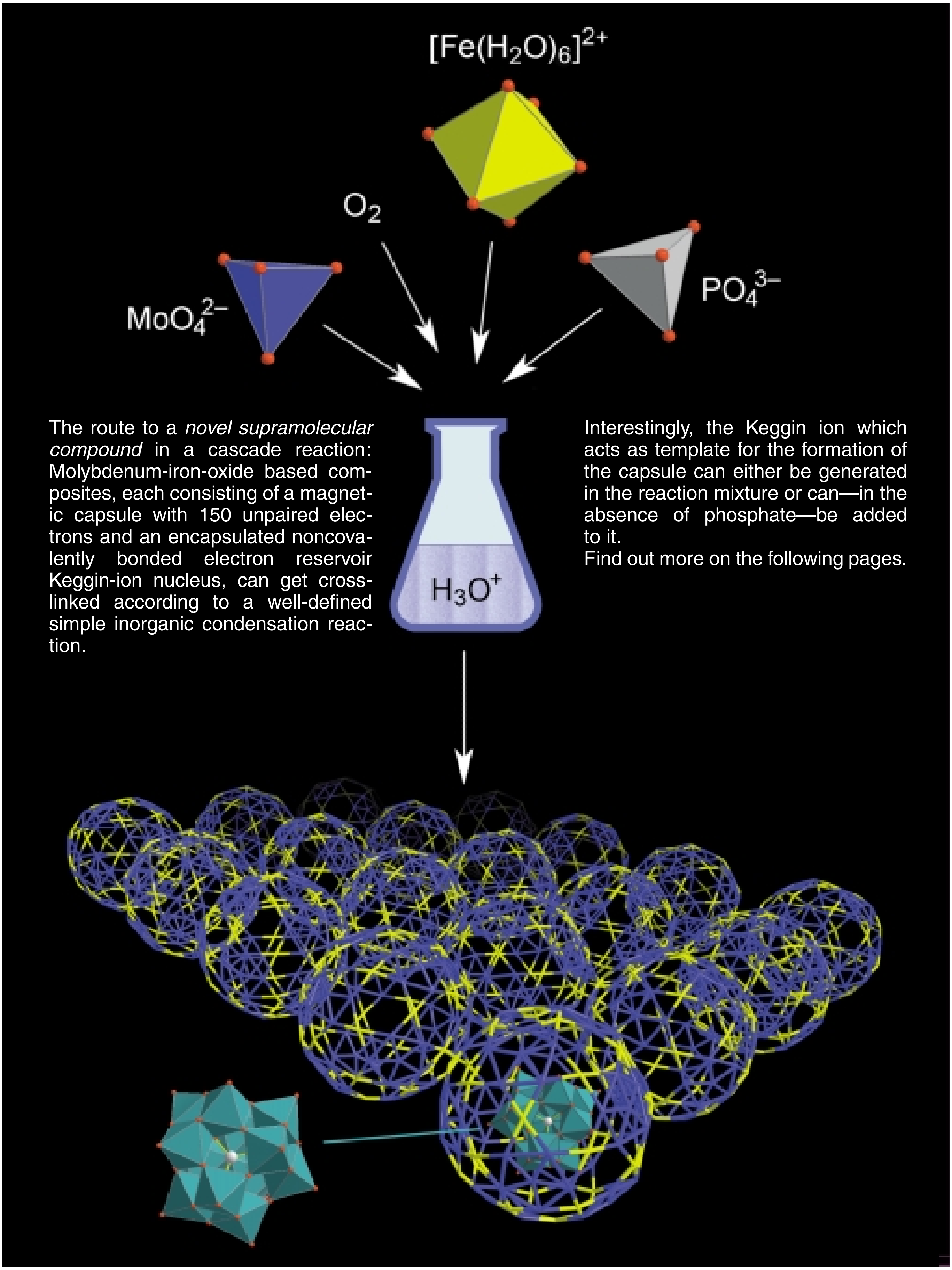

The route to a *novel supramolecular compound* in a cascade reaction: Molybdenum-iron-oxide based composites, each consisting of a magnetic capsule with 150 unpaired electrons and an encapsulated noncovalently bonded electron reservoir Keggin-ion nucleus, can get cross-linked according to a well-defined simple inorganic condensation reaction.

Interestingly, the Keggin ion which acts as template for the formation of the capsule can either be generated in the reaction mixture or can—in the absence of phosphate—be added to it.
Find out more on the following pages.

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A New Type of Supramolecular Compound: Molybdenum-Oxide-Based Composites Consisting of Magnetic Nanocapsules with Encapsulated Keggin-Ion Electron Reservoirs Cross-Linked to a Two-Dimensional Network**

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Hartmut Bögge, Marc Schmidtmann,
Alfred X. Trautwein, Volker Schünemann,
Erich Krickemeyer, and Wilhelm Preetz

Dedicated to Professor Gérard Férey
on the occasion of his 60th birthday

The fabrication of ordered arrays of well-defined nanoparticles or clusters is of fundamental and technological interest. As this is a difficult task, different techniques have been employed.[1] An elegant approach would be to link well-defined building blocks in a chemically straightforward procedure yielding a monodisperse or a completely homogeneous material. We have succeeded now even to cross-link assembled nanosized metal-oxide-based composites—novel supramolecular entities—under one-pot conditions. The supramolecular metal-oxide-based entity, we are dealing with, consists of an oxidized icosahedral capsule as host (internal cavity diameter ~16 Å) corresponding to a paramagnet of the type $\{Mo_{72}^{VI}Fe_{30}^{III}\}$ and the reduced Keggin cluster $[H_xPMo_{12}O_{40}]^{3-}$ ($x = 1$ or 2; diameter of the Keggin anion ~14 Å) as nucleus (guest). Interestingly, the linking is based on a well known inorganic condensation process and the guest (nucleus) acts as a template for the generation of the host (capsule). This was our prior assumption, as according to a modeling investigation it turned out that the Keggin anion just fits exactly into the capsule.

In an acidified aqueous solution (pH 2) containing only polymolybdate, iron(II) chloride, and acetic acid as well as a relatively small amount of phosphate in the presence of air, a stepwise assembly process takes place leading to a new type of material, that is the neutral layer compound **1**. Compound **1** was characterized by elemental analyses, thermogravimetry (to determine the crystal water content), single-crystal X-ray structure analysis[2] (including the calculation of bond valence sums[3] in order to distinguish between (terminal) O and OH_2 ligands), and spectroscopic methods (IR, resonance-Raman, UV/Vis, NIR, ^{57}Fe Mössbauer) as well as magnetic measurements (Table 1).

$$[H_xPMo_{12}O_{40} \subset H_4Mo_{72}^{VI}Fe_{30}^{III}(CH_3COO)_{15}O_{254}(H_2O)_{98}] \cdot \text{ca. } 60\,H_2O$$
$$\mathbf{1} \equiv \mathbf{1a} \cdot \text{ca. } 60\,H_2O$$

As **1** can also be assembled by adding the normal Keggin anion $[PMo_{12}O_{40}]^{3-}$ directly to the aqueous reaction mixture containing no phosphate according to our first approach, the other reaction (see Experimental Section, method 1) corresponds to a molecular cascade with the formation of the Keggin ion as the initial step. Correspondingly, the reaction takes a different route (with no formation of **1**!) in the presence of larger amounts of phosphate, while adding the Keggin unit seems to accelerate the capsule formation as a template. It is important to start from Fe^{II} (which gets gradually oxidized) rather than from Fe^{III}, as the latter starting material immediately results in a not well-defined precipitate.

The building block of each layer of **1** is the spherical icosahedral giant oxidized cluster cage of the $\{(Mo^{VI})Mo_5^{VI}\}_{12}Fe_{30}^{III}$ type, comparable to that reported[4] earlier, but which now has a reduced metal-oxide-based cluster—the tetrahedral reduced Keggin $[H_xPMo_{12}O_{40}]^{3-}$ ion[2]—as nucleus (Figure 1). Each of the cluster–cluster composites is linked to four others through Fe-O-Fe bonds to form a layer structure (Figure 2). The spherical capsule comprises 12 pentagonal fragments of the type $\{(Mo)Mo_5O_{21}\}$ (built up by a central bipyramidal MoO_7 group linked by edge-sharing to five MoO_6 octahedra) which are connected by 30 $\{Fe^{III}(H_2O)_2\}^{3+}$ linkers. The (disordered) acetate ligands, which make the assembly neutral in result, are located inside

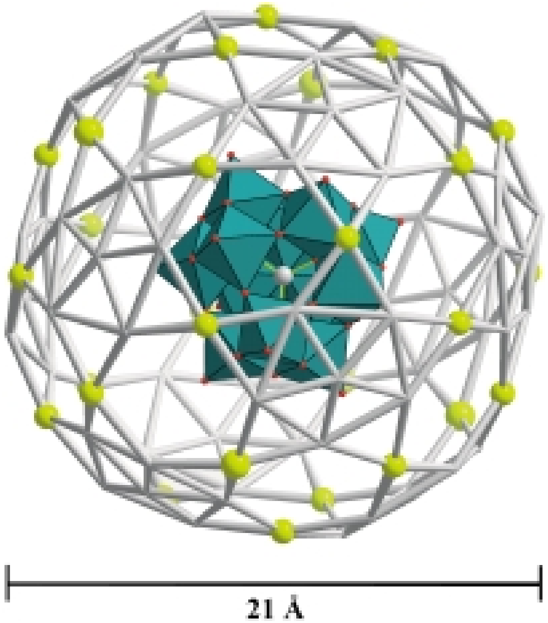

Figure 1. Demonstration of the structure of the building block of **1** with the capsule (host) and encapsulated Keggin-type cluster nucleus (guest idealized): the metal $\{Mo_{72}Fe_{30}\}$ capsule in wire frame representation—with 30 Fe^{III} centers (highlighted as yellow spheres) linking the 12 $\{(Mo^{VI})Mo_5^{VI}\}$ pentagons—and the Keggin nucleus in polyhedral representation.

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Table 1. Characteristics of the two-dimensional layer structure formed by cross linking novel supramolecular-type (composite) building blocks: $\{Mo_{12} \subset Mo_{72}Fe_{30}\}$ (spherical icosahedral capsule and an encapsulated nucleus of tetrahedral symmetry).

	Building block (capsule and nucleus)		Interaction characteristics
	capsule (host)	Keggin nucleus (guest)	
imposed Platonic/ Archimedean solids	icosidodecahedron (Fe_{30}) icosahedron ($\{(Mo)Mo_5\}_{12}$)	cuboctahedron (Mo_{12}) rhombicuboctahedron (O_{24})	topological host–guest complementarity
symmetry	icosahedral metal framework (I_h)	tetrahedral (T_d)	
geometrical data	diameter: ca. 2.5 nm		min. O(shell)$\cdots$ O(nucleus) = ca. 2.6 Å
building units	90 octahedra ($Fe^{III}O_4(H_2O)_2$, $Mo^{VI}O_6$)	1 tetrahedron (P^VO_4)	
	12 pentagonal bipyramids ($Mo^{VI}O_7$)	12 octahedra ($Mo^{VI/V}O_6$)	
electronic transitions [cm^{-1}]	O $\rightarrow$ Mo^{VI} charge transfer: $\sim$ 27000	intervalence charge transfer ($Mo^V \rightarrow Mo^{VI}$): $\sim$ 11600/$\sim$ 9500[a]	nucleus $\rightarrow$ shell charge transfer: $\sim$ 18100
vibrations [cm^{-1}][b]	$\nu(MoO_t)$ (IR): 960	$\nu(O_{br})$-breathing(resonance Raman)[c]: 830	
		ν_{as} (PO_4) (IR): 1068	
redox state[d]	oxidized (72 Mo^{VI} and 30 Fe^{III})	reduced (electron reservoir)	
magnetism	strong paramagnet corresponding to 26 antiferromagnetically coupled Fe^{III} ($S = 5/2$) centers (at RT, $\chi_{mol}T = 114$ emu K mol^{-1})[e]		
nuclei properties [mm s^{-1}]	^{57}Fe Mössbauer isomer shift/quadrupole splitting (180 K): $\delta = 0.48/\Delta E_Q = 0.70$ (characteristic for $Fe^{III}O_6$)		

[a] Solid, transmission of a film obtained from the pure substance by pressure (10 kbar) between saphir pistils (the electronic spectra of reduced Keggin ions strongly depend on their environment, for example the type of solvent). [b] KBr pellet (the band at 1068 cm^{-1} supports the presence of a Keggin ion[2]). [c] $\lambda_e = 1064$ nm. [d] Potentiometric titration using $Ce(SO_4)_2$. [e] Whereas the susceptibility of discrete $\{Mo_{72}Fe_{30}\}$ units which exist in the wet crystals (measured directly after filtration) at room temperature corresponds to 30 nearly uncorrelated Fe^{III} centers, due to the linking of the building blocks through four Fe^{III}-O-Fe^{III} bonds (see also ref. [4] for a related problem) the magnetic moment corresponds effectively to only 26 uncorrelated Fe^{III} centers at room temperature.

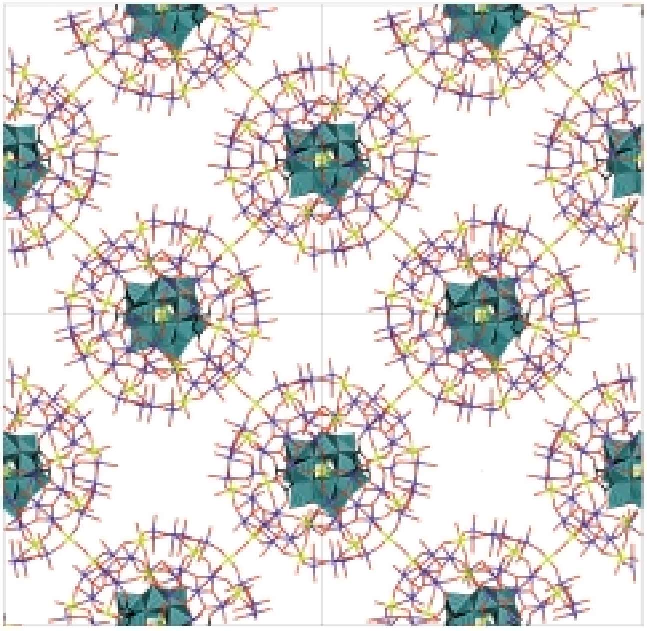

Figure 2. Schematic structural depiction of a layer segment in crystals of **1** with the capsules (including O atoms in contrast to Figure 1) in wire frame (O: red; Fe: yellow; Mo: blue) and the Keggin ions (idealized) in polyhedral representation.

the sphere and coordinate as bidentate ligands to the metal centers, preferably bridging Fe and Mo sites.

Selected physical properties of **1** are summarized in Table 1 and displayed in Figure 3. They not only prove the existence of the two separate, noncovalently bonded parts of each supramolecular entity (the capsule and its nucleus), but show also its interesting topological, spectroscopic, electronic, and magnetic properties. The reduced Keggin cluster can be identified nicely by means of the resonance-Raman effect (Figure 3d) showing only the vibrational bands of this unit. The nanocapsules of the type $\{(Mo^{VI})Mo_5^{VI}\}_{12}Fe_{30}^{III}$, which form a system of magnetic dots (each individual discrete dot represents as yet the strongest known molecular paramagnet due to the presence of 30 Fe^{III} centers with 150 (!) unpaired electrons, that is, $S = 150/2$ at room temperature), encapsulate the reduced nuclei (quantum dots) as guests which can be regarded as potential electron-storage elements. Notably, the free Keggin cluster can be reduced in several steps in association with concomitant protonation thus keeping its charge constant.[5]

The noncovalent host–guest interactions are worthy of consideration as the reduced electron reservoir-type Keggin ion fits exactly into the capsule cavity (the shortest $O_{host} \cdots O_{guest}$ bond lengths, typical for hydrogen bonding, are of the order of 2.6 Å). This type of composite/supramolecular entity with a reduced nucleus in an oxidized shell is unprecedented. The band observed at $\sim$ 550 nm ($\sim 18.1 \times 10^3$ cm^{-1}; Figure 3b) which contributes to the color can tentatively be assigned to a novel charge transfer transition of the type *reduced nucleus $\rightarrow$ oxidized shell*.[6]

The knowledge of the chemistry of nanocapsules which are variable in size[4a] and linkable[4b] allows us the synthesis of new types of materials. It is even possible to open the capsules, exchange their contents, and close them again[7] which allows

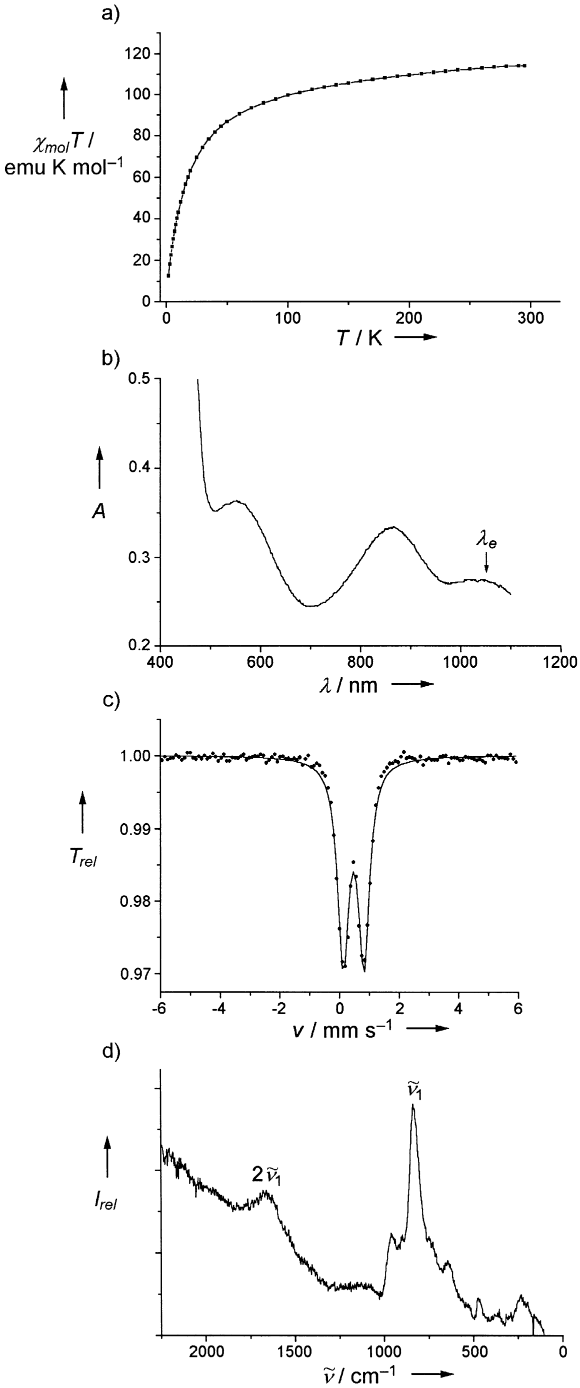

Figure 3. Physical/spectroscopic data of **1** that characterize the capsule and encapsulated nucleus: a) magnetic susceptibility as function of temperature, b) electronic absorption with λ_e for the resonance Raman spectrum, c) ^{57}Fe Mössbauer, and d) resonance-Raman spectra (for details see Table 1).

the fabrication of different types of cross-linked composites. We refer to a new class of novel composite (a cluster encapsulated in a cluster) type materials, in which the electronic/magnetic structure of the composite (quantum/magnetic dot) can, in principle, be tuned by changing the relevant properties of the constituents, for instance by changing the electron population of the nucleus (Keggin anion).

Experimental Section

1: Method 1: $NaH_2PO_4 \cdot 2H_2O$ (0.21 g, 1.35 mmol) was added to a solution obtained by treating a mixture of H_2O (75 mL), $FeCl_2 \cdot 4H_2O$ (1.0 g, 5.03 mmol), and $Na_2MoO_4 \cdot 2H_2O$ (5.0 g, 20.66 mmol) with CH_3COOH (100%, 10 mL). After acidification with about 3 mL of 32% hydrochloric acid (pH of the reaction mixture ~2.0), the solution was stirred for 15 min at room temperature and filtered. The filtrate was kept for seven days at 20°C in an open 250 mL beaker for crystallization. The greenish crystals (thin plates) were filtered, washed with water, and dried at room temperature. Yield: 0.45 g (14.8% based on Fe) (correct analysis).

Method 2: $H_3[P(Mo_3O_{10})_4]$ (2.5 g, 1.37 mmol) was added to a solution obtained by treating a mixture of H_2O (75 mL), $FeCl_2 \cdot 4H_2O$ (1.0 g, 5.03 mmol), and $Na_2MoO_4 \cdot 2H_2O$ (2.0 g, 8.27 mmol) with CH_3COOH (100%, 10 mL). After acidification with about 0.5 mL 32% HCl acid (pH of the reaction mixture ~2.0), the solution was stirred for 45 min at room temperature and filtered. The filtrate was kept in an open 250 mL beaker for crystallization for five days. The crystals were filtered, washed with water, and dried at room temperature. Yield: 0.5 g (correct analysis).

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[2] Crystal structure analysis of **1**: Space group *Cmca*, $a = 36.621(2)$, $b = 34.778(2)$, $c = 34.824(2)$ Å, $V = 44351(4)$ Å^3, $Z = 4$, $\rho = 2.727$ g cm^{-3}, $\mu = 3.367$ mm^{-1}, $F(000) = 34904$, crystal dimensions $0.36 \times 0.18 \times 0.02$ mm^3. Dry crystals were cooled to 183(2) K on a Bruker axs SMART diffractometer ($Mo_{K\alpha}$, graphite monochromator). A total of 112330 reflections ($1.50 < \theta < 25.06°$) was collected, of which 19640 unique reflections ($R_{int} = 0.1328$) were used. The structure was solved by using the program SHELXS-97 and refined (1423 parameters) by using the program SHELXL-93 to $R = 0.073$ for 11094 reflections with $I > 2\sigma(I)$ (both programs from G. M. Sheldrick, University of Göttingen, **1993/1997**, respectively). Several molecules of water of crystallization could not be located due to their disorder. For the encapsulated Keggin ion only the central P atom and partly disordered Mo atoms (but not the O atoms because of the disorder) could be detected for which the occupancy factors, however, add up to 12. This together with the analysis, the vibrational spectrum (for related IR ν(PO) bands see C. Rocchiccioli-Deltcheff, R. Thouvenot, *J. Chem. Res. (S)* **1977**, 46–47; C. Rocchiccioli-Deltcheff, R. Thouvenot, *J. Chem. Res. (M)* **1977**, 549–571) and the used pH value supports the presence of a complete Keggin ion rather than a lacunary type one. Due to the disorder and related basic analytical problems in connection with the error limit of the number of acetate ligands differently protonated and reduced (singly/doubly) Keggin ions cannot be completely excluded (see also L. A. Combs-Walker and C. L. Hill, *Inorg. Chem.* **1991**, *30*, 4016–4026. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-140422 (**1**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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[6] Neither a relevant reduced Keggin ion $[H_xPMo_{12}O_{40}]^{3-}$ nor the $\{Mo_{72}Fe_{30}\}$-type compounds containing only Mo^{VI} and Fe^{III} centers without an encapsulated Keggin ion (see ref. [4]) taken separately show this electronic absorption band at 550 nm. Using blue or green excitation lines give Raman spectra of the capsule with changing intensity only of the 830 cm^{-1} band.

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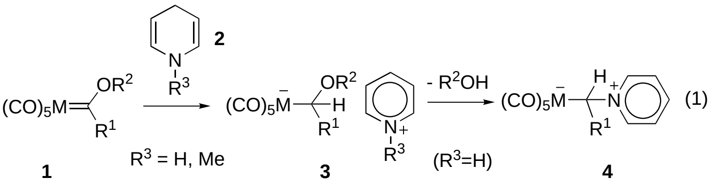
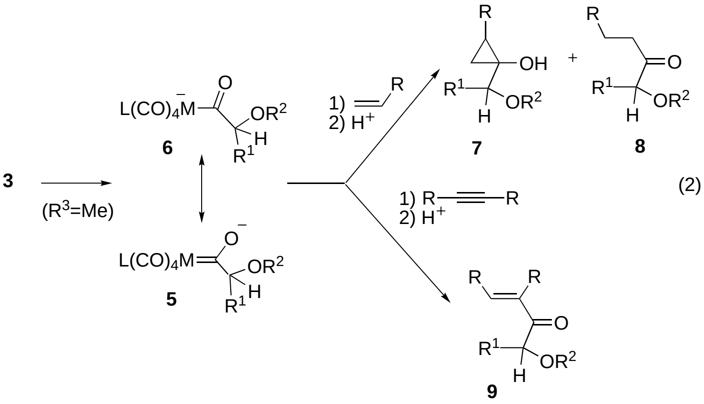
Linear Coupling of Three CO Ligands of Chromium Hexacarbonyl Leading to Functionalized Butenolides via Fischer Carbene Complexes

Henri Rudler,* Andrée Parlier, Victor Certal, and Jacqueline Vaissermann

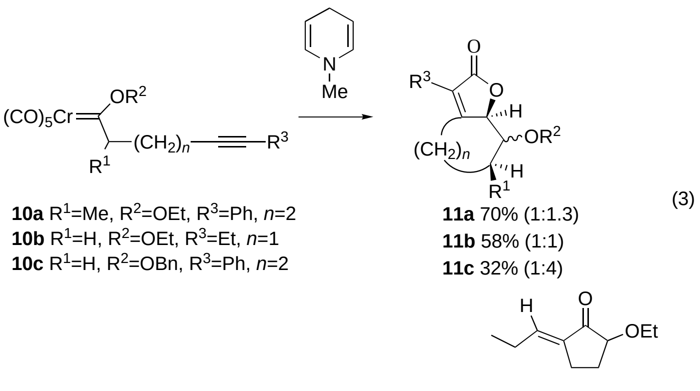
Fischer carbene complexes have been widely used for the synthesis of a broad spectrum of organic compounds.[1, 2] By far the best known applications are the formation of cyclopropanes and phenols by reaction with olefins and alkynes, respectively. Whereas in the former, besides the olefin, one CO ligand of $[Cr(CO)_6]$ is incorporated as a carbene group, in the latter, besides the alkyne, two CO ligands are included in the final product, the first one again as a carbene group. Here we describe the first general synthesis of functionalized polycyclic butenolides by incorporation of three CO groups of $[Cr(CO)_6]$, besides an alkyne. This reaction involves successive insertion reactions of a carbene complex of chromium, an alkyl chromate, an acylium chromate, and a ketene complex of chromium.

In previous papers, we have described a general dihydropyridine-induced reduction of alkoxycarbene complexes of chromium and tungsten to pyridinium metalates **3** [Eq. (1)].[3–5] When $R^3 = H$, isolable pyridinium ylide complexes **4** were formed in high yield; for $R^3 = Me$, unstable *N*-methylpyridinium metalates **3** could be characterized by NMR spectroscopy. Interestingly, the latter complexes underwent a CO insertion reaction, akin to that observed for other (carbonyl)metalates,[6–12] to give oxycarbene complexes **5**, a resonance form of the acylium metalates **6**. These complexes gave hydroxycyclopropanes **7** and/or ketones **8** with alkenes, whereas reaction with alkynes gave *α,β*-unsaturated ketones **9** [Eq. (2)].





However the most gratifying transformation occurred in the case of alkynylalkoxycarbene complexes of chromium. When complex **10a** was treated with a twofold excess of *N*-methyldihydropyridine at $-10\,^{\circ}C$ and the reaction mixture warmed to room temperature overnight, the bicyclic butenolide **11a** was obtained in 70% yield as a 1/1.3 mixture of *cis*/*trans* isomers which differ in the relative configuration of the hydrogen atoms at the ring junction and on the carbon atom bearing the ethoxyl group [Eq. (3)]. Their structures were established by NMR spectroscopy.



12 (11%)

Changing the nature of the substituents on the triple bond and the number of methylene groups in the alkynyl chain did not affect the course of the reaction: complex **10b** gave **11b** in 58% yield as a 1/1 mixture of isomers together with 11% of **12**. The alkoxyl group was modified by a known procedure, which in the case of benzyl alcohol led to **10c**.[13, 14] Reaction of **10c** with *N*-methyldihydropyridine gave the butenolide **11c**, again as a mixture of isomers (1:4), in 32% yield.

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