Teaching the Cummins Complex Heterodimerization: Formation of Unorthodox Heteroleptic $X_3Mo\equiv MoY_3$ Dimers with Ultralong Metal-Metal Triple Bonds

Daniel Rütter,[a] Nils Nöthling,[a] Markus Leutzsch,[a] Alois Fürstner*[a]

[a] Max-Planck-Institut für Kohlenforschung, 45470 Mülheim/Ruhr, Germany

ABSTRACT: Attempts to stabilize mononuclear trigonal-planar Mo(+3) complexes by (tripodal) silanolates or alkoxides, which had recently been shown to synergize exceedingly well with high valent molybdenum or tungsten alkylidynes, afforded unsymmetrical dimolybdenum complexes of the general type $[X_3Mo\equiv MoY_3]$; not only is this ligand pattern unprecedented, but these dimers incorporate the intact Cummins complex $[(tBu)(Ar)N]_3Mo$ (Ar = 3,5-dimethylphenyl), which is famous for not engaging in metal-metal triple bonding otherwise. The remarkable ease of heterodimerization likely reflects a pronounced kinetic selectivity. The new complexes were characterized by crystallographic and spectroscopic means; they show highly deshielded ^{95}Mo NMR signals and comprise unusually long yet robust Mo≡Mo bonds.

The chemistry of Mo(+3) is dominated by the massive bias of $[X_3Mo]$ units to dimerize. It is the stability of the resulting $\sigma^2\pi^4$ metal-metal triple bond between the two d^3 electron fragments that provides a formidable thermodynamic driving force for the formation of homo-bimetallic complexes of the general type $[X_3Mo\equiv MoX_3]$ (X = alkyl, (pseudo)halide, alkoxy, silyloxy, dialkylamido etc.). Ever since the first such complex had been described by Wilkinson and coworkers in 1971,[1] the field flourished, leading to a plethora of homoleptic representatives.[2,3] Some of them have been transformed into heteroleptic variants by partial ligand exchange via protonolysis or salt metathesis, whereby "symmetrical" ligand distributions ($[X_2YMo\equiv MoYX_2]$, "1,2-pattern")[4,5] were far more commonly attained than "unsymmetrical" ones ($[XY_2Mo\equiv MoX_3]$, "1,1-pattern").[6-9] Such isomers tend not to interconvert, suggesting that the barriers for group transfer between the two neighboring molybdenum centers under thermal conditions are high in most cases.[7,10] Heteroleptic examples of the type $[X_2YMo\equiv MoX_3]$ or $[XY_2Mo\equiv MoX_3]$ are exceedingly rare,[11-16] and heterodimers of the general constitution $[X_3Mo\equiv MoY_3]$ seem to be unknown.[17]

The challenge to access a kinetically stable monomeric Mo(+3) complex was first met in 1995 by Cummins and coworkers, who disclosed the preparation, structure and stunning reactivity of the trigonal planar complex $[(tBu)(Ar)N]_3Mo$ (Ar = 3,5-dimethylphenyl) (**1**) (Figure 1).[18-22] This particular trisamidomolybdenum species and its siblings are capable of activating numerous small molecules under mild conditions, including substrates as unreactive as N_2 or N_2O. The serendipitous discovery in our laboratory that **1** also reacts with CH_2Cl_2 to generate alkyne metathesis catalysts in situ that proved highly chemoselective and therefore appropriate for applications to polyfunctionalized substrates opened an interface to advanced organic synthesis as well.[23-26] In any case, the strongly π-donating and very bulky amido ligands safeguard the Mo(+3) center so effectively that dimerization of **1** has never been observed, not even as a side reaction in any of the applications that this complex has found so far in the literature.

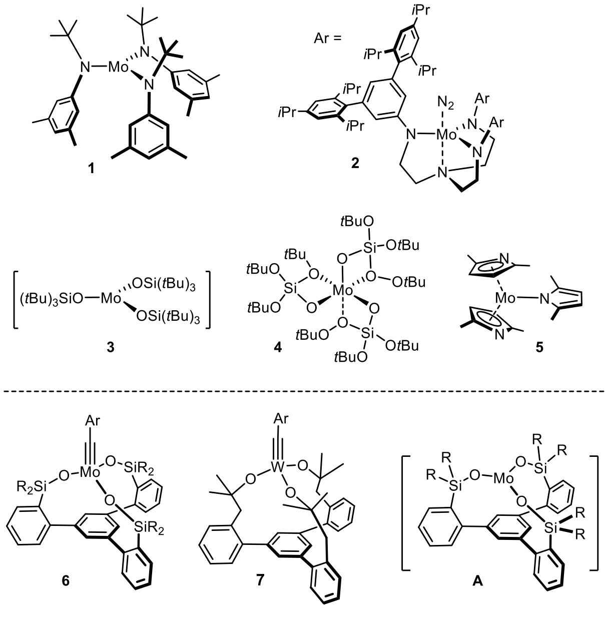
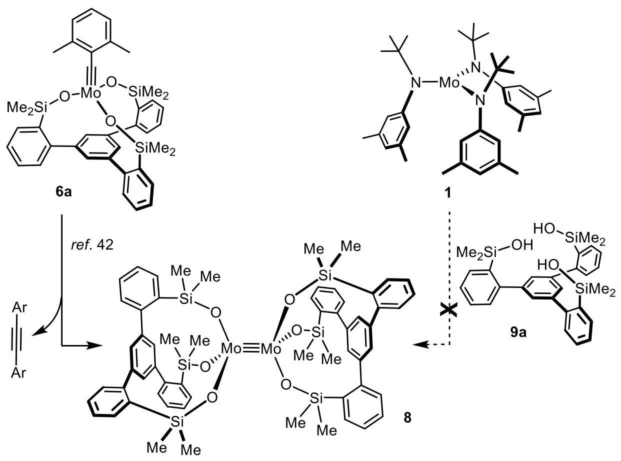


Figure 1. Top: known monomeric Mo(+3) complexes; bottom: "canopy catalysts" for alkyne metathesis and envisaged use of the tripodal ligands they incorporate for the stabilization of Mo(+3)

Very few other monomeric Mo(+3) complexes were described ever since. Arguably most prominent are complexes such as **2** comprising a trisamidoamine ligand framework,[27-29] which served as entry point for the reductive cleavage of N_2 with formation of NH_3 in a catalytic mode.[30] Though much less π-donating than amides, bulky silanolates were also shown to be adequate ligands, as witnessed by complex $[(t\mathrm{Bu}_3\mathrm{SiO})_3\mathrm{Mo}]$ (**3**), even though the structure of **3** proper is unknown and its monomeric nature was inferred from a crystalline phosphine adduct.[31,32] Complex $[[(t\mathrm{BuO})_3\mathrm{SiO}]_3\mathrm{Mo}]$ (**4**) constitutes an interesting variation on that theme: by virtue of the additional lateral oxygen atoms, each siloxide engages in weak κ^2 binding; **4** is hence a coordinatively saturated octahedral entity, yet retains the prototypical reactivity of a monomeric Mo(+3) species towards N_2 and other small molecules.[33] A higher level of coordinative and electronic saturation also helps stabilize complex **5**, in which two of the three 2,5-dimethylpyrrolide ligands are η^5-bound, thus rendering the bonding situation analogous to that of a bent metallocene.[34]

Scheme 1. A dumbbell dimer with two tripodal silanolate endcaps; Ar = 2,6-dimethylphenyl

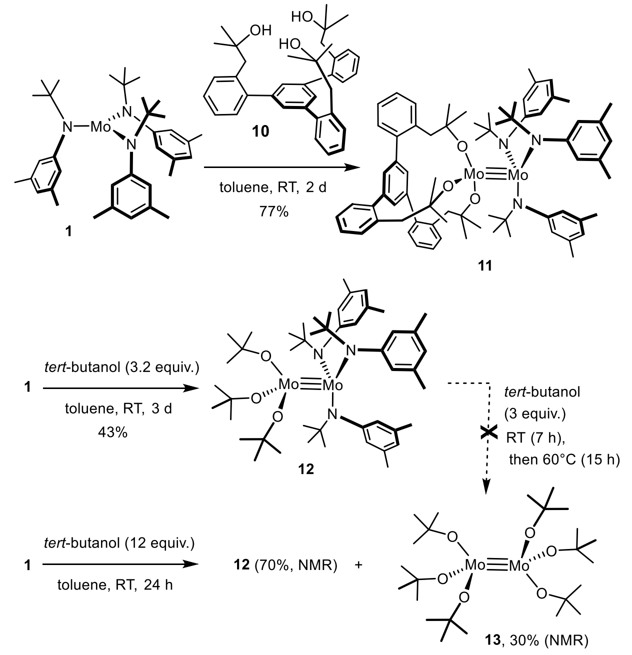


Intrigued by these reports, we wondered whether tripodal silanolates or alkoxides of the types recently used to support high-valent molybdenum or tungsten alkylidynes could serve similar purposes. For the excellent synergy between these ligands and the respective high-valent metal centers, catalysts such as **6** and **7** excel in alkyne metathesis for reasons that are now fairly well understood.[35-41] When applied to Mo(+3), the phenyl ring forming the basal plane of the "canopy" ligand framework would effectively block one side of the hypothetical complex **A**, whereas the fence of upward-pointing substituents R on the tethers encircling the Mo(+3) atom potentially shields the opposite face.

To prevent dimerization from occurring, the size and shape of R is likely of critical importance. This notion is corroborated by our previous observation that the alkylidyne complex **6a** decomposes by bimolecular coupling with formation of the corresponding tolane and the homobimetallic dimer **8** (Scheme 1).[42] Methyl substituents on the silicon linkers do obviously not suffice to prevent metal-metal bonding from occurring. Interestingly though, reaction of **1** with the free ligand **9a** failed to afford this product but gave an ill-defined oligomer.

A more auspicious result was obtained with the tripodal alcohol derivative **10**, which had originally been designed to bolster the activity of tungsten alkylidyne catalysts **7**.[40] Though hardly more encumbered than **9a**, addition of **10** to a solution of **1** in C_6D_6 showed the clean formation of a defined product as judged by ^{1}H NMR; surprisingly though, ca. 50% of the ligand remained unchanged at the point when the molybdenum complex was fully consumed. Analysis of the crude material by HR-MS indicated that a product of formal composition $[C_{72}H_{93}Mo_2N_3O_3]^+$ had formed;[43] this data suggested that **1** had somehow been incorporated into a dimeric species. To confirm this paradoxical result, the experiment was repeated with a 1:2 ratio of the reaction partners in toluene, which allowed the new complex **11** to be isolated in analytically pure form in 77% yield (Scheme 2).

Scheme 2. Heterodimers by alcoholysis of **1**



The diamagnetic nature of the complex suggested that a Mo≡Mo bond might have been formed. ROESY cross peaks showed that two chemically different ligand spheres are present as part of one and the same molecule. The recorded ^{15}N NMR shift (δ_N = −147 ppm) differs significantly from that of the free aniline (tBu)(Ar)NH (δ_N = −289 ppm), thus indicating that the ligand is metal-bound. High barriers for rotation about the N–Ar bond render the *ortho*-H atoms on the aryl ring diastereotopic on the NMR timescale; one of them resides in the anisotropy cone of a neighboring aryl ring and is therefore highly shielded (δ_H = 4.19 ppm).[44]

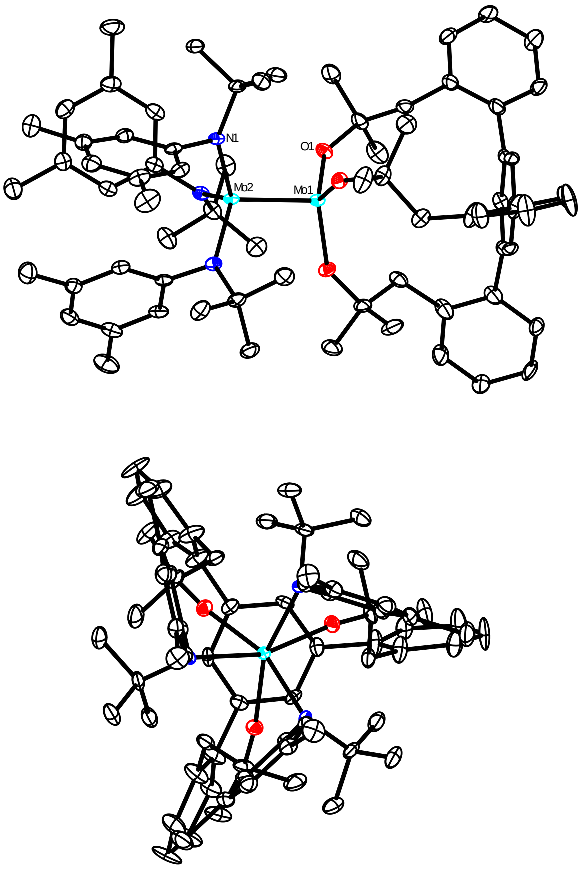


Figure 2. Molecular structure of the heterodimeric complex **11** in the solid state; top: side view; bottom: projection along the threefold crystallographic Mo–Mo axis; H-atoms, disordered parts, and solute solvent molecules in the unit cell not shown for clarity; the full structure is contained in the Supporting Information

The structure of **11** in the solid state confirms the conclusions drawn from the NMR data; to the best of our knowledge, **11** is the first example of a heterodimeric species of the type $[X_3Mo{\equiv}MoY_3]$ (Figure 2). Truly perplexing is that fact that **11** incorporates an intact "Cummins fragment" as one of the subunits, even though complex **1** is famous for *not* engaging in metal-metal triple bonding otherwise. The Newman-type projection shows that the ligands are not perfectly staggered about the Mo–Mo axis, despite their bulk;[45] the smallest torsion (O1-Mo1-Mo2-N1) is only 39.6° (rather than 60°). The arguably most striking feature, however, is the unusually long Mo–Mo distance of 2.2955(7) Å) (see below).

To probe whether the formation of **11** is caused by the peculiar ligand framework, in which the three arms carrying the tertiary alcohol substituents are tied back onto a rigidifying arene linker, **1** was reacted with ordinary *tert*-butanol (Scheme 2). Once again, the corresponding heterodimer **12** was formed. It shows the same distinctive structural features, namely a very long Mo≡Mo bond (2.2944(2) Å) and small torsional angles (O-Mo-Mo-N: 32.57, 33.35, 34.72°) even further away from the ideal 60° that one might intuitively expect to find in such a crowded ligand environment (Figure 3); the barrier to rotation about the N–Ar bond was determined to be on the order of 12.5 $kcal\cdot mol^{-1}$ (for details, see the Supporting Information).

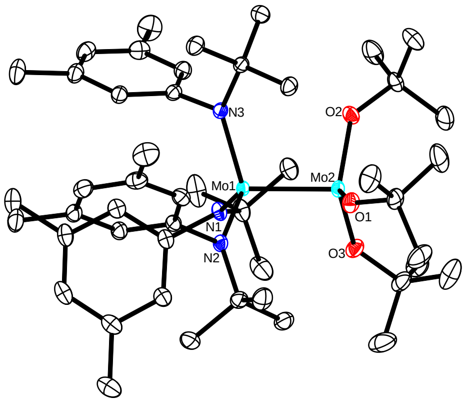
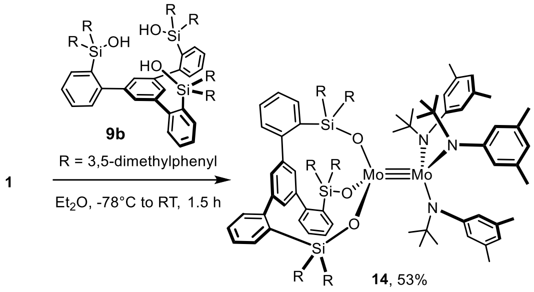


Figure 3. Molecular structure of complex **12** in the solid state; H-atoms and disordered solvent in the unit cell are not shown for clarity

Perplexed by the ease with which these unorthodox heterodimers are formed, the alcoholysis of **1** was repeated with *tert*-butanol in excess. Although a mixture was obtained in this case, the heterodimer **12** was still the major species in the crude product, whereas the homoleptic dimer $[Mo_2(OtBu)_6]$ (**13**) was minor. Similarly instructive was another control experiment, in which purified heterodimer **12** was treated with *tert*-butanol; the recorded spectra showed no sign of formation of **13** even when the temperature was raised to 60°C for 15 h.[46] This result is all the more surprising if one considers that the alcoholysis of $[Mo_2(NMe_2)_6]$ with *tert*-butanol in a hydrocarbon solvent is the standard method for the preparation of $[Mo_2(OtBu)_6]$ (**13**).[47] Moreover, $[Mo_2(OtBu)_6]$ is the final product of and thermodynamic sink in many different reactions starting from various molybdenum sources.[5,12,48-52] The remarkable preference for the formation of the heterodimer **12** is therefore likely kinetic in origin: putative $[(tBuO)_3Mo]$ (or a mixed species $[(tBuO)_n[(tBu)(Ar)N]_mMo]$, $n+m = 3$) *in statu nascendi* is so "hot" that it instantly traps any remaining **1** with formation of **12**.[53] Once formed, the crowded ligand sphere precludes protonolysis of the remaining Mo–N bonds, at least by an encumbered partner such as *tert*-butanol.

The higher acidity of the silanol groups in **9b** in combination with bulky aryl groups on silicon does not change the outcome either (Scheme 3).[54] A monomeric complex of type **A**, as initially targeted, has neither been observed nor isolated; its heterodimerization must hence be fast and facile.[55] The constitution of the resulting heterodimeric complex **14** was again ascertained by X-ray crystallography (Figure 4). With 2.3440(3) Å, the Mo≡Mo bond of **14** is the longest triple bond between two unbridged Mo(+3) centers with CN = 4 each (CN = coordination number) documented in the literature (Figure 5).[56,57]



Scheme 3. Heterodimer with a trisilanolate podand cap

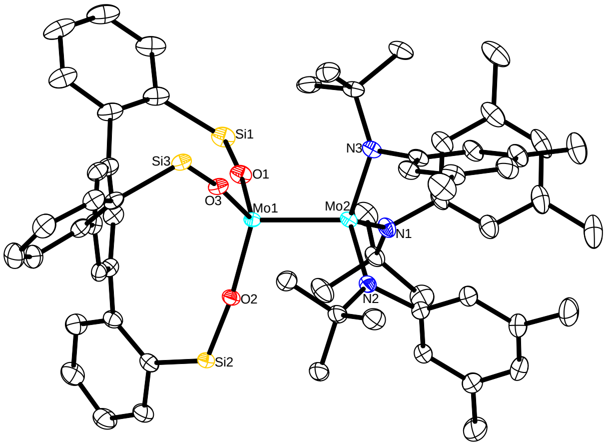


Figure 4. Truncated molecular structure of complex **14** in the solid state; the 3,5-dimethylphenyl substituents on the silicon linkers, disordered parts, and H-atoms are not shown for clarity; the full structure is contained in the Supporting Information

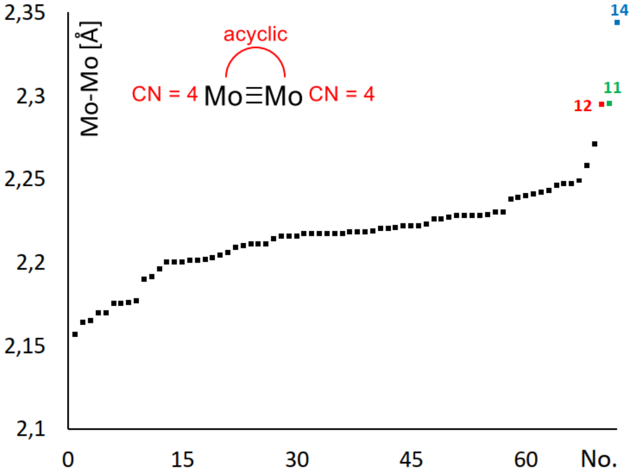
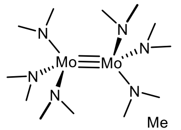
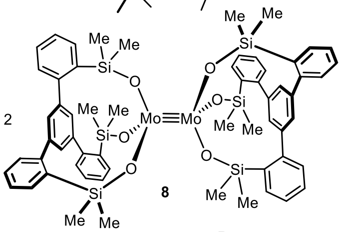
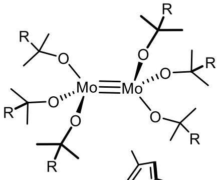
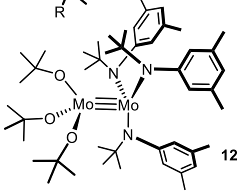
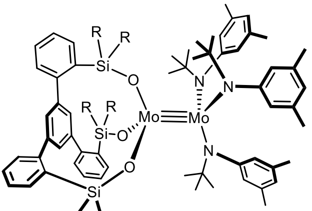
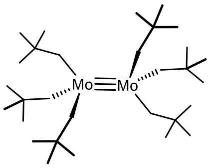


Figure 5. Plot of the Mo–Mo bond distances of complexes comprising an unbridged Mo≡Mo core and a CN = 4 on both metal atoms found in the Cambridge Crystallographic Data Centre (black dots); comparison with the new heterodimeric complexes reported herein (for details, see the Supporting Information)

Table 1. ^{95}Mo NMR shifts ([D$_8$]-toluene, 333 K (unless stated otherwise)) and Mo–Mo distances of selected dimeric complexes.

##	Complex	δ_{Mo} (ppm)	Mo-Mo (Å)
1		2441[a]	2.211(2) 2.217(2)[b],66
2		2632[42]	-----
3		2640 (R = Me)[c,d],52	--- (R = Me) 2.2388(6) (R = Ph)[67] 2.226(3) (R = CF_3)[68]
4		3260/3127 (br)	2.2944(2)
5	 **14** (R = 3,5-dimethylphenyl)	3314 (br)/n.d.	2.3440(3)
6		3695[c],61	2.1654(7)[64]

[a] ref. 61: 2430 ppm (C_6D_6, RT); [b] two independent complexes in the asymmetric unit cell; [c] in C_6D_6, RT; [d] ref. 61: 2645 ppm (C_6D_6, RT)

In this context, a brief comment on the ^{95}Mo NMR shifts of the heterodimeric complexes is warranted. Because this molybdenum isotope is a spin 5/2 nucleus with low natural abundance (≈15.9%), an unfavorable gyromagnetic ratio and a low quadrupole moment, ^{95}Mo NMR is not without challenges.[58-60] Early work, however, had shown that the nuclei in dimeric Mo≡Mo complexes are strongly deshielded and can therefore be easily distinguished from other molybdenum species;[61] Table 1 includes the data of some pertinent examples. Although the problems caused by the quadrupolar nature of ^{95}Mo are massively enhanced by lowering symmetry and increasing the molecular weight of the compounds, we managed to record *two* distinct ^{95}Mo resonances for the new heterodimeric complex **12**: the sharper signal at 3260 ppm is tentatively attributed to the ≡Mo(OtBu)$_3$ unit, whereas a much broader signal at 3127 ppm likely stems from bound $\equiv$Mo[N(Ar)(*t*Bu)]$_3$.[62] For complex **14**, however, only one very broad peak at 3314 ppm was detected even after 5 d acquisition time, likely belonging to the Mo center carrying the tripodal siloxide. In any case, Table 1 shows that the Mo centers of the heterodimers are strongly deshielded (≈600-800 ppm) relative to relevant homodimeric siblings carrying the same or similar alkoxide, siloxide or dialkylamino ligands. Although the data set is currently too small for a generalization, the comparison seems to imply that a heterodimeric constitution results in a peculiar electronic character of the Mo≡Mo core, potentially with a higher paramagnetic contribution; the ultralong Mo–Mo distances could be another manifestation thereof, even though the diamagnetism of **12** and **14** shows that net triple bonding is preserved.[63] Importantly, however, the example of the homoleptic complex [$Mo_2(CH_2CMe_3)_6$] devoid of any π-donating ligands must be taken as a warning against too rapid an interpretation: this complex resonates at δ_{Mo} = 3695 ppm,[61] yet shows an extremely short Mo≡Mo bond (2.1654(7) Å).[64]

These ostensibly difficult-to-reconcile experimental results make a detailed yet non-trivial analysis of the ^{95}Mo NMR shift tensors and of the electronic character of the complexes necessary once additional data are available as indispensable calibration points for high-level computational studies.[65] Until then, we have to leave the question open whether or not there exists an innate link between the remarkable spectroscopic fingerprints and the equally astounding structural attributes of the new family of heterodimeric complexes disclosed herein.

ASSOCIATED CONTENT

Supporting Information.

The Supporting Information is available free of charge at #####

Experimental Section including characterizatioin data and NMR spectra of new compounds

Single crystal structure analysis

AUTHOR INFORMATION

Corresponding Author

Alois Fürstner – *Max-Planck-Institut für Kohlenforschung, D-45470 Mülheim/Ruhr, Germany*; orcid.org/0000-0003-0098-3417; Email: fuerstner@kofo.mpg.de

Authors

Daniel Rütter – *Max-Planck-Institut für Kohlenforschung, D-45470 Mülheim/Ruhr, Germany*
Nils Nöthling – *Max-Planck-Institut für Kohlenforschung, D-45470 Mülheim/Ruhr, Germany*
Markus Leutzsch – *Max-Planck-Institut für Kohlenforschung, D-45470 Mülheim/Ruhr, Germany;* orcid.org/0000-0001-8171-9399

Notes

The authors declare no competing financial interest.

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(44) This interpretation is corroborated by the fact that the structure of **11** in the solid state shows this exact orientation as evident form Figure S2 contained in the Supporting Information.

(45) The coordination geometry about the two individual Mo-centers is in between trigonal monopyramidal and tetrahedral (compare: O1-Mo1-Mo2 100.44(7)°; N1-Mo2-Mo1 106.29(8)°).

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(56) Compare the computed bond lengths of hypothetical "Cummins dimers" of type $[(Ar)(R)N]_3Mo{\equiv}Mo[N(R)(Ar)]_3$: 2.367 Å for R = *i*Pr; for R = *t*Bu, however, the hypothetical distance (2.466 Å) is still much larger, see ref. 57.

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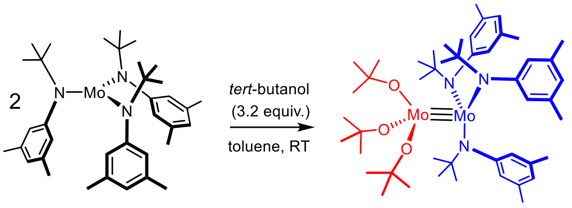

Synopsis

The Cummins complex $[(t\mathrm{Bu})(\mathrm{Ar})\mathrm{N}]_3\mathrm{Mo}$ was the historically first example of a monomeric Mo(+3) species escaping dimerization with formation of a [Mo≡Mo] triple bond; exceptionally high reactivity vis-à-vis many different small molecules does ensue. Despite this famous prequel, it is surprisingly easy to engage this complex into heterodimerization to give unsymmetrical dimolybdenum complexes of type $[(t\mathrm{Bu})(\mathrm{Ar})\mathrm{N}]_3\mathrm{Mo{\equiv}MoX}_3$, which are unprecedented in the literature.