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Fast "Wittig-Like" Reactions As a Consequence of the Inorganic Enamine Effect

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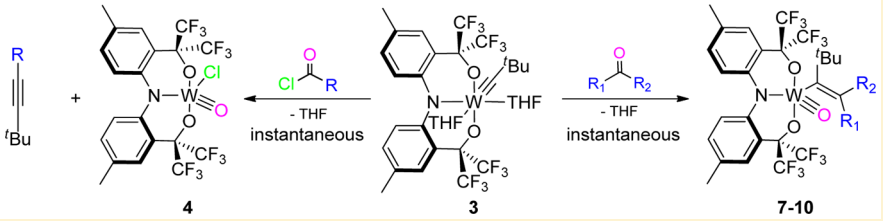
Supporting Information



ABSTRACT: The tungsten alkylidyne $[CF_3{-}ONO]W{\equiv}CC(CH_3)_3(THF)_2$ (**3**) {where $CF_3{-}ONO$ = $(MeC_6H_3[C(CF_3)_2O])_2N^{3-}$} supported by a trianionic pincer-type ligand demonstrates enhanced nucleophilicity in unusually fast "Wittig-like" reactions. Experiments are designed to provide support for an inorganic enamine effect that is the origin of the enhanced nucleophilicity. Treating complex **3** with various carbonyl-containing substrates provides tungsten-oxo-vinyl complexes upon oxygen atom transfer. The rates of reactivity of **3** are compared with the known alkylidyne $(DIPP)_3W{\equiv}CC(CH_3)_3$ (DIPP = 2,6-diisopropylphenoxide). In all cases (except acetone), complex **3** exhibits significantly faster overall rates than $(DIPP)_3W{\equiv}CC(CH_3)_3$. New oxo-vinyl complexes are characterized by NMR, combustion analysis and single crystal X-ray diffraction. Treating **3** with acid chlorides provides the tungsten oxo chloride species $[CF_3{-}ONO]W(O)Cl$ (**4**) and disubstituted alkynes. In the case of acetone the oxo-vinyl complex results in two rotational isomers $\mathbf{10}_{syn}$ and $\mathbf{10}_{anti}$. The rate of isomerization was determined for the forward and reverse directions and was complimented with DFT calculations.

INTRODUCTION

Creating highly nucleophilic metal−carbon multiple bonds is an important synthetic challenge and can result in new and unusual reactivity. For example, the trianionic ONO^{3-} pincer alkylidene $[CF_3{-}ONO]W{=}CHCH_2CH_3(O^tBu)$ deprotonates its own *tert*-butoxide ancillary ligand to release isobutylene producing the tungsten oxo-alkyl complex $[CF_3{-}ONO]W(O)CH_2CH_2CH_3$.[1] From Mindiola's laboratories, the pincer supported titanium alkylidyne $[(PNP)Ti{\equiv}CC(CH_3)_3]$[2−4] (where PNP^- = $N[2\text{-}P^iPr_2\text{-}4\text{-methylphenyl}]_2$) can activate C−H bonds from benzene, methane, ethane, propane, linear alkanes C4−C8, and some cyclic alkanes.[5−7] A method to elevate the nucleophilicity of metal−carbon multiple bonds is to apply the "inorganic enamine" effect.[1] Figure 1 depicts the relationship between organic enamines[8] and an inorganic enamine via a straightforward resonance depiction. Constraining an N atom lone pair to be collinear with a metal−carbon multiple bond is the basis for the interaction. In both cases, the resonance contributions effectively delocalize the N atom lone pair electron density across the unsaturated bond to the carbon two bonds away.

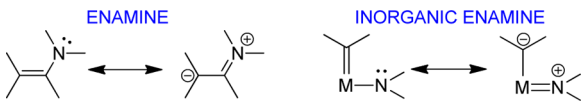


Figure 1. Resonance contributions for an enamine (left) and the analogous inorganic enamine (right).

Figure 2 depicts a truncated molecular orbital diagram that summarizes previous work on the electronic consequences of the inorganic enamine effect.[1] In Figure 2A, the amido ligand rotates freely, thus the lone pair on nitrogen preferentially orients to maximize overlap with the empty d_{xy} orbital on the metal. The interaction stabilizes the N atom lone pair in a bonding molecular orbital as the HOMO. It is clear that no electron density resides on the α-carbon of the alkylidyne. In contrast, a trianionic ONO^{3-} pincer ligand constrains the N atom lone pair in Figure 2B to be coplanar with one of the metal−carbon π-bonds. The forced interaction has three important effects: (1) the interaction splits the energies of M-C π-bonding orbitals; (2) the HOMO orbital is π^* in character, and thus overall is destabilized; and (3) the HOMO orbital contains significant electron density on the α-carbon, akin to an enamine. Taken together the inorganic enamine effect destabilizes the complex and accentuates the nucleophilicity of the α-carbon.

Positive support that the inorganic enamine effect is indeed real requires the α-carbon to not only react with protons, but other electrophiles as well, and the reactivity should be accelerated, i.e., demonstrably more nucleophilic. Herein, we

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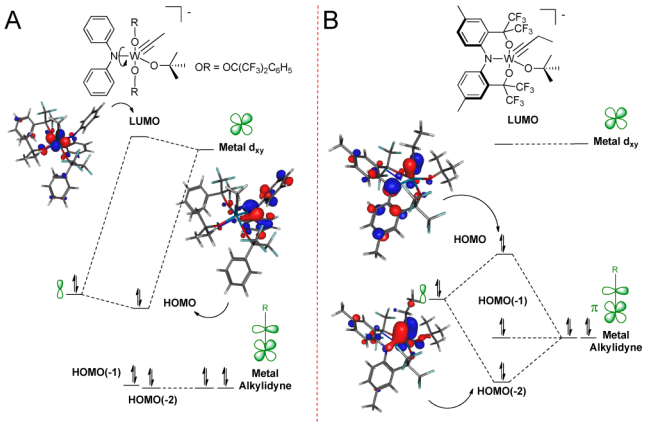


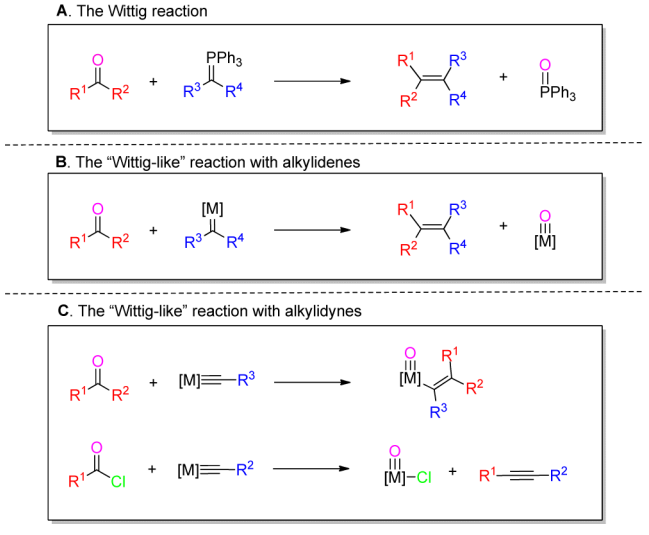
Figure 2. Truncated molecular orbital diagram illustrating the electronic consequences of an inorganic enamine. (A) Amido ligand freely rotates and preferentially orients to overlap with the N atom lone pair with the unoccupied d_{xy} orbital and (B) constrained within a pincer ligand the N atom lone pair is forced to overlap with one of the W−C π-bonds.[1]

present extraordinarily rapid Wittig-like reactions with the trianionic pincer alkylidyne complex $[CF_3{-}ONO]W{\equiv}CC(CH_3)_3(THF)_2$. A combined, synthetic, kinetic, and theoretical analysis provides conclusive evidence for the accentuated nucleophilicity of metal−carbon multiple bonds within an inorganic enamine.

RESULTS AND DISCUSSION

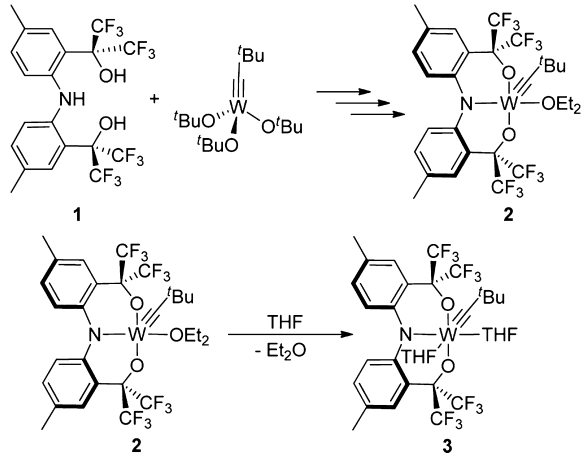
Predicting chemical outcomes based solely on the electronic structure of molecules is critical to discovering new reactivity. A classic case is the juxtaposition of Schrock alkylidenes/ynes[9,10] and Fischer carbenes/ynes.[11] As predicted by their electronic structure, high-oxidation-state metal carbon multiple bonds are nucleophilic and exhibit Wittig chemistry (Scheme 1). Tebbe's reagents $Cp_2Ti(\mu\text{-}CH_2)(\mu\text{-}X)Al(CH_3)_2$ (X = Cl, Me)[12−15] and Schrock's $(Me_3CCH_2)_3M(=CHCMe_3)$ (M = Nb and Ta) alkylidenes[16] react with aldehydes, ketones, esters, and amides (Scheme 1B). Alkylidynes can also participate in Wittig-like chemistry.[17,18] $(DIPP)_3W{\equiv}CC(CH_3)_3$ (DIPP = 2,6-diisopropylphenoxide)[17] cleaves C=O bonds to form oxo-vinyl complexes according to Scheme 1C. In an interesting example, acid chlorides react with $(DIPP)_3W{\equiv}CC(CH_3)_3$ to produce disubstituted acetylenes in a single step,[18] an overall three bond group transfer. In this work, we use Wittig reactions to evaluate the relative nucleophilicity of metal−carbon multiple bonds.

Scheme 1. Wittig and "Wittig-Like" Reactions with Alkylidenes and Alkylidynes



Reported previously, treating the proligand $[CF_3{-}ONO]H_3$ (**1**) with $(^tBuO)_3W{\equiv}CC(CH_3)_3$ in Et_2O leads to the trianionic pincer alkylidyne complex $[CF_3{-}ONO]W{\equiv}CC(CH_3)_3(Et_2O)$ (**2**) (Scheme 2).[19] The Et_2O complex can be challenging to prepare in pure form. To improve the preparation, treating complex **2** with a few drops of THF produces the bis-THF complex $[CF_3{-}ONO]W{\equiv}CC(CH_3)_3(THF)_2$ (**3**), which is more amenable to purification and a significant improvement to the synthesis.

Scheme 2. Improved Synthesis of the Tungsten Alkylidyne $[CF_3{-}ONO]W{\equiv}CC(CH_3)_3(THF)_2$ (3)



Scheme 3 depicts the room-temperature reactivity of complex **3** with various carbonyl-containing substrates. The reaction between **3** and *p*-methoxybenzoyl chloride results in an instantaneous color change from blue to green, to form the oxo-chloride complex $[CF_3{-}ONO]W(O)Cl$ (**4**) and 1-(3,3-dimethylbut-1-yn-1-yl)-4-methoxybenzene (**5**), in 91% yield. The net reaction is a peculiar three bond swap, C=O and C−Cl for W=O and W−Cl. The reaction presumably proceeds via first formation of a metallaoxetane[18,20] followed by β-chloride elimination.[21] N−atom transfers to acid chlorides proceed via a similar mechanism.[22,23] Complete conversion and confirmation of the identity of the alkyne was confirmed by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy. Complex **3** also reacts with pivaloyl chloride to produce **4** and 2,2,5,5-tetramethylhex-3-yne (**6**) in 76% yield.

Following the same procedure, the reactivity of **3** with esters, ketones, and amides, was also explored (Scheme 3). An instantaneous color change from blue to red occurs upon adding 1 equiv of methyl phenylpropiolate to **3**. The red color signals the production of the oxo-vinyl complex $[CF_3{-}ONO]W(O)\{\kappa\text{-}C{-}O{-}(CH_3)_3CC{=}C(OCH_3)(C{\equiv}CC_6H_5)\}$ (**7**), in 82% yield. Interestingly, the alkylidyne attacks the carbonyl group of phenylpropiolate rather than the alkyne. Attack at the carbonyl must occur first because attack at the alkyne would form a metallacyclobutadiene complex, which is irreversible.[19] Evidence for the identity of complex **7** comes from a combination of solution phase NMR studies and solid-state structural characterization. The $^{19}F\{^1H\}$ NMR spectrum

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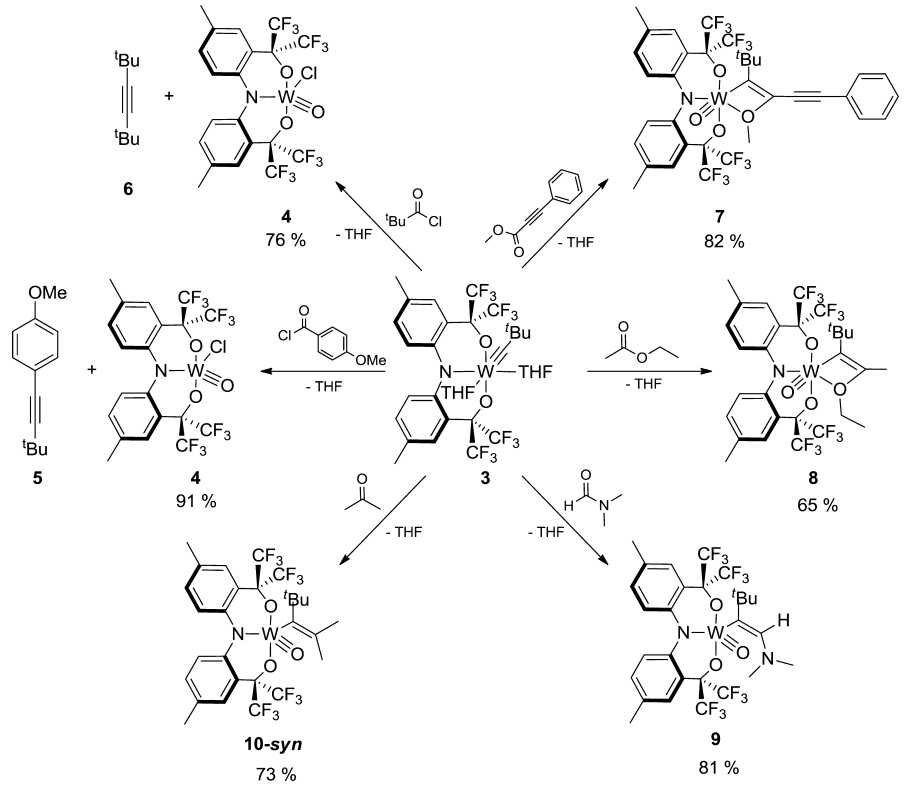
Scheme 3. Reactivity of 3 with Various Carbonyl Compounds



of 7 exhibits four quartets at −70.28, −70.56, −75.51, and −75.94 ppm, corresponding to each CF_3 group in a C_1-symmetric compound. The ^{1}H NMR spectrum exhibits a singlet at 3.23 ppm attributable to the methyl group and the ^{t}Bu protons resonate at 1.63 ppm.

An X-ray diffraction experiment performed on single crystals of 7 provides its unambiguous assignment (Figure. 3).

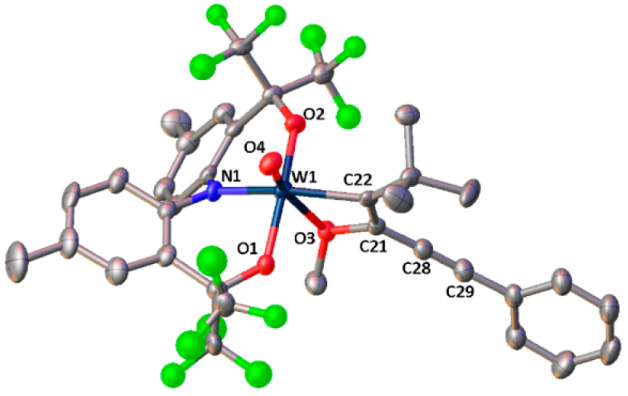


Figure 3. Molecular structure of 7. Ellipsoids are drawn at the 50% probability level, and hydrogen and disordered fluorine atoms are removed for clarity.

Importantly, the molecular structure reveals that the OMe group coordinates to the tungsten ion *trans* to the oxo ligand rendering the complex with a distorted octahedral geometry (∠O4−W1−O3 = 163.27(12)°, ∠O1−W1−O2 = 159.42(12)°, and ∠N1−W1−C22 = 146.04(15)°). A long W1−O3 bond length of 2.413(3) Å indicates the OMe is weakly bound. For comparison, complex **2** contains a W-OEt_2 bond length that is shorter (2.1144(19) Å).[19] The W1−O4 distance is 1.691(3) Å and is consistent with related tungsten-oxo complexes.[23−27] The C28−C29 bond distance is 1.194(6) Å, indicating that the C≡C triple bond remains intact. A bond length of 1.348(6) Å between C21 and C22 confirms that a newly formed double bond is present in 7.

Complex **3** also reacts immediately in benzene with 1 equiv of ethyl acetate to produce the green oxo-vinyl complex [CF_3−ONO]W(O){κ−C-O-$(CH_3)_3$CC═C(OCH_2CH_3)CH_3} (**8**), in 65% yield. ^{1}H NMR spectroscopic characterization indicates **8** is also C_1-symmetric and exhibits diastereotopic protons resonating at 3.40 and 3.80 ppm for the −OCH_2CH_3 protons. The methyl protons (−OCH_2CH_3) appear as a doublet of doublets centered at 0.33 ppm and the ^{t}Bu protons resonate at 1.43 ppm. Four quartet resonances at −69.74, −70.59, −75.12, and −76.09 ppm in the ^{19}F{^{1}H} spectrum of **8** offer additional support for a C_1 complex.

Upon treating a benzene solution of **3** with dimethylformamide (DMF), an instantaneous color change from blue to red occurs. Removing the solvent under reduced pressure provides the red oxo-vinyl complex [CF_3−ONO]W(O){$(CH_3)_3$CC═CH($N(CH_3)_2$)} (**9**) in 81% yield. Crystals suitable for X-ray diffraction deposit from a slowly evaporating solution of **9** in diethyl ether. A combination of ^{1}H, ^{19}F{^{1}H}, and ^{13}C{^{1}H} NMR spectroscopy, combustion analysis, and X-ray diffraction studies confirm the identity of **9** (Figure. 4). Clearly different from complex 7, the N atom of the vinyl group in **9** does not coordinate to form a chelate. The metal center adopts a distorted square-pyramidal geometry (τ = 0.32)[28] with basal plane angles of ∠O1−W1−O2 = 156.46(9)° and ∠C21−W1−N1 = 137.13(11)°. The W1−O3 distance of 1.699(2) Å is statistically identical to 7. Without a chelate such as in 7, the ^{t}Bu group in **9** orients toward open space on the opposite side of the oxo ligand.

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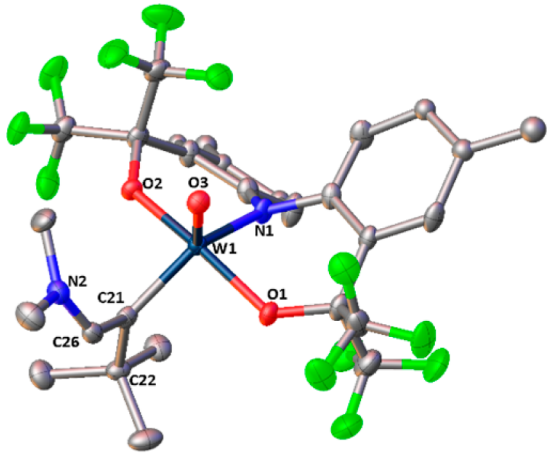
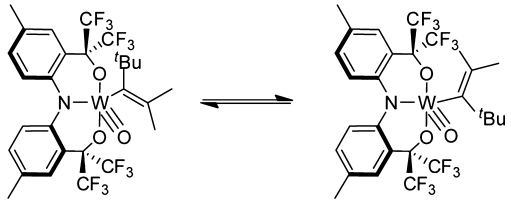


Figure 4. Molecular structure of **9**. Ellipsoids are drawn at the 50% probability level, and hydrogen and disordered arene atoms are removed for clarity.

Complex **3** also deoxygenates acetone to yield the green oxo-vinyl complex $[CF_3{-}ONO]W(O)\{(CH_3)_3CC{=}C(CH_3)_2\}$ (**10**) in 73% yield. Confirmation for the identity of **10** comes from ^1H, $^{19}F\{^1H\}$, and $^{13}C\{^1H\}$ spectroscopy, elemental analysis, and solid-state characterization. NMR studies indicate that **10** exists as two rotational isomers due to restricted rotation about the W−C bond as $\mathbf{10}_{syn}$ and $\mathbf{10}_{anti}$ in a 2:1 ratio (25 °C); where *syn* and *anti* refer to the orientation of the vinyl double bond relative to the oxo ligand (Scheme 4). Similar rotation isomers were assigned to products that form upon reacting $(DIPP)_3W{\equiv}CC(CH_3)_3$ with acetone, but no X-ray structural data were provided.[17]

Scheme 4. Rotational Isomers $\mathbf{10}_{syn}$ and $\mathbf{10}_{anti}$



Complex $\mathbf{10}_{syn}$ forms initially as the kinetic product, and then gradual isomerization to $\mathbf{10}_{anti}$ establishes the equilibrium. The isomerization occurs at room temperature over a period of 20 h and is easily monitored by $^{19}F\{^1H\}$ NMR spectroscopy. For the forward reaction of $\mathbf{10}_{syn}$ to $\mathbf{10}_{anti}$ a barrier of 23.7 ± 0.4 kcal·mol^{-1} was determined. In the reverse direction ($\mathbf{10}_{anti}$ to $\mathbf{10}_{syn}$), a barrier of 23.3 ± 0.4 kcal·mol^{-1} was found. The difference of 0.4 kcal·mol^{-1} between the two isomers is in agreement with the NMR determined equilibrium distribution of 2:1 for $\mathbf{10}_{syn}$:$\mathbf{10}_{anti}$.

Insight into the rotation about the W−C bond comes also from DFT calculations at the B3LYP level of theory,[29−31] where the OWCC dihedral angle was scanned in 10° increments. Figure 5 depicts an asymmetric potential energy surface (PES) as expected for a C_1-symmetric complex. The PES displays two minima corresponding to $\mathbf{10}_{syn}$ and $\mathbf{10}_{anti}$ and two high-energy barriers that prevent free rotation about the W−C bond. These barriers result from the large steric hindrance between the flanking CF_3 groups of the pincer and

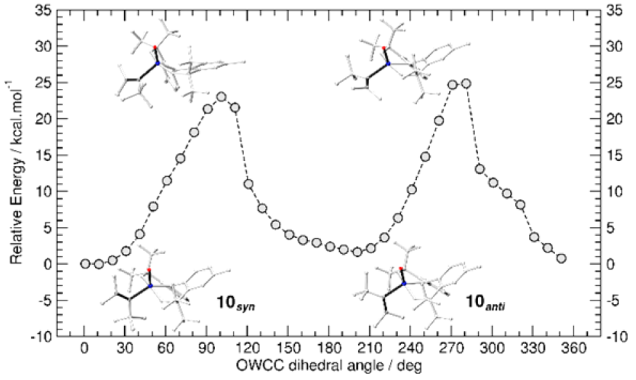


Figure 5. PES scan for the highlighted (black) OWCC dihedral angle of **10**.

the vinyl group. The calculated rotational barriers of 23.04 kcal·mol^{-1} for the forward reaction and 21.38 kcal·mol^{-1} for the reverse process are in good agreement with the experimental values.

Green crystals suitable for X-ray diffraction studies grow upon slow diffusion of pentane into a concentrated diethyl ether solution of $\mathbf{10}_{syn}$ at −23 °C. The solid-state structure (Figure 6) confirms the *syn* orientation. Redissolving the

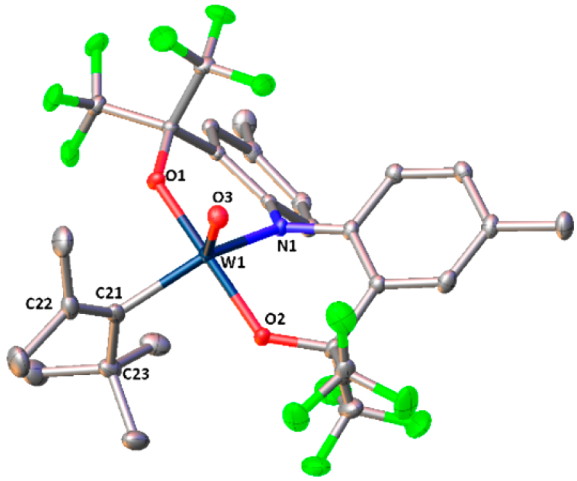


Figure 6. Molecular structure of $\mathbf{10}_{syn}$. Ellipsoids are drawn at the 50% probability level, and hydrogen atoms are removed for clarity.

crystals in C_6D_6 and obtaining a ^1H NMR spectrum reveals only resonances attributable to $\mathbf{10}_{syn}$, though as before $\mathbf{10}_{anti}$ slowly forms to establish equilibrium once dissolved. The crystallographic data indicate the tungsten ion adopts a distorted square-pyramidal geometry (τ = 0.37)[28] with basal plane angles of ∠O1−W1−O2 = 159.52(7)° and ∠C21−W1−N1 = 137.46(9)°. The bond length of 1.365(4) Å between C21 and C22 is appropriate for a C=C double bond, and again the tungsten-oxo bond is similar to **7** and **9** with a bond length of 1.6967(16) Å.

Rates of Reactions: $(DIPP)_3W{\equiv}CC(CH_3)_3$ vs 3. Table 1 lists the results from the kinetic analysis for the reaction of various C=O-containing substrates with **3** and $(DIPP)_3W{\equiv}CC(CH_3)_3$. Impressively, complex **3** exhibits extraordinarily fast overall reaction rates. Schrock reported "Wittig-like" reactivity for the tungsten alkylidyne $(DIPP)_3W{\equiv}CC(CH_3)_3$,[17] however reaction times of hours were observed for most substrates. For complex **3** each reaction end point occurs within 10 s.

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Table 1. Reaction Times and Rates for "Wittig-Like" Reactions Performed with Complexes 3 and $(DIPP)_3W{\equiv}CC(CH_3)_3$

	3		$(DIPP)_3W{\equiv}CC(CH_3)_3$	
substrate	t	rate[a] $M^{-1}{\cdot}s^{-1}$	t	rate[a] $M^{-1}{\cdot}s^{-1}$
acetone	≤10 s	≥0.002	≤10 s	≥0.002
DMF	≤10 s	≥0.002	12 h[b]	–
EtOAc	≤10 s	≥0.002	2 d	1.2×10^{-7}
Ph_2CO	≤10 s	≥0.002	90 min	3.7×10^{-6}
p-MeOBzCO$_2$Cl	≤10 s	≥0.002	12 h	4.6×10^{-7}

[a]Rate refers to the time frame to complete full conversion. [b]Temperature had to be increased to 50 °C.

Comparing these observations with the ones reported by Schrock,[17] the overall rates for **3** are surprisingly faster (>4 orders of magnitude).

$(DIPP)_3W{\equiv}CC(CH_3)_3$, synthesized according to literature precedent from $\{(CH_3)_3CH_2\}_3W{\equiv}CC(CH_3)_3$,[32] was subjected to the identical reaction conditions as **3**. Monitored by ^{1}H NMR spectroscopy and in sealed NMR tubes, the same concentration of each alkylidyne was used in all cases (0.02 M in C_6D_6). Complex **3** consumes all substrate within 10 s, thus an estimated minimum overall reaction rate of 0.002 $M^{-1}{\cdot}s^{-1}$ for acetone, ethyl acetate, DMF, *p*-methoxybenzoyl chloride, and methyl phenylpropiolate was determined. In contrast, changing from brown to deep red, the reaction of $(DIPP)_3W{\equiv}CC(CH_3)_3$ (0.02 M in C_6D_6) with acetone was the only reaction with an instantaneous color change. More typical, adding 1 equiv of ethyl acetate to $(DIPP)_3W{\equiv}CC(CH_3)_3$ results in complete conversion after 2 days. For comparison, complex **3** reacts within 10 s with ethyl acetate with a minimum rate of 0.002 M^{-1} s^{-1}, whereas $(DIPP)_3W{\equiv}CC(CH_3)_3$ requires 2 days demonstrating a rate of approximately 1.2×10^{-7} $M^{-1}{\cdot}s^{-1}$. The acceleration is 4 orders of magnitude faster for **3**. Complex **3** also reacts within 10 s with the larger substrate benzophenone, whereas $(DIPP)_3W{\equiv}CC(CH_3)_3$ requires 90 min. Treating $(DIPP)_3W{\equiv}CC(CH_3)_3$ with DMF instantaneously forms the DMF adduct,[17] however complete conversion to the oxo-vinyl complex requires 12 h heating at 50 °C. For DMF, a direct comparison of reaction rates is not possible since higher temperatures are needed for $(DIPP)_3W{\equiv}CC(CH_3)_3$ to react, but again **3** reacts instantaneously at 25 °C. Formation of acetylene from $(DIPP)_3W{\equiv}CC(CH_3)_3$ and *p*-methoxybenzoyl chloride requires 12 hours to achieve complete conversion resulting in a rate of approximately 4.6×10^{-7} $M^{-1}{\cdot}s^{-1}$, again 4 orders of magnitude slower than **3**.

The increased reactivity is not due to the fact **3** contains a trianionic pincer ligand alone. The nitrogen atom in the pincer framework is critical to the inorganic enamine effect. For example, the trianionic OCO^{3-} supported tungsten alkylidyne complex $[^t$BuOCO$]W{\equiv}CC(CH_3)_3(THF)_2$[33] only binds DMF without further reaction even after heating at 65 °C for 12 h.

CONCLUSION

The trianionic pincer supported complex $[CF_3{-}ONO]W{\equiv}CC(CH_3)_3(THF)_2$ (**3**) reacts instantaneously with carbonyl-containing compounds resulting in C=O bond cleavage. The purpose of the study was to establish reactivity rates as a means to support the contention that complex **3** has enhanced nucleophilic character as a consequence of the inorganic enamine effect. A compelling conclusion is possible since complex **3** reacts up to 4 orders of magnitude faster than $(DIPP)_3W{\equiv}CC(CH_3)_3$. An important result discounts the notion that **3** could be less sterically encumbered than $(DIPP)_3W{\equiv}CC(CH_3)_3$. DMF binds to $(DIPP)_3W{\equiv}CC(CH_3)_3$ instantaneously but takes hours to complete the C=O bond cleavage. The instantaneous binding indicates steric impedance to the metal is not a problem, yet the reaction requires heating to 50 °C for hours to complete. In contrast, complex **3** binds and cleaves the C=O bond in DMF within 10 s. Other Schrock alkylidynes are slow to react; the alkylidyne $(^t$BuO$)_3W{\equiv}CC(CH_3)_3$ requires 16 h and 60 °C to react with acetone.[17] Combined with the fact that the trianionic OCO^{3-} pincer alkylidyne complex $[^t$BuOCO$]W{\equiv}CC(CH_3)_3(THF)_2$ does not react with DMF, it is clear that an electronic factor must be responsible for the increased rates observed for **3**. The diverse chemistry of metal−carbon multiple bonds is intimately related to the nucleophilicity/electrophilicity of the α-carbon. The "inorganic enamine" effect provides synthetic chemists a new design tool to tailor catalysts.

ASSOCIATED CONTENT

Supporting Information

Full experimental procedures, NMR spectra, and X-ray crystallographic details for CCDC 1048942−1048944. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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