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Introduction

Transition metal-catalyzed alkyne cross metathesis (ACM),¹⁻¹² nitrile-alkyne cross metathesis (NACM),^{1,13-20} ring-closing alkyne metathesis (RCAM),²¹⁻²⁴ ring-opening alkyne metathesis polymerization (ROAMP),²⁵⁻²⁸ and acyclic diyne metathesis (ADIMET)²⁹⁻³¹ continue to attract considerable interest as useful catalytic methods for creating C=C triple bonds. Work still remains to create highly active catalysts that tolerate a broad scope of substrates comparable to their alkene metathesis counterparts.

Jia and Lin³² examined alkyne metathesis computationally and some striking results emerged regarding the use of amido *vs.* alkoxide *vs.* Mo(v1) *vs.* W(v1) catalysts on the rates of metathesis. Dissecting the transition state for catalyst (MeO)₃W \equiv C (Me), the authors determined that ligand deformation (trigonal \rightarrow T-shape; Fig. 1) accounted for ~24 kcal mol⁻¹ of the relative energy difference during transition, while alkyne binding was surprisingly exothermic by ~16 kcal mol^{-1.32} Therefore, an ideal catalyst would remove the ligand

Unusually stable tungstenacyclobutadienes featuring an ONO trianionic pincer-type ligand†

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This report presents the synthesis of the first neutral trianionic ONO pincer-type tungsten alkylidyne complex, $[CF_3-ONO]W \equiv C({}^{t}Bu)(OEt_2)$ (5) {where $CF_3-ONO = (MeC_6H_3[C(CF_3)_2O])_2N^{3-}$ }. Treating 5 with 1-phenylpropyne, 4,4-dimethyl-2-pentyne, and cyclooctyne yields the corresponding tungstenacyclobutadiene complexes $[CF_3-ONO]W[\kappa^2-C({}^{t}Bu)C(Me)C(Ph)]$ (6), $[CF_3-ONO]W[\kappa^2-C({}^{t}Bu)C(Me)C({}^{t}Bu)]$ (7), and $[CF_3-ONO]W[\kappa^2-C({}^{t}Bu)C(CH_2)_6C]$ (8). Complexes 6, 7, and 8 do not undergo retro-[2 + 2]-cycloaddition even at 200 °C or in the presence of PMe₃. DFT methods to elucidate the electronic structure of complexes 5 and 6 reveal important electronic factors that contribute to the lack of reactivity for the tungsten-acyclobutadienes. An important bonding combination between the pincer N-atom lone pair and the W \equiv C bond within 5, termed an inorganic enamine, provides an explanation for the lack of retro-[2 + 2]-cycloaddition from 6, 7, and 8. ¹⁵N NMR spectroscopy was used to confirm the computational finding of an inorganic enamine bonding combination. Single crystal X-ray analysis of 5, 6, 7, and 8 provides insight into possible steric inadequacies within the CF₃-ONO³⁻ ligand to promote catalytic metathesis.



Fig. 1 Ancillary ligand rearrangement during alkyne metathesis.

reorganization energy, making alkyne binding the rate-determining step.

In addition to mitigating the activation energy for the forward and reverse [2 + 2]-cycloaddition, the relative energies of the alkylidyne and metallacyclobutadiene intermediates must be tailored to permit reversibility (Fig. 1). The stability of a metallacyclobutadiene relative to the alkylidyne precursor is dependent on a combination of steric and electronic contributors.33-35 Schrock and co-workers first demonstrated poorly ancillary ligands that basic stabilize metallacyclobutadienes.33-35 Some relevant examples are the tungstenacyclobutadiene $W(\kappa^2-C_3R_3)(OR)_3$ with weakly basic alkoxides -OC(CF₃)₂CH₃,³⁵ -OCH(CF₃)₂,³⁵ and -OC₆H₃(ⁱPr)₂.³⁴ In contrast, $W(\kappa^2-C_3R_3)(O^tBu)_3$, bearing the strongly basic alkoxide -OC(CH₃)₃, has never been isolated. Poorly basic

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alkoxides also facilitate alkyne binding by creating a more electrophilic metal center, thus lowering the [2 + 2]-cycloaddition activation barrier.³² A computational study by Eisenstein *et al.* provides additional support for these ligand effects in analogous *alkene* metathesis.³⁶

Using sterically cumbersome alkoxides arguably raises the energy barrier for ligand rearrangement (trigonal \rightarrow T-shape) and hinders substrate access, but serves an important role in destabilizing the corresponding metallacyclobutadiene. For example, W(κ^2 -C₃Me_3)(OC(CF₃)₂*CH*₃)₃ will metathesize 20 equiv. of 3-heptyne with $t_{1/2} < \sim 2.5$ min in pentane or diethyl ether, but W(κ^2 -C₃Me_3)(OCH(CF₃)₂)₃, with sterically smaller alkoxides, only slowly converts 3-heptyne in pentane ($t_{1/2} = 21$ h).³⁵ The slower rate is attributable to a more stable WC₃ intermediate caused by poor steric repulsion between the alkoxides and the WC₃ ring. Adding donor solvents can compensate and the rate increases to $t_{1/2} = 10$ min for W(C₃Me₃)(OCH-(CF₃)₂)₃ in Et₂O. Interestingly, ΔS^{\dagger} for the retro-[2 + 2]-cycloaddition of W(κ^2 -C₃Et₃)(OCH(CF₃)₂)₃ is consistent with an associative transition state.³⁵

Our initial approach^{37,38} has focused on eliminating or significantly reducing the kinetic barrier to [2 + 2]-cycloaddition by employing trianionic pincer ligands³⁹⁻⁴² that are rigid and pre-organized to adopt a T-shape. Another advantage provided by the trianionic pincer ligand is an open/labile^{43,44} coordination site to allow large substrates access to the metal center. The [CF₃-ONO]³⁻ ligand⁴⁵ depicted in Fig. 2 incorporates a push-pull^{12,28,46-49} electronic environment created by pairing an electron-rich amido with fluorinated alkoxides.35 In addition to confining the anionic donors to a T-shape, the $[CF_3-ONO]^{3-}$ constrains the pincer N-atom lone pair to establish the inorganic equivalent⁴⁵ of an enamine^{50,51} (Fig. 2, N-W=CR \leftrightarrow $N^+ = W = C^- R$), thus providing enhanced nucleophilicity, a property that should facilitate [2 + 2]-cycloaddition. Unfortunately, our previous attempts to isolate a neutral W-alkylidyne bearing the $[CF_3-ONO]^{3-}$ ligand from the anionic propylidyne complex A were met with synthetic challenges (Scheme 1). Owing to the high nucleophilic character of the W=C bond, the neutral species B self-destructs via C-H bond activation and isobutylene expulsion, to provide the corresponding alkylidene C.⁴⁵

Having overcome this obstacle, we now report the successful isolation of the neutral ONO^{3-} trianionic pincer-type tungsten alkylidyne complex [CF₃-ONO]W=C^tBu(OEt₂) (5). Moreover, as expected, complex 5 reacts rapidly with alkyne substrates PhC=CMe, ^tBuC=CMe, and cyclooctyne; with the cyclooctyne



Fig. 2 The push-pull electronic effect of the $[CF_3-ONO]$ pincer-type ligand (left) and the inorganic enamine bonding structure (right).



Scheme 1 Isobutylene expulsion from $[CF_3-ONO]W(\equiv CEt)(O^tBu)$ upon addition of Me₃SiOTf.⁴⁵

derivative providing the first example of a bicyclic metallacyclobutadiene. Curiously, the tungstenacyclobutadienes are remarkably stable. Presented below are data and a discussion regarding the factors promoting their inherent stability.

Results and discussion



Our synthetic strategy to avoid isobutylene expulsion was to replace the propylidyne within complex A with the larger 2,2dimethylpropylidyne in an effort to provide enough steric hindrance to prevent CH bond activation. Treating [CF₃-ONO]H₃ (1) with $({}^{t}BuO)W \equiv C^{t}Bu^{52}$ in benzene yields complex 2, a tungsten alkylidene supported by a [CF₃-ONO]³⁻ pincer-type ligand (eqn (1)). Complex 2 crystallizes from a pentane solution at -35 °C. The ¹H NMR spectrum of 2 exhibits protons at 1.15 and 1.24 ppm attributable to the W=CHC(CH₃)₃ and OC- $(CH_3)_3$ protons, respectively. The W=CH^tBu proton resonates at 6.44 ppm with ${}^{2}J_{HW}$ = 8.80 Hz, and the corresponding carbon signal appears at 262.6 ppm in the ${}^{13}C{}^{1}H$ NMR spectrum. The aryl rings of $[CF_3-ONO]^{3-}$ are unable to lie coplanar rendering the complex C_1 -symmetric as exemplified by two separate Ar– CH_3 proton resonances at 1.99 and 1.94 ppm. As a further consequence of the C_1 -symmetry, the ¹⁹F{¹H} NMR spectrum of 2 contains four quartets, one for each $-CF_3$ group, at -70.7, -71.5, -73.4, and -77.3 ppm.



Treating a pentane solution of 2 with Ph_3PCH_2 deprotonates the alkylidene and precipitates the anionic alkylidyne,



complex 3, as an analytically pure pink powder (eqn (2)). The ¹H NMR spectrum of 3 contains a doublet at 2.36 ppm (${}^{2}J_{\rm HP}$ = 13.31 Hz) corresponding to the H₃CPPh₃⁺ counter cation, and the ³¹P{¹H} spectrum contains a single resonance at 21.6 ppm. The W=*C*^{*t*}Bu carbon resonates downfield in the ¹³C{¹H} NMR spectrum at 286.0 ppm; and again the ¹⁹F{¹H} NMR spectrum reveals the characteristic four quartets indicative of *C*₁-symmetry at -68.7, -71.2, -74.4, and -76.2 ppm.

Upon treating a benzene solution of complex 3 with excess methyl triflate, a color change from red to deep blue occurs over 0.5 h. Evaporating the solvent under vacuum yields a deep blue oil, which was further purified by dissolving in a minimal amount of benzene and adding dropwise to a cold pentane solution to precipitate a deep blue oil of 4. Unfortunately, some decomposition occurs, and free [CH₃PPh₃][OTf] cannot be removed (Scheme 2). Nonetheless, ¹H, ¹⁹F{¹H}, and 2D NMR spectra unambiguously confirm the identity of 4. The ¹H NMR spectrum displays one ^tBu proton resonance at 1.07 ppm and two Ar- CH_3 proton resonances at 2.10 and 2.07 ppm. The 19 F{ 1 H} NMR spectrum of 4 contains four quartets at -69.0, -73.2, -73.9, and -76.7 ppm, and two additional singlet resonances at -76.7 and -78.2 ppm corresponding to coordinated and free $-OSO_2CF_3$ anions. The W $\equiv C^tBu$ carbon appears at 309.4 ppm in the ¹³C{¹H} NMR spectrum. For practical reasons, the isolation of 4 is not necessary, since dissolving blue 4 in Et₂O yields a light blue solution of 5 and a colorless precipitate of [CH₃PPh₃][OTf] (Scheme 2). The majority of the [CH₃PPh₃][OTf] can be removed initially by filtration, and an additional small amount precipitates in Et₂O at -35 °C. However, variable amounts of [CH₃PPh₃][OTf] always remain during bulk scale synthesis of 5, thus thwarting combustion analysis.

The ¹H NMR spectroscopic characterization of 5 reveals one coordinated Et₂O molecule. The $-CH_2$ - protons of the coordinated ether are diastereotopic, appearing as two multiplets at 3.83 and 3.64 ppm. The ^{*t*}Bu protons resonate at 0.84 ppm, and the two Ar- CH_3 protons appear at 2.04 and 2.06 ppm. The ¹⁹F {¹H} spectrum displays the prototypical quartets at -69.2, -71.8, -75.4, and -77.2 ppm. The signal from the W= C^t Bu carbon appears downfield at 311.5 ppm in the ¹³C{¹H} NMR spectrum.

Blue crystals of 5 co-crystallize with residual $[CH_3PPh_3]$ -[OTf] by slowly evaporating a concentrated Et₂O solution of the mixture. Depicted in Fig. 3 is the solid state structure of 5. The alkylidyne 5 contains a tungsten(v1) ion in a square pyramidal geometry ($\tau = 0.266$),⁵³ with the $[CF_3-ONO]^{3-}$ ligand and the coordinated Et₂O occupying the basal positions (Fig. 3). The



Fig. 3 Molecular structure of $[CF_3-ONO]W(\equiv C^tBu)(OEt_2)$ (5) with ellipsoids drawn at 50% probability level, with hydrogens removed for clarity. Only one of two disordered conformation at C28 are shown for clarity.



Scheme 3 Synthesis of tungstenacyclobutadienes 6, 7, and 8.

alkylidyne bond sits in the apical position and is nearly linear (∠W1-C21-C22 is 171.2(2)°) with a W1-C21 bond length of 1.754(3) Å, consistent with other W=C bond lengths ranging between 1.745-1.838 Å for neutral W(vi) alkylidynes.^{28,33,38,47,48,54–67} The C_1 -symmetry of 5 is apparent in Fig. 3 by the underlying twist of the $[CF_3-ONO]^{3-}$ ligand. The nitrogen atom, N1, adopts a planar sp² hybridized geometry, evidenced by a 358.8(3)° sum of angles around N1. The vector perpendicular to the C3-N1-C13 plane representing the nitrogen lone pair forms a ~45° angle from parallel with the W≡C bond.

Complex 5 (or 4 generated *in situ*) readily reacts with excess PhC=CCH₃ to yield the tungstenacyclobutadiene complex 6 (Scheme 3). The ¹H NMR spectrum of 6 exhibits the WC₃-CH₃ protons at 2.79 ppm. Protons for the ^{*t*}Bu group (1.21 ppm) shift downfield relative to 5 (0.84 ppm) and the WC₃-C₆H₅ protons appear between 7.02 and 7.13 ppm. Complex 6 is C_1 -symmetric yielding four quartets in the ¹⁹F{¹H} NMR at

-71.5, -72.1, -76.1, and -76.5 ppm, and the ${}^{13}C{}^{1}H$ NMR spectrum contains two W–C_{α} resonances at 245.4 and 243.0 ppm.

Table 1 Selected metric parameter	rs for the WC_3 r	ings of 6 , 7 , and	8
Bond length (Å) and angles (°)	6	7	8
W1-C21 W1-C23 C21-C22 C22-C23 W1-N1 \angle N1-W1-C21 \angle N1-W1-C23 \angle O1-W1-O2	$\begin{array}{c} 1.9046(16)\\ 1.9106(18)\\ 1.450(3)\\ 1.473(2)\\ 2.0158(14)\\ 122.99(7)\\ 153.60(6)\\ 147.78(5)\end{array}$	$\begin{array}{c} 1.882(3)\\ 1.908(3)\\ 1.456(4)\\ 1.453(4)\\ 2.022(2)\\ 122.65(10)\\ 154.02(10)\\ 147.39(8)\end{array}$	$\begin{array}{c} 1.911(3)\\ 1.897(3)\\ 1.443(4)\\ 1.473(4)\\ 2.023(2)\\ 123.66(10)\\ 153.22(10)\\ 147.80(7)\end{array}$



Fig. 4 Molecular structure of $[CF_3-ONO]W[\kappa^2-C(^tBu)C(Me)C(Ph)]$ (6) with ellipsoids drawn at 50% probability level, with hydrogens removed for clarity.

Crystals were initially grown by slowly evaporating a diethyl ether solution of 6. However, crystals more suitable for an X-ray diffraction experiment were obtained from a slowly evaporating pentane solution of 6. Table 1 lists pertinent bond length and angle data. The solid state structure of 6, presented in Fig. 4, contains a tungsten atom in a distorted-square pyramidal geometry ($\tau = 0.097$)⁵³ with the C^tBu (C21) occupying the apical position. The W1-C21 and W1-C23 bond distances are 1.9046(16) Å and 1.9106(18) Å, respectively, which are consistent with other reported WC_3 rings (Fig. 5). Quite interesting is that the two W-C bond lengths are nearly equal, with a difference of only 0.006(3) Å, whereas other reported structures display a larger difference between the W– C_{α} bonds, ranging from 0.023 to 0.113 Å (Fig. 5). The W1–N1 bond distance is 2.0158(14) Å and the vector perpendicular to the C3-N1-C13 plane representing the nitrogen lone pair forms an angle of ~42.3° to the WC₃ plane.

The phenyl ring (C29–C34) attached to the WC₃ ring is ~44.7° from collinearity with the WC₃ plane. This may be attributed to steric interactions from the nearby WC₃–*CH*₃ group (C28). An interesting structural feature arising from the constrained pincer-type geometry is the O1–W1–O2 angle of complex **6** is tied-back resulting in an angle of 147.78(5)°, which is significantly more acute (10°–18°) than other crystallographically characterized tungstenacyclobutadienes (see Fig. 5).^{34,35,48,68} Overall, the WC₃ ring of complex **6** contains similar structural features to the other reported WC₃ ring moieties depicted in Fig. 5.

To our surprise, complex **6** does not react further with $PhC \equiv CCH_3$ to yield any cross-metathesis products, even after heating at 200 °C, with Et_2O as a free donor ligand. Despite the seemingly similar electronic features of the $[CF_3-ONO]^{3-}$ ligand and structural components of the WC₃ ring to reported alkyne metathesis catalysts, complex **6** does not undergo retro-



Fig. 5 Reported X-ray crystallographic bond length and angles of W(κ^2 -C₃Et₃)(ImN){OCMe(CF₃)₂}₂ (A),⁴⁸ W[κ^2 -C(^tBu)C(Me)C(Me)]Cl₃ (B),⁶⁸ W(κ^2 -C₃Et₃)[O-2,6-C₆H₃(ⁱPr)₂]₃ (C),³⁴ W(κ^2 -C₃Et₃)[OCH(CF₃)₂]₃ (D),³⁵ **6**, **7**, and **8**.

[2 + 2]-cycloaddition. Something unique to the $[CF_3-ONO]^{3-}$ pincer-type ligand must render the tungstenacyclobutadiene fragment exceptionally stable. One possibility is the pincer-type ligand, being overly rigid, may prevent the fluxional exchange between the apical and equatorial positions within the WC₃ ring as illustrated in Fig. 6. The solid state structure of **6** contains only a single conformer, where ^{*t*}Bu occupies the apical position, but does the $[CF_3-ONO]^{3-}$ ligand allow a conformer change in solution? Since complex **6** contains different groups in position R₁ and R₃, it is impossible to determine if a fluxional process occurs in solution. However, if the process is fluxional and R₁ = R₃ = ^{*t*}Bu, a single resonance should be present in the ¹H NMR spectrum.

Heating complex 5 in the presence of ^{*t*}BuC=CMe in C₆H₆ at 60 °C for 3 h yields complex 7, where R₁ and R₃ contain the same ^{*t*}Bu appendage (Scheme 3). Single crystals suitable for X-ray diffraction experiments grow by slowly evaporating an Et₂O solution of 7. Table 1 lists pertinent bond lengths and angles and Fig. 7 depicts the molecular structure. Complex 7 is C_1 -symmetric with the tungsten ion again in a distorted square pyramidal geometry ($\tau = 0.111$).⁵³ The refined X-ray data contains a slight disorder (7%) in the tungsten position. A salient feature in the solid state structure is that the ^{*t*}Bu groups are not equivalent. Evidence includes different W–C bond lengths for W1–C21 = 1.882(3) Å and W1–C23 = 1.908(3) Å, and different N–W–C bond angles (\angle N1–W1–C21 = 122.65(10)° and \angle N1–W1–C23 = 154.02(10)°). However, the asymmetry only exists in the solid state, because the ¹H NMR spectrum of 7



Fig. 6 Fluxional WC₃ ring conformations.



Fig. 7 Molecular structure of $[CF_3-ONO]W[C({}^{t}Bu)C(Me)C({}^{t}Bu)]$ (7) with ellipsoids drawn at 50% probability level, with hydrogens removed for clarity. A disordered W ion position (7%) is removed for clarity.

exhibits a single resonance for both ^{*t*}Bu groups at 1.19 ppm, affirming a fluxional process between the two conformers. The rapid exchange in solution produces an overall C_2 -symmetry as evidenced in the ¹⁹F{¹H} MMR spectrum of 7, which exhibits only two quartets at -71.9 and -76.5 pm. Similarly, the ¹³C {¹H} MMR spectrum contains only a single resonance for both C_{α} in the WC₃ ring at 252.8 ppm. Despite the increased steric bulk within the WC₃ ring compared to **6**, complex 7 again does not react with additional PhC=CMe, even at 200 °C in the presence of Et₂O.

If thermolysis does not provide the energy necessary to cleave the WC₃ ring, an internal driving force that weakens the WC₃ ring may be necessary. Treating complex 5 with cyclooctyne in C_6H_6 provides complex 8, which contains a WC₃ ring fused to a cyclooctene (Scheme 3). The internal ring strain within cyclooctene contributes 7.4 kcal mol^{-1 69} directed towards destabilizing the WC3 unit. The ¹H NMR spectrum of 8 is indicative of a C_1 -symmetric complex with six aromatic resonances at 7.69 (s), 7.61 (s), 7.12 (d), 7.10 (d), 6.88 (d), and 6.85 (d) ppm. The Ar- CH_3 resonances appear at 2.05 and 2.01 ppm and the ^tBu protons resonate at 1.18 ppm. Within the fused cyclooctene structure, the two -CH2- protons adjacent to the WC₃ ring are diastereotopic appearing as four multiplets at 3.82, 3.66, 3.36, and 3.18 ppm. The remaining -CH₂protons (8H) appear as several broad resonances between 0.90 and 1.55 ppm. The ¹⁹F{¹H} NMR spectrum contains four quartets at -70.9, -72.2, -76.1, and -76.6 ppm, and the ${}^{13}C{}^{1}H{}$ spectrum exhibits two unique resonances for W-C_{α} atoms at 252.8 and 238.6 ppm.

Single crystals grow from slow evaporation of a concentrated Et₂O solution of **8**. Table 1 lists pertinent bond lengths and angles and Fig. 8 depicts the molecular structure of **8**. The solid state structure consists of a distorted square pyramidal tungsten ion. Attached to the WC₃ ring is a ^tBu group (C24–27) and a fused cyclooctene ring (C28–C32). The cyclooctene ring is disordered, containing two different conformations at C30 and C31. The $C_{\alpha}^{t}Bu$ again occupies the apical position and



Fig. 8 Molecular structure of $[CF_3-ONO]W[C(^tBu)C(CH_2)_6C]$ (8) with ellipsoids drawn at 50% probability level, with hydrogens removed for clarity. Only one of two disordered conformation at C30 and C31 are shown for clarity.

forms a 123.66(10)° bond angle with N1 of the pincer ligand (N1–W1–C21) and the adjacent N1–W1–C23 bond angle is 153.22(10)°. The apical W1–C21 bond length of 1.911(3) Å is slightly longer by 0.014(4) Å than the W–C23 bond length of 1.897(3) Å. Overall the bond lengths and angles for the WC₃ ring within complexes **6**, **7**, and **8** are comparable (see Table 1).

Again, despite the strain imposed by the fused cyclooctene ring, treating complex 8 with excess PhC=CMe and diethyl ether at 200 °C in toluene-d₈ does not yield metathesis products. One salient feature within the molecular structures of 6, 7, and 8 is the acute O1-W1-O1 bond angles of 147.78(5)°, 147.39(8)°, and 147.80(7)°, respectively. As a result of this acute angle and the overall pincer-type architecture, the -CF₃ groups are tied-back and prevented from exerting steric pressure on the tungstenacyclobutadiene ring. In contrast are the crystallographically characterized tungstenacyclobutadiene of active alkyne metathesis catalysts (Fig. 5, structures A, C, and D), where the large ancillary ligands reside over the WC₃Et₃ ring. As mentioned earlier, the stability of the metallacyclobutadiene complexes depends on the steric repulsion between the ancillary ligand and the substituents attached to the WC₃ ring. Consequently, these isolated structures feature small ethyl substituents attached to the tungstenacyclobutadiene ring to minimize the destabilizing steric repulsion. Despite complexes 6-8 containing larger ^tBu substituents, the WC₃ ring is exceptionally inert. For complexes 6, 7, and 8, the closest distances between the -CF₃ of the pincer-type ligand and the WC₃-R groups (R = ${}^{t}Bu$, Ph, -C₆H₁₂-) are 3.54, 3.52, and 3.53 Å, respectively. For complex A (Fig. 5), the closest contact between the $-CF_3$ and the -Et group is 3.11 Å.⁴⁸

Considering the poor steric pressure from the $[CF_3-ONO]^{3-}$ ligand on the WC₃R₃ rings of **6**, **7**, and **8**, perhaps adding a stronger donor ligand (*e.g.* PMe₃) will promote retro-[2 + 2]-cycloaddition, similar to adding Et₂O to W(C₃Me₃)(OCH-(CF₃)₂)₃.³⁵ Treating complexes **6–8** with excess PhC=CMe and PMe₃, as a potential strong σ -donor ligand, at 100 °C did not generate any metathesis products. Interestingly, a C₆D₆ solution of complex **6** turns violet upon addition of PMe₃, accompanied by a broadening of proton resonances in the ¹H NMR, but eventually slow decomposition occurs in solution. The ¹H NMR spectra of complexes 7 and 8 displayed no signs of reaction with PMe₃. The unusual stability of complexes 6-8 prompted us to investigate a possible electronic component to the apparent energetic disparity between 6, 7, and 8 and a putative alkylidyne.

Computational studies

Fig. 9 depicts the geometry optimized structure of both 5 and 6, as calculated by DFT methods. For complex 5, the calculated bond lengths and angles of the tungsten ion core are in good agreement with the crystallographically determined values. For example, the W1–C21–C22 bond angle of 172.35° matches the experimental value of $171.2(2)^{\circ}$. Similarly, the O1–W1–O2 angle of 143.64° agrees with the experimental value of $144.97(8)^{\circ}$. The vector perpendicular to the C3–N1–C13 plane representing the nitrogen lone pair is ~42.4° from parallel with the tungsten alkylidyne bond (W1–C21). This angle is slightly more acute than the experimental angle of ~45°.

The calculated metric parameters for complex **6** are also reasonable, although some bond angle differences deserve mentioning. The N1–W1–C21 angle of 129.77° is 6.78° larger than the crystallographically determined angle of 122.99(7). Correspondingly, the adjacent angle, N1–W1–C23, of 148.39° is smaller by 5.21° than the experimental value of 153.60(6)°. These deviations are not uncommon and are observed for other reported WC₃ structures.^{47,48} A more significant deviation is the O1–W1–O2 angle of 155.13° from the experimental angle of 147.78(5)°. In agreement though, the nitrogen lone pair represented by a vector perpendicular to the C3–N1–C13 plane forms a ~42.8° to the WC₃ ring, matching the experimentally value of ~42.3°.

Fig. 2 above relates the electronic consequence of having an amido lone pair aligned with the W=C bond axis (inorganic enamine). To assess this interaction in 5 and its fate upon [2 + 2]-cycloaddition and possible role in preventing retro-[2 + 2]-cycloaddition, Gaussian single point calculations were performed on both complexes 5 and 6. Fig. 10 depicts a truncated



Fig. 9 DFT geometry optimized structures of 5 and 6 with calculated bond lengths (red) and crystallographic determined lengths (black).

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Fig. 10 Truncated MO diagram of 5 (left) and 6 (right) (isovalues = 0.051687).

molecular orbital diagram of 5. The inorganic enamine interaction is clearly observed in the HOMO and HOMO–2 orbitals. The HOMO–2 contains a bonding interaction between the W=C π -bond and the aligned N-atom p-orbital, thereby stabilizing the HOMO–2 relative to the unperturbed HOMO–1 by 0.01822 AU. The HOMO is correspondingly destabilized in the anti-bonding combination. This bonding combination is analogous to highly nucleophilic enamines.^{50,51}

Analysis of the electronic structure of **6** reveals that the inorganic enamine bonding combination within **5** is lost. From the single point calculation of **6**, the nitrogen lone pair (HOMO) is lower in energy than the HOMO of **5** by 0.0155 AU, while the W–C π -bonds of **5** and **6** retain similar energy levels (-0.22214 and -0.22268 AU, respectively). *The N-atom lone pair is essentially non-bonding*. The LUMO consists of the π^* interaction between the d_{xy} orbital and p-orbitals of the WC₃ ring. The HOMO–1 contains a d_{yz} orbital in π -overlap with the two C_{α} p-orbitals of the WC₃ ring. This WC₃ π -bonding interaction is consistent with other theoretical models.^{70–75} The HOMO–1 also shows a small amount of bonding overlap with the nitrogen p-orbital, though it is unclear whether this interaction contributes much to the stability of **6**. The most important feature is the restricted orientation caused by chelation; the nitrogen lone pair does not π -donate into the LUMO, which would help destabilize the WC₃ ring by populating a π^* orbital.

The drastic changes in the nitrogen bonding environment from the alkylidyne complexes of 3–5 and the tungstenacyclobutadiene complexes 6–8 are evident by ¹⁵N NMR spectroscopy. Table 2 lists the ¹⁵N resonances for complexes 2–8 (C_6D_6). The N-atom lone pair in the alkylidene complex 2 does not have the appropriate orientation to overlap with the W=C double bond, and as a consequence the lone pair is essentially non-bonding.⁴⁵ The ¹⁵N resonance for 2 appears downfield at 225.7 ppm. In contrast, the ¹⁵N resonance shifts dramatically upfield to 149.3, 165.5, and 178.3 ppm upon forming the W=C triple bonds in 3, 4 and 5, respectively. Clearly, the

Table 2 ¹⁵N NMR chemical shifts of 2-8

	2	3	4	5	6	7	8
ppm	225.7	149.3	165.5	178.3	208.6	204.4	202.1

N-atom lone pair experiences a new environment involving overlap with the W \equiv C bond. This dramatic change in the ¹⁵N NMR chemical shift provides experimental evidence for an inorganic enamine orbital interaction. The interaction is lost upon [2 + 2]-cycloaddition to form **6**, 7, and **8**. From the calculated electronic structure of **6**, the N-atom lone pair is non-bonding, and consequently the ¹⁵N resonance reverts back downfield to 208.6 ppm. Similarly, tungstenacyclobutadienes 7 and **8** also exhibit downfield signals at 204.4 and 202.1 ppm, respectively.

The thermodynamic irreversibility of the [2 + 2]-cycloaddition products 6, 7, and 8 is astonishing. As mentioned earlier, complexes 6-8 lack significant steric repulsion between the ancillary ligand and the WC₃R₃ ring. Unlike the example of $W(\kappa^2-C_3Me_3)(OCH(CF_3)_2)_3$, where poor sterics were compensated for by adding $\text{Et}_2\text{O}_3^{35}$ adding a strong σ -donating PMe₃ ligand was not sufficient to break apart the WC₃ ring. Moreover, these results are intriguing since the [CF₃-ONO]³⁻ ligand incorporates similar electronic features to the fluorinated alkoxides paired with an amido donor, utilized in Tamm's highly active catalysts.^{12,28,46-48,67} This leads us to think another factor plays a significant part in the overly stable tungstenacyclobutadienes 6, 7, and 8. Fig. 11 depicts the $[CF_3-ONO]^{3-}$ pincer-type ligand where the amido lone pair is 45° from parallel to the tungsten alkylidyne bond (I). For comparison, also depicted are Tamm's active catalysts, in which the amido ligand either freely rotates (Fig. 11; II)^{47,48} or is restricted (Fig. 11; III).⁴⁷ In both II and III, the nitrogen lone pair orients perpendicular to the tungsten-alkylidyne bond, thus avoiding the inorganic enamine interaction. In case II where the imidazolin-2-iminato ligand can freely rotate, the nitrogen lone pair reorients 90° upon [2 + 2]-cycloaddition to lie coplanar to the WC₃ ring.^{47,48} In the case of III, the computational models predict that the bulkier tert-butyl-3,5-(dimethylphenyl)-amido ligand is unable to rotate, remaining perpendicular to the WC₃ plane.⁴⁷ Both II and III undergo retro-[2 + 2]-cycloaddition. Thus, one electronic difference between I and cases II and III, is II and III are able to avoid the unfavourable inorganic enamine.

As retro-[2 + 2]-cycloaddition occurs, the inorganic enamine interaction turns on according to Fig. 12 and is endergonic. Removing the amido-alkylidyne interaction should permit facile retro-[2 + 2]-cycloaddition. One way to do this is to attempt Nitrile-Alkyne Cross Metathesis (NACM). Upon formation of an azametallacyclobutadiene, retro-[2 + 2]-cycloaddition would provide a W \equiv N bond instead of a W \equiv C, which would not have the correct energy match to overlap with the N-atom lone pair, and moreover, W \equiv N bond formation should make the overall reaction exergonic. Importantly, the



Fig. 11 Amido lone pair orientation for varying ligand systems of tungsten alkylidyne and tungstenacyclobutadiene complexes (I, II, 47,48 and III 47).



Fig. 12 Reaction progress *vs.* free energy diagram for retro-[2 + 2]-cycloaddition.

sterics remain the same if not somewhat reduced, since the nitrile-N-atom does not bear a substituent.

Indeed, treating complex 5 with excess acetonitrile in C_6D_6 yields a 57:43 mixture of free 4,4-dimethyl-2-pentyne and 7 along with unidentifiable species as evidenced by ¹H NMR spectroscopy (eqn (3)). 4,4-Dimethyl-2-pentyne is removed by vacuum and the ¹H and ¹⁹F{¹H} NMR spectra unambiguously confirm the identity of 7. The unidentifiable products are presumably tungsten nitrido species, though their identity is not clear from the spectroscopic data. Broad resonances in the ¹H

and ¹⁹F{¹H} NMR spectra of the reaction mixture may represent several multi-nuclear species; it is well-known for W-nitrido complexes to exist as dimers,^{20,76–79} trimers,^{77–80} and larger oligomers.^{77,78} Most importantly, complex 7 and the free 4,4-dimethyl-2-pentyne indicate retro-[2 + 2]-cycloaddition occurred. In fact, retro-[2 + 2]-cycloaddition must occur swiftly because 7 is the product of alkylidyne 5 and free 4,4-dimethyl-2-pentyne. Adding excess ^tBuC=CMe to the reaction mixture does not result in any further nitrile–alkyne cross metathesis from the presumed tungsten–nitrido species.



Conclusions

Presented is the first synthesis of a neutral trianionic pincertype tungsten alkylidyne (5). Complex 5 reacts with PhC \equiv CMe, ^{*t*}BuC \equiv CMe, and cyclooctyne to yield tungstenacyclobutadiene complexes 6, 7, and 8, respectively. Complex 8 is the first example of a bicyclic metallacyclobutadiene, a remarkable find considering cyclooctyne is typically polymerized as a consequence of its internal ring strain.^{27,81,82} Tungstenacyclobutadienes 6–8 contain bond angles and lengths that are similar to known crystallographically characterized metallacyclobutadienes of active metathesis catalysts. Despite the similar metric parameters, the WC₃ rings of 6, 7, and 8 do not cleave to regenerate the alkylidyne, even at 200 °C.

DFT calculations elucidate the key electronic features of 5 and 6. Complex 5 exhibits a bonding combination between the N-atom lone pair on the pincer and the W=C bond that is best described as an inorganic enamine. Evidence for substantial overlap between the N-atom lone pair and the alkylidyne π -bond comes from ¹⁵N NMR spectroscopy. A dramatic 47 ppm shift upfield occurs upon formation of the alkylidyne complex 5 (178.3 ppm) from the alkylidene complex 2 (225.7 ppm). In contrast, the inorganic enamine interaction is lost upon formation of the tungstenacyclobutadiene 6, and the ¹⁵N NMR resonance shifts back downfield to 208.6 ppm.

Both steric and electronic features influence the thermodynamic stability of **6**, **7**, and **8** relative to the corresponding alkylidyne. The chelating nature of the pincer ties back the pendant perfluoroalkoxides, and as a consequence, the CF₃– ONO^{3-} pincer-type ligand exerts minimal steric pressure on the WC₃ core. Surprisingly, adding excess donor ligands such as Et₂O and PMe₃ and heating does not induce cycloreversion. Evidence points to an inorganic enamine interaction as a substantial electronic impediment to cycloreversion. The retro-[2 + 2]-cycloaddition is prevented thermodynamically by reestablishing the inorganic enamine orbital interaction. Proof to support this claim comes from the addition of $CH_3C\equiv N$ to 5 to generate an azatungstenacyclobutadiene intermediate. Retro-[2 + 2]-cycloaddition from the azatungstenacyclobutadiene forms a stable W \equiv N bond, which is unable to participate in an inorganic enamine bonding combination. The reaction of 5 with CH₃C \equiv N yields the metathesis product MeC \equiv C^tBu and unidentifiable tungsten-nitride products. Additional support comes from Tamm's catalysts.^{28,46-48,67} Both complexes **II** and **III** (Fig. 12) are able to avoid the inorganic enamine bonding combination, and are consequently active catalysts.

There is merit in employing a trianionic ONO pincer ligand for alkyne metathesis catalysts; [2 + 2]-cycloaddition occurs swiftly at room temperature, and the confined geometry allows sterically cumbersome substrates access to the metal center as evidenced by the formation of 7. However, the design of the $[CF_3-ONO]^{3-}$ pincer ligand underestimated the steric and electronic factors contributing to the stability of the metallacyclobutadiene. Current work involves designing a new ONO ligand to destabilize the metallacyclobutadiene by increasing the peripheral steric bulk and mitigating/avoiding any inorganic enamine interactions.

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