ORGANOMETALLICS

pubs.acs.org/Organometallics Article

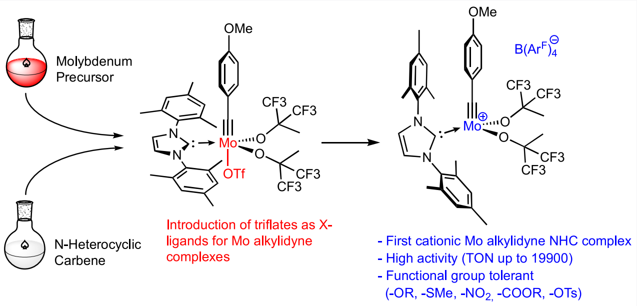
Highly Reactive Cationic Molybdenum Alkylidyne *N*-Heterocyclic Carbene Catalysts for Alkyne Metathesis

Jonas Groos, Philipp M. Hauser, Maximilian Koy, Wolfgang Frey, and Michael R. Buchmeiser*

Cite This: *Organometallics* 2021, 40, 1178−1184 Read Online

ACCESS | Metrics & More | Article Recommendations | Supporting Information

ABSTRACT: The tetracoordinated cationic molybdenum alkylidyne *N*-heterocyclic carbene (NHC) complexes $[\mathrm{Mo}(\equiv\mathrm{CC_6H_4}\text{-}p\text{-}\mathrm{OMe})(\mathrm{IMes})(\mathrm{OCMe}(\mathrm{CF_3})_2)_2][\mathrm{BPh_4}]$ (**Mo5**) and $[\mathrm{Mo}(\equiv\mathrm{CC_6H_4}\text{-}p\text{-}\mathrm{OMe})(\mathrm{IMes})(\mathrm{OCMe}(\mathrm{CF_3})_2)_2][\mathrm{B}(\mathrm{Ar^F})_4]$ (**Mo6**, IMes = 1,3-dimesitylimidazol-2-ylidene)) were synthesized from the pentacoordinated progenitor $\mathrm{Mo}(\equiv\mathrm{CC_6H_4}\text{-}p\text{-}\mathrm{OMe})(\mathrm{IMes})(\mathrm{OCMe}(\mathrm{CF_3})_2)_2(\mathrm{OTf})$ (**Mo4**). Complexes **Mo4**−**Mo6** were evaluated for their ability to catalyze the self-metathesis of several internal alkynes. The presence of a triflate group facilitates formation of a cationic species while preformation of the cationic molybdenum center in molybdenum alkylidyne NHC complexes indeed results in a strong increase in catalyst productivity and activity, also in the presence of functional groups, compared to previously reported neutral congeners. The most striking feature of this class of tetracoordinate cationic complexes is the excellent catalytic activity in the alkyne metathesis of non-protic substrates, thereby supporting our previously published proposal of a tetracoordinate cationic active species in alkyne metathesis formed from the neutral, pentacoordinate molybdenum alkylidyne NHC progenitors. Catalyst productivity, expressed as turnover number, reached 20 000 in the self-metathesis of 1-phenyl-1-propyne (**S1**) using $\mathrm{Mo}(\equiv\mathrm{CC_6H_4}\text{-}p\text{-}\mathrm{OMe})$(1,3-dimesitylimidazol-2-ylidene)$(\mathrm{OCMe}(\mathrm{CF_3})_2)_2[\mathrm{B}(\mathrm{Ar^F})_4]$ (**Mo6**) and 5-(benzyloxy)-2-pentyne (**S2**) at catalyst loadings as low as 0.005 mol %.



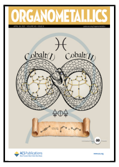
Introduction of triflates as X-ligands for Mo alkylidyne complexes

- First cationic Mo alkylidyne NHC complex
- High activity (TON up to 19900)
- Functional group tolerant (-OR, -SMe, -NO$_2$, -COOR, -OTs)

Starting from "ill-defined" metathesis catalysts, the number of well-defined homogeneous alkyne metathesis catalysts has grown unceasingly to the point that structure and reactivity can be precisely controlled.[1] The groups of Schrock,[2−10] Fürstner,[11−15] Tamm,[16−25] Veige,[26−28] Zhang,[29−31] Moore,[32−34] Fischer,[35−37] and Cummins[38−40] developed current state-of-the-art catalysts bearing silanolates, amides, fluorinated alkoxides, iminato or multidentate ligands. A common feature is the tetracoordinate nature of the active catalyst systems. In contrast, we recently reported on pentacoordinate molybdenum alkylidyne complexes, e.g., $\mathrm{Mo}(\equiv\mathrm{CC_6H_4}\text{-}p\text{-}\mathrm{OMe})(\mathrm{NHC})(\mathrm{OCMe}(\mathrm{CF_3})_2)_3$, bearing mono-, bi-, and tridentate *N*-heterocyclic carbene (NHC) ligands, which showed moderate productivity in alkyne metathesis reactions with turnover numbers (TONs) < 1000.[41] For strongly σ-donating NHCs, the active species was postulated to be the cationic tetracoordinate species after dissociation of one fluorinated alkoxide as weakly coordinating anion (WCA). Encouraged by the successful implementation of triflate ligands into molybdenum imido alkylidene NHC catalysts,[41−44] we targeted the synthesis of complexes with better leaving groups than the previously employed fluorinated alkoxides, namely, triflates, to shift the equilibrium toward the cationic species, thereby further enhancing the formation of the active species. In view of the results obtained with tetra-, penta-, and hexacoordinated, cationic tungsten alkylidyne NHC complexes,[45] we aimed on the synthesis of a cationic, preferably tetracoordinate complex, which would represent the stable active species in alkylidyne metathesis reactions.

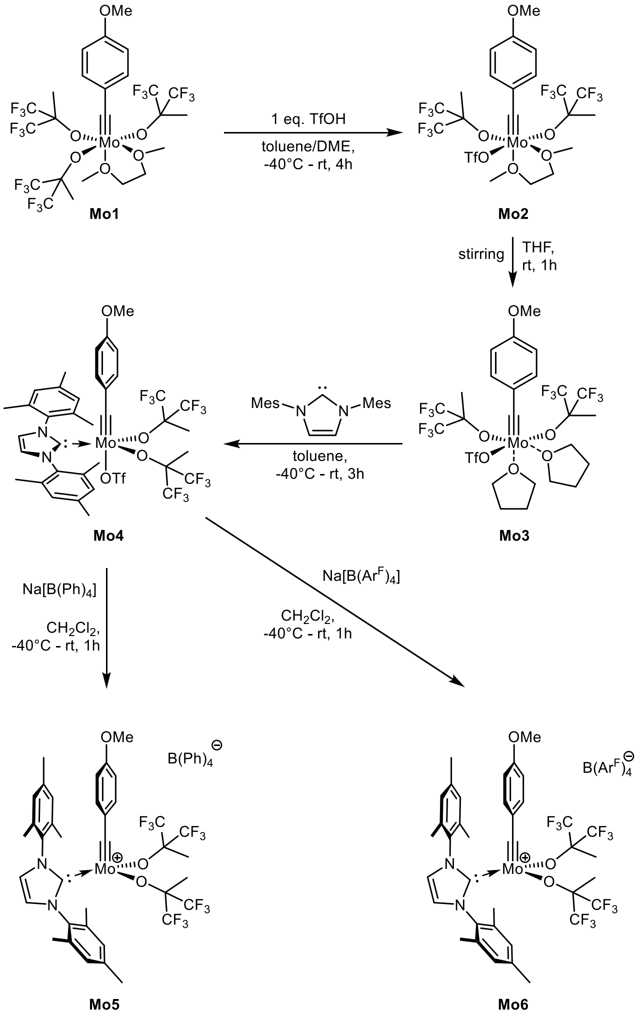
We started with molybdenum *p*-methoxybenzylidyne tris(hexafluoro-*tert*-butoxide) complexes bearing sterically less demanding NHCs, e.g., 1,3-diisopropylimidazol-2-ylidene (IiPr); however, their reaction with *N*,*N*-dimethylanilinium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate only resulted in unstable tetracoordinate cationic species, decomposing in the course of a few hours. Also, coordination of sterically demanding carbenes, e.g., 1,3-dimesitylimidazol-2-ylidene (IMes), to $\mathrm{Mo}(\equiv\mathrm{CC_6H_4}\text{-}p\text{-}\mathrm{OMe})(\mathrm{DME})(\mathrm{OCMe}(\mathrm{CF_3})_2)_3$ (**Mo1**, DME = 1,2-dimethoxyethane) resulted in immediate decomposition and formation of several byproducts. To circumvent these issues, we focused on the synthesis of new precursors with sterically less demanding anionic ($\mathrm{X^-}$) ligands. For these purposes, the triflate ligand was deemed as the target, additionally serving as an excellent leaving group. Hence, the

Received: March 22, 2021
Published: April 13, 2021



trisalkoxide precursor **Mo1** was carefully treated with 1 equiv of triflic acid to obtain the molybdenum alkylidyne monotriflate bisalkoxide complex Mo(≡CC$_6$H$_4$-*p*-OMe)(DME)(OCMe(CF$_3$)$_2$)$_2$(OTf) **Mo2** in 64% isolated yield. However, coordination of the NHC toward **Mo2** resulted in the formation of [1,3-dimesityl-2-methylimidazolium][OTf], most probably formed through carbene-induced DME activation, followed by transmethylation as previously shown for tungsten alkylidene complexes.[46] The DME ligand was therefore exchanged by two THF molecules by stirring a solution of **Mo2** in THF for 1 h to yield Mo(≡CC$_6$H$_4$-*p*-OMe)(THF)$_2$(OCMe(CF$_3$)$_2$)$_2$(OTf) **Mo3** in 84% isolated yield (Scheme 1). The monotriflate precursor **Mo3** was then reacted with **IMes** to yield 86% of Mo(≡CC$_6$H$_4$-*p*-OMe)(IMes)(OCMe(CF$_3$)$_2$)$_2$(OTf) **Mo4** (Scheme 1). The NHC coordination toward **Mo3** containing THF proceeded smoothly in contrast to the DME-containing precursors **Mo1** and **Mo2**. Thereupon, the triflate in **Mo4** was replaced by the noncoordinating anion B(Ph)$_4^-$ via reaction with NaB(Ph)$_4$ to yield the tetracoordinate species [Mo(≡CC$_6$H$_4$-*p*-OMe)(DME)(OCMe(CF$_3$)$_2$)$_2$][BPh$_4$] **Mo5** in 88% isolated yield. Alternatively, triflate was exchanged by tetrakis(3,5-bis(trifluoromethyl)phenyl)borate, (B(Ar^F)$_4^-$), via reaction of **Mo4** with NaB(Ar^F)$_4$ to yield the tetracoordinate species [Mo(≡CC$_6$H$_4$-*p*-OMe)(DME)(OCMe(CF$_3$)$_2$)$_2$][B(Ar^F)$_4$] **Mo6** in 86% isolated yield.

Scheme 1. Synthesis of the Neutral Monotriflate NHC Complex Mo4 (Middle) and the Respective Cationic NHC Complexes with B(Ph)$_4^-$ (Mo5) and B(Ar^F)$_4^-$ (Mo6) as Anion



Crystals of the monotriflate complex **Mo4** suitable for single crystal X-ray analysis were obtained from CH$_2$Cl$_2$ and *n*-pentane. Complex **Mo4** crystallizes in the monoclinic space group $P2_1/n$ (a = 1270.26(5) pm, α = 90°, b = 1757.39(8) pm, β = 106.230(2)°, c = 1922.24(8) pm, γ = 90°, Z = 4) (Figure 1). The metal complex adopts a slightly distorted trigonal bipyramidal (TBP) geometry based on the τ_5 value of 0.88 with the alkylidyne moiety and the triflate in the apices and the NHC as well as the alkoxides in the plane.[47] The alkoxides are strongly bound to molybdenum as judged from the Mo−O bond lengths (Mo−O1: 188.23 pm and Mo−O3: 188.69 pm) and do not experience any *trans* influence due to their in-plane position in the TBP geometry. In contrast, the Mo−O$_{\text{triflate}}$ bond (235.24 pm) is exceptionally long compared to the structurally related alkylidene complex Mo(N-2,6-Me$_2$-C$_6$H$_3$)(CH(CMe$_2$Ph))(IMesH$_2$)(OTf)(OCMe(CF$_3$)$_2$) in which the Mo−O$_{\text{alkoxide}}$ and the Mo−O$_{\text{triflate}}$ bonds are 200.9 and 218.5 pm, respectively. It is even substantially longer compared to the alkylidene complex Mo(N-3,5-Me$_2$-C$_6$H$_3$)(CH(CMe$_2$Ph))(IMes)(OTf)$_2$, which is already considered cationic at room temperature in solution with a Mo−O$_{\text{triflate}}$ bond length of 214.0 pm in the solid state.[48,49] The cationic character of **Mo4** with a dissociated triflate in solution is further vindicated by the triflate signal at δ = −78.92 pm in CD$_2$Cl$_2$ at 25 °C, virtually identical to the signal of "free" triflate found for NBu$_4^+$OTf$^-$ (−78.89 ppm).[48] The alkylidyne ligand in **Mo4** shows an almost perfectly linear arrangement with a Mo−C(30)−C(31) angle of 179.05°.

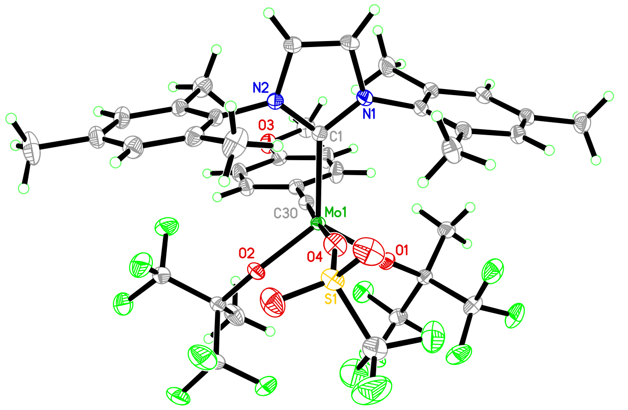


Figure 1. Single crystal X-ray structure of complex **Mo4**. Selected bond lengths [pm] and angles [deg]: Mo(1)−C(30) 176.75(14), Mo(1)−O(1) 188.23(10), Mo(1)−O(2) 188.69(10), Mo(1)−C(1) 220.48(13), Mo(1)−O(4) 235.24(11), C(30)−Mo(1)−O(1) 103.03(5), C(30)−Mo(1)−O(2) 102.28(5), O(1)−Mo(1)−O(2) 113.75(5), C(30)−Mo(1)−C(1) 90.36(6), O(1)−Mo(1)−C(1) 117.76(5), O(2)−Mo(1)−C(1) 122.14(5), C(30)−Mo(1)−O(4) 175.08(5), O(1)−Mo(1)−O(4) 79.52(4), O(2)−Mo(1)−O(4) 80.29(4), C(1)−Mo(1)−O(4) 84.72(5).

The cationic complex **Mo6** crystallizes in the triclinic space group $P\bar{1}$ (a = 1575.70(10) pm, α = 97.815(4)°, b = 1618.41(11) pm, β = 95.823(4)°, c = 1650.04(10) pm, γ = 95.894(3)°, Z = 2) and adopts a slightly distorted tetrahedral structure (τ_4 = 0.91, τ_4' = 0.90) (Figure 2). The alkylidyne bond is shorter (173.90 pm) compared to the neutral species

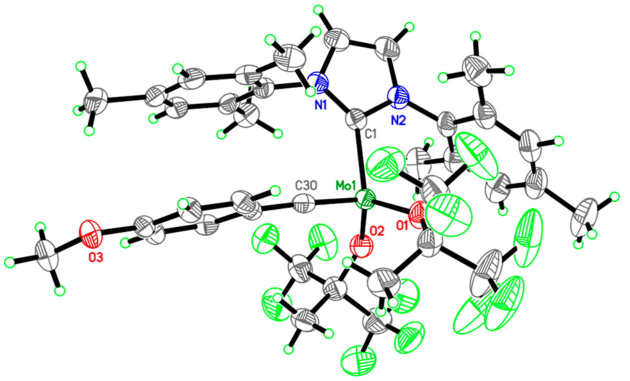


Figure 2. Single crystal X-ray structure of complex **Mo6**. Selected bond lengths [pm] and angles [deg]: Mo1−C(30) 173.9(3), Mo1−O(2) 187.6(2), Mo1−O(1) 187.7(2), Mo1−C(1) 2.132(3), C(30)−Mo1−O(2) 106.37(12), C(30)−Mo1−O(1) 106.57(12), O(2)−Mo1−O(1) 114.39(10), C(30)−Mo1−C(1) 95.44(12), O(2)−Mo1−C(1) 114.01(10), O(1)−Mo1−C(1) 117.26(11). The $B(Ar^F)_4^-$ anion was omitted for clarity.

Mo4 (176.75 pm). The NHC is bound considerably stronger (213.20 pm) compared to **Mo4** (220.48 pm), which is most probably a result of the substantial charge delocalization between the NHC and the formally cationic metal center, rendering the cationic complexes rather "soft" according to the HSAB principle, as already elaborated for NHC alkylidene complexes.[50] In contrast, the alkoxides are almost unaffected in the cationic complex and the bond lengths are only negligibly shorter (**Mo6**: 187.6 pm, 187.7 pm; **Mo4**: 188.2 pm, 188.7 pm). Particularly interesting is the comparison between the neutral and cationic complex regarding the ligand arrangement. In the neutral monotriflate complex **Mo4**, the IMes ligand is orthogonal to the alkylidyne ligand and in the same plane than the two alkoxides. The triflate is *trans* to the IMes ligand.

In the cationic species **Mo6**, one of the mesityl substituents occupies the now empty former triflate site, whereas the other mesityl substituent engages in a $\pi-\pi$ interaction with the aromatic *para*-anisole alkylidyne substituent, therefore shielding and stabilizing the cationic species. The aromatic systems of the anisole and the mesityl are displaced in a parallel manner with an interlayer distance of ca. 340 pm, typical for π-stacking.

Complexes **Mo4−Mo6** were examined for their activity in the self-metathesis of 1-phenyl-1-propyne (**S1**) in three different solvents (toluene, 1,2-dichloroethane, 1,2-dichlorobenzene) and at different temperatures (35 and 80 °C) in the presence of powdered 5 Å molecular sieves (MS) as 2-butyne scavenger[14] using a catalyst loading of 0.1 mol %. Gratifyingly, both the neutral monotriflate complex **Mo4** and the tetracoordinate cationic complexes **Mo5** and **Mo6** showed an unexpected high level of activity. In the case of **Mo6**, full conversion of **S1** was reached in less than 1 h with a catalyst loading of 0.1 mol % in 1,2-dichlorobenzene. The novel triflate complexes thus outperform the to date most active neutral molybdenum alkylidyne NHC catalysts[51] by far: tested under similar conditions, $Mo(\equiv CC_6H_4OMe)(NHC)(OCMe(CF_3)_2)_3$[51] with NHC = 1,3-diisopropylimidazol-2-ylidene reached a conversion of 37% after 3 h. These findings are fully in line with our hypothesis of a cationic tetracoordinate NHC molybdenum alkylidyne species acting as the active species.[41,51] Complexes **Mo4**, **Mo5**, and **Mo6** were then investigated with regard to their activity in self-metathesis reactions of a wider substrate scope. 5-(Benzyloxy)-2-pentyne (**S2**), 2-pentyne-5-yl benzoate (**S3**), 2-pentyne-5-yl 4-nitrobenzoate (**S4**), 2-pentyne-5-yl tosylate (**S5**), and 5-(4-methylthio-benzoate)-2-pentyne (**S6**) were chosen as substrates. Substrates **S1−S6** (Figure 3) were tested under optimized reactions conditions with a catalyst loading of 0.1 mol % in 1,2-dichlorobenzene at 35 °C in the presence of 5 Å MS.

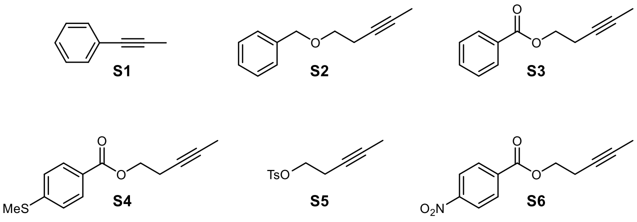


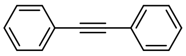
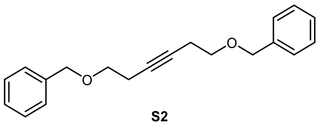
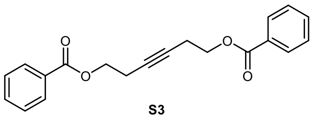
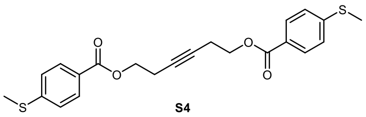
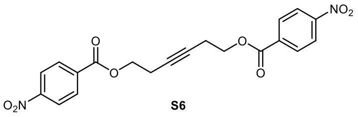
Figure 3. Substrates **S1−S6**.

Complexes **Mo4**, **Mo5**, and **Mo6** were able to reach full conversion in all metathesis experiments (Table 1), in the case of **Mo6**, in less than 3 h. **Mo6** turned out to be the most active catalyst in all alkyne metathesis reactions. Full conversion for **S1**, **S2**, **S3**, and **S5** was reached within 1 h. Reaction with **Mo4** and **Mo5** proceeded slightly slower than with **Mo6**; values for conversion and TONs after 3 h are listed in the Supporting Information (Table S1). The alkyne metathesis reactions were repeated with a lower catalyst loading using **Mo6** and carried out at different substrate concentrations. A diluted system with a substrate concentration of 13 mM, the hitherto used system with a concentration of 130 mM and a more concentrated system with a substrate concentration of 660 mM were chosen. The catalyst loading was reduced to 0.05 mol %, allowing TONs up to 20 000. All reactions were stirred for 48 h at 35 °C due to the low concentration in the diluted system and the therefore expected slow conversion rate (Table 1). Values for the conversion after 3 h can be found in the Supporting Information (Table S2). For substrate **S1**, the substrate concentration was additionally set to 1.3 M as an increase in substrate concentration usually leads to an increased conversion. This is particularly the case with **S1**. In the highly diluted system (13 mM), only 41% of the starting material was consumed; however, conversion increased up to 99%, resulting in a TON of 19 900 for a substrate concentration of 1.3 M. However, **Mo4** and **Mo6** are decomposing upon exposure to air for 1 day (Figures S1−S4) or when reacted with alkynols such as 3-pentyn-1-ol (Figures S5 and S6).

In terms of catalytic performance, the cationic molybdenum alkylidyne NHC complexes are at least comparable to the catalysts recently published by Fürstner et al., which showed exceptional tolerance against functional groups and to some degree against water at high catalyst loadings (>1 mol %),[11,52] as well as to the catalysts reported by Tamm et al., which reached TONs > 180 000, though only for carefully and highly purified **S1**,[17,18] in that the catalysts presented here allow for high TONs for various substrates *without* extensive purification. Furthermore, the turnover frequencies after 5 min (TOF_{5min}) were determined for the conversion of **S1−S6** with **Mo6** at a catalyst loading of 0.005% and a concentration of 660 mM (Table 2). For substrate **S2**, a TON of 3600 was reached after 5 min, translating into a TOF_{5min} of 12 s^{-1}.

In conclusion, we have synthesized the first cationic molybdenum alkylidyne NHC complexes with the aim to increase activity, productivity, and functional group tolerance

Table 1. Turnover Numbers (TONs) and Conversion in Alkyne Self-Metathesis of Substrates S1−S6 with Complexes Mo4, Mo5, and Mo6 at Different Concentrations and Catalyst Loadings[a]

Entry	Catalyst	Substrate: Catalyst	Concentration [mM]	Product	Time [h]	TON	Conversion [%]
1	**Mo4**	1000	130	 **S1**	12	990	99
2	**Mo5**	1000	130		12	990	99
3	**Mo6**	1000	130		1	990	99
4	**Mo6**	20000	13		48	8100	41
5	**Mo6**	20000	130		48	10800	54
6	**Mo6**	20000	660		48	16000	80
7	**Mo6**	20000	1300		48	19900	99
8	**Mo4**	1000	130	 **S2**	3	990	99
9	**Mo5**	1000	130		3	990	99
10	**Mo6**	1000	130		1	990	99
11	**Mo6**	20000	13		48	16600	83
12	**Mo6**	20000	130		48	18900	94
13	**Mo6**	20000	660		48	19700	99
14	**Mo4**	1000	130	 **S3**	3	990	99
15	**Mo5**	1000	130		3	990	99
16	**Mo6**	1000	130		1	990	99
17	**Mo6**	20000	13		48	13800	69
18	**Mo6**	20000	130		48	11800	59
19	**Mo6**	20000	660		48	15800	79
20	**Mo4**	1000	130	 **S4**	12	990	99
21	**Mo5**	1000	130		12	990	99
22	**Mo6**	1000	130		3	990	99
23	**Mo6**	20000	13		48	13600	68
24	**Mo6**	20000	130		48	13300	66
25	**Mo6**	20000	660		48	14300	71
26	**Mo4**	1000	130	 **S5**	12	990	99
27	**Mo5**	1000	130		12	990	99
28	**Mo6**	1000	130		3	990	99
29	**Mo6**	20000	13		48	10000	50
30	**Mo6**	20000	130		48	11100	55
31	**Mo6**	20000	660		48	12300	61
32	**Mo4**	1000	130	 **S6**	12	990	99
33	**Mo5**	1000	130		12	990	99
34	**Mo6**	1000	130		12	990	99
35	**Mo6**	20000	13		48	9000	45
36	**Mo6**	20000	130		48	11300	57
37	**Mo6**	20000	660		48	9400	47

[a] Solvent: 1,2-dichlorobenzene; internal standard: *t*Bu-benzene; temperature: 35 °C; with the addition of ground 5 Å molecular sieves as 2-butyne scavenger.[14]

Table 2. Conversion and Turnover Frequencies after 5 min (TOF_{5min}) in the Alkyne Self-Metathesis of Substrates S1−S6 with Complex Mo6 at a Concentration of 660 mM

substrate: catalyst	substrate	conversion [%]	TOF_{5min} [s^{-1}]
5000	**S1**	31	5
5000	**S2**	72	12
2500	**S3**	37	3
2500	**S4**	40	3.3
2500	**S5**	34	2.6
2500	**S6**	33	2.6

and demonstrated that they indeed present the catalytic species that form from neutral pentacoordinate molybdenum alkylidyne NHC complexes via dissociation of one anionic ligand. In that regards, particularly the triflate complexes were found suitable. Tetracoordinate, solvent-free cationic complexes demonstrate high catalytic activity and productivity in the self-metathesis of several alkyne substrates, do not require extensive purification of the substrates, and demonstrate tolerance versus ether, ester-, thioether, and nitro groups.

EXPERIMENTAL SECTION

General Information. All operations were performed under an inert gas atmosphere (N_2), either with standard Schlenk techniques or in a glovebox (LabMaster 130, MBraun, Garching, Germany), unless stated otherwise. Diethyl ether, *n*-pentane, CH_2Cl_2, tetrahydrofuran, and toluene were dried by a solvent purification system (SPS, MBraun). All NMR measurements were conducted on a Bruker Avance III 400 instrument. Chemical shifts are reported in ppm relative to the solvent signal; coupling constants are listed in Hz. ^{13}C NMR spectra were measured using broadband decoupling. Single-crystal X-ray measurements were carried out on a Bruker Kappa APEXII Duo diffractometer with Mo Kα radiation at the Institute of Organic Chemistry, University of Stuttgart. Crystal data have been deposited with the Cambridge Crystallographic Data Centre (CCDC): **Mo4** CCDC 2063125, **Mo6** CCDC 2063124.

Reagents and starting materials were purchased from ABCR (Karlsruhe, Germany), Alfa Aesar (Karlsruhe, Germany), and Merck (Munich, Germany) and used as received unless stated otherwise. **S1** was dried over CaH_2 and distilled under N_2. All solvents were purchased anhydrous and stored over 3 Å molecular sieves. 1,3-Dimesitylimidazol-2-ylidene,[53] **S2**,[21] **S3**,[21] **S4**,[21] **S5**,[21] **S6**,[52] and **Mo1**[51] were synthesized according to the literature.

Mo2. A solution of triflic acid (28 mg, 0.19 mmol) in 2 mL of toluene:DME (5:1) was cooled to −40 °C and slowly added at −40 °C to **Mo1** (150 mg, 0.18 mmol) dissolved in 4 mL of toluene. The reaction mixture was stirred for 4 h at room temperature; then the volatiles were removed *in vacuo*. The residue was coevaporated with *n*-pentane (8 × 1 mL) and diethyl ether (8 × 1 mL), washed with *n*-pentane (2 × 2 mL), and crystallized from diethyl ether/*n*-pentane. The product was isolated in the form of red crystals (92 mg, 0.11 mmol, 64%): ^1H NMR (400 MHz, $CDCl_3$): δ = 7.36 (d, $^3J_{H-H}$ = 8.9 Hz, 2H), 6.81 (d, $^3J_{H-H}$ = 9.0 Hz, 2H), 4.41 (s, 3H), 4.29 (td, $^3J_{H-H}$ = 11.4 Hz, $^2J_{H-H}$ = 3.2 Hz, 1H), 3.91−3.83 (m, 2H), 3.80 (s, 3H), 3.57−3.51 (m, 1H), 3.37 (s, 3H), 2.02 (s, 3H), 1.97 (s, 3H) ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ = −76.35 (q, $^4J_{F-F}$ = 9.7 Hz, 3F), −76.73 to −76.85 (m, 3F), −77.30 (q, $^4J_{F-F}$ = 3.4 Hz, 3F), −77.55 to −77.69 (m, 3F), −77.92 to −78.10 (m, 3F) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 303.2, 161.3, 136.8, 133.7, 123.7 (q, $^1J_{C-F}$ = 287 Hz, CF_3), 123.6 (q, $^1J_{C-F}$ = 287 Hz, CF_3), 123.5 (q, $^1J_{C-F}$ = 287 Hz, CF_3), 123.1 (q, $^1J_{C-F}$ = 287 Hz, CF_3), 119.5 (q, $^1J_{C-F}$ = 318 Hz, CF_3), 113.6, 85.6 (hept., $^1J_{C-F}$ = 29.4 Hz), 84.5 (hept., $^1J_{C-F}$ = 29.3 Hz), 76.0, 73.2, 69.4, 59.6, 55.6, 18.9, 18.8 ppm. Anal. Calcd (%) for $C_{21}H_{23}F_{15}MoO_8S$: C, 30.90; H, 2.84. Found: C, 30.83; H, 2.91.

Mo3. Mo2 (500 mg, 0.61 mmol) was dissolved in 10 mL of THF and stirred for 1 h at room temperature. All volatiles were removed *in vacuo*; the residue was coevaporated with *n*-pentane (5 × 2 mL) and diethyl ether (5 × 2 mL) and crystallized from diethyl ether/*n*-pentane/CH_2Cl_2. The product was isolated in the form of red crystals (450 mg, 0.52 mmol, 84%): ^1H NMR (400 MHz, $CDCl_3$): δ = 7.39 (d, $^3J_{H-H}$ = 9.0 Hz, 2H), 6.82 (d, $^3J_{H-H}$ = 9.1 Hz, 2H), 4.62 (s, 2H), 4.37 (s, 2H), 3.80 (s, 3H), 3.76−3.71 (m, 4H), 2.13−2.05 (m, 4H), 1.99 (s, 3H), 1.90 (s, 3H), 1.82−1.77 (m, 4H) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = −77.16 to −77.48 (m, 9F), −77.54 to −77.94 (m, 6F) ppm. ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 304.7, 161.8, 137. 7, 134.3, 124.23 (q, *J* = 287.7 Hz), 123.99 (q, *J* = 287.2 Hz), 123.86 (q, *J* = 287.4 Hz), 120.07 (q, *J* = 317.5 Hz), 113.8, 86.20 (hept, *J* = 28.4 Hz), 84.84 (hept, *J* = 28.2 Hz), 79.9, 69.2, 56.0, 26.5, 25.8, 19.7, 19.1 ppm. Anal. Calcd (%) for $C_{25}H_{29}F_{15}MoO_8S$: C, 34.49; H, 3.36. Found: C, 34.15; H, 3.41.

Mo4. A cold (−40 °C) solution of 1,3-dimesitylimidazol-2-ylidene (139.9 mg, 0.46 mmol, 1 equiv) in toluene (50 mL) was added to a solution of **Mo3** (400 mg, 0.46 mmol) in toluene (50 mL), cooled to −40 °C. The reaction was stirred for 3 h; then the solvent was removed *in vacuo* and the residue was coevaporated with *n*-pentane (5 × 4 mL) and diethyl ether (5 × 4 mL). The resulting solid residue was washed with *n*-pentane (3 × 10 mL) and crystallized from diethyl ether/*n*-pentane. The product was isolated in the form of orange crystals (405 mg, 0.39 mmol, 86%): ^1H NMR (400 MHz, CD_2Cl_2): δ = 7.95 (s, 2H), 6.86 (s, 4H), 6.77 (d, $^3J_{H-H}$ = 9.0 Hz, 2H), 6.66 (d, $^3J_{H-H}$ = 8.9 Hz, 2H), 3.84 (s, 3H), 2.17 (s, 6H), 2.02 (s, 12H), 1.77 (s, 6H) ppm. ^{19}F NMR (376 MHz, CD_2Cl_2): δ = −76.92 (q, $^4J_{F-F}$ = 9.0 Hz), −78.67 (q, $^4J_{F-F}$ = 9.2), −78.93 ppm. ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 311.0, 185.6, 162.8, 142.9, 137.7, 135.3, 134.0, 132.3, 130.6, 128.2, 122.80 (q, *J* = 286.7 Hz), 122.76 (q, *J* = 286.6 Hz), 113.7, 85.25 (hept, *J* = 30.1 Hz), 56.2, 21.3, 20.9, 17.6 ppm. Anal. Calcd (%) for $C_{38}H_{37}F_{15}MoN_2O_6S$: C, 44.28; H, 3.62; N, 2.72. Found: C, 44.29; H, 3.74; N, 2.80.

Mo5. Na[B(Ph)$_4$] (33.1 mg, 0.10 mmol, 1 equiv) was slowly added to a solution of **Mo4** (100 mg, 0.10 mmol) in CH_2Cl_2 (4 mL), cooled to −40 °C, and the mixture was stirred for 1 h at room temperature. The resulting suspension was filtered through a pad of Celite, the solvent was removed *in vacuo*, and the oily residue was excessively coevaporated with *n*-pentane (10 × 2 mL) and diethyl ether (10 × 2 mL). The residue was washed with *n*-pentane (2 × 6 mL) and crystallized from CH_2Cl_2/*n*-pentane. The product was isolated in the form of dark red crystals (103 mg, 0.09 mmol, 88%): ^1H NMR (400 MHz, CD_2Cl_2): δ = 7.32 (s, 8H), 6.95 (m, 8H), 6.84 (s, 4H), 6.82−6.74 (m, 4H), 6.77−6.70 (m, 4H), 6.67−6.60 (m, 2H), 3.82 (s, 3H), 2.18 (s, 6H), 1.91 (s, 12H), 1.76 (s, 6H) ppm. ^{19}F NMR (376 MHz, CD_2Cl_2): δ = −76.93 (q, *J* = 9.0 Hz), −78.74 (q, *J* = 9.1 Hz) ppm. ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 310.7, 185.3, 165.53−163.58 (m), 162.8, 142.9, 137.6, 136.4, 135.1, 133.9, 132.1, 130.6, 127.6, 126.2, 122.8 (q, *J* = 286.9 Hz), 122.7 (q, *J* = 286.6 Hz), 122.3, 113.7, 85.31 (hept, *J* = 29.7 Hz), 56.2, 21.3, 20.9, 17.5 ppm. Anal. Calcd (%) for $C_{61}H_{57}BF_{12}MoN_2O_3\cdot(CH_2Cl_2)_{0.5}$: C, 59.41; H, 4.70; N, 2.25. Found: C, 59.62; H, 4.79; N, 2.34.

Mo6. A suspension of Na[B(Ar^F)$_4$] (343 mg, 0.39 mmol, 1 equiv) in CH_2Cl_2 (12 mL), cooled to −40 °C, was slowly added to a solution of **Mo4** (400 mg, 0.39 mmol) dissolved in CH_2Cl_2 (12 mL), and the resulting mixture was stirred for 1 h at room temperature. Then, the suspension was filtered through a pad of Celite, the solvent was removed *in vacuo*, and the oily residue was excessively coevaporated with *n*-pentane (10 × 2 mL) and diethyl ether (10 × 2 mL). The residue was washed with *n*-pentane (2 × 6 mL) and crystallized from CH_2Cl_2/*n*-pentane. The product was isolated in the form of dark red crystals (580 mg, 0.24 mmol, 86%): ^1H NMR (400 MHz, CD_2Cl_2): δ = 7.84−7.63 (m, 10H), 7.56 (s, 4H), 6.86 (s, 4H), 6.77 (d, $^3J_{H-H}$ = 9.0 Hz, 2H), 6.65 (d, $^3J_{H-H}$ = 9.0 Hz, 2H), 3.81 (s, 3H), 2.16 (s, 6H), 2.00 (s, 12H), 1.79 (s, 6H) ppm. ^{19}F NMR (376 MHz, CD_2Cl_2): δ = −62.87 (24F), −76.95 (q, $^4J_{F-F}$ = 8.7 Hz), −78.78 (q, $^4J_{F-F}$ = 9.0 Hz) ppm. ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 311.1, 185.0, 162.5, 162.0, 161.5, 161.0, 142.8, 137.2, 134.8, 134.5, 133.5, 131.5, 130.2, 128.7 (qq, *J* = 30.8 Hz, 5.7 Hz), 126.7, 126.0, 123.2, 122.3 (q, $^1J_{C-F}$ = 286.7 Hz), 122.2 (q, $^1J_{C-F}$ = 286.7 Hz), 120.5, 117.46, 113.2, 85.0 (hept, $^2J_{C-F}$ = 30.3 Hz, C(CF$_3$)$_2$Me), 55.6, 20.7, 20.4, 16.9 ppm. Anal. Calcd (%) for $C_{69}H_{49}BF_{36}MoN_2O_3$: C, 47.50; H, 2.83; N, 1.61. Found: C, 47.54; H, 3.02; N, 1.66.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.1c00175.

Detailed experimental procedures, NMR data and spectra for all compounds (PDF)

Accession Codes

CCDC 2063124 and 2063125 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

AUTHOR INFORMATION

Corresponding Author

Michael R. Buchmeiser − *Institute of Polymer Chemistry, University of Stuttgart, 70569 Stuttgart, Germany;* orcid.org/0000-0001-6472-5156; Email: michael.buchmeiser@ipoc.uni-stuttgart.de

Authors

Jonas Groos − *Institute of Polymer Chemistry, University of Stuttgart, 70569 Stuttgart, Germany*
Philipp M. Hauser − *Institute of Polymer Chemistry, University of Stuttgart, 70569 Stuttgart, Germany*
Maximilian Koy − *Institute of Polymer Chemistry, University of Stuttgart, 70569 Stuttgart, Germany*
Wolfgang Frey − *Institute of Organic Chemistry, University of Stuttgart, 70569 Stuttgart, Germany*

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.organomet.1c00175

Funding

Financial support by the Deutsche Forschungsgemeinschaft DFG (grant number 358283783 − CRC 1333) is gratefully acknowledged.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

Dedicated to Prof. Christian Bruneau for his outstanding contributions to catalysis.

REFERENCES

(1) Schrock, R. R. Multiple Metal−Carbon Bonds for Catalytic Metathesis Reactions (Nobel Lecture). *Angew. Chem.* **2006**, *118* (23), 3832−3844.

(2) Zhai, F.; Schrock, R. R.; Hoveyda, A. H.; Müller, P. Syntheses of "Phosphine-Free" Molybdenum Oxo Alkylidene Complexes through Addition of Water to Alkylidyne Complexes. *Organometallics* **2020**, *39* (13), 2486−2492.

(3) Tonzetich, Z. J.; Lam, Y. C.; Müller, P.; Schrock, R. R. Facile Synthesis of a Tungsten Alkylidyne Catalyst for Alkyne Metathesis. *Organometallics* **2007**, *26* (3), 475−477.

(4) Schrock, R. R. High-oxidation-state molybdenum and tungsten alkylidyne complexes. *Acc. Chem. Res.* **1986**, *19* (11), 342−348.

(5) Toreki, R.; Vaughan, G. A.; Schrock, R. R.; Davis, W. M. Metathetical reactions of rhenium(VII) alkylidene-alkylidyne complexes of the type $Re(CR')(CHR')[OCMe(CF_3)_2]_2$ (R′ = CMe_3 or CMe_2Ph) with terminal and internal olefins. *J. Am. Chem. Soc.* **1993**, *115* (1), 127−137.

(6) Freudenberger, J. H.; Schrock, R. R. Multiple metal-carbon bonds. 42. Formation of tungstenacyclobutadiene complexes containing a proton in the ring and their conversion to deprotio tungstenacyclobutadiene complexes. *Organometallics* **1986**, *5* (7), 1411−1417.

(7) Listemann, M. L.; Schrock, R. R. Multiple metal carbon bonds. 35. A general route to tri-tert-butoxytungsten alkylidyne complexes. Scission of acetylenes by ditungsten hexa-tert-butoxide. *Organometallics* **1985**, *4* (1), 74−83.

(8) Freudenberger, J. H.; Schrock, R. R. Multiple metal-carbon bonds. 37. Preparation of di-tert-butoxytungsten(VI) alkylidene complexes by protonation of tri-tert-butoxytungsten(VI) alkylidyne complexes. *Organometallics* **1985**, *4* (11), 1937−1944.

(9) Freudenberger, J. H.; Schrock, R. R.; Churchill, M. R.; Rheingold, A. L.; Ziller, J. W. Metathesis of acetylenes by (fluoroalkoxy)tungstenacyclobutadiene complexes and the crystal structure of $W(C_3Et_3)[OCH(CF_3)_2]_3$. A higher order mechanism for acetylene metathesis. *Organometallics* **1984**, *3* (10), 1563−1573.

(10) Schrock, R. R.; Clark, D. N.; Sancho, J.; Wengrovius, J. H.; Rocklage, S. M.; Pedersen, S. F. Tungsten(VI) neopentylidyne complexes. *Organometallics* **1982**, *1* (12), 1645−1651.

(11) Hillenbrand, J.; Leutzsch, M.; Yiannakas, E.; Gordon, C. P.; Wille, C.; Nothling, N.; Coperet, C.; Fürstner, A. Canopy Catalysts" for Alkyne Metathesis: Molybdenum Alkylidyne Complexes with a Tripodal Ligand Framework. *J. Am. Chem. Soc.* **2020**, *142* (25), 11279−11294.

(12) Heppekausen, J.; Stade, R.; Kondoh, A.; Seidel, G.; Goddard, R.; Fürstner, A. Optimized synthesis, structural investigations, ligand tuning and synthetic evaluation of silyloxy-based alkyne metathesis catalysts. *Chem. - Eur. J.* **2012**, *18* (33), 10281−99.

(13) Heppekausen, J.; Fürstner, A. Rendering Schrock-type Molybdenum Alkylidene Complexes Air Stable: User-Friendly Precatalysts for Alkene Metathesis. *Angew. Chem.* **2011**, *123* (34), 7975−7978.

(14) Heppekausen, J.; Stade, R.; Goddard, R.; Fürstner, A. Practical New Silyloxy-Based Alkyne Metathesis Catalysts with Optimized Activity and Selectivity Profiles. *J. Am. Chem. Soc.* **2010**, *132*, 11045−11057.

(15) Fürstner, A.; Mathes, C.; Lehmann, C. W. $Mo[N(t\text{-}Bu)(Ar)]_3$ Complexes As Catalyst Precursors: In Situ Activation and Application to Metathesis Reactions of Alkynes and Diynes. *J. Am. Chem. Soc.* **1999**, *121* (40), 9453−9454.

(16) Bittner, C.; Ehrhorn, H.; Bockfeld, D.; Brandhorst, K.; Tamm, M. Tuning the Catalytic Alkyne Metathesis Activity of Molybdenum and Tungsten 2,4,6-Trimethylbenzylidyne Complexes with Fluoroalkoxide Ligands $OC(CF_3)_nMe_{3-n}$ (n = 0−3). *Organometallics* **2017**, *36* (17), 3398−3406.

(17) Estes, D. P.; Gordon, C. P.; Fedorov, A.; Liao, W. C.; Ehrhorn, H.; Bittner, C.; Zier, M. L.; Bockfeld, D.; Chan, K. W.; Eisenstein, O.; Raynaud, C.; Tamm, M.; Coperet, C. Molecular and Silica-Supported Molybdenum Alkyne Metathesis Catalysts: Influence of Electronics and Dynamics on Activity Revealed by Kinetics, Solid-State NMR, and Chemical Shift Analysis. *J. Am. Chem. Soc.* **2017**, *139* (48), 17597−17607.

(18) Estes, D. P.; Bittner, C.; Arias, O.; Casey, M.; Fedorov, A.; Tamm, M.; Coperet, C. Alkyne Metathesis with Silica-Supported and Molecular Catalysts at Parts-per-Million Loadings. *Angew. Chem.* **2016**, *128* (45), 14166−14170.

(19) Haberlag, B.; Freytag, M.; Jones, P. G.; Tamm, M. Tungsten and Molybdenum 2,4,6-Trimethylbenzylidyne Complexes as Robust Pre-Catalysts for Alkyne Metathesis. *Adv. Synth. Catal.* **2014**, *356* (6), 1255−1265.

(20) Haberlag, B.; Freytag, M.; Daniliuc, C. G.; Jones, P. G.; Tamm, M. Efficient Metathesis of Terminal Alkynes. *Angew. Chem.* **2012**, *124* (52), 13195−13198.

(21) Haberlag, B.; Wu, X.; Brandhorst, K.; Grunenberg, J.; Daniliuc, C. G.; Jones, P. G.; Tamm, M. Preparation of imidazolin-2-iminato molybdenum and tungsten benzylidyne complexes: a new pathway to highly active alkyne metathesis catalysts. *Chem. - Eur. J.* **2010**, *16* (29), 8868−77.

(22) Lysenko, S.; Haberlag, B.; Wu, X.; Tamm, M. Ring-Opening Metathesis Polymerization of Cyclooctyne Employing Well-Defined Tungsten Alkylidyne Complexes. *Macromol. Symp.* **2010**, *293* (1), 20−23.

(23) Beer, S.; Brandhorst, K.; Grunenberg, J.; Hrib, C. G.; Jones, P. G.; Tamm, M. Preparation of Cyclophanes by Room-Temperature Ring-Closing Alkyne Metathesis with Imidazolin-2-iminato Tungsten Alkylidyne Complexes. *Org. Lett.* **2008**, *10*, 981−984.

(24) Beer, S.; Hrib, C. G.; Jones, P. G.; Brandhorst, K.; Grunenberg, J.; Tamm, M. Efficient room-temperature alkyne metathesis with well-defined imidazolin-2-iminato tungsten alkylidyne complexes. *Angew. Chem.* **2007**, *119* (46), 9047−9051.

(25) Melcher, D.; Àrias, Ò.; Freytag, M.; Jones, P. G.; Tamm, M. Synthesis of Alkyne Metathesis Catalysts from Tris(dimethylamido)

tungsten Precursors. *Eur. J. Inorg. Chem.* **2020**, *2020* (47), 4454−4464.

(26) Roland, C. D.; VenkatRamani, S.; Jakhar, V. K.; Ghiviriga, I.; Abboud, K. A.; Veige, A. S. Synthesis and Characterization of a Molybdenum Alkylidyne Supported by a Trianionic OCO^{3-} Pincer Ligand. *Organometallics* **2018**, *37* (23), 4500−4505.

(27) VenkatRamani, S.; Ghiviriga, I.; Abboud, K. A.; Veige, A. S. A new ONO($^{3-}$) trianionic pincer ligand with intermediate flexibility and its tungsten alkylidene and alkylidyne complexes. *Dalton. Trans.* **2015**, *44* (42), 18475−86.

(28) McGowan, K. P.; O'Reilly, M. E.; Ghiviriga, I.; Abboud, K. A.; Veige, A. S. Compelling mechanistic data and identification of the active species in tungsten-catalyzed alkyne polymerizations: conversion of a trianionic pincer into a new tetraanionic pincer-type ligand. *Chem. Sci.* **2013**, *4* (3), 1145.

(29) Yang, H.; Liu, Z.; Zhang, W. Multidentate Triphenolsilane-Based Alkyne Metathesis Catalysts. *Adv. Synth. Catal.* **2013**, *355* (5), 885−890.

(30) Jyothish, K.; Wang, Q.; Zhang, W. Highly Active Multidentate Alkyne Metathesis Catalysts: Ligand-Activity Relationship and Their Applications in Efficient Synthesis of Porphyrin-Based Aryleneethynylene Polymers. *Adv. Synth. Catal.* **2012**, *354* (11−12), 2073−2078.

(31) Jyothish, K.; Zhang, W. Introducing a podand motif to alkyne metathesis catalyst design: a highly active multidentate molybdenum(VI) catalyst that resists alkyne polymerization. *Angew. Chem.* **2011**, *123* (15), 3497−3500.

(32) Cho, H. M.; Weissman, H.; Moore, J. S. Synthetic applications with use of a silica-supported alkyne metathesis catalyst. *J. Org. Chem.* **2008**, *73* (11), 4256−8.

(33) Weissman, H.; Plunkett, K. N.; Moore, J. S. A Highly Active, Heterogeneous Catalyst for Alkyne Metathesis. *Angew. Chem.* **2006**, *118* (4), 599−602.

(34) Cho, H. M.; Weissman, H.; Wilson, S. R.; Moore, J. S. A Mo(VI) alkylidyne complex with polyhedral oligomeric silsesquioxane ligands: homogeneous analogue of a silica-supported alkyne metathesis catalyst. *J. Am. Chem. Soc.* **2006**, *128* (46), 14742−3.

(35) von Kugelgen, S.; Piskun, I.; Griffin, J. H.; Eckdahl, C. T.; Jarenwattananon, N. N.; Fischer, F. R. Templated Synthesis of End-Functionalized Graphene Nanoribbons through Living Ring-Opening Alkyne Metathesis Polymerization. *J. Am. Chem. Soc.* **2019**, *141* (28), 11050−11058.

(36) Bellone, D. E.; Bours, J.; Menke, E. H.; Fischer, F. R. Highly selective molybdenum ONO pincer complex initiates the living ring-opening metathesis polymerization of strained alkynes with exceptionally low polydispersity indices. *J. Am. Chem. Soc.* **2015**, *137* (2), 850−6.

(37) Paley, D. W.; Sedbrook, D. F.; Decatur, J.; Fischer, F. R.; Steigerwald, M. L.; Nuckolls, C. Alcohol-promoted ring-opening alkyne metathesis polymerization. *Angew. Chem.* **2013**, *125* (17), 4689−4692.

(38) Tsai, Y.-C.; Diaconescu, P. L.; Cummins, C. C. Facile Synthesis of Trialkoxymolybdenum(VI) Alkylidyne Complexes for Alkyne Metathesis. *Organometallics* **2000**, *19* (25), 5260−5262.

(39) Cummins, C. C. Reductive cleavage and related reactions leading to molybdenum−element multiple bonds: new pathways offered by three-coordinate molybdenum(III). *Chem. Commun.* **1998**, *0*, 1777−1786.

(40) Laplaza, C. E.; Johnson, M. J. A.; Peters, J. C.; Odom, A. L.; Kim, E.; Cummins, C. C.; George, G. N.; Pickering, I. J. Dinitrogen Cleavage by Three-Coordinate Molybdenum(III) Complexes: Mechanistic and Structural Data1. *J. Am. Chem. Soc.* **1996**, *118* (36), 8623−8638.

(41) Elser, I.; Groos, J.; Hauser, P. M.; Koy, M.; van der Ende, M.; Wang, D.; Frey, W.; Wurst, K.; Meisner, J.; Ziegler, F.; Kästner, J.; Buchmeiser, M. R. Molybdenum and Tungsten Alkylidyne Complexes Containing Mono-, Bi-, and Tridentate N-Heterocyclic Carbenes. *Organometallics* **2019**, *38* (21), 4133−4146.

(42) Pucino, M.; Mougel, V.; Schowner, R.; Fedorov, A.; Buchmeiser, M. R.; Coperet, C. Cationic Silica-Supported N-Heterocyclic Carbene Tungsten Oxo Alkylidene Sites: Highly Active and Stable Catalysts for Olefin Metathesis. *Angew. Chem.* **2016**, *128* (13), 4372−4374.

(43) Herz, K.; Unold, J.; Hänle, J.; Schowner, R.; Sen, S.; Frey, W.; Buchmeiser, M. R. Mechanism of the Regio- and Stereoselective Cyclopolymerization of 1,6-Hepta- and 1,7-Octadiynes by High Oxidation State Molybdenum−Imidoalkylidene N-Heterocyclic Carbene Initiators. *Macromolecules* **2015**, *48* (14), 4768−4778.

(44) Buchmeiser, M. R.; Sen, S.; Unold, J.; Frey, W. Komplexe N-heterocyclischer Carbene mit Molybdän-Alkylidenen der höchsten Oxidationsstufe: funktionalitätstolerante kationische Katalysatoren für die Olefinmetathese. *Angew. Chem.* **2014**, *126* (35), 9538−9542.

(45) Hauser, P. M.; van der Ende, M.; Groos, J.; Frey, W.; Wang, D.; Buchmeiser, M. R. Cationic Tungsten Alkylidyne N-Heterocyclic Carbene Complexes: Synthesis and Reactivity in Alkyne Metathesis. *Eur. J. Inorg. Chem.* **2020**, *2020*, 3070−3082.

(46) Imbrich, D. A.; Frey, W.; Buchmeiser, M. R. N-Heterocyclic carbene-induced transmethylation in tungsten imido alkylidene bistriflates: unexpected formation of an N-heterocyclic olefin complex. *Chem. Commun.* **2017**, *53* (88), 12036−12039.

(47) Addison, A. W.; Rao, T. N.; Reedijk, J.; van Rijn, J.; Verschoor, G. C. Synthesis, Structure, and Spectroscopic Properties of Copper(II) Compounds containing Nitrogen-Sulphur Donor Ligands; the Crystal and Molecular Structure of Aqua[1,7-bis(N-methylbenzimidazol-2'-yl)2,6-dithiaheptane]copper(II) Perchlorate. *J. Chem. Soc., Dalton Trans.* **1984**, *0*, 1349−1356.

(48) Herz, K.; Podewitz, M.; Stohr, L.; Wang, D.; Frey, W.; Liedl, K. R.; Sen, S.; Buchmeiser, M. R. Mechanism of Olefin Metathesis with Neutral and Cationic Molybdenum Imido Alkylidene N-Heterocyclic Carbene Complexes. *J. Am. Chem. Soc.* **2019**, *141* (20), 8264−8276.

(49) Buchmeiser, M. R.; Sen, S.; Lienert, C.; Widmann, L.; Schowner, R.; Herz, K.; Hauser, P.; Frey, W.; Wang, D. Molybdenum Imido Alkylidene N-Heterocyclic Carbene Complexes: Structure-Productivity Correlations and Mechanistic Insights. *ChemCatChem* **2016**, *8* (16), 2710−2723.

(50) Benedikter, M.; Musso, J.; Kesharwani, M. K.; Sterz, K. L.; Elser, I.; Ziegler, F.; Fischer, F.; Plietker, B.; Frey, W.; Kästner, J.; Winkler, M.; van Slageren, J.; Nowakowski, M.; Bauer, M.; Buchmeiser, M. R. Charge Distribution in Cationic Molybdenum Imido Alkylidene N-Heterocyclic Carbene Complexes: A Combined X-ray, XAS, XES, DFT, Mössbauer, and Catalysis Approach. *ACS Catal.* **2020**, *10* (24), 14810−14823.

(51) Koy, M.; Elser, I.; Meisner, J.; Frey, W.; Wurst, K.; Kastner, J.; Buchmeiser, M. R. High Oxidation State Molybdenum N-Heterocyclic Carbene Alkylidyne Complexes: Synthesis, Mechanistic Studies, and Reactivity. *Chem. - Eur. J.* **2017**, *23* (61), 15484−15490.

(52) Hillenbrand, J.; Leutzsch, M.; Fürstner, A. Molybdenum Alkylidyne Complexes with Tripodal Silanolate Ligands: The Next Generation of Alkyne Metathesis Catalysts. *Angew. Chem., Int. Ed.* **2019**, *58* (44), 15690−15696.

(53) Arduengo, A. J.; Krafczyk, R.; Schmutzler, R.; Craig, H. A.; Goerlich, J. R.; Marshall, W. J.; Unverzagt, M. Imidazolylidenes, imidazolinylidenes and imidazolidines. *Tetrahedron* **1999**, *55* (51), 14523−14534.