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The First Earlier Transition Metal Alkynyl Cubane Cluster Mn₄C₄

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While the coordination chemistry of monometallic complexes and the surface properties of extended metal particles are well understood, the control of metal nanocluster formation has remained challenging. The isolation of discrete metal clusters constitutes an especially rare snapshot at the nanoscale of cluster growth. This work reports the synthesis and full characterization of the first early-transition metal alkynyl cubane and the first μ^3 -alkynyl-Mn₃ motif.

Discrete metal nanoclusters constitute unique molecular architectures between the regimes of monometal coordination compounds and larger particles (Scheme 1).[1]-[3] The synthesis of metal nanoclusters has direct ramifications for the understanding of nanoparticle growth, materials design, metal-catalyzed reaction mechanisms, and biological processes. $\ensuremath{^{[1]-[3]}}$ The presence of several metal-metal interactions within a low-molecular weight compound often results in optical and magnetic properties that are distinct from monometal complexes.^{[2],[4]} However, the synthesis of well-defined nanoclusters of low-valent transition metals is generally limited by low control over size, shape, and coordination properties and the operation of undesired side reactions including rapid cluster growth, metal oxidations, and redox disproportions. The vast majority of literature reports involve sterically shielded clusters with stable ligands (i.e. bridging carbonyl or heteroatomic oxo, imido, nitrido ligands at coordinatively saturated metal centers).^{[2],[5]} These have mostly been studied toward the nature and extent of metal-metal cooperativity.^{[6],[7]} Catalytic applications, however, have largely been neglected.^{[6],[7]} Our group and Ohki et al. have successfully exploited the implementation of µ2-amido and µ3-hydrido ligands for the stabilization of various novel nanocluster architectures.^{[8]-[10]} This enabled the synthesis of discrete Mn₆, Fe₄, Fe₆, and Fe₇ clusters that exhibited planar geometries (Scheme 2).^{[9],[10]} Alkyne ligands constitute a distinct and versatile class of ligands for the design of metal cluster architectures. They offer various coordination modes (σ , π^2 , π^4 ; terminal and bridging), are competent stabilizers of atomically precise nanoclusters, and provide the opportunity for facile removal or ligand exchange under mild condition.[11],[12]b Mostly, stable alkynyl clusters of the coinage metals (Cu, Ag, Au) were prepared - that benefit from the soft carbophilicity of the group 11 metals - and studied toward their photophysical properties and catalytic activities (Scheme 1).^{[11],[12]} Despite the broad availability

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of alkynylmetal complexes and their significance as catalytic intermediates in many organic transformations, there are only very few reports of discrete μ_3 -alkynylmetal nanoclusters bearing late transition metals other than group 11 metals (i.e. Ru, Rh and Ni) and ancillary ligands.^[13] Documented herein is the facile and high-yielding synthesis of a well-defined heteroleptic alkynyl-Mn₄ cluster, comprising the first σ , μ_3 -alkynyl-Mn₃ and the first early-transition metal-alkynyl cubane motifs (Scheme 2), its full characterization, and application to nanoparticle formation and catalysis.



Scheme 1. Transition metal clusters: The scarcity of CO-free alkynyl metal clusters other than with coinage metals.



Scheme 2. The μ_3 -X-M motif in planar hydridomanganese and 3D-alkynyl-manganese clusters (R=SiMe_3).

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We envisioned the synthesis of alkynylmetal clusters based on a formal exchange of the µ3-bridging hydrido ligands of our previously reported planar transition metal clusters with σ,μ_3 alkynyl ligands which are well documented for the soft carbophilic coinage metals and very few other late transition metals.[11].[13] Accordingly, the reaction of divalent Mn[N(SiMe₃)₂]₂ (1) with phenylacetylene in *n*-hexane afforded a yellow-orange solution which upon cooling led to the novel alkynylmanganese complex $\{Mn(\mu_3-C=CPh)(N[SiMe_3]_2)\}_4$ (2, Scheme 3). This nanocluster crystallized in an unprecedented Mn₄C₄ cubane structure in 80% yield. The yellow-orange crystals turned into a khaki solid upon drying under vacuum (mp. 118 °C, which gave an orange-yellow liquid; decomp. at 166 °C). The UV-VIS spectrum in n-hexane exhibited two bands at 405 nm (broad) and 479 nm (weak). The characteristic C≡C IR absorption of the solid at 2012 cm⁻¹ is in full agreement with that of dicopper $\mu_2 - \eta^1 : \eta^1$ - and tricopper μ_3 - η^{1} : η^{1} : η^{1} -alkynyl complexes.^[14] The ¹H NMR signals of the paramagnetic complex 2 were very broad and weak (-100 to 100 ppm).



Scheme 3. Synthesis and reactivity of the Mn₄C₄-cubane cluster 2.

The molecular structure of 2 was confirmed by single crystal Xray crystallography (Figure 1). The central Mn₄C₄ core is an almost perfect cube containing alternating Mn and C atoms in slightly distorted T_d symmetry. Each Mn₃ triangle of the Mn₄ tetrahedron is capped with one $\mu_3 \cdot \eta^1 : \eta^1 \cdot \eta^1 \cdot \eta^1$ -bridging σ -alkynyl ligand; each Mn center coordinates one terminal hexamethyldisilazide (hmds) ligand. In comparison, the μ_3 -H-bridged Mn₃ units in [MnH(hmds)]₆ arranged in a nearly planar nanosheet geometry.^[10] The Mn-C distances (2.21771(4), 2.27113(4), 2.31275(7) Å) and C=C bond lengths (1.22291(2) Å) in 2 are comparable with those of the bimetallic $\mu_2 - \eta^1 : \eta^1$ -alkynyl complexes [(nacnac)Mn(C=CPh)]₂ and [CpMn(C=CPh)(THF)]₂ $(nacnac = HC{CMeN(2,6-iPr_2C_6H_3)}_2, Cp = cyclopentadienyl).^{[15]}$ The $\mu_3 - \eta^1 : \eta^1 : \eta^1 - bridging$ alkynylmetal motif is very well documented for the coinage metals Cu, Ag, and Au.^[11] Examples containing other transition metals are very rare, with only a handful of μ_3 -alkynyl complexes of the late transition metals Ru, Rh and Ni reported.^[13] Related Mn complexes have hitherto been unknown. The distorted Mn₄ tetrahedron of 2 contains two different environments around Mn comprising two shorter Mn-Mn distances (3.07999(4) Å) with smaller Mn–C–Mn angles of 86.6° and four longer Mn-Mn distances (3.22525(6) Å) with wider MnC-Mn angles (89.4 and 90.8°). The Mn-Mn distances are in good agreement with those of other Mn^{II}₄N₄^{[16],[17]} heterocubane clusters and only slightly longer than in Mn₆H₆(hmds)₆ (2.85622(3)-2.97627(3) Å).^[10] The tetranuclear Mn cluster 2 is the first welldefined, isolated alkynyl-bridged cubane containing low-valent, open-shell Mn ions. This structural motif has so far been exclusively known from alkynyl coinage metal clusters. Beside the general interest in the special electronic and magnetic properties of multi-metallic complexes for materials and catalysis applications, cubic manganese clusters bear a close structural relationship to the central Mn₄O₄ cluster of the oxygen-evolvingcomplex.^[18] Other known examples of such Mn₄X₄ cluster topologies involve group 15 and 16 ligands.^{[17]-[19]} A similar M₄X₄ heterocubane structure with two different groups of Fe^{III} atoms was recently observed in a [Fe₄S₄(SAr)₄] cluster.^[20]

We further investigated the structure and reactivity of the cubane. The solution magnetic moment of **2** (5.7 μ_B in C₆D₆; $\chi_M T = 4.1$ cm³mol⁻¹K) is indicative of strong antiferromagnetic interactions between the Mn(II) ions (spin-only value of four uncoupled Mn(II) ions: 11.8 μ_B ; 17.5 cm³mol⁻¹K). Temperature-dependent magnetic measurements on solid 2 were in full agreement: Starting at 6.1 cm³mol⁻¹K at r.t., $\chi_M T$ decreased to almost zero at 15 K indicating a diamagnetic $S_T = 0$ ground state (Figure 2). The experimental magnetic data were simulated based on the Heisenberg-Dirac-van-Vleck (HDvV) spin Hamiltonian for two isotropic exchange coupling constants (Figure 2, inset) and Zeeman splitting (PHI program,^[21] see ESI for more details): The coupling J_1 (-24.5 cm⁻¹) represents the interaction via the two cubane faces with shorter Mn–Mn distances (3.08 Å) and J_2 (– 10.4 cm⁻¹) via the four faces with longer Mn–Mn distances (3.23 Å). So far, μ_3 -alkynyl-Mn complexes have not been reported. Even for the simplest dinuclear μ_2 -alkynyl complexes^{[15],[22]} only one structure was magnetically characterized ($J = -30.5 \text{ cm}^{-1}$, $d(Mn-Mn) = 2.97 \text{ Å}).^{[15]}$ The observed coupling constants in 2 correlate well with the Mn-Mn distances and are much higher than for dinuclear Mn(II) complexes containing heteroatomic bridging ligands (phenoxides, halides, azides: $|J| \le 5 \text{ cm}^{-1})^{[23]}$ due to the more covalent Mn-C bond character.



Figure 1. Solid state structure of 2 (50% probability level; H atoms omitted).

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Figure 2. Temperature-dependent magnetization $\chi_M T$ for **2**. Solid red line is the best fit with $J_1 = -24.5 \text{ cm}^{-1}$, $J_2 = -10.4 \text{ cm}^{-1}$, g = fixed at 2.0. Inset: Magnetic coupling scheme used for the simulation.

The modular structure of 2 offers ample opportunities for catalytic applications^[24] and further cluster manipulation by ligand exchange toward functionalized cubanes and supramolecular Mn-cages.^{[20],[25]} We investigated conditions for small molecule coordination or bond activation and the exchange of the residual amido ligands with other n-, σ - and π -ligands. In the presence of alcohols or water, 2 underwent rapid decomposition, most likely by ligand protonation. No reactivities were observed for reactions between 2 and cyclohexyl bromide and diphenyldiazene, respectively. With 1 equiv. benzyl azide, the formation of an unidentified paramagnetic species was observed. Addition of the S,O-ligand and CH-acid 2-acetylthiophene bifunctional (equimolar to 2) resulted in complete consumption of the substrate and elimination of HN(SiMe₃)₂. Attempts to obtain suitable single crystals of the resultant paramagnetic light yellow product were unsuccessful. The IR spectrum of the solid exhibited a C=O absorption at 1594 cm⁻¹ that is 56 cm⁻¹ lower in energy than free 2-acetylthiophene. The C=C-IR stretch (2048 cm⁻¹) appeared as a weak band at slightly lower energy than for cluster ${\bf 2}$ (2012 cm⁻¹).^[26] The presence of an alkynyl transition metal moiety in 2 prompted us to study the catalytic activity of 2 in alkyne reactions. A recent report from our group has successfully demonstrated the cyclotrimerization of terminal alkynes with catalytic Fe(hmds)2.[27] A similarly effective reaction with Mn catalysts has not been reported.^{[10],[28]} An equimolar solution of 2 with phenylacetylene in *n*-hexane afforded an off-white insoluble precipitate (Scheme 3). Complete consumption of phenylacetylene and elimination of HN(SiMe₃)₂ was verified by ¹H NMR (see SI). We postulate the formation of oligomeric bis(alkynyl)manganese complexes [Mn(C=CPh)₂]_n that decomposed at 151 °C. A suspension of the insoluble oligomer in THF underwent color change at 60 °C to give a dark brown mixture. The concomitant formation of 1,4-diphenyl-1,3-butadiyne suggests the operation of a reductive elimination pathway that would lead to the formation of Mn(0) particles (Scheme 3). Paralleling our report of iron-catalyzed cyclotrimerization, Mn(hmds)₂ and 2 proved to be moderately active in the catalytic cyclotrimerization of phenylacetylene, respectively (Scheme 4A). The remaining substrate presumably underwent polymerization, which resulted in an orange solid with the

characteristic broad ¹H resonances at 5.5-8 ppm.^[29] The initially formed white suspension and slow color change to dark-brown may indicate the intermediacy of alkynyl-manganese oligomers under catalytic conditions. The reaction of Mn(hmds)₂ with 2 equiv. phenylacetylene (or 2 with 1 equiv. phenylacetylene) presumably gave rise to the formation of heterogeneous Mn(0) species upon deprotonation, coordination, and reductive elimination of 1,4-diphenylbutadiyne. Under related conditions, we have recently reported the first efficient Mn-catalyzed hydrogenation of alkenes, alkynes, and imines under mild conditions.[10] Various Mn catalysts have recently been reported for the hydrogenation of carbonyl derivatives, [30], [31] whereas olefin hydrogenations are very rare.^[10] Some of the reported Mn catalysts even tolerate the presence of alkenes under hydrogenation conditions.[31] We therefore evaluated combinations of 1/phenylacetylene as catalysts in hydrogenations. Various alkenes and alkynes underwent clean hydrogenation to the fully saturated products at 5 bar H₂ and 70°C (Scheme 4B). The cubane 2 (1.25 mol%) also catalyzed the hydrogenation of alkenes but with significantly lower activity for diphenylacetylene than the in situ catalyst mixture (5 mol% 1 + 10 mol% phenylacetylene). Mono- and di- substituted alkenes were hydrogenated with very high yields (Scheme 4). However, the compatibility with other polar functional groups is limited (Scheme 4 and Table S1). Rapid hydrodebromination was observed with 4-bromo- α -methylstyrene.



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In summary, we have demonstrated that the formal substitution of μ_3 -hydrido with μ_3 -alkynyl ligands effects a change from a 2D to a 3D Mn cluster topology. The resultant Mn₄ nanocluster constitutes the first earlier transition metal cubane cluster comprising an Mn₄C₄ core and a heteroleptic ligand periphery of alkynyl and amido groups; the former motif was hitherto known only from coinage metal clusters. The crystal structure documents the presence of two sets of Mn(II) environments; SQUID magnetic studies exhibited strong antiferromagnetic interactions via two different Mn-Mn coupling patterns. The reactivity profile of the novel Mn₄ cluster was explored in Mn(0) nanoparticle formation and acid-base, alkyne cyclotrimerization, and hydrogenation reactions. The simple combination of Mn(hmds)₂ and phenyl-acetylene provides a rare example of a Mn alkene hydrogenation catalyst and leaves ample opportunities for further development.

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Keywords: cluster • manganese • alkyne • cubane • hydrogenation • cyclotrimerization

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The first non-coinage metal M_4C_4 cubane has been prepared and characterized. The nanocluster contains two sets of Mn(II) environments that exhibit strong antiferromagnetic coupling. Facile amido ligand exchange and formation of Mn nanoparticles have been evaluated in catalytic studies.



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