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Tungsten Alkylidynes

Cationic Tungsten Alkylidyne *N*-Heterocyclic Carbene Complexes: Synthesis and Reactivity in Alkyne Metathesis

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Abstract: The first cationic and neutral tungsten alkylidyne *N*-heterocyclic carbene (NHC) complexes bearing one triflate ligand were synthesized and tested for their reactivity in alkyne metathesis. Both types of tungsten alkylidyne complexes display a higher productivity in alkyne metathesis than the analogous neutral tungsten alkylidyne NHC trisalkoxide complexes. Reaction of W(≡CC$_6$H$_4$OMe)(1,3-bis(1-hydroxy-1,1-trifluoromethylethyl)-imidazol-2-ylidene)Cl (**W18**) with AgB(Ar^F)$_4$ (Ar^F = 3,5-bis(trifluoromethyl)phenyl) resulted in the unexpected formation of, to the best of our knowledge, the first cationic ditungstatetrahedrane W$_2$(1,3-bis(1-hydroxy-1,1-trifluoromethylethyl)-imidazol-2-ylidene)$_2$(MeCN)(μ-((Ar)CC(Ar)))$^+$ (B(Ar^F)$_4$)$^-$ (**W19**, Ar = C$_6$H$_4$OMe), which suggests bimolecular decomposition as a possible decomposition pathway of cationic tungsten alkylidyne NHC complexes. Reaction of the cationic tungsten alkylidyne NHC complex W(≡CC$_6$H$_4$OMe)(1,3-diisopropylimidazol-2-ylidene)(OC(CF$_3$)$_2$Me)$_2$(NC*t*Bu)$^+$ (B(Ar^F)$_4$)$^-$ (**W7**) with 1-phenyl-1-propyne allowed for the isolation of a cationic tungstacyclobutadiene W(C$_3$(Ph)(Me)(C$_6$H$_4$OMe))(1,3-diisopropylimidazol-2-ylidene)(OC(CF$_3$)$_2$Me)$_2$(NC*t*Bu)$^+$ (B(Ar^F)$_4$)$^-$ (**W20**). Its formation strongly supports a cationic active species in the alkyne metathesis with tungsten alkylidyne NHC complexes.

Introduction

The metathesis of alkynes was first discovered in 1968 as the disproportionation of 2-pentyne with the heterogeneous catalyst WO_3 supported on silica.[1] In the following years, several well-defined homogeneous catalyst systems were developed by the groups of Schrock,[2] Fürstner,[3] Tamm,[4] Moore,[5] Cummins,[6] Zhang,[7] Nuckolls,[8] Fischer[9] and Veige[10] and advanced the field of alkyne metathesis. The close relation to olefin metathesis allows for inspiration in catalyst design, as shown by the development of imidazolin-2-iminato tungsten and molybdenum alkylidyne complexes[4a,4b,11] derived from Schrock's tungsten and molybdenum imido alkylidene complexes.[12]

Cationic molybdenum and tungsten alkylidene *N*-heterocyclic carbene (NHC) complexes are highly active olefin metathesis catalysts and represent the active species in neutral molybdenum and tungsten alkylidene NHC complexes.[13] In view of these findings, we recently developed molybdenum and tungsten alkylidyne NHC complexes. Particularly, the molybdenum alkylidyne NHC complexes showed moderate activity in alkyne metathesis, while the analogous tungsten complexes turned out to be virtually unreactive.[14] We proposed that the active species in these complexes are cationic with a dissociated alkoxide ligand in case a strongly σ-donating NHC was coordinated to the metal center. Based on this proposal, it should be possible to improve the reactivity of otherwise inactive tungsten alkylidyne NHC complexes by replacing one alkoxide by a better leaving group, such as a triflate, similar to neutral molybdenum and tungsten alkylidene NHC complexes.[13a,13g] Alternatively, one alkoxide can be replaced by a non-coordinating anion (e.g. B(Ar^F)$_4^-$) in order to bypass ligand dissociation, as proven successful in olefin metathesis with cationic molybdenum and tungsten alkylidene NHC complexes.[13b,13c,13e,15] Although reports on cationic tungsten alkylidyne complexes exist,[16] we report herein the synthesis of the *first cationic tungsten alkylidyne NHC complexes* and their reactivity in selected alkyne metathesis reactions.

Results and Discussion

Synthesis of Neutral and Cationic W Alkylidyne NHC Complexes

We recently reported on the first tungsten alkylidyne complexes bearing bidentate NHC ligands. Surprisingly, these complexes did not show any activity in alkyne metathesis while the analogous molybdenum complexes did.[14b] Since molybdenum alkylidyne complexes with monodentate NHCs proved to be more

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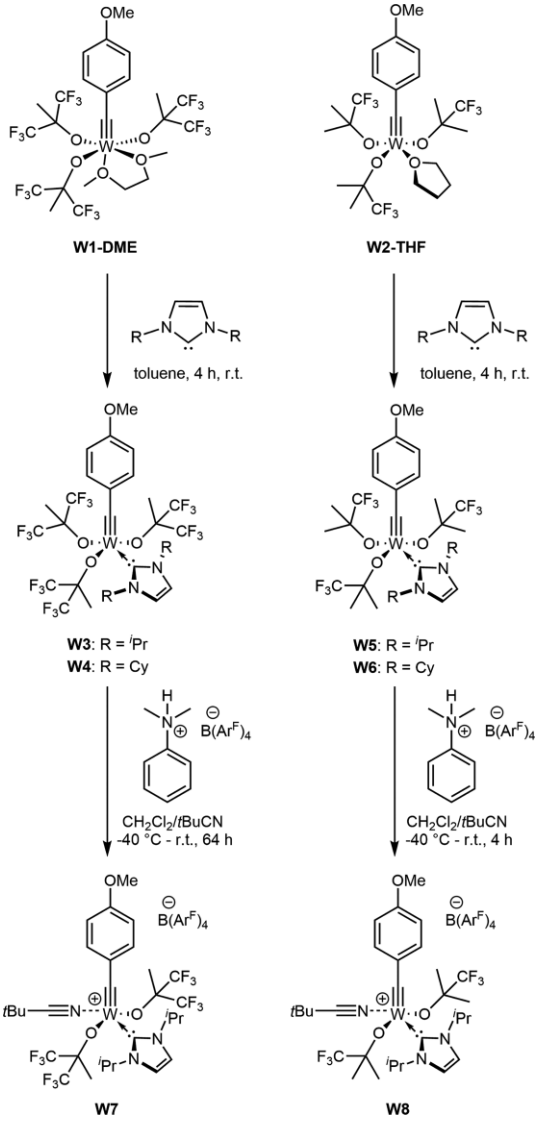
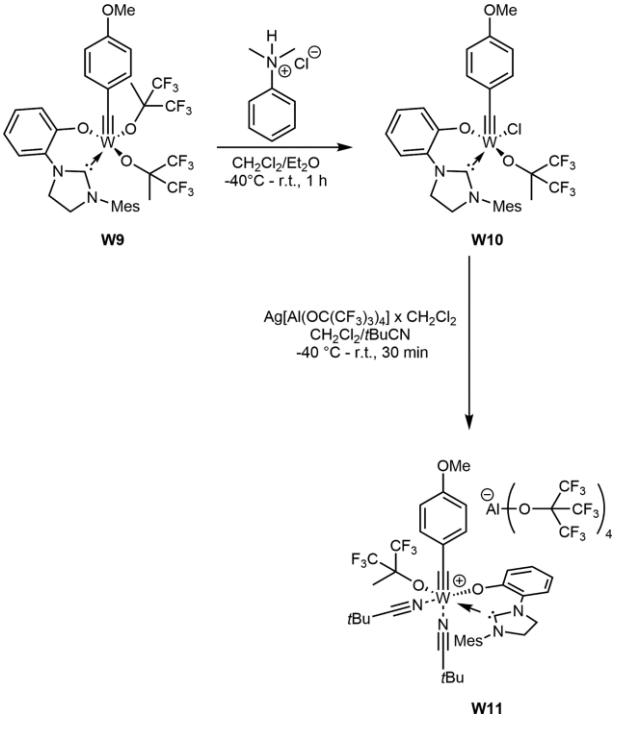
reactive than those bearing bidentate NHCs, the corresponding tungsten complexes were synthesized.[14] Tamm and Copéret already demonstrated that the reactivity of molybdenum- and tungsten-based, Schrock-type alkylidyne complexes strongly depends on the degree of fluorination of the alkoxide ligands, with a maximum in reactivity for tungsten complexes residing at the trifluoro-*tert*-butoxide.[4e,4f]

In view of this information, we first synthesized complexes bearing monodentate NHCs with hexafluoro-*tert*-butoxides as well as complexes bearing trifluoro-*tert*-butoxides (Scheme 1). In analogy to the previously published molybdenum complexes,[14a] the tungsten precursors **W1-DME** and **W2-THF** were reacted with the strongly σ-donating NHCs 1,3-diisopropylimidazol-2-ylidene (Tolman electronic parameter (TEP) = 2051.5 cm^{-1}) and 1,3-dicyclohexylimidazol-2-ylidene (TEP = 2049.7 cm^{-1}),[17] respectively, to afford complexes **W3**, **W4**, **W5** and **W6** in 43–80 % isolated yield. In an effort to enhance reactivity in alkyne metathesis by the use of cationic tungsten alkylidyne NHC complexes, **W3** and **W5** were treated with *N*,*N*-dimethylanilinium $B(Ar^F)_4^-$ etherate in order to replace one of the fluorinated alkoxides by the non-coordinating anion $B(Ar^F)_4$. To stabilize the cationic metal center, an additional donor ligand turned out be necessary. Here, pivalonitrile was used. Complexes **W7** and **W8** were isolated in 62 and 79 % yield, respectively. Notable, in the case of **W7**, the addition of a large excess of pivalonitrile resulted in a complex with two pivalonitrile molecules coordinated to the metal center as evidenced by the integrals of the signals at δ = 1.41 - 1.27 ppm in the ^1H NMR spectra, which can be assigned to the four methyl groups of the NHC as well as to the three and six methyl groups of the nitrile, respectively, which amount to 21 or 30 protons for a single or double pivalonitrile-coordinated complex (Figures S 36, S 39, SI).

Since the neutral tungsten alkylidyne complexes bearing bidentate NHCs were virtually inactive in alkyne metathesis,[14b] we aimed on the synthesis of an analogous cationic complex to improve activity. First, one alkoxide in **W9** was protonated off using *N*,*N*-dimethylaniline hydrochloride and replaced by chloride. The chloro complex **W10** was isolated in 59 % yield and reacted with $AgB(Ar^F)_4 \cdot 3CH_3CN$, which lead to the formation of a cationic complex with two acetonitriles coordinated to the metal center. The complex did not crystallize in our hands and decomposed after a few days. To enhance the stability of the cationic complex, acetonitrile was replaced by the more bulky pivalonitrile; concomitantly, a change in the anion from $B(Ar^F)_4^-$ to $Al(OC(CF_3)_3)_4)^-$ was envisaged to facilitate crystallization of the complex. Accordingly, **W10** was treated with $Ag[Al(OC(CF_3)_3)_4] \cdot CH_2Cl_2$ and pivalonitrile and allowed for the isolation of **W11** in 63 % yield (Scheme 2, Figure 2).



Scheme 1. Synthesis of complexes **W3**–**W6** bearing monodentate NHCs and subsequent transformation into the cationic complexes **W7** and **W8**.



Scheme 2. Synthesis of cationic **W11** via the chloro-substituted complex **W10**.

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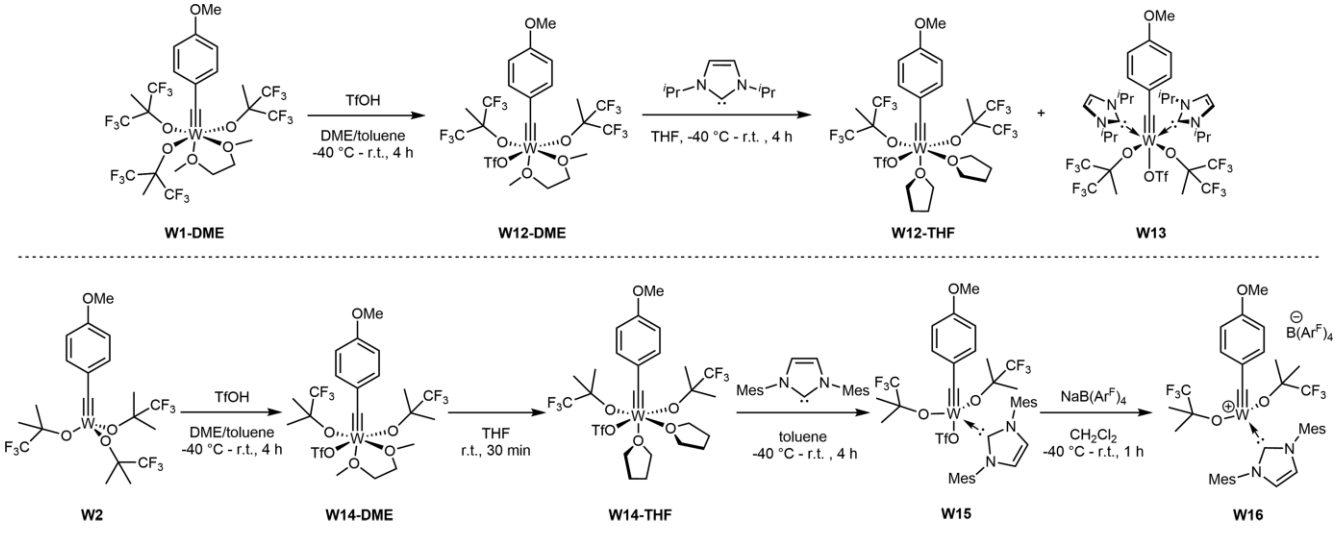
Given the proposed cationic active species in our molybdenum alkylidyne NHC complexes, we also attempted to replace one of the fluorinated alkoxide ligands in the above-mentioned complexes by both a non-coordinating anion and a better leaving group. In neutral molybdenum imido alkylidene NHC mono- or bistriflate complexes, one triflate dissociates either thermally or in the presence of an olefin to form the active species.[13g] We therefore sought to introduce a triflate ligand in our complexes to increase the formation of a cationic species and consequently enhance their reactivity in alkyne metathesis.

The implementation of a triflate ligand was realized by the reaction of the tungsten alkylidyne precursors **W1-DME** and **W2-DME** with one equivalent of triflic acid to obtain **W12-DME** and **W14-DME**, respectively. The reaction of **W12-DME** with one equivalent 1,3-diisopropylimidazol-2-ylidene in THF resulted in a 1:1 mixture of the tungsten alkylidyne bis-NHC complex **W13** and the precursor complex **W12-THF** (Scheme 3), which was successfully extracted from the reaction mixture with *n*-pentane. In case **W12-DME** and **W14-DME** were treated with a bulkier NHC such as 1,3-dimesitylimidazol-2-ylidene, no formation of the desired product was observed at all. Reports on DME activation in tungsten alkylidene complexes[18] led us to believe that the DME ligand had to be exchanged to successfully coordinate 1,3-dimesitylimidazol-2-ylidene. Stirring complexes **W12-DME** and **W14-DME** in THF for 30 minutes generated the THF-coordinated complexes **W12-THF** and **W14-THF**. In contrast to **W14-DME**, we were indeed able to coordinate 1,3-dimesitylimidazol-2-ylidene to the trifluoro-*tert*-butoxide complex **W14-THF** to obtain **W15** in 88 % yield. Notably, at least in our hands, it could *not* be coordinated to **W12-THF** bearing hexafluoro-*tert*-butoxides. In this reaction, only decomposition of the starting material was observed. The triflate in **W15** was easily replaced by the non-coordinating anion $B(Ar^F)_4$ via reaction of **W15** with $NaB(Ar^F)_4$ to obtain **W16** in 73 % isolated yield. In contrast to **W7** and **W8**, the mesityl groups of the NHC in complex **W16** provide enough steric bulk to render the cationic metal complex stable in the absence of an additional donor.

In analogy to the previously published molybdenum complex,[14b] we sought to realize a W alkylidyne complex containing a tridentate NHC to stabilize the cationic charge at the metal center via the chelate effect. Trifluoromethyl groups in α-position to the chelating oxygen atoms were expected to mirror the electron-withdrawing character of the fluorinated alkoxides in complexes containing monodentate NHCs such as **W3**–**W6**. The reaction of **W1-DME** with a tridentate NHC resulted in the formation of **W17** in 57 % isolated yield (Scheme 4). For the synthesis of the corresponding cationic complex, the remaining alkoxide was first replaced by chloride via the reaction with *N*,*N*-dimethylaniline hydrochloride to obtain **W18** in 25 % isolated yield. The reaction of **W18** with $AgB(Ar^F)_4$•3MeCN was expected to result in the formation of a cationic alkylidyne NHC complex, but the ^{1}H NMR spectrum (Figure S78, SI.) showed only half of the expected integrals for the $B(Ar^F)_4$-anion; also, no signals were observed in the alkylidyne region of the ^{13}C NMR spectrum (Figure S80, SI.). Single crystal X-ray analysis of the crystalline product (Figure 5, vide infra) revealed a dimeric structure with a ditungstatetrahedrane core, a bridging chloride and one acetonitrile bound to one of the tungsten centers. The positive charge is formally distributed between the tungsten centers. A complex with a similar dimolybdatetrahedrane core was reported by Fürstner et al. and identified as the decomposition product of the corresponding precursor catalyst $[(Ph_3SiO)_3Mo{\equiv}CC_6H_4OMe]$(phenanthroline) after treatment with $ZnCl_2$ to generate the active catalyst $(Ph_3SiO)_3Mo{\equiv}CC_6H_4OMe$.[19] In addition to a bridging chloride, the molybdenum atoms were also bridged by one of the silyloxide ligands. Other ditungstatetrahedrane structures, which derived from alkylidynes or W≡W species were published by the groups of Fischer[20] and Chisholm.[21] Especially interesting are Chisholm's complexes that are generated by the addition of alkynes to $W_2(OR)_6$ and form ditungstatetrahedranes instead of the expected alkylidyne



Scheme 3. Synthesis of the precursor **W12-DME** and reaction with 1,3-diisopropylimidazol-2-ylidene in THF yielding the tungsten alkylidyne bis-NHC complex **W13** (top). Synthesis of the precursor **W14-THF** and isolation of complex **W15** with subsequent reaction with $NaB(Ar^F)_4$ to obtain the cationic complex **W16** (bottom).

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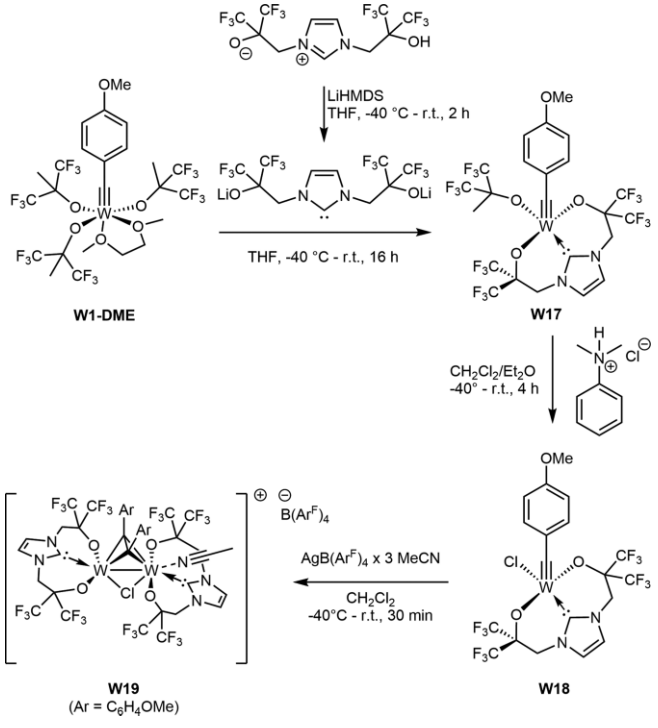
complexes, as observed by Schrock et al. by scission of the W≡W bond.[22] These ditungstatetrahedranes are in equilibrium with the alkylidyne complexes.[21b,21c] For **W19** neither an equilibrium with **W18** nor any reactivity in test reactions with 1-phenyl-1-propyne (**S1**) was observed. The formation of **W19** with loss of the alkylidyne moiety during transformation to a cationic complex and the identification of the dimetallatetrahedrane by Fürstner et al. as one decomposition product of their catalyst, leads us to believe that bimolecular decomposition might indeed be a possible decomposition pathway for cationic alkylidyne NHC complexes. However, it has to be noted that there is no experimental data showing that this decomposition occurs during metathesis reactions. Still, the observation of the ditungstatetrahedrane **W19** strongly underlines the necessity to immobilize the complexes to prevent bimolecular decomposition.



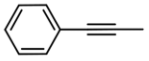
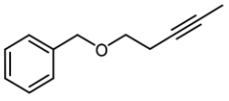
Scheme 4. Synthesis of tungsten alkylidyne complexes bearing tridentate NHCs and formation of the ditungstatetrahedrane **W19**.

Reactivity in Alkyne Metathesis

To confirm our hypothesis that cationic tungsten alkylidyne NHC complexes perform better in alkyne metathesis reactions compared to their neutral analogs, complexes **W3**–**W8**, **W15,** and **W16** were tested in some benchmark self-metathesis reactions. Powdered 5 Å molecular sieves were added to the reaction mixture to remove 2-butyne formed during the reaction.[3c] The neutral tungsten alkylidyne NHC tris(trifluoro-*tert*-butoxide) complexes **W5** and **W6** showed low turnover numbers (TONs) in the self-metathesis of **S1** at 80 °C while being non-reactive at 35 °C. Complexes **W5** and **W6** did not show any reactivity with **S1** without the addition of molecular sieves. The analogous tris(hexafluoro-*tert*-butoxide) complexes **W3** and **W4** were unreactive at both temperatures. For comparison, the corresponding Mo alkylidyne NHC tris(hexafluoro-*tert*-butoxide) complexes showed moderate activity at room temperature or 35 °C.[14] Although a strong σ-donor is present in complexes **W3**–**W6**, they follow a similar trend as observed for the activity of W alkylidyne complexes of the type $MesC{\equiv}W(OR^F)_3$ in alkyne metathesis reactions. In these complexes, the maximum in reactivity was observed for the tris(trifluoro-*tert*-butoxide) complex. Higher degrees of fluorination resulted in a loss of reactivity, which was explained by calculations of a significantly stabilized metallacyclobutadiene (MCBD) intermediate. For Mo, the most active complex was the one based on hexafluoro-*tert*-butoxides.[4c,4e,4f]

The neutral complexes **W10**, **W17** and **W13** as well as the cationic complex **W11** did not show any reactivity in alkyne metathesis of **S1**, neither at 35 °C or 80 °C. **W13** is a 16 electron complex, which explains its inertness in alkyne metathesis reactions. By contrast, the cationic 14 electron complex **W8** showed a substantially increased reactivity compared to the neutral congener **W5** at 80 °C. While **W5** was not reactive at 35 °C, the cationic complex **W8** already reacted with **S1** at room temperature, though only to a minor extent. At 80 °C, **W8** showed the highest TON of 550 for all tungsten alkylidyne NHC complexes with **S1**. This increase in reactivity as well as the reactivity displayed by cationic tungsten complex **W7** in the self-metathesis of **S1** at 80 °C compared to the neutral complex **W3**, which was not reactive at all, supports the proposed cationic active species for metal alkylidyne NHC complexes. With 5-(benzyloxy)-2-pentyne (**S2**) as substrate, complexes **W5**, **W6**, **W8**, **W15,** and **W16** showed TONs around 500 even without the addition of molecular sieves. Indeed, higher TONs cannot be expected without the elimination of 2-butyne from the reaction mixture.[3c] In fact with **S2** the neutral catalysts **W5** and **W6** even show slightly higher productivities than the cationic complexes; however, without molecular sieves all productivities are roughly around equilibrium. Surprisingly, the addition of molecular sieves actually resulted in lower TONs for all catalysts with both substrates in 1,2-dichloroethane and in some cases even in a total loss of activity (**W7**, **W8**). This can be rationalized by the fact that 1,2-dichloroethane is taken up by the 5 Å molecular sieves, which can then no longer remove 2-butyne from the reaction mixture. Impurities inside the molecular sieves together with an elevated sensitivity of the cationic complexes can finally result in even lower TONs. For that reason, the metathesis reactions with **S1** were repeated in chlorobenzene as solvent. In that case, the TONs for **W15** and **W16** increased or at least stayed the same in the presence of molecular sieves, but again decreased for the catalysts **W7** and **W8** bearing pivalonitriles. Why the productivities decrease for these two complexes upon addition of molecular sieves is still not clear. An explanation could be that **W7** and **W8** are less stable than **W15** and **W16**, which is also why they have to be stabilized by additional solvent molecules. Complexes **W15** and **W16** showed similar TONs of 200 and 230 for **S1** at 80 °C without the addition of molecular sieves (Table 1). The cationic tungsten alkylidyne NHC bis(hexafluoro-*tert*-butoxide) complex **W7** was inactive in alkyne metathesis at 35 °C, whereas cationic **W8**

Table 1. Turnover numbers (TONs) after 3 h for metathesis reactions with complexes **W5**–**W8**, **W15,** and **W16**, with and without the addition of grated 5 Å molecular sieves (MS) as 2-butyne scavenger.[3c]

Substrate	T / °C		W5[a]	W6[a]	W7[b]	W8[b]	W15[b]	W16[b]
 **S1**	35	with 5 Å MS	0	0	0 (0)	0 (0)	50 (110)	50 (80)
		without 5 Å MS	0	0	0 (0)	140 (60)	130 (80)	150 (60)
	80	with 5 Å MS	120	130	0 (0)	200 (0)	40 (280)	70 (370)
		without 5 Å MS	0	0	60 (0)	550 (600)	200 (120)	230 (360)
 **S2**	35	with 5 Å MS	0	0	0	0	170	380
		without 5 Å MS	470	510	0	460	510	460
	80	with 5 Å MS	330	330	0	0	80	240
		without 5 Å MS	570	560	0	590	500	420

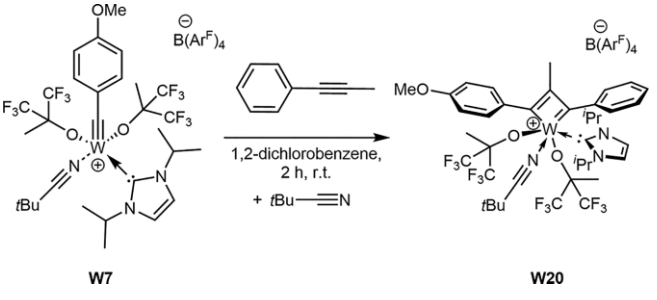
[a] Toluene, substrate:catalyst = 1000:1, internal standard: *t*Bu-Ph. [b] 1,2-dichloroethane, substrate:catalyst = 1000:1, internal standard: *t*Bu-Ph, values in parenthesis indicate productivities when chlorobenzene was used as solvent.

bearing two trifluoro-*tert*-butoxides showed reactivity at the same temperature. A similar trend was found in Tamm's tungsten trialkoxide complexes[4e] among which the tungsten alkylidyne tris(hexafluoro-*tert*-butoxide) complex was inactive, while the tungsten alkylidyne tris(trifluoro-*tert*-butoxide) complex showed the highest catalytic activity,[4c,4e] The finding that **W7** was inactive at 35 °C but active at 80 °C led us to believe that similar to the aforementioned trialkoxide complexes the tungstacyclobutadiene intermediate is overly stabilized and requires higher temperatures to undergo cycloreversion.[23] Even though increased productivities compared to the previously published tungsten alkylidyne NHC complexes were observed,[14b] the cationic tungsten alkylidyne NHC complexes do not rival already established systems for alkyne metathesis.[3c,3d,4c,4e,4g]

Since no preceding reaction such as alkoxide dissociation in neutral alkylidyne NHC complexes should be necessary to activate the cationic alkylidyne NHC complexes, the low reactivity of the cationic alkylidyne NHC complexes **W7** and **W11** towards **S1** in 1,2-[D_4]dichlorobenzene was investigated by ^{1}H and ^{19}F NMR. Five equivalents of **S1** were added to the catalyst solutions and the reaction mixtures were monitored over a period of one hour by NMR. The same experiment was conducted with the alkyne metathesis-active cationic complex **W16**. The ^{1}H NMR spectra of the reaction of **W16** with **S1** (Figure S1, SI) showed the instantaneous formation of the desired product diphenylacetylene (δ = 7.21, 7.50 ppm) and quickly decreasing signals for **S1** (δ = 7.16, 7.38 ppm). Formation of diphenylacetylene was confirmed by GC-MS. The ^{19}F NMR spectra (Figure S2, SI) showed the ($B(Ar^F)_4$) signal at δ = –62.06 ppm, which did not shift after substrate addition. However, the singlet for the alkoxides (δ = –82.41 ppm, 6F) split into two new signals (δ = –78.30 ppm, 3F; –80.53 ppm, 3F). Within 10 min after substrate addition the signals of the parent complex had vanished.

By contrast, after the addition of **S1** to **W11** (Figure S4, SI), the ^{1}H NMR spectrum showed no signals of the metathesis product and probably decomposed upon substrate addition since no clean formation of a new species was observed. Complex **W7**, which only showed metathesis activity with **S1** at 80 °C, did not show any formation of diphenylacetylene in the ^{1}H NMR spectra (Figure S6, SI) at room temperature despite the consumption of one equivalent of **S1** within 60 minutes (Figure S7, SI). For **W7**, we surmised the formation of a tungstacyclobutadiene, for which cycloreversion and release of the metathesis product do not occur at this temperature. And indeed, as observed for **W16**, the ^{19}F NMR spectra of **W7** (Figure S8, SI) did not show a shift in the $(B(Ar^F)_4)^-$ signal (δ = –62.09 ppm) but the two quartets at δ = –76.88 ppm (6F) and δ = –77.33 ppm (6F) slowly vanished over 60 minutes, while two new singlets at δ = –76.55 and –76.65 ppm appeared.

To isolate the proposed tungstacyclobutadiene **W20** (Scheme 5), **S1** was added to a solution of **W7** in 1,2-dichlorobenzene. After stirring the reaction mixture for 2 hours, a drop of pivalonitrile was added and the solution was overlaid with *n*-pentane. The obtained crystals were suitable for single-crystal X-ray analysis and indeed confirmed the formation of the tungstacyclobutadiene (Figure 1). Metallacyclobutadienes were early identified as intermediates in alkyne metathesis and isolated from reaction mixtures of catalyst and substrate.[2e,4a,23,24] Recently, a molybdatetrahedrane complex was also detected as a reaction intermediate in a Mo alkylidyne complex bearing a



Scheme 5. Synthesis of the cationic tungstacyclobutadiene complex **W20** via reaction of **W7** with **S1**.

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siloxide ligand.[25] Similar to some previously published metallacyclobutadienes,[23] **W7** does not perform a full metathesis cycle at room temperature but stops at the stage of the metallacyclobutadiene. **W20** was tested in the metathesis of 1-phenyl-1-propyne (**S1**) without the addition of molecular sieves in 1,2-dichloroethane. Like the parent complex **W7**, **W20** did not show any reactivity in the metathesis of **S1** at 35 °C but exactly the same TON of 60 at 80 °C. To gain further insights in the reactivity of **W20**, ^{1}H and ^{19}F NMR spectra of **W20** at higher temperatures were recorded. The temperature was increased from 25 °C to 80 °C in 5 K steps. Already at 45 °C signals for the parent complex **W7** reappeared in the ^{1}H NMR (Figure S19, SI), for example the doublet at δ = 6.89 ppm. In the ^{19}F NMR (Figure S20, SI) at the same temperature the singal at δ = –77.31 ppm appeared, assignable to **W7**. However, it has to be noted that that **W20** does not solely convert back to **W7** at higher temperatures, since the metallacyclobutadiene has more than one possibility to open. In W alkylidyne imidazolin-2-iminato complexes it was shown that the metallacyclobutadiene forms *trans* to the imidazolin-2-iminato ligand, which represents the strongest σ-donor in this complex.[4a] The same was observed in Mo alkylidene NHC complexes, in which the olefin coordinates *trans* to the NHC.[13g] Consequently, the MCBD in **W20** was also expected to be *trans* to the strongest σ-donor, i.e. to the NHC. However, the crystal structure of **W20** revealed that the NHC is actually *cis* to the MCBD in the octahedral complex structure (Figure 1). If one assumes that the solvent must dissociate prior MCBD formation, as it is the case for the tungsten alkylidyne complex bearing a trianionic ONO pincer ligand reported by Veige and co-workers,[24f] one can explain the structure of **W20** with dissociation of pivalonitrile, addition of the substrate *trans* to the NHC, and recoordination of pivalonitrile pushing the NHC into the *cis* position. A similar release of stabilizing solvent was found for molybdenum alkylidene NHC complexes.[13g]

To investigate the active species in **W15**, a ^{1}H and ^{19}F NMR-based experiment was conducted in which trifluoro-*tert*-butanol was added to a solution of **W15** in o-[D_4]dichlorobenzene followed by five equivalents of **S1**.[14] In case of any dissociated, free NHC, the NHC should be protonated by the acidic alcohol to give the imidazolium salt, which can then easily be observed by ^{1}H NMR. While a new signal indeed appeared in the imidazolium region (Figure S9, SI) it did not fit the chemical shift for 1,3-dimesitylimidazolium trifluoro-*tert*-butoxide (Figure S15, SI). Instead, it was assignable to 1,3-dimesitylimidazolium *triflate* (Figure S17, SI). However, this species is also observed in the NMR spectra recorded in course of the alkyne metathesis reaction of **W15** with **S1** *without the addition of alcohol* (Figure S11, SI). In both experiments, the signal of the imidazolium salt amounts to ca. 10 % after 30 minutes; it therefore must rather form in course of a general catalyst decomposition than an NHC dissociation and formation of a Schrock-type W alkylidyne complex. After addition of **S1** to **W15**, the ^{19}F NMR spectra showed new signals upfield of the parent triflate signal. The integrals suggest that the new signals belong to the alkoxides, while the triflate signal remains unaffected. Equally important, the W–O bond (233.0(2) pm) between tungsten and the triflate in **W15** (Figure 3, vide infra), is exceptionally long. Compared to the one in the alkylidene complex Mo(N-3,5-Me_2-C_6H_3)(CH(CMe_2Ph))-(IMes)$(OTf)_2$ (214.0(3) pm), which is considered already cationic at room temperature in solution, the triflate bond in **W15** is even longer.[13g,15b] Considering the chemical shift of the triflate of δ = –78.14 ppm ($CDCl_3$, Figure S67, SI) which is close to, but not identical to the shift of free triflate found during ring opening metathesis polymerization with molybdenum alkylidene

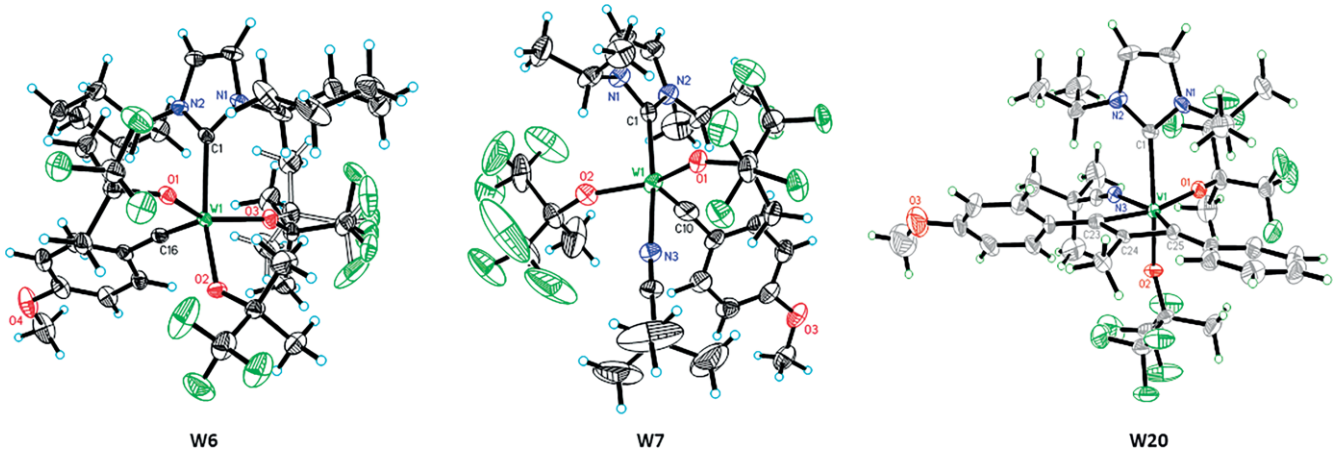

Figure 1. Single crystal X-ray structures of complexes **W6** (left), **W7** (middle) and **W20** (right). $B(Ar^F)_4$-anions in **W7** and **W20** are omitted for clarity. Selected bond lengths [pm] and angles [°] for **W6**: W(1)–C(16) 175.9(2), W(1)–C(1) 225.8(2); W(1)–O(1) 193.75(14), W(1)–O(2) 197.22(15), W(1)–O(3) 193.25(15), O(2)–W(1)–C(1) 165.06(7), O(3)–W(1)–O(1) 141.90(6), O(3)–W(1)–C(1) 83.59(7), O(1)–W(1)–C(1) 83.23(7), C(16)–W(1)–O(3) 108.88(8), C(16)–W(1)–O(1) 107.99(8). Selected bond lengths [pm] and angles [°] for **W7**: W(1)–C(10) 172.3(11), W(1)–C(1) 219.0(8), W(1)–O(1) 188.5(5), W(1)–O(2) 190.6(6), W(1)–N(3) 221.2(7), C(10)–W(1)–O(1) 106.6(3), C(10)–W(1)–O(2) 110.6(3), O(1)–W(1)–O(2) 141.1(2), C(10)–W(1)–C(1) 100.1(3), O(1)–W(1)–C(1) 92.5(2), O(2)–W(1)–C(1) 92.0(2), C(10)–W(1)–N(3) 89.8(3), O(1)–W(1)–N(3) 84.5(2), O(2)–W(1)–N(3) 84.6(2), C(1)–W(1)–N(3) 170.1(3). Selected bond lengths [pm] and angles [°] for **W20**: W(1)–C(23) 194.9(4), W(1)–C(25) 188.4(4), W(1)–C(24) 218.2(4), C(23)–C(24) 140.7(6), C(24)–C(25) 150.4(5), W(1)–C(1) 226.7(4), W(1)–O(1) 190.3(3), W(1)–O(2) 197.3(3), W(1)–N(3) 245.5(4), C(25)–W(1)–O(1) 112.69(14), C(25)–W(1)–C(23) 81.89(16), O(1)–W(1)–C(23) 163.92(14), C(25)–W(1)–O(2) 101.31(13), O(1)–W(1)–O(2) 89.42(11), C(23)–W(1)–O(2) 94.42(13), O(2)–W(1)–C(1) 165.91(12), C(24)–C(23)–W(1) 79.3(2), C(23)–C(24)–C(25) 119.4(3), C(24)–C(25)–W(1) 79.3(2).

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NHC catalysts (ca. –79 ppm),[13a] we propose that in **W15** the triflate is dissociated and that **W15** is cationic in solution. The aforementioned NMR experiment was also conducted with **W16** but no new signal in the imidazolium region was observed (Figure S11, SI).

Single Crystal X-ray Analyses

To gain more insight into the structures of our tungsten alkylidyne NHC complexes, crystal structures of the most important complexes were determined by single-crystal X-ray analysis. Complex **W6** crystallizes in the monoclinic space group $P2_1/n$ (a = 1091.45(3) pm, α = 90°, b = 2142.85(7) pm, β = 104.3430(10)°, c = 1662.48(5) pm, γ = 90°) and shows a geometry index of τ = 0.38, which more likely resembles a distorted square pyramidal (SP) geometry with the alkylidyne ligand in the apex, than a trigonal bipyramidal (TBP) geometry with the NHC and one alkoxide in the apex (Figure 1). Due to the *trans* influence, the alkoxide *trans* to the NHC is bound more weakly (W(1)–O(2) 197.22(15) pm) than the other two alkoxides (W(1)–O(1) 193.75(14) and W(1)–O(3) 193.25(15) pm). The alkylidyne bond in **W6** is 175.9(2) pm and thus comparable to the NHC free complex W(≡CMes)(OC(CF$_3$)Me$_2$)$_3$ (176.89(19) pm)[4e] but slightly longer than the one in a similar Mo complex Mo(≡CC$_6$H$_4$OMe)(ICy)(OC(CF$_3$)$_2$Me)$_3$ (174.4(4) pm).[14b] Notably, the alkoxide bonds in **W6** are substantially longer than in the NHC-free complex W(≡CMes)(OC(CF$_3$)Me$_2$)$_3$ (187.05(13) – 187.90(12) pm). **W7** crystallizes in the triclinic space group $P\bar{1}$ (a = 1300.43(10) pm, α = 97.387(4)°, b = 1468.67(11) pm, β = 92.661(4)°, c = 1847.02(13) pm, γ = 92.100(3)°). The geometry index of τ = 0.48 indicates a structure in between SP with the alkylidyne in the apex and TBP with NHC and pivalonitrile in the apices. Compared to the crystal structure of the neutral complex **W6**, the alkoxide ligand with the longest W–O bond is replaced by pivalonitrile, *trans* to the NHC in **W7**. The alkylidyne bond with 172.3(11) pm is considerably shorter than in **W6** (175.9(2) pm) as well as in W(≡CMes)(OC(CF$_3$)$_2$Me)$_3$ (176.0(4) pm).[4c] The NHC in **W7** (219.0(8) pm) is bound more closely than in **W6** (225.8(2) pm), which is most probably a result of the cationic charge distribution between the metal center and the NHC. **W20** crystallizes in the triclinic space group $P\bar{1}$ (a = 1043.82(3) pm, α = 94.468(2)°, b = 1795.15(5) pm, β = 97.791(2)°, c = 2135.60(7) pm, γ = 94.6430(10)°). In the octahedral structure; the tungstacyclobutadiene lies in one plane with one alkoxide and the pivalonitrile. Perpendicular to this plane is the NHC ligand and the second alkoxide, *trans* to each other. The tungstacyclobutadiene shows the expected alternating contraction of bond lengths (W(1)–C(23) 194.9(4) pm, C(23)–C(24) 140.7(6) pm, C(24)–C(25) 150.4(5) pm, W(1)–C(25) 188.4(4) pm).

There is a disorder of 37 % in the crystal structure, in which the aromatic substituents in the metallacyclobutadiene are exchanged. The metal–NHC bond with 226.7(4) pm in **W20** is substantially longer than in the cationic alkylidyne complex **W7** but more similar to the one in **W6** (225.8(2) pm). Because of the *trans* influence of the NHC ligand, the tungsten–alkoxide bond, *trans* to the NHC is longer (197.3(3) pm) than the alkoxide bond *cis* to the NHC (190.3(3) pm). The pivalonitrile lies in a plane with the MCBD and is bound to the tungsten center with an angle of 164.8(3)°. Even though in **W20** the pivalonitrile is not influenced by the *trans* effect of the NHC, the length of the W(1)–N(3) bond is 245.5(4) pm and thus significantly longer than in the cationic complex **W7** (221.2(7) pm). This large bond hints towards a weakly bound pivalonitrile, which supports the theory that the pivalonitrile dissociates from the metal center prior to the formation of the MCBD and then rebinds to the metal. Complex **W11** crystallizes in the triclinic space group $P\bar{1}$ (a = 1099.83(5) pm, α = 83.947(2)°, b = 1809.71(7) pm, β = 88.265(3)°, c = 1924.33(9) pm, γ = 77.565(2)°) (Figure 2). It shows an octahedral symmetry, with the two pivalonitriles *cis* to each other and *trans* to the alkylidyne and phenoxide-group of the NHC, while the carbene of the NHC ligand and the alkoxide are *trans* to each other. This marks a major difference to the cationic complex **W7** in which the NHC is *trans* to the nitrile. Thus, in **W11** the *trans* influence of the NHC does not aid in the dissociation of the nitriles to activate the 16-electron complex. Similar to **W20**, the nitriles are coordinated in a slightly bent manner (163.5(5)° and 156.1(5)°). The metal alkylidyne bond (178.4(6) pm) is longer than in both isomers of its neutral precursor **W9**[14b] (176.3 pm and 162.6 pm). The tungsten–carbene bond (223.5(5) pm) is comparable to the one in the two isomers of **W9** (221.5 and 225.7 pm). The bond lengths of the nitriles are very dissimilar to each other with the one *trans* to the phenoxide-moiety being considerably shorter than the one *trans* to the alkylidyne (218.2(5) vs. 237.1(5) pm). **W15** crystallizes in the triclinic space group $P\bar{1}$ (a = 1054.39(4) pm, α = 98.738(3)°, b = 1138.88(4) pm, β = 100.773(3)°, c = 2126.48(11) pm, γ = 108.517(2)°). Unlike all other pentacoordinate Mo and W alkylidyne NHC complexes, which are mostly distorted SP or at least in between SP and TBP,[14] **W15** shows an slightly disordered TBP symmetry with the alkylidyne and the triflate in the apices, while the NHC and the alkoxides are in the plane (τ = 0.91, Figure 3). The metal alkylidyne (177.6(3) pm) bond is similar to

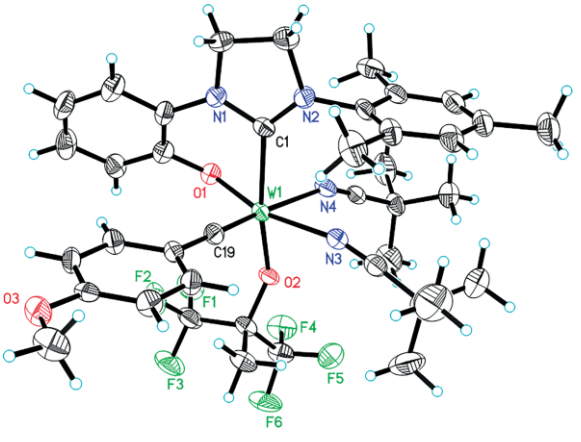

Figure 2. Crystal structure of **W11**. Selected bond lengths [pm] and angles [°]: W(1)–C(19) 178.4(6), W(1)–C(1) 223.5(5), W(1)–O(1) 191.1(4), W(1)–O(2) 195.0(4), W(1)–N(3) 218.2(5), W(1)–N(4) 237.1(5), C(19)–W(1)–O(1) 99.3(2), C(19)–W(1)–O(2) 103.6(2), O(1)–W(1)–N(3) 163.50(17), C(19)–W(1)–C(1) 87.9(2), O(2)–W(1)–C(1) 168.43(17), C(19)–W(1)–N(4) 174.1(2), N(3)–W(1)–N(4) 79.69(18), C(1)–W(1)–N(4) 91.95(18). The Al(OC(CF$_3$)$_3$)$_4$-anion and 1,2-dichloroethane were omitted for clarity.

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the one in **W6** (175.9(2) pm), a neutral tungsten complex that is also based on a monodentate NHC. Even though the NHC in **W15** is bulkier than in **W6** (36.5 % for IMes vs. 27.5 % V_{bur} for ICy at 200 pm M–NHC bond length)[26] the tungsten–NHC bond in **W15** (217.1(3) pm) is notably shorter than in **W6** (225.8(2) pm) and compares better to the one in the cationic complex **W7** (219.0(8) pm), which can be attributed to the better leaving-group character of triflate compared to trifluoro-*tert*-butoxide, generating a cationic complex more easily. The same conclusion can be made if one considers the bond length for the tungsten-triflate bond, which is rather long (233.0(2) pm). The two alkoxides have a uniform bond length (187.0(2) and 187.22(19) pm), on which, because of the TBP structure, the NHC only has a negligible *trans* influence. **W16** crystallizes in the triclinic space group $P\bar{1}$ (a = 1292.17(6) pm, α = 60.943(2)°, b = 1809.44(8) pm, β = 75.820(3)°, c = 1848.56(8) pm, γ = 88.964(2)°) and adopts a slightly distorted tetrahedral structure (τ_4 = 0.91, τ'_4 = 0.91, Figure 4). The metal alkylidyne (176.4(2) pm) is only slightly shorter than in **W15** (177.6(3) pm). The W–carbene bond is 212.9(2) pm, which is shorter than in the mono triflate complex **W15** (217.1(3) pm) as well as in the cationic tungsten alkylidyne NHC complex **W7** (219.0(8) pm). The tungsten alkoxide bonds (186.11(16) and 185.09(15) pm) are virtually the same, but marginally shorter than in **W15** (187.0(2) and 187.22(19) pm) but substantially shorter than in complex **W6** (193.25(15) - 197.22(15) pm). Finally, **W19** crystallizes in the monoclinic space group $P2_1/c$ (a = 1511.15(6) pm, α = 90°, b = 2153.53(9) pm, β = 93.274(2)°, c = 2766.22(12) pm, γ = 90°). The nitrile in **W19** binds to only one tungsten center in the binuclear complex, resulting in a difference in the bond lengths to the bridging carbons. The W center with coordinated nitrile has significantly longer W–C bond lengths (233.0(4) and 228.2(3) pm) than in the other tungsten center (203.5(4) and 208.1(4) pm). In Chisholm's complex derived from the reaction of $W_2(OtBu)_6$ and acetylene, a pyridine also coordinates to only one tungsten center, but there are no substantial differences in W–C-bond lengths (211.9(9) and 209.5(9) pm for the two W center without pyridine vs. 209.0(10) and 209.3(9) pm for the tungsten center with pyridine).[21b] The W–W bond in **W19** (267.09 pm) is comparable to the one in Chisholm's complex (266.5(2) pm) and longer than the Mo–Mo bond in Fürstner's dimolybdatetrahedrane (256.18(3) pm), whereas the C–C bond in the ditungstatetrahedrane core of **W19** with 139.2(5) pm is similar to the one in Fürstner's dimolybdatetrahedrane complex (139.0(3) pm) and shorter than in Chisholm's ditungstatetrahedrane (144.1(14) pm), (Figure 5).[19,21b]

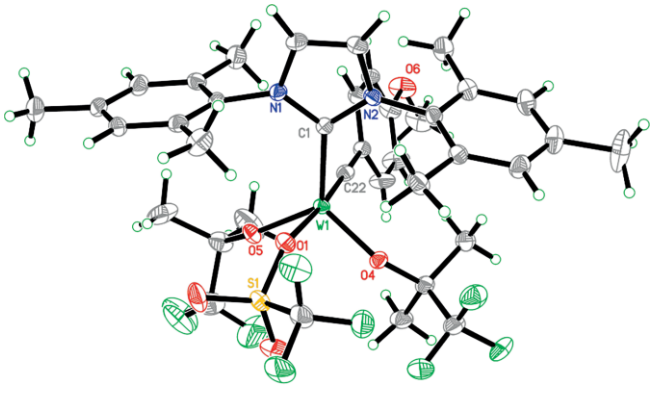

Figure 3. Crystal structure of **W15**. Selected bond lengths [pm] and angles [°]: W(1)–C(22) 177.6(3), W(1)–C(1) 217.1(3), W(1)–O(1) 233.0(2), W(1)–O(4) 187.0(2), W(1)–O(5) 187.22(19), C(22)–W(1)–O(4) 103.89(11), C(22)–W(1)–O(5) 102.22(11), O(4)–W(1)–O(5) 116.95(9), C(22)–W(1)–C(1) 92.51(12), O(4)–W(1)–C(1) 116.11(10), O(5)–W(1)–C(1) 118.84(10), C(22)–W(1)–O(1) 173.35(11), O(4)–W(1)–O(1) 80.55(8), O(5)–W(1)–O(1) 79.76(8); C(1)–W(1)–O(1) 81.02(9). 1,2-Dichloroethane was omitted for clarity.

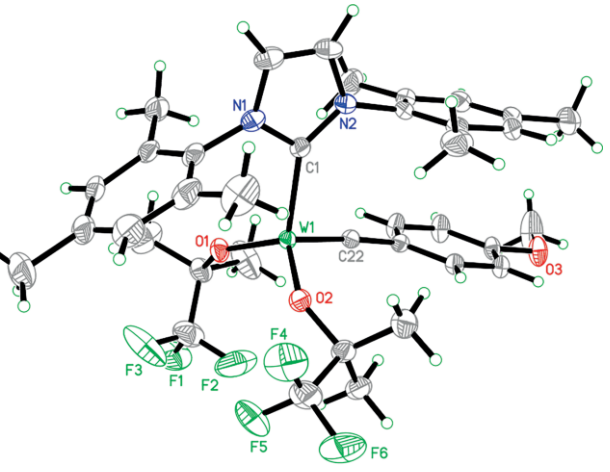

Figure 4. Crystal structure of **W16**. Important bond lengths [pm] and angles [°]: W(1)–C(22) 176.4(2), W(1)–C(1) 212.9(2), W(1)–O(1) 186.11(16), W(1)–O(2) 185.09(15), C(22)–W(1)–O(2) 108.12(8), C(22)–W(1)–O(1) 108.79(8), O(2)–W(1)–O(1) 115.64(7), C(22)–W(1)–C(1) 96.07(9), O(2)–W(1)–C(1) 110.64(8), O(1)–W(1)–C(1) 115.54(8). The $B(Ar^F)_4$-anion was omitted for clarity.

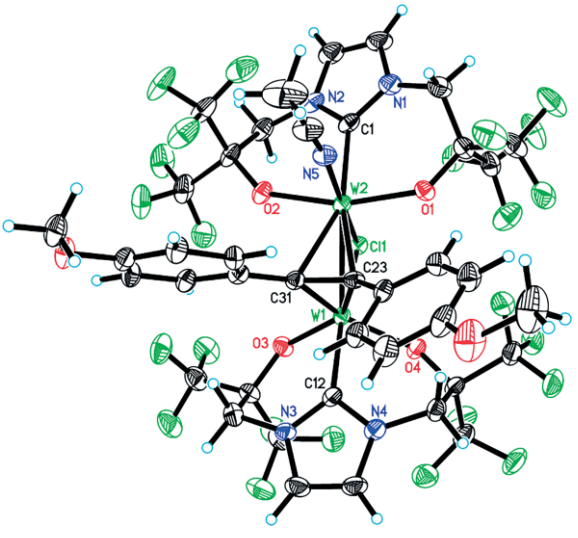

Figure 5. Crystal structure of **W19**. Selected bond lengths [pm] and angles [°]: W(1)–W(2) 267.09(2), W(1)–C(31) 203.5(4), W(1)–C(23) 208.1(4), W(2)–C(31) 233.0(4), W(2)–C(23) 228.2(3), C(23)–C(31) 139.2(5), W(1)–C(12) 214.1(4), W(2)–C(1) 218.2(4), W(2)–N(5) 213.7(3), W(1)–Cl(1) 243.53(9), W(2)–Cl(1) 239.07(8), W(1)–O(3) 196.5(2), W(1)–O(4) 195.7(2), W(2)–O(1) 196.8(2), W(2)–O(2) 195.8(2), O(4)–W(1)–O(3) 113.88(11), C(31)–W(1)–C(23) 39.52(14), O(4)–W(1)–C(12) 80.34(12), C(31)–W(1)–C(12) 85.86(14), C(23)–W(1)–C(12) 84.95(14), O(2)–W(2)–O(1) 162.89(11), C(1)–W(2)–C(23) 162.90(13), C(1)–W(2)–C(31) 156.44(13), C(23)–W(2)–C(31) 35.12(12), W(2)–CL1–W(1) 67.20(2), C(31)–C(23)–W(1) 68.5(2), C(31)–C(23)–W(2) 74.3(2), W(1)–C(23)–W(2) 75.33(11), W(1)–C(31)–W(2) 75.12(11). The $B(Ar^F)_4$-anion was omitted for clarity.

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Conclusions

The first cationic tungsten alkylidyne NHC complexes were synthesized and showed higher productivities in alkyne metathesis reactions than the neutral precursor complexes containing three alkoxides. The introduction of triflate as a better leaving group also results in an improved reactivity in alkyne metathesis. In the reaction with 1-phenyl-1-propyne, a cationic tungstacyclobutadiene intermediate has been isolated. Its formation strongly supports our previously published proposal of a cationic active species in tungsten and analogous molybdenum alkylidyne NHC complexes. The formation of a ditungstatetrahedrane complex was observed and suggests bimolecular decomposition as a possible decomposition pathway of cationic tungsten alkylidyne NHC complexes.

Experimental Section

Unless stated otherwise, all reactions were performed under inert gas atmosphere (N_2), either in a glove box (LabMaster 130, MBraun, Garching, Germany) or with standard Schlenk techniques. CH_2Cl_2, diethyl ether, toluene, *n*-pentane, and tetrahydrofuran were dried by a solvent purification system (SPS, MBraun). 1,2-Dimethoxyethane (DME) was dried with LiH and distilled under N_2, 1,2-Dichloroethane and 1-phenyl-1-propyne (**S1**) were dried with CaH_2 and distilled under N_2. Anhydrous chlorobenzene and anhydrous 1,2-dichlorobenzene were purchased and as all solvents stored over 3 Å molecular sieves. NMR measurements were recorded on a Bruker Avance III 400. Chemical shifts are reported in ppm relative to the solvent signal;[27] coupling constants are listed in Hz. Single crystal X-ray measurements were carried out on a Bruker Kappa APEXII Duo diffractometer with Mo-K_α radiation at the Institute of Organic Chemistry, University of Stuttgart. Starting materials and reagents were purchased from Sigma Aldrich/Merck (Munich, Germany), Alfa Aesar (Karlsruhe, Germany), or ABCR (Karlsruhe, Germany) and were used as received unless stated otherwise.

W(≡CC_6H_4OMe)$(OC(CF_3)_2Me)_3$(DME) (**W1-DME**),[4b,28] 1,3-diisopropylimidazol-2-ylidene,[29] 1,3-dicyclohexylimidazol-2-ylidene,[30] W(≡CC_6H_4OMe)$(OC(CF_3)Me_2)_3$(THF) (**W2-THF**),[14b] *N*,*N*-dimethylanilinium $B(Ar^F)_4^-$ etherate,[31] 1-(1,1,1-trifluoro)-2-(trifluoromethyl)-2-hydroxyprop-3-yl)imidazolium-3-(1,1,1-trifluoro)-2-(trifluoromethyl)propan-2-olate,[32] $AgB(Ar^F)_4$•3MeCN,[33] 1,3-dimesitylimidazol-2-ylidene,[34] W(≡CC_6H_4OMe)(1-(mesityl)-3-(2-hydroxyphenyl)-imidazolin-2-ylidene)$(OC(CF_3)_2Me)_2$ (**W9**),[14b] $Ag[Al(OC(CF_3)_3)_4]$•CH_2Cl_2[35] and $NaB(Ar^F)_4$,[36] 5-(benzyloxy)-2-pentyne (**S2**)[4b] were prepared according to the literature.

W(≡CC_6H_4OMe)(1,3-diisopropylimidazol-2-ylidene)$(OC(CF_3)_2Me)_3$ (W3): 1,3-Diisopropylimidazol-2-ylidene (67 mg, 0.44 mmol, 1 equiv.) was dissolved in toluene, cooled to –40 °C and added to a solution of W(≡CC_6H_4OMe)$(OC(CF_3)_2Me)_3$(DME) (**W1-DME**) (410 mg, 0.44 mmol, 1 equiv.) in toluene at –40 °C. The reaction mixture was stirred at room temperature for four hours. All volatiles were removed under reduced pressure. The residue was washed with *n*-pentane and crystallized from diethyl ether and *n*-pentane to yield **W3** as red crystals (350 mg, 0.35 mmol, 80 %). ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.12 (d, $^3J_{H\text{-}H}$ = 13.4, 1H), 7.11 (d, $^3J_{H\text{-}H}$ = 13.4 Hz, 1H), 6.95 (d, $^3J_{H\text{-}H}$ = 9.0 Hz, 2H), 6.89 (d, $^3J_{H\text{-}H}$ = 9.1 Hz, 2H), 5.59 (sept, $^3J_{H\text{-}H}$ = 6.7 Hz, 1H), 4.27 (sept, $^3J_{H\text{-}H}$ = 6.6 Hz, 1H), 1.71 (s, 3H), 1.65 (s, 6H), 1.45 (d, $^3J_{H\text{-}H}$ = 6.6 Hz, 6H), 1.39 (d, $^3J_{H\text{-}H}$ = 6.7 Hz, 6H) ppm. ^{19}F NMR (376 MHz, CD_2Cl_2): δ = –76.74 (q, $^4J_{F\text{-}F}$ = 9.7 Hz, 6F), –76.96 (m, 6F), –77.85 (s, 6F) ppm. ^{13}C NMR (101 MHz,CD_2Cl_2): δ = 283.5, 192.4, 160.0, 138.9, 134.6, 124.6 (q, $^1J_{C\text{-}F}$ = 289 Hz), 124.3 (q, $^1J_{C\text{-}F}$ = 292 Hz) 117.9, 117.5, 113.0, 83.3 (sept*, $^2J_{C\text{-}F}$ = 28.3 Hz), 82.7 (sept*, $^2J_{C\text{-}F}$ = 28.2 Hz) 55.8, 54.0, 24.0, 23.2, 20.0, 19.5 ppm. Elemental anal. calcd. for $C_{29}H_{32}F_{18}N_2O_4W$: C, 34.89; H, 3.23; N, 2.81; found C, 34.81, H, 3.239, N, 2.81. *terminal signals of the septet were not observed.

W(≡CC_6H_4OMe)(1,3-dicyclohexylimidazol-2-ylidene)$(OC(CF_3)_2Me)_3$ (W4): W4 was synthesized in analogy to **W3** via the reaction of W(≡CC_6H_4OMe)$(OC(CF_3)_2Me)_3$(DME) (**W1-DME**) and 1,3-dicyclohexylimidazol-2-ylidene to yield the product as red crystals (25 mg, 0.02 mmol, 43 %). ^{1}H NMR (400 MHz, C_6D_6): δ = 7.17 (d, $^3J_{H\text{-}H}$ = 9.1 Hz, 2H), 6.73 (d, $^3J_{H\text{-}H}$ = 8.8 Hz, 2H), 6.33 (s, 2H), 5.18 (tt, $^3J_{H\text{-}H}$ = 11.9, 3.5 Hz, 1H), 3.92 (tt, $^3J_{H\text{-}H}$ = 11.7, 3.4 Hz, 1H), 3.24 (s, 3H), 2.28 (d, $^3J_{H\text{-}H}$ = 12.2 Hz, 2H), 2.07 (d, $^3J_{H\text{-}H}$ = 11.9 Hz, 2H), 1.85 (s, 3H), 1.79 (s, 6H), 1.71–1.67 (m, 2H), 1.52–1.29 (m, 6H), 1.19–0.80 (m, 8H) ppm. ^{19}F NMR (376 MHz, C_6D_6): δ = –76.15 (q, $^4J_{F\text{-}F}$ = 9.7 Hz, 6F), –76.50 (m, 6F), –77.28 (s, 6F) ppm. ^{13}C NMR (101 MHz, C_6D_6): δ = 283.1, 192.4, 160.1, 138.7, 135.0, 124.9 (q, $^1J_{C\text{-}F}$ = 287.6 Hz), 124.4 (q, $^1J_{C\text{-}F}$ = 286.4 Hz), 117.4, 117.1, 112.9, 83.3 (sept*, $^2J_{C\text{-}F}$ = 28.8 Hz), 82.9 (sept*, $^2J_{C\text{-}F}$ = 29.3 Hz), 61.6, 60.6, 54.8, 34.3, 33.4, 25.6, 25.4, 25.3, 19.7, 19.3 ppm. Elemental anal. calcd. for $C_{35}H_{40}F_{18}N_2O_4W$: C, 38.98; H, 3.74; N, 2.60; found C, 39.06; H, 3.840; N, 2.64. *terminal signals of the septet were not observed.

W(≡CC_6H_4OMe)(1,3-diisopropylimidazol-2-ylidene)$(OC(CF_3)Me_2)_3$ (W5): W5 was synthesized in analogy to **W3** via the reaction of W(≡CC_6H_4OMe)$(OC(CF_3)Me_2)_3$(THF) (**W2-THF**) and 1,3-diisopropylimidazol-2-ylidene to yield the product as yellow crystals (106 mg, 0.13 mmol, 64 %). ^{1}H NMR (400 MHz, C_6H_6): δ = 7.15 (d, $^3J_{H\text{-}H}$ = 8.9 Hz, 2H), 6.77 (d, $^3J_{H\text{-}H}$ = 8.9 Hz, 2H), 6.18 (m, 2H), 5.81 (sept, $^3J_{H\text{-}H}$ = 6.7 Hz, 1H), 4.42 (sept, $^3J_{H\text{-}H}$ = 6.6 Hz, 1H), 3.31 (s, 3H), 1.77 (s, 12H), 1.28 (s, 6H), 1.00 (d, $^3J_{H\text{-}H}$ = 6.7 Hz, 6H), 1.00 (d, $^3J_{H\text{-}H}$ = 6.6 Hz, 6H) ppm. ^{19}F NMR (376 MHz, C_6D_6): δ = –81.24 (9F) ppm. ^{13}C NMR (100 MHz, C_6H_6): δ = 273.0, 193.5, 158.8, 140.7, 134.1, 128.7 (q, $^1J_{C\text{-}F}$ = 287 Hz), 128.5 (q, $^1J_{C\text{-}F}$ = 287 Hz), 116.7, 115.7, 113.1, 80.5 (q, $^2J_{C\text{-}F}$ = 27.7 Hz), 65.9, 54.8, 52.8, 52.5, 25.9, 25.7, 25.7, 23.2, 22.8, 15.6 ppm. Elemental anal. calcd. for $C_{29}H_{41}F_9N_2O_4W$: C, 41.64; H, 4.94; N, 3.35; found C, 41.64; H, 4.823; N, 3.31.

W(≡CC_6H_4OMe)(1,3-dicyclohexylimidazol-2-ylidene)$(OC(CF_3)Me_2)_3$ (W6): W6 was synthesized in analogy to **W3** via the reaction of W(≡CC_6H_4OMe)$(OC(CF_3)Me_2)_3$(THF) (**W2-THF**) and 1,3-dicyclohexylimidazol-2-ylidene to yield the product as yellow crystals (120 mg, 0.13 mmol, 66 %). ^{1}H NMR (400 MHz, C_6D_6): δ = 7.22 (d, $^3J_{H\text{-}H}$ = 8.7 Hz, 2H), 6.78 (d, $^3J_{H\text{-}H}$ = 8.8 Hz, 2H), 6.36 (d, $^3J_{H\text{-}H}$ = 14.8 Hz, 1H), 6.36 (d, $^3J_{H\text{-}H}$ = 14.7 Hz, 1H), 5.42 (tt, $^3J_{H\text{-}H}$ = 12.0, 3.7 Hz, 1H), 4.24 (tt,$^3J_{H\text{-}H}$ = 11.8, 3.4 Hz, 1H), 3.29 (s, 3H), 2.36 (d, $^3J_{H\text{-}H}$ = 12.0 Hz, 2H), 2.01 (d, $^3J_{H\text{-}H}$ = 11.0 Hz, 2H), 1.75 (s, 6H), 1.73 (s, 6H), 1.70–1.62 (m, 2H), 1.51–1.27 (m, 12H), 1.12 (m, 4H), 1.02–0.75 (m, 4H) ppm. ^{19}F NMR (376 MHz, C_6D_6): δ = –81.40 (s, 6F), –81.77 (s, 3F) ppm. ^{13}C NMR (101 MHz, C_6D_6): δ = 271.5, 192.7, 157.8, 139.5, 133.6, 127.5 (q, $^1J_{C\text{-}F}$ = 286.4 Hz), 127.4 (q, $^1J_{C\text{-}F}$ = 287.5 Hz), 115.9, 115.0, 111.8, 78.9 (q, $^2J_{C\text{-}F}$ = 27.5 Hz), 79.3 (q, $^2J_{C\text{-}F}$ = 28.0 Hz), 59.3, 58.8, 53.7, 33.0, 32.4, 24.5, 24.4, 24.3, 24.3, 24.1 ppm. Elemental anal. calcd. for $C_{35}H_{49}F_9N_2O_4W$: C, 45.86; H, 5.39, N, 3.06; found C, 45.98; H, 5.393; N, 3.14.

W(≡CC_6H_4OMe)(1,3-diisopropylimidazol-2-ylidene)$(OC(CF_3)_2Me)_2$ $(NCtBu)^+$ $(B(Ar^F)_4)^-$ (W7): W3 (160 mg, 0.162 mmol, 1 equiv.) and pivalonitrile (20 mg, 0.33 mmol, 2 equiv.) were dissolved in CH_2Cl_2 and cooled to –40 °C. A cooled solution of *N*,*N*-dimethylanilinium $B(Ar^F)_4^-$ etherate (170 mg, 0.16 mmol, 0.98 equiv.) in CH_2Cl_2 was added and the reaction mixture was stirred for 64 hours at room temperature. All volatiles were removed under reduced pressure and then co-evaporated with diethyl ether. The residue was twice extracted with *n*-pentane for 30 minutes. The residue was crystallized

from 1,2-dichloroethane and *n*-pentane to obtain the product as dark violet crystals (180 mg, 0.10 mmol, 62 %). ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.72 (s, 8H), 7.56 (s, 4H), 7.31 (s, 2H), 7.00 (m, 4H), 5.30 (s, 2H), 4.02 (s, 1H), 3.84 (s,3H), 1.99 (s, 6H), 1.48–1.32 (m, 21H) ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ = –62.48 (s, 24F), –77.25 (q, $^4J_{F\text{-}F}$ = 8.3 Hz, 6F), –77.64 (q, $^4J_{F\text{-}F}$ = 8.2 Hz, 6F) ppm. ^{13}C NMR (101 MHz, CD_2Cl_2): δ = 304.5, 189.4, 162.6, 162.2 (q, $^1J_{C\text{-}B}$ = 50 Hz), 137.2, 135.8, 135.2, 129.3 (qq, $^2J_{C\text{-}F}$ = 32 Hz, $^3J_{C\text{-}B}$ = 3 Hz), 125.0 (q, $^1J_{C\text{-}F}$ = 272 Hz), 123.8 (q, $^1J_{C\text{-}F}$ = 288 Hz), 122.9 (q, $^1J_{C\text{-}F}$ = 286 Hz), 120.1, 119.2, 117.9, 113.6, 85.1 (sept*, $^2J_{C\text{-}F}$ = 30 Hz), 55.9, 55.1, 27.3, 23.6, 23.0, 20.4 ppm. Elemental anal. calcd. for $C_{62}H_{50}BF_{36}N_3O_3W$: C, 42.22; H, 2.86; N, 2.38; found C, 42.19; H, 2.921; N, 2.33. *terminal signals of septet were not observed.

[W(≡CC$_6$H$_4$OMe)(1,3-diisopropylimidazol-2-ylidene)(OC(CF$_3$)Me$_2$)$_2$ (NC*t*Bu)$^+$ (B(Ar^F)$_4$)$^-$] (W8): W5 (101 mg, 0.12 mmol, 1 equiv.) and two drops of pivalonitrile were dissolved in CH_2Cl_2 and cooled to –40 °C. A cooled solution of *N*,*N*-dimethylanilinium $B(Ar^F)_4^-$ etherate (128 mg, 0.12 mmol, 0.98 equiv.) was added and the reaction mixture was stirred for four hours at room temperature. All volatiles were removed and then co-evaporated with diethyl ether. The residue was stirred twice with *n*-pentane for 30 minutes. The solvent was decanted and the residue was dried in vacuo. The product was isolated as red powder (160 mg, 0.10 mmol, 79 %). ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.79 (s, 8H), 7.62 (s, 4H), 7.25 (s, 2H), 7.10 (d, $^3J_{H\text{-}H}$ = 8.7 Hz, 2H), 6.97 (d, $^3J_{H\text{-}H}$ = 8.9 Hz, 2H), 5.43 (s, 1H), 4.30 (s, 1H), 3.82 (s, 3H), 1.75 (s, 6H), 1.49 (m, 27H) ppm. ^{19}F-NMR (376 MHz, CD_2Cl_2): δ = –62.80 (s, 24F), –82.31(s, 6F) ppm. ^{13}C-NMR (101 MHz, CD_2Cl_2): δ = 299.0, 188.8, 187.9, 163.6 (q, $^1J_{C\text{-}B}$ = 50 Hz), 161.8, 138.7, 135.5 (br), 129.7 (qq, $^2J_{C\text{-}F}$ = 32 Hz, $^3J_{C\text{-}B}$ = 3 Hz), 127.2 (q, $^1J_{C\text{-}F}$ = 285 Hz), 125.4 (q, $^1J_{C\text{-}F}$ = 273 Hz), 119.5 (br), 118.2, 113.7, 84.5 (q, $^2J_{C\text{-}F}$ = 29 Hz), 56.0, 55.9, 54.9, 35.9, 30.2, 27.6, 26.2, 26.0, 23.5 ppm. Elemental anal. calcd. for $C_{62}H_{56}BF_{30}N_3O_3W$: C, 44.98; H, 3.41; N, 2.54; found C, 44.91; H, 3.639; N, 2.56.

WCl(≡CC$_6$H$_4$OMe)(1-(mesityl)-3-(2-hydroxyphenyl)imidazolin-2-ylidene)(OC(CF$_3$)$_2$Me) (W10): A solution of W(≡CC$_6$H$_4$OMe)(1-(mesityl)-3-(2-hydroxyphenyl)imidazolin-2-ylidene)(OC(CF$_3$)$_2$Me)$_2$ (100 mg, 0.11 mmol, 1 equiv.) in CH_2Cl_2 was cooled to –40 °C and a cooled solution of *N*,*N*-dimethylanilinium hydrochloride (16 mg, 0.11 mmol, 1 equiv.) in CH_2Cl_2 was added. The reaction mixture was stirred for one hour at room temperature. All volatiles were removed, the residue was taken up in CH_2Cl_2 and the solvent was removed under reduced pressure again. The residue was then taken up in a minimal amount of CH_2Cl_2, filtered and overlaid with *n*-pentane to isolate the product as dark red crystals (50 mg, 0.06 mmol, 59 %). ^{1}H NMR (400 MHz, C_6D_6): δ = 7.41 ppm (d, $^3J_{H\text{-}H}$ = 7.9 Hz, 1H), 7.04 (td, 1H, $^3J_{H\text{-}H}$ = 7.8 Hz, $^4J_{H\text{-}H}$ = 1.5 Hz), 6.83 (td, $^3J_{H\text{-}H}$ = 7.8 Hz, $^4J_{H\text{-}H}$ = 1.4 Hz, 1H), 6.70 (s, 1H), 6.58 (s, 1H), 6.45 – 6.56 (m, 5H), 3.13 (s, 3H), 2.81 – 3.10 (m, 4H), 2.18 (s, 3H), 2.09 (s, 3H), 1.91 (s, 3H), 1.87 (s, 3H) ppm. ^{19}F NMR (376 MHz, C_6D_6): δ = –76.82 (q, 3F, *J* = 9.3 Hz), –77.09 ppm (q, 3F, *J* = 9.4 Hz); ^{13}C NMR (101 MHz, C_6D_6): δ = 301.2, 218.8, 160.7, 157.7, 138.3, 138.1, 137.2, 135.9, 135.7, 135.1, 131.8, 129.6, 129.5, 125.4, 123.4 (q*), 120.9, 118.3, 117.2, 112.4, 83.5 (sept)*, 54.7, 52.1, 47.4, 21.1, 20.4, 18.5, 18.1 ppm. Elemental anal. calcd. for $C_{30}H_{29}ClF_6N_2O_3W$: C, 45.11; H, 3.66; N, 3.51; found C, 45.19; H, 3.790; N, 3.61. *quartet poorly resolved. **terminal signals of the expected septet were not observed.

[W(≡CC$_6$H$_4$OMe)(1-(mesityl)-3-(2-hydroxyphenyl)imidazolin-2-ylidene)(OC(CF$_3$)$_2$Me)(NC*t*Bu)$_2$$^+$ (Al(OC(CF$_3$)$_3$)$_4$)$^-$] (W11): W10 (40 mg, 0.05 mmol, 1 equiv.) and two drops of pivalonitrile were dissolved in CH_2Cl_2 and cooled to –40 °C. A solution of $Ag[Al(OC(CF_3)_3)_4]\cdot CH_2Cl_2$ (58 mg, 0.05 mmol, 1 equiv.) in CH_2Cl_2 was cooled to –40 °C and added to the reaction mixture and stirred for one hour at room temperature. The reaction mixture was filtered through celite and the solvent was removed under reduced pressure. The residue was crystallized from 1,2-dichloroethane and *n*-pentane; the product was isolated as brown crystals (55 mg, 0.03 mg, 63 %). ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.27 (td, $^3J_{H\text{-}H}$ = 7.8 Hz, $^3J_{H\text{-}H}$ = 1.6 Hz, 1H), 7.17– 6.98 (m, 5H), 6.67 (d, $^3J_{H\text{-}H}$ = 8.8 Hz, 2H), 5.92 (d, $^3J_{H\text{-}H}$ = 8.3 Hz, 2H), 4.68 – 4.58 (m, 1H), 4.26–4.15 (m, 1H), 4.03–3.90 (m, 2H), 3.73 (s, 3H), 2.36 (s, 3H), 2.28 (s, 6H), 1.70 (s, 3H), 1.34 (m, 18H) ppm. ^{19}F NMR (376 MHz, CD_2Cl_2): δ = –75.72 (s 36F), –77.52 (m 6F) ppm. ^{13}C NMR (101 MHz, CD_2Cl_2): δ = 304.0, 219.4, 162.4, 160.8, 143.4, 140.5, 137.4, 136.9, 136.1, 133.7 (q, $^1J_{C\text{-}F}$ = 302 Hz), 130.8, 130.5, 125.49, 121.9 (q, $^1J_{C\text{-}F}$ = 292 Hz) 118.0, 116.0, 112.6, 83.8 (sept*), 55.8, 49.76, 30.82, 29.15, 27.80, 27.52, 21.39, 19.82, 18.36 ppm. Elemental anal. calcd. for $C_{56}H_{47}AlF_{42}N_4O_7W$: C, 35.46; H, 2.50; N, 2.95; found C, 35.24; H, 2.580; N, 2.95. *septet poorly resolved.

W(≡CC$_6$H$_4$OMe)(OC(CF$_3$)$_2$Me)$_2$(OTf)(DME) (W12-DME): W(≡CC$_6$H$_4$OMe)(OC(CF$_3$)$_2$Me)$_3$(DME) (200 mg, 0.21 mmol, 1 equiv.) was dissolved in a mixture of toluene and DME and cooled to –40 °C. A cold solution (–40 °C) of triflic acid (34 mg, 0.22 mmol, 1.05 equiv.) in toluene and DME was slowly added and stirred for four hours at room temperature. All volatiles were removed under reduced pressure and the residue was crystallized from CH_2Cl_2 and *n*-pentane to obtain the product as dark red crystals (130 mg, 0.14 mmol, 72 %). ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.00 (d, $^3J_{H\text{-}H}$ = 9.0 Hz, 2H), 6.92 (d, $^3J_{H\text{-}H}$ = 9.0 Hz, 2H), 4.65 (s, 3H), 4.32–4.24 (m, 1H), 3.98 (m, 1H), 3.93–3.84 (m, 1H), 3.80 (s, 3H), 3.61–3.54 (m, 1H), 3.47 (s, 3H), 1.98 (s, 6H) ppm. ^{19}F NMR (376 MHz, CD_2Cl_2): δ = –76.78 (q, $^4J_{F\text{-}F}$ = 9.8 Hz, 3F), –77.40 (m, 3F), –77.79 (m, 3F), –77.84 –77.98 (m, 3F), –78.38 (m, 3F) ppm. ^{13}C NMR (101 MHz, CD_2Cl_2): δ = 285.6, 161.4, 137.1, 136.6, 124.5 (q, $^1J_{H\text{-}H}$ = 287 Hz), 124.2 (q, $^1J_{H\text{-}H}$ = 288 Hz), 124.2 (q, $^1J_{H\text{-}H}$ = 287 Hz), 123.7 (q, $^1J_{H\text{-}H}$ = 286 Hz), 112.9, 84.8 (sept*, $^2J_{C\text{-}F}$ = 29 Hz), 84.2 (sept*, $^2J_{C\text{-}F}$ = 29 Hz), 77.2, 77.0, 70.4, 60.5, 55.9, 19.0, 18.9 ppm. Elemental anal. calcd. for $C_{21}H_{23}F_{15}O_8SW$: C, 27.89; H 2.56; found C, 28.05, H 2.62. *terminal signals for septet were not observed.

W(≡CC$_6$H$_4$OMe)(OC(CF$_3$)$_2$Me)$_2$(OTf)(THF)$_2$ (W12-THF): W12-DME (140 mg, 0.15 mmol) was dissolved in THF and stirred for 30 minutes. All volatiles were removed and the residue was extracted with *n*-pentane. The solution was concentrated under reduced pressure and then stored at –40 °C to obtain the product as red crystals (92 mg, 0.11 mmol, 72 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.04 (d, $^3J_{H\text{-}H}$ = 8.9 Hz, 2H), 6.89 (d, $^3J_{H\text{-}H}$ = 8.9 Hz, 2H), 4.73 (s, 2H), 4.46 (s, 2H), 3.87 – 3.81 (m, 4H), 3.80 (s, 3H), 2.13–2.06 (m, 4H), 2.00 (s, 3H), 1.91–1.80 (m, 7H) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –77.00 to –77.15 (m, 6F), –77.18 to –77.23 (m, 3F), –77.30 to –77.43 (m, 3F), –77.62 to –77.80 (m, 3F) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 286.1, 160.7, 136.8, 124.0 (q, $^1J_{C\text{-}F}$ = 285 Hz), 123.9 (q, $^1J_{C\text{-}F}$ = 290 Hz), 123.7 (q, $^1J_{C\text{-}F}$ = 289 Hz), 123.4 (q, $^1J_{C\text{-}F}$ = 288 Hz), 119.4 (q, $^1J_{C\text{-}F}$ = 318 Hz), 112.5, 84.6 (sept*, $^2J_{C\text{-}F}$ = 29 Hz), 83.7 (sept*, $^2J_{C\text{-}F}$ = 29 Hz), 81.0, 69.2, 55.4, 26.4, 25.5, 19.3, 18.5 ppm. Elemental anal. calcd. for $C_{25}H_{29}F_{15}O_8SW$: C, 31.33; H, 3.05; found C, 31.06; H, 3.165. *terminal signals of septet were not observed.

W(≡CC$_6$H$_4$OMe)(1,3-diisopropylimidazol-2-ylidene)$_2$(OC(CF$_3$)$_2$Me)$_2$ (OTf) (W13): 1,3-Diisopropylimidazol-2-ylidene (7 mg, 0.05 mmol, 1 equiv.) was dissolved in THF, cooled to –40 °C and added to a solution of **W12-DME** (42 mg, 0.05 mmol, 1 equiv.) in THF at –40 °C. The solution was stirred for four hours at room temperature. All volatiles were removed under reduced pressure. The residue was washed with *n*-pentane several times and the residue crystallized from CH_2Cl_2 and *n*-pentane to obtain the product as red crystals (18 mg, 0.016 mmol, 32 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 (d, $^3J_{H\text{-}H}$ = 21.4 Hz, 2H), 7.39 (d, $^3J_{H\text{-}H}$ = 21.2 Hz, 2H), 7.19 (d, $^3J_{H\text{-}H}$ =

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9.0 Hz, 2H), 6.98 (d, $^3J_{H-H}$ = 9.0 Hz, 2H), 5.31(sept, $^3J_{H-H}$ = 6.6 Hz 2H), 5.30 (s, 1H, 0.5 eq CH_2Cl_2), 4.29 (sept, $^3J_{H-H}$ = 6.6 Hz, 2H), 3.89 (s, 3H), 1.85 (s, 6H), 1.52 (d, $^3J_{H-H}$ = 6.6 Hz, 12H), 1.27 (d, $^3J_{H-H}$ = 6.7 Hz, 12H) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –76.77 (s, 12F), –78.15 (s, 3F) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 294.3, 191.3, 161.5, 136.9, 136.0, 122.9 (q, $^1J_{C-F}$ = 288 Hz), 121.1 (q, $^1J_{C-F}$ = 322 Hz), 119.3, 118.9, 113.5, 84.0 (sept* $^2J_{C-F}$ = 28 Hz), 55.7, 53.6 (overlaps with CH_2Cl_2 signal), 52.9, 23.7, 23.1, 20.6 ppm. The ^{1}H NMR spectrum showed that 0.5 equivalents of CH_2Cl_2 remained in the product, which could not be removed under vacuum. Therefore, elemental analysis was calculated for **W13**·0.5CH_2Cl_2. Elemental anal. calcd. for $C_{35.5}H_{46}F_{15}ClN_4O_6SW$: C, 36.72; H, 3.99; N, 4.83; found C, 36.57; H, 4.158; N, 4.91. *terminal signals of the septet were not observed.

W(≡CC$_6$H$_4$OMe)(OC(CF$_3$)Me$_2$)$_2$(OTf)(DME) (W14-DME): W14-DME was synthesized in analogy to **W12-DME** via the reaction of W(≡CC$_6$H$_4$OMe)(OC(CF$_3$)Me$_2$)$_3$ (175 mg, 0.26 mmol, 1 equiv.) with triflic acid (38 mg, 0.26 mmol, 1 equiv.) and isolated as brown crystals (120 mg, 0.15 mmol, 58 %) ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.07 (d, $^3J_{H-H}$ = 8.8 Hz, 2H), 6.88 (d, $^3J_{H-H}$ = 8.8 Hz, 2H), 4.49 (s, 3H), 4.26–4.16 (m, 1H), 3.93–3.81 (m, 2H), 3.79 (s, 3H), 3.60–3.52 (m, 1H), 3.49 (s, 3H), 1.77 (s, 3H), 1.65 (s, 3H), 1.61 (s, 6H) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –77.42 (s, 3F), –82.20 (s, 3F), –82.35 (s, 3F) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 277.4, 160.0, 137.6, 136.2, 127.8 (q, $^1J_{C-F}$ = 285 Hz), 127.3 (q, $^1J_{C-F}$ = 285 Hz), 119.6 (q, $^1J_{C-F}$ = 318 Hz), 112.5, 83.8 (q, $^2J_{C-F}$ = 28 Hz), 81.9 (q, $^2J_{C-F}$ = 28 Hz), 75.6, 74.0, 69.9, 60.0, 55.4, 25.2, 25.1, 25.0, 24.0 ppm. Elemental anal. calcd. for $C_{21}H_{29}F_9O_8SW$: C, 31.67; H, 3.67; found C, 31.29; H, 3.706.

W(≡CC$_6$H$_4$OMe)(OC(CF$_3$)Me$_2$)$_2$(OTf)(THF)$_2$ (W14-THF): W14-THF was prepared in analogy to **W12-THF** via the reaction of **W14-DME** with THF to obtain the product as brown crystals (86 mg, 0.10 mmol, 67 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.11 (d, $^3J_{H-H}$ = 8.9 Hz, 2H), 6.88 (d, $^3J_{H-H}$ = 9.0 Hz, 2H), 4.59 (s, 2H), 4.34 (s, 2H), 3.90 – 3.82 (m, 4H), 3.79 (s, 3H), 2.08 – 2.00 (s, 4H), 1.88 – 1.81 (s, 4H), 1.75 (s, 3H), 1.64 – 1.55 (m, 9H) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ –77.39 (s, 3F), –82.11 (s, 3F), –82.69 (s, 3F) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 278.1, 159.9, 137.9, 136.4, 127.7 (q, $^1J_{C-F}$ = 286 Hz), 119.6 (q, $^1J_{C-F}$ = 317 Hz), 112.5, 83.5 (q, $^2J_{C-F}$ = 28 Hz), 81.8 (q, $^2J_{C-F}$ = 28 Hz), 79.1, 69.0, 55.4, 26.3, 25.5, 25.2, 24.4 ppm. Elemental anal. calcd. for $C_{25}H_{35}F_9O_8SW$: C, 35.31; H, 4.15; found C, 33.49; H, 4.006. Despite numerous efforts, no satisfactory elemental analysis was obtained, probably due to a minor by-product in which only one THF was coordinated to the metal center.

W(≡CC$_6$H$_4$OMe)(1,3-dimesitylimidazol-2-ylidene)(OC(CF$_3$)Me$_2$)$_2$-(OTf) (W15): A solution of 1,3-dimesitylimidazol-2-ylidene (67 mg, 0.22 mmol, 1 equiv.) in toluene was cooled to –40 °C and added to a solution of **W14-THF** (188 mg, 0.22 mmol, 1 equiv.) in toluene at –40 °C. The reaction mixture was stirred for four hours. All volatiles were removed under reduced pressure and the residue was crystallized from CH_2Cl_2 and *n*-pentane to obtain the product as red crystals (196 mg, 0.19 mmol, 88 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.49 (s, 2H), 6.95 (s, 4H), 6.77 (d, $^3J_{H-H}$ = 8.9 Hz, 2H), 6.68 (d, $^3J_{H-H}$ = 8.7 Hz, 2H), 3.81 (s, 3H), 2.30 (s, 6H), 2.15 (s, 12H), 1.34 (s, 6H), 1.20 (s, 6H) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –78.05 (s, 3F), –81.84 (s, 6F) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 285.9, 195. 160.3, 141.2, 137.7, 135.9, 135.7, 133.2, 129.9, 127.8, 125.9 (q, $^1J_{C-F}$ = 285 Hz), 120.4 (q, $^1J_{C-F}$ = 320 Hz), 112.2, 84.4 (q, $^2J_{C-F}$ = 29 Hz), 55.4, 25.5, 23.6, 21.1, 18.1. Elemental anal. calcd. for $C_{38}H_{43}F_9N_2O_6SW$: C, 45.16; H, 4.29; N, 2.77; found C, 44.90; H, 4.418; N, 2.84.

[W(≡CC$_6$H$_4$OMe)(1,3-dimesitylimidazol-2-ylidene)(OC(CF$_3$)Me$_2$)$_2$$^+$ (B(Ar^F)$_4$)$^-$] (W16): W15 (87 mg, 0.09 mmol, 1 equiv.) was dissolved in CH_2Cl_2 and cooled to –40 °C. A solution of NaB(Ar^F)$_4$ (76 mg, 0.09 mmol, 1 equiv.) in a mixture of CH_2Cl_2 and diethyl ether was cooled to –40 °C and added to the reaction mixture, which was then stirred for one hour. The reaction mixture was filtered through celite and the solvent was removed under reduced pressure and co-evaporated with diethyl ether and *n*-pentane. The residue was crystallized from 1,2-dichloroethane and *n*-pentane to obtain the product as red crystals (108 mg, 0.07 mmol, 73 %). ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.74 (s, 8H), 7.70 (s, 2H), 7.57 (s, 4H), 6.87 (s, 4H), 6.69 (d, $^3J_{H-H}$ = 8.9 Hz, 2H), 6.54 (d, $^3J_{H-H}$ = 8.9 Hz, 2H), 3.80 (s, 3H), 2.18 (s, 6H), 2.00 (s, 12H), 1.63 (s, 6H), 1.52 (s, 6H) ppm. ^{19}F NMR (376 MHz, CD_2Cl_2): δ = –62.84 (s, 24F), –82.82 (s, 6F) ppm. ^{13}C NMR (101 MHz, CD_2Cl_2): δ = 288.6, 191.6, 162.4 (q, $^1J_{C-B}$ = 50 Hz), 162.0, 143.0, 136.9, 136.7, 135.4, 134.8, 132.8, 130.7, 129.5 (qq, $^2J_{C-F}$ = 32 Hz, $^3J_{C-B}$ = 3 Hz), 128.0, 126.0 (q, $^1J_{C-F}$ = 284 Hz), 125.2 (q, $^1J_{C-F}$ = 274 Hz), 118.1, 112.7, 85.8 (q, $^2J_{C-F}$ = 30 Hz), 55.9, 26.3, 25.6, 21.3, 17.8 ppm. Elemental anal. calcd. for $C_{69}H_{55}BF_{30}N_2O_3W$: C, 48.05; H, 3.21; N, 1.62; found C, 47.98; H, 3.349; N, 1.67.

W(≡CC$_6$H$_4$OMe)(1,3-bis(1-hydroxy-1,1-trifluoromethylethyl)-imidazol-2-ylidene)(OC(CF$_3$)$_2$Me) (W17): LiHMDS (147 mg, 0.88 mmol, 2.05 equiv.) was added as a solid to a suspension of 1-(1,1,1-trifluoro)-2-(trifluoromethyl)-2-hydroxyprop-3-yl)imidazolium-3-(1,1,1-trifluoro)-2-(trifluoromethyl)propan-2-olate (183 mg, 0.43 mmol, 1 equiv.) in THF at –40 °C and the reaction mixture was stirred at room temperature for two hours. The resulting solution was cooled to –40 °C, added to a solution of W(≡CC$_6$H$_4$OMe)(OC(CF$_3$)$_2$Me)$_3$(DME) (400 mg, 0.43 mmol, 1 equiv.) in THF at –40 °C and stirred at room temperature for 16 h. All volatiles were removed under reduced pressure and co-evaporated with *n*-pentane. The residue was then taken up in toluene, filtered through celite and the solvent was removed under reduced pressure. The resulting residue was stirred in *n*-pentane for one hour, filtered and dried in vacuo to receive the product as red powder (221 mg, 0.24 mmol, 57 %). ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.21 (s, 2H), 6.79 (d, $^3J_{H-H}$ = 9.0 Hz, 2H), 6.66 (d, $^3J_{H-H}$ = 8.9 Hz, 2H), 4.50 (s, 4H), 3.75 (s, 3H), 1.85 (s, 3H) ppm. ^{19}F NMR (376 MHz, CD_2Cl_2): δ = –75.27 (q, $^4J_{F-F}$ = 9.8 Hz, 6F), –77.06 (q, $^4J_{F-F}$ = 9.8 Hz, 6F), –78.59 (s, 6F) ppm. ^{13}C NMR (101 MHz, CD_2Cl_2): δ = 295.7, 195.5, 160.4, 138.9, 124.5 (q, $^1J_{C-F}$ = 288 Hz), 123.8 (q*, $^1J_{C-F}$ = 289 Hz), 123.4 (q, $^1J_{C-F}$ = 291 Hz), 135.0, 122.3, 112.8, 83.0 (sept**, $^2J_{C-F}$ = 29 Hz), 81.2 (sept**, $^2J_{C-F}$ = 29 Hz), 55.8, 50.8, 20.7 ppm. Elemental anal. calcd. for $C_{23}H_{16}F_{18}N_2O_4W$: C, 30.35; H, 1.77; N, 3.08; found C, 30.09; H, 1.946; N, 3.25. *one signal of the quartet is overlaid by the signal at 122.3 ppm. **terminal signals of the septet were not observed.

WCl(≡CC$_6$H$_4$OMe)(1,3-bis(1-hydroxy-1,1-trifluoromethylethyl)-imidazol-2-ylidene) (W18): *N*,*N*-Dimethylanilinium hydrochloride (26 mg, 0.17 mmol, 1 equiv.) was dissolved in CH_2Cl_2 and diethyl ether, cooled to –40 °C and added to a solution of **W17** (150 mg, 0.17 mmol, 1 equiv.) in CH_2Cl_2 and diethyl ether at –40 °C. The reaction mixture was stirred at room temperature for four hours. All volatiles were removed under reduced pressure and the residue was washed with diethyl ether and dried in vacuo, to obtain the product as a blue solid (31 mg, 0.04 mmol, 25 %). ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.24 (s, 2H), 6.82 (d, $^3J_{H-H}$ = 8.9 Hz, 2H), 6.54 (d, $^3J_{H-H}$ = 8.8 Hz, 2H), 4.58 (d, $^2J_{H-H}$ = 14.3 Hz, 2H), 4.48 (d, $^2J_{H-H}$ = 14.3 Hz, 2H), 3.77 (s, 3H) ppm. ^{19}F NMR (376 MHz, CD_2Cl_2): δ = –74.94 (q, $^4J_{F-F}$ = 9.6 Hz, 6F), –76.63 (q, $^4J_{H-H}$ = 9.7 Hz, 6F) ppm. ^{13}C-NMR (101 MHz, CD_2Cl_2): δ = 310.4, 192.9, 161.3, 137.9, 135.3, 123.7 (q, $^1J_{C-F}$ = 288 Hz), 123.2 (q, $^1J_{C-F}$ = 298 Hz) 122.4, 112.3, 81.4 (sept*, $^2J_{C-F}$ = 28.9 Hz), 55.8, 50.7 ppm. Despite numerous efforts, no adequate elemental analysis was obtained. *terminal signals of the septet were not observed.

[W$_2$Cl(1,3-bis(1-hydroxy-1,1-trifluoromethyl-ethyl)-imidazol-2-ylidene)$_2$(MeCN)(μ-((Ar)CC(Ar)))$^+$ (B(Ar^F)$_4$)$^-$] (Ar = C$_6$H$_4$OMe) (W19): W18 (27 mg, 0.04 mmol, 1 equiv.) was dissolved in CH_2Cl_2

and cooled to –40 °C. A cooled solution of $AgB(Ar^F)_4$•3MeCN (38 mg, 0.04 mmol, 1 equiv.) in CH_2Cl_2 was added and the mixture was stirred for one hour at room temperature. The reaction mixture was filtered through celite, then all volatiles were removed under reduced pressure and the residue was crystallized from CH_2Cl_2 and *n*-pentane to obtain the product in form of black crystals (14 mg, 0.01 mmol, 33 %). ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.71 (s, 8H), 7.55 (s, 4H), 7.31 (s, 2H), 7.19 (s, 2H), 6.95 (d, $^3J_{H-H}$ = 8.8 Hz, 4H), 6.89 (d, $^3J_{H-H}$ = 9.2 Hz, 4H), 4.70 (d, $^2J_{H-H}$ = 15.0 Hz, 2H), 4.40–4.31 (m, 4H), 4.27 (d, $^2J_{H-H}$ = 14.8 Hz, 2H), 3.84 (s, 6H), 2.46 (s, 3H) ppm. ^{19}F NMR (376 MHz, CD_2Cl_2): δ = –62.86 (24F), –73.00 (6F), –73.35 (6F), –75.08 (6F), –75.28 (6F) ppm. ^{13}C NMR (176 MHz, CD_2Cl_2): δ = 185.9, 176.8, 165.7, 162.2, 162.2 (q, $^1J_{C-B}$ = 50 Hz), 142.1, 135.2, 133.9, 133.7, 131.6, 129.5 (qq, $^2J_{C-F}$ = 32 Hz, $^3J_{C-B}$ = 3 Hz), 125.1, 125.0 (q, $^1J_{C-F}$ = 271 Hz), 123.8, 122.7 (q*, $^1J_{C-F}$ = 290 Hz), 122.0 (q*, $^1J_{C-F}$ = 291 Hz), 121.6 (q*, $^1J_{C-F}$ = 290 Hz), 121.3 (q*, $^1J_{C-F}$ = 291 Hz), 117.9 (sept**, $^3J_{C-F}$ = 3 Hz), 112.5, 86.6 (sept***), 84.3 (sept**, $^2J_{C-F}$ = 29 Hz), 55.7, 50.7, 46.9, 4.2 ppm. Elemental anal. calcd. for $C_{72}H_{41}BF_{48}ClN_5O_6W_2$: C, 36.06; H, 1.72; N, 2.92; found C, 36.26; N, 1.983; H, 2.85. *terminal signals of the quartet were not observed. **terminal signals of septet were not observed. ***septet poorly resolved.

[W(C$_3$(Ph)(Me)(C$_6$H$_4$OMe))(1,3-diisopropylimidazol-2-ylidene)-(OC(CF$_3$)$_2$Me)$_2$(NC*t*Bu)]$^+$ (B(Ar^F)$_4$)$^-$] (W20): A solution of **S1** (67.5 mg, 0.581 mmol, 5 equiv.) in o-dichlorobenzene was added to a solution of **W7** (205 mg, 0.116 mmol, 1 equiv.) in o-dichlorobenzene and stirred for two hours. One drop of pivalonitrile was added and the solution was overlayed with *n*-pentane and cooled to –40 °C overnight. The crystalline product was dried in vacuo, washed several times with *n*-pentane to remove residual o-dichlorobenzene and dried in vacuo again to obtain the product as dark red crystals (123.5 mg, 0.065 mmol, 57 %). ^{1}H NMR (400 MHz, $C_2D_2Cl_4$): δ = 7.75–7.65 (m, 2H), 7.63 (s, 8H), 7.54–7.43 (m, 8H), 7.38 (dd, $^3J_{H-H}$ = 6.1 Hz, $^3J_{H-H}$ = 4.1 Hz, 1H), 7.21–7.17 (m, 1H), 7.15 (dd, *J* = 6.0, 4.5 Hz, 1H), 6.83–6.71 (m, 2H), 4.52–4.27 (m, 2H), 3.93–3.51 (m, 6H), 1.59–1.50 (m, 3H), 1.27 (s, 9H), 1.22–1.14 (m, 6H), 1.00 (s, 2H), 0.48 (d, $^3J_{H-H}$ = 6.5 Hz, 2H), 0.43–0.39 (m, 2H) ppm. ^{19}F NMR (376 MHz, $C_2D_2Cl_4$): δ = –67.90 (s, 24F), –82.10 to –83.05 (m, 12F). ^{13}C NMR (101 MHz, $C_2D_2Cl_4$): δ = 252.9, 251.8, 182.1, 164.0, 161.9 (q, $^1J_{C-B}$ = 49.7 Hz), 140.3, 135.3, 135.1, 134.2, 132.6, 132.0, 130.9, 129.7, 129.1 (qq, $^2J_{C-F}$ = 31 Hz, $^3J_{C-B}$ = 3 Hz), 128.2, 124.8 (q, $^1J_{C-F}$ = 273Hz), 123.1 (q, $^1J_{C-F}$ = 290 Hz), 123.0 (q, $^1J_{C-F}$ = 289 Hz), 120.7, 119.1, 117.8, 115.2, 85.8 (sept*), 81.9 (sept*), 66.0, 56.0, 53.7, 53.6, 28.4, 24.9, 24.6, 22.3, 18.1, 17.0 ppm. Elemental anal. calcd. for $C_{71}H_{58}BF_{36}N_3O_3W$: C, 45.36; H, 3.11; N, 2.24; found C, 45.33; H, 3.312; N, 2.25.

Associated Content

Experimental details and characterization data. The Supporting Information is available free of charge from the publisher.

Deposition Numbers 1995648 (**W6**), 1995649 (**W7**), 1995650 (**W11**), 1995651 (**W19**), 1995652 (**W20**), 1995653 (**W16**) and 1995654 (**W15**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

Conflict of Interest

The authors declare no competing financial interest.

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