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A facile and novel route to unprecedented manganese C_4 cumulenic complexes†

Koushik Venkatesan, Francisco J. Fernández, Olivier Blacque, Thomas Fox, Montserrat Alfonso, Helmut W. Schmalle and Heinz Berke*
Anorganisch-Chemisches Institut der Universität Zürich, Winterthurerstrasse 190, CH-8057 Zürich, Switzerland. E-mail: hberke@aci.unizh.ch

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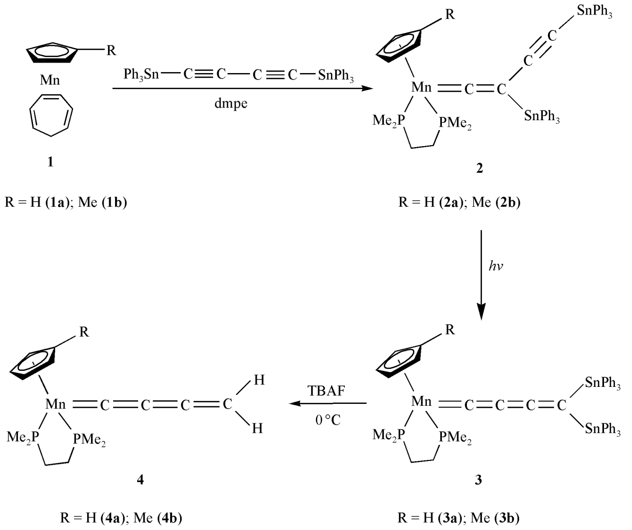
The theoretically characterized (DFT) C_4 cumulenic species $Mn(C_5H_4R)(dmpe)\{=C=C=C=C(SnPh_3)_2\}$ was obtained by photolysis of the C_{sp^2}–Sn bond in the vinylidene complex $Mn(C_5H_4R)(dmpe)[=C=C(SnPh_3)–C\equiv CSnPh_3]$, which in turn was prepared by a thermal reaction from $MnC_5H_4R(dmpe)(C_7H_8)$ and $Ph_3Sn–C_4–SnPh_3$.

Owing to their high degree of unsaturation metallacumulene complexes $L_nM=(C=)_mCR_2$ are a matter of great theoretical and preparative interest.[1] Metallacumulenes with $m = 1$ or 2 (vinylidenes and allenylidenes) are very common and have been well studied during the past years.[2] Complexes with $m = 4$ are less common, but some examples of such complexes are known.[3] However, species with a four carbon chain ($m = 3$) appear to be of extraordinarily low stability and therefore have been accessed only rarely. Recently, Werner's group has prepared the first stable neutral C_4 metallacumulene compound containing an $Ir=C=C=C=CPh_2$ unit[4] and also have later reported reactivity studies of this complex.[5,6] Furthermore, *in situ* preparations of cationic species containing a $[Ru=C=C=C=CRH]^+$ fragment were reported: (R = H) by Bruce,[3d–e,7] ($R \neq H$) Dixneuf[8] and Winter.[3a,3c,8,9] The $Ru=C_4$ species were quite short-lived preventing spectroscopic characterization. Lapinte's group managed to stabilize a peculiar complex containing a $Fe=C_4$ cumulenic motif by attaching a $FeCp^*(CO)_2$ moiety to the terminal carbon atom of the cumulenic chain.[3f]‡

Previous to this paper we have explored the chemistry and reactivity of Mn^{II} and Mn^{III} halfsandwich dmpe alkynyl complexes and their conversion to Mn^I vinylidene species.[10a–c] A first conclusion of this study was that vinylidene complexes gained considerably in stability through the presence of the bis(dimethylphosphino)ethane ligand (dmpe) in comparison with the reported CO substituted species $Mn(Cp)L^1L^2(C=CR_2)$ where $L^1 = L^2 = CO$, or $L^1 = CO$, $L^2 = PR_3$.[11a] Our interest in this area focuses on the preparation of redox-active di- or polynuclear organometallic complexes containing manganese (end)groups and we consequently sought to utilize the stability and electron-richness of dmpe substituted halfsandwich Mn^I moieties for the build-up of molecular redox wires.[11b] A major route to dinuclear metal systems bearing cumulene bridges utilizes coupling processes of appropriate mononuclear species.[2s,10a–b,12a–k]

A common method to obtain vinylidene complexes makes use of the high propensity of terminal acetylene derivatives to rearrange to vinylidene compounds.[7g–k,2b,2e–f,2l–m,3c,13] For such a process to be initiated in the realm of halfsandwich Mn^I chemistry, we thought the complexes $Mn(C_5H_4R^1)(\eta^6\text{-heptatriene})$ ($R^1 = C_5H_5$, **1a**; C_5H_4Me, **1b**)[14] to be excellent starting materials due to the labile character of the Mn–heptatriene interaction. Facile ligand exchange with donating ligands, such as phosphines or acetylenes, was expected to occur. Conversions with tin mono- or disubstituted acetylenes were anticipated to also lead to the desired vinylidene species $Mn(C_5H_4R^1)(dmpe)(=C=CR^2R^3)$. Indeed, the reaction of $Mn(C_5H_4R^1)(\eta^6\text{-heptatriene})$ ($R^1 = C_5H_5$, **1a**; C_5H_4Me, **1b**) with $Ph_3Sn–C_4–SnPh_3$ and dmpe gave the corresponding vinylidene species $Mn(C_5H_4R^1)(dmpe)(=C=CSnPh_3–C\equiv CSnPh_3)$ (R^1 = H, **2a**; Me, **2b**) in about 98 % yield (Scheme 1). This reaction required initial formation of a Mn-alkyne species.[13] However, NMR studies of the reaction carried out in the range of −70 to 20 °C did not reveal any intermediate. The ^{13}C NMR spectrum of **2** shows the C_α and the C_β around 328 ppm and 114 ppm, respectively. The ^{31}P NMR resonances appear at 93.8 (**2a**) and 92.8 ppm (**2b**). These data are comparable to those which were obtained for the related $Mn(Cp^1)(dmpe)(=C=CRH)$ complexes.[10b,12a,b,13] The ^{119}Sn NMR spectra of species **2** show two signals, a triplet corresponding to the C_{sp^2}–Sn at −130 (**2a**) and −132 ppm (**2b**) with $^4J(^{31}P, ^{119}Sn) \approx 77$ Hz and a singlet for the C_{sp^3}–Sn at −162 ppm.

The X-ray diffraction studies for **2b** (Fig. 1) show the Mn=C1 and C1=C2 distances of 1.742(5) and 1.330(6) Å in the same



Scheme 1

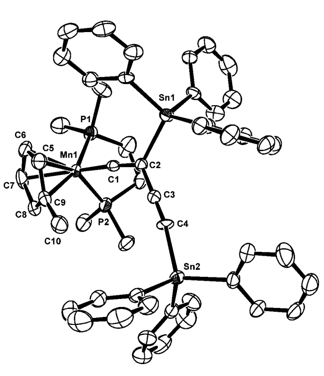


Fig. 1 Molecular structure of **2b**. Selected bond lengths (Å) and angles (°): Mn1–C1 1.742(5), C1–C2 1.330(6), C2–C3 1.430(6), C3–C4 1.223(5), C2–Sn1 2.123(4), C4–Sn2 2.073(4), Mn1–C(g) 1.767(6), C1–C2–C3 120.8(4), C1–C2–Sn1 122.3(3), C3–C2–Sn1 116.5(3).

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† Electronic supplementary information (ESI) available: experimental and computational details. See http://www.rsc.org/suppdata/cc/b3/b304882a/

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range as those reported for other Mn-vinylidene complexes.[1h,2d,3f,11a] The C2–Sn1 and C4–Sn2 distances are 2.123(4) and 2.073(4) Å, respectively.

When toluene solutions of **2** were irradiated at 20 °C using a 125 W medium pressure mercury lamp the C_{sp^2}–Sn bonds were activated and subsequent transformations into the remarkably stable C_4 cumulene species **3** were observed. Both complexes **3** were isolated as green solids in approximately 80% yield. The ^{13}C NMR spectra of the species **3** exhibit four resonances for the C_4 cumulenic chain at 266.5 (**3a**), 267.5 (**3b**) (Mn=C_1), 130.8 (**3a**), 131.6 (**3b**) (=C_2=), 124.8 (**3a**), 121.4 (**3b**) (=C_3=) and 140.0 (**3a**), 139.9 ppm (**3b**) (=CSn_2). The ^{31}P NMR spectrum exhibits a resonance at 91.8 (**3a**) and 91.6 (**3b**) ppm slightly shifted to higher field in comparison with the value obtained for species **2**. The ^{119}Sn NMR spectra display one triplet for the two Sn nuclei at around −125 ppm (t, $^6J(^{31}P, ^{119}Sn) = 64$ Hz). The structure of complex **3a** was confirmed by an X-ray diffraction study (Fig. 2). The unsaturated carbon chain slightly deviates from linearity as shown for instance by the Mn–C1···C4 bond angle of 170.6°. The bond angles C3–C4–Sn are surprisingly different with values of 112.0(3)° and 122.6(3)° for C3–C4–Sn1 and C3–C4–Sn2, respectively. The Mn=C bond distance of 1.769(4) Å is slightly longer than that observed for **2b** but comparable to those found in other Mn-vinylidene complexes.[10b,12a,b,15] The length of the two internal C–C double bonds are shorter (1.296(5) Å and 1.264(5) Å) than the external one (1.316(5) Å).‡ A similar behaviour was reported for the mentioned Ir–C_4 cumulenic species.[4–6]

Complexes **3** constitute the first examples of C_4 metallacumulene species with main group metal substituents as endgroups, which were assumed to be reactive and were expected to be readily removable. Indeed, deprotection of species **3** was accomplished with tetrabutylammonium fluoride[16] (TBAF). The parent C_4 cumulenic species $Mn(C_5H_4R)(dmpe)\{=C=C=C=CH_2\}$ (R = H **4a**, Me **4b**) were formed by selective replacement of the terminal $SnPh_3$ moieties. They were unstable above −5 °C and were therefore characterized in solution at −40 °C. The presence of the terminal CH_2 group in **4** was confirmed by (^1H,^{13}C) correlation, ^{13}C-DEPT, and $^1H\{^{31}P\}$ decoupling NMR experiments. The CH_2 protons appear at 1.93 ppm as a triplet with $^6J(^1H,^{31}P) = 2.0$ Hz. The ^{13}C chemical shifts for compounds **3** and **4** have been assigned under the assumption that the ^{13}C, ^{31}P coupling constants decrease with increasing coupling pathway in the linear C_4 chain. The ^{13}C NMR spectrum shows four signals corresponding to the cumulenic carbon chain at 281.8 (**4a**), 280.8 (**4b**) (Mn=C_1), 158.7 (**4a**), 157.9 (**4b**) (=C_2=), 141.0 (**4a**), 140.2 (**4b**) (=C_3=) and 44.4 (**4a**), 44.3 (**4b**) (=CH_2). The cationic complexes containing the fragment $[Ru=C=C=C=CH_2]^+$ were reported earlier by Bruce[7] in 1996, however, their existence could only be made plausible by reactivity studies analyzing follow-up complexes. Compounds **4** are the first examples of complexes with $[M=C=C=C=CH_2]$ unit whose structures have been fully established by NMR spectroscopy in solution. At higher temperatures (0 °C and above) compounds **4** decomposed to a mixture of as yet unidentified compounds.

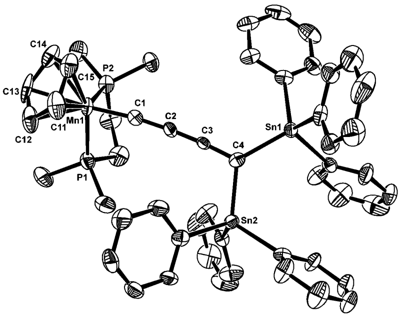
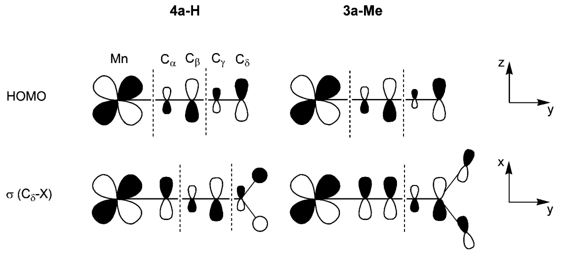


Fig. 2 Molecular structure of **3a**. Selected bond lengths (Å) and angles (°): Mn1–C1 1.769(4), C1–C2 1.296(5), C2–C3 1.264(5), C3–C4 1.316(5), C4–Sn1 2.130(5), C4–Sn2 2.132(5), Mn1–C1–C2 173.5(4), C2–C3–C4 175.5(5), C3–C4–Sn1 112.0(3), C3–C4–Sn2 122.6(3), Sn1–C4–Sn2 124.5(2).



Scheme 2

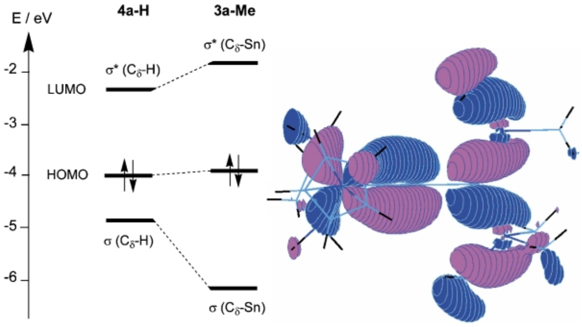


Fig. 3 a) Energy levels of frontier molecular orbitals for model complexes **3a-Me** and **4a-H**. b) Calculated occupied MO σ(C_δ–Sn) of **3a-Me** showing the bonding interactions between C_δ and the terminal tin groups.

An attempt to analyse this striking difference in stability between the two types of complexes **3** and **4** has been made using DFT calculations.[17] For this **3** has been modelled by **3a-Me** and **4** by **4a-H** replacing dmpe by two PH_3 groups in both cases, and $SnPh_3$ substituents by $SnMe_3$ moieties in **3a-Me**. The molecular orbital analysis shows that the HOMO's of both structurally optimized complexes have similar shapes and energies and clearly imply strong Mn-chain interactions (Scheme 2). However, these HOMO's of **3a-Me** and **4a-H** cannot account for the differences in stability of **3** and **4**, since no participation of tin orbital character is observed.

The stabilising role of the tin groups of complexes **3** in comparison with **4** is mirrored in the shape and energy of an occupied MO in the HOMO range of **3a-Me** displaying bonding interaction in the *xy* plane between the carbon chain and $C_\delta/\sigma_p(Sn)$. This leads to its energetic stabilization (about 1.3 eV) relative to its counterpart in **4a-H**. The excellent donor properties of the energetically high-lying tin orbitals allow for a high-lying out-of-phase Sn–C_δ–Sn σ-type function (Fig. 3), which possesses the right symmetry to interact in a stabilizing fashion with one of the higher-lying π-orbitals of the residual carbon chain. For complex **4a-H** the corresponding $C_\delta H_2$ σ-type interaction appears at much lower energies and is therefore even repelling filled π-orbitals by out-of-phase participation. Overall this electronic destabilization is assumed to be the cause for the instability of the series of parent compounds **4**.

The experimental details and computational details of the DFT calculations reported in this paper are available as ESI.†

Since solutions containing the parent species **4** were easily prepared and can be stored at least for a short time at low temperature further studies regarding its general reactivity and its particular utilisation in oxidative coupling processes to Mn–C_8–Mn units are in progress.

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Notes and references

‡ *Crystal data for* **[2b]**: $C_{52}H_{53}MnP_2Sn_2$, $M_r = 1032.20$, red, monoclinic, space group $P2_1/c$, $a = 11.1101(5)$, $b = 16.0437(5)$, $c = 26.5040(5)$ Å, $\alpha = 90°$, $\beta = 96.074(6)$, $\gamma = 90°$, $V = 4697.7(3)$ Å^3, $T = 183(2)$ K, $Z = 4$,

μ = 1.421 mm^{-1}, 13734 independent reflections (R_{int} = 0.1194), R_1 = 0.0396, wR_1 = 0.0760 [5333 reflections, $I > 2\sigma(I)$] and R_2 = 0.1146, wR_2 = 0.0897 (all data), GoF(F^2) = 0.612.

[3a]: $C_{55}H_{61}MnOP_2Sn_2$, M_r = 1092.30, olive green, orthorhombic, space group $Pna2_1$, a = 19.9343(10), b = 21.6102(9), c = 12.0206(5) Å, $\alpha = \beta = \gamma = 90°$, V = 5178.3(4) Å^3, T = 183(2) K, Z = 4, μ = 1.295 mm^{-1}, 15414 independent reflections, (R_{int} = 0.0801). R_1 = 0.0350, wR_1 = 0.0491 [8294 reflections, $I > 2\sigma(I)$], R_2 = 0.0867, wR_2 = 0.0541 (all data), GoF(F^2) = 0.799. Data were collected on a Stoe IPDS diffractometer[19a] and structure solutions performed by using SHELXS-97.[19b] Refinement calculations were done with SHELXL-97.[19c] CCDC 202584 and 202585. See http://www.rsc.org/suppdata/cc/b3/b304882a/ for crystallographic data in .cif or other electronic format

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