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High Oxidation State Molybdenum *N*-Heterocyclic Carbene Alkylidyne Complexes: Synthesis, Mechanistic Studies and Reactivity

Maximilian Koy,[a] Iris Elser,[a] Jan Meisner,[b] Wolfgang Frey,[c] Klaus Wurst,[d] Johannes Kästner[b] and Michael R. Buchmeiser*[a]

Abstract: The first synthetic protocol to high oxidation state molybdenum (VI) *N*-heterocyclic carbene (NHC) alkylidyne complexes (NHC = 1,3-diisopropylimidazol-2-ylidene, 1,3-dimethyl-4,5-R_2-imidazol-2-ylidene, R_2 = H, Cl, CN) is reported. Steric limitations of the NHCs and the benzylidyne are described. All novel complexes were characterized by single crystal X-ray diffraction and solution NMR techniques. It was shown that all complexes presented here show activity in the self-metathesis of 1-phenyl-1-propyne at room temperature. To identify mechanistic differences, an experimental sequence to detect dissociation of ligands was developed. Results reveal dissociation of less electron-donating NHCs in course of the reaction. Mechanistic and reactivity differences were attributed to electronic and steric effects through Tolman's electronic parameter and the percentage of buried volume. Furthermore, **Mo-1** containing the 1,3-dimethylimidazol-2-ylidene ligand showed good activity in self-metathesis reactions of *p*-substituted 1-phenyl-1-propynes with electron-donating moieties at room temperature.

N-Heterocyclic carbenes (NHCs) represent a privileged class of ligands in organometallic chemistry allowing for significant developments, e.g., in cross coupling chemistry and ruthenium-catalyzed olefin metathesis.[1] In particular, catalyst stability and reactivity has been impressively improved through the implementation of NHCs and variations of the NHC ligand allowed for a substantial fine-tuning of catalyst properties. Recently, our group expanded the portfolio of NHC transition metal complexes to neutral and cationic high oxidation state group VI metal NHC alkylidene complexes and obtained highly active catalysts for various olefin metathesis reactions, which upon immobilization allowed for productivities >$1.1 \cdot 10^6$.[2]
High oxidation state group VI alkylidyne complexes are known for their activity in alkyne metathesis reactions.[3]

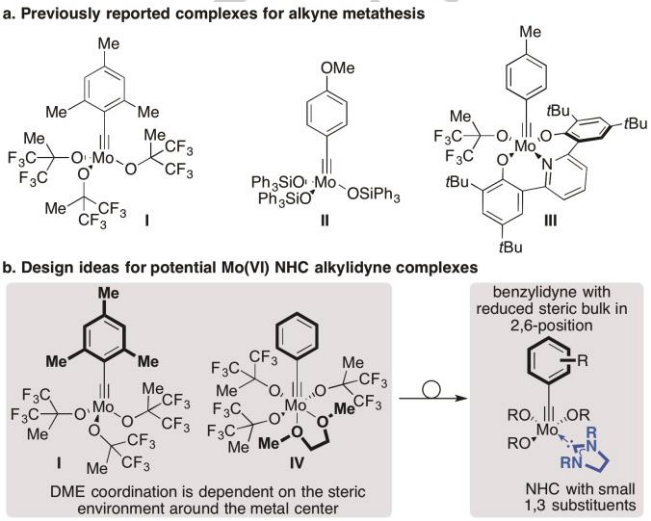
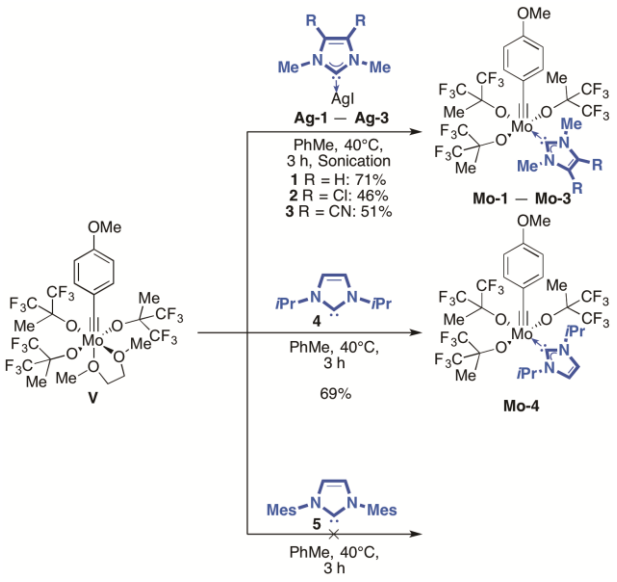


Figure 1. Selected Mo(VI) alkylidyne complexes and design ideas for related NHC complexes.

The development of this reaction was driven by the discovery of high oxidation state tungsten and molybdenum alkylidyne complexes as potent catalysts by Schrock and co-workers.[4]



Scheme 1. Synthetic elaboration of Mo(VI) alkylidyne complexes.

[a] M. Koy, I. Elser, Prof. Dr. M. R. Buchmeiser
Universität Stuttgart, Institut für Polymerchemie
Pfaffenwaldring 55, 70569 Stuttgart (Germany)
E-mail: michael.buchmeiser@ipoc.uni-stuttgart.de
[b] J. Meisner, Prof. Dr. J. Kästner
Universität Stuttgart, Institut für Theoretische Chemie
Pfaffenwaldring 55, 70569 Stuttgart (Germany)
[c] Dr. Wolfgang Frey
Universität Stuttgart, Institut für Organische Chemie
Pfaffenwaldring 55, 70569 Stuttgart (Germany)
[d] Dr. Klaus Wurst
Universität Innsbruck, Institut für Allgemeine, Anorganische und Theoretische Chemie
Innrain 80-82, 6020 Innsbruck (Austria)

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Current state-of-the-art catalysts containing fluorinated alkoxides, silanolates, amides, iminato ligands or multidentate ligands were developed by the groups of Schrock,[4-5] Fürstner,[6] Tamm,[7] Zhang,[8] Fischer,[9] Veige,[10] Moore[11] and Nuckolls[12] (e.g., compounds **I–III**, Figure 1). These catalysts found widespread application in advanced organic synthesis,[3d, 13] polymer chemistry and materials science.[8b, 9, 10b, 14] Advanced applications require tailor-made catalysts to improve stability, handling and/or reactivity. Therefore, the introduction of a new ligand class provides further possibilities to tackle the aforementioned issues by tuning the electronic and steric properties of the catalysts through innovative ligand design.

Motivated by the success story of NHCs in organometallic chemistry and especially in olefin metathesis, we envisioned NHC alkylidyne complexes to be of high interest as potential catalysts for alkyne metathesis reactions. As a starting point, we decided to focus on tris(hexafluoro)-*tert*-butoxide complexes developed by Tamm and coworkers.[7] Based on the observation that the coordination of 1,2-dimethoxyethane in those complexes is dependent on the steric requirement of the substitution pattern of the benzylidyne (complex **I** vs. **IV**),[7b, c] a complex bearing small benzylidyne ligands combined with NHCs bearing sterically less demanding residues in 1,3-position was anticipated to be the ideal match for our purposes (Figure 1b). To overcome the limitation of relatively low kinetic stability of 1,3-dimethyl-substituted imidazol-2-ylidenes, the corresponding NHC silver complexes were selected for transmetalation with the tris(hexafluoro)-*tert*-butoxide alkylidyne complex **V**.[15] Much to our delight, complexes **Mo-1** – **Mo-3** bearing 1,3-dimethyl-4,5-R_2-imidazol-2-ylidenes (R_2 = H, Cl, CN) were isolated as red solids in good yields (71 %, 46 % and 51 %). To further stress our hypothesis that the accessibility of Mo(VI) alkylidyne complexes is dictated through the steric environment around the metal center, 1,3-diisopropylimidazol-2-ylidene **4** with sterically more demanding groups was reacted with complex **V** to yield **Mo-4** as a brown solid in good yield (69 %). With NHC **5** containing bulky and conformationally less fluxional mesityl-substituents in 1,3-position of the imidazol-2-ylidene, only decomposition of the starting material was observed (Scheme 1).

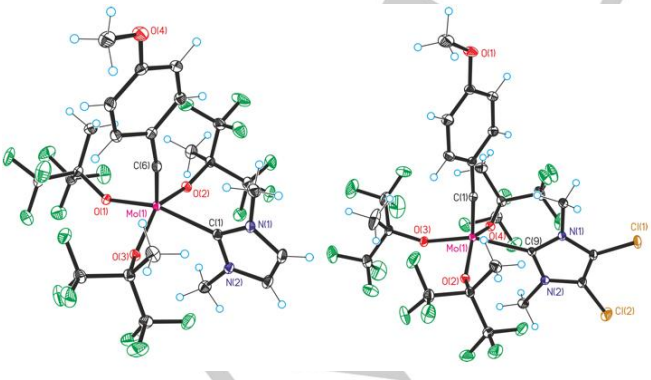

Figure 2. Single crystal X-ray structure of **Mo-1** (left) and **Mo-2** (right). Selected bond lengths [pm] for **Mo-1**: Mo(1)-C(6): 173.8(2); Mo(1)-C(1): 224.41(18); τ = 0.18[16]. Selected bond lengths [pm] for **Mo-2**: Mo(1)-C(1): 174.26(18); Mo(1)-C(9): 225.21(17); τ = 0.24.

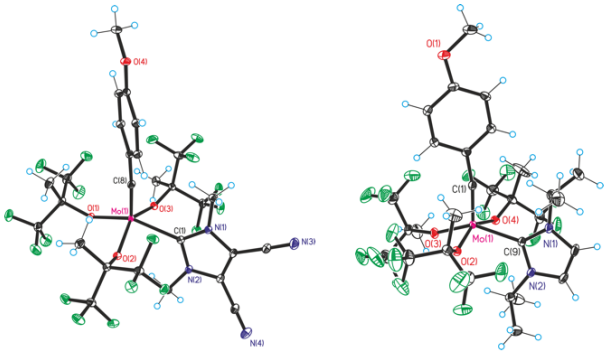

Figure 3. Single crystal X-ray structure of **Mo-3** (left) and **Mo-4** (right). Selected bond lengths [pm] for **Mo-3**: Mo(1)-C(8): 174.46(14); Mo(1)-C(1): 226.63(5); τ = 0.17. Selected bond lengths [pm] for **Mo-4**: Mo(1)-C(1): 173.7(3); Mo(1)-C(9): 225.2(3); τ = 0.05.

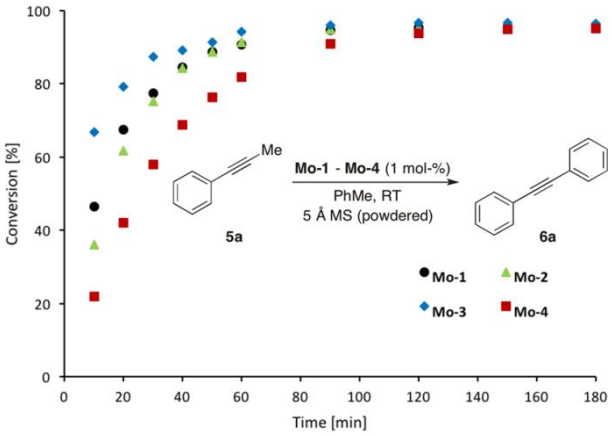

Figure 4. Kinetic profiles for the self-metathesis of 1-phenyl-1-propyne with **Mo-1** – **Mo-4** at room temperature (see S.I. for further details).

To shed light on structural features of our complexes, single crystal X-ray crystallography and NMR experiments were conducted. **Mo-1** – **Mo-3** crystalize in the triclinic space group $P\bar{1}$, while **Mo-4** crystalizes in the monoclinic space group $P2_1/c$. Distorted square pyramidal (SP) coordination spheres ($0.04 < \tau^{[16]} < 0.24$) around the metal center with the benzylidyne in the apical position and the NHC and the alkoxides forming the basal plane were found. With four new NHC alkylidyne complexes at hand, we were curious about their performance as catalysts in standard alkyne metathesis reactions. Therefore, kinetic profiles for the self-metathesis of 1-phenyl-1-propyne **5a** were elaborated for complexes **Mo-1** – **Mo-4**. Gratifyingly, all complexes allowed for quantitative conversion within less than 2 hours at room temperature; the order of reactivity was **Mo-3** > **Mo-1** ≈ **Mo-2** > **Mo-4** (Figure 4). Key questions to be answered were: i) what is the nature of the active species; and ii) are there differences in reactivity or mechanism that can be attributed to certain properties of the NHC. Initially, we hypothesized three different potential active species, namely the pentacoordinated neutral complexes **Mo-1** – **Mo-4** themselves, a cationic species

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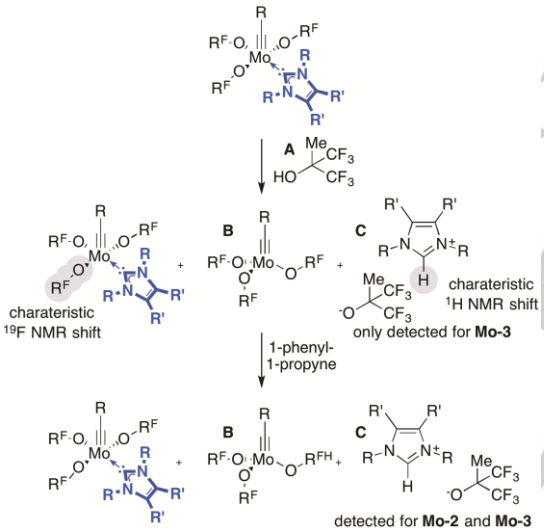
with dissociated alkoxide or a tetracoordinated neutral Schrock-type alkylidyne complex with dissociated NHC. Mechanistic experiments were designed to provide evidence for any of the possible species. Due to the high basicity of NHCs, it was expected that any dissociated NHC would react irreversibly with a proton source to form the neutral tetracoordinated complex **B** and the corresponding imidazolium salt **C**, which should conveniently be detectable by ^{1}H NMR spectroscopy (Scheme 2, Figures S2, S6, S10 and S14, S.I.). Hexafluoro-*tert*-butanol **A** was chosen as the acidic compound, because any ligand exchange reaction with hexafluoro-*tert*-butanolate would not affect the experiment as such. As anticipated, free NHCs react smoothly with hexafluoro-*tert*-butanol **A** to form the corresponding imidazolium salts (see S.I. for further details). In the same sequence of experiments, the formation of a cationic species can be followed by monitoring the signals of the alkoxides via ^{19}F NMR spectroscopy (Figures S4, S8, S12 and S16, S.I.). In a typical experiment, **A** was added to the respective complex in C_6D_6 and the potential formation of imidazolium salt was monitored by ^{1}H NMR spectroscopy. To the same reaction mixture was added 1-phenyl-1-propyne and the feasible formation of imidazolium salt was checked by NMR spectroscopy again. Finally, product formation was proven by GC-MS analysis of the reaction mixture.



Scheme 2. Mechanistic experiments to elucidate the active species of **Mo-1** – **Mo-4**. (R^F = hexafluoro-*tert*-butanolate).

Mo-1 and **Mo-4** showed no dissociation of the NHC by ^{1}H NMR in C_6D_6 (Figures S3 and S15, S.I.), while very minor but detectable amounts of free imidazolium salt were observed for **Mo-2** after addition of substrate and for **Mo-3** after addition of the proton source (<1 % NHC dissociation for both complexes, Figures S7 (**Mo-2**) and S11 (**Mo-3**), S.I.). Upon addition of 1-phenyl-1-propyne to **Mo-4** in C_6D_6 a signal attributable to hexafluoro-*tert*-butanolate was observed by ^{19}F NMR at δ = -78.8 ppm, which in turn suggests formation of a cationic species, though to a very minor extent. Thus, integration revealed only ~1 % alkoxide dissociation (Figure S16, S.I.). For **Mo-1**, however, this signal was not observed under the same conditions (Figure S4, S.I.). Additionally, ^{1}H and ^{19}F NMR spectra of **Mo-1** – **Mo-4** were measured in CD_3CN to investigate whether the addition of a coordinating solvent would encourage alkoxide dissociation and the formation of a cationic species. In line with the results outlined above, some minor replacement of the NHC by CD_3CN was observed by ^{19}F NMR for both **Mo-2** and **Mo-3** (~1 % dissociation). This finding was confirmed by comparison of the corresponding ^{19}F NMR spectra with the ^{19}F NMR spectrum of **V** in CD_3CN (Figures S9 and S13, S.I.). By contrast, for **Mo-1** in CD_3CN two new signals at δ = -78.9 and -76.7 ppm (2:1 ratio) were observed in the ^{19}F NMR spectrum (Figure S5, S.I.). This is in accordance with the formation of a cationic species, with two chemically and magnetically equivalent hexafluoro-*tert*-butoxides and one dissociated hexafluoro-*tert*-butoxide serving as the anion. Integration revealed ~3 % alkoxide dissociation. **Mo-4** containing the sterically more demanding diisopropylimidazol-2-ylidene, however, showed significant formation of a new species in CD_3CN. In the ^{1}H NMR spectrum, the most prominent new signal was the resonance of the protons adjacent to the nitrogen atoms of the imidazol-2-ylidene at δ = 4.55 ppm (sept, J = 6.54 Hz). By contrast, in the parent complex the signals are split into two pseudo-septets at δ = 5.40 ppm (sept., J = 6.53 Hz) and δ = 4.05 ppm (sept, J = 6.53 Hz), respectively (Figure S17, S.I.). This finding can be rationalized by a change of the complex geometry from SP in the parent complex to trigonal bipyramidal (TBP) with the NHC in an apical position. Compared to the basal position in the SP configuration, the apex in the TBP would allow for a free rotation of the substituents at the nitrogens of the NHC. This hypothesis is supported by the ^{19}F NMR spectrum of **Mo-4** in CD_3CN in which only one new signal can be observed at δ = -76.7 ppm, in line with three magnetically equivalent hexafluoro-*tert*-butoxides in the plane of the TBP complex (Figure S18, S.I.). According to both ^{1}H and ^{19}F NMR spectroscopy, approximately 12 % of the complex reorganized into the TBP geometry after twelve hours in CD_3CN. A comparison of the ^{1}H NMR spectra of free carbene **4** and **Mo-4** in CD_3CN ensured that the new imidazol-2-ylidene signals did not stem from dissociated NHC (Figure S19, S.I.). Whether this reorganization proceeds via a cationic species remains speculative. Based on the data outlined above, the observed reactivity of complexes **Mo-1** – **Mo-4** in the self-metathesis reaction of 1-phenyl-1-propyne **5a** can be explained if different active species proven by mechanistic studies (*vide supra*) are taken into account. For these purposes, two molecular descriptors - namely Tolman's electronic parameter (TEP) for electronic properties and the percentage of buried volume $\%V_{bur}$ - were regarded.[17] TEP values for NHCs[18] and calculated $\%V_{bur}$ for complexes[19] in this study are given in Table 1.

Donor properties of the NHCs **1** – **4** significantly decrease in the series **Mo-4** > **Mo-1** > **Mo-2** > **Mo-3**. While $\%V_{bur}$ of the NHCs in **Mo-1** – **Mo-3** is virtually the same, it is slightly higher for **Mo-4**. A reasonable explanation for the increasing tendency for NHC dissociation in the series **Mo-1** < **Mo-2** < **Mo-3** can be found in the weaker electron-donor properties of the corresponding NHCs (indicated by the TEP values), which is in line with decreasing Mo-C_{NHC} bond lengths in the same series. This accounts for the finding that the corresponding NHC dissociates from both **Mo-2** and **Mo-3** to a small extent. In view of the lowest

TEP, the NHC in **Mo-3** should dissociate more easily. This is supported by the fact that NHC dissociation from **Mo-3** is already observed once the proton source is added, whereas **Mo-2** remains stable under these conditions. We therefore reason that the alkyne metathesis-active species for **Mo-2** and **Mo-3** are either the neutral complexes **Mo-2** and **Mo-3** as such or the parent Schrock-type alkylidyne complexes *without* NHC ligand.

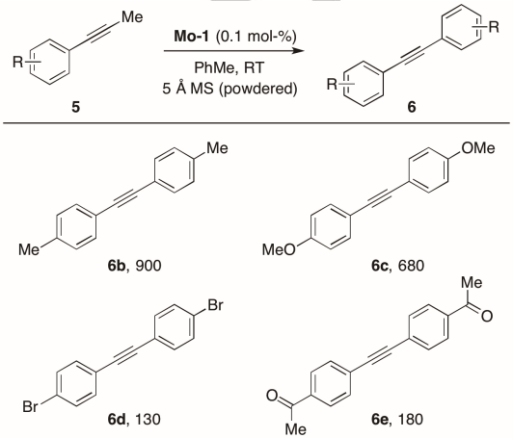
Table 1. Tolman's electronic parameter (TEP) for NHCs in this study and percentage of buried volume $\%V_{bur}$ for **Mo-1** – **Mo-4**.

Complex	TEP[a]	$\%V_{bur}$[b]
Mo-1	2054.1	23.1
Mo-2	2059.0	23.0
Mo-3	2066.2	22.6
Mo-4	2051.5	23.9

[a] According to ref. [18]. [b] Determined with SambVca 2.0, see ref. [19].

By contrast, for complexes **Mo-1** and **Mo-4** containing the stronger electron donating NHCs, dissociation of a fluorinated alkoxide leading to the formation of a cationic and potentially more active species is possible. However, these cationic species only form to a small extent (3 and 1%, respectively, *vide supra*). Despite the *highest* TEP value of NHC **4** in **Mo-4**, this Mo-alkylidyne NHC complex shows the *lowest* alkyne metathesis activity. This is in line with the above-proposed, neutral pentacoordinated species with one benzylidyne, three alkoxides and one NHC ligand and the low degree of alkoxide dissociation (1%). By contrast the increased activity of **Mo-1** over **Mo-4** is proposed to be related to the cationic nature of **Mo-1** in CD_3CN, which can well be anticipated in the presence of substrate, too. Its formation is proposed to be a result of the smaller buried volume for **Mo-1** compared **Mo-4**, resulting in easier access of substrates to the metal core. Thus, cation formation is believed to occur simultaneously with substrate (or CD_3CN) coordination, similar to the formation of cationic species in Mo and W imido/oxo alkylidene NHC complexes.[2a-c] With this mechanistic understanding at hand, the slower reactions rates of **Mo-1** – **Mo-4** compared to complex **I** are comprehensible, because tetracoordinated species **I** requires no dissociation of the NHC or an alkoxide ligand. Several attempts to isolate cationic complexes were unsuccessful, mostly due to synthetic difficulties to selectively remove one alkoxide (see S.I. for further details). Therefore, other mechanistic pathways cannot strictly be excluded at the current stage of our investigations, since no direct proof of a cationic species under the reaction conditions was provided so far.

Finally, we investigated the reactivity of **Mo-1** towards several *p*-substituted 1-phenyl-1-propynes **5**. **Mo-1** was the catalyst of choice, due to its higher reactivity, respectively stability compared to the other complexes. Productivity of **Mo-1** in the self-metathesis of the *p*-substituted 1-phenyl-1-propynes **5b-e** at room temperature increased with the electron-donating character of the *p*-substituents (Scheme 3). The presence of electron withdrawing bromo- and aceto-group (**5d** and **5e**) resulted in rather low TONs of 130 and 180, respectively, whereas with the methoxy- and the methyl-substituent high TONs of 680 and 900 were reached after only three hours reaction time at room temperature. Substrates containing terminal alkynes were not suitable for **Mo-1** (see S.I. for further details).



Scheme 3. Productivities (TONs) for self-metathesis reactions of *p*-substituted 1-phenyl-1-propynes **5b-e** with **Mo-1.** Reaction conditions: toluene, room temperature, 3 hours, internal standard for GC-MS: *n*-dodecane, 250 mg 5 Å molecular sieves, catalyst:substrate = 1:1000.

In conclusion, the first high oxidation state molybdenum alkylidyne complexes bearing structurally different NHCs have been synthesized and characterized. Kinetic profiles for the self-metathesis of 1-phenyl-1-propyne revealed different reactivity patterns. Mechanistic experiments indicated that no dissociation of NHC ligands occurs for strongly coordinating NHCs with large TEPs while NHC dissociation was observed for weakly coordinating NHCs. TEP and the percentage of buried volume were used as useful descriptors to ascribe a distinct mechanism and reactivity observations. For **Mo-1**, good activity in the self-metathesis of *p*-substituted 1-phenyl-1-propynes with electron-donating substituents was demonstrated at room temperature within less than three hours. A cationic Mo-alkylidyne NHC species was proposed to be the active species.

Experimental Section

General

All reactions were performed under the exclusion of air and moisture in a N_2-filled glove box (MBraun Labmaster) unless noted otherwise. Chemicals were purchased from ABCR, Acros Organics, Alfa Aesar, Sigma Aldrich and TCI. CH_2Cl_2, diethyl ether, pentane and toluene were dried using an MBraun SPS-800 solvent purification system and stored over 4 Å molecular sieves. Deuterated solvents were stored over activated alumina and 4 Å molecular sieves for a minimum of 24 h prior to use.

p-OMe-$C_6H_4C{\equiv}MoBr_3{\cdot}$DME,[6d, e, 7b] $KOCMe(CF_3)_2$,[7b] 1,3-dimethylimidazol-2-ylidene·AgI (**Ag-1**),[15] 4,5-dichloro-1,3-

dimethylimidazol-2-ylidene·AgI (**Ag-2**),[15] 4,5-dicyano-1,3-dimethylimidazol-2-ylidene·AgI (**Ag-3**)[15] and 1,3-diisopropylimidazol-2-ylidene (**4**)[20] were prepared according to literature-known procedures. 1-Phenyl-1-propyne was purchased from Alfa Aesar, stirred over CaH_2, vacuum transferred, degassed through three consecutive freeze-pump-thaw cycles and stored at -40°C over 4 Å molecular sieve. 5 Å molecular sieve was crushed outside the glove box, dried for 12 h at 180°C, 4 h at 300°C and 30 min at 600°C under high vacuum and subsequently stored inside the glove box.

NMR spectra were recorded on a Bruker Avance III 400 spectrometer. NMR spectra were internally calibrated to solvent signals.[21] Abbreviations for multiplicities: s (singlet), bs (broad singlet), d (dublet), q (quartet), sept. (septet), m (multiplet). GC-MS analyses were performed on an Agilent Technologies 5975C inert MSD device consisting of a triple-axis detector, a 7693 autosampler and a 7890A GC system equipped with an SPB-5 fused silica column (34.13 m×0.25 mm×0.25 µm film thickness). The injection temperature was set to 150°C. The column temperature ramped from 45 to 250°C within 8 min, and was then held for further 5 min. The column flow was 1.05 mL min^{-1}. Elemental analyses were measured on a Perkin Elmer 240 device at the Institut für Anorganische Chemie, Universität Stuttgart, Germany. Single crystal X-ray measurements were carried out on a Nonius KappaCCD 4-circle diffractometer equipped with graphite-monochromatized Mo-Kα radiation, a Micracol Fiber Optics collimator, and a Nonius FR590 generator at the Institut für Allgemeine, Anorganische und Theoretische Chemie, Universität Innsbruck, Austria (structures of **Mo-1**, **Mo-2**, **Mo-4**) and on a Bruker Kappa APEXII Duo diffractometer with Mo-Kα radiation at the Institut für Organische Chemie, Universität Stuttgart, Germany (structure of **Mo-3**). CCDC-1531387-1531390 contain the supplementary crystallographic data for compounds **Mo-1** – **Mo-4**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data%5Frequest/cif.

***p*-OMe-C_6H_4C≡Mo$(OCMe(CF_3)_2)_3$·DME (V)**

In a glove box, *p*-OMe-C_6H_4C≡$MoBr_3$·DME (400 mg, 0.734 mmol) was suspended in diethyl ether and $KOCMe(CF_3)_2$ (500 mg, 2.275 mmol) was dissolved in diethyl ether. Both mixtures were cooled to -40°C. The solution of $KOCMe(CF_3)_2$ was slowly added to the suspension of *p*-OMe-C_6H_4C≡$MoBr_3$·DME. The formation of a light brown solid was observed. The reaction mixture was allowed to stir at room temperature for 16 h. The suspension was filtered and all volatiles were removed under reduced pressure. The brownish solid was dissolved in pentane, filtered and stored at -40°C over night to give the title compound as brown crystals (440 mg, 0.52 mmol, 71%). **^{1}H-NMR** (400 MHz, CD_2Cl_2): δ 7.16-7.13 (m, 2H), 6.83-6.79 (m, 2H), 3.80 (s, 3H), 3.71 (s, 4H), 3.58 (s, 6H), 1.86 (s, 9H) ppm; **^{13}C-NMR** (100 MHz, CD_2Cl_2): δ 296.2, 160.7, 138.2, 132.5, 124.4 (q, J_{CF} = 290.21 Hz), 113.8, 84.0 (sept, $^2J_{CF}$ = 28.75 Hz)*, 72.2, 63.8, 55.8, 19.4 ppm; **^{19}F-NMR** (377 MHz, CD_2Cl_2): δ -77.40 (s) ppm; **EA** calcd.: $C_{24}H_{26}F_{18}MoO_6$: C, 33.98; H, 3.09. Found: C, 33.97; H, 3.16. *Terminal signals of the expected septet are not observable.

General transmetalation procedure

In a glove box, **V** was dissolved in toluene in a Schlenk tube equipped with a magnetic stir bar. The corresponding silver complex was suspended in toluene and added to the reaction mixture. The reaction mixture was removed from the glove box and was sonicated for 3 h at 40°C. In course of the reaction, typically a color change from brown to red was observed. The reaction mixture was concentrated *in vacuo* and brought back into the glove box. The reaction mixture was extracted with diethyl ether and filtered. The solvent was removed under reduced pressure and the remaining solid was crystallized from diethyl ether/pentane to give the product as a red solid.

***p*-OMe-C_6H_4C≡Mo(1,3-dimethylimidazol-2-ylidene)$(OCMe(CF_3)_2)_3$ (Mo-1)**

The title compound was prepared according to the general transmetalation procedure using **V** (654 mg, 0.77 mmol) and 1,3-dimethylimidazol-2-ylidene·AgI (**Ag-1**) (306 mg, 0.93 mmol). The product was obtained as a red solid (471 mg, 0.55 mmol, 71%). **^{1}H-NMR** (400 MHz, CD_2Cl_2): δ 7.30-7.26 (m, 2H), 6.93-6.90 (m, 2H), 6.85-6.81 (m, 2H), 3.85 (s, 3H), 3.81 (s, 3H), 3.56 (s, 3H), 1.69 (s, 3 H), 1.61 (s, 6H) ppm; **^{13}C-NMR** (100 MHz, CD_2Cl_2): δ 297.1, 188.3, 160.5, 138.3, 132.6, 122.8, 122.7, 124.59 (q, J_{CF} = 289.97 Hz), 124.26 (q, J_{CF} = 290.64 Hz), 124.11 (q, J_{CF} = 288.56 Hz), 122.0, 121.1, 113.8, 83.4-82.2 (m)*, 55.8, 39.5, 36.7, 20.0, 19.7 ppm; **^{19}F-NMR** (377 MHz, CD_2Cl_2): δ -77.91 – -77.96 (m, 6F), -77.33 – -77.41 (m, 3F) ppm; **EA** calcd.: $C_{25}H_{24}F_{18}MoN_2O_4$: C, 35.14; H, 2.83; N, 3.28. Found: C, 34.84; H, 2.99; N, 3.39. Red crystals suitable for single crystal X-ray diffraction were obtained by over layering an almost saturated solution of **Mo-1** in diethyl ether with pentane and storing the solution at -40°C overnight. *The expected septets are reported as a multiplet due to strong overlapping.

***p*-OMe-C_6H_4C≡Mo(4,5-dichloro-1,3-dimethylimidazol-2-ylidene)$(OCMe(CF_3)_2)_3$ (Mo-2)**

The title compound was prepared according to the general transmetallation procedure using **V** (90 mg, 0.106 mmol) and 4,5-dichloro-1,3-dimethylimidazol-2-ylidene·AgI (**2**) (51 mg, 0.127 mmol). The product was obtained as a red solid (45 mg, 0.049 mmol, 46%). **^{1}H-NMR** (400 MHz, CD_2Cl_2): δ 7.28-7.26 (m, 2H), 6.85-6.82 (m, 2H), 3.85 (s, 3H), 3.82 (s, 3H), 3.53 (s, 3H), 1.69 (s, 9H) ppm; **^{13}C-NMR** (100 MHz, CD_2Cl_2): δ 298.2, 188.5, 160.8, 138.3, 132.7, 124.5 (q, J_{CF} = 288.72 Hz), 124.2 (q, J_{CF} = 290.72 Hz), 117.9, 116.9, 113.9, 84.0-82.4 (m)*, 55.9, 37.9, 34.9, 20.1, 19.8 ppm; **^{19}F-NMR** (377 MHz, C_6D_6): δ -76.96 (s, 6F), -77.47 – -77.54 (m, 6F), -77.60 – -77.62 (m, 6F) ppm; **EA** calcd.: $C_{25}H_{22}Cl_2F_{18}MoN_2O_4$: C, 32.52; H, 2.40; N, 3.03. Found: C, 32.49; H, 2.47; N, 3.13. Red crystals suitable for single crystal X-ray diffraction were obtained by over layering an almost saturated solution of **Mo-2** in diethyl ether with pentane and storing the solution at -40°C overnight. *The expected septets are reported as a multiplet due to strong overlapping.

***p*-OMe-C_6H_4C≡Mo(4,5-dicyano-1,3-dimethylimidazol-2-ylidene)$(OCMe(CF_3)_2)_3$ (Mo-3)**

The title compound was prepared according to the general transmetallation procedure using **V** (231 mg, 0.273 mmol) and 4,5-dicyano-1,3-dimethylimidazol-2-ylidene·AgI (**3**) (125 mg, 0.328 mmol). The product was obtained as a red solid (126 mg,

0.139 mmol, 51%). **^{1}H-NMR** (400 MHz, CD_2Cl_2): δ 7.13-7.09 (m, 2H), 6.52-6.49 (m, 2H), 3.20 (s, 3H), 3.15 (s, 3H), 3.00 (s, 3H), 1.75 (s, 3 H), 1.64 (s, 6H) ppm; **^{13}C-NMR** (100 MHz, CD_2Cl_2): δ 300.3, 196.4, 161.3, 138.1, 132.9, 124.3 (q, J_{CF} = 289.08 Hz), 124.1 (q, J_{CF} = 287.31 Hz), 115.6, 114,7. 114.2, 106.9, 106.4, 84.3-82.4 (m)*, 55.9, 39.7, 34.9, 37.1, 20.1, 19.8 ppm; **^{19}F-NMR** (377 MHz, C_6D_6): δ -77.67 (s, 6F), -77.80 – -77.88 (m, 6F), -78.24 – -78.27 (m, 6F) ppm; **EA** calcd.: $C_{27}H_{22}F_{18}MoN_4O_4$: C, 35.86; H, 2.45; N, 6.19. Found: C, 35.73; H, 2.73; N, 5.89. Crystals suitable for single crystal X-ray diffraction were obtained by over layering an almost saturated solution of **Mo-3** in diethyl ether with pentane and allowing to stand the solution at -40°C overnight. *The expected septets are reported as a multiplet due to strong overlapping.

***p*-OMe-C_6H_4C≡Mo(1,3-diisopropylimidazol-2-ylidene)(OCMe(CF_3)$_2$)$_3$ (Mo-4)**

In a glove box, **V** and 1,3-diisopropylimidazol-2-ylidene **4** (36 mg, 0.24 mmol) were dissolved in toluene in a Schlenk tube equipped with a magnetic stir bar. Both mixtures were cooled to -40°C. The solution of **4** was slowly added to the solution of **V.** The reaction mixture was removed from the glove box and stirred 20 min at room temperature, then for 3 h at 40°C. In course of the reaction, a color change from brown to red was observed. The reaction mixture was concentrated *in vacuo* and brought back into the glove box. The remaining solid was crystallized from diethyl ether/pentane to give the product as a brown solid (36 mg, 0.24 mmol). The reaction mixture was stirred a 40°C for 3 h. The product was obtained as a brown solid (149 mg, 0.164 mmol, 69%). **^{1}H-NMR** (400 MHz, C_6D_6): δ 7.35-7.33 (m, 2H), 6.54-6.52 (m, 2H), 6.21-6.20 (m, 2H), 5.36 (sept., $^{3}J_{HH}$ = 6.56 Hz, 1H), 4.17 (sept., $^{3}J_{HH}$ = 6.52 Hz, 1H), 3.19 (s, 3H), 1.90 (s, 3H), 1.74 (s, 6H), 1.05 (d, $^{3}J_{HH}$ = 6.60 Hz, 6H), 1.02 (d, $^{3}J_{HH}$ = 6.68 Hz, 6H) ppm; **^{13}C-NMR** (100 MHz, CD_2Cl_2): δ 298.2, 186.1, 160.4, 138.2, 132.1, 124.68 (q, J_{CF} = 288.64 Hz), 124.47 (q, J_{CF} = 289.46 Hz), 124.32 (q, J_{CF} = 290.22 Hz), 117.3, 116.6, 113.6, 83.5 (sept., $^{2}J_{CF}$ = 28.57 Hz)*, 82.91 (sept., $^{2}J_{CF}$ = 28.87 Hz)*, 55.8, 53.1, 52.9, 24.0, 23.13, 23.08, 20.0, 19.4 ppm; **^{19}F-NMR** (377 MHz, C_6D_6): δ -76.12 – -76.19 (m, 6F), -76.30 – -76.34 (m, 6F), -76.87 (s, 6F) ppm; **EA** calcd.: $C_{29}H_{32}F_{18}MoN_2O_4$: C, 38.26; H, 3.54; N, 3.08. Found: C, 38,17; H, 3.60; N, 3.24. Dark brown crystals suitable for single crystal X-ray diffraction were obtained by over layering an almost saturated solution of **Mo-4** in diethyl ether with pentane storing the solution at -40°C overnight. *Terminal signals of the septet are not observable.

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Conflict of interest

The authors declare no conflict of interests.

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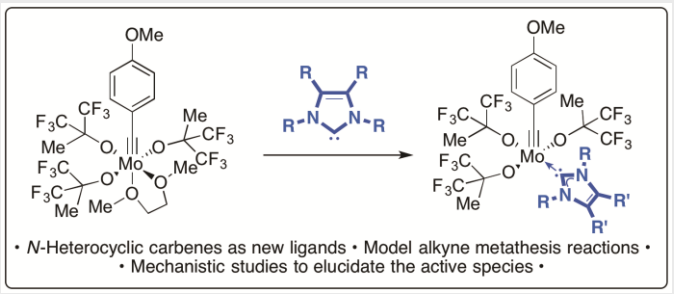

*M. Koy, I. Elser, J. Meisner, K. Wurst, W. Frey, J. Kästner, M. R. Buchmeiser**

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High Oxidation State Molybdenum *N*-Heterocyclic Carbene Alkylidyne Complexes: Synthesis, Mechanistic Studies and Reactivity

The synthesis and characterization of high oxidation state molybdenum *N*-heterocyclic carbene alkylidyne complexes is presented. All complexes show activity in model alkyne metathesis reactions. Mechanistic studies reveal different active species depending on distinct electronic and steric properties of the NHC.