

Rendering Schrock-type Molybdenum Alkylidene Complexes Air Stable: User-Friendly Precatalysts for Alkene Metathesis**

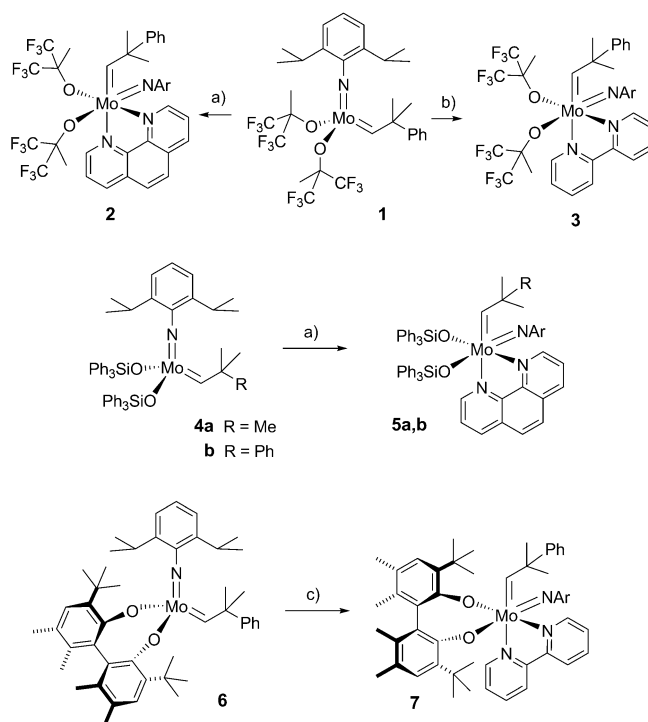
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Complex **1** and related tetracoordinate molybdenum alkylidenes developed by Schrock and co-workers range amongst the most powerful alkene metathesis catalysts known to date.^[1,2] They are distinguished by exceptional reactivity, good functional group tolerance and a remarkable scope, encompassing olefins that are considered difficult substrates on steric and/or electronic grounds.^[3,4] The modularity of the established synthesis route allowed the operative motif of **1** to be systematically edited and hence gave rise to several generations of descendant catalysts with tailored properties. Most notable among them are Schrock alkylidenes with chiral alkoxide or diolate ligands and/or alkylidenes that are chiral at metal for all sorts of asymmetric metathesis reactions,^[3,5] as well as catalysts that impose high *Z*-selectivity on certain metathesis reactions.^[6]

As complex **1** and relatives, however, are very sensitive to air and moisture, their handling is clearly more demanding than that of the competing ruthenium carbenes introduced by Grubbs.^[7] To overcome this disadvantage, we now present a simple way of rendering prototype Schrock alkylidenes largely air-stable, which facilitates their handling and may hence encourage more widespread use of these able catalysts in preparative laboratories.

Based on recent observations made in the alkyne metathesis arena,^[8,9] solutions of **1** in toluene were reacted at room temperature with equimolar amounts of 1,10-phenanthroline or 2,2'-bipyridine. The resulting crystalline adducts **2** and **3** turned out to be surprisingly robust in the solid state as well as in solution.^[10] Their integrity can be easily checked by NMR spectroscopy due to the characteristic downfield shift of the alkylidene proton from $\delta_{\text{H}}(\text{CD}_2\text{Cl}_2) = 12.19$ ppm in the parent complex **1** to $\delta_{\text{H}}(\text{CD}_2\text{Cl}_2) = 13.88$ and 13.74 ppm in **2** and **3**, respectively. According to this distinctive signature, a sample of the bipyridine adduct **3** stored at the bench in an open flask was fully intact after eight weeks, whereas the corresponding phenanthroline adduct **2** was found to be somewhat less stable (only ca. 50% intact after four weeks). Other prototype molybdenum alkylidenes such as the triphenylsilanolates

complex **4**^[11] and the chiral variant **6**^[12] also form adducts that remain intact when stored without any precautions for extended periods (Scheme 1).



Scheme 1. a) 1,10-Phenanthroline, toluene, RT, 95% (**2**), 81% (**5a**), 85% (**5b**); b) 2,2'-bipyridine, toluene, RT, 93% (**3**); c) 2,2'-bipyridine, Et₂O, RT, 74% (**7**); Ar = 2,6-diisopropylphenyl.

The structure of the particularly robust complex **3** in the solid state is depicted in Figure 1. The coordination geometry about the Mo^{VI} center can be described as distorted octahedral, with the imido ligand and one of the two inequivalent hexafluoro-*tert*-butanolates residing *trans* to each other, even though the corresponding N3-Mo1-O2 angle (167.04(4)°) strongly deviates from linearity. Likewise, the angle between the alkylidene C19 carbon and the *trans*-positioned N2 atom of the bipyridine is reduced to 167.02(4)°. The distortion of the ligand sphere also manifests in very uneven bond distances between the Mo center and the N atoms of the chelating bipyridine unit. The fact that the Mo1-N2 bond (2.3503(11) Å) is considerably longer than the corresponding Mo1-N1 bond (2.2462(10) Å) reflects the significant *trans* influence of the alkylidene unit^[13] and may be an essential structural precondition for the decomplexation behavior described below. The alkylidene Mo1-C19 bond length

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[**] Generous financial support by the MPG and the Fonds der Chemischen Industrie is gratefully acknowledged. We thank Dr. C. W. Lehmann and J. Rust for solving the X-ray structures and all analytical departments of our institute for their excellent support of our program.

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/anie.201102012>.

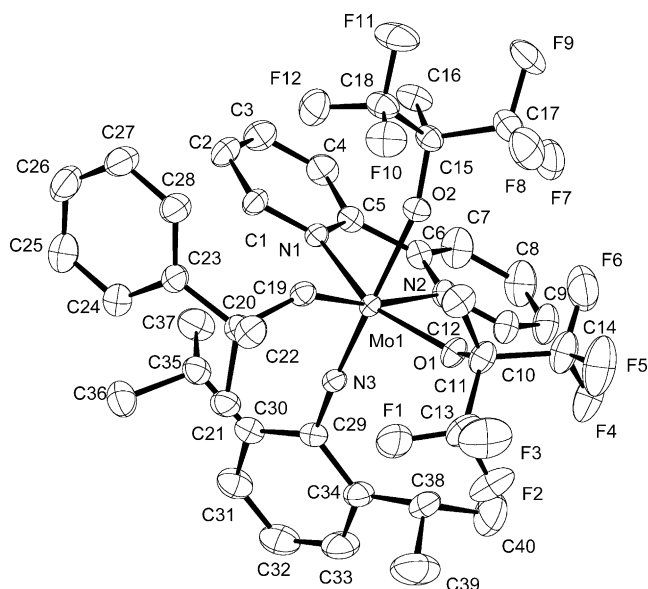


Figure 1. Structure of the bipyridine adduct **3** in the solid state.^[14] The structures of the analogous phenanthroline complexes **2** and **5b** are contained in the Supporting Information.

itself (1.9361(12) Å) falls in the normal range and the neophylidene group shows the expected *syn* conformation (orientation toward the imido substituent).^[1,2] The overall structures of the related 1,10-phenanthroline complexes **2** and **5b** (Supporting Information) as well as of the chiral bipyridine adduct **7** (Figure 2) in the solid state are largely similar in that they exhibit distorted octahedral coordination geometries, unequal distances between the metal center and the two inequivalent N atoms of the chelating donor ligand, as well as *syn*-oriented molybdenum alkylidene units.^[14]

In contrast to the known adducts of Schrock alkylidenes with various monodentate donor ligands (ethers, phosphines,

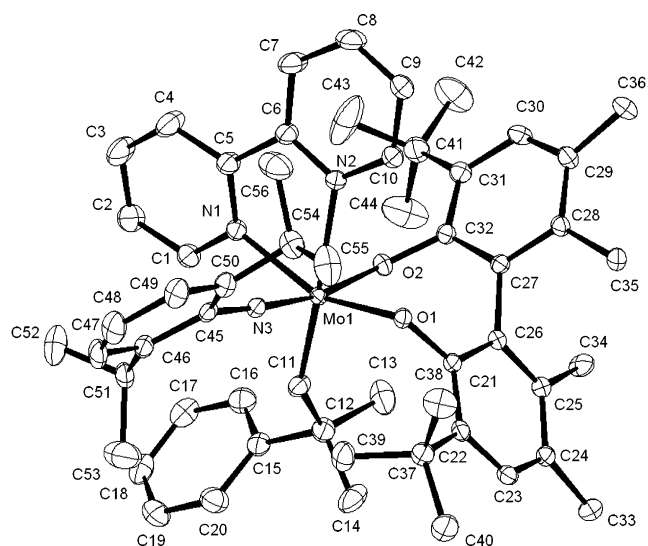


Figure 2. Structure of complex **7** in the solid state.^[14] Selected bond length [Å] and angles [°]: Mo1–N3 1.7626(16), Mo1–C11 1.967(2), Mo1–N1 2.2561(17), Mo1–N2 2.3352(17), N3–Mo1–O2 169.57(7), C11–Mo1–N2 168.12(7), Mo1–N3–C45 176.26(16).

pyridine, quinuclidine), in which the coordination of the base is partially reversible in solution at ambient temperature,^[15] the NMR spectra of **2**, **3**, **5**, and **7** give no indications for partial dissociation of the chelating bipyridine or phenanthroline residues.^[16] As a result, these complexes are devoid of catalytic activity in prototype ring closing metathesis (RCM) reactions even at higher temperatures. Gratifyingly though, the bidentate N ligands can be readily pulled off upon treatment of these adducts with one equivalent of anhydrous ZnCl₂ in toluene at ≤ 100°C, thus releasing the structurally intact and catalytically competent parent Schrock alkylidene from which they derive. As judged by NMR spectroscopy, the reaction is complete in less than 30 min.^[17] It is believed that the structural distortion of the adducts and, in particular, the weakened Mo–N bond *trans* to the alkylidene unit are essential for making this ligand interchange possible. In case of complex **7**, the decomplexation was performed at 60–80°C to avoid racemization of the enantiopure biaryl moiety.

The possibility to remove the phenanthroline (bipyridine) unit from adducts **2**, **3**, **5**, and **7** without compromising the reactive metal core distinguishes the current method from previous attempts to stabilize high valent alkylidene catalysts with the aid of external donor ligands. Specifically, complexation of Schrock alkylidenes with hydrotris(1-pyrazolyl)borate or derivatives thereof is known to afford indefinitely air stable adducts. However, treatment with Lewis acids such as AlCl₃ did not cleanly regenerate the parent complexes but rather produced mixtures containing one or even more than one structurally undefined new species of low catalytic competence.^[18–20]

In striking contrast, the decomplexation of the phenanthroline or bipyridine ligand from **2** or **3**, respectively, released the intact parent tetracoordinate molybdenum alkylidene **1** as judged by NMR spectroscopy; its excellent reactivity was found uncompromised by the presence of the precipitated yellow bipyridine–ZnCl₂ or phenanthroline–ZnCl₂ that need not be filtered off.^[17] As expected for complex **1** as the active principle, all chosen test reactions shown in Table 1 were high-yielding under mild conditions.^[21,22] This includes the formation of sterically hindered and even tetrasubstituted products at room temperature, the cyclization of electronically disfavored alkenes (vinylsilane, enol ether, enoate), the smooth conversion of an azide-containing substrate (which is destroyed by Grubbs-type catalysts bearing R₃P ligands) to an immediate precursor of the protein kinase inhibitor balanol (entry 8),^[23] as well as a desymmetrization reaction (entry 11) and a kinetic resolution (entry 12) catalyzed by the chiral complex **7** activated with ZnCl₂. We hence conclude that our new method combines the convenience of handling of a crystalline and bench-stable precatalyst with the benefits of a well defined active species of proven versatility. It is hoped that this approach will foster the use of the remarkably powerful Schrock alkylidenes and fertilize further investigations into metathesis reactions using non-noble transition metal catalysts in general.

Received: March 22, 2011

Published online: July 1, 2011

Table 1: RCM using precatalyst **2** (5 mol%) activated with ZnCl₂ (5 mol%); E = COOEt.^[a]

Entry	Substrate	t	Product	Yield [%]
1		10 min		98
2		12 h		94
3		12 h		95, R = tBu
4		12 h		98, R = Ph
5		3 h		93, R = COOEt ^[b]
6		12 h		95
7		1 h		96
8		1 h		92 ^[c]
9		12 h		85
10		1 h		93
11		6 h		85 (90% ee) ^[d]
12		1 h		[e]

[a] Unless stated otherwise, the precatalyst was activated by reaction with ZnCl₂ in toluene at 100 °C for 30 min; the subsequent RCM reactions were then performed at ambient temperature. [b] The RCM was performed at 50 °C. [c] In CH₂Cl₂ at reflux. [d] Using precatalyst **7** activated with ZnCl₂ in toluene at 80 °C. [e] Using precatalyst **7** activated with ZnCl₂ in toluene at 65 °C; at 72% conversion (determined by NMR spectroscopy using dodecane as internal standard), the recovered substrate (27%) showed an ee of 99%, and the product (33%) had an ee of 70%.

Keywords: alkene metathesis · alkylidene complexes · molybdenum · precatalysts

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