Predicting Catalytic Activity from $^{13}$CCH Alkylidene Chemical Shift in Cationic Tungsten Oxo Alkylidene N-Heterocyclic Carbene Complexes

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A series of cationic tungsten oxo alkylidene N-heterocyclic carbene (NHC) complexes was synthesized and structurally characterized by single crystal X-ray diffraction. The $^{13}$C NMR chemical shifts of the alkylidene C atoms of these complexes were correlated with the diamagnetic, paramagnetic and spin-orbit chemical shifts calculated by DFT. A good correlation ($R^2 = 0.90$) between the DFT isotropic chemical shifts and the experimental chemical shift as well as a strong correlation between the DFT isotropic chemical shifts and the TOF for the RCM of 1,7-octadiene was found. Further, a comparison of the catalyst geometries allowed for assigning tetracoordinate pseudotetrahedral catalysts to the most deshielded alkylidenes and to the highest TOF pentacoordinate square-planar catalysts to the intermediate deshielded alkylidenes and intermediate TOF, and hexacoordinate and octahedral catalyst to the most shielded alkylidene and lowest TOF.

Analysis of the magnetic shielding tensors allowed for ascribing variations in the chemical shifts to electronic transitions between occupied molecular orbitals corresponding to the alkylidene-C and alkylidene-H $\sigma$-bonds and the empty molecular orbital corresponding to the W-alkylidene $\sigma^*$-bond.

Introduction

Molybdenum (VI) and tungsten (VI) alkylidene N-heterocyclic carbene (NHC) complexes are highly active and productive catalysts for olefin metathesis allowing for productivities (turnover numbers, TONs) $> 500,000$ in solution.[1] Upon immobilization on silica, TONs $> 1,200,000$ have been reported for cationic tungsten oxo alkylidene NHC complexes.[2] We were interested in the question, whether highly active representatives of this class of olefin metathesis catalysts, i.e. catalysts that allow for high turnover frequencies, TOFs, could be identified or even predicted by any theoretical or analytical means, e.g. by the $^{13}$C NMR chemical shifts of the alkylidene carbon. Indeed, Copéret et al. recently outlined the importance of the analysis of the chemical shift tensors for an in-depth understanding of the reactivity of metal olefin complexes, e.g. towards oxidative cyclization and protonolysis.[3]

Here, we report on a correlation between the magnetic shielding and the $^{13}$C NMR chemical shifts of the alkylidene carbon of cationic tungsten oxo alkylidene NHC complexes based on 1,3-dimethyl-4,5-dichloroimidazol-2-ylidene (IMeCl), the 1,3-dimesitylimidazol-2-ylidene (IMes), and the 1,3-diisopropylimidazol-2-ylidene ligand (iPr), respectively, containing different anionic ligands such as chlorides, alkoxides, phenoxides and carboxylates. We finally put forward a correlation between the magnetic shielding tensors and transition between occupied and empty molecular orbitals around the alkylidene center. These values have additionally been correlated with the activity of selected complexes in the ring-closing metathesis (RCM) of 1,7-octadiene and in the cross-metathesis (CM) of 1-octene, 1-dodecene as well as allylbenzene, expressed as turnover frequency after 1 min (TOF).
However, upon addition of two equiv. of remaining phosphine from 1 via Scheme 1.

Results and Discussion

Synthesis of Complexes

Complexes 2–5 were prepared exploiting the route outlined in Scheme 1.1a-d The tungsten oxo alkylidene NHC dichloride complex 2a was prepared from W(O)(CHCMePh)Cl(PMePh)₂ (1) via reaction with IMes. The use of CuCl to remove the remaining phosphine from 2a resulted in decomposition. However, upon addition of two equiv. of tris(pentafluorophenyl)borane as phosphine scavenger, this case, all attempts to purify the mixture by recrystallization failed. 2b crystallizes in the triclinic space group P̅1 with a = 1064.85 pm, b = 1274.94 pm, c = 1723.47 pm, α = 88.65°, β = 87.78°, γ = 80.77° with two molecules in the unit cell. Relevant bond lengths and angles are summarized in Table 1. The tungsten center has a distorted square pyramidal ligand sphere (rₜ = 0.38).1f

As might be expected, the W-oxo bond is stretched after borane coordination (W–O₁ = 176 pm). The W–NHC bond length is comparable to the one in 2a.1g The W–O₁–B₁ angle was found to be 166°; the stretched alkylidene ligand (W–C₂O–C₄₁) shows an angle of 160°. Consequently, the W alkylidene bond is significantly shorter than in 2a (184 vs. 195 pm) and the alkylidene proton is in proximity to the W center (W–H₄0 = 210 pm). In solution, the alkylidene proton is observed at δ = 3.57 ppm (CDCl₃). This is very unusual for alkylidene resonances but is clearly a result of borane coordination and the concomitant distortion of the alkylidene ligand. A second complex (approximately 20%) with H₄0 at δ = 9.70 ppm was observed in solution. This signal is assigned to the borane-free complex, which is in equilibrium with 2b, indicating that borane coordination is reversible in solution. The reaction of 2a with one equiv. of the silver or lithium salts of various alkoxides, carboxylates or trifluoromethanesulfonate resulted in the formation of complexes 3 and 4a-f. The mixed monotriflate-monochloride NHC complex 3 still contained the phosphine ligand. In the solid state the metal in the carboxylate-ligated complex 4c adopts an octahedral configuration with the NHC and the chloride in the apices (Figure 1). Consequently, the chloride is almost trans to the NHC (C₁–W–C₁₁ = 158.32°). 4c crystallizes in the monoclinic space group P2₁/n with a = 1156.72 pm, b = 1258.11 pm, c = 2927.0 pm, α = 90°, β = 95.92°, γ = 90°, Z = 4. The pentfluorocarboxylate is bound in an unsymmetrical η²-fashion (W–O₃ = 239 pm, W–O₂ = 224 pm). In solution, the carboxylate ligand most likely switches between η²- and η¹-binding as suggested by the very broad ¹H NMR signals of this compound.

Complex 4d, which features the defluoroorotphenolate (DFTP) ligand, crystallizes from acetoniitrile (MeCN) in the triclinic space group P̅1 with a = 1088.15 pm, b = 1173.07 pm, c = 835.25 pm, α = 92.88°, β = 91.06°, γ = 105.43°, Z = 4.

Table 1. Relevant bond lengths [pm], angles [°], NHCs, rₜ values and isotropic displacement parameters (Uₐ) of the neutral complexes 2b, 4c, 8b, 6, 9, 8c and 4a, determined by single crystal X-ray diffraction.

|        | 2b | 4c | 6a | 9a | 8c | 4a |
|--------|----|----|----|----|----|----|
| bond lengths [pm] | | | | | | |
| a | 224.8 | 220.7 | 221.16 | 221.7 | 223.8 | 223.3 | 223.5 | 225.2 | 229.90 |
| b | 190.9 | 190.9 | 191.09 | 189.4 | 189.4 | 190.9 | 189.8 | 190.75 |
| c | 233.4 | 232.8 | 238.9 | 201.94 | 195.68 | 201.7 | 196.8 | 197.1 | 198.53 |
| rₜ | 0.38 | 0.39 | 0.39 | 0.18 | 0.14 | 0.05 | 0.42 | 0.54 |

[a] One of two conformers. [b] Octahedral geometry [c] X₁, X₂ = anionic ligands (chloride, alkoxide, carboxylate).

**Scheme 1. Synthesis of complexes 2a, 2b, 3, 4a-4d, 5a-5f.**
The metal center has a distorted square pyramidal ligand sphere \((\tau_S = 0.39)\). The fluorinated ligand is fairly trans to the NHC. The aryloxy is highly bent \((W-O_2 > C_22 = 131.7^\circ)\). All other bonds and angles are inconspicuous and comparable to similar structures in Table 1. The highly distorted trigonal bipyramidal \((\tau_S = 0.54)\) crystal structure of \(4e\) is depicted in Figure S62, S.I.

The coordination of phosphines to scavengers are present and the steric hindrance around the phosphine ligand still is coordinated, since no efficient abstraction of the chloride ligand. A mixture of unidentified products was obtained. However, the reaction with the silver chloride. Finally, the cationic tungsten oxo alkylidene NHC complex was prepared from the monoalkoxide/chloride precursors \(4a-f\) via reaction with Ag(MeCN)\(_2\)B-(Ar\(^f\))\(_2\) and NaB(Ar\(^f\))\(_2\) respectively. In the presence of acetonitrile, the corresponding MeCN adducts were isolated in high yield (typically >90%). In most cases, solvent-free NaB(Ar\(^f\))\(_2\) facilitated the formation of the four-coordinate cationic complexes. Surprisingly, \(4d\) did not react readily with NaB(Ar\(^f\))\(_2\) via abstraction of the chloride ligand. A mixture of unidentified products was obtained. However, the reaction with the silver salt proceeded smoothly to the corresponding cationic complex, coordinated by MeCN, and accompanied by the precipitation of silver chloride. Finally, the cationic tungsten oxo alkylidene IMes monochloro complex \(5d\) was prepared via the reaction of the dichloro complex \(2a\) with NaB(Ar\(^f\))\(_2\). In \(5d\), the phosphine ligand still is coordinated, since no efficient scavengers are present and the steric hindrance around the metal is comparably low. The coordination of phosphines to cationic complexes is expected to lower the reactivity in metathesis reactions dramatically and to lead to a crowded coordination sphere.\(^5\) Indeed, in the preparation of the compounds discussed here, the fast separation of any free phosphines or phosphine-adducts was crucial to the successful isolation of the products. It is assumed that the oxo ligand is readily removed by free phosphine to form the corresponding phosphine oxides and unstable tungsten (IV) complexes. In view of these difficulties, an alternative, more direct synthetic approach was developed (Scheme 2). For these purposes, compound 1 was reacted with two equiv. of lithium hexafluoro-2-butoxide, followed by the addition of one equiv. of IMes. This way, the tungsten oxo alkylidene NHC bisalkoxide complex \(6\) was obtained in 76% isolated yield after precipitation in hexane and quick filtration, since it decomposes in concentrated solution in the presence of phosphines. Subsequent protonation of one of the alkoxide ligands by dimethylphenyliminium B(Ar\(^f\))\(_2\) resulted in the formation of \(5b\) in high yield (89%). Additionally, reduced pressure was applied during the reaction to quickly remove the volatile alcohol that formed upon protonation. Dimethylamine was easily removed by washing the product with pentane. Compound \(6\) (Figure S65, S.I.) crystallizes in the triclinic space group \(P1\) with \(a = 1110.33\) pm, \(b = 1787.91\) pm, \(c = 2131.8\) pm, \(\alpha = 66.06^\circ\), \(\beta = 78.43^\circ\), \(\gamma = 83.27^\circ\), \(Z = 4\) in form of two conformers. Both metal centers have a distorted square pyramidal ligand sphere \((\tau_S = 0.14\) and 0.13). Both W-alkoxide bond lengths are virtually identical (200 and 201 pm). All other angles and bond distances are comparable to the other structures discussed earlier.

The structural analysis of cationic complexes \(5a-h\) and \(12\) was particularly challenging since they are less prone to form crystals suitable for single-crystal X-ray analysis compared to their imido counterparts.\(^6\) Complex \(5g\) is one of the rare

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**Figure 1.** Single crystal X-ray structures of neutral W oxo NHC complexes; \(2b\) (left), \(4c\) (center), \(4d\) (right), X-ray structures of other complexes depicted in the S.I. (Figures S62, S65–S68), solvent molecules omitted for clarity.

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**Scheme 2.** Preparation of \(5b\) through protonation of the tungsten oxo alkylidene NHC bisalkoxide complex \(6\).
Tungsten Oxo Alkylidene NHC Complexes Bearing Bulky Aryloxides and Small NHCs

Further, complexes featuring a small NHC in combination with terphenoxides of different steric demand have been prepared (Scheme 3). The cationic complex 10a was prepared via two different routes. First, the terphenoxide ligand was introduced to yield the phosphine-coordinated monoaryloxide monochloro complexes 7a–c. Then, the silver iodide adduct of IMeCl or iPr (2,3-disopropylimidazol-2-ylidene) was reacted with complexes 7a–c. Silver iodide was found to be an excellent phosphine scavenger and thus, transmetalation proceeded smoothly to yield the pentacoordinate neutral complexes 8a–c in good yield (60–75%). Complex 8b crystallizes in the monoclinic space group P21/c with a = 1884.32 pm, b = 1232.86 pm, c = 2193.75 pm, α = 83.53°, β = 77.39°, γ = 82.58°, Z = 2. The structure is disordered in a ratio of 94:6 and a second weakly populated, strongly disordered tungsten alkylidyne species was found. Its structure could not unambiguously be solved. Lastly, we also obtained single crystals of 5b-MeCN from a mixture of 1,2-dichloroethane and diethyl ether. 5b-MeCN crystallizes in the monoclinic space group P21/c with a = 2229.73 pm, b = 1620.08 pm, c = 2411.41 pm, α = 90°, β = 117.367°, Z = 4. The strongly coordinating MeCN is not replaced by diethyl ether in the solvent mixture. A non-resolvable density-peak at W (dist. ~ 0.8 Å) causes a large Hirschfeld factor for the W=O bond, which is not uncommon for structures of this type.

All relevant bond lengths and angles of the cationic complexes are summarized in Table 2. In general, all NH–W bond lengths are shorter than in their neutral precursors, which can be attributed to a delocalization of the positive charge by the NHC. In the same way, the alkoxide ligands are more tightly bound to the cationic metal centers, which is reflected in bond distances of only between 185.0 and 194.2 Å, whereas in the neutral complexes these are mostly > 200 Å. The alkylidene-W and W-oxo bond distances, on the contrary, do not significantly differ from those observed in neutral W oxo alkylidene NHC complexes.

Table 2. Relevant bond lengths (pm), angles [°], NHCs, τ and isotropic displacement parameters (Ueq) values of the cationic complexes 12, 5b-MeCN, 5g and 5h-Et2O determined by single crystal X-ray diffraction.

|          | Sg | 12    | 5h-Et2O | 5b-MeCN |
|----------|----|-------|---------|---------|
| NH–W     | IMes | IMes  | IMes    | IMes    |
| alkylidene-W | 214.7 | 213.7 | 219.4   | 219.7   |
| alkoxide-W | 189.8 | 187.6 | 189.5   | 189.9   |
| L–W      | 19.0  | 188.4 | 185.0   | 194.2   |
| oxo-W    | 168.2 | 167.6 | 170.6   | 159.6   |
| NH–W-alkylidene | 100.11 | 100.03 | 98.1    | 100.1   |
| NH–W-oxo | 97.27 | 106.64 | 93.18   | 92.8    |
| τ        | 74.0  | 74.1  | 74.2    | 74.2    |
| Ueq      | 0.36  | 0.38  | 0.38    | 0.38    |
| Ueq(C100) | 22(1) | 30(1) | 21(1)   | 36(1)   |
| Ueq(C90)  | 28(1) | 39(1) | 27(1)   | 41(1)   |
| Ueq(C11)  | 25(1) | 26(1) | 23(1)   | 41(1)   |
| Ueq(C12)  | 31(1) | 49(1) | 32(1)   | 80(2)   |
| Ueq(X1)   | 25(3) | 59(1) | 17(1)   | 40(1)   |
| Ueq(L)    | 74.1  | 74.2  | 74.2    | 74.2    |

[a] Tetrahedral geometry.

Figure 2. Single crystal X-ray structures of cationic W oxo NHC complexes; 12 (left), 5b–MeCN (center), 5g (right). X-ray structures of 5h–Et2O depicted in Figure S64. S.I., B(Ar), ion omitted for clarity.
The use of \( [\text{Ag(MeCN)}]_2\text{B(Ar)}_2 \) or the addition of coordinating molecules to the reaction mixture of \( \text{NaB(Ar)}_2 \) and \( 8b \) led to the formation of the cationic complexes. Compound 10a was also synthesized from the bisaryloxide complex 9. In principle, the same approach as presented in Scheme 2 for the synthesis of 5b was used. The intermediary bisaryloxide phosphine complex 7d was reacted with AgIMeCl. 9 crystallizes in the monoclinic space group \( P2_1/c \) with \( a = 1228.84 \, \text{pm}, b = 4555.8 \, \text{pm}, c = 1626.55 \, \text{pm}, \alpha = 90^\circ, \beta = 111.08^\circ, \gamma = 90^\circ, Z = 8 \) (Figure S68, S.I.). Two conformers co-crystallized in the unit cell. In these two conformers, the tungsten center adopts either an almost perfect or a slightly distorted square pyramidal geometry (\( r_3 = 0.05 \) or 0.11, respectively). The aryloxide ligand trans to the NHC has a slightly longer W–O bond than the one trans to the oxo ligand (201 vs. 197 pm). Interestingly, the aryloxide ligand trans to the NHC is bent (C24A–O3A–W1A = 136.1\(^\circ\)) while the one trans to the oxo functionality is almost linear (C6A–O2A–W1A = 165.5\(^\circ\)).

Reactivity

The reactivity of complexes 5a–d, 5f–g, 10a–b, 12, 5b–MeCN and 5c–MeCN was tested in the RCM of 1,7-octadiene and the HM of 1-octene, 1-dodecene and allylbenzene, respectively. Figure 4 shows an overview of all complexes used in the catalytic testing and DFT calculations. Although cationic tungsten oxo alkylidene complexes proved to possess an outstandingly high functional group tolerance, e.g. against nitriles, sec-amines or thioethers,\(^{[1g]}\) we intentionally avoided chloride bonds are elongated (240 vs. 248 pm), whereas the oxo bonds are about the same length. Other bond distances and angles are summarized in Figure 3.

1173.60 pm, \( c = 1687.54 \, \text{pm}, \alpha = \gamma = 90^\circ, \beta = 97.59^\circ, Z = 4 \). The metal center is coordinated by a distorted square pyramidal ligand sphere (\( r_3 = 0.18 \)). Unlike in \( 4b \), the smaller NHC leads to a much less distorted structure, even though the aryloxide ligand is more sterically demanding. The tungsten–NHC distance is comparable to distances observed in complexes bearing the IMes ligand. Thus, the significantly less pronounced electron-donation does not have an influence on the structure. As in \( 4b \), the chloride is fairly trans to the NHC (Cl(1)–W–Cl(1) = 156.87). All other bond lengths and angles are in the expected range (Figure S66, S.I.). By increasing the steric bulk employing the HIPTO aryloxide, compound 8c was successfully prepared. Its structure is significantly more distorted (Figure S67, S.I.). Here, the metal center adopts an intermediate geometry between trigonal bipyramidal and square pyramidal (\( r_3 = 0.42 \)). Complex \( 8c \) crystallizes in the monoclinic space group \( P2_1/n \) with \( a = 1303.42 \, \text{pm}, b = 2163.3 \, \text{pm}, c = 1810.01 \, \text{pm}, \alpha = \gamma = 90^\circ, \beta = 111.01^\circ, Z = 4 \). The bond lengths are mostly similar to those found in \( 8b \).

In an attempt to prepare a cationic complex from \( 8b \) and \( \text{NaB(Ar)}_2 \) no precipitation of NaCl was observed. Instead, the bimolecular complex 11 formed quantitatively, containing one equivalent of \( \text{NaB(Ar)}_2 \). Its solid-state structure reveals a Na\(^+\) cation that is incorporated into a square pyramidal structure with the oxo and chloride ligands in the pyramidal plane (Na-oxo = 231 pm, Na-chloride = 270 pm) and one of the phenyl rings from the HIPTO ligand in the apex (Na–C distance = 293 pm). This structure is remarkably stable and is only disrupted by the addition of coordinating solvents.

Complex 11 crystallizes in the triclinic space group \( P1 \) with \( a = 1286.04 \, \text{pm}, b = 2121.30 \, \text{pm}, c = 2323.08 \, \text{pm}, \alpha = 110.47^\circ, \beta = 96.11^\circ, \gamma = 97.47^\circ, Z = 2 \). The two tungsten centers adopt distorted and highly distorted square pyramidal geometries (\( r_3 = 0.29 \) and 0.43, respectively). Compared to \( 8b \), the tungsten geometry.
substrates bearing possibly coordinating functional groups to eliminate any unwanted, additional influence on catalytic activity. In earlier studies, this strategy was successfully utilized to eliminate any unwanted, additional influence on catalytic activity. In nitrile-free complexes, TOF\textsubscript{1min} and the \textsuperscript{13}C NMR shift of the alkylidene for 1,7-octadiene with R\textsuperscript{2} = 0.981 was obtained (Figure S61, S.I.).

Notably, the reaction of 5\textsubscript{a} with 1,7-octadiene resulted in a mixture of the RCM and acyclic diene metathesis (ADMET) products of which only the dimer, 1,7,14-tetradecatriene, could be found in GC/MS. Nonetheless, higher ADMET products cannot be ruled out due to the detection limit of GC/MS for larger molecules.

In addition to the \(\sigma\)-donor strength of the NHC, the coordination of L-type ligands such as nitriles, phosphines or pyridines can well be expected to have an influence on both the activity and productivity of cationic tungsten and molybdenum alkylidene complexes.\cite{5} In some cases and especially in tungsten alkylidene complexes this can lead to complete loss of activity\cite{5} and, indeed, 10\textsubscript{a} and 5\textsubscript{d}, which contain two acetonitrile molecules or a sterically demanding phosphine in combination with the O-2,6-Ph\textsubscript{2}C\textsubscript{6}H\textsubscript{3} ligand did not show any catalytic activity.

We, therefore, strived to rule out the influence of any additional coordinating ligand such as nitriles and compared the TOF\textsubscript{1min} of five nitrile-free complexes with three pure hydrocarbon-based substrates (Table 3, Figure 5), i.e. with 1-octene, 1,7-octadiene and 1-dodecene. Very good linear correlations with high R\textsuperscript{2} values of 0.95, 0.97 and 0.93, respectively, were found for all three substrates. Again, catalysts with higher shielding of the alkylidene carbon showed higher activity. Obviously, in nitrile-free complexes, TOF\textsubscript{1min} can be

![Figure 4. Structures of complexes used in catalytic testing and calculations.](image)

Table 3. TOF\textsubscript{1min} (min\textsuperscript{-1}) and TON values for 1,7-octadiene, 1-octene, and 1-dodecene using nitrile- and phosphine-free complexes.

| Substrate | Catalyst | 1-octene TOF\textsubscript{1min} | TON | 1,7-octadiene TOF\textsubscript{1min} | TON | 1-dodecene TOF\textsubscript{1min} | TON |
|-----------|----------|-------------------------------|-----|--------------------------------|------|-------------------------------|------|
| 12        | sc       | 4220                          | 8760| 15400                         | 18900| 4880                          | 8120 |
| 12        | sb       | 1180                          | 8650| 10830                         | 19500| 3050                          | 7890 |
| 12        | sg       | 6100                          | 8400| 18300                         | 19600| 5500                          | 8260 |
| 12        | sh       | 5600                          | 6930| 17110                         | 17220| 5030                          | 6520 |
| 12        | 5h       | 4450                          | 5790| 15570                         | 16390| 4700                          | 5140 |

![Figure 5. \textsuperscript{13}C\textsubscript{\textsubscript{NMR}} Shift vs TOF\textsubscript{1min} for 1-octene (blue circle), 1,7-octadiene (green circle) and 1-dodecene (red circle) using nitrile- and phosphine-free complexes.](image)
reliably predicted for both reactions, RCM and HM, from the $^{13}$C alkylidene shift.

**DFT modeling**

Starting from the single-crystal X-ray structural data available, DFT geometry optimizations (at the PBE0-D3/SVP level of theory using the Gaussian D.01 package),[9] and NMR analysis (using the gauge-including atomic orbital (GIAO) method at the PBE0/ZORA/TZ2P level of theory, with inclusion of spin-orbit coupling using the ADF 2019 package),[10][11] were performed for the nine IMes-containing complexes $5\text{a–c, } 5\text{f–g, } 12, 5\text{b–MeCN and } 5\text{c–MeCN}$ (for computational details see the SI). The following discussion is based on ample literature on the calculation of IMes-containing complexes.

To benchmark the chosen protocol, we initially compared the X-ray and the DFT optimized geometries of $12, 5\text{b–MeCN and } 5\text{g}$, by calculating the root-mean-square deviation (RMSD) between the cores of the two geometries, composed of the W atoms and the atoms up to two bonds from W. The resulting RMSDs of 0.29, 0.20 and 0.14 Å indicate that the DFT geometries well reproduce the coordination sphere around the W atom, which is the region of the complex influencing mostly the electronic structure and NMR properties at the alkylidene C atom. Comparison of the DFT and experimental $^{13}$C NMR chemical shifts of the alkylidene carbon, also resulted in good correlation ($R^2 = 0.90$, see Figure 6), and validated further the following analysis.

Analysis of the diamagnetic, $\delta_{\text{dia}}$, paramagnetic, $\delta_{\text{para}}$, and spin-orbit, $\delta_{\text{SO}}$, components of the chemical shift tensors (Table 4)[12] indicated that within the examined nine complexes, $\delta_{\text{dia}}$ and $\delta_{\text{SO}}$ span a range of only 3.4 and 4.9 ppm, respectively, while $\delta_{\text{para}}$ spans a range of 18.2 ppm, almost matching the isotropic DFT chemical shift ($\delta_{\text{DFT}}$) window of 20.3 ppm. This suggests that the following analysis can be focused on the paramagnetic plus spin-orbit term, $\delta_{\text{para}+\text{SO}}$. Analysis of the principal components of the chemical shift tensor, $\delta_{\text{sp}}$, $\delta_{\text{ip}}$ and $\delta_{\text{para}}$, indicates that the most and the least deshielding components, $\delta_{\text{ip}}$ and $\delta_{\text{para}}$, span a range of 24.5 and 23.1 ppm, respectively, while the intermediate deshielding component $\delta_{\text{ip}}$ spans a slightly larger range of 34.6 ppm, indicating that all the components similarly affect $\delta_{\text{DFT}}$. This preliminary analysis is in line with similar studies[12] and, more specifically, with previous work on metal-alkylidene complexes,[13] which thus set the basis for the following analysis of the magnetic shielding tensor and of the molecular orbitals (MO) responsible for the variation in the paramagnetic term. Consistently with a previous study on metal-alkylidene complexes,[14] this MO analysis is performed within a molecular axes frame, with the W–C(alkylidene) bond along the $Y_C$ axis and the W–C(NHC) bond in the $Y_ZC$ plane, which results in the $X_C$ axis being nearly orthogonal to the W–C(alkylidene) bond and nearly laying in the mean W–C(H)(R) plane (see Figure 7).

Next, we checked if there was a correlation between the chemical shifts and the number of ligands or geometry around the W center. This analysis (see Table 4) indicated that the tetracoordinate pseudotetrahedral (pt) complexes are systematically more shielded than the pentacoordinate square pyramidal (sp) ones, with the hexacoordinate octahedral (oh) complex $5\text{a}$ being the least shielded. Considering that the experimental chemical shifts range in a window of only 27.0 ppm (20.3 ppm by DFT), which renders a detailed analysis hard to be conclusive, we focused on the two complexes corresponding to the most and to the least shielded ones, which are $5\text{g}$ and $5\text{a}$, as representative cases.

Representation of the directions corresponding to the principal components in these complexes indicate that $\delta_{\text{ip}}$ is approximately in the plane of the C(H)(R) alkylidene moiety and nearly perpendicular to the W–C $\pi$-bond (see Figure 7), almost

![Figure 6. Correlation plot between the experimental and the calculated $^{13}$C$_{\text{CH}}$ shift of complexes reported in Table 4.](image)

| $\Delta\delta$ (ppm) | $\delta_{\text{dia}}$ (ppm) | $\delta_{\text{para}}$ (ppm) | $\delta_{\text{SO}}$ (ppm) | $\delta_{\text{ip}}$ (ppm) | $\delta_{\text{para}+\text{SO}}$ (ppm) | $\delta_{\text{ip}+\text{SO}}$ (ppm) |
|---------------------|----------------------------|-----------------------------|--------------------------|------------------------|---------------------------------|----------------------------------|
| $5\text{g}$ pth     | $-13.2$                    | $314.3$                     | $12.7$                   | $685.9$                | $141.3$                         | $114.2$                          | $313.8$                         | $300.6$                         | $-18.8$                          |
| $5\text{b}$ pth     | $-13.8$                    | $318.4$                     | $11.4$                   | $684.8$                | $140.6$                         | $122.6$                          | $316.0$                         | $297.3$                         | $-13.6$                          |
| $12$ pth            | $-12.6$                    | $317.9$                     | $12.8$                   | $687.3$                | $146.5$                         | $120.3$                          | $318.0$                         | $301.4$                         | $-15.6$                          |
| $5\text{h}$ pth     | $-15.3$                    | $317.7$                     | $16.2$                   | $677.7$                | $152.2$                         | $125.6$                          | $318.5$                         | $303.9$                         | $-16.4$                          |
| $5\text{c}$ pth     | $-16.0$                    | $321.0$                     | $13.8$                   | $687.8$                | $146.2$                         | $124.5$                          | $319.5$                         | $310.8$                         | $-23.1$                          |
| $5\text{c–MeCN}$ sp | $-15.4$                    | $324.3$                     | $13.7$                   | $686.5$                | $145.2$                         | $133.8$                          | $321.7$                         | $309.9$                         | $-20.8$                          |
| $5\text{b–MeCN}$ sp | $-12.6$                    | $324.0$                     | $11.3$                   | $700.8$                | $135.5$                         | $131.9$                          | $322.7$                         | $309.6$                         | $-20.1$                          |
| $5\text{f–MeCN}$ sp | $-14.4$                    | $328.4$                     | $13.7$                   | $702.2$                | $151.0$                         | $129.8$                          | $327.7$                         | $319.4$                         | $-23.3$                          |
| $5\text{a}$ oh      | $-13.9$                    | $332.4$                     | $15.6$                   | $695.0$                | $170.1$                         | $137.3$                          | $334.1$                         | $324.3$                         | $-22.5$                          |
coincident with the $X_C$ axis in the molecular frame. In strict similarity to the direction of the most deshielding component, $\delta_{11}$, only changes by 9 ppm from $5g$ to $5a$, being the least relevant for the 20 ppm variation in $\delta_{10}$. On the basis of a natural chemical shielding (NCS) analysis using the NBO 6.0 program, $\delta_{11}$ is mostly impacted by electronic transitions from the occupied MO corresponding to the $\sigma_{W^{\text{alk}}}$ bond to the empty MO corresponding to the $\pi_{W^{\text{alk}}}$ bond, or by transitions from the MO corresponding to the $\pi_{W^{\text{alk}}}$ bond to the MO corresponding to the $\sigma_{W^{\text{alk}}}$ bond, both through a coupling via 90° rotation around the $X_C$ direction.

Differently, the intermediate and less shielding components are neither collinear nor perpendicular to the $W-C$ bond, both in $5g$ and $5a$ (see Figure 7), preventing a straightforward description of these variations based on MOs centered at the $W-C$ moiety. Nevertheless, the occupied MOs that should mostly contribute to $\delta_{22}$ and $\delta_{33}$ should correspond again to the $\sigma_{W^{\text{alk}}}$ and $\pi_{W^{\text{alk}}}$ bonds, via coupling with the MOs corresponding to the empty $\sigma_{W^{\text{alk}}}$ and $\pi_{W^{\text{alk}}}$ bonds, with the addition of transitions from the occupied $\sigma_{W^{\text{alk}}}$ and $\sigma_{W^{\text{alk}}}$ MOs to the empty $\pi_{W^{\text{alk}}}$ and $\sigma_{W^{\text{alk}}}$ MOs.

Visual inspection of Figure 7 shows that one among the $\delta_{32}$ and $\delta_{13}$ components is more aligned to the $W-C$ bond, specifically $\delta_{32}$ in $5g$, forming an angle of 30° with the $W-C$ axis, and $\delta_{13}$ in $5a$, forming an angle of 27°. Instead, the other component is more perpendicular to the $W-C$ bond, namely $\delta_{13}$ for $5g$, forming an angle of 60° with the $W-C$ axis, and $\delta_{32}$ for $5a$, forming an angle of 63°. We thus compared contributions to $\delta_{32}$ for $5g$ with those to $\delta_{13}$ for $5a$, and similarly we compared those to $\delta_{13}$ for $5g$ with those to $\delta_{32}$ for $5a$. This means we compared components according to similarity in their direction in the molecular frame, rather than based on their magnitude.

With this caveat in mind, the variation of the principal components reported in Table 4 is 9, 14 and 66 ppm for the components mostly aligned with the $X_C$, $Y_C$ and $Z_C$ axes, pointing to the component perpendicular to the mean $= C(H)(R)$ plane as the one resulting in a clearly larger deshielding in $5a$ compared to $5g$. Inspection of the NCS contribution to the components aligned to the $Y_C$ and $Z_C$ axes for $5a$ and $5g$ (see Table 5), shows negligible variations for the $\sigma_{W^{\text{alk}}}$ and $\pi_{W^{\text{alk}}}$ terms, and reduced variations for the $\sigma_{W^{\text{alk}}}$ and $\sigma_{W^{\text{alk}}}$ terms for the component aligned to the $Y_C$ axis. Instead, clearly larger variations in the shielding of the $\sigma_{W^{\text{alk}}}$ and $\sigma_{W^{\text{alk}}}$ terms occur for the component aligned to the $Z_C$ axis. As already shown, these terms are dominated by transitions from the filled $\sigma_{W^{\text{alk}}}$ and $\sigma_{W^{\text{alk}}}$ MOs to the empty $\sigma_{W^{\text{alk}}}$ MO (Figure 8). Finally, non-negligible contributions are also due to the $\sigma_{W^{\text{alk}}}$, $\sigma_{W^{\text{alk}}}$ and $\pi_{W^{\text{alk}}}$ bonds, indicating participation of the NHC and oxo moieties in determining the chemical shift of the alkylidene C atom.

As a last check, we focused on the different lengths of the $W$-alkylidene bond in $5g$ and $5a$, which are 1.902 and 1.942 Å, respectively, as the shielding is impacted by both the energy gap between the MOs involved in the transition, and their overlap (see Figure 8). The latter, of course is impacted by the distance between the bonded atoms. We thus rigidly translated the entire $= C(H)(R)$ alkylidene group in $5g$ along the $W-C$ bond to a $W$-alkylidene bond length of 1.942 Å, as in $5a$. This deformed complex $5g$ experiences a downfield shift of 12.8 ppm, reducing the difference between $5g$ and $5a$ from 20.3 to only 8.1 ppm.

### Table 5. Natural chemical shift analysis of the $\alpha_{\text{NCS}}$ contributions of the principal components of the shielding tensor. Contributions are assigned to $X_C$, $Y_C$ and $Z_C$ depending on the orientation of principal components (PC) in the molecular frame.

| PC aligned to | $5g$ | $5a$ | $5a-5g$ |
|--------------|------|------|--------|
| $X_C$        | $\sigma_{W^{\text{alk}}}$ $-471$ | $-498$ | $-27$ |
|              | $\pi_{W^{\text{alk}}}$ $-147$  | $-104$ | $43$  |
| $Y_C$        | $\sigma_{W^{\text{alk}}}$ $-91$  | $-92$  | $0$   |
|              | $\sigma_{W^{\text{alk}}}$ $-28$  | $-55$  | $-27$ |
| $Z_C$        | $\sigma_{W^{\text{alk}}}$ $-5$   | $-3$   | $2$   |
|              | $\pi_{W^{\text{alk}}}$ $-91$  | $-98$  | $-8$  |
|              | $\pi_{W^{\text{alk}}}$ $-3$    | $-3$   | $0$   |
|              | $\sigma_{W^{\text{alk}}}$ $-46$ | $-34$  | $13$  |
|              | $\sigma_{W^{\text{alk}}}$ $-50$ | $-27$  | $23$  |
|              | $\pi_{W^{\text{alk}}}$ $1$    | $0$    | $1$   |
|              | $\pi_{W^{\text{alk}}}$ $-1$   | $-1$   | $0$   |
|              | $\sigma_{W^{\text{alk}}}$ $-34$ | $-30$  | $4$   |
|              | $\pi_{W^{\text{alk}}}$ $5$    | $0$    | $-5$  |
|              | $\sigma_{W^{\text{alk}}}$ $-52$ | $-80$  | $-28$ |
|              | $\sigma_{W^{\text{alk}}}$ $-76$ | $-121$ | $-45$ |
|              | $\pi_{W^{\text{alk}}}$ $-4$   | $-4$   | $0$   |
|              | $\pi_{W^{\text{alk}}}$ $1$    | $1$    | $0$   |
|              | $\pi_{W^{\text{alk}}}$ $-2$   | $-30$  | $1$   |

![Figure 7](image1.png) **Figure 7.** Principal axes of the NMR shift tensors for the compounds $5g$ and $5a$, together with a line structure of the (NHC)$W=C(H)(R)$ moiety showing the molecular axes frame used in the analysis.

![Figure 8](image2.png) **Figure 8.** a) Schematic localized occupied and vacant orbitals contributing to the deshielding variation of the $\delta_{11}$ term at the alkylidene C atom; b) representation of the equation determining the magnitude of the induced field upon electronic transition from one filled MO, $\Psi_{\text{occ}}$, to an empty MO, $\Psi_{\text{vac}}$, coupled by rotation of 90° of $\Psi_{\text{occ}}$ promoted by the angular momentum operator $I$, $\varepsilon_{\text{vac}} - \varepsilon_{\text{occ}}$ is the energy gap between the $\Psi_{\text{vac}}$ and $\Psi_{\text{occ}}$ orbitals.
Conclusion

A correlation between the catalytic activity of a series of cationic tungsten oxo alkylidene complexes in olefin metathesis and, both, the experimentally determined $^{13}$C alkylidene shift and the DFT isotropic chemical shifts was found. Further analysis confirmed that the variance of the total isotropic shielding, in agreement with literature, can be mainly attributed to the paramagnetic term. Comparison between catalysts geometries, the $^{13}$C alkylidene shifts and TOF$_{\text{max}}$, allowed to classify catalysts into three categories, depending on the coordination geometry around the W atom. Most shielding and higher TOF$_{\text{max}}$ values correspond to tetrahedral complexes, intermediate shielding and TOF$_{\text{min}}$ values correspond to pentacoordinate complexes, while the least shielding and lowest TOF$_{\text{min}}$ values correspond to the hexacoordinate complex.

Analysis of the magnetic shielding tensors of the most and least shielded complexes allowed for ascribing variations in the chemical shifts to electronic transitions between occupied molecular orbitals corresponding to the alkylidene-C and alkylidene-H o-bonds and the empty molecular orbital corresponding to the W-alkylidene o-bond. Those findings provide a better understanding of the activity of tungsten oxo alkylidene NHC complexes and will be a useful tool for a more rational approach to the design of novel cationic group 6 alkylidene NHC complexes.

Experimental Section

All reactions were carried out inside a N$_2$-filled glove box (Labmaster 130, MBraun) or by using standard Schlenk techniques. Diethyl ether, CH$_2$Cl$_2$, n-pentane and toluene were dried by a solvent purification system (MBraun). Deuterated solvents were purchased from Eurisotop and dried by storage over 4 Å molecular sieves. The following compounds were prepared according to literature procedures: IMes$_{[1g]}$, IMesMe$_{[19]}$, Na(BAr$_{4}$)$_{4}$, IMesMe$_{[19]}$ (2 equiv), IMes$_{[19]}$, 1,3-bis(diethylphosphino)propane (2 equiv), Na(BAr$_{4}$)$_{4}$ (1 equiv), 4,4,5,5-tetramethyl-2-pyrrolidinone (2 equiv), CaCl$_{2}$. Activation of tungsten oxide was performed by stirring in MeCN in the presence of AgCl$_{2}$PMe$_{2}$, AgCl$_{2}$ was washed with another 15 mL of pentane. The crude product was recrystallized from MeCN.

Elemental analysis (%) calcd. for C$_{38}$H$_{38}$Cl$_{6}$F$_{30}$N$_{2}$: C, 51.69; H, 4.11; N, 3.17. Found: C, 51.78; H, 4.13; N, 3.23.

WO(CH$_{2}$Me$_{4}$Ph)(IMes)(Cl)$_{2}$: 4d. 2a (102 mg, 0.121 mmol) was dissolved in 6 mL of CH$_{2}$Cl$_{2}$. Li$_{2}$-6,6-dipentafluorophenylphosphonate ethane (62 mg, 1 equiv) was added as a solid at room temperature. The solution became turbid and was stirred for 1 h. The solvent was reduced to half the volume. The colorless precipitate was filtered off over celite. The filtrate was further reduced to 1 mL then the solution was put in the freezer at −40 °C. Overnight, a yellow crystalline solid formed. (60 mg, 45 %).

W(O)(CH$_{2}$Me$_{4}$Ph)(IMes)(Cl)$_{2}$: 4c. 2a (173 mg, 0.204 mmol) was dissolved in 7 mL of CH$_{2}$Cl$_{2}$ and cooled to −40 °C. This solution was added to solid silver pentaffluorobenzoate (66 mg, 1 equiv). A colorless precipitate formed. The suspension was stirred for 60 min under the exclusion of light and then filtered over celite. After removing the solvent, the residual oily product was dissolved in a minimum amount of CH$_{2}$Cl$_{2}$ and filtered again. This step had to be repeated several times to remove residual AgCl. Then, all volatiles were removed in vacuo. The residual orange oil was washed with 10 mL of pentane and stirred with a minimum amount of MeCN. An orange solid precipitated, which was filtered off quickly. Prolonged stirring in MeCN in the presence of AgCl$_{2}$PMe$_{2}$ led to decomposition. After AgCl$_{2}$PMe$_{2}$ was removed, the product was recrystallized from cold MeCN. Yield: 111 mg (61 %) of an orange solid.

NMR spectra of this compound are very broad at room temperature due to the presence and slow interconversion (on the NMR time scale) of at least 3 isomers. $^{13}$C NMR (400 MHz, CDCl$_{3}$) δ 105.7 (W=CH), 10.14 (W=CH), 9.76 (W=CH), 7.39, 7.38, 7.31, 7.28, 7.21, 7.18, 6.95, 6.92, 6.60, 6.52, 6.49, 2.31, 2.15, 2.03, 1.93, 1.87, 1.64, 1.57. Assignment of protons was not possible due to presence of more than 3 isomers. $^{13}$C NMR (101 MHz, CDCl$_{3}$) δ 300.6 (W=CH), 298.1 (W=CH), 192.9 (NCN–NHC), 192.6 (N–NHC), 150.8, 149.6, 146.7, 144.2, 141.2, 139.9, 138.9, 136.3, 135.8, 135.5, 134.9, 134.7, 129.6, 129.4, 129.2, 128.1, 126.3, 126.2, 125.9, 124.9, 124.6, 124.3, 116.5, 51.1 (CMe$_{3}$), 38.1 (CMe$_{3}$), 35.9 (CMe$_{3}$), 28.2 (CMe$_{3}$), 27.9 (CMe$_{3}$), 21.2 (Me–Mes), 18.7 (Me–Mes), 18.4 (Me–Mes), 18.2 (Me–Mes). $^{19}$F NMR (376 MHz, CDCl$_{3}$) δ −136.52, −136.61, −149.44, −152.12, −161.59, −162.32. Elemental analysis (%) calcd. for C$_{38}$H$_{38}$Cl$_{6}$F$_{30}$N$_{2}$: C, 51.69; H, 4.11; N, 3.17. Found: C, 51.78; H, 4.13; N, 3.23.
added as a solid at room temperature. The solution became turbid and was stirred for 12 h. The colorless precipitate was filtered off over celite. The filtrate was further filtered to remove the excess of AgNHC. The crude product was recrystallized from CHCl₃/pentane at -40 °C to yield yellow crystals (192 mg, 65%). ¹H NMR (400 MHz, CDCl₃) δ 8.37 (s, 1H, W–CH), 7.24–7.18 (m, 5H, Ar), 7.15–6.91 (m, 5H, Ar), 6.87 (s, 2H, Ar), 6.78 (s, 2H, Ar), 6.71 (s, 2H, Ar), 5.85 (s, 2H, CH–CH–NHC), 2.71–1.44 (m, 42H, Me–Mes, CH₂MePh). ¹³C NMR (101 MHz, CDCl₃) δ 288.5 (W–CH), 196.3 (NCN–NHC), 160.5 (Ar), 151.9 (Ar), 139.2 (Ar), 135.9 (Ar), 133.6 (Ar), 129.7 (Ar), 129.2 (Ar), 129.0 (Ar), 128.4 (Ar), 128.1 (Ar), 126.5 (Ar), 125.9 (Ar), 124.5 (Ar), 118.4 (Ar), 50.2 (CMe₂Ph), 39.4, 29.0, 21.7, 21.4, 20.5, 19.4, 19.2. Elemental analysis (% calcld for C₃₂H₂₅Cl₃N₇O₃W: C, 65.97; H, 6.14; N, 2.80. Found: C, 65.96, H, 6.27; N, 2.80.

(WO)(CH₂MePh)(Mes)OTf (Cl(2PMe)(Ph)(BAr₄)₅). 5d: 2a (80 mg, 0.0943 mmol) was dissolved in 5 mL of CHCl₃ and cooled to -40 °C. The solution was added to solid NaBAr₄ (84 mg, 1 equiv) and the suspension was stirred for 30 min. A colorless precipitate formed. The mixture was again cooled to -40 °C and then filtered through celite. The filtrate was further filtered to remove one third of the volume and filtered again. After removing the solvent, an oil foam formed that was triturated with pentane until a bright yellow solid precipitated. The pentane phase was decanted and the solid was dried in vacuo. Yield: 750 mg (89%). Analytical data were in accordance to already published data.¹⁸

(WO)(CH₂MePh)(Mes)(OC₆Me(CF₃)₂) was dissolved in 15 mL toluene and cooled to -40 °C. To this solution 485 mg of dimethylaminolithium (BAr₄)₂ (etherate (0.98 equiv) was added as a solid. After 5 min of stirring, vacuum was applied for approx. 30 min. to remove the alcohol that formed and to reduce the amount of solvent by ca. 50%. An orange oily residue was obtained, which was triturated with 15 mL pentane until an orange solid precipitated. The product was filtered off and washed with pentane. Yield 750 mg (89%). Analytical data were in accordance to already published data.¹⁸

Preparation of 5b from 6: 500 mg of W-(O)(CH₂MePh)(Mes)(OCH₂CF₃)₂ was dissolved in 15 mL toluene and cooled to -40 °C. To this solution 485 mg of dimethylaminolithium (BAr₄)₂ (etherate (0.98 equiv) was added as a solid. After 5 min of stirring, vacuum was applied for approx. 30 min. to remove the alcohol that formed and to reduce the amount of solvent by ca. 50%. An orange oily residue was obtained, which was triturated with 15 mL pentane until an orange solid precipitated. The product was filtered off and washed with pentane. Yield 750 mg (89%). Analytical data were in accordance to already published data.¹⁸

(WO)(CH₂MePh)(Mes)(Cl)(PMe₂Ph)(BAr₄)₅. 5d: 2a (80 mg, 0.0943 mmol) was dissolved in 5 mL of CHCl₃ and cooled to -40 °C. The solution was added to solid NaBAr₄ (84 mg, 1 equiv) and the suspension was stirred for 30 min. A colorless precipitate formed. The mixture was again cooled to -40 °C and then filtered through celite. The filtrate was further filtered to remove one third of the volume and filtered again. After removing the solvent, an oil foam formed that was triturated with pentane until a bright yellow solid precipitated. The pentane phase was decanted and the solid was dried in vacuo. Yield: 115 mg (73%). ¹H NMR (400 MHz, CDCl₃) δ 10.12 (d, 1JCH = 117.4 Hz, 1JCH = 10.6 Hz, 1H), 7.80 (brs, 8H, o–CH–(BAr₄)₂), 7.61 (brs, 4H, p–CH–BAr₄)₂), 7.49 (m, 1H, Ar), 7.37 (m, 2H, Ar), 7.34 (m, 2H, CH–CH–NHC), 2.79 (m, 4H, Ar), 7.14 (m, 2H, Ar), 7.12 (brs, 2H, Ar–Mes), 7.00 (m, 2H, Ar), 6.94 (brs, 2H, Ar–Mes), 2.39 (s, 6H, Me–Mes), 2.18 (s, 6H, Me–Mes), 1.99 (s, 6H, Me–Mes), 1.86 (s, 3H, CMe₂Ph), 1.39 (d, 1JCH = 10.6 Hz, 1H, Me–P), 1.17 (d, 1JCH = 10.6 Hz, 1H, Me–P). ¹³C NMR (376 MHz, CDCl₃) δ 302.5 (W–CH), 191.1 (NCN–NHC), 162.2 (Ar), 141.6 (Ar), 131.6 (Ar), 135.5 (Ar), 134.6 (Ar), 131.8 (Ar), 131.5 (Ar), 131.4 (Ar), 130.8 (Ar), 130.5 (Ar), 130.1 (Ar), 129.8 (Ar), 129.7 (Ar), 129.7 (Ar), 129.5 (Ar), 129.4 (Ar), 129.2 (Ar), 128.8 (Ar), 128.1 (Ar), 126.7 (Ar), 126.2 (Ar), 126.1 (Ar), 125.9 (Ar), 123.9 (Ar), 121.2 (Ar), 118.2 (Ar), 52.2 (CMe₂Ph), 32.8 (CMe₂Ph), 28.6 (CMe₂Ph), 21.5 (Me–Mes), 18.7 (Me–Mes), 13.9 (d, 1JCH = 31.4 Hz), 11.6 (d, 1JCH = 35.4 Hz). ¹⁷F NMR (376 MHz, CDCl₃) δ 62.76 (s, 24F, BAr₄)₂. ¹³P NMR (162 MHz, CDCl₃) δ 17.5 (s, 1JCP = 320.3 Hz, 1P).

Elemental analysis (% calcld for C₆H₂Br₂N₂O₆W: C, 50.96; H, 3.35; N, 1.67. Found: C, 51.20; H, 3.35; N, 1.44.
−35°C and added to solid NaB(Ar)₂. (49.4 mg, 1 equiv.). The resulting suspension was stirred for 1 h. A colorless precipitate formed. The solution was reduced in vacuo to one third of the volume and filtered over celite. After removing the solvent, an oily foam formed that was triturated with pentane (2 mL) and a light-yellow solid formed which was dried in vacuo. Yield: 90 mg (88%).

1H NMR (400 MHz, CDCl₃) δ 11.23 (s, 1H, W−CH), 7.73 (s, 8H, Ar−CH(BAr²)), 7.56 (s, 4H, p−CH−BAr²), 7.34−7.16 (m, 6H, Ar), 7.00 (dd, J = 19.2, 7.3 Hz, 4H, Ar), 6.91 (s, 2H, Ar), 6.85 (s, 2H, Ar), 6.78 (d, J = 11.3 Hz, 4H, Ar), 2.35 (d, J = 10.7 Hz, 12H, −Me−Mes), 1.84 (s, 6H, Me−Mes), 1.78 (s, 6H, Me−Mes), 1.72 (s, 6H, Me−Mes), 1.53 (s, 6H, Me−Mes), 1.47 (s, 3H, CMePh), 1.24 (s, 3H, CMePh). 13C NMR (101 MHz, CDCl₃) δ 300.6 (−W−CH), 178.1 (NCN−NHC), 163.1 (Ar), 162.6 (Ar), 162.1 (Ar), 161.6 (Ar), 158.7 (Ar), 148.1 (Ar), 142.1 (Ar), 139.5 (Ar), 137.3 (Ar), 136.2 (Ar), 135.8 (Ar), 134.5 (Ar), 134.4 (Ar), 133.8 (Ar), 133.5 (Ar), 131.8 (Ar), 131.4 (Ar), 130.9 (Ar), 130.5 (Ar), 130.4 (Ar), 129.7 (Ar), 129.6 (Ar), 129.2 (Ar), 127.9 (Ar), 127.5 (Ar), 126.5 (Ar), 126.4 (Ar), 125.8 (Ar), 123.8 (Ar), 121.1 (Ar), 118.0 (Ar), 51.9 (CMePh), 33.8, 31.2, 22.9, 21.6, 21.4, 21.1, 18.2, 17.2, 14.4. 19F NMR (376 MHz, CDCl₃) δ −62.83 (s, 2F, BAr²). Elemental analysis (%); calcd. for C₇₀H₅₁F₂O₇N₉W:C, 57.13; H, 4.02; N, 1.53. Found: C, 57.13; H, 4.09; N, 1.55.

W(O)(CHMe₂Ph)(Mes)OTf(BAr²) OSP(C₂Ph₂) N₂O₂, W: C, 57.13; H, 4.02; N, 1.53. Found: C, 57.13; H, 4.09; N, 1.55.

W(O)(CHMe₂Ph)(Mes)OTf(BAr²)OSP(C₂Ph₂) N₂O₂, W: C, 57.13; H, 4.02; N, 1.53. Found: C, 57.13; H, 4.09; N, 1.55.
off. The filtrate was reduced to 1 mL and filtered again. Then the solution was cooled at –35 °C overnight. An off-white solid material precipitated (74%). 400 MHz (CDCl3) δ 129.5 (s, JCH = 122.9 Hz, 1H, W-CH), 7.16 (m, 1H, Ar), 7.07 (m, 1H, Ar), 7.05 (m, 1H, Ar), 6.94 (m, 4H, Ar), 6.86 (m, 4H, Ar), 6.75 (m, 1H, Ar), 3.34 (m, 2H, CH-IPr), 2.56 (br s, 6H, Me–NE–CH2), 2.83 (m, 2H, CH-IPr), 2.24 (m, 2H, CH-IPr), 1.61 (s, 3H, CMe2Ph), 1.34 (s, 3H, CMe2Ph). 13d (d, JCH = 6.7 Hz, 3H, IPr), 1.23 (d, JCH = 6.6 Hz, 3H, IPr), 1.22 (d, JCH = 6.9 Hz, 3H, IPr), 1.20 (d, JCH = 6.9 Hz, 3H, IPr), 1.17 (d, JCH = 6.8 Hz, 3H, IPr), 1.15 (d, JCH = 6.9 Hz, 3H, IPr), 1.14 (d, JCH = 6.9 Hz, 3H, IPr), 1.01 (d, JCH = 6.8 Hz, 3H, IPr), 0.89 (d, JCH = 6.9 Hz, 3H, IPr), 0.79 (d, JCH = 6.8 Hz, 3H, IPr), 0.49 (d, JCH = 6.8 Hz, 3H, IPr), 0.30 (d, JCH = 6.9 Hz, 3H, IPr). 14 NMR (101 MHz, CDCl3) δ 295.4 (W-CH), 190.9 (NHC–NHC), 161.9 (Ar), 150.5 (Ar), 148.9 (Ar), 148.5 (Ar), 148.4 (Ar), 147.6 (Ar), 135.5 (Ar), 134.8 (Ar), 131.8 (Ar), 130.9 (Ar), 130.7 (Ar), 130.4 (Ar), 128.5 (Ar), 126.0 (Ar), 122.9 (Ar), 121.1 (Ar), 120.5 (Ar), 120.4 (Ar), 119.6 (Ar), 118.6 (Ar), 49.7 (CMe2Ph), 36.9, 35.0, 34.8, 31.5, 31.3, 31.0, 30.7, 30.5, 30.2, 27.5, 27.4, 26.2, 25.4, 24.9, 24.8, 24.7, 24.5, 24.4, 23.3, 22.8, 21.1. Elemental analysis (%) calcd. for C22H35N5O6W: C, 59.45; H, 6.55; N, 2.72. Found: C, 59.37; H, 6.19; N, 2.53.

W(O)(CHMe2Ph)(iPr)(HMTO)(Cl)2, 8d: Compound 7b (150 mg, 180 µmol) was dissolved in 1 mL of benzene. iPr2 (28.7 mg, 1.05 equiv) was dissolved in 10 mL of toluene. Solid was reduced to 2 mL and filtered once again. Then the solution was filtered to dryness to obtain a yellow foam. The foam was triturated with pentane until a yellow solid formed. The pentane phase was decanted and the remaining solid was in vacuo. The product was precipitated from propyl ether or diethyl ether and pentane. Yield: 136 mg, 79%. 1H NMR (400 MHz, CDCl3) δ 11.62 (s, JCH = 122.9 Hz, 1H, W–CH), 7.71 (br m, 8H, O–Ar–B(Ar)3), 7.52 (m, 4H, p–Ar–B(Ar)3), 7.41 (m, 4H, Ar), 7.18 (m, 2H, Ar), 7.10 (m, 3H, Ar), 7.00 (br s, 1H, Ar), 6.82 (d, 8H, Ar), 3.55 (br s, 6H, Me–NE–CH2), 3.11 (s, 3H, CMe2Ph), 1.79, 1.52 (br s, 6H, MeCN), 1.47 (s, 3H, CMe2Ph). 1C NMR (101 MHz, CDCl3) δ 299.7 (W–CH), 183.7 (NHC–NHC), 161.4 (Ar), 154.8 (Ar), 146.9 (Ar), 135.0 (Ar), 131.2 (Ar), 129.0 (Ar), 128.6 (Ar), 128.5 (Ar), 127.5 (Ar), 126.1 (Ar), 124.9 (Ar), 124.5 (Ar), 123.4 (Ar), 120.0 (Ar), 117.6 (Ar), 50.9 (CMe2Ph), 36.5 (Me–NE–CH2), 29.7 (CMe2Ph), 29.1 (MeCN). 13F NMR (376 MHz, CDCl3) δ –62.40 (s, 24F, B(Ar)3).

Elemental analysis (%) calcd. for C22H35F35N5O6W: C, 50.33; H, 3.55; N, 3.13. Found: C, 50.69; H, 3.82; N, 3.05.

Preparation of 10a from 9: W(O)(CHMe2Ph)(MeCl)(ODP), 200 mg, 0.202 mmol) was dissolved in 15 mL CH2Cl2, the solution was cooled to –40 °C and 1 equiv. of N,N-dimethylanilinium B(Ar)3, ethereal (210 mg) was added as a solid. After 30 min the solvent was removed. The residue was filtered and washed with pentane. The product was filtered and washed with pentane. Yield: 270 mg, 83%.

W(O)(CHMe2Ph)(MeCl)(iPr)(HMTO)(MeCN)[B(Ar)4], 10c: 8c (64 mg, 0.0621 mmol) was dissolved in 2 mL CH2Cl2 and the solution was cooled to –35 °C. Solid NaB(Ar)4 (1 equiv) was added under stirring. Immediately, the color changed to bright yellow and a few drops of MeCN were added. The reaction was stirred for 30 min at room temperature. Subsequently, the solvent was removed to 50% and the mixture was cooled to –35 °C. All insoluble solids were filtered off over celite. The filtrate was reduced to dryness to obtain a yellow foam. The foam was triturated with pentane until a yellow solid formed. The pentane phase was decanted and the remaining solid was in vacuo. Yield: 101 mg, 86%. 1H NMR (400 MHz, CDCl3) δ 12.23 (s, JCH = 126.6 Hz, 1H, W–CH), 7.73 (br m, 8H, O–Ar–B(Ar)3, 7.57 (br m, 4H, p–Ar–B(Ar)3), 7.37–7.30 (m, 3H, Ar), 7.27–7.20 (m, 4H, Ar), 7.05–6.97 (m, 3H, Ar), 6.87–6.80 (m, 2H, CH–IPr), 1.87 (s, 3H, CMe2Ph), 1.53 (s, 3H, CMe2Ph), 1.35 (d, JCH = 5.7 Hz, 6H, Me–IPr), 1.34 (d, JCH = 5.7 Hz, 6H, Me–IPr), 0.99 (d, JCH = 6.6 Hz, 6H, Me–IPr), 0.77 (d, JCH = 6.6 Hz, 6H, Me–IPr). 13C NMR (101 MHz, CDCl3) δ 305.9 (W–CH), 177.6 (NHC–NHC), 161.9 (Ar), 158.4 (Ar), 152.6 (Ar), 149.9 (Ar), 147.0 (Ar), 145.2 (Ar), 132.8 (Ar), 131.8 (Ar), 130.1 (Ar), 129.1 (Ar), 128.7 (Ar), 127.6 (Ar), 126.5 (Ar), 125.8 (Ar), 125.1 (Ar), 124.8 (Ar), 124.5 (Ar), 123.6 (Ar), 121.4 (Ar), 120.9 (Ar), 117.8 (Ar), 51.9 (CMe2Ph), 36.7 (Me–NE–CH2), 35.0, 31.2, 31.0, 30.0, 28.5, 25.6, 24.5, 24.2, 24.1, 23.7, 23.1, 1.1 (MeCN). 19F NMR (376 MHz, CDCl3) δ –62.85 (s, 24F, B(Ar)3). Elemental analysis (%) calcd. for C22H35F35Cl3N5O6W: C, 53.76; H, 4.35; N, 2.21. Found: C, 53.41; H, 4.23; N, 2.01.

W(O)(CHMe2Ph)(iPr)(HMTO)[B(Ar)4], 10d: 8d (100 mg, 118 µmol) was dissolved in 2 mL CH2Cl2 and the solution was cooled to –35 °C. Solid NaB(Ar)4 (104 mg, 1 equiv) was added under stirring. The reaction was stirred for 1 h at room temperature. Subsequently, all insoluble solids were filtered off over celite. The filtrate was reduced to dryness to obtain an orange foam. The foam was triturated with pentane until an orange solid formed. The pentane
phase was decanted and the remaining solid was washed in vacuo.

Yield: 169 mg, 86%. \(^1\)H NMR (400 MHz, CD\(_2\)Cl\(_2\)) \(\delta\) 11.18 (1H, 1H, Ar), 7.75 (8H, o-Ar–B(\(\text{Ar}^\text{Me}\))\(\text{Ph}\)) – 7.58 (8H, p-Ar–B(\(\text{Ar}^\text{Me}\))\(\text{Ph}\)) – 7.45 – 7.35 (m, 1H, Ar), 7.32 – 7.14 (m, 7H, Ar), 7.06 (d, \(J = 12.3\) Hz, 4H, Ar), 6.92 (2H, CH–NH–Ar), 3.82 (hept, \(J = 6.7\) Hz, 2H,Pr), 2.33 (s, 6H, Me–Mes), 2.02 (s, 6H, Me–Mes), 1.85 (s, 6H, Me–Mes), 1.63 (d, \(J = 11.5\) Hz, 6H), 1.19 (s, \(J = 6.6\) Hz, 6H), 1.04 (d, \(J = 6.6\) Hz, 6H). \(^{13}\)C NMR (101 MHz, CD\(_2\)Cl\(_2\)) \(\delta\) 298.2 (W–CH), 174.7 (NCC–NH), 163.1 (Ar), 162.6 (Ar), 162.1 (Ar), 156.9 (Ar), 147.5 (Ar), 139.5 (Ar), 137.0 (Ar), 143.6 (Ar), 135.4 (Ar), 133.7 (Ar), 131.8 (Ar), 130.6 (Ar), 130.2 (Ar), 129.7 (Ar), 129.4 (Ar), 129.3 (Ar), 127.9 (Ar), 127.3 (Ar), 126.5 (Ar), 126.2 (Ar), 123.8 (Ar), 122.1 (Ar), 121.1 (Ar), 118.1 (Ar), 113.6 (CHMe\(\text{Me}\)), 55.6 (CHMe\(\text{Me}\)), 52.2 (CMe\(\text{Ph}\)), 34.7, 31.1, 30.2, 24.0, 23.0, 22.7, 21.4, 21.1, 20.5, 14.4. \(^{19}\)F NMR (376 MHz, CD\(_2\)Cl\(_2\)) \(\delta\) –62.82 (s, 24F, B(\(\text{Ar}^\text{Me}\))\(\text{Ph}\)).

Elemental analysis (% calcd.) for C\(_{53}\)H\(_{37}\)F\(_{24}\)N\(_{2}\)O\(_{2}\): C, 53.72; H, 3.91; N, 1.67. Found: C, 53.80; H, 3.99; N, 1.69.

\[\text{[WO}(\text{CHMe}\(\text{Ph})(\text{MeCl})\text{HMATOCl}])\text{Na(B(\text{Ar}^\text{Me}\text{Ph}))} = 11: 8 b (70 mg, 0.0811 mmol) was dissolved in 4 mL CH\(_2\)Cl\(_2\) and the solution was cooled to \(-35\) °C. Solid NaB(\(\text{Ar}^\text{Me}\text{Ph})) (1 equiv) was added under stirring. The reaction mixture was then stirred for another 30 min; then the solvent was reduced to 50% and the mixture was cooled to \(-35\) °C. All insoluble solids were filtered off over celite. The filtrate was dried with the Cambridge Crystallographic Data Centre (CCDC): 2084479 H, 3.82; N, 2.20.\[\text{[W(O)(CHCMe}

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**Conflict of Interest**

The authors declare no conflict of interest.

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