CHEMCOMM
Communication
www.rsc.org/chemcomm

Dynamic equilibration of η^1-carbene and η^2-alkyne moieties within an alkynylcarbene dimanganese complex†

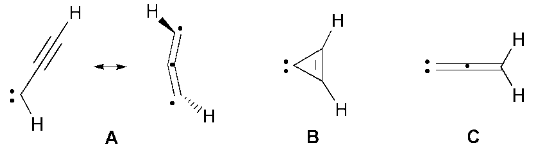
Yannick Ortin, Yannick Coppel, Noël Lugan,* René Mathieu and Michael J. McGlinchey‡

Laboratoire de Chimie de Coordination du CNRS, 205 route de Narbonne, 31077 Toulouse Cedex 4, France. E-mail: lugan@lcc-toulouse.fr

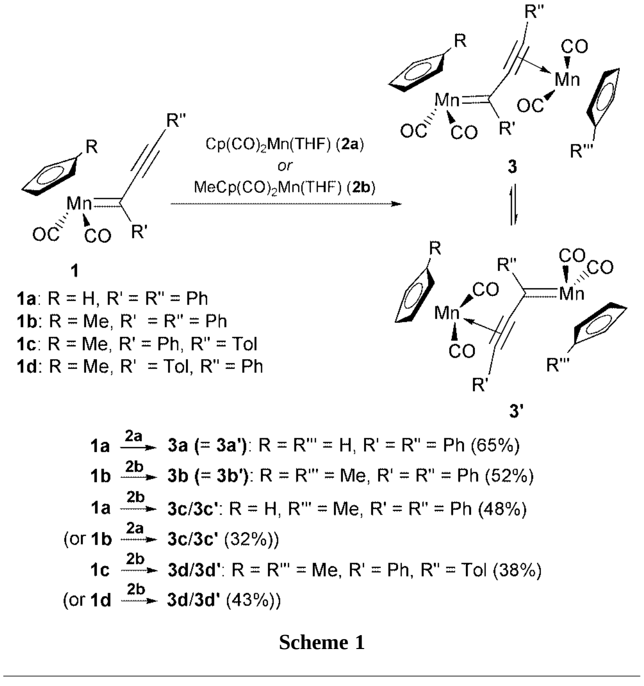
Received (in Cambridge, UK) 30th May 2001, Accepted 24th July 2001
First published as an Advance Article on the web 16th August 2001

The coordination of an additional [Cp(CO)$_2$Mn] fragment to the alkyne linkage of an alkynylcarbene complex of the type Cp(CO)$_2$Mn=C(R′)C≡CR″ yields a highly fluxional molecule, in which the [η^1-carbene] and [η^2-alkyne] moieties are seen to exchange rapidly on the NMR time scale.

The energy surface of the C$_3$H$_2$ system continues to attract considerable attention.[1] Among the numerous possible isomers that can exist and interconvert are propynylidene **A**, cyclopropenylidene **B**, and allenylidene **C**, and many such species have been isolated as stable organometallic complexes. In continuation of our studies on manganese carbene complexes,[2] our current work has focussed on non-heteroatom-substituted alkynylcarbenes of the type (RC$_5$H$_4$)Mn=C(R′)C≡CR″, where R = H, Me.[3,4] A recent report by Casey *et al.*[4] that related rhenium systems undergo a fascinating dimerization[4] prompts us to present our own findings in this area.



The alkynylcarbene complexes (RC$_5$H$_4$)Mn=C(R′)C≡CR″ **1** shown in Scheme 1 were synthesised in a straightforward manner and in high yields (81–85%) upon treatment of the corresponding carbyne complexes [(RC$_5$H$_4$)Mn≡CR′][BPh$_4$] with the appropriate alkynyllithium reagents LiC≡CR″.† With the general idea of inducing remote activation of the carbene carbon atom by coordination of a transition metal to the alkyne function in alkynylcarbene complexes, **1a** was treated with Cp(CO)$_2$Mn(THF) **2a**, at room temperature. This yielded **3a**, whose IR spectrum showed four bands in the *ν*CO region, strongly indicative of a polymetallic structure.



Scheme 1

The structure of **3a**, as determined by X-ray diffraction§ (Fig. 1) shows that, as anticipated, the molecule consists of a Mn alkynylcarbene complex in which the alkyne is coordinated to an additional Cp(CO)$_2$Mn fragment. Both Cp(CO)$_2$Mn units are bonded in the conventional fashion so as to maximise the overlap between the frontier orbitals of the metal fragments and of the carbene and alkyne units, respectively.[5] Indeed, the interplanar angle {cent1–Mn1–C3}–{Mn1–C3–C4} is 2.4° (ideal 0°), whereas the corresponding value for {cent2–Mn2–cent3}–{Mn2–C4–C5} is 83.6° (ideal 90°) [cent1 and cent2 are the centroids of the Cp rings attached to Mn1 and Mn2, respectively, and cent3 is the middle of the C4–C5 vector]. The angle between the plane containing the two alkyne carbon atoms and Mn2, and the plane of the carbene unit attached to Mn1 is 74.6°. The Mn1–C3 distance compares well with the Mn=C bond distance found in mononuclear non-heteroatom-substituted Mn carbene complexes.[6] The alkyne moiety is coordinated to Mn2 in an unsymmetrical fashion, whereby the Mn2–C4 and the Mn2–C5 distances represent, respectively, the longest and the shortest Mn–C bonds ever reported for an alkyne η^2-coordinated to a Cp(CO)$_2$Mn fragment.[7]

The variable-temperature ^{13}C{^{1}H} NMR spectra of **3a** are particularly informative. At 183 K, the spectrum is in full agreement with the X-ray crystal structure; in particular, the carbene carbon atom, C3, and two carbon atoms of the alkyne moiety, C4 and C5, are observed at δ 317.9, and 76.9 and 106.3,

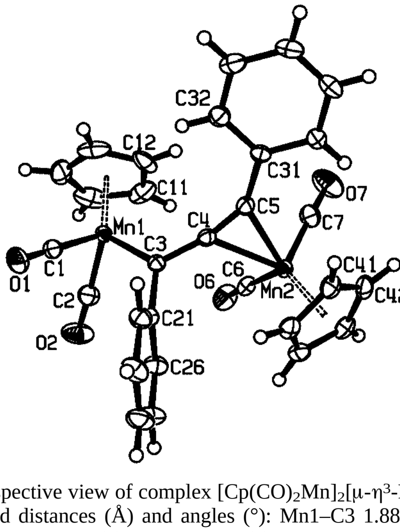


Fig. 1 A perspective view of complex [Cp(CO)$_2$Mn]$_2$[μ-η^3-PhCCCPh] **3a**. Selected bond distances (Å) and angles (°): Mn1–C3 1.888(2), Mn2–C4 2.186(2), Mn2–C5 2.082(2), C3–C4 1.411(3), C4–C5 1.261(3); C3–C4–C5 166.7(2), C4–C5–C31 145.5(2).

---

† Electronic supplementary information (ESI) available: details of synthesis and spectral characterisation of the new complexes. See http://www.rsc.org/suppdata/cc/b1/b104712b/

‡ On sabbatical leave from: Department of Chemistry, McMaster University, Hamilton, Ontario, Canada L8S 4M1.

DOI: 10.1039/b104712b

respectively. As a consequence of the lack of symmetry, the Cp rings appear as two sharp singlets at δ 91.9 and 85.9, the CO ligands give rise to four resonances at δ 235.6, 235.4, 232.6 and 231.4, and the signals due to each of the Ph rings are clearly differentiated. However, as the temperature is gradually raised, the signals for the two Cp rings coalesce (T_c = 213 K), as do the pairs of Ph ring absorptions as well as the four CO resonances. Over the same temperature range, the signals attributed to the C3 and C5 sites rapidly collapse, ultimately giving a barely observable broad resonance centred at δ 212 at 298 K. Clearly, the molecule executes a dynamic process that averages the two Mn environments. Additional spin saturation transfer experiments, performed at 188 K, confirmed the exchange between the C3 and C5 sites. In other words, the results indicate that equilibration of the [η^1-carbene] and the [η^2-alkyne] moieties in **3a** occurs readily on the NMR time-scale, as depicted in Scheme 1. The coalescence behaviour of the Cp ring resonances (both ^{13}C and ^{1}H) yields an activation energy barrier of 9.3 ± 0.5 kcal mol^{-1}.

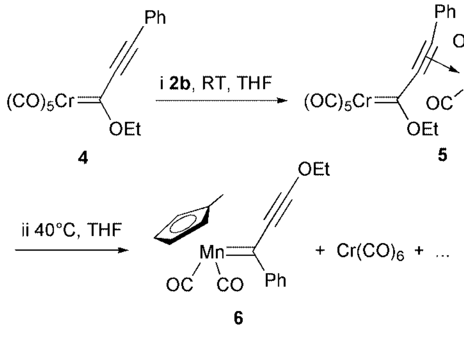
The MeCp analogue, **3b**, behaved similarly, and the non-dissociative character of the exchange was established by a crossover experiment, whereby no trace of the mixed Cp/MeCp product was detected when **3a** and **3b** were mixed. In fact, the mixed Cp/MeCp complex can be obtained by reaction of *either* **1a** with **2b**, *or* **1b** with **2a**, as a mixture of interconverting isomers **3c**/**c′**, and this provides additional support for the equilibration process shown in Scheme 1.

Likewise, complexes **3d**/**d′**, in which an η^3-PhCCCTol ligand bridges two MeCp(CO)$_2$Mn fragments, is preparable by reaction of *either* **1c** *or* **1d** with **2b**. Gratifyingly, subsequent reaction of **3d**/**d′** with carbon monoxide gave a 1 : 1 mixture of **1c** *and* **1d** through loss of the alkyne-bonded Mn fragment in each isomer, as shown in eqn. (1).

$$\left.\begin{matrix}\mathbf{1c}\\ \mathbf{1d}\end{matrix}\right] \xrightarrow[\text{RT, THF}]{\mathbf{2b}} \mathbf{3d/3d'} \xrightarrow[80\ ^\circ\text{C, THF}]{\text{CO (4 atm)}} \mathbf{1c} + \mathbf{1d} + \text{MeCpMn(CO)}_3 \qquad (1)$$

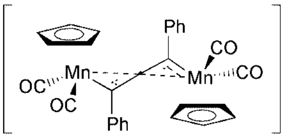
These observations raise the possibility of alkynylcarbene transfer from a metal fragment to an other one upon a bond shift isomerism within a transient bimetallic bridging η^3-alkynylcarbene complex. We now report that this can be realized in the case of (CO)$_5$Cr=C(OEt)C≡CPh **4**, for which treatment with **2b** yields MeCp(CO)$_2$Mn=C(Ph)C≡COEt **6**, through the intermediacy of **5** (Scheme 2). This rearrangement is readily accounted for by the same mechanism that gives rise to fluxionality in the **3**/**3′** system; the difference lies in the fact that the MeCp(CO)$_2$Mn=C linkage is favored over the (OC)$_5$Cr=C moiety, and that (OC)$_5$Cr[η^2-alkyne] complexes are unstable, thus rendering the isomerization irreversible.

This may also be relevant to the postulated alkynyl carbenoid rearrangement observed in the Rh(II)-catalysed cyclisation reaction of dialkynyl-substituted α-diazoketones, reported by Padwa *et al.*[8] Moreover, it is not inconceivable that the slow equilibrium between isomeric monometallic Re alkynylcarbene complexes briefly mentioned by Casey *et al.*[4] may be mediated by traces of a dirhenium complex analogous to the Mn systems described here.

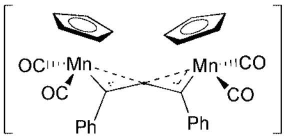


Scheme 2

A more complete analysis of the transition state for these processes must await the full DFT study that is currently under way, however, the variable-temperature NMR data provide some insight. At the low-temperature limit, the ^{13}C spectrum of **3a** exhibits *four* different CO environments but, as the temperature is raised, these signals coalesce into a *single* peak. This implies that the molecule passes through a highly symmetrical conformation allowing the pairs of carbonyls bonded to each manganese to lose their diastereotopic character. Planar transition states of C_{2h} or C_{2v} symmetry, such as those shown below, in which the central carbon possesses carbene character with some stabilisation provided by the two manganese fragments, would be consistent with the NMR data. We favour the C_{2h} conformation on steric grounds, and hypothesize that the reaction proceeds by a stretching of the alkyne-bonded manganese fragment—evidenced by the elongated Mn2–C4 bond in the X-ray structure of **3a**—while the carbene-bonded Cp(CO)$_2$Mn unit approaches the central carbon atom. We emphasise, however, that unlike a conventional organic S$_N$2 process in which the incoming nucleophile and the leaving group maintain a rectilinear relationship, this process involves a quasi-helical, twisting motion since in the initial and final structures, the planes bisecting the Cp(CO)$_2$Mn fragments adopt mutually almost orthogonal orientations.



[3a]$^\#$ (C_{2h})



[3a]$^\#$ (C_{2v})

Notes and references

§ *Crystal data*: C$_{29}$H$_{20}$Mn$_2$O$_4$, M = 542.33, monoclinic, space group $P2_1/c$ (no. 14), a = 12.843(2), b = 8.358(1), c = 22.265(6) Å, U = 2368.8(8) Å^3, T = 160 K, Z = 4, μ(Mo-K$_\alpha$) = 1.10 mm^{-1}, 14485 reflections measured, 3520 unique (R_{int} = 0.039) which were used in all calculations. The final $wR(F^2)$ was 0.0628 (all data).

CCDC reference number 168123. See http://www.rsc.org/suppdata/cc/b1/b104712b/ for crystallographic data in CIF or other electronic format.

1 M. Rubio, J. Stalring, A. Bernhardsson, R. Lindh and B. O. Roos, *Theor. Chem. Acc.*, 2000, **105**, 15 and references therein; A. M. Mebel, W. M. Jackson, A. H. H. Chang and S. H. Lin, *J. Am. Chem. Soc.*, 1998, **120**, 5751; R. A. Seburg, E. V. Patterson, J. F. Stanton and R. J. McMahon, *J. Am. Chem. Soc.*, 1997, **119**, 5847; M. Noro, T. Masude, A. S. Ichimura, N. Koga and H. Iwamura, *J. Am. Chem. Soc.*, 1994, **116**, 6179.

2 A. Rabier, N. Lugan and R. Mathieu, *J. Organomet. Chem.*, 2001, **617–618**, 681.

3 For other non-heteroatom-stabilised alkynylcarbene complexes, see for instance: M. A. Esteruelas, A. V. Gomez, A. M. Lopez, J. Modrego and E. Onate, *Organometallics*, 1997, **16**, 5826; M. R. Terry, C. Kelley, N. Lugan, G. L. Geoffroy, B. S. Haggerty and A. L. Rheingold, *Organometallics*, 1993, **12**, 3607.

4 C. P. Casey, S. Kraft and D. R. Powell, *J. Am. Chem. Soc.*, 2000, **122**, 3771.

5 N. M. Kostic and R. F. Fenske, *J. Am. Chem. Soc.*, 1982, **104**, 3979; B. E. R. Schilling, R. Hoffmann and D. L. Lichtenberger, *J. Am. Chem. Soc.*, 1979, **101**, 585.

6 W. A. Herrmann, J. L. Hubbard, I. Bernal, J. D. Korp, B. L. Haymore and G. L. Hillhouse, *Inorg. Chem.*, 1984, **23**, 2878 and references therein.

7 C. Lowe, H.-U. Hund and H. Berke, *J. Organomet. Chem.*, 1989, **378**, 211; G. G. Cash and R. C. Pettersen, *J. Chem. Soc., Dalton Trans.*, 1979, 1630.

8 A. Padwa, D. J. Austin, Y. Gareau, J. M. Kassir and S. L. Xu, *J. Am. Chem. Soc.*, 1993, **115**, 2637.