

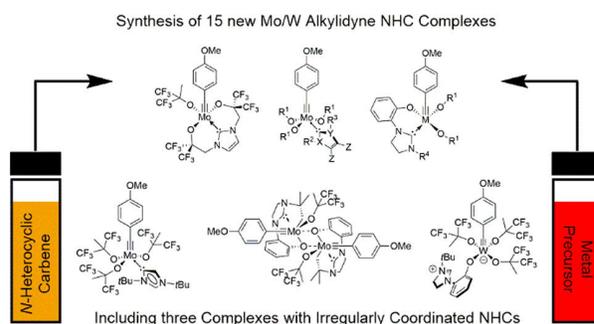
# Molybdenum and Tungsten Alkylidyne Complexes Containing Mono-, Bi-, and Tridentate *N*-Heterocyclic Carbenes

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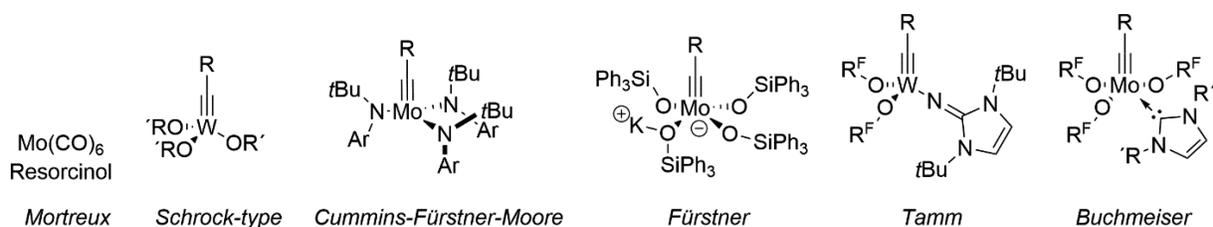
**ABSTRACT:** New tungsten and molybdenum alkylidyne complexes bearing mono-, bi-, and tridentate *N*-heterocyclic carbenes (NHCs) have been synthesized. Formation of unprecedented structures in complexes bearing *N*-*tert*-butyl substituents on the imidazol(in)-2-ylidene was observed, leading to molybdenum complexes containing an abnormal carbene (**Mo-4**) and a bridging O,C,C-pincer ligand (**Mo-10**) and to a tungsten complex containing a cationic imidazolium-tagged alkoxide forming an inner salt with an anionic tungsten center (**W-5**). Both the abnormal carbene binding in **Mo-4** and the O,C,C-pincer-type structure of **Mo-10** were confirmed by single-crystal X-ray analysis, and the proposed structure of **W-5** is supported by the single-crystal X-ray structure of a minor byproduct (**W-8**) formed during the synthesis of **W-4**, displaying the aforementioned inner-salt-like structure. The novel alkylidyne complexes were also investigated for their capability to form a previously postulated quasi-cationic species with a weakly coordinating anion (WCA) during the alkyne homometathesis of 1-phenyl-1-propyne. Overall, incorporation of bidentate and strongly  $\sigma$  donating NHCs as well as introduction of better leaving groups did not lead to the expected increase in catalytic activity. Despite identical ligand spheres, changing from molybdenum to tungsten led to complete loss of activity in the bidentate systems.



## INTRODUCTION

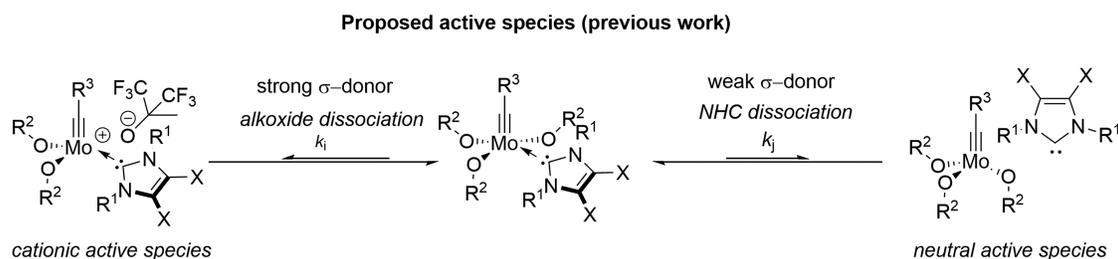
During the last 30 years, alkyne metathesis has made enormous progress, starting from “ill-defined” metathesis catalysts to those whose structure and reactivity in solution can be controlled with high precision.<sup>1</sup> Enormous synthetic efforts made by a multitude of organometallic chemists paved the way from the first catalytically active  $\text{WO}_3$  or  $\text{MoO}_3$  compounds supported on silica to the sophisticated catalyst systems applied today.<sup>2</sup> Seminal work by Schrock,<sup>3</sup> Fürstner,<sup>4</sup> Tamm,<sup>5</sup> Mortreux,<sup>6</sup> Cummins,<sup>7</sup> Moore<sup>8</sup> and Zhang<sup>2e,9</sup> contributed to the development of well-defined alkyne metathesis catalysts.<sup>10</sup> Apart from Schrock-type tris(alkoxy) metal alkylidyne complexes, catalysts bearing multidentate ligands,<sup>2e,9b,11</sup> electronically and sterically flexible silyloxy ligands,<sup>4c,d</sup> or imidazolin-2-iminato ligands<sup>5a-d</sup> have been reported (Figure 1). In all catalyst systems tetracoordinated species have been identified as the active species. Even the Fürstner-type pentacoordinated complexes dissociate one of the silanolates to form a neutral tetracoordinated active species prior to alkyne coordination.<sup>4d</sup> In this context, the alkyne metathesis activity of our recently published pentacoordinated 14-VE molybdenum tris(hexafluoro-*tert*-butoxide) *N*-heterocyclic car-

bene (NHC) alkylidyne complexes deserves an explanation (Figure 1, right).<sup>12</sup> Mechanistic investigations suggested that, depending on the incorporated NHC, the pentacoordinated complexes either dissociate the carbene under the formation of a neutral Schrock-type alkylidyne complex or form a quasi-cationic species with the alkoxide serving as a weakly coordinating anion (WCA, Scheme 1, top). Here, strongly  $\sigma$  donating NHCs, allowing for strong metal–carbene bonds, promote the latter. However, the proposed quasi-cationic species was found to form to a very minor extent (approximately 1%). We assumed this low concentration of the active species to translate into the observed moderate activity in alkyne metathesis. Unfortunately, up to this point, we were not able to isolate the cationic species or unambiguously prove its existence. Two factors were expected to foster the formation of the proposed active species: first, the stabilization of the positive partial charge at the metal complex and, second, the stabilization of the anionic charge in the WCA.

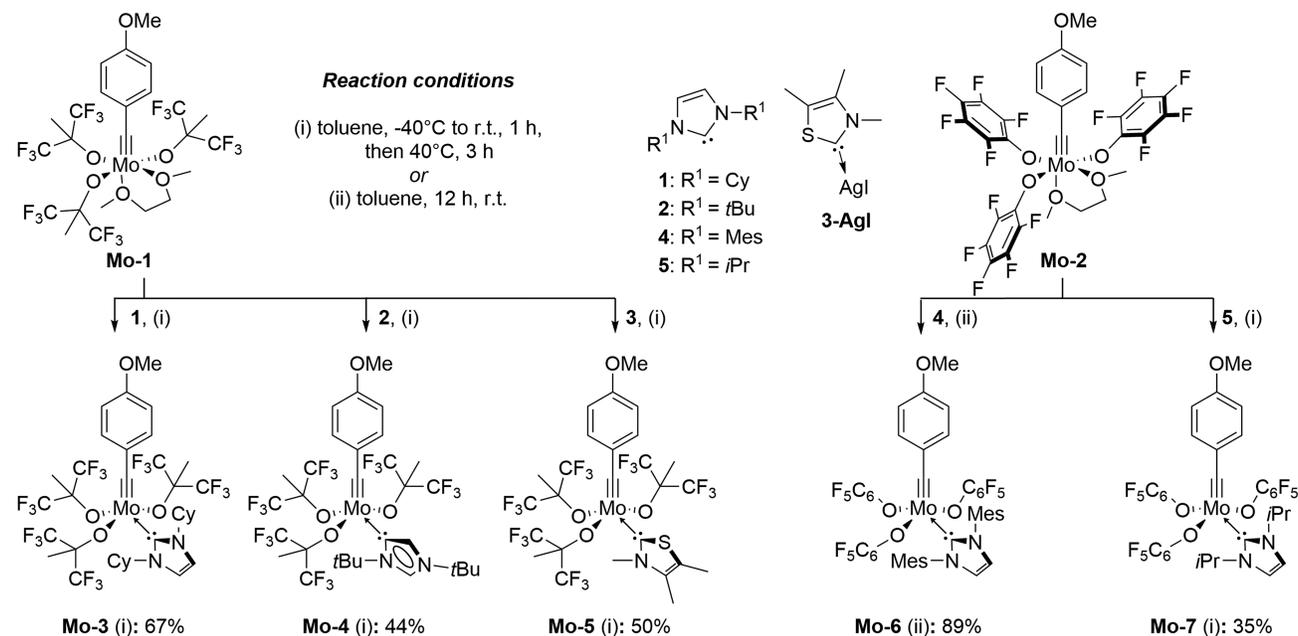


**Figure 1.** Well-defined alkyne metathesis catalysts developed in the groups of Mortreux,<sup>6</sup> Schrock,<sup>3a-i</sup> Cummins,<sup>7</sup> Fürstner,<sup>4a-d</sup> Moore,<sup>8</sup> Tamm<sup>5b-e</sup> and Buchmeiser.<sup>12</sup>

**Scheme 1. (Top) Proposed Active Species (Previous Work) and Measures Taken in This Work to Increase the Concentration and Stability of the Proposed Active Species and (Bottom) Synthesis of New Molybdenum Alkyldiyne NHC Complexes Bearing Monodentate NHCs<sup>4</sup>**



**This work: Stabilization of assumed cationic active species by introduction of bidentate ligands, strong  $\sigma$ -donors, good leaving groups**



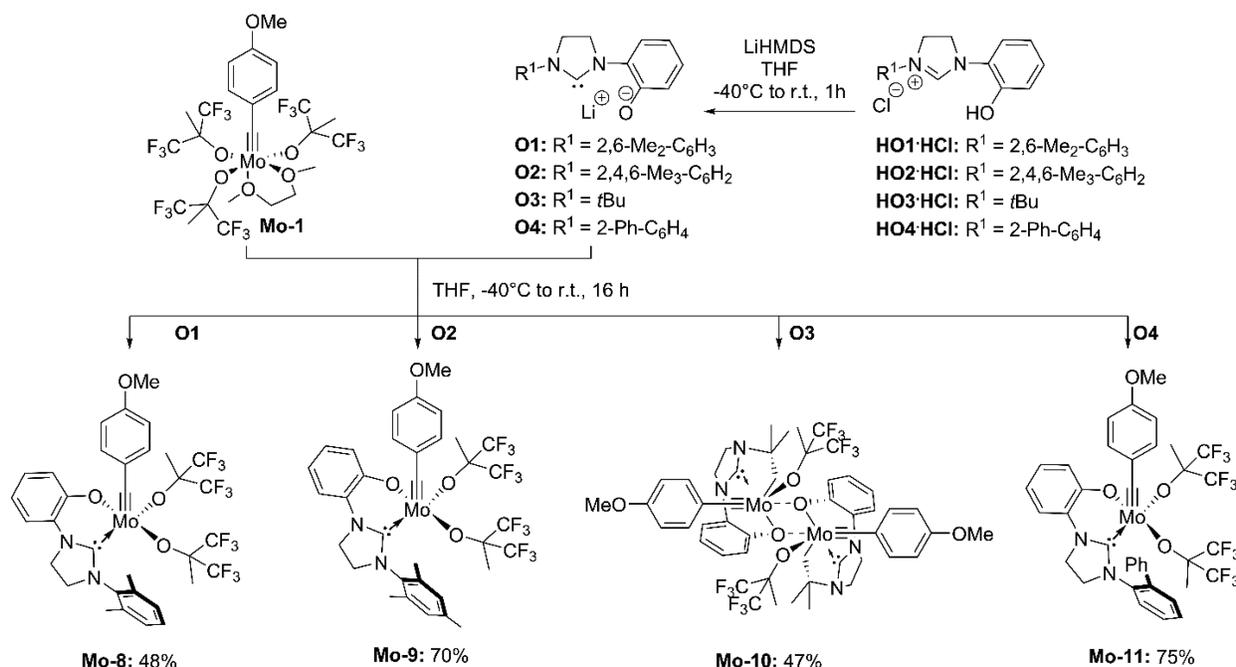
<sup>a</sup>Isolated yields are given in percent.

In this work, stabilization of the cationic charge on the metal center was attempted by introduction of strong  $\sigma$  donors and by incorporation of bi- and tridentate ligands into the catalyst structures. Stabilization of the anionic charge on the WCA was addressed by the introduction of more acidic alcohols. Strong  $\sigma$  donors were additionally expected to result in a stronger trans effect, thereby lowering the activation energy for the formation of the catalytically active metal complex. Incorporation of multidentate NHCs also minimizes the chances of generating the tetracoordinated active species by NHC dissociation (Scheme 1, top).

## SYNTHESIS

**Monodentate NHC Alkyldiyne Complexes.** Several novel complexes bearing monodentate NHCs based on the tris(hexafluoro-*tert*-butoxide) precursor  $\text{Mo}(\equiv\text{C}-p\text{-OMe}-\text{C}_6\text{H}_4)(\text{OCMe}(\text{CF}_3)_2)_3(\text{DME})$  (**Mo-1**) were synthesized. The applied NHC ligands were chosen for several reasons: both 1,3-dicyclohexylimidazol-2-ylidene (**1**) and 1,3-di-*tert*-butylimidazol-2-ylidene (**2**) are strong  $\sigma$  donors (Tolman electronic parameter (TEP):<sup>13</sup> **1**, 2049.7  $\text{cm}^{-1}$ ; **2**, 2050.6  $\text{cm}^{-1}$ ). Due to their low TEPs, they were expected to enhance the formation of the proposed quasi-cationic reactive species

**Scheme 2. Synthesis of Molybdenum Alkylidyne Complexes with Bidentate O-Chelating NHCs (Mo-8–Mo-11) by Conversion with NHCs O1–O4<sup>a</sup>**



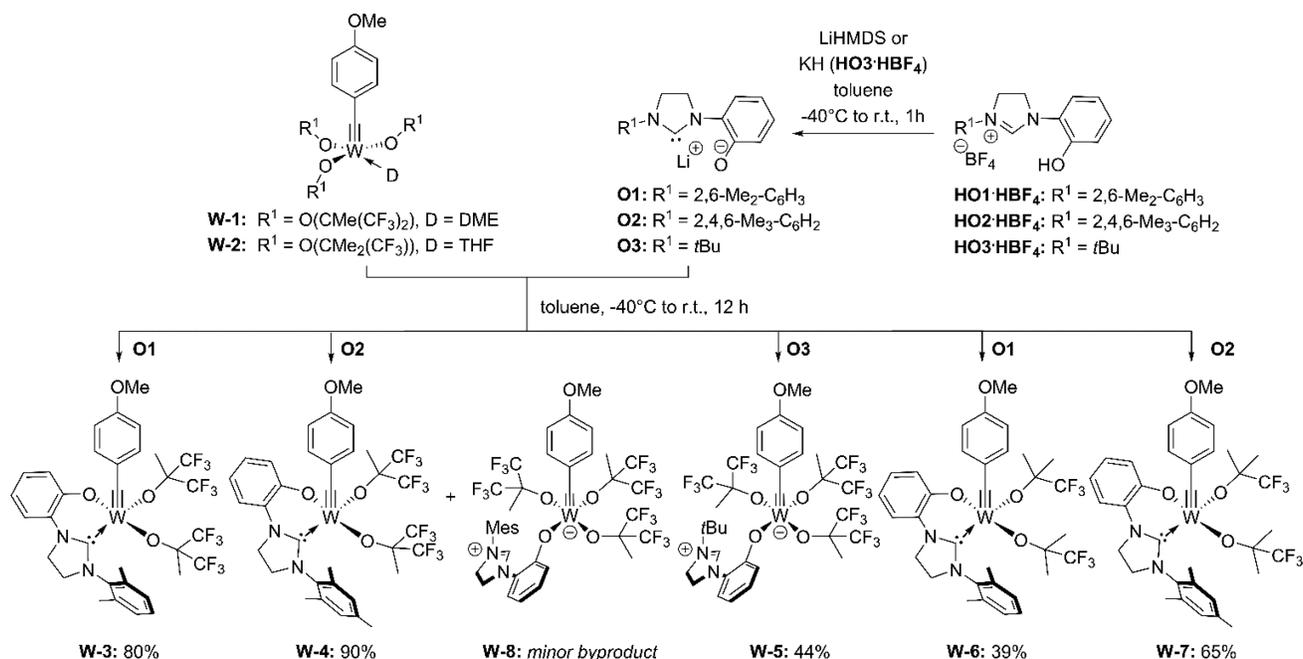
<sup>a</sup>NHCs were generated without isolation *prior* to metal complex synthesis by deprotonation of the respective imidazolium chlorides HOX·HCl. Isolated yields are given in percent.

by their trans effect on the weakly coordinating anion OCMe(CF<sub>3</sub>)<sub>2</sub>. Furthermore, strong  $\sigma$  donors can stabilize the positive partial charge on the metal complex. On the other hand, 3,4,5-trimethylthiazol-2-ylidene (**3**), although a weak  $\sigma$  donor (TEP = 2058.5 cm<sup>-1</sup>, calculated in analogy to the literature<sup>13</sup>), was envisioned to form a strong metal–carbene bond, due to the decrease in steric bulk resulting from the missing 1-substituent in the thiazol-2-ylidene. It therefore seemed unlikely that the NHC would dissociate to form the proposed neutral tetracoordinated active species (Scheme 1, top). Consequently, the precursor complex **Mo-1** was reacted with the *N*-heterocyclic carbenes **1** and **2** and the carbene silver salt **3-Agl**, respectively, in toluene at 40 °C to afford the complexes Mo( $\equiv$ C-*p*-OMe-C<sub>6</sub>H<sub>4</sub>)(OCMe(CF<sub>3</sub>)<sub>2</sub>)<sub>3</sub>(X) (**Mo-3** (X = **1**), **Mo-4** (X = **2**), and **Mo-5** (X = **3**)) in 67, 44, and 50% isolated yields, respectively. **Mo-3** and **Mo-5** showed the expected <sup>1</sup>H and <sup>19</sup>F NMR spectra in C<sub>6</sub>D<sub>6</sub>. Interestingly, **Mo-3** with the sterically demanding cyclohexyl-substituted NHC showed a rearrangement from a square-pyramidal (SP) to a trigonal-bipyramidal (TBP) structure in CD<sub>3</sub>CN (Figures S69 and S70 in the Supporting Information). This change in geometry was already reported for Mo( $\equiv$ C-*p*-OMe-C<sub>6</sub>H<sub>4</sub>)(OCMe(CF<sub>3</sub>)<sub>2</sub>)<sub>3</sub>(**5**) (**Mo-12**).<sup>12</sup>

The two protons on the carbon atom adjacent to the nitrogen atoms become magnetically equivalent. Also, the imidazol-2-ylidene backbone protons show up as a singlet at  $\delta$  7.43 ppm instead of the two doublets at  $\delta$  7.24 ppm (d, 1H, <sup>3</sup>J<sub>H-H</sub> = 2.0 Hz) and  $\delta$  7.28 ppm (d, 1H, <sup>3</sup>J<sub>H-H</sub> = 2.0 Hz) in the corresponding parent complex. In the <sup>19</sup>F NMR spectrum only one new signal for all three OCMe(CF<sub>3</sub>)<sub>2</sub> ligands at  $\delta$  -76.7 ppm could be observed. Complex **Mo-4** shows a surprising <sup>1</sup>H NMR spectrum: the two protons in the backbone of the 1,3-di-*tert*-butylimidazol-2-ylidene show up as a doublet at  $\delta$  7.86

ppm (d, <sup>4</sup>J<sub>HH</sub> = 1.8 Hz) and a broad singlet at  $\delta$  7.09 ppm. The small coupling constant of 1.8 Hz hints toward a <sup>4</sup>J<sub>H-H</sub> coupling. In combination with the splitting of the *N-tert*-butyl groups into two overlapping singlets at  $\delta$  1.64 ppm in the <sup>1</sup>H NMR spectrum, we expected a structure with an abnormally bound imidazol-2-ylidene, which was later confirmed by single-crystal X-ray measurements (*vide infra*). The <sup>19</sup>F NMR spectra of **Mo-3–Mo-5** indicate a square-pyramidal (SP) structure in solution, with one of the alkoxide ligands in the apex, since three distinct resonances for the CF<sub>3</sub> groups are observed. This indicates that the CF<sub>3</sub> groups are diastereotopic, in turn indicating that the molybdenum center is chiral. Chirality in pentacoordinated complexes of the type Ma<sub>3</sub>bc is only present in a SP structure with one of the three equal ligands in the apex. **Mo-3–Mo-5** are all based on the OCMe(CF<sub>3</sub>)<sub>2</sub> ligand; however, a careful choice of the alkoxide ligand can drastically alter the catalytic performance. Consequently, we targeted an exchange of the alkoxide ligand into a better leaving group (weaker base) to foster the formation of the active species. Pentafluorophenoxide is a better leaving group than hexafluoro-*tert*-butoxide (pK<sub>a</sub>: HOC<sub>6</sub>F<sub>5</sub>, 5.53;<sup>14</sup> HOCMe(CF<sub>3</sub>)<sub>2</sub>, 9.8<sup>15</sup>). Hence, we first synthesized the new precursor complex Mo( $\equiv$ C-*p*-OMe-C<sub>6</sub>H<sub>4</sub>)(OC<sub>6</sub>F<sub>5</sub>)<sub>3</sub>(DME) (**Mo-2**) from Mo( $\equiv$ C-*p*-OMe-C<sub>6</sub>H<sub>4</sub>)Br<sub>3</sub>(DME) via reaction with 3 equiv of LiOC<sub>6</sub>F<sub>5</sub> in 60% isolated yield in analogy to the literature.<sup>5d</sup> Subsequently, 1,3-dimesitylimidazol-2-ylidene (**4**) was successfully coordinated to **Mo-2** in toluene at room temperature, affording Mo( $\equiv$ C-*p*-OMe-C<sub>6</sub>H<sub>4</sub>)(OC<sub>6</sub>F<sub>5</sub>)<sub>3</sub>(**4**) (**Mo-6**) in 89% isolated yield (Scheme 1). Furthermore, **Mo-2** was reacted with 1,3-diisopropylimidazol-2-ylidene (**5**) to provide Mo( $\equiv$ C-*p*-OMe-C<sub>6</sub>H<sub>4</sub>)(OC<sub>6</sub>F<sub>5</sub>)<sub>3</sub>(**5**) (**Mo-7**) in 35% isolated yield as an analogue to the previously reported complex **Mo-12** bearing

Scheme 3. Synthesis of Tungsten Alkylidyne Complexes with Bidentate O-Chelating NHCs (W-3–W-7) by Conversion with NHCs O1–O3<sup>a</sup>



<sup>a</sup>NHCs were generated without isolation *prior* to metal complex synthesis by deprotonation of the respective imidazolium tetrafluoroborates HOX·HBF<sub>4</sub>. Isolated yields are given in percent.

three OCMe(CF<sub>3</sub>)<sub>2</sub> ligands. As judged from the <sup>19</sup>F NMR spectrum, two of the three OC<sub>6</sub>F<sub>5</sub> ligands in **Mo-6** are equivalent, whereas the third occupies another coordination site. Whether two of the OC<sub>6</sub>F<sub>5</sub> ligands are in the plane of a TBP structure and the other is in the apex or one of the three OC<sub>6</sub>F<sub>5</sub> groups experiences a trans effect (for example from the NHC) in an SP structure with all three OC<sub>6</sub>F<sub>5</sub> ligands in the plane cannot be distinguished.

**Bidentate NHC Alkylidyne Complexes.** Apart from molybdenum-based alkylidyne complexes with monodentate NHCs, we were interested in the synthesis of catalysts containing bidentate ligands. The hypothesis was that the proposed active, cationic species is stabilized by the chelate effect, which would in turn result in a better catalytic performance. Beneficially, kinetic reasons lead to a decreased propensity for bidentate vs monodentate NHCs to dissociate from the corresponding metal complexes, thereby preventing formation of a neutral active species (Scheme 1, top). Complementary, in the case of tungsten, the alkoxide ligand was varied to probe the influence of the degree of fluorination on activity.<sup>5j</sup> Several O-chelating NHCs were synthesized according to or in analogy to the literature.<sup>16</sup> Ligand properties of the NHCs were varied by altering the nonchelating N-substituent from the *N-tert*-butyl (**O3**) to the *N-2,6*-dimethylphenyl (**O1**), the *N-2,4,6*-trimethylphenyl (**O2**), and the *N-2*-phenylphenyl (**O4**) substituent to span a wide range of steric hindrance. Also, the 2-phenylphen-1-yl-substituted NHC (**O4**) offers flexibility, allowing the phenyl group to either shield the metal center or open it to attacks. Carbenes were synthesized directly *prior* to metal complex formation by deprotonation of the respective imidazolium salt with LiHMDS, KHMDS, or KH. The molybdenum-based complexes Mo(≡C-*p*-OMe-C<sub>6</sub>H<sub>4</sub>)(OCMe(CF<sub>3</sub>)<sub>2</sub>)<sub>2</sub>(**OX**) (**Mo-8** (**O1**), **Mo-9** (**O2**), **Mo-11** (**O4**)) and [Mo(≡C-*p*-OMe-

C<sub>6</sub>H<sub>4</sub>)(OCMe(CF<sub>3</sub>)<sub>2</sub>)(**O3**)]<sub>2</sub> (**Mo-10**) were synthesized from **Mo-1** (Scheme 2). For this purpose, imidazolium salts HOX·HCl were deprotonated with LiHMDS in THF and then reacted with **Mo-1** in THF. The corresponding complexes bearing bidentate NHCs were formed in 47–75% isolated yield. **Mo-8**, **Mo-9**, and **Mo-11** showed the expected NMR spectra. Since the pentacoordinated complexes **Mo-8–Mo-11** are all chiral at the metal center, the CF<sub>3</sub> groups and the OCMe(CF<sub>3</sub>)<sub>2</sub> ligands in the complexes are diastereotopic. This results in four multiplets (**Mo-8**, **Mo-11**) or three multiplets with a ratio of 3:3:6 (**Mo-9**) in the <sup>19</sup>F NMR spectra. Also, the diastereotopic protons in the backbones of the imidazol-2-ylidenes are fully split for all three complexes. In case of **Mo-10**, only three methyl groups instead of the expected five methyl groups were observed in the <sup>1</sup>H NMR spectrum as three singlets at δ 1.69, 1.51, and 1.33 ppm (CD<sub>2</sub>Cl<sub>2</sub>). Additionally, at δ 2.46 ppm (br s, 1H) and δ 2.00 ppm (d, <sup>2</sup>J<sub>H-H</sub> = 10.6 Hz, 1H) two unexpected signals were found, hinting toward a methylene group bearing two diastereotopic protons. We therefore envisioned a structure containing an O,C,C-pincer-type NHC, derived from abstraction of one proton from the *tert*-butyl substituent on the NHC and replacement of one OCMe(CF<sub>3</sub>)<sub>2</sub> ligand by the resulting carbanion (Scheme 2). In line with this proposal, two distinct signals for the two diastereotopic CF<sub>3</sub> groups can be observed in the <sup>19</sup>F NMR spectrum at δ -78.1 and -78.4 ppm due to the chirality at the metal center. The formation of **Mo-10** is proposed to proceed via an intramolecular C–H activation of the *tert*-butyl group followed by release of HOCMe(CF<sub>3</sub>)<sub>2</sub>. Comparable C–H activations on NHC ligands by replacement of an anionic ligand have been observed in molybdenum imido alkylidyne NHC complexes or in ruthenium NHC alkylidyne complexes.<sup>17</sup> The tungsten-based complexes W(≡C-*p*-OMe-C<sub>6</sub>H<sub>4</sub>)(OCMe(CF<sub>3</sub>)<sub>2</sub>)<sub>2</sub>(**OX**) (**W-3** (**O1**) and **W-4** (**O2**)) and

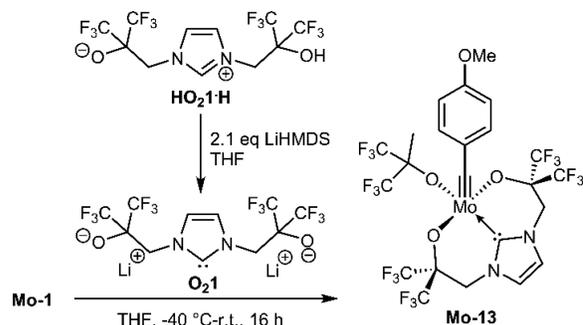
W( $\equiv$ C-*p*-OMe-C<sub>6</sub>H<sub>4</sub>)(OCMe(CF<sub>3</sub>)<sub>2</sub>)<sub>3</sub>(O<sub>3</sub>-H) (**W-5**) were synthesized from W( $\equiv$ C-*p*-OMe-C<sub>6</sub>H<sub>4</sub>)(OCMe(CF<sub>3</sub>)<sub>2</sub>)<sub>3</sub>(DME) (**W-1**). The complexes W( $\equiv$ C-*p*-OMe-C<sub>6</sub>H<sub>4</sub>)(OCMe(CF<sub>3</sub>)<sub>2</sub>)<sub>2</sub>(O<sub>1</sub>) (**W-6** (**O1**)) and W( $\equiv$ C-*p*-OMe-C<sub>6</sub>H<sub>4</sub>)(OCMe(CF<sub>3</sub>)<sub>2</sub>)<sub>2</sub>(O<sub>2</sub>) (**W-7** (**O2**)) were derived from W( $\equiv$ C-*p*-OMe-C<sub>6</sub>H<sub>4</sub>)(OCMe<sub>2</sub>(CF<sub>3</sub>)<sub>3</sub>)(THF) (**W-2**) (Scheme 3). All reactions employing tungsten precursors were done in toluene, and the imidazolium tetrafluoroborates HOX·HBF<sub>4</sub> were used instead of the chlorides. Deprotonation of imidazolium salts HOX·HBF<sub>4</sub> was performed in toluene with LiHMDS (**O1**, **O2**) or KH (**O3**). Complexes **W-3–W-7** were isolated by crystallization in 39–90% yield. **W-3**, **W-4**, **W-6**, and **W-7** showed regular structures, as judged from the NMR spectra. As already mentioned for molybdenum, **W-3–W-7** are chiral at the metal center. Therefore, **W-3** and **W-4** each display four distinct multiplets in the <sup>19</sup>F NMR spectrum, representing two diastereotopic CF<sub>3</sub> groups in two diastereotopic OCMe(CF<sub>3</sub>)<sub>2</sub> ligands. For **W-6** and **W-7**, two singlets can be observed in the <sup>19</sup>F NMR spectrum, which is in accordance with two diastereotopic OCMe<sub>2</sub>CF<sub>3</sub> ligands. Interestingly, for the reaction of carbene **O3** bearing the *N-tert*-butyl substituent with the precursor **W-1** an irregular structure was observed, as indicated by the NMR spectra. The resulting complex **W-5** shows an unexpected signal at  $\delta$  8.63 ppm (s, 1H) in the <sup>1</sup>H NMR spectrum. This signal is assigned to an imidazolium species, pointing toward a structure where only the phenolate group is coordinated to the metal center, yielding a tungstate complex (Scheme 3). The existence of an imidazolium species is also supported by <sup>13</sup>C NMR spectroscopy; the signal at  $\delta$  159.7 ppm can be clearly assigned to the imidazolium salt. A structure in which one OCMe(CF<sub>3</sub>)<sub>2</sub> ligand was replaced by the phenolate can be ruled out, since nine protons are observed for the OCMe(CF<sub>3</sub>)<sub>2</sub> ligand. The inner-salt-like structure is further confirmed by the absence of a BF<sub>4</sub><sup>-</sup> signal in the <sup>19</sup>F NMR spectrum. **W-5** shows two multiplets in the <sup>19</sup>F NMR spectrum, with a ratio of 12:6. In order to elucidate the formation of the unusual structure of **W-5** we investigated the reaction by <sup>1</sup>H NMR spectroscopy. Interestingly, the fact that the ligand binds only via the phenoxy moiety originates from exclusive deprotonation of the phenolic moiety of the imidazolium tetrafluoroborate HO<sub>3</sub>·HBF<sub>4</sub> even in the presence of 2 equiv of KH in THF (Figure S1 in the Supporting Information). A change of the base to LiHMDS and LiHMDS also resulted in exclusive deprotonation of the phenolic moiety; the imidazolium proton remained untouched in all cases. For the imidazolium chloride HO<sub>3</sub>·HCl, however, complete 2-fold deprotonation was easily achieved under the same conditions (Figure S2 in the Supporting Information). Such selective deprotonation could be advantageous, since it offers an attractive access to cationically tagged alkylidyne complexes that might be used under biphasic conditions as realized with ionic olefin metathesis catalysts.<sup>18</sup>

**Tridentate NHC Molybdenum Alkylidyne Complex.** Tridentate NHCs, like bidentate NHCs, offer the possibility of stabilizing metal complexes by the chelate effect. This was envisioned to be beneficial for the stabilization of the proposed quasi-cationic active species. Also, NHC ligand dissociation is highly unlikely in such a system.

The tridentate O,O,C-pincer-type ligand **O<sub>2</sub>1** with trifluoromethyl groups adjacent to the alkoxides was chosen to ensure sufficient Lewis acidity at the metal center. Mo( $\equiv$ C-(*p*-OMe-C<sub>6</sub>H<sub>4</sub>))(OCMe(CF<sub>3</sub>)<sub>2</sub>)<sub>2</sub>(**O<sub>2</sub>1**) (**Mo-13**) bearing the tridentate O,O,C-pincer-type NHC ligand **O<sub>2</sub>1** was synthesized by

converting **Mo-1** with **O<sub>2</sub>1** in THF (Scheme 4). **O<sub>2</sub>1** was prepared by deprotonation of the inner salt HO<sub>2</sub>1·H

**Scheme 4. Synthesis of a Molybdenum Alkylidyne Complex Bearing a Tridentate NHC in 75% Yield**

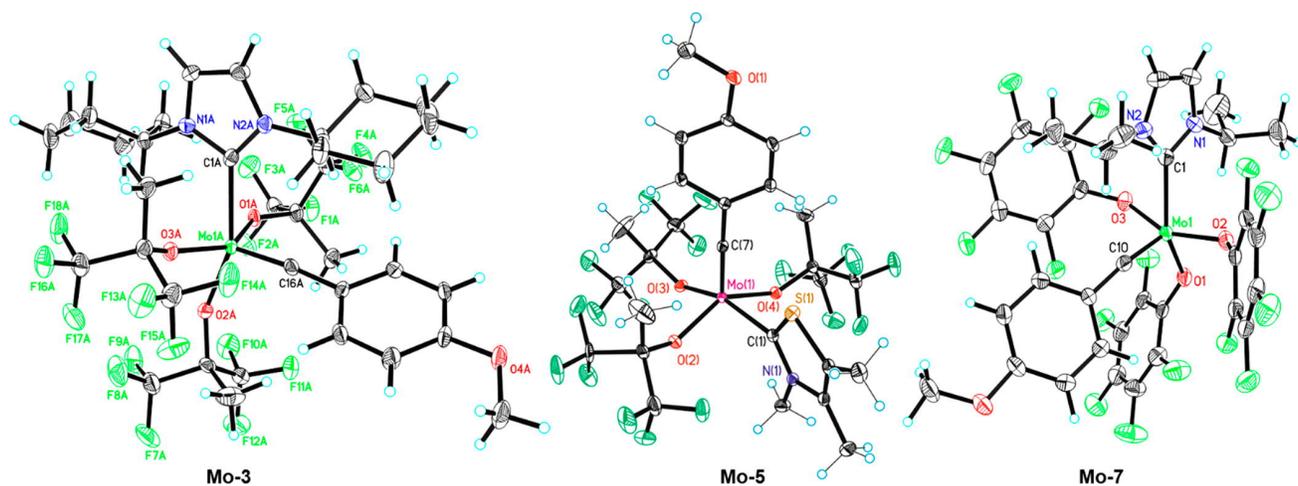


immediately prior to complex synthesis. **Mo-13** was isolated in 75% yield by crystallization from diethyl ether. The <sup>1</sup>H NMR spectrum shows two doublets for the methylene protons of the NHC ligand at  $\delta$  4.54 and 4.48 ppm (<sup>2</sup>J<sub>H-H</sub> = 14.3 Hz). **Mo-13** is not chiral at the metal center (plane of symmetry through the NHC, the alkylidyne, and the OCMe(CF<sub>3</sub>)<sub>2</sub> group); consequently, the <sup>19</sup>F NMR spectrum shows only three resonances. The two equivalent CF<sub>3</sub> groups on distinct tethers of the NHC show up at  $\delta$  -75.5 ppm (q, <sup>4</sup>J<sub>F-F</sub> = 9.8 Hz) and the other two at  $\delta$  -77.0 ppm (q, <sup>4</sup>J<sub>F-F</sub> = 9.9 Hz). Both are quartets, since they couple with the other adjacent diastereotopic CF<sub>3</sub> group.

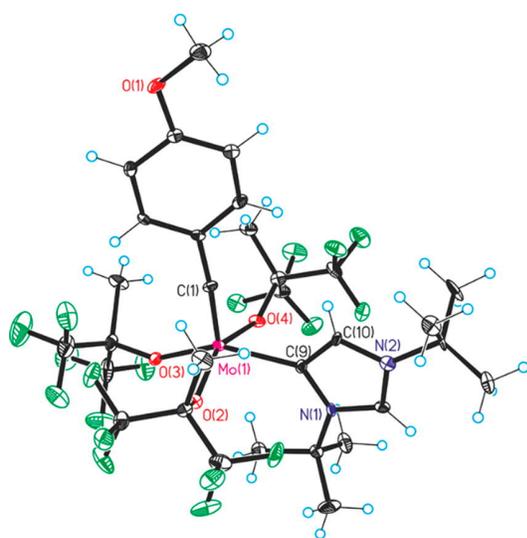
On the other hand, the CF<sub>3</sub> groups at the OCMe(CF<sub>3</sub>)<sub>2</sub> ligand are observed as a singlet at  $\delta$  -78.6 ppm (s, OCMe(CF<sub>3</sub>)<sub>2</sub>), since those CF<sub>3</sub> groups are not diastereotopic.

## ■ SINGLE-CRYSTAL X-RAY STRUCTURES

To elucidate the structural peculiarities of the synthesized complexes, single-crystal X-ray structures of several compounds were measured. As already judged from NMR spectra, complexes **Mo-3**, **Mo-5**, and **Mo-7** with monodentate NHCs showed the expected structures with the NHCs coordinated via the C2 carbon of the imidazol-2-ylidene (Figure 2). **Mo-3** crystallizes in the monoclinic space group *P2<sub>1</sub>/n* (*a* = 2274.0(2) pm, *b* = 1066.42(9) pm, *c* = 3316.6(3) pm;  $\alpha$  = 90°,  $\beta$  = 95.299(4)°,  $\gamma$  = 90°). **Mo-5** crystallizes in the orthorhombic space group *Pbca* (*a* = 1034.86(5) pm, *b* = 1933.02(11) pm, *c* = 3258.38(19) pm;  $\alpha$  =  $\beta$  =  $\gamma$  = 90°). Comparable to our previously published complexes,<sup>12</sup> **Mo-3** and **Mo-5** show a distorted-square-pyramidal (SP) structure in the solid state, with  $\tau^{19}$  = 0.18 and 0.28, respectively.<sup>20</sup> The benzyldiene ligand occupies the apex of the SP structure in **Mo-3** and **Mo-5**. **Mo-4** crystallizes in the monoclinic space group *P2<sub>1</sub>/c* (*a* = 2074.36(19) pm, *b* = 3454.3(3) pm, *c* = 1053.88(9) pm;  $\alpha$  = 90°,  $\beta$  = 90.876(3)°,  $\gamma$  = 90°). As anticipated from the NMR spectra, **Mo-4** was shown to contain carbene **2** bound in the abnormal fashion (vide supra, Figure 3). Reports on abnormally C4 bound carbene ligands that are not blocked with an additional substituent at the acidic C2 position are scarce.<sup>21</sup> This rather unusual structural motif can directly be deduced from the high steric constraint introduced by the *N-t*-Bu substituents. The abnormal binding mode results in a considerably higher TEP for the carbene (TEP = 2043.9 cm<sup>-1</sup>, calculated in analogy to the literature;<sup>13</sup> see the Supporting Information) and was therefore expected to



**Figure 2.** Single-crystal X-ray structures of **Mo-3**, **Mo-5**, and **Mo-7** displaying regular structures. Bond lengths (pm) and angles (deg): **Mo-3**, Mo–C16 174.4(4), Mo–O1 195.5(2), Mo–O3 195.9(3), Mo–O2 196.2(2), Mo–C1 226.5(4), C16–Mo–O1 105.08(14), C16–Mo–O3 106.93(14), O1–Mo–O3 146.28(10), C16–Mo–O2 105.20(14), O1–Mo–O2 90.98(10), O3–Mo–O2 90.67(11), C16–Mo–C1 97.48(16), O1–Mo–C1 84.03(11), O3–Mo–C1 81.62(12), O2–Mo–C1 157.30(12); **Mo-5**, Mo–C7 174.0(2), Mo–O4 194.61(15), Mo–O3 195.96(14), Mo–O2 196.17(14), Mo–C1 224.4(2), C7–Mo–O4 106.04(8), C7–Mo–O3 108.42(8), O4–Mo–O3 91.77(6), C7–Mo–O2 106.78(8), O4–Mo–O2 144.54(6), O3–Mo–O2 90.37(6), C7–Mo–C1 90.30(9), O4–Mo–C1 84.14(7), O3–Mo–C1 161.23(7), O2–Mo–C1 82.63(7); **Mo-7**, Mo–C10 173.7(2), Mo–O2 195.69(17), Mo–O1 198.17(17), Mo–O3 199.23(18), Mo–C1 220.5(2), C10–Mo–O2 101.84(10), C10–Mo–O1 107.84(9), O2–Mo–O1 95.99(7), C10–Mo–O3 100.45(10), O2–Mo–O3 154.83(7), O1–Mo–O3 88.15(7), C10–Mo–C1 101.41(10), O2–Mo–C1 83.27(8), O1–Mo–C1 150.20(9), O3–Mo–C1 81.00(8).



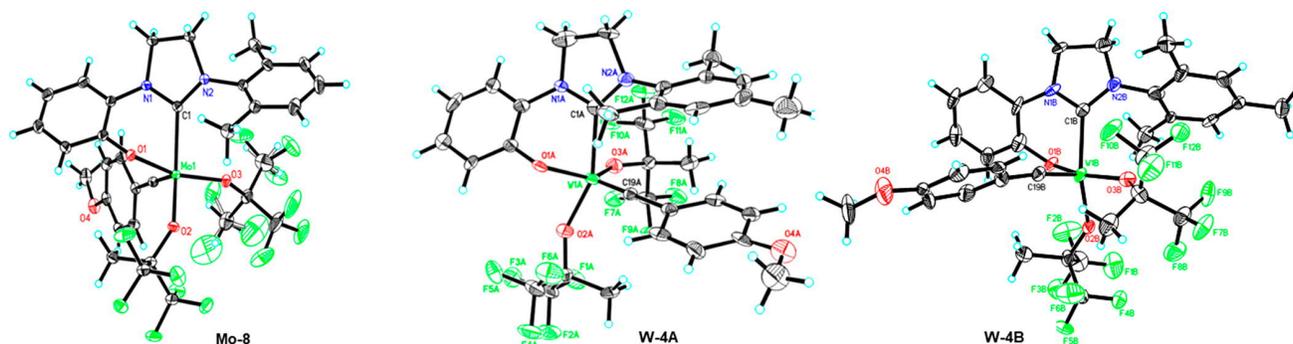
**Figure 3.** Single-crystal X-ray structure of **Mo-4**. **Mo-4** displays an irregular structure with the 1,3-di-*tert*-butylimidazol-2-ylidene bond in an abnormal fashion (small crystals with low diffraction were obtained). Bond lengths and angles are within experimental accuracy, but data are not included for further discussion. See the Supporting Information for details).

result in even higher activity in alkyne metathesis. **Mo-5** showed a shorter molybdenum–carbene bond of 224.4(2) pm in comparison to previously published complexes<sup>12</sup> based on rather weak  $\sigma$  donors such as Mo( $\equiv$ C-(*p*-OMe-C<sub>6</sub>H<sub>4</sub>))-(OCMe(CF<sub>3</sub>)<sub>2</sub>)<sub>3</sub>(1,3-dimethyl-4,5-dichloroimidazol-2-ylidene) and Mo( $\equiv$ C-(*p*-OMe-C<sub>6</sub>H<sub>4</sub>))-(OCMe(CF<sub>3</sub>)<sub>2</sub>)<sub>3</sub>(1,3-dimethyl-4,5-dicyanoimidazol-2-ylidene) (Mo–C<sub>carbene</sub> = 225.21(17) and 226.63(15) pm, respectively).

This can be attributed to the decrease in steric demand derived from replacement of one of the *N*-Me groups by sulfur.

**Mo-7** crystallizes in the monoclinic space group  $P2_1$  ( $a = 1066.04(06)$  pm,  $b = 1283.87(9)$  pm,  $c = 1296.41(8)$  pm;  $\alpha = 90^\circ$ ,  $\beta = 98.076(2)^\circ$ ,  $\gamma = 90^\circ$ ). In the solid state, **Mo-7** displays an almost perfect SP structure ( $\tau = 0.077$ ) with the alkylidyne ligand in the apex. In comparison to the previously published complex Mo( $\equiv$ C-(*p*-OMe-C<sub>6</sub>H<sub>4</sub>))(OCMe(CF<sub>3</sub>)<sub>2</sub>)<sub>3</sub> (**Mo-12**) based on the OCMe(CF<sub>3</sub>)<sub>2</sub> ligand, the increased steric bulk of OCMe(CF<sub>3</sub>)<sub>2</sub> vs OC<sub>6</sub>F<sub>5</sub> is only mirrored in the substantially longer Mo–C<sub>NHC</sub> bond (225.2(3) pm for **Mo-12** vs 220.5(2) pm for **Mo-7**).<sup>12</sup> Generally, the Mo–C<sub>alkylidyne</sub> bonds in the complexes bearing monodentate NHCs, **Mo-3** (174.4(4) pm), **Mo-5** (174.0(2) pm), and **Mo-7** (173.7(2) pm), are shorter than those in the recently reported donor-free complex Mo( $\equiv$ C-(*p*-OMe-C<sub>6</sub>H<sub>4</sub>))(OCMe(CF<sub>3</sub>)<sub>2</sub>)<sub>3</sub> (175.03 pm) and the doubly THF coordinated complex Mo( $\equiv$ C-(*p*-OMe-C<sub>6</sub>H<sub>4</sub>))(OCMe(CF<sub>3</sub>)<sub>2</sub>)<sub>3</sub>(THF)<sub>2</sub> (175.7(2) pm).<sup>51</sup> This could be due to either the change in geometry and coordination number or to a more positive polarization of the Mo in the complexes **Mo-3**, **Mo-5**, and **Mo-7**. Two complexes bearing bidentate NHCs were additionally characterized by single-crystal X-ray measurements. Molybdenum-based **Mo-8** crystallizes in the triclinic space group  $P\bar{1}$  ( $a = 1151.90(6)$  pm,  $b = 1251.45(7)$  pm,  $c = 1417.59(1)$  pm;  $\alpha = 98.704(4)^\circ$ ,  $\beta = 109.748(3)^\circ$ ,  $\gamma = 113.041(2)^\circ$ ). **Mo-8** displays a slightly distorted SP structure ( $\tau = 0.099$ ) with the benzylidyne in the apical position (Figure 4). Tungsten-based **W-4** crystallizes in the triclinic space group  $P\bar{1}$  ( $a = 1524.31(18)$  pm,  $b = 1701.61(16)$  pm,  $c = 1795.5(2)$  pm;  $\alpha = 106.139(6)^\circ$ ,  $\beta = 109.867(6)^\circ$ ,  $\gamma = 94.334(5)^\circ$ ).

The crystal structure of **W-4** reveals two independent conformers. In both conformers the ligands adopt a distorted SP geometry with the benzylidyne in the apical position. The geometry index  $\tau$  was 0.095 for conformer B and 0.25 for conformer A, indicating a higher deviation from the SP structure for conformer A. Since, apart from the metal center, **Mo-8** and **W-4** only differ by one methyl group in the



**Figure 4.** Single-crystal X-ray structures of **Mo-8** and both isomers of **W-4**. All of the complexes show the expected structure with the bidentate NHC coordinated via the phenolate and the carbene moiety. Important bond lengths can be found in Table 1.

**Table 1. Comparison of the Metal–Ligand Bond Lengths and Angles in Mo-8 and the Conformers of W-4<sup>a</sup>**

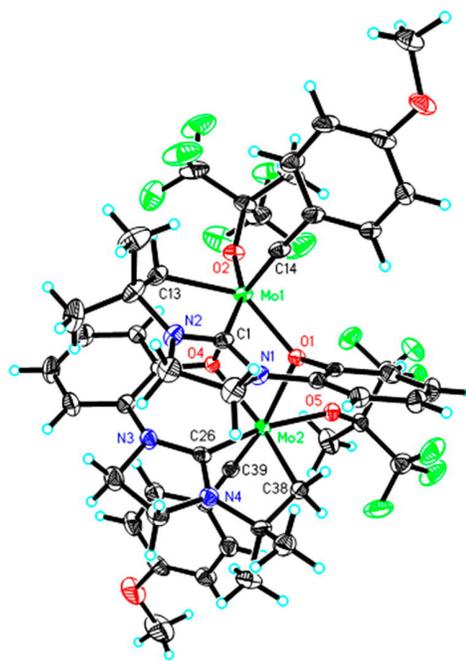
	$\tau$	M–C <sub>carbene</sub> (pm)	M–O <sub>trans carbene</sub> <sup>b</sup> (pm)	M–O <sub>chelate</sub> <sup>c</sup> (pm)	M–O <sub>trans chel</sub> <sup>d</sup> (pm)	M–C <sub>alkylidyne</sub> (pm)	O <sub>trans NHC</sub> –M–C <sub>NHC</sub> (deg)
<b>Mo-8</b>	0.099	223.4	196.2	201.75	193.25	174.38	151.1
<b>W-4B</b>	0.095	221.5	196.9	190.9	198.3	176.3	155.5
<b>W-4A</b>	0.250	225.7	196.4	198.4	191.1	162.6	151.3

<sup>a</sup>Derived from single-crystal X-ray analysis. <sup>b</sup>Oxygen atom trans to the NHC. <sup>c</sup>Chelating oxygen atom of the NHC. <sup>d</sup>Oxygen atom trans to the chelating oxygen of the NHC.

nonchelating substituent of the imidazolin-2-ylidene, a comparison between the corresponding Mo and W complexes in terms of bond lengths and angles seemed appropriate (Table 1). It is noteworthy that the lengths of the M–O<sub>trans NHC</sub> bond are almost identical in **Mo-8**, **W-4A**, and **W-4B**, irrespective of the differences in the M–C<sub>NHC</sub> bond length and the O<sub>trans NHC</sub>–M–C<sub>NHC</sub> angle (Table 1). Conformers A and B of **W-4** show a substantial difference of 13.7 pm in the W–C<sub>alkylidyne</sub> bond lengths. Furthermore, the structure of **Mo-10** was measured to confirm the proposed O,C,C-pincer-type structure. **Mo-10** crystallizes in the monoclinic space group  $P2_1/n$  with  $a = 1248.62(6)$  pm,  $b = 2131.16(9)$  pm,  $c = 2111.02(9)$  pm,  $\alpha = \gamma = 90^\circ$ ,  $\beta = 103.530(2)^\circ$ , and  $Z = 4$ . Interestingly, the crystal structure revealed a binuclear structure in the solid state (Figure 5).

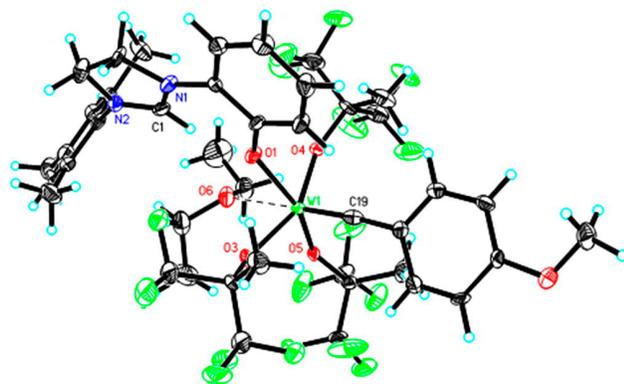
The two molybdenum centers are double-bridged via the two oxygen atoms O1 and O4 of the O,C,C-pincer-type NHC. The bridging oxygen atom O1 is closer to Mo1 (Mo1–O1 = 202.67(18) pm), whereas O4 is closer to Mo2 (Mo2–O4 = 203.09(18) pm). In comparison, the bond lengths Mo1–O4 and Mo2–O1 are substantially elongated (243.42(17) and 241.22(17) pm). The Mo–C bond lengths Mo1–C13 and Mo2–C38 in the unexpectedly formed chelate in **Mo-10** are 218.2(3) and 218.4(3) pm. Generally, the Mo–O<sub>alkoxide</sub> bonds in all described NHC-coordinated complexes, whether bi- or monodentate, with bond lengths ranging from 193.25 pm (**Mo-8**) to 196.2(2) pm (**Mo-3**) are substantially longer than those in Mo( $\equiv$ C-(*p*-OMe-C<sub>6</sub>H<sub>4</sub>))(OCMe(CF<sub>3</sub>)<sub>2</sub>)<sub>3</sub> with bond lengths between 189.6(2) and 190.8(2) pm.<sup>51</sup>

We attribute this to the increase in steric congestion induced by the additional NHC ligands. We furthermore successfully characterized the crystal structure of a minor byproduct, W( $\equiv$ C-*p*-OMe-C<sub>6</sub>H<sub>4</sub>)(OCMe(CF<sub>3</sub>)<sub>2</sub>)<sub>3</sub>(**O3-H**) (**W-8**), formed during the synthesis of **W-4** (Scheme 3). In **W-8**, the supposedly bidentate NHC ligand **O2** is exclusively bound via the phenolate moiety (**W-8**; Figure 6). The imidazolium moiety remained intact and forms a zwitterion with an anionic tungsten center. **W-8** crystallizes in the monoclinic space group



**Figure 5.** Single-crystal X-ray structure of dimeric **Mo-10**. Bond lengths (pm): Mo1–C14 175.8(3), Mo1–O2 197.41(17), Mo1–O1 202.67(18), Mo1–C1 214.7(3), Mo1–C13 218.2(3), Mo1–O4 243.42(17), Mo2–C39 176.2(3), Mo2–O5 197.21(18), Mo2–O4 203.09(18), Mo2–C26 214.4(3), Mo2–C38 218.4(3), Mo2–O1 241.22(17).

$P2_1/c$  ( $a = 1286.93(12)$  pm,  $b = 1693.92(13)$  pm,  $c = 2151.28(18)$  pm;  $\alpha = 90^\circ$ ,  $\beta = 102.129(4)^\circ$ ,  $\gamma = 90^\circ$ ). **W-8** displays an SP geometry ( $\tau = 0.052$ ) with the alkylidyne ligand in the apex. Anionic **W-8** is coordinated by one molecule of diethyl ether trans to the alkylidyne ligand in the solid state. The comparable tungstate complex [W( $\equiv$ C-*p*-OMe-C<sub>6</sub>H<sub>4</sub>)-(OSiPh<sub>3</sub>)<sub>4</sub>][K]<sup>22</sup> with the same alkylidyne ligand has a W–C<sub>alkylidyne</sub> bond length of 176.9(7) pm, which is almost identical



**Figure 6.** Single-crystal X-ray structure of zwitterionic **W-8**, a very minor byproduct in the synthesis of **W-4**, with the supposedly bidentate NHC bound exclusively via the phenolic moiety. Bond lengths (pm) and angles (deg): W–C19 176.4(9), W–O5 195.4(5), W–O4 196.1(5), W–O3 198.6(5), W–O1 205.4(5); C19–W–O5 101.8(3), C19–W–O4 103.8(3), O5–W–O4 92.5(2), C19–W–O3 102.4(3), O5–W–O3 90.3(2), O4–W–O3 152.5(2), C19–W–O1 102.5(3), O5–W–O1 155.6(2), O4–W–O1 83.5(2), O3–W–O1 82.7(2).

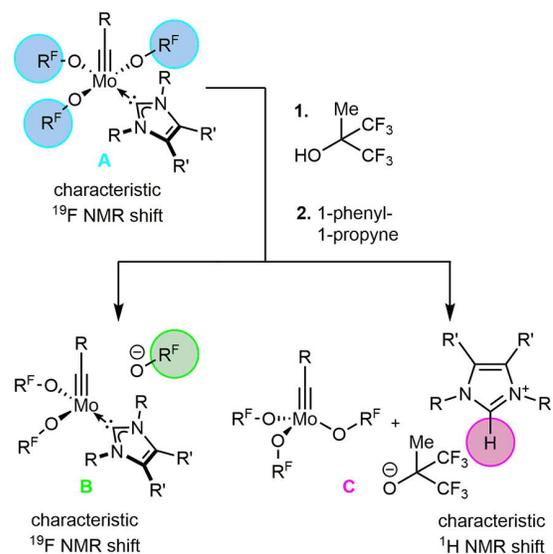
with the W–C19 bond length of 176.4(9) pm in **W-8**. Although providing no final proof, the crystal structure of **W-8** corroborates the inner-salt-type structure proposed above for **W-5** (Scheme 3).

## ■ REACTIVITY AND ACTIVE SPECIES

All novel complexes **Mo-3**–**Mo-11** and **Mo-13** and **W-3**–**W-7** were used in the homometathesis (HM) of 1-phenyl-1-propyne (**S1**) at 35 °C in toluene in the presence of 5 Å molecular sieves.<sup>4c</sup> The complexes showed moderate productivities with TONs in the range of 0–800 (Table 2). Pentacoordinated complexes **Mo-6** and **Mo-7** bearing the OC<sub>6</sub>F<sub>5</sub> ligand did *not* exhibit any metathesis activity. At first glance this was surprising, since pentafluorophenoxide was expected to be a good leaving group. However, as already outlined, in addition to a good leaving group a stabilized molybdenum center is also required for improved formation of the proposed quasi-cationic active species. Likely, the reduced steric bulk of the OC<sub>6</sub>F<sub>5</sub> ligands and the reduced donor strength result in a very unstable cation, thereby counterbalancing the favorable leaving-group character. Disappointingly, all tungsten-based complexes were inactive, whereas the molybdenum-centered complexes showed moderate activity (Table 2). This becomes particularly interesting for complexes **Mo-8** vs **W-3** and **Mo-9** vs **W-4**. These two groups of metal complexes only differ in the metal. The origin of the complete loss of activity caused by the replacement of molybdenum by

tungsten remains unclear at this point and cannot be explained by the solid-state structures described above. An increase in the reaction temperature to 80 °C led to complete loss of activity for all molybdenum-based complexes. The most reactive catalyst was **Mo-13**, with a tridentate NHC, with TONs of 780 after 3 h and 800 after 15 h. To identify the active species, all complexes were analyzed according to a previously published reaction sequence<sup>12</sup> (Scheme 5): Hexafluoro-*tert*-

## Scheme 5. Determination of the Active Species by NMR Spectroscopy (C<sub>6</sub>D<sub>6</sub>)<sup>a</sup>



<sup>a</sup>The proposed cationic active species **B** can be detected in the <sup>19</sup>F NMR spectrum, whereas observation of the imidazolium salt in the <sup>1</sup>H NMR spectrum is indicative for the formation of neutral active species **C**.

butyl alcohol and 1-phenyl-1-propyne were added to a solution of the respective complex in C<sub>6</sub>D<sub>6</sub>. The reaction was then carefully monitored by <sup>1</sup>H and <sup>19</sup>F NMR spectroscopy to check for the formation of either a proposed quasi-cationic active species with a weakly coordinating anion (visible as partially dissociated OCMe(CF<sub>3</sub>)<sub>2</sub> in the <sup>19</sup>F NMR, structure **B** in Scheme 5) or the assumed neutral active species indicated by the observation of imidazolium salts (characteristic proton signal in the <sup>1</sup>H NMR spectrum, structure **C** in Scheme 5), stemming from dissociation of the NHC and reaction with the acidic alcohol (Figures S66–S68 and S71–S81 in the Supporting Information). In contrast to our assumptions we could not observe an enhanced formation of the active species (maximum: approximately 1% for both **Mo-3** and **Mo-4**) in comparison to the previously reported complex

**Table 2.** TONs of Mo Catalysts Containing Monodentate and Multidentate NHCs in the HM of 1-Phenyl-1-propyne with Addition of 0, 20, and 500 Equiv of KOCMe(CF<sub>3</sub>)<sub>2</sub><sup>a</sup>

	catalyst							
	Mo-3	Mo-4	Mo-5	Mo-8	Mo-9	Mo-10	Mo-11	Mo-13
TON	390 (580)	500 (640)	660 (880)	270*	400 (400)	0	250 (260)	780 (800)
TON (20 equiv)	300 (560)	200 (340)	320 (610)		90 (100)		20 (20)	450 (580)
TON (500 equiv)	0 (0)	0 (0)	0 (0)		0 (0)		0 (0)	0 (0)

<sup>a</sup>Reaction conditions: toluene, 35 °C, 4 h (\*3 h), catalyst:substrate = 1:1000, internal standard *tert*-butylbenzene, molecular sieves 5 Å (according to Fürstner et al.<sup>4c</sup>). Values in parentheses: TON after 15 h.

bearing the 1,3-diisopropylimidazol-2-ylidene ligand (**Mo-12**)<sup>12</sup> for all novel synthesized complexes. Gratifyingly, also no dissociation of the NHC was observed.

To probe the effect of free alkoxide on the reactivity of the active complexes, the homometathesis of 1-phenyl-1-propyne with addition of 20 and 500 equiv of KOCMe(CF<sub>3</sub>)<sub>2</sub> was examined. Under the same conditions the TONs decreased for all tested complexes when 20 equiv of KOCMe(CF<sub>3</sub>)<sub>2</sub> was added. The addition of 500 equiv of KOCMe(CF<sub>3</sub>)<sub>2</sub> resulted in complete loss of reactivity. This decrease in reactivity supports the existence of a cationic active species, since the addition of free alkoxide shifts the equilibrium to the nonreactive neutral pentacoordinated complex. We hold the tris(hexafluoro-*tert*-butoxide) precursor accountable for the observed moderate activity. Probably, insufficient stabilization of the negative charge on the dissociated hexafluoro-*tert*-butoxide prevents the formation of higher amounts of the proposed cationic species. X-type ligands with an improved leaving-group character and ample steric demand are required.

## CONCLUSIONS

Mono-, bi-, and tridentate Mo- and W-alkylidene NHC complexes have been prepared and evaluated for their propensity to form alkyne-metathesis-productive, presumably cationic metal alkylidyne NHC complexes, which we believe to represent the active species in alkyne-metathesis-active pentacoordinated metal alkylidyne NHC complexes. Stabilization of the partial positive charge at the metal was considered essential. Contrary to our assumptions, the introduction of strongly  $\sigma$  donating or chelating NHCs did *not* promote the formation of the catalytically active cationic species. Evidently, in analogy to the corresponding metal alkylidene triflate complexes, which show substantial formation of a cationic active species,<sup>23</sup> the incorporation of good leaving groups with sufficient steric demand, e.g. triflates, might eventually lead to higher activity and productivity. Whether the resulting cationic metal alkylidynes are stable enough to be used in solution or will have to be immobilized on suitable supports is still to be evaluated. The results will be reported in due course.

## EXPERIMENTAL SECTION

**General Information.** Unless stated otherwise, all reactions were performed under an inert gas atmosphere (N<sub>2</sub>), either in a glovebox (LabMaster 130, MBraun, Garching, Germany) or with standard Schlenk techniques. CH<sub>2</sub>Cl<sub>2</sub>, diethyl ether, toluene, *n*-pentane, and tetrahydrofuran were dried by a solvent purification system (SPS, MBraun). NMR measurements were recorded on a Bruker Avance III 400 instrument. Chemical shifts are reported in ppm relative to the solvent signal; coupling constants are listed in Hz. Single-crystal X-ray measurements were carried out on a Nonius KappaCCD four-circle diffractometer equipped with graphite-monochromated Mo K $\alpha$  radiation, a Micracol Fiber Optics collimator, and a Nonius FR590 generator at the Institute of General, Inorganic and Theoretical Chemistry, University of Innsbruck, Austria (structures of **Mo-4** and **Mo-5**), and on a Bruker Kappa APEXII Duo diffractometer with Mo K $\alpha$  radiation at the Institute of Organic Chemistry, University of Stuttgart (structures of **Mo-3**, **Mo-8**, **Mo-10**, **W-4**, and **W-8**). Starting materials and reagents were purchased from Sigma-Aldrich (Munich, Germany), Alfa Aesar (Karlsruhe, Germany), or ABCR (Karlsruhe, Germany) and were used as received unless stated otherwise. The syntheses of the novel precursor complexes (**Mo-2**, **W-2**) and imidazolium salts as well as alternative procedures for the synthesis of **W-3** and **W-6** are described in the Supporting Information Literature for previously published compounds is provided in the Supporting Information CCDC 1531391 (**Mo-3**), CCDC 1531392

(**Mo-4**), CCDC 1531393 (**Mo-5**), CCDC 1861323 (**Mo-7**), CCDC 1861321 (**Mo-8**), CCDC 1861322 (**W-4**), CCDC 1897061 (**Mo-10**), CCDC 1861324 (**W-8**) contain supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre by The Cambridge Crystallographic Data Centre.

**Mo( $\equiv$ C-(*p*-OMe-C<sub>6</sub>H<sub>4</sub>))(1)(OCMe(CF<sub>3</sub>)<sub>2</sub>)<sub>3</sub> (**Mo-3**).** 1·HBF<sub>4</sub> (35 mg, 0.11 mmol) was suspended in toluene, and KHMDS (22 mg, 0.11 mmol) was dissolved in toluene in 10 mL glass vials. Both mixtures were cooled to -40 °C. The solution of KHMDS was slowly added to the solution of 1·HBF<sub>4</sub> with stirring. The reaction mixture was stirred for 1 h at room temperature and then filtered, cooled again to -40 °C, and then added to a cold solution of **Mo-1** (100 mg, 0.12 mmol) in a Schlenk tube equipped with a magnetic stir bar. The reaction mixture was removed from the glovebox and stirred for 20 min at room temperature and then for 3 h at 40 °C. In course of the reaction a color change from brown to red was observed. The reaction mixture was concentrated in vacuo and brought back into the glovebox. The remaining solid was crystallized from diethyl ether/*n*-pentane to give the product as a red solid (79 mg, 0.080 mmol, 67%). <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  7.42–7.40 (m, 2H), 6.56–6.54 (m, 2H), 6.37–6.36 (m, 2H), 5.01–4.95 (m, 1H), 3.86–3.81 (m, 1H), 3.17 (s, 3H), 2.29 (d, <sup>3</sup>J<sub>H-H</sub> = 11.8 Hz, 2H), 2.08 (d, <sup>3</sup>J<sub>H-H</sub> = 11.6 Hz, 2H), 1.88 (s, 3H), 1.73 (s, 6H), 1.68 (s, 2H), 1.51–1.13 (m, 14H) ppm. <sup>19</sup>F NMR (375 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  -76.19 to -76.27 (m, 6F), -76.41 (s, 6F), -77.22 (s, 6F) ppm. <sup>13</sup>C NMR (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  297.6 (Mo $\equiv$ C), 186.2 (NCN), 160.5, 138.1, 132.7, 124.7 (q, <sup>1</sup>J<sub>C-F</sub> = 289.0 Hz, CF<sub>3</sub>), 124.6 (q, <sup>1</sup>J<sub>C-F</sub> = 290.0 Hz, CF<sub>3</sub>), 124.4 (q, <sup>1</sup>J<sub>C-F</sub> = 290.3 Hz, CF<sub>3</sub>), 117.6, 117.2, 113.5, 83.5 (hept, <sup>2</sup>J<sub>C-F</sub> = 28.4 Hz, C(CF<sub>3</sub>)<sub>2</sub>Me), 82.8 (hept, <sup>2</sup>J<sub>C-F</sub> = 28.8 Hz, C(CF<sub>3</sub>)<sub>2</sub>Me)\*, 61.2, 60.4, 55.8, 34.7, 33.7, 25.8, 25.7, 25.6, 19.8 ppm. Anal. Calcd for C<sub>33</sub>H<sub>40</sub>F<sub>18</sub>MoN<sub>2</sub>O<sub>4</sub>: C, 42.44; H, 4.07; N, 2.83. Found: C, 42.12; H, 4.16; N, 2.83. \*Only five signals of the septet were observed. Red crystals suitable for single-crystal X-ray diffraction were obtained by layering an almost saturated solution of **Mo-3** in CH<sub>2</sub>Cl<sub>2</sub> with *n*-pentane followed by storage at -40 °C for several days.

**Mo( $\equiv$ C-(*p*-OMe-C<sub>6</sub>H<sub>4</sub>))(2)(OCMe(CF<sub>3</sub>)<sub>2</sub>)<sub>3</sub> (**Mo-4**).** **Mo-1** (200 mg, 0.24 mmol) and **2** (43 mg, 0.24 mmol) were separately dissolved in toluene (2 mL each). Both solutions were cooled to -40 °C, and the solution of **2** was slowly added to that of **Mo-1**. The resulting reaction mixture was stirred at 40 °C for 3 h and then concentrated in vacuo. The remaining solid was crystallized from diethyl ether/*n*-pentane to give the product as a red solid (98 mg, 0.104 mmol, 44%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.86 (d, <sup>4</sup>J<sub>H-H</sub> = 1.8 Hz, 1H), 7.19–7.16 (m, 2H), 7.09 (bs, 1H), 6.84–6.80 (m, 2H), 3.81 (s, 3H), 1.65 and 1.64 (2x, 18H), 1.62 (s, 9H) ppm. <sup>19</sup>F NMR (375 MHz, CDCl<sub>3</sub>):  $\delta$  -75.33 to -75.41 (m, 6F), -77.64 to -77.68 (m, 6F), -77.92 (s, 6F) ppm. <sup>13</sup>C NMR (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  292.2 (Mo $\equiv$ C), 170.2, 159.8, 138.5, 131.6, 127.3, 126.1, 124.9 (q, <sup>1</sup>J<sub>C-F</sub> = 289.7 Hz, CF<sub>3</sub>), 124.4 (q, <sup>1</sup>J<sub>C-F</sub> = 291.0 Hz, CF<sub>3</sub>), 113.7, 83.4 (hept, <sup>2</sup>J<sub>C-F</sub> = 28.0 Hz, C(CF<sub>3</sub>)<sub>2</sub>Me)\*, 81.7 (hept, <sup>2</sup>J<sub>C-F</sub> = 28.4 Hz, C(CF<sub>3</sub>)<sub>2</sub>Me)\*, 60.2, 57.8, 55.7, 30.8, 30.2, 19.5, 19.3 ppm. Anal. Calcd for C<sub>31</sub>H<sub>36</sub>F<sub>18</sub>MoN<sub>2</sub>O<sub>4</sub>: C, 39.65; H, 3.87; N, 2.98. Found: C, 39.66; H, 3.85; N, 3.07. Red crystals suitable for single crystal X-ray diffraction were obtained by layering an almost saturated solution of **Mo-4** in diethyl ether with *n*-pentane followed by storage at -40 °C overnight. \*Only 5 signals of the septet were observed.

**Mo( $\equiv$ C-(*p*-OMe-C<sub>6</sub>H<sub>4</sub>))(3)(OCMe(CF<sub>3</sub>)<sub>2</sub>)<sub>3</sub> (**Mo-5**).** Under exclusion of light, **3-HI** (100 mg, 0.118 mmol), 4 Å molecular sieves (100 mg), Ag<sub>2</sub>O (55 mg, 0.236 mmol), and CH<sub>2</sub>Cl<sub>2</sub> (4 mL) were placed in a Schlenk tube equipped with a magnetic stir bar. The reaction mixture was stirred at room temperature for 1 h under exclusion of light. Volatile components were removed under reduced pressure. Toluene (2 mL) and **Mo-1** (333 mg, 0.393 mmol) in toluene (2 mL) were added to the reaction mixture. The reaction mixture was removed from the glovebox, sonicated for 3 h at 40 °C under the exclusion of light, concentrated in vacuo, and brought back into the glovebox. The brownish green solid was extracted with diethyl ether, filtered, and concentrated in vacuo to give a dark red solid. Crystallization from diethyl ether/*n*-pentane at -40 °C gave the

product as a red solid (175 mg, 0.198 mmol, 50%).  $^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  7.45–7.41 (m, 2H), 6.60–6.56 (m, 2H), 3.20 (s, 3H), 2.96 (s, 3H), 1.98 (s, 3H), 1.80 (s, 6H), 1.36 (s, 3H), 1.17 (s, 3H) ppm.  $^{19}\text{F}$  NMR (375 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  -76.66 to -76.78 (m, 12F), -77.14 to -77.22 (m, 6F) ppm.  $^{13}\text{C}$  NMR (100 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  300.7 (Mo $\equiv$ C), 209.0 (NCS), 160.6, 140.2, 138.4, 133.0, 132.5, 124.7 (q,  $^1J_{\text{C-F}} = 289.7$  Hz,  $\text{CF}_3$ ), 124.28 (q,  $^1J_{\text{C-F}} = 290.0$  Hz,  $\text{CF}_3$ ), 124.1 (q,  $^1J_{\text{C-F}} = 289.8$  Hz,  $\text{CF}_3$ ), 113.7, 83.8–82.7 (m,  $\text{C}(\text{CF}_3)_2\text{Me}$ )\*, 55.8, 40.6, 20.0, 19.7, 12.2, 12.0 ppm. Anal. Calcd for  $\text{C}_{26}\text{H}_{25}\text{F}_{18}\text{MoNO}_4\text{S}$ : C, 35.27; H, 2.85; N, 1.58. Found: C, 35.08; H, 3.09; N, 1.59. \*Septet poorly resolved. Red crystals suitable for single-crystal X-ray diffraction were obtained by layering a saturated solution of **Mo-5** in diethyl ether with *n*-pentane followed by storage at  $-40^\circ\text{C}$  overnight.

**Mo( $\equiv$ C-(*p*-OMe- $\text{C}_6\text{H}_4$ ))(4)(OC $_6\text{F}_5$ ) $_3$  (Mo-6).** **Mo-2** (226 mg, 0.3 mmol) was dissolved in toluene (approximately 15 mL) and cooled to  $-40^\circ\text{C}$ . **4** (81 mg, 0.3 mmol) was added to toluene (approximately 5 mL), and the solution was slowly added to the metal complex solution. The mixture was stirred for 3 h at room temperature, and the solvent was removed. The resulting greenish residue was washed with diethyl ether to afford **Mo-6** (252 mg, 0.23 mmol, 89%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.16 (s, 2H), 6.65 (br s, 4H)\*, 6.48 (s, 4H), 3.75 (s, 3H), 2.15 (s, 6H), 1.99 (s, 12H) ppm.  $^{19}\text{F}$  NMR (375 MHz,  $\text{CDCl}_3$ ):  $\delta$  -160.3 (m, 4F), -162.4 (m, 2F), -166.2 (m, 4F), -168.0 (m, 2F), -171.1 (m, 2F), -174.0 (m, 1F) ppm.  $^{13}\text{C}$  NMR\* (100 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  310.2 (Mo $\equiv$ C), 189.9 (NCN), 160.8, 143.3–136.1 (m,  $\text{C}_{\text{ar}}$ , OC $_6\text{F}_5$ ), 140.1, 135.5, 133.0, 129.1, 124.1, 111.8, 55.4, 21.0, 17.5 ppm. Anal. Calcd for  $\text{C}_{47}\text{H}_{31}\text{F}_{15}\text{MoN}_2\text{O}_4$ : C, 52.82; H, 2.92; N, 2.62; Found: C, 52.86; H, 2.959; N, 2.70. \*Only seven out of the expected nine aromatic signals are observed; however, this is in accordance with the  $^1\text{H}$  NMR spectrum, in which only one broad signal for all aromatic protons of the benzyldiene ligand is visible.

**Mo( $\equiv$ C-(*p*-OMe- $\text{C}_6\text{H}_4$ ))(5)(OC $_6\text{F}_5$ ) $_3$  (Mo-7).** **Mo-2** (101.7 mg, 0.120 mmol) was suspended in toluene and cooled to  $-40^\circ\text{C}$ . A solution of **5** (18.1 mg, 0.12 mmol) in toluene was cooled to  $-40^\circ\text{C}$  and added dropwise to the suspension. The reaction mixture was stirred for 1 h while it was warmed to room temperature and then stirred for 3 h at  $40^\circ\text{C}$ . All volatiles were removed under reduced pressure, and the resulting solid was crystallized in  $\text{CH}_2\text{Cl}_2$ , diethyl ether, and *n*-pentane to yield the product as dark brown crystals (39.0 mg, 0.04 mmol, 35%).  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  7.19 (s, 2H), 6.69 (s, 4H), 5.01 (m, 2H), 3.76 (s, 3H), 1.27 (d,  $^3J_{\text{H-H}} = 6.6$  Hz, *i*Pr 12H) ppm.  $^{19}\text{F}$  NMR (375 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  -162.44 (s, 6F), -166.33 (s, 4F), -167.45 (s, 2F), -171.44 (s, 2F), -173.20 (s, 1F) ppm.  $^{13}\text{C}$  NMR (100 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  304.4 (Mo $\equiv$ C), 184.6 (NCN), 161.4, 143.8, 139.7 (d, CF,  $^1J_{\text{C-F}} = 241.8$  Hz), 138.5 (d, CF,  $^1J_{\text{C-F}} = 248.0$  Hz), 137.4, 134.8 (d, CF,  $^1J_{\text{C-F}} = 245.5$  Hz), 131.9, 117.3, 113.6, 54.8, 53.2, 23.2 ppm. Anal. Calcd for  $\text{C}_{35}\text{H}_{23}\text{F}_{15}\text{MoN}_2\text{O}_4$ : C, 45.87; H, 2.53; N, 3.06. Found: C, 45.55; H, 2.74; N, 3.20.

**Mo( $\equiv$ C-(*p*-OMe- $\text{C}_6\text{H}_4$ ))(O1)(OCMe( $\text{CF}_3$ ) $_2$ ) $_2$  (Mo-8).** **HO1-HCl** (53.5 mg, 0.18 mmol) in THF (2 mL) and LiHMDS (59.8 mg, 0.36 mmol) in THF (2 mL) were cooled to  $-40^\circ\text{C}$ . The LiHMDS solution was added dropwise to the **HO1-HCl** suspension. The reaction mixture was stirred for 1 h at room temperature and cooled to  $-40^\circ\text{C}$ . The cooled mixture was then added dropwise to a solution of **Mo-1** (150 mg, 0.18 mmol) in THF (2 mL) at  $-40^\circ\text{C}$ . After the reaction mixture was stirred for 16 h at room temperature, the volatiles were removed in vacuo and the residue was washed with *n*-pentane (2 mL) and redissolved in  $\text{CH}_2\text{Cl}_2$ . The mixture was filtered through a pad of Celite, and all volatiles were removed in vacuo. The solid residue was crystallized from diethyl ether and *n*-pentane. The product was isolated in the form of dark violet crystals (72 mg, 0.21 mmol, 48%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.14–7.01 (m, 4H), 6.91 (m, 2H), 6.74 (d,  $^3J_{\text{H-H}} = 7.3$  Hz, 1H), 6.54–6.45 (m, 4H), 4.38 (d,  $^3J_{\text{H-H}} = 10.5$  Hz, 1H), 4.28–4.18 (m, 1H), 4.18–4.07 (m, 1H), 3.87 (q,  $^3J_{\text{H-H}} = 10.7$  Hz, 1H), 3.72 (s, 3H), 2.38 (s, 3H), 2.23 (s, 3H), 1.72 (s, 3H), 1.28 (s, 3H) ppm.  $^{19}\text{F}$  NMR (375 MHz,  $\text{CDCl}_3$ ):  $\delta$  -77.12 to -77.26 (m, 3F), -77.32 (q,  $^4J_{\text{F-F}} = 9.8$  Hz, 3F), -77.38 to -77.51 (m, 3F), -77.72 to -77.88 (m, 3F) ppm.  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  307.1 (Mo $\equiv$ C), 208.2 (NCN), 160.3, 158.7, 139.1,

137.8, 136.4, 135.2, 132.5, 132.2, 129.7, 129.3, 128.7, 126.2, 124.7 (q,  $^1J_{\text{C-F}} = 287.7$  Hz), 124.1 (q,  $^1J_{\text{C-F}} = 290.3$  Hz), 120.3, 118.8, 118.2, 112.9, 83.7–81.6 (m,  $\text{C}(\text{CF}_3)_2\text{Me}$ )\*, 55.8, 50.3, 20.0, 19.5, 19.3, 18.9 ppm. Despite numerous efforts, no satisfactory elemental analysis data could be obtained due to fast decomposition. Nonetheless, its structure was unambiguously confirmed by single-crystal X-ray analysis. \*Septet poorly resolved.

**Mo( $\equiv$ C-(*p*-OMe- $\text{C}_6\text{H}_4$ ))(O2)(OCMe( $\text{CF}_3$ ) $_2$ ) $_2$  (Mo-9).** **HO2-HCl** (56.0 mg, 0.18 mmol) in THF (2 mL) and LiHMDS (59.8 mg, 0.36 mmol) in THF (2 mL) were cooled to  $-40^\circ\text{C}$ . The LiHMDS solution was added dropwise to the **HO2-HCl** suspension. The reaction mixture was stirred for 1 h at room temperature and cooled to  $-40^\circ\text{C}$ . The cooled mixture was then added dropwise to a solution of **Mo-1** (150 mg, 0.18 mmol) in THF (2 mL) at  $-40^\circ\text{C}$ . After the reaction mixture was stirred for 16 h at room temperature, all volatiles were removed in vacuo and the residue was washed with *n*-pentane (2 mL) and redissolved in  $\text{CH}_2\text{Cl}_2$ . The mixture was filtered through a pad of Celite and all volatiles were removed in vacuo. The solid residue was crystallized from diethyl ether and *n*-pentane. The product was isolated in the form of dark red crystals (106 mg, 0.12 mmol, 70%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.12–7.08 (m, 2H), 7.02–6.96 (m, 1H), 6.93–6.86 (m, 1H), 6.79 (s, 1H), 6.51 (m, 4H), 6.31 (s, 1H), 4.29–4.20 (m, 2H), 3.98 (m, 2H), 3.75 (s, 3H), 2.30 (s, 3H), 2.26 (s, 3H), 2.03 (s, 3H), 1.69 (s, 3H), 1.25 (s, 3H) ppm.  $^{19}\text{F}$  NMR (375 MHz,  $\text{CDCl}_3$ ):  $\delta$  -77.09 (q,  $^4J_{\text{F-F}} = 9.6$  Hz, 3F), -77.29 (s, 3F), -77.47 (q,  $^4J_{\text{F-F}} = 9.6$  Hz, 6F) ppm.  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  307.9 (Mo $\equiv$ C), 208.9 (NCN), 159.8, 138.2, 137.4, 136.5, 135.8, 135.1, 131.8, 131.7, 129.7, 129.4, 129.2, 128.4, 126.3, 125.5, 124.1 (q,  $^1J_{\text{C-F}} = 288.8$  Hz)\*, 123.7 (q,  $^1J_{\text{C-F}} = 288.0$  Hz)\*, 120.4, 119.5, 118.1, 112.4, 83.2–81.0 (m,  $\text{C}(\text{CF}_3)_2\text{Me}$ )\*, 55.3, 53.2, 49.4, 20.9, 19.9, 19.0, 18.4, 18.1 ppm. Anal. Calcd for  $\text{C}_{34}\text{H}_{32}\text{F}_{12}\text{MoN}_2\text{O}_4$ : C, 47.67; H, 3.77; N, 3.27. Found: C, 47.42; H, 4.063; N, 3.29. \*Quartet poorly resolved. \*\*Septet poorly resolved.

**[Mo( $\equiv$ C-(*p*-OMe- $\text{C}_6\text{H}_4$ ))(O3)(OCMe( $\text{CF}_3$ ) $_2$ ) $_2$ ] (Mo-10).** **HO3-HCl** (54.1 mg, 0.21 mmol) in THF (2 mL) and LiHMDS (71.7 mg, 0.43 mmol) in THF (2 mL) were cooled to  $-40^\circ\text{C}$ . The LiHMDS solution was added dropwise to the **HO3-HCl** solution. The reaction mixture was stirred for 1 h at room temperature and cooled to  $-40^\circ\text{C}$ . The cooled mixture was then added dropwise to a solution of **Mo-1** (180 mg, 0.21 mmol) in THF (2 mL) at  $-40^\circ\text{C}$ . After the reaction mixture was stirred for 16 h at room temperature, all volatiles were removed in vacuo and the residue was washed with *n*-pentane (2 mL) and redissolved in  $\text{CH}_2\text{Cl}_2$ . The mixture was filtered through a pad of Celite, and all volatiles were again removed in vacuo. The solid residue was crystallized from  $\text{CH}_2\text{Cl}_2$ . The product was isolated in the form of a yellow solid (73 mg, 0.10 mmol, 47%).  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  7.19 (d,  $^3J_{\text{H-H}} = 8.0$  Hz, 1H), 7.04–6.96 (m, 1H), 6.82 (s, 1H), 6.82 (dd,  $^3J_{\text{H-H}} = 5.3$  Hz,  $^4J_{\text{H-H}} = 1.0$  Hz, 1H), 6.64 (d,  $^3J_{\text{H-H}} = 8.5$  Hz, 2H), 6.57 (d,  $^3J_{\text{H-H}} = 8.9$  Hz, 2H), 4.37–4.22 (m, 1H), 4.14–3.97 (m, 1H), 3.78–3.59 (m, 5H), 2.46 (s, 1H), 2.00 (d,  $^3J_{\text{H-H}} = 10.6$  Hz, 1H), 1.69 (s, 3H), 1.51 (s, 3H), 1.33 (s, 3H) ppm.  $^{19}\text{F}$  NMR (375 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  -78.08 (s, 3F), -78.74 (q,  $^4J_{\text{F-F}} = 9.4$  Hz, 3F) ppm.  $^{13}\text{C}$  NMR (100 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  302.4 (Mo $\equiv$ C), 220.1 (NCN), 159.4, 156.4, 139.9, 131.6, 131.4, 124.9 (q,  $^1J_{\text{C-F}} = 288.3$  Hz), 124.0, 119.7, 119.5, 114.3, 113.3, 81.4 (sept.,  $^2J_{\text{C-F}} = 28.4$  Hz,  $\text{C}(\text{CF}_3)_2\text{Me}$ ), 67.8, 63.9, 55.7, 49.8, 43.8, 29.9, 26.7, 20.9 ppm. Despite numerous efforts, no satisfactory elemental analysis data could be obtained due to substoichiometric incorporation of tetrahydrofuran and  $\text{CH}_2\text{Cl}_2$  (as confirmed by single-crystal X-ray analysis).

**Mo( $\equiv$ C-(*p*-OMe- $\text{C}_6\text{H}_4$ ))(O4)(OCMe( $\text{CF}_3$ ) $_2$ ) $_2$  (Mo-11).** **HO4-HCl** (82.7 mg, 0.24 mmol) in THF (2 mL) and LiHMDS (79.7 mg, 0.48 mmol) in THF (2 mL) were cooled to  $-40^\circ\text{C}$ . The LiHMDS solution was added dropwise to the **HO4-HCl** solution. The reaction mixture was stirred for 1 h at room temperature and cooled to  $-40^\circ\text{C}$ . The cooled mixture was then added dropwise to a solution of **Mo-1** (200 mg, 0.24 mmol) in THF (2 mL) at  $-40^\circ\text{C}$ . After the reaction mixture was stirred for 16 h at room temperature, all volatiles were removed in vacuo and the residue was washed with *n*-pentane (2 mL) and redissolved in  $\text{CH}_2\text{Cl}_2$ . The mixture was filtered through a pad of

Celite, and all volatiles were again removed in vacuo. The solid residue was crystallized from diethyl ether and *n*-pentane. The product was isolated in the form of a dark solid (153 mg, 0.18 mmol, 75%). <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 7.52–7.25 (m, 6H), 7.18 (d, <sup>3</sup>J<sub>H-H</sub> = 5.8 Hz, 1H), 6.99 (m, 3H), 6.83 (s, 2H), 6.75–6.64 (m, 1H), 6.41 (d, <sup>3</sup>J<sub>H-H</sub> = 8.9 Hz, 2H), 6.27 (s, 2H), 4.80–4.64 (m, 1H), 4.55–4.43 (m, 1H), 4.15–3.93 (m, 2H), 3.64 (s, 3H), 1.60 (s, 3H), 1.39 (s, 3H) ppm. <sup>19</sup>F NMR (375 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ -75.77 (d, <sup>4</sup>J<sub>F-F</sub> = 7.4 Hz, 3F), -76.26 (d, <sup>4</sup>J<sub>F-F</sub> = 8.2 Hz, 3F), -77.18 to -77.33 (m, 3F), -77.37 to -77.49 (m, 3F) ppm. <sup>13</sup>C NMR (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 302.9 (Mo≡C), 208.1 (NCN), 163.2, 159.8, 139.4, 139.3, 138.2, 137.1, 132.6, 132.0, 128.9, 128.7, 128.1, 127.5, 125.7, 125.0, 124.8 (q, <sup>1</sup>J<sub>C-F</sub> = 289.5 Hz), 118.7, 118.3, 116.1, 112.8, 82.7 (m, C(CF<sub>3</sub>)<sub>2</sub>Me)\*, 55.7, 49.7, 21.2, 19.4 ppm\*\*. Anal. Calcd for C<sub>37</sub>H<sub>30</sub>F<sub>12</sub>MoN<sub>2</sub>O<sub>4</sub>: C, 49.90; H, 3.40; N, 3.15. Found: C, 49.50; H, 3.548; N, 3.23. \*Septet poorly resolved. \*\*Missing signals in the aromatic region are due to peak overlapping and broad peaks.

**Mo(≡C-(*p*-Ome-C<sub>6</sub>H<sub>4</sub>))(O<sub>2</sub>)(OCMe(CF<sub>3</sub>)<sub>2</sub>)<sub>2</sub> (Mo-13).** HO<sub>2</sub>·H (131.2 mg, 0.31 mmol) and LiHMDS (103.6 mg, 0.62 mmol) were suspended/dissolved in THF (each 10 mL) and cooled to -40 °C. The LiHMDS solution was added to the imidazolium salt suspension, and the mixture was stirred at room temperature for 1 h. Mo-1 (260 mg, 0.31 mmol) was dissolved in THF (15 mL) and cooled to -40 °C. The reaction mixture was cooled to -40 °C and was then slowly added to the solution of the metal complex. The reaction mixture was stirred at room temperature for 16 h, and then all volatiles were removed in vacuo and the residue was washed with *n*-pentane (2 × 30 mL). The resulting residue was crystallized from diethyl ether. The product was isolated in the form of a red solid (189 mg, 0.23 mmol, 75%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.20 (s, 2H), 6.89 (d, <sup>3</sup>J<sub>H-H</sub> = 8.9 Hz, 2H), 6.72 (d, <sup>3</sup>J<sub>H-H</sub> = 9.0 Hz, 2H), 4.54 (d, <sup>2</sup>J<sub>H-H</sub> = 14.3 Hz, 2H), 4.48 (d, <sup>2</sup>J<sub>H-H</sub> = 14.3 Hz, 2H), 3.76 (s, 3H), 1.82 (s, 3H) ppm. <sup>19</sup>F NMR (375 MHz, CDCl<sub>3</sub>): δ -75.46 (q, <sup>4</sup>J<sub>F-F</sub> = 9.8 Hz, 6F), -77.01 (q, <sup>4</sup>J<sub>F-F</sub> = 9.9 Hz, 6F), -78.55 (s, 6F) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 310.1 (Mo≡C), 189.4 (NCN), 160.2, 138.0, 131.3, 123.9 (q, <sup>1</sup>J<sub>C-F</sub> = 287.0 Hz), 123.0 (q, <sup>1</sup>J<sub>C-F</sub> = 289.2 Hz), 122.9 (q, <sup>1</sup>J<sub>C-F</sub> = 291.4 Hz), 121.8, 113.0, 82.5 (sept., <sup>2</sup>J<sub>C-F</sub> = 29.1 Hz), 80.8 (sept., <sup>2</sup>J<sub>C-F</sub> = 28.4 Hz), 55.3, 49.8, 20.2 ppm\*\*. Anal. Calcd for C<sub>23</sub>H<sub>16</sub>F<sub>18</sub>MoN<sub>2</sub>O<sub>4</sub>: C, 33.59; H, 1.96; N, 3.41. Found: C, 33.79; H, 2.139; N, 3.48.

**W(≡C-(*p*-Ome-C<sub>6</sub>H<sub>4</sub>))(O<sub>1</sub>)(OCMe(CF<sub>3</sub>)<sub>2</sub>)<sub>2</sub> (W-3).** HO<sub>1</sub>·HBF<sub>4</sub> (0.1 g, 0.28 mmol, 1 equiv) was suspended in toluene, and LiHMDS (99 mg, 0.59 mmol, 2.1 equiv) was added as a solid at -40 °C. The yellow reaction mixture was stirred for 2 h at room temperature and then cooled again to -40 °C. Separately, W-1 (0.26 g, 0.28 mmol) was dissolved in toluene and added dropwise at -40 °C to the NHC solution. The reaction mixture was stirred overnight and filtered through Celite, and the solvent was removed under reduced pressure. The residue was washed with *n*-pentane, and the clean orange product W-3 was isolated from diethyl ether (0.11 g, 0.12 mmol, 44%). <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>): δ 7.38 (dd, <sup>3</sup>J<sub>H-H</sub> = 8.1 Hz, <sup>4</sup>J<sub>H-H</sub> = 0.9 Hz, 1H), 7.02 (ddd, <sup>3</sup>J<sub>H-H</sub> = 8.1 Hz, 7.5 Hz, <sup>4</sup>J<sub>H-H</sub> = 1.6 Hz, 1H), 6.85–6.70 (m, 4H), 6.56–6.47 (m, 3H), 6.46–6.41 (m, 2H), 3.13 (s, 3H), 3.11–2.93 (m, 2H), 2.80–2.71 (m, 1H), 2.59–2.47 (m, 1H), 2.17 (s, 3H), 2.10 (s, 3H), 1.99 (s, 3H), 1.72 (s, 3H) ppm. <sup>19</sup>F NMR (375 MHz, C<sub>6</sub>D<sub>6</sub>): δ -75.91 (q, <sup>4</sup>J<sub>F-F</sub> = 8.9 Hz, 3F), -76.46 (q, <sup>4</sup>J<sub>F-F</sub> = 9.8 Hz, 3F), -76.98 (q, <sup>4</sup>J<sub>F-F</sub> = 9.1 Hz, 3F), -77.31 (q, <sup>4</sup>J<sub>F-F</sub> = 9.1 Hz, 3F) ppm. <sup>13</sup>C NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>): δ 292.9 (W≡C), 215.1 (NCN), 160.4, 160.1, 138.8, 138.2, 135.4, 135.2, 134.1, 133.1, 129.7, 129.5, 125.9, 122.0 (m, CF<sub>3</sub>)\*, 119.7, 118.3, 117.9, 112.3, 82.9 (m, C(CF<sub>3</sub>)<sub>2</sub>Me)\*\*, 54.6, 53.1, 49.2, 20.7, 19.7, 19.2, 19.1 ppm. Anal. Calcd for C<sub>33</sub>H<sub>30</sub>F<sub>12</sub>WN<sub>2</sub>O<sub>4</sub>: C, 42.60; H, 3.25; N, 3.01. Found: C, 42.75; H, 3.22; N, 3.15. \*Quartet signals poorly resolved, overlapping with the C<sub>6</sub>D<sub>6</sub> signals. \*\*Septet poorly resolved. An alternative synthetic route to this compound is provided in the Supporting Information.

**W(≡C-(*p*-Ome-C<sub>6</sub>H<sub>4</sub>))(O<sub>2</sub>)(OCMe(CF<sub>3</sub>)<sub>2</sub>)<sub>2</sub> (W-4).** HO<sub>2</sub>·HBF<sub>4</sub> (0.401 g, 1.1 mmol, 1 equiv) was suspended in toluene, and LiHMDS (0.383 g, 2.3 mmol, 2.1 equiv) was added as a solid at -40 °C. The yellow reaction mixture was stirred for 2 h at room temperature and

then cooled to -40 °C. Separately, W-1 (1.03 g, 1.1 mmol) was dissolved in toluene and added dropwise at -40 °C to the NHC solution. The reaction mixture was stirred overnight and filtered through Celite, and the solvent was removed in vacuo. The orange residue was washed with *n*-pentane, and the pure product W-4 was crystallized from diethyl ether (0.62 g, 0.66 mmol, 60%). <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>): δ 7.39 (dd, <sup>3</sup>J<sub>H-H</sub> = 8.1, <sup>4</sup>J<sub>H-H</sub> = 0.8 Hz, 1H), 7.02 (ddd, <sup>3</sup>J<sub>H-H</sub> = 8.1 Hz, 7.5 Hz, <sup>4</sup>J<sub>H-H</sub> = 1.6 Hz, 1H), 6.75 (td, <sup>3</sup>J<sub>H-H</sub> = 7.7 Hz, <sup>4</sup>J<sub>H-H</sub> = 1.4 Hz, 1H), 6.57–6.52 (m, 2H), 6.51–6.42 (m, 5H), 3.15 (s, 3H), 3.11–3.04 (m, 1H), 2.98 (dd, <sup>2</sup>J<sub>H-H</sub> = 20.7 Hz, <sup>3</sup>J<sub>H-H</sub> = 10.2 Hz, 1H), 2.88–2.81 (m, 1H), 2.65 (dd, <sup>2</sup>J<sub>H-H</sub> = 21.2 Hz, <sup>3</sup>J<sub>H-H</sub> = 10.1 Hz, 1H), 2.18 (s, 3H), 2.12 (s, 3H), 2.01 (s, 3H), 1.99 (s, 3H), 1.69 (s, 3H) ppm. <sup>19</sup>F NMR (375 MHz, C<sub>6</sub>D<sub>6</sub>): δ -75.98 to -76.15 (m, 3F), -76.46 (q, <sup>4</sup>J<sub>F-F</sub> = 9.8 Hz, 3F), -77.01 (q, <sup>4</sup>J<sub>F-F</sub> = 9.4 Hz, 3F), -77.38 (q, <sup>4</sup>J<sub>F-F</sub> = 9.2 Hz, 3F) ppm. <sup>13</sup>C NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>): δ 293.0 (W≡C), 215.1 (NCN), 160.0, 159.3, 138.1, 138.0, 136.6, 135.3, 135.2, 133.8, 133.0, 130.2, 130.0, 126.0, 124.7 (q, <sup>1</sup>J<sub>C-F</sub> = 288.1 Hz), 120.0, 118.3, 112.2, 82.7 (m, C(CF<sub>3</sub>)<sub>2</sub>Me)\*, 54.6, 53.1, 49.1, 20.7, 20.3, 19.8, 19.1, 19.0 ppm. Anal. Calcd for C<sub>34</sub>H<sub>32</sub>F<sub>12</sub>N<sub>2</sub>O<sub>4</sub>W: C, 43.24; H, 3.42; N, 2.97. Found: C, 43.53; H, 3.77; N, 2.83. \*Septet poorly resolved. Crystals suitable for single-crystal X-ray analysis were obtained from diethyl ether.

**W(≡C-(*p*-Ome-C<sub>6</sub>H<sub>4</sub>))(O<sub>3</sub>)(OCMe(CF<sub>3</sub>)<sub>2</sub>)<sub>3</sub> (W-5).** HO<sub>3</sub>·HBF<sub>4</sub> (33 mg, 0.11 mmol, 1 equiv) was dissolved in diethyl ether, and KH (9 mg, 0.23 mmol, 2.1 equiv) was added. After 3 h of stirring at room temperature, the potassium salt of the ionically tagged alkoxide was filtered off, suspended in toluene, and slowly added dropwise at -40 °C to a toluene solution of W-1 (0.11 g, 0.12 mmol, 1 equiv). The reaction mixture was stirred at room temperature for 3 h and filtered through Celite, and the solvent was removed in vacuo. The red residue was washed with *n*-pentane and dried (65.6 mg, 0.06 mmol, 53%). <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>): δ 8.63 (s, 1H), 7.92 (d, <sup>3</sup>J<sub>H-H</sub> = 8.2 Hz, 1H), 7.23 (d, <sup>3</sup>J<sub>H-H</sub> = 8.7 Hz, 2H), 7.12–7.04 (m, 1H), 6.84–6.78 (m, 2H), 6.62 (td, <sup>3</sup>J<sub>H-H</sub> = 7.9 Hz, <sup>4</sup>J<sub>H-H</sub> = 1.0 Hz, 1H), 6.48–6.43 (m, 1H), 3.31 (s, 3H), 2.94–2.87 (m, 2H), 2.45–2.36 (m, 2H), 2.11 (s, 3H), 1.97 (s, 6H), 0.82 (s, 9H) ppm. <sup>19</sup>F NMR (375 MHz, C<sub>6</sub>D<sub>6</sub>): δ -76.87 to -77.01 (m, 12F), -77.13 to -77.20 (m, 6F) ppm. <sup>13</sup>C NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>): δ 272.3 (W≡C), 159.7 (NCN), 157.1, 155.1, 139.2, 134.8, 128.8, 126.0, 125.3 (q, <sup>1</sup>J<sub>C-F</sub> = 290.0 Hz), 120.5, 120.2, 118.3, 113.1, 82.5 (sept., <sup>2</sup>J<sub>C-F</sub> = 27.0 Hz, C(CF<sub>3</sub>)<sub>2</sub>Me)\*, 56.8, 54.9, 53.3, 50.0, 43.3, 27.2, 20.2, 19.8 ppm. Anal. Calcd for C<sub>33</sub>H<sub>34</sub>F<sub>18</sub>N<sub>2</sub>O<sub>5</sub>W: C, 37.24; H, 3.22; N, 2.63. Found: C, 37.19; N, 3.34; H, 2.75. \*Only five signals of the septet were observed.

**W(≡C-(*p*-Ome-C<sub>6</sub>H<sub>4</sub>))(O<sub>1</sub>)(OCMe<sub>2</sub>(CF<sub>3</sub>)<sub>2</sub>)<sub>2</sub> (W-6).** W-6 was synthesized analogously to W-3 by the reaction of HO<sub>1</sub>·HBF<sub>4</sub> with W-2 and isolated as a yellow solid (95 mg, 0.12 mmol, 39%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.17–7.11 (m, 4H), 7.07 (m, 2H), 6.91–6.83 (m, 1H), 6.56 (d, <sup>3</sup>J<sub>H-H</sub> = 9.0 Hz, 2H), 6.12 (d, <sup>3</sup>J<sub>H-H</sub> = 8.9 Hz, 2H), 4.55–4.43 (m, 1H), 4.20–4.04 (m, 2H), 3.69 (s, 3H), 3.62 (m, 1H), 2.42 (s, 3H), 2.21 (s, 3H), 1.62 (s, 3H), 1.50 (s, 3H), 1.35 (s, 3H), 0.74 (s, 3H) ppm. <sup>19</sup>F NMR (375 MHz, CDCl<sub>3</sub>): δ -80.97 (s, 3F), -82.01 (s, 3F) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 284.9 (W≡C), 217.7 (NCN), 161.8, 158.5, 139.5, 139.3, 135.1, 134.6, 134.2, 133.1, 129.9, 129.6, 128.3, 127.9 (q, <sup>1</sup>J<sub>C-F</sub> = 285.3 Hz, CF<sub>3</sub>), 126.6 (q, <sup>1</sup>J<sub>C-F</sub> = 286.9 Hz, CF<sub>3</sub>)\*, 125.2, 118.5, 117.5, 117.0, 112.0, 80.7 (q, <sup>2</sup>J<sub>C-F</sub> = 28.6 Hz, C(CF<sub>3</sub>)<sub>2</sub>Me), 98.0 (q, <sup>2</sup>J<sub>C-F</sub> = 28.3 Hz, C(CF<sub>3</sub>)<sub>2</sub>Me), 55.3, 53.6, 49.5, 26.1, 25.6, 25.3, 23.2, 20.0, 19.1 ppm. Anal. Calcd for C<sub>33</sub>H<sub>36</sub>F<sub>6</sub>WN<sub>2</sub>O<sub>4</sub>: C, 48.19; H, 4.41; N, 3.41. Found: C, 48.18; H, 4.50; N, 3.39. \*One signal of quartet overlaps with signal at δ 125.19 ppm. An alternative route to this compound is provided in the Supporting Information.

**W(≡C-(*p*-Ome-C<sub>6</sub>H<sub>4</sub>))(O<sub>2</sub>)(OCMe<sub>2</sub>(CF<sub>3</sub>)<sub>2</sub>)<sub>2</sub> (W-7).** W-7 was synthesized analogously to W-4 by the reaction of HO<sub>2</sub>·HBF<sub>4</sub> with W-2 and isolated as a yellow solid (45 mg, 0.05 mmol, 65%). <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>): δ 7.41 (dd, <sup>3</sup>J<sub>H-H</sub> = 8.1 Hz, <sup>4</sup>J<sub>H-H</sub> = 1.3 Hz, 1H), 7.11 (ddd, <sup>3</sup>J<sub>H-H</sub> = 8.0 Hz, 7.5 Hz, <sup>3</sup>J<sub>H-H</sub> = 1.6 Hz, 1H), 6.83 (td, <sup>3</sup>J<sub>H-H</sub> = 7.6 Hz, <sup>3</sup>J<sub>H-H</sub> = 1.4 Hz, 1H), 6.68–6.44 (m, 7H), 3.18 (m, 1H), 3.13 (s, 3H), 3.10–3.01 (m, 1H), 2.81–2.72 (m, 1H), 2.46 (m, 1H), 2.07 (s, 3H), 2.05 (s, 3H), 2.03 (s, 3H), 1.96 (s, 3H), 1.83 (s,

3H), 1.64 (s, 3H), 1.03 (s, 3H; CH<sub>3</sub>) ppm. <sup>19</sup>F NMR (375 MHz, C<sub>6</sub>D<sub>6</sub>): δ -81.50 (s, 3F), -80.65 (s, 3F) ppm. <sup>13</sup>C NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>): δ 285.2 (W≡C), 217.4 (NCN), 162.9, 159.3, 139.8, 137.8, 137.3, 134.7, 134.6, 133.8, 133.6, 130.8, 130.1, 128.8 (q, <sup>1</sup>J<sub>C-F</sub> = 285.5 Hz, CF<sub>3</sub>), 127.6 (q, <sup>1</sup>J<sub>C-F</sub> = 286.2 Hz, CF<sub>3</sub>), 125.4, 118.2, 117.8, 117.3, 112.5, 81.3 (q, <sup>2</sup>J<sub>C-F</sub> = 28.4 Hz, C(CF<sub>3</sub>)Me<sub>2</sub>), 80.4 (q, <sup>2</sup>J<sub>C-F</sub> = 27.8 Hz, C(CF<sub>3</sub>)Me<sub>2</sub>), 54.6, 53.2, 48.7, 26.7, 26.0, 25.6, 23.6, 20.7, 19.8, 18.8, ppm. Anal. Calcd for C<sub>34</sub>H<sub>38</sub>F<sub>6</sub>N<sub>2</sub>O<sub>4</sub>W: C, 48.82; H, 4.58; N, 3.35. Found: C, 48.83; H, 4.59; N, 3.47.

### Accession Codes

CCDC 1531391–1531393, 1861321–1861324, and 1897061 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](http://www.ccdc.cam.ac.uk/data_request/cif), or by emailing [data\\_request@ccdc.cam.ac.uk](mailto: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.

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#### Notes

The authors declare no competing financial interest.

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