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Molybdenum Alkylidyne Silyloxy N-Heterocyclic Carbene Complexes – Highly Active Alkyne Metathesis Catalysts that can be Handled in Air

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A series of molybdenum alkylidyne silyloxy N-heterocyclic carbene (NHC) complexes of the general formula [Mo(≡C-(R))$(OSiPh_3)_3$(NHC)] (R = *t*Bu, 4-methoxyphenyl, 2,4,6-trimethylphenyl; NHC = 1,3-diisopropylimidazol-2-ylidene, 1,3-dicyclohexylimidazol-2-ylidene, 1,3-dicyclohexyl-4,5-dihydroimidazol-2-ylidene, 1,3-dimethylimidazol-2-ylidene, 1,3-dimethyl-4,5-dichloroimidazol-2-ylidene) was synthesized. Single crystal X-ray analyses revealed that with increasing steric demand of the alkylidyne group, enhanced air-stability of the complexes in the solid-state is achieved with the most stable complex (R = 2,4,6-trimethylphenyl, NHC = 1,3-diisopropylimidazol-2-ylidene) being stable in air for 24 h without showing signs of decomposition in ^{1}H NMR. In contrast to previously reported air-stable molybdenum-based complexes, the novel catalysts proved to be highly active in alkyne metathesis, allowing for turnover numbers (TONs) of up to 6000 without further activation, and tolerant towards several functional groups such as tosyl, ether, ester, thioether and nitro moieties. Their air stability allows for facile handling of the catalysts in air and even after exposure to ambient atmosphere for one week, the most stable representative still displayed high productivity in alkyne metathesis.

Introduction

Alkyne metathesis is a versatile tool in the fields of polymer[1] and supramolecular[2] chemistry as well as in organic synthesis, especially for macrocyclizations in complex natural products.[3] After the initial discovery of heterogeneous alkyne metathesis catalyzed by tungsten trioxide on silica at high temperatures in 1968,[4] homogeneous systems were developed in the following years. Those systems either comprise in situ-generated active species, for example, the Mortreux catalyst,[5] or well-defined Schrock-type alkylidyne complexes.[6] Since the first catalytically active d^0 tungsten-based catalysts were synthesized by Schrock and co-workers in 1981,[6a] a plethora of group 6 alkylidyne catalysts was created including complexes bearing fluorinated alkoxide,[7] amide,[8] imidazoline-2-iminato[9] or silyloxy[10] ligands. Also, Schrock-type alkylidyne complexes supported on partially dehydroxylated silica have been synthesized and displayed high turnover numbers (TON), albeit accompanied by a usually lower activity than their homogeneous congeners.[11] It was found that the reduced catalytic activity in those silica-supported systems most likely stems from a decreased electrophilicity at the active sites.[12] In general, it is hypothesized that in Schrock-type alkylidyne complexes up to a certain degree, a low-energy $\pi^*_{C\equiv M}$ orbital caused by electron deficient ligands (such as hexafluoro-*t*-butoxide) leads to increased catalytic activity. However, at some point with decreasing electron donation of ligands an adverse effect on catalytic activity occurs (as observed in complexes with nonafluoro-*t*-butoxide ligands), which is likely caused by an overly stable metallacyclobutadiene intermediate.[7b,13] On the other hand, another contributing factor to catalytic activity in those complexes, is the conformational rigidity of ligands – the complex must be able to accommodate various different geometries within the catalytic cycle.[14] In this context, the flexibility of the Si–O–M linkage in silyloxy ligands proved advantageous and, hence, those complexes often possess very high activity.[3c,10a,b]

In the last decade, increasing efforts have been devoted to the synthesis of air-stable alkylidyne complexes. Notable examples are displayed in Figure 1.

Fürstner and co-workers presented air-stable phenanthroline and bipyridine adducts of conventional Schrock-type alkylidyne complexes.[10a,b] The 1,10-phenantroline adduct in Figure 1 (left) was stable enough to allow facile handling in air.[10a] Later, it was shown that in its crystalline form, stability in air of up to one year was reached and complexes of this type only decompose slowly over several days in CD_2Cl_2 solution

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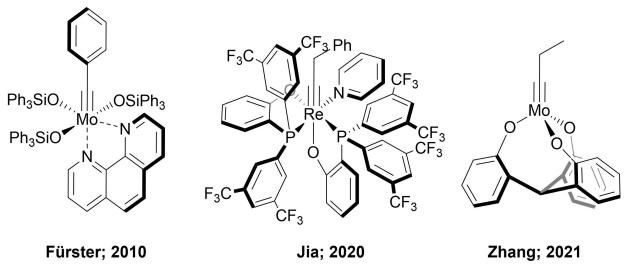


Figure 1. Notable examples of air-stable alkylidyne complexes and alkylidyne complexes that can operate under open-air conditions.[10a,b,15]

containing 10 ppm water.[10b] It was found that the moisture stability is strongly linked to the donor strength of the chelating phenanthroline or bipyridine ligand.[10b] However, the complexes do not possess any catalytic activity and have to be triggered by the addition of a Lewis acid such as $MnCl_2$ or $ZnCl_2$, which renders the whole system less user-friendly and comes with further drawbacks. Thus, $ZnCl_2$ and many other Lewis acids are hygroscopic and must be dried prior to use. On the other hand, while $MnCl_2$ is not hygroscopic, it causes paramagnetic line-broadening in NMR studies.[10a,b] More recently, a breakthrough in catalytic alkyne metathesis using d^2 Re(V) complexes has been achieved by Jia and co-workers (Figure 1, middle).[15a] The complex tolerates a broad range of functional groups, even carboxylic acids, can operate in wet solvents, and is even in solution air-stable for several weeks.[15a] Nevertheless, rhenium is one of the rarest metals in the earth's crust with an abundance of only 1 ppb[16] and relatively high catalyst loadings of 2–3 mol% had to be used to ensure high conversions for most substrates.[15a] Therefore, it is still desirable to develop highly active, air-stable alkylidyne complexes based on more abundant metals such as molybdenum or tungsten. An approach using a tridentate tris(2-hydroxyphenyl)methane ligand (Figure 1, right) enabled alkyne metathesis with a molybdenum-based catalyst under open-air conditions.[15b] The complex was formed in situ by the addition of the ligand to a Mo alkylidyne triamide precursor.[15b] Although the catalyst performed well in a flask open to ambient atmosphere, which also served as an efficient method to remove 2-butyne, this was limited to operation in CCl_4, which is virtually immiscible with water and is a potential occupational carcinogen. Other restrictions of the system are that even immersed in paraffin wax, the catalyst's activity drastically decreased over several weeks when stored in air and, also, comparably high catalyst loadings of 2–3 mol% had to be used.[15b] It should be mentioned that there are further alkylidyne catalyst systems that tolerate air, such as the aforementioned Mortreux catalyst that suffers from low activity,[5,17] or another more exotic example that cannot be discussed in detail; we therefore refer to the corresponding literature.[18]

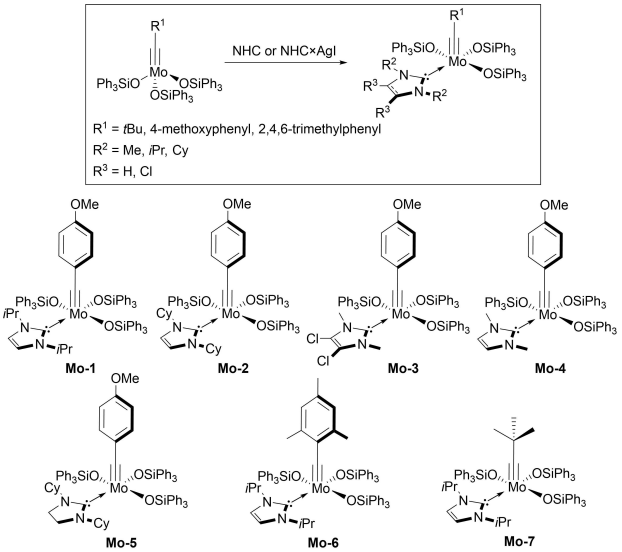
Another class of highly active, yet air-sensitive alkylidyne complexes was first presented in 2017 by our group by coordinating N-heterocyclic carbenes (NHCs) to molybdenum alkylidyne precursors,[19] which was shortly thereafter followed by analogous complexes bearing chelating alkylidyne ligands[20] and cationic molybdenum and tungsten alkylidyne complexes with weakly coordinating anions.[21] As outlined above, the synthesis of highly active, air-stable alkylidyne complexes based on abundant metals such as molybdenum is a very recent and sought-after synthetic target for organometallic chemists. In consequence and inspired by the approach of Fürstner, we strived to utilize our expertise in NHC-coordinated group 6 complexes and coordinate an NHC to Schrock-type alkylidyne complexes instead of a chelating bipyridine or phenanthroline ligand. We were confident that this could lead to air-stable alkyne metathesis catalysts that do not require any further activation, especially, since we succeeded with a similar catalyst design for air-stable alkylidene complexes that are remarkably active and functional group tolerant in olefin metathesis.[22]

Results and Discussion

Synthesis of Metal Complexes

The synthesis of NHC-coordinated alkylidyne complexes was achieved by reacting a molybdenum silyloxy precursor of the type $[Mo(\equiv C(R))(OSiPh_3)_3]$ (R = *t*Bu, 4-methoxyphenyl, 2,4,6-trimethylphenyl) with either a free NHC (NHC = 1,3-diisopropylimidazol-2-ylidene = I*i*Pr, 1,3-dicyclohexylimidazol-2-ylidene = ICy and 1,3-dicyclohexyl-4,5-dihydroimidazol-2-ylidene = SiCy) in benzene or by a transmetallation with an NHC silver iodide adduct (NHC = 1,3-dimethyl-4,5-dichloroimidazol-2-ylidene = $IMeCl_2$ and 1,3-dimethylimidazol-2-ylidene = IMe) in CH_2Cl_2 (Scheme 1).

The formed complexes were obtained in sufficient purity after filtration (only required for the silver iodide adducts) and washing with diethyl ether. The reaction proceeds without the formation of any notable side-products and, thereby, the yields



Scheme 1. Synthesis of molybdenum alkylidyne silyloxy NHC complexes of the general formula $[Mo(\equiv C(R))(OSiPh_3)_3NHC]$ and scope of the reaction.

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only depend on the solubility of the complexes in diethyl ether. Consequently, the isolated yields span a broad range from 41 to 81 %. In ^{1}H NMR the chemical shifts of the two *N*-substituents of the NHCs as well as the protons on the backbone of the NHC are not identical indicating a rotational inhibition of the NHCs on the timescale of the NMR measurement. This is most likely caused by the crowded coordination sphere around the metal center and was previously also observed for complexes of the type [Mo(≡C(4-methoxyphenyl))(OC(CF$_3$)$_2$(CH$_3$))$_3$(NHC)] but only for NHC=I*i*Pr and not for the sterically less bulky IMe or IMeCl$_2$.[19] However, in our novel complexes, the silyloxy ligands are sterically more demanding and, therefore, this effect is observed for all representatives of this class of complexes even for the ones bearing small NHCs. The attempted coordination of the relatively bulky 1,3-dimesitylimidazol-2-ylidene to [Mo(≡C(4-methoxyphenyl))(OSiPh$_3$)$_3$] did not lead to any product formation as evidenced by ^{1}H NMR and clearly displays the limitation in size of the NHCs that can be used in the reaction. We also tried to synthesize a cyclic(alkyl)(amino)carbene (CAAC) coordinated alkylidyne complex by adding (2,6-diisopropylphenyl)-2,2,4,4-tetramethyl-pyrrolidin-5-ylidene to the same precursor. In this case presumably the high steric demand of the 2,6-diisopropylphenyl group prevented binding of the CAAC ligand to the complex.

Single Crystal X-Ray Analyses

The crowded coordination sphere of silyloxy NHC complexes is also evidenced by subsequently conducted single crystal X-ray analyses. Single crystals of **Mo-1**, **Mo-6** and **Mo-7** were successfully grown from 1,2-dichloroethane/acetonitrile solutions at −35 °C; a comparison of the structures is depicted in Figure 2 in the order of increasing steric demand of the alkylidyne ligand. The most important structural features such as lengths and angles of relevant bonds as well as the geometry indexes[23] and buried volume (%V_{bur})[24] of the alkylidyne ligand are summarized in Table 1.

Mo-1 crystallizes in the triclinic space group $P\bar{1}$, a = 1404.08(6) pm, b = 1465.82(7) pm, c = 1518.22(7) pm, α = 96.894(3)°, β = 93.627(3)°, γ = 90.775(3)°, Z = 2. In the solid state, **Mo-1** adopts a distorted square pyramidal (SPy) geometry (τ_5 = 0.16) with the alkylidyne ligand in the apex and the silyloxy ligands as well as the NHC in the equatorial plane. The bond length of the Mo-alkylidyne bond (174.1(3) pm) and the Mo–NHC bond (224.0(2)) are both in the range observed for previously reported five-coordinate Mo 4-methoxyphenylidyne complexes bearing an NHC ligand with bond lengths of the Mo-alkylidyne bond between 173.7(3) and 174.46(14) pm and a distance of the Mo–NHC bond in the range of 224.41(18)–226.63(15) pm.[19] Likewise, a distorted SPy geometry (τ_5 = 0.05–0.24) was reported in literature for similar complexes.[19]

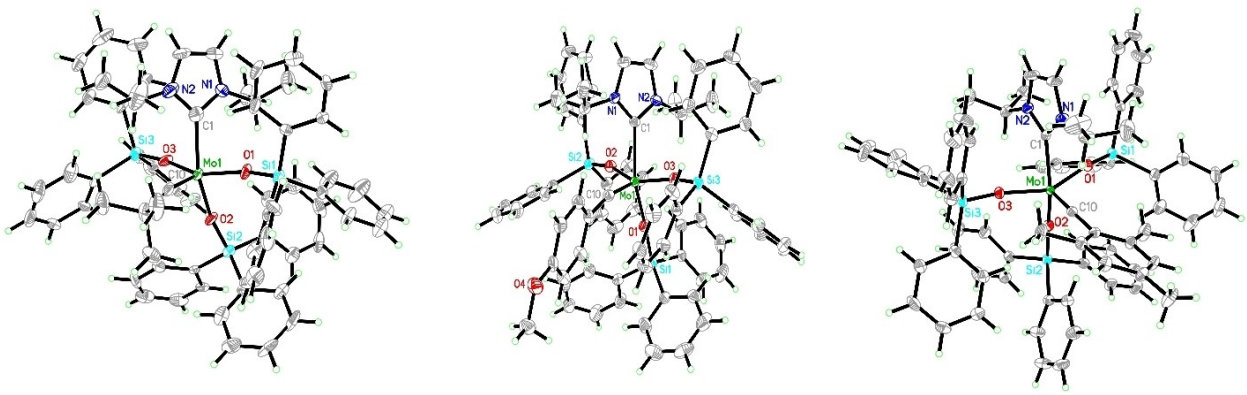

Figure 2. Single crystal X-ray structures of **Mo-7** (left), **Mo-1** (middle), and **Mo-6** (right), depicted in the order of increasing steric demand of the alkylidyne ligand, solvent molecules omitted for clarity.

Table 1. NHCs, alkylidyne ligands, %V_{bur} of the alkylidyne ligand and τ_5-values as well as relevant bond lengths [pm] and angles [°] of complexes **Mo-7**, **Mo-1** and **Mo-6**.

	Mo-7	Mo-1	Mo-6
NHC	I*i*Pr	I*i*Pr	I*i*Pr
Alkylidyne	*t*Bu	4-methoxyphenyl	Mes
%V_{bur} of the Alkylidyne Ligand	12.4	20.0	23.0
τ_5 Geometry	0.02, SPy	0.16, SPy	0.21, SPy
Mo–NHC	220.9(9)	224.0(2)	224.9(3)
Mo-Alkylidyne	174.4(10)	174.1(3)	174.3(2)
Mo–OSiPh$_3$	193.9(5)–194.6(5)	192.70(17)–196.29(16)	194.87(17)–195.24(17)
Alkylidyne-Mo–NHC	99.4(4)	99.34(10)	96.37(10)
Alkylidyne-Mo–OSiPh$_3$	102.4(3)–104.4(3)	102.46(10)–106.79(10)	104.27(10)–106.19(9)

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Mo-6 crystallizes in the monoclinic space group $P2_1/n$, $a=$ 1306.61(6) pm, $b=3702.53(16)$ pm, $c=1393.17(7)$ pm, $\alpha=\gamma=$ 90°, $\beta=102.166(3)°$, $Z=4$. Like **Mo-1**, **Mo-6** adopts a SPy geometry with the alkylidyne ligand in the apical position. However, a higher degree of distortion was observed for **Mo-6** ($\tau_5=0.21$), most probable stemming from the sterically more demanding mesitylidyne ligand. To compare the steric demand of the different alkylidyne ligands, $\%V_{bur}$ was calculated using the SambVca 2.1 application developed by Cavallo and co-workers (for details see S.I., Figure S23).[24] The comparison of the 4-methoxyphenylidyne ligand of **Mo-1** ($\%V_{bur}=20.0$) and the mesitylidyne ligand of **Mo-6** ($\%V_{bur}=23.0$) confirms the assumption that the mesitylidyne ligand, indeed, occupies a larger space in the coordination sphere. This also goes along with a slightly longer Mo–NHC bond in **Mo-6** (224.9(3) pm) compared to the corresponding bond length in **Mo-1** (224.0(2) pm). In addition, the angles of the alkylidyne-Mo–NHC and the alkylidyne-Mo–$OSiPh_3$ bonds in **Mo-1** and **Mo-6** differ by 2–3°. This again reflects the influence of the steric demand of the alkylidyne ligand on the structure as a whole and might be a decisive factor for the air-stability as shielding of the metal atom could protect the complex from decomposition, for example via hydrolysis of the ligands.

Lastly, the structural features of **Mo-7** were elucidated by single crystal X-ray analysis. Due to the poor crystallization propensity of **Mo-7** and the resulting small size of the crystals obtained, the measured intensities were weak and the obtained data quality was limited. Also, the small proportion (37%) of observed data ($>4\sigma(I)=$ greater than four times the standard deviation) directly indicates that it is, indeed, a data set with weak intensities. Nevertheless, the overall standard deviations of the C–C bonds were 1.3 pm and R1 was ~7.8%, which is relatively high but still tolerable. Nonetheless, the structure of **Mo-7** shall be discussed with caution and the standard deviations of bond lengths and angles (Table 1) must be considered.

In the solid-state **Mo-7** adapts the monoclinic space group $P2_1/n$, $a=1359.2(3)$ pm, $b=1882.8(5)$ pm, $c=2325.5(5)$ pm, $\alpha=\gamma=90°$, $\beta=91.023(5)°$, $Z=4$. Similar to the two other complexes discussed earlier, **Mo-7** possesses a SPy geometry. The relatively small *tert*-butylidyne ligand has low steric bulk ($\%V_{bur}=12.4$), which consequently results in a low distortion of the complex and an almost perfect SPy geometry ($\tau_5=0.02$). This is accompanied by an approximately 4 pm shorter Mo–NHC bond compared to **Mo-1** and **Mo-6** and again pinpoints the large influence of the alkylidyne ligand and its steric demand on the structure in the solid state.

Catalytic Activity

Next, we sought to probe the catalytic activity of complexes **Mo-1**–**Mo-7** in alkyne metathesis. In academic setups, molecular sieves are often used in alkyne metathesis reactions to remove the formed 2-butyne from the equilibrium, thereby allowing the reaction to reach full conversion.[7b,10a,b,15b,21b,25] Usually, a large excess of molecular sieves is added (up to 10 times the weight of the substrate).[7b,10a,b,15b,21b,25] However, this renders the reaction conditions less user-friendly. Especially on a larger scale, excess solvent has to be used to rinse the molecular sieves to extract remaining product, which results in higher waste production in the form of molecular sieve soaked with solvent. Examples in the literature show that other methods such as conducting the reactions at elevated temperature under open-air condition can serve as an efficient way to remove 2-butyne from the reaction mixture.[15b] Since we were planning to tackle this issue in a similar fashion at a later stage, we conducted the first assessment of catalytic activity under a N_2-atmosphere without the addition of molecular sieves. Notably, this must be expected to limit the maximum conversion to the equilibrium state between starting material, product, and 2-butyne. To find the optimal reaction conditions, an initial screening was conducted. In this context, the catalytic activity of **Mo-4** was tested in different solvents (toluene, 1,2-dichlorobenzene, and 1,2-dichloroethane) and at two different temperatures (room temperature (r.t.) and 80 °C) at a catalyst loading of 0.1 mol% with phenylpropyne (**S1**, S.I., Table S1). While the catalyst proved to be completely inactive in all solvents at room temperature, good activity was found at elevated temperatures (80 °C) with the highest TON obtained in 1,2-dichloroethane. For this reason, all subsequent reactions have been run at these conditions using a catalyst loading of 0.1 and 0.01 mol%, respectively. The highest productivities in each case are depicted in Table 2. The structures of the substrates are summarized in Figure 3. Conversions were determined by GC-MS; products were not isolated but unambiguously identified in the GC-MS traces.[21]

Table 2. Productivities (TONs) for alkyne metathesis reactions of **Mo-1**–**Mo-7** with substrates **S1**–**S7** determined by GC-MS.

	Mo-1	Mo-2	Mo-3	Mo-4	Mo-5	Mo-6	Mo-7
S1	650[a]	650[a]	620[a]	560[a]	720[a]	710[a]	570[a]
S2	3700[b]	5400[b]	700[b]	6000[b]	5800[b]	5700[b]	5600[b]
S3	690[a]	2300[b]	710[a]	1300[b]	3300[b]	2600[b]	710[a]
S4	2000[b]	2200[b]	3300[b]	660[a]	830[a]	4700[b]	2000[b]
S5	640[a]	640[a]	590[a]	580[a]	600[a]	640[a]	390[a]
S6	450[a]	410[a]	240[a]	630[a]	200[a]	340[a]	350[a]
S7	450[a]	710[a]	700[a]	760[a]	800[a]	660[a]	540[a]

[a] Reaction conditions: substrate (1 M) in 1,2-dichloroethane with 1,4-di-*tert*-butylbenzene (0.1 M) as internal standard, 80 °C, 12 h; catalyst:substrate = 1:1000. [b] Reaction conditions: substrate (1 M) in 1,2-dichloroethane with 1,4-di-*tert*-butylbenzene (0.1 M) as internal standard, 80 °C, 12 h; catalyst: substrate = 1:10000.

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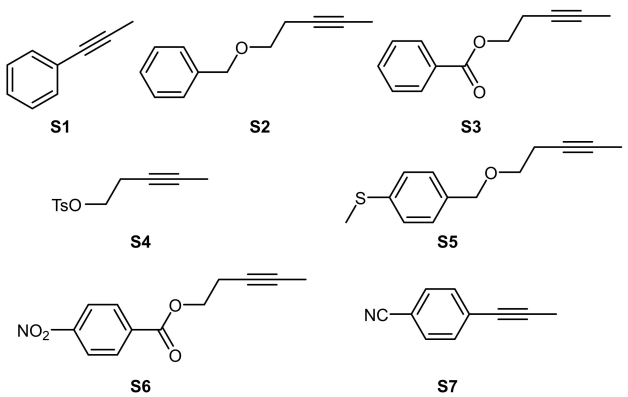

Figure 3. Substrates **S1**–**S7**.

With phenylpropyne (**S1**) all catalysts performed similarly, allowing for TONs between 560 and 720. Much higher productivities (TON up to 6000) were found in the reaction with substrate **S2**. For this substrate, all catalysts showed excellent results with the only exception being **Mo-3**, which allowed for a TON of 700. Compared to the other catalysts, **Mo-3** possesses a considerably weaker σ-donating NHC. The Tolman electronic parameter (TEP) of $IMeCl_2$ is 2058.5 cm^{-1},[26] which is almost in the range of phosphines (TEP($PiPr_3$) = 2059.2 cm^{-1}[27]) and renders it a much weaker σ-donor than all other NHCs used (range of the TEP of other NHCs used between 2049.5–2051.2 cm^{-1}[26]). Consequently, the metal has vastly altered electronics, which could contribute to lower activity. This is also reflected in the catalytic testing with **S3** in which **Mo-3** displays one of the lowest productivities as well. However, this trend does not hold for **S4**. Here, the lowest activities were found for **Mo-4** and **Mo-5**. The TONs for substrates **S5**–**S7** bearing the more challenging nitro, thioether and nitrile groups were all in the range between 200–800 with the TONs for **S6** being on the lower end. In an overall comparison, it becomes apparent that there is no clear trend between the alkylidyne or the NHC ligand of a complex and its catalytic activity in alkyne metathesis other than the one mentioned for **Mo-3**. The differences in productivity between the complexes for different substrates might be caused by a complex interplay between subtle differences in the electron donating capability of the different NHC ligands and the stability of the metallacyclobutadiene intermediate (as outlined in the introduction) with every particular substrate, which seems difficult to predict.[7b,13] Nevertheless, the productivity of our Mo alkylidyne silyloxy NHC complexes exceeds the one of any other neutral NHC-coordinated alkylidyne complexes[19–20,21c] to this date and also rivals the TONs obtained for conventional Mo alkylidyne silyloxy complexes[10] (although a direct comparison might be difficult since mostly other reaction conditions and substrates were used).

Handling of the Catalyst in Air

To confirm our initial working hypothesis that NHC-coordinated Mo alkylidyne silyloxy complexes like the previously presented bipyridine and phenanthroline adducts developed by Fürstner and co-workers possess improved stability towards moisture and air, we exposed solid samples of every catalyst to ambient atmosphere and analyzed those by ^{1}H NMR spectroscopy after 24 h and 1 week, respectively (S.I., Figure S16–S22). This procedure was conducted in a similar study confirming the air-stability of olefin metathesis catalysts.[22c,28] Most complexes showed slight signs of decomposition after 24 h in air. Notable exceptions were **Mo-3**, which bears the small and weakly σ-donating $IMeCl_2$, and **Mo-5** with the only saturated NHC among all complexes. Both complexes already showed the formation of an imidazolium and imidazolinium salt, respectively, as indicated by a highly downfield shifted peak after 24 h in air stemming from the undesired protonation of the NHC ligand. **Mo-1** and **Mo-6** with the strongly donating and sterically shielding I*i*Pr, on the other hand, did not display any change after exposure to air for 24 h. After 1 week in air, a majority of complexes showed slight formation of imidazolium salt along with other signs of progressed decomposition in the aliphatic and aromatic regions of the NMR spectra. As the only complex, **Mo-3** decomposed completely after 1 week in air. We found that the combination of the sterically demanding mesitylidyne ligand (%V_{bur} = 23.0) in combination with I*i*Pr in **Mo-6** led to the most stable complex and even after 1 week in air only very small peaks at the detection limit of the ^{1}H NMR were apparent for this complex (corresponds to an estimate of 2–3 % decomposition).

Admittedly, the air-stability of **Mo-6** lacks behind the one reported for bipyridine and phenanthroline adducts of Mo silyloxy complexes, which proved to be bench-stable for up to 1 year in their crystalline form.[10a,b] Considering that bipyridine and phenanthroline are chelating ligands and, thereby, occupying two binding sites, a higher steric shielding of the metal center is achieved, which consequently yields higher stability of the complexes. Nonetheless, those complexes require activation by treatment with a Lewis acid to remove the chelating ligand. The Lewis acids are often hygroscopic and require tedious drying as well as storage in a desiccator or can cause paramagnetic line-broadening in NMR, which considerably limits the user-friendliness of those systems. **Mo-6** in contrast, offers the advantage that it can be activated by simple heating to 80 °C.

We strived to utilize this feature for the handling of **Mo-6** in air followed by use in alkyne metathesis reactions. **Mo-6** was weighed in under ambient atmosphere and subsequently placed in a Schlenk tube followed by the addition of the substrate in 1,2-dichloroethane and heating to 80 °C under nitrogen atmosphere. This process is illustrated in S39 (S.I.). To remove the formed 2-butyne from the reaction mixture, the Schlenk tube was opened under a flow of nitrogen after 5, 30 and 90 min to take a sample that was subjected to analysis via GC-MS. A higher catalyst loading of 0.2 mol% was chosen compared to the initial testing of catalytic activity. This was

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done for several reasons: 1. We were seeking robust reaction conditions that are applicable universally to a variety of different substrates and sufficient to reach full conversion (whereas the loading of 0.1 mol% in the previous testing only led to conversions of 50% or even less for some substrates). 2. A catalyst loading of 0.2 mol% is already very low and, indeed, one order of magnitude lower than the loading of other catalysts that can be handled in air or operate under open-air conditions (usually 2–3 mol% were used in similar studies[10a,b,15]). 3. On the scale the reactions were conducted (1.9 mL, substrate 1 M) only milligram amounts of the catalyst were used (4.6 mg). Any further reduction of the catalyst loading would have resulted in the required amounts of catalysts being too small to be handled in our laboratory setup reproducibly. The TONs and conversions after 12 h are summarized in Table 3. Except for **S6** bearing the challenging nitro group, the conversions of all substrates were at least 83% indicating that the 2-butyne removal was successful, thereby allowing for higher conversions compared to the previous catalytic testing in a closed vial. The reactions with **S1**, **S2**, **S3**, and **S7** even reached conversions $>90\%$. Obviously, the TONs are lower than in the initial catalytic testing under ideal glove box conditions and are also limited by the higher catalyst loading. Nevertheless, the TONs in some cases, for example for **S1**, **S5**, **S6**, and **S7** only lack behind by 25–35% compared to the previous testing under ideal conditions (Table 2, **Mo-6** at a catalyst loading of 1:1000).

In line with the high stability towards air in the solid state as indicated by ^{1}H NMR spectra (S.I., Figure S21), indeed, we could prove that **Mo-6** retains most of its catalytic activity in the reaction with phenylpropyne after exposure to ambient atmosphere for 1 week (86% conversion and a TON of 430). As mentioned earlier, samples of the reaction were taken after 5, 30, and 90 min to monitor the reaction and to remove 2-butyne that is formed in the course of the reaction. The conversion over time for selected substrates is displayed in Figure 4 (the conversion over time for all substrates is shown in S.I., Figure S39). For all substrates, there was a steep increase in conversion within the first 90 min of the reaction whereas after that virtually no further product formation takes place. This indicated that at a catalyst loading of 0.2 mol% and a reaction time of 90 min might be sufficient to reach the maximal conversion.

Subsequently, we tried to conduct alkyne metathesis under open air conditions (**Mo-6**, catalyst loading, substrates, temperature, and concentrations were the same) in a vial open to ambient atmosphere. However, this led to very low conversions of only up to 20% and we, therefore, assume that the active species in solution, unlike the catalyst in the solid state, does not well tolerate moisture and air. This observation is supported by the fact that even under glove box conditions no product formation was observed for substrates bearing protic groups (the attempted alkyne metathesis of pent-3-yn-1-ol even at 1 mol% did not lead to any product formation, tested for all catalysts under glove box conditions). This highlights the need for further elucidation of the metathetically active species as well as the investigation of possible decomposition pathways in solution.

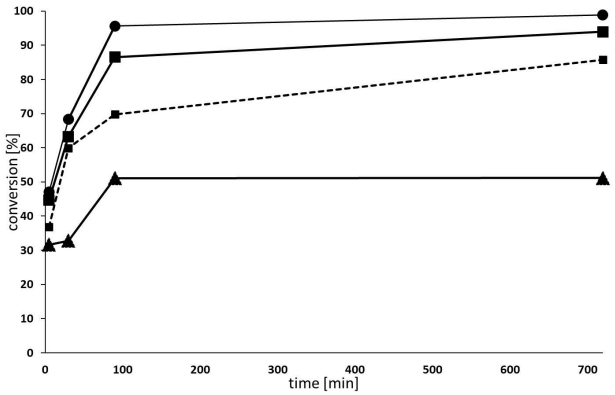

Figure 4. Reaction conditions: **Mo-6** was weighed under ambient atmosphere or kept in air for 1 week and then placed in a Schlenk tube under N_2. Substrate (1 M) in 1,2-dichloroethane (1.9 mL) with 1,4-di-tert-butylbenzene (0.1 M) as internal standard was added and the mixture was heated to 80 °C for 12 h. After 5, 30 and 90 min aliquots were taken under a flow of N_2; catalyst:substrate = 1:500; 0.2 mol%; conversion over time is displayed for selected substrates; circles, **S7**; big square, **S1**; small square and dashed line, **S1** after 1 week in air; triangle, **S6**.

Mechanistic Investigations

Molybdenum alkylidyne triphenylsilyloxy complexes are among the catalytically most active and versatile alkylidyne complexes reported to this date.[10b] Therefore, we were intrigued by the question if upon activation of our NHC-coordinated Mo silyloxy complexes, the NHC dissociates and a triphenylsilyloxy complex forms. In previous studies, the activation of complexes of the type [Mo(≡C(4-methoxyphenyl))$(OC(CF_3)_2(CH_3))_3$NHC] was investigated showing that the activation can either proceed via the mentioned dissociation of the NHC or by dissociation of one of the alkoxides leading to the formation of a cationic species (Scheme 2, top).[19–20] It was shown that the mode of activation highly depends on the properties of the NHC. To distinguish between the two activation pathways, either only triphenylsilanol or triphenylsilanol and substrate (phenylpropyne) were added to complexes **Mo-1**–**Mo-7** at room temperature or 80 °C in deuterated 1,2-dichloroethane and ^{1}H NMR spectra were recorded after 30 min (Scheme 2, bottom). The formation of imidazolium salt indicates a loosely bound NHC, which would point towards an activation via dissociation of an NHC ligand that is subsequently protonated by triphenylsilanol. The absence of any imidazolium peaks, on the other hand, especially in the presence of substrate and product formation would indicate an activation via a cationic species. Furthermore, examples of isolated, highly active cationic Mo alkylidyne NHC complexes are present in literature,[21b] which renders their existence as an active intermediate likely.

To prove that the basicity of a free NHC is sufficient to deprotonate the quite acidic triphenylsilanol, a preliminary experiment was conducted in which $IMeCl_2$ (the weakest σ-

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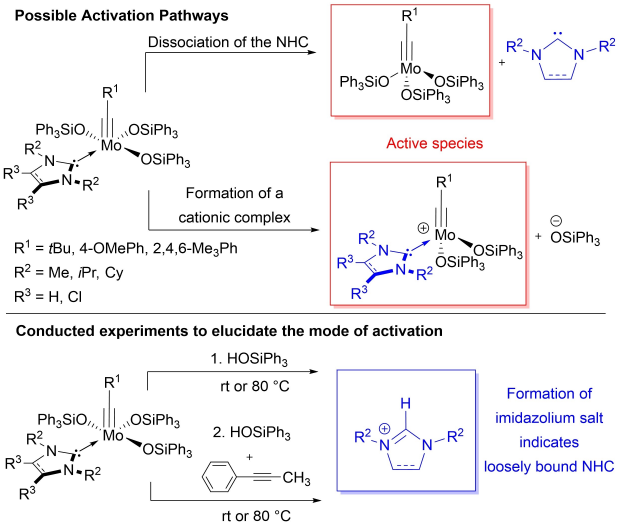

Scheme 2. Possible activation pathways of NHC-coordinated Mo alkylidyne complexes based on findings in previous studies[19–20] and the conducted experiments to investigate the possible formation of imidazolium salts.

donor[26] and presumably the least basic of all NHCs used) and triphenylsilanol were mixed in deuterated 1,2-dichloroethane. Indeed, the formation of imidazolium salt was indicated by a broad peak around $\delta = 8.4$ ppm (S.I., S24). This was followed by the experiments as outlined in Scheme 2, bottom; the individual spectra are shown in the Supporting Information (S25–S38).

In general, the catalysts **Mo-1**–**Mo-7** can be classified into two different categories. Complexes **Mo-3** and **Mo-4** bearing the small NHC ligands IMe and $IMeCl_2$ belong to the first category. Those complexes did not show the formation of imidazolium salt at any of the stated reaction conditions. At room temperature **Mo-4** is inactive and no formation of 2-butyne was observed in the ^{1}H NMR spectrum, whereas **Mo-3** is already active at lower temperatures. However, the peaks of **Mo-3** belonging to the alkylidyne complex did not change indicating a poor initiation efficiency of the catalyst below the detection limit of the NMR at room temperature. At a higher temperature of 80 °C, on the contrary, **Mo-3** and **Mo-4** are both active and also the formation of new alkylidyne species is evidenced by additionally formed signals between 6.0 and 6.5 ppm. That means a relatively high proportion of the alkylidyne complex reacted with phenylpropyne without the formation of any imidazolium salt (the dissociation of the NHC would lead to instantaneous protonation by triphenylsilanol). This strongly supports the presence of a cationic active intermediate. Nevertheless, this is no final proof and any other activation pathway that does not involve the dissociation of the NHC, although highly unlikely, cannot be ruled out completely for those two catalysts.

For the other catalysts, namely **Mo-1**, **Mo-2**, **Mo-5**, **Mo-6**, and **Mo-7**, the formation of imidazolium salt at 8.5–9.5 ppm was observed and, therefore, their mode of activation could be different. All these complexes have in common that they possess the sterically more demanding *i*Pr-, ICy- or SICy-based NHCs resulting in a higher steric pressure around the metal center, which presumably facilitates dissociation of the bulky NHC and the formation of a Schrock-alkylidyne complex.

At room temperature, imidazolium salt formation was solely observed for **Mo-6** after the addition of silanol and substrate. A viable explanation could be the activation of **Mo-6** via dissociation of the NHC in the presence of phenylpropyne and the formation of a Mo alkylidyne triphenylsilyloxy complex as well as the free NHC that is readily protonated by the silanol. The other complexes of this category (**Mo-1**, **Mo-2**, **Mo-5**, and **Mo-7**) only show imidazolium formation at an elevated temperature of 80 °C. However, in those cases, the imidazolium salt forms in the presence of substrate and silanol but also when only triphenylsilanol is added. This makes it difficult to distinguish between the simple decomposition of the catalyst by the action of protic reagents in solution and the possible activation via the dissociation of the NHC ligand in the presence of substrate. Considering that the catalysts from both categories show very similar productivities and functional group tolerance in alkyne metathesis reactions, it is unlikely that the mode of activation for both is inherently different and we, therefore, assume that although the catalysts **Mo-1**, **Mo-2**, **Mo-5**, **Mo-6**, and **Mo-7** possess a more labile NHC ligand the activation pathway might still be via a cationic species or both modes of activation coexist as it was shown in previous studies for similar NHC-coordinated alkyne metathesis catalysts that both modes of activation can be present for this type of catalyst.[19]

In any case, the finding that high steric demand will favor dissociation of the NHC is crucial not only for determining the activation pathway but also as explanation for the moisture-sensitivity of complexes in solution and is giving a hint for potential decomposition pathways in the presence of protic groups in solution.

Conclusion

We developed a new class of alkyne metathesis catalysts that in their solid state can be handled in air for extended periods of time and even after 1 week in air providing high activity in alkyne metathesis reactions at a low catalyst loading of 0.2 mol%. This allows for use of the catalysts without the requirement of a glove box by using Schlenk technique provided the catalyst is kept under inert atmosphere for longer storage. Furthermore, single crystal X-ray analyses showed that the stability of the complexes can be correlated with the shielding by sterically demanding ligands. Nevertheless, the factors contributing to moisture and air stability in the solid state have a vastly different effect in solution and steric pressure leads to a more labile NHC ligand that can be easily protonated and, therefore, results in lower moisture stability in solution and decomposition of the catalyst in the presence of protic groups. This knowledge is sought to be used in further studies and guide future catalyst design to develop even more stable alkyne metathesis catalysts. For example, the utilization of CAAC ligands (relatively small substituents on the CAAC would be required to allow for coordination to the sterically

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crowded Mo silyloxy complexes) could, due to their stronger σ-donor properties,[29] lead to a more robust Mo-carbene bond. Indeed, it was shown that metal-CAAC complexes in many cases excel their NHC counterparts in terms of stability and catalytic activity.[29] In addition, it might be beneficial to investigate advanced strategies for a more efficient 2-butyne removal to reach higher conversions. This could, for example, be achieved by conducting the reaction under a constant flow of N_2. Those experiments are underway; results will be reported in due course.

Experimental Section

General considerations: All oxygen and moisture-sensitive reactions were carried out under nitrogen atmosphere unless stated otherwise using standard Schlenk techniques or a glove box (Labmaster 130, Mbraun, Garching, Germany; oxygen and water levels were kept below 0.1 ppm). The glassware used for Schlenk line manipulations was stored overnight at 140 °C in a drying cabinet or heated to 600 °C for 15 minutes under vacuum immediately before use. Glassware used inside the glove box was stored overnight at 140 °C in a drying oven and placed into an antechamber under vacuum for 30 minutes before use. Starting materials and reagents were purchased from Alfa Aesar (Karlsruhe, Germany), Merck (Darmstadt, Germany), TCI (Eschborn, Germany) or abcr (Karlsruhe, Germany) and used as received unless stated otherwise. Dichloromethane, diethyl ether, toluene and n-pentane used for the reactions were dried over a solvent purification system (SPS, MBraun) and stored over molecular sieves (4 Å). Benzene was dried over CaH_2, distilled and stored over molecular sieves (4 Å). 1,2-Dichloroethane (anhydrous) and CH_3CN (anhydrous) were purchased from Merck (Darmstadt, Germany) and as well stored over 4 Å molecular sieves. Elemental analyses were carried out at the Institute of Inorganic Chemistry, University of Stuttgart, Germany, using a Perkin Elmer Analyzer 240. NMR spectra were recorded on a Bruker Avance III 400; chemical shifts are reported in ppm relative to the solvent signal (C_6D_6 7.16 ppm, CD_2Cl_2 5.13 ppm, 1,2-dichloroethane-d_4 3.76 ppm) and the data are reported in the following format: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sept = septet, br = broad, m = multiplet), coupling constants (Hz) and integration. GC-MS analyses were performed on an Agilent Technologies 5975 C inert MSD device consisting of a triple-axis detector, a 7693 autosampler and a 7890 A GC system equipped with an SPB-5 fused silica column (34.13 m × 0.25 mm × 0.25 μm film thickness). Single-crystal X-ray analyses were performed on a Bruker Kappa APEXII Duo diffractometer at the Institute of Organic Chemistry, University of Stuttgart at 130 K or 135 K using Cu Kα (λ = 1.54178 Å) or Mo Kα (λ = 0.71073 Å) irradiation. The SAINT program package was used for cell refinement and the absorption correction was conducted with SADBAS. SHELXL97 was used to solve the structure by direct methods and also for isotropic (least squares methods) and anisotropic refinements (on F2 of all non-hydrogen atoms).[30] Riding models were employed to calculate the position of H-atoms geometrically. Crystal data have been deposited with the Cambridge Crystallographic Data Centre (CCDC): **Mo-1** CCDC 2211989, **Mo-6** CCDC 2211990, **Mo-7** CCDC 2211991.

Preparation of precursor reagents: The following reagents have been prepared according to previously published literature procedures: [Mo(≡C(tBu))($OSiPh_3$)$_3$],[10a] [Mo(≡C(4-methoxyphenyl))($OSiPh_3$)$_3$],[10c] [Mo(≡C(2,4,6-trimethylphenyl))($OSiPh_3$)$_3$],[31] 1,3-diisopropylimidazol-2-ylidene,[32] 1,3-dicyclohexylimidazol-2-ylidene,[33] 1,3-dicyclohexyl-4,5-dihydroimidazol-2-ylidene,[34] 1,3-dimethylimidazol-2-ylidene,[35] 1,3-dimethyl-4,5-dichloroimidazol-2-ylidene.[35]

Synthesis of complexes

[Mo(≡C(4-methoxyphenyl))($OSiPh_3$)$_3$(1,3-diisopropylimidazol-2-ylidene)] (Mo-1): To a solution of [Mo(≡C(Ar))($OSiPh_3$)$_3$] (Ar = 4-methoxyphenyl) (200 mg, 192 μmol, 1.00 equiv.) in benzene (1 mL) was slowly added I*i*Pr (30.7 mg, 202 μmol, 1.05 equiv.) in benzene (1 mL) and the reaction solution was stirred for 2 h at rt. The solvent was removed *in vacuo* and the remaining solid was then washed with diethyl ether (3 × 1 mL). After drying *in vacuo* the product was isolated as a grey-green solid (131 mg, 57 %). More product can be crystallized by storing the washing solution at −35 °C overnight. The product can be recrystallized from CH_2Cl_2/MeCN solution at −35 °C overnight resulting in burgundy-colored crystals.^{1}H NMR (400 MHz, C_6H_6) δ 7.93–7.80 (m, 6H, O–Si–Ar), 7.68–7.51 (m, 12H, O–Si–Ar), 7.14–7.07 (m, 9H, O–Si–Ar), 7.06–6.99 (m, 12H, O–Si–Ar), 6.98–6.92 (m, 6H, O–Si–Ar), 6.64 (d, J = 8.9 Hz, 2H, Mo≡C–Ar), 6.47 (d, J = 8.9 Hz, 2H, Mo≡C–Ar), 6.18 (d, J = 1.8 Hz, 1H, NHC-backbone), 6.11 (d, J = 1.7 Hz, 1H, NHC-backbone), 5.38 (h, J = 6.9 Hz, 1H, $CH(CH_3)_2$), 4.74 (h, J = 6.9 Hz, 1H, $CH(CH_3)_2$), 3.19 (s, 3H, OMe), 0.86 (d, J = 6.6 Hz, 6H, $CH(CH_3)_2$), 0.51 (d, J = 6.7 Hz, 6H, $CH(CH_3)_2$). ^{13}C NMR (101 MHz, CD_2Cl_2) δ 292.9 (Mo≡C), 188.9 (N–C–N), 159.0 (Ar), 139.4 (Ar), 139.0 (Ar), 138.9 (Ar), 136.2 (Ar), 136.1 (Ar), 136.0 (Ar), 132.9 (Ar), 132.9 (Ar), 129.3 (Ar), 129.2 (Ar), 129.0 (Ar), 128.9 (Ar), 128.9 (Ar), 127.9 (Ar), 127.8 (Ar), 127.6 (Ar), 127.5 (Ar), 116.9 (Ar), 116.7 (Ar), 116.4 (Ar), 116.2 (Ar), 112.6 (NHC-backbone), 112.5 (NHC-backbone), 55.7 (N–$CH(CH_3)_2$), 55.6 (N–$CH(CH_3)_2$), 52.4 (O–Me), 23.7 (N–$CH(CH_3)_2$), 23.6 (N–$CH(CH_3)_2$), 23.3 (N–$CH(CH_3)_2$), 23.2 (N–$CH(CH_3)_2$). Anal. calcd. for $C_{71}H_{68}MoN_2O_4Si_3$: C, 71.45; H, 5.74; N, 2.35; Found: C, 71.14; H, 5.70; N, 2.40.

[Mo(≡C(4-methoxyphenyl))($OSiPh_3$)$_3$(1,3-dicyclohexylimidazol-2-ylidene)] (Mo-2): To a solution of [Mo(≡C(Ar))($OSiPh_3$)$_3$] (Ar = 4-methoxyphenyl) (200 mg, 192 μmol) in benzene (1 mL) was slowly added ICy (46.9 mg, 202 μmol, 1.05 equiv.) in benzene (1 mL) and the reaction solution was stirred for 2 h at rt. The solvent was removed *in vacuo* and the dark red solid was then washed with diethyl ether (3 × 2 mL) and dried *in vacuo*. The product was finally isolated as a green solid (100 mg, 41 %). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.55–7.47 (m, 6H, O–Si–Ar), 7.36 (s, 1H, O–Si–Ar), 7.28–7.14 (m, 20H, O–Si–Ar), 7.04–6.98 (m, 12H, O–Si–Ar), 6.95–6.88 (m, 7H, O–Si–Ar, NHC-backbone), 6.84 (d, J = 1.5 Hz, 1H, NHC-backbone), 6.35 (d, J = 8.7 Hz, 2H, Mo≡C–Ar), 6.10 (d, J = 8.7 Hz, 2H, Mo≡C–Ar), 4.92 (tt, J = 12.0, 3.3 Hz, 1H, N–CH-$(CH_2)_5$), 4.14 (tt, J = 11.5, 2.9 Hz, 1H, N–CH$(CH_2)_5$), 3.72 (s, 3H, OMe), 1.75–1.59 (m, 3H, N–CH($CH_2)_5$), 1.58–0.92 (m, 14H, N–CH($CH_2)_5$), 0.85–0.69 (m, 1H, N–CH($CH_2)_5$), 0.38–0.10 (m, 2H, N–CH($CH_2)_5$). ^{13}C NMR (101 MHz, CD_2Cl_2) δ 292.2 (Mo≡C), 189.1 (N–C–N), 159.1 (Ar), 139.5 (Ar), 139.0 (Ar), 138.8 (Ar),

136.2 (Ar), 136.1 (Ar), 133.4 (Ar), 129.2 (Ar), 129.0 (Ar), 128.9 (Ar), 127.8 (Ar), 127.6 (Ar), 117.0 (Ar), 116.9 (NHC-backbone), 112.6 (NHC-backbone), 60.3 (N–CH(CH$_2$)$_5$), 60.0 (N–CH(CH$_2$)$_5$), 55.8 (O–Me), 34.1 (N–CH(CH$_2$)$_5$), 33.9 (N–CH(CH$_2$)$_5$), 26.2 (N–CH(CH$_2$)$_5$), 25.7 (N–CH(CH$_2$)$_5$), 25.5 (N–CH(CH$_2$)$_5$), 25.1 (N–CH(CH$_2$)$_5$). Anal. calcd. for $C_{77}H_{76}MoN_2O_4Si_3$: C, 72.61; H, 6.01; N, 2.20; Found: C, 72.60; H, 6.12; N, 2.04.

[Mo(≡C(4-methoxyphenyl))(OSiPh$_3$)$_3$(1,3-dimethyl-4,5-dichloroimidazol-2-ylidene)] (Mo-3): To a solution of [Mo(≡C(Ar))(OSiPh$_3$)$_3$] (Ar = 4-methoxyphenyl) in benzene (1.5 mL) a suspension of the NHC-silver adduct of IMeCl$_2$ (present as (NHC)$_4$Ag$_6$I$_6$; 208 mg, 101 μmol, 0.35 equiv) in benzene (2 mL) was added slowly and the reaction mixture was then stirred for 2 h at rt. The mixture was filtered over celite and the solvent was removed *in vacuo*. The residual solid was washed with diethyl ether (3 × 2 mL) and subsequently dried under reduced pressure. The product was isolated as a red solid (280 mg, 81 %). ^{1}H NMR (400 MHz, CD$_2$Cl$_2$) δ 7.84–7.75 (m, 6H, O–Si–Ar), 7.65–7.50 (m, 12H, O–Si–Ar), 7.35–7.28 (m, 6H, O–Si–Ar), 7.23–7.10 (m, 15H, O–Si–Ar), 6.99–6.89 (m, 6H, O–Si–Ar), 6.45 (d, J = 8.8 Hz, 2H, Mo≡C–Ar), 6.32 (d, J = 8.8 Hz, 2H, Mo≡C–Ar), 3.75 (s, 3H, OMe), 3.46 (s, 3H, N–Me), 2.78 (s, 3H, N–Me). ^{13}C NMR (101 MHz, CD$_2$Cl$_2$) δ 294.4 (Mo≡C), 189.6 (N–C–N), 159.4 (Ar), 139.5 (Ar), 139.5 (Ar), 139.2 (Ar), 138.1 (Ar), 136.1 (Ar), 135.7 (Ar), 133.2 (Ar), 129.6 (Ar), 129.3 (Ar), 128.0 (Ar), 127.8 (Ar), 116.5 (Ar), 116.4 (NHC-backbone), 112.9 (NHC-backbone), 55.8 (O–Me), 37.4 (N–Me), 35.7 (N–Me). Anal. calcd. for $C_{67}H_{58}MoN_2O_4Si_3$: C, 66.71; H, 4.85; N, 2.32; Found: C, 66.76; H, 5.09; N, 2.08.

[Mo(≡C(4-methoxyphenyl))(OSiPh$_3$)$_3$(1,3-dimethylimidazol-2-ylidene)] (Mo-4): A solution of [Mo(≡C(Ar))(OSiPh$_3$)$_3$] (Ar = 4-methoxyphenyl) (200 mg, 192 μmol, 1.00 equiv.) in CH$_2$Cl$_2$ (2 mL) was added to the NHC-silver adduct of IMe (present as (NHC)$_4$Ag$_6$I$_6$; 121 mg, 67.2 μmol, 0.35 equiv.) and the resulting suspension was stirred for 1.5 h at rt. The mixture was filtered over celite and the solvent was removed *in vacuo*. The remaining solid was then washed with diethyl ether (3 × 2 mL). After drying *in vacuo* the product was isolated as a pale pink solid. (168 mg, 77 %). ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.00–7.87 (m, 6H, O–Si–Ar), 7.73–7.67 (m, 12H, O–Si–Ar), 7.48–7.39 (m, 6H, O–Si–Ar), 7.38–7.32 (m, 3H, O–Si–Ar), 7.31–7.19 (m, 12H, O–Si–Ar), 7.18–7.03 (m, 6H, O–Si–Ar), 6.65 (d, J = 9.0 Hz, 2H, Mo≡C–Ar), 6.60 (d, J = 9.0 Hz, 2H, Mo≡C–Ar), 6.40–6.33 (m, 1H, NHC-backbone), 6.08–6.07 (m, 1H, NHC-backbone), 3.96 (s, 3H, OMe), 3.68 (s, 3H, N–Me), 2.71 (s, 3H, N–Me). ^{13}C NMR (101 MHz, CDCl$_3$) δ 291.3 (Mo≡C), 189.5 (N–C–N), 158.5 (Ar), 139.2 (Ar), 138.7 (Ar), 138.1 (Ar), 135.7 (Ar), 135.5 (Ar), 132.7 (Ar), 128.8 (Ar), 128.6 (Ar), 127.3 (Ar), 127.2 (Ar), 120.6 (Ar), 119.4 (NHC-backbone), 112.3 (NHC-backbone), 55.2 (O–Me), 38.8 (N–Me), 37.1 (N–Me). Anal. calcd. for $C_{67}H_{60}MoN_2O_4Si_3$: C, 70.75; H, 5.32; N, 2.46; Found: C, 70.69; H, 5.27; N, 2.40.

[Mo(≡C(4-methoxyphenyl))(OSiPh$_3$)$_3$(1,3-dicyclohexyl-4,5-dihydroimidazol-2-ylidene)] (Mo-5): [Mo(≡C(Ar))(OSiPh$_3$)$_3$] (Ar = 4-methoxyphenyl) (200 mg, 192 μmol, 1.00 equiv.) was dissolved in benzene (1 mL). A solution of SICy (47.2 mg, 202 μmol, 1.05 equiv.) in benzene (1 mL) was added slowly and the reaction solution was stirred for 3 h at rt. The solvent was removed in vacuo, the solid was washed several times with n-pentane (3 × 2 mL) and then recrystallized in a mixture of Et$_2$O/n-pentane (1 : 1, 2 mL). The crude product was washed again with n-pentane (2 × 2 mL) and after drying *in vacuo* the product could be isolated as a grey solid (180 mg, 73 %). ^{1}H NMR (400 MHz, CD$_2$Cl$_2$) δ 7.53–7.43 (m, 17H, O–Si–Ar), 7.29–7.22 (m, 6H, O–Si–Ar), 7.22–7.14 (m, 4H, O–Si–Ar), 7.11–7.03 (m, 12H, O–Si–Ar), 6.97–6.86 (m, 6H, O–Si–Ar), 6.33 (d, J = 8.9 Hz, 2H, Mo≡C–Ar), 6.08 (d, J = 8.9 Hz, 2H, Mo≡C–Ar), 4.67 (tt, J = 12.3, 3.8 Hz, 1H, N–CH(CH$_2$)$_5$), 3.71 (s, 3H, OMe), 3.45 (tt, J = 12.2, 3.6 Hz, 1H, N–CH(CH$_2$)$_5$), 3.25 (dd, J = 12.6, 8.8 Hz, 2H, NHC-backbone), 3.04 (dd, J = 12.7, 8.9 Hz, 2H, NHC-backbone), 1.97 (s, 1H, N–CH(CH$_2$)$_5$), 1.65–1.34 (m, 6H, N–CH(CH$_2$)$_5$), 1.34–1.11 (m, 5H, N–CH(CH$_2$)$_5$), 1.05–0.80 (m, 5H, N–CH(CH$_2$)$_5$), 0.79–0.63 (m, 1H, N–CH(CH$_2$)$_5$), 0.46–0.27 (m, 2H, N–CH(CH$_2$)$_5$). ^{13}C NMR (101 MHz, CD$_2$Cl$_2$) δ 291.6 (Mo≡C), 208.5 (N–C–N), 158.8 (Ar), 141.7 (Ar), 139.4 (Ar), 139.1 (Ar), 138.7 (Ar), 136.7 (Ar), 136.3 (Ar), 136.2 (Ar), 135.8 (Ar), 133.1 (Ar), 129.3 (Ar), 129.0 (Ar), 127.7 (Ar), 127.6 (Ar), 112.4 (Ar), 59.0 (N–CH(CH$_2$)$_5$), 58.7 (N–CH(CH$_2$)$_5$), 55.7 (O–Me), 43.6, 43.2, 31.3 (NHC-backbone), 30.9 (NHC-backbone), 26.1 (N–CH(CH$_2$)$_5$), 25.8 (N–CH(CH$_2$)$_5$), 25.6 (N–CH(CH$_2$)$_5$), 25.1 (N–CH(CH$_2$)$_5$). Anal. calcd. for $C_{77}H_{78}MoN_2O_4Si_3$: C, 72.50; H, 6.16; N, 2.20; Found: C, 72.57; H, 6.23; N, 2.14.

[Mo(≡C(2,4,6-trimethylphenyl))(OSiPh$_3$)$_3$(1,3-diisopropylimidazol-2-ylidene)] (Mo-6): To a solution of [Mo(≡C(Ar))(OSiPh$_3$)$_3$] (Ar = 2,4,6-trimethylphenyl) (200 mg, 190 μmol, 1.00 equiv.) in benzene (1 mL) was slowly added I*i*Pr (30.4 mg, 199 μmol, 1.05 equiv.) in benzene (1 mL) and the reaction solution was stirred for 2 h at rt. The solvent was removed *in vacuo* and the remaining solid was then washed with diethyl ether (3 × 1 mL). After drying *in vacuo*, the product was isolated as a lavender-colored solid. More product can be crystallized by storing the wash solution at −35 °C overnight. The product can be recrystallized from CH$_2$Cl$_2$/pentane solution at −35 °C overnight resulting in deep purple crystals (144 mg, 63 %). Single crystals suitable for X-ray analysis were grown from a mixture of CH$_2$Cl$_2$/acetonitrile. ^{1}H NMR (400 MHz, CD$_2$Cl$_2$) δ 7.45–7.39 (m, 6H, Ar), 7.28–7.20 (m, 18H, Ar), 7.10–7.01 (m, 16H, Ar), 6.85–6.74 (m, 7H, Ar), 6.47–6.40 (m, 2H, NHC-backbone), 5.59 (hept, J = 6.5 Hz, 1H, CH(CH$_3$)$_2$), 4.40 (hept, J = 6.9 Hz, 1H, CH(CH$_3$)$_2$), 2.19 (s, 3H, Mes-*p*-CH$_3$), 2.05 (s, 6H, Mes-*o*-CH$_3$), 0.92 (d, J = 6.7 Hz, 6H, CH(CH$_3$)$_2$), 0.44 (d, J = 6.6 Hz, 6H, CH(CH$_3$)$_2$). ^{13}C NMR (101 MHz, CD$_2$Cl$_2$) δ 298.4 (Mo≡C), 189.1 (N–C–N), 142.4 (Ar), 141.4 (Ar), 139.3 (Ar), 139.2 (Ar), 138.0 (Ar), 136.3 (Ar), 136.1 (Ar), 129.2 (Ar), 129.2 (Ar), 129.0 (Ar), 127.8 (Ar), 127.7 (Ar), 127.4 (Ar), 127.3 (Ar), 117.2 (NHC-backbone), 117.1 (NHC-backbone), 53.2 (O–Me), 52.2 (N–CH(CH$_3$)$_2$), 52.1 (N–CH(CH$_3$)$_2$), 23.7 (Me), 23.7 (Me), 23.5 (Me), 23.4 (Me), 21.6 (Me), 21.5 (Me), 21.4 (Me), 21.3 (Me). Anal. calcd. for $C_{73}H_{72}MoN_2O_3Si_3$: C, 72.73; H, 6.02; N, 2.32; Found: C, 72.97; H, 6.37; N, 2.08.

[Mo(≡C(*t*Bu))(OSiPh$_3$)$_3$(1,3-diisopropylimidazol-2-ylidene)] (Mo-7): To a solution of [Mo(≡C(*t*Bu))(OSiPh$_3$)$_3$] (200 mg, 202 μmol, 1.00 equiv.) in benzene (1 mL) was slowly added I*i*Pr (32.3 mg, 212 μmol, 1.05 equiv.) in benzene (2 mL) and the reaction solution was stirred for 2 h at rt. The solvent was removed *in vacuo* and the remaining solid was then

washed with diethyl ether (3×1 mL). After drying *in vacuo* the product was isolated as a brown powder (140 mg, 61%). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.60–7.47 (m, 8H, O–Si–Ar), 7.33–7.14 (m, 21H, O–Si–Ar), 7.12–6.97 (m, 19H, O–Si–Ar, NHC-backbone), 6.91 (d, J = 2.0 Hz, 1H, NHC-backbone), 5.71 (hept, J = 6.8 Hz, 1H, $CH(CH_3)_2$), 4.71 (sept, J = 6.8 Hz, 1H, $CH(CH_3)_2$), 1.08 (d, J = 6.8 Hz, 6H, $CH(CH_3)_2$), 1.02 (d, J = 6.7 Hz, 6H, $CH(CH_3)_2$), 0.66 (s, 9H, *t*Bu). ^{13}C NMR (101 MHz, CD_2Cl_2) δ 312.3 (Mo≡C), 189.5 (N–C–N), 139.5 (Ar), 139.2 (Ar), 136.3 (Ar), 136.1 (Ar), 136.0 (Ar), 129.2 (Ar), 129.1 (Ar), 127.7 (Ar), 127.6 (Ar), 127.6 (Ar), 117.2 (Ar), 117.0 (Ar), 116.3 (NHC-backbone), 116.2 (NHC-backbone), 52.8 (CMe_3), 52.2 (N–$CH(CH_3)_2$), 52.2 (N–CH-$(CH_3)_2$), 29.8 (Me), 29.8 (Me), 23.7 (Me), 23.7 (Me), 23.6 (Me), 23.5 (Me). Anal. calcd. for $C_{68}H_{70}MoN_2O_3Si_3$: C, 71.42; H, 6.17; N, 2.45; Found: C, 71.26; H, 6.02; N, 2.31.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

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