilibrium whereby the $CpRe(CO)_2$ fragment in **A** undergoes a "[1,1.5] metal shift" to give the transient species $Cp(CO)_2Re[[\eta^2\text{-}RC{\equiv}C(R')CR']$ (**B**), and hence develop carbenoid reactivity at the remote site.

We have recently reported that the *manganese* carbyne complexes $[MeCp(CO)_2Mn{\equiv}CR][BPh_4]$ ($[\mathbf{1}][BPh_4]$) react with alkynyllithium reagents $LiC{\equiv}CR'$, to give the corresponding alkynylcarbene complexes $MeCp(CO)_2Mn{=}C(R)C{\equiv}CR'$ (**2**; **2a**: R = R′ = Ph; **2b**: R = Ph, R′ = Tol; **2c**: R = Tol, R′ = Ph) in high yields (81–85%) (Scheme 1).[3a] During such studies, we were intrigued by the fact that the chromatographic workups were erratically showing trace amounts of a pink species, **3**. This species could not be characterized until the preparations were scaled up, then allowing monocrystals of **3a** (R = R′ = Ph), and eventually **3b** (R = Ph, R′ = Tol) to be obtained.

The X-ray diffraction analysis showed **3a** to be the ene-diyne dimanganese complex $[MeCp(CO)_2Mn]_2[\eta^4\text{-}(E)\text{-}PhC{\equiv}CC(Ph){=}C(Ph)C{\equiv}CPh]$ shown in Figure 1.‡ Clearly, complex **3a** appears as the dimerisation product of complex **2a**. The alkyne moieties adopt the so-called "horizontal" coordination mode,[4] and interestingly, the two possible rotamers of complex **3a**—namely, the *meso* form and the racemic form—co-crystallise and are both seen in the solid state structure. Later on, the X-ray structure analysis of **3b**,‡ $[MeCp(CO)_2Mn]_2[\eta^4\text{-}(E)\text{-}PhC{\equiv}CC(Tol){=}C(Tol)C{\equiv}CPh]$, showed the tolyl groups to be in an adjacent position relative to the C=C bond, thereby revealing that dimerisation occurs through a coupling *via* the terminal alkynyl carbon atoms, just like in the parent rhenium system.



Scheme 1

Yet, considering the reaction conditions in which the formation of **3** was initially observed (reducing reaction conditions, very low temperature *vs.* 120 °C for the rhenium analogs) and taking into account earlier observations by Ustynyuk *et al.* of a Na/K-promoted dimerisation of acetylide complexes[5] and the recent report by Sierra *et al.*, on the C_8K-promoted self-condensation-cycloisomerisation of group 6 alkynylcarbene complexes,[6] we reasoned that a radical process might also be effective here.§ In an initial approach, complex **2a** was reacted with readily available sodium benzophenone ketyl radical anion (NaBPK), in THF. As a matter of fact, IR monitoring of the reaction showed that only a sub-stoichiometric quantity of NaBPK (10%) was needed to drive the reaction to completion. After chromatographic workup, the dimerisation product **3a** could be obtained in up to 70% yield.¶

With a view to the emerging evidence for a reductive electrocatalytic coupling process, still undocumented for Fischer carbenes, we became interested in substantiating such a reaction pathway.

Clearly, a reductive ETC mechanism can be considered if and only if the starting material **2** can be reduced the radical anion of reaction product, $\mathbf{3}^{\cdot-}$.[7] This is indeed the case as the cyclic voltammogram (CV) of a THF solution of complex **2a** displays a quasi-reversible system with $E_{pc}(\mathbf{2a}) = -1.14$ V *vs.* SCE while the CV of **3a** shows an irreversible system with $E_{pc}(\mathbf{3a}) = -1.51$ V *vs.* SCE (6.10^{-3} M THF soln., $[^nBu_4N][BF_4]$ (0.1 M), gold electrode (125 μm), 20 °C, 0.01 V s^{-1}). Considering these preliminary observations, we finally turned our attention to *preparative* electrosyntheses of complexes **3**.

An electrolysis of **2a** was undertaken under galvanostatic conditions at $E = -1.30$ V, *i.e.* at a potential between $E_{pc}(\mathbf{2a})$ and $E_{pc}(\mathbf{3a})$. After 300 s, the CV of the reaction medium (Figure 2) revealed the total disappearance of **2a** ($E_{pc}(\mathbf{2a}) = -1.05$ V under these experimental conditions), and displayed a pattern characteristic of **3a** (solid line). Complex **3a** could easily be extracted from the electrolysis medium with diethyl oxide, and obtained in 78% yield after purification.‖ The **2b**/**3b** and **2c**/**3c** couples present redox properties similar to those of the **2a**/**3a** couple. The controlled potential electrolyses of complexes **2b** and **2c**, both performed at −1.30 V *vs.* SCE, nicely afforded complexes **3b** (80% yield), and $[MeCp(CO)_2Mn]_2[\eta^4\text{-}(E)\text{-}$

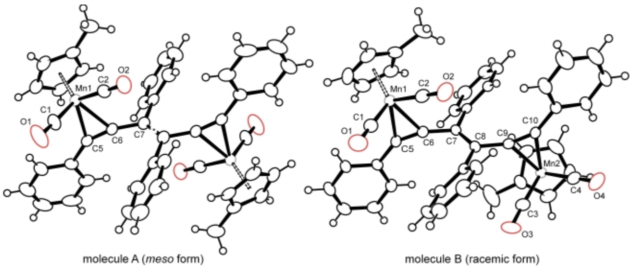
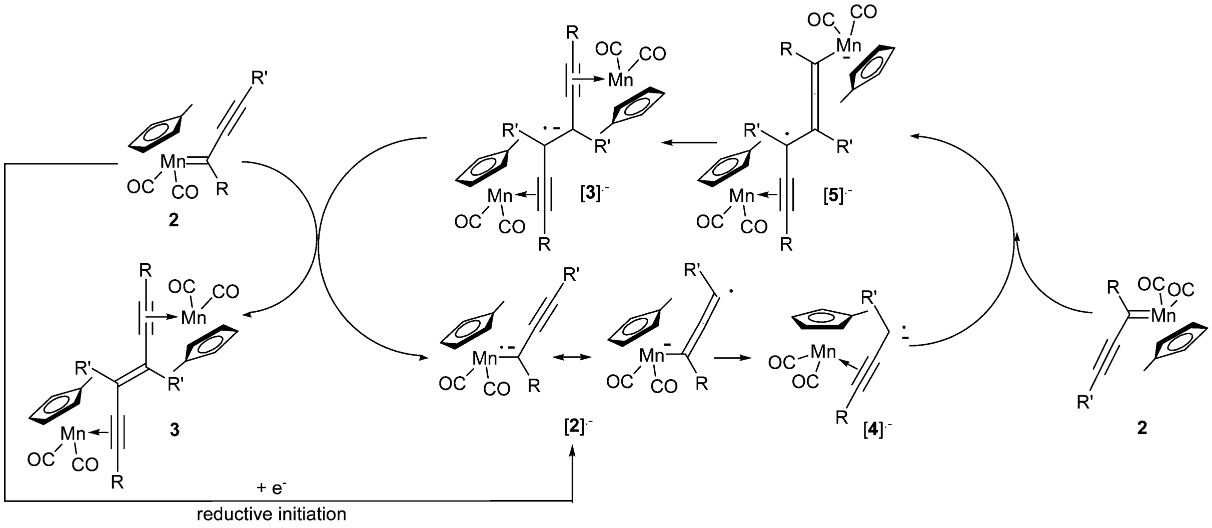


Fig. 1 Juxtaposed perspective views of the two independent units of $[MeCp(CO)_2Mn]_2[\eta^4\text{-}PhC{\equiv}C(Ph)C{=}C(Ph)C{\equiv}CPh]$ (**3a**).

[†] Electronic supplementary information (ESI) available: details of syntheses and spectral characterisation of the new complexes, ORTEP plot of complex **3b**. See http://www.rsc.org/suppdata/cc/b3/b300623a/

DOI: 10.1039/b300623a



Scheme 2

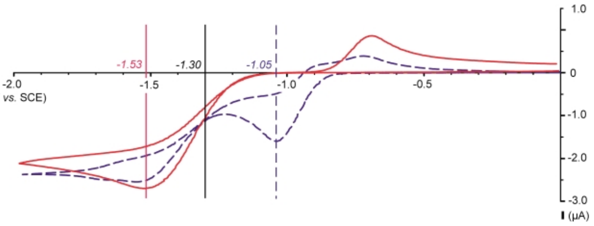


Fig. 2 CVs of the reaction medium before (dotted line) and after (solid line) the electrosynthesis of complex **3a** from **2a** (210 mg, 0.55 mmol) (THF soln. (10 mL), [^{n}Bu$_4$N][BF$_4$] (0.3 M), gold electrode (125 μm), 20 °C, 0.1 V s^{-1}).

TolC≡CC(Ph)=C(Ph)C≡CTol], **3c** (84% yield), respectively.|| The electrosyntheses were conducted up to a 1.6 millimole scale and in terms of coulombic efficiency, we found that only 0.0027 to 0.0051 e$^-$ mole^{-1} of **2** was required to induce total conversions.

A plausible interpretation for the electrocatalytic dimerisation of **2** is given in Scheme 2. The initiation step would be a single electron reduction of complex **2** to form the radical anion [**2**]$^{\cdot-}$.[6,8] Rather than being engaged in a *stoichiometric* tail-to-tail dimerisation, as proposed by Sierra for Cr analogs,[6] the latter would rearrange to an η^2-alkyne radical-anion complex [**4**]$^{\cdot-}$ undergoing rapid nucleophilic attack onto the terminal alkynyl carbon atom of a neighbouring unit **2**** to produce the dinuclear radical anion [**5**]$^{\cdot-}$, then [**3**]$^{\cdot-}$ by virtue of the same rearrangement as [**2**]$^{\cdot-}$ → [**4**]$^{\cdot-}$. The [**2**]$^{\cdot-}$ → [**4**]$^{\cdot-}$ and [**5**]$^{\cdot-}$ → [**3**]$^{\cdot-}$ rearrangements we propose are somewhat similar to the "[1,1.5] metal shift" invoked by Casey[2] to account for the thermally induced dimerisation of rhenium analogs.§ Finally, an electron transfer from [**3**]$^{\cdot-}$ to a new molecule of **2**, which might be thermodynamically favoured due to a larger delocalisation of the odd electron in [**2**]$^{\cdot-}$, would generate **3** and [**2**]$^{\cdot-}$, thereby allowing the propagation to occur.

In the prospect of new organic reactions currently emerging from recent studies of reduced Fischer carbenes,[6,9] the present observation brings a new facet in this field, and offers a valuable mean to promote carbon–carbon bond forming reactions. Significantly, the enyne (*E*)-PhC≡CC(Ph)=C(Ph)–C≡CPh[10] could be quantitatively released from **3a** by simply stirring a hot acetonitrile solution of the complex (80 °C) in an open Erlenmeyer for 45 min.

Notes and references

‡ Crystal data for **3a**: 1.5($C_{46}H_{34}Mn_2O_4$, M = 1140.92, monoclinic, a = 10.816(1), b = 18.331(2), c = 28.208(4) Å, β = 100.24(2)°, U = 5503(1) Å^3, T = 160 K, space group $P2_1/n$ (no. 14), Z = 4, μ(Mo–K_α) = 0.73 mm^{-1}, 32196 reflections measured, 7903 unique (R_{int} = 0.0635) which were used in all calculations. The final $wR(F^2)$ was 0.0449 (all data). Crystal data for **3b**: $C_{48}H_{38}Mn_2O_4$, M = 788.66, monoclinic, a = 11.373(2), b = 18.282(3), c = 19.260(5) Å, β = 106.65(2)°, U = 3837(1) Å^3, T = 160 K, space group $P2_1/n$ (no. 14), Z = 4, μ(Mo–K_α) = 0.70 mm^{-1}, 28664 reflections measured, 7405 unique (R_{int} = 0.064) which were used in all calculations. The final $wR(F^2)$ was 0.0717 (all data) CCDC 201834 and 201835. See http://www.rsc.org/suppdata/cc/b3/b300623a/ for crystallographic data in .cif or other electronic format.

§ During the reviewing process, we became aware of a publication by Casey *et al.* reporting that the *thermal activation* (65 °C, 19 h) of manganese alkynyl carbene complexes also produces ene-diynes complexes, and eventually mixtures of stereo- and regioisomers of ene-diynes upon further heating at 100 °C: C. P. Casey, T. L. Dzwiniel, S. Kraft, M. A. Kozee, D. R. Powell, *Inorg. Chim. Acta*, 2003, **345**, 320.

¶ The reproducibility in the yields of **3** following that method appears to be highly sensitive to the purity of the starting material.

|| ^{1}H NMR of the crude reaction mixture (93–98% raw yield) showed traces of other MeCp-containing complexes. Accordingly, traces of the minor (*Z*)-ene-diyne isomers, in particular, cannot be excluded.

** The electrophilic character of the terminal alkynyl carbon in **2** can be demonstrated, for instance, by the reaction of **2b** with PPh$_3$ leading to the zwitterionic σ-allenyl complex MeCp(CO)$_2$Mn(η^1-C(Ph)C=C=C(Tol)PPh$_3$) in a nearly quantitative yield: Y. Ortin, *PhD Thesis*, Université Paul Sabatier, Toulouse, 2002.

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