

Electronic Supplementary Information (ESI)

**Dual nucleophilic substitution at a W(II) η^2 -coordinated
diiodo acetylene leading to an amidinium carbyne complex**

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1. Crystallographic Details

Single crystals suitable for X-ray diffraction analysis were selected in Fomblin YR-1800 perfluoropolyether oil (Alfa Aesar) at ambient temperature and mounted on a glass fiber. During the measurement the samples were cooled to 173(2) K. Diffraction data were collected on a Bruker-Nonius Apex X8 and a Bruker Kappa Apex II diffractometer using graphite monochromated Mo-K α radiation. Structure solutions were found by direct methods (SHELXS-2013)^[S1] and were refined by full-matrix least-squares procedures on F^2 (SHELXL-2013).^[S2] All non-hydrogen atoms were anisotropically refined. Hydrogen atoms were included at calculated positions with fixed thermal parameters.

Table S1. Crystallographic details for **3**-PF₆ and **4a**-PF₆.

	3 -PF ₆	4a -PF ₆
empirical formula	C ₂₅ H ₃₂ BF ₆ I ₂ N ₈ OPW	C ₃₃ H ₃₈ BF ₆ N ₈ O ₂ PW
$M_w / \text{g}\cdot\text{mol}^{-1}$	1054.01	918.34
colour, habit	green, needle	green, plate
crystal system	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$
$a / \text{\AA}$	8.3520(2)	25.7178(9)
$b / \text{\AA}$	22.5729(6)	11.6201(4)
$c / \text{\AA}$	18.2914(5)	25.7435(8)
$\alpha / ^\circ$	90	90
$\beta / ^\circ$	100.772(2)	97.686(2)
$\gamma / ^\circ$	90	90
$V / \text{\AA}^3$	3387.69(15)	7624.2(4)
Z	4	8
$\rho_{\text{calcd.}} / \text{g}\cdot\text{cm}^{-3}$	2.067	1.600
μ / mm^{-1}	5.347	3.143
$\lambda_{\text{MoK}\alpha} / \text{\AA}$	0.71073	0.71073
T / K	173	173
collected refl.	44292	50914
unique refl.	10842	14472
refl. $I > 2\sigma(I)$	8987	11088
R_{int}	0.1337	0.0708
parameters/restraints	439	994
$R_1 [I > 2\sigma(I)]$	0.0635	0.0512
wR_2 (all data)	0.1327	0.1052
Goof	1.005	1.018
resid. density [$\text{e}\text{\AA}^{-3}$]	2.264/−1.670	1.140/−1.596
CCDC	1428746	1428747

2. Experimental Section

2.1. General Information

All operations were carried out in an atmosphere of dry argon using Schlenk and glove box techniques. Solvents were dried and saturated with argon by standard methods and freshly distilled prior to use. One- and two-dimensional NMR spectra were recorded at 300 K using Bruker Avance 250, 300 or 500 MHz spectrometer, respectively. In ^1H and ^{13}C NMR, the chemical shifts were internally referenced to the solvent residual peak. IR spectroscopy was conducted on a Nicolet 380 FT-IR with a Smart Orbit ATR module. Elemental analyses were performed with a Thermo Finnigan Flash EA 1112 Series. Mass spectrometry was obtained with an Agilent 6210 Time-of-Flight LC/MS for electrospray ionization (ESI) and with a Thermo Electron Finnigan MAT 95-XP GC/MS for electron ionization (EI). UV/vis data was collected on a Perkin Elmer lambda 19 spectrometer. The starting materials $[(2,4,6\text{-trimethylpyridine})_2][\text{PF}_6]^{[S3]}$, $\text{Tp}'\text{W}(\text{CO})_3^{[S4]}$, $[\text{Cp}_2\text{Fe}][\text{PF}_6]^{[S5]}$ and $\text{Tp}'\text{W}(\text{CO})_2\equiv\text{CBr}^{[S6]}$ were synthesized according to literature procedures. Technical acetylene was purified by passing successively a KOH and a P_2O_5 column prior to use. All other reagents were used as purchased from commercial sources.

2.2. Synthetic Procedures

Caution: Diiodoacetylene decomposes heavily to carbon and iodine by friction, heating or when mixed as a solid with strong oxidizing agents. The reported decomposition points as well as the explosion power vary from 80°C to 128°C .

i. Diiodoacetylene C_2I_2 (slightly modified procedure of Brunel and Rousseau)^[S7]

A moderate acetylene gas flow was passed through a solution of $[(2,4,6\text{-trimethylpyridine})_2][\text{PF}_6]$ (5 g, 9.72 mmol) in 100 ml CH_2Cl_2 . After 45 min the solution was noticeably cloudy and slightly yellow. The volume was reduced *in vacuo* at 0°C to 10 ml. The residue was immediately purified by flash chromatography on SiO_2 . Fast elution with 1:5 $\text{CH}_2\text{Cl}_2/n$ -hexane allowed collection of a single slightly pink band. The eluate was smoothly concentrated at rt. / 10 mbar, before the remaining solvents were removed subsequently at $0^\circ\text{C} / 10^{-3}$ mbar. The colorless crystals were kept in a closed flask at a cold and dark place preventing any decomposition or sublimation of the product. Yield: 908 mg (3.26 mmol, 67 %). ^{13}C NMR (CDCl_3 , 63 MHz, 300 K): $\delta = 0.53$ ppm. MS (EI): m/z calcd for C_2I_2 : 278, found: 278 [M^+].

ii. [Tp'W(CO)₂(η²-C₂I₂)](PF₆) 1-PF₆

A concentrated solution of C₂I₂ (164 mg, 0.59 mmol) in CH₂Cl₂ was added to a CH₂Cl₂ solution (30 ml) of Tp'W(CO)₃ (300 mg, 0.53 mmol). Solid [Cp₂Fe][PF₆] (176 mg, 0.53 mmol) was added in small portions within 60 min. After 3 h of further stirring the solvents were removed *in vacuo*. The green residue was washed with 3 x 10 ml Et₂O to remove excess alkyne and Cp₂Fe. The product was used directly for reactions without further purification. Yield: 387 mg (0.41 mmol, 76 %). ¹H NMR (CDCl₃, 250 MHz, 300 K): δ = 6.21 (s, 1 H, CH(CCH₃)₂), 6.12 (s, 2 H, CH(CCH₃)₂), 2.63 (s, 3 H, CCH₃), 2.61 (s, 6 H, CCH₃), 2.42 (s, 3 H, CCH₃), 1.71 (s, 6 H, CCH₃) ppm. IR (CH₂Cl₂, cm⁻¹): ν̃ = 2568 (w, BH), 2073, 2006 (s, CO), 1543 (m, pyrazolyl). MS (ESI-TOF, CH₃CN): *m/z* calcd for C₁₉H₂₂Bl₂N₆O₂W⁺: 814.95, found: 814.95 [M⁺], 827.98 [M⁺-CO+CH₃CN].

iii. [Tp'W(CO)(κ¹-CH₃CN)(η²-C₂I₂)](PF₆) 2-PF₆

CH₃CN (10 mL) were added to freshly prepared 1-PF₆ (using 200 mg, 0.354 mmol Tp'W(CO)₃). After stirring for 3 h, volatiles were removed *in vacuo*. The green crude product was recrystallized three times from CH₂Cl₂/*n*-pentane. Yield: 92 mg (0.095 mmol, 27 %). **Elemental analysis** C₂₀H₂₅BF₆I₂N₇OPW (972.88 g mol⁻¹): C 24.77 (calcd. 24.69), H 2.64 (2.59), N 9.61 (10.08) %. ¹H NMR (CDCl₃, 250 MHz, 300 K): δ = 6.17, 6.04, 5.87 (s, 1 H, CH(CCH₃)₂), 2.94 (s, 3 H, NCCH₃), 2.61 (s, 3 H, CCH₃), 2.56 (s, 3 H, CCH₃), 2.53 (s, 3 H, CCH₃), 2.38 (s, 3 H, CCH₃), 2.18 (s, 3 H, CCH₃), 1.48 (s, 3 H, CCH₃). ¹³C NMR (CDCl₃, 63 MHz, 300 K): δ = 224.8 (WCO), 175.0, 165.9 (WCl), 154.3 (CCH₃), 154.0 (NCCH₃), 152.6, 151.1, 147.8, 147.7, 145.7 (CCH₃), 109.4, 109.4, 108.5 (CH(CCH₃)₂), 16.8, 16.0, 15.8, 12.9, 12.7, 12.6 (CCH₃), 4.45 (NCCH₃) ppm. IR (CH₂Cl₂, cm⁻¹): ν̃ = 2564 (b, BH), 2280 (w, CN), 1972 (s, CO), 1544 (m, pyrazolyl). MS (ESI-TOF, CH₃CN): *m/z* calcd for C₂₀H₂₅Bl₂N₇OW⁺: 827.98, found: 827.98 [M⁺].

iv. [Tp'W(CO){NC₅H₄N(CH₃)₂}(η²-C₂I₂)](PF₆) 3-PF₆

To a CH₂Cl₂ solution (15 ml) of freshly prepared 1-PF₆ (using 190 mg, 0.33 mmol Tp'W(CO)₃) was added solid DMAP (41 mg, 0.33 mmol). After stirring for 12 h solvents were removed *in vacuo*. The crude product was washed with 10 ml Et₂O before it was recrystallized from CH₂Cl₂/pentane. Yield: 275 mg (0.26 mmol, 78 %). **Elemental analysis** C₂₅H₃₂BF₆I₂N₈OPW·CH₂Cl₂ (1138.93 g mol⁻¹): C 27.56 (calcd. 27.42), H 2.94 (3.01), N 9.67 (9.84) %. ¹H NMR (CD₂Cl₂, 250 MHz, 300 K): δ = 7.84 (d, 1 H, NCH), 6.48 (d, 1 H, NCH), 6.45 (m, 1 H, NCHCH), 6.23 (m, 1 H, NCHCH), 6.18 (s, 1 H,

CH(CCH₃)₂), 5.93 (s, 1 H, CH(CCH₃)₂), 5.87 (s, 1 H, CH(CCH₃)₂), 3.06 (s, 6 H, N(CH₃)₂), 2.61 (s, 3 H, CCH₃), 2.50 (s, 3 H, CCH₃), 2.40 (s, 3 H, CCH₃), 1.89 (s, 3 H, CCH₃), 1.59 (s, 3 H, CCH₃), 1.51 (s, 3 H, CCH₃) ppm. ¹³C NMR (CD₂Cl₂, 63 MHz, 300 K): δ = 233.1 (WCO), 170.4, 166.7 (WCl), 155.3 (CN(CH₃)₃), 154.4 (CCH₃), 153.0 (NCH), 152.6, 152.4 (CCH₃), 150.0 (NCH), 148.2, 148.1, 146.8 (CCH₃), 110.0, 109.4 (CH(CCH₃)₂), 108.7 (NCHCH), 108.6 (CH(CCH₃)₂), 108.2 (NCHCH), 39.8 (N(CH₃)₂), 17.4, 15.7, 14.9, 13.2, 13.0, 13.0 (CCH₃) ppm. IR (CH₂Cl₂, cm⁻¹): $\tilde{\nu}$ = 2561 (w, BH), 1948 (s, CO), 1649, 1626, 1562 (m, DMAP) 1544 (m, pyrazolyl); (ATR, cm⁻¹): $\tilde{\nu}$ = 2569 (w, BH), 1936 (s, CO), 1650, 1626, 1572 (m, DMAP) 1541 (m, pyrazolyl). MS (ESI-TOF, CH₃CN): *m/z* calcd for C₂₅H₃₂Bl₂N₈OW⁺: 909.04, found: 909.04 [M⁺].

v. [Tp'W(CO)₂{κ¹-CC(NHBn)₂}] [PF₆] 4a-PF₆

Freshly prepared 1-PF₆ (using 300 mg, 0.53 mmol Tp'W(CO)₃) was solved in 30 ml CH₂Cl₂. Neat benzylamine (0.12 ml, 1.06 mmol) was added to the green solution, which turned brown after 10 min. Stirring was continued for 2 h before volatiles were removed *in vacuo*. The residue was rinsed with 20 ml toluene and the suspension was stirred for 30 min before the green precipitate was filtered off under an argon atmosphere. Extraction with some CH₂Cl₂ and subsequent removal of the solvent led to the product as a green solid. The colorless residue remaining on the filter was identified by NMR as [BnNH₃][PF₆]. Yield: 151 mg (0.164 mmol, 31 %). **Elemental analysis** C₃₃H₃₈BF₆N₈O₂PW·0.5 C₅H₁₂ (954.40 g mol⁻¹): C 44.98 (calcd. 44.68), H 4.44 (4.65), N 11.63 (11.74) %. ¹H NMR (CDCl₃, 250 MHz, 300 K): δ = 8.37 (b, 2 H, NH)¹, 7.40–6.85 (m, 10 H, Ph-H), 5.97 (s, 2 H, CH(CCH₃)₂), 5.80 (s, 1 H, CH(CCH₃)₂), 4.65 (s, 4 H, NCH₂), 2.48 (s, 6 H, CCH₃), 2.44 (s, 3 H, CCH₃), 2.34 (s, 3 H, CCH₃), 2.31 (s, 6 H, CCH₃) ppm. ¹³C NMR (CDCl₃, 63 MHz, 300 K): δ = 248.1 (WCC), 225.5 (WCO), 159.5 (WCC). 152.5, 152.0, 146.7, 145.7 (CCH₃), 135.4 (C_{ipso}), 129.3–126.9 (Ar-C), 107.5, 107.4 (CH(CCH₃)₂), 47.4 (CH₂), 16.8, 15.1, 12.6, 12.6 (CCH₃) ppm. IR (CH₂Cl₂, cm⁻¹): $\tilde{\nu}$ = 3358 (NH), 2558 (w, BH), 2020, 1936 (s, CO), 1605 (m, CN) 1543 (m, pyrazolyl); (ATR, cm⁻¹): $\tilde{\nu}$ = 3376 (NH), 2558 (w, BH), 2021, 1936 (s, CO), 1616 (m, CN) 1546 (m, pyrazolyl). MS (ESI-TOF, CH₃CN): *m/z* calcd for C₃₃H₃₈BN₈O₂W⁺: 773.27, found: 773.27 [M⁺], 745.28 [M⁺-CO], 717.28 [M⁺-2 CO].

¹ signal not always present (depends on concentration and choice of solvent)

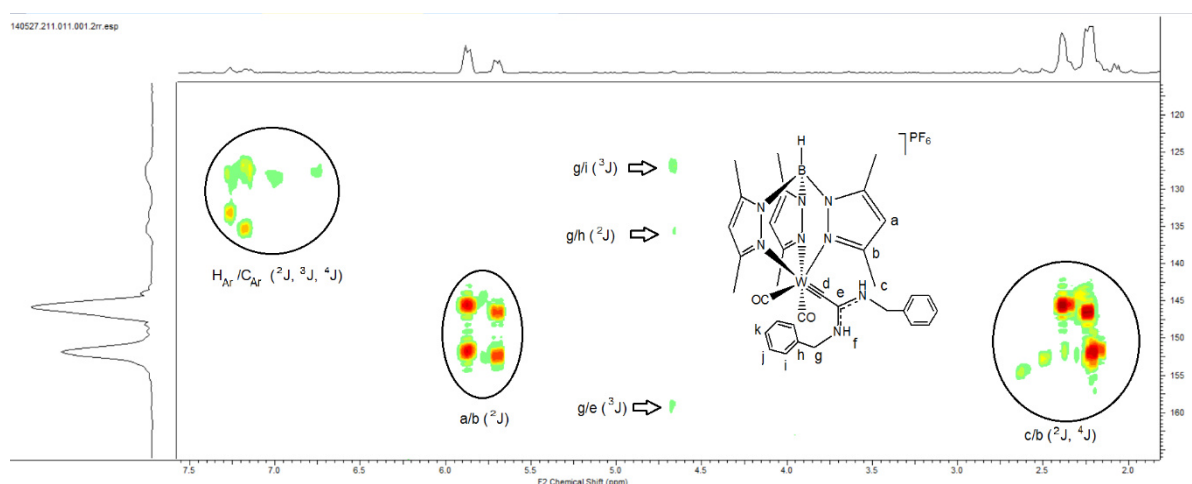


Figure S1. Selected detail of the gHMBC Spectrum of **4a**-PF₆.

2.3. Reaction of *in situ* generated [Tp'W(CO)₂≡C-Li] with carbodiimides

A solution of Tp'W(CO)₂≡CBr in thf was cooled to -80 °C and treated with 1.2 eq. *n*-butyllithium (2.5 M solution in *n*-hexane). The yellow solution turned orange and *in situ* IR spectroscopy indicated the formation of Tp'W(CO)₂≡CLi ($\nu_{\text{CO}} = 1916, 1890 \text{ cm}^{-1}$)^[S8b]. After stirring for 30 min at -80 °C, 1 eq. of carbodiimides (dicyclohexylcarbodiimide or diisopropylcarbodiimide) was added. The solution was allowed to reach room temperature in the course of 2 h. IR spectroscopy showed the formation of only one product, whereas the vibration bonds of carbodiimide remained unchanged. The product was identified as Tp'W(CO)₂≡CH and could be isolated in substance after chromatographic work up. The analytical data (IR, XRD, ¹H and ¹³C NMR) is in accordance with literature.^[S8a]

This negative result indicates that proton abstraction from the solvent or *n*-butylbromide proceeds faster than the desired insertion of carbodiimides. Related problems were frequently described, when the electrophile does not react smoothly.^[S9]

3. DFT computational results

The calculations were performed with either the G09w program package^[S10] or the ORCA program suite.^[S11] The computations were carried out as closed shell calculations for the isomeric cationic complexes $[\text{Tp}'\text{W}(\text{CO})_2(\eta^2\text{-C}_2\text{I}_2)]^+$, $[\text{Tp}'\text{W}(\text{CO})_2(\kappa^1\text{-CCl}_2)]^+$, $[\text{Tp}'\text{W}(\text{CO})_2\{\eta^2\text{-C}_2\text{I}(\text{NMe})\}]^+$, $[\text{Tp}'\text{W}(\text{CO})_2\{\kappa^1\text{-CCl}(\text{NMe})\}]^+$ (in both conformations *syn* and *anti* with respect to the pyrazole pocket) and $[\text{Tp}'\text{W}(\text{CO})_2\{\eta^2\text{-C}_2(\text{NMe})_2\}]^+$, $[\text{Tp}'\text{W}(\text{CO})_2\{\kappa^1\text{-CC}(\text{NMe})_2\}]^+$, respectively. In addition, the isomeric intermediates **11**⁺ and **12**⁺, generated by addition of MeNH₂ to $[\text{Tp}'\text{W}(\text{CO})_2(\eta^2\text{-C}_2\text{I}_2)]^+$, **1**⁺, at the W-bound alkyne carbon atom (in *syn*-position to the CO co-ligands for accessibility reasons) were included in the calculations. The molecular geometries of the complexes (**1**⁺) and model complexes (Me groups instead of Bn at N) were optimized in the gas phase without symmetry constraints by DFT. The functionals were varied from the GGA type BP86^[S12] to the hybrid type b3lyp;^[S13] and basis sets of different levels {LanI2DZ, def2-TZVP and 6-311G(d,p)} were used for comparison. In combination with the latter two W was described by a pseudo-relativistic effective core potential (ECP) of the Stuttgart/Cologne group^[S14] and a (8s7p6d2f1g)/[6s5p3d2f1g] basis set. Frequency calculations were performed to identify all stationary points as minima or transition state. The *synchronous transit-guided quasi-Newton* (STQN) method^[S15] was used to locate the transition state; and the intrinsic reaction coordinates (IRC)^[S16] were calculated for the transition state to confirm that such structure indeed connects **11**⁺ and **12**⁺. Table 3 and 4 contain a compilation of ΔH values (sum of electronic and thermal enthalpies at 298.15 K), using the most stable isomer as reference, respectively, for the identified starting materials, substitution intermediates and products. Table 5 contains the coordinates of **11**⁺, **12**⁺ and the transition state connecting them for optional reproduction. In addition, a movie file in gif-format illustrating the imaginary frequency (-122 cm^{-1}) is provided.

In addition, for the calculation of bond dissociation energies (*BDE*) with $[\text{Tp}'\text{W}(\text{CO})_2\{\kappa^1\text{-CC}(\text{NMe})_2\}]^+$, ^{Me}**4a**⁺ and $[\text{Tp}'\text{W}(\text{CO})_2\{\kappa^1\text{-CCO}\}]^+$ the hybrid correlation-exchange-parameter-free functional PBE0^[S17] and the def2-TZVP basis set with ECP for W as stated above were used. The fragments of homolytic CC bond fission were calculated as open shell $S = 1/2$ systems and the fragments of heterolytic cleavage as closed shell systems and additionally, for comparison, as open shell triplet species. The ΔH values (sum of electronic and thermal enthalpies at 298.15 K) of geometry optimized structures were used for calculation of the *BDE* values (Table S2). Finally, for the structure comparison of ^{Me}**4a**⁺ and **8a**⁺ (Figure 3) scalar relativistic effects have been incorporated by applying the zero order regular approximation (ZORA)^[S18] implemented in the ORCA program suite. This procedure further improved the congruency of the experimentally determined and the calculated structure parameters (**4a**⁺, solid state versus ^{Me}**4a**⁺, gas phase).

Table S2. Electronic and thermal enthalpies at 298.15 K of all geometry optimized fragments in a.u.

	homolytic CC cleavage doublet states		heterolytic CC cleavage singlet states (triplet states)	
$[\text{Tp}'\text{W}(\text{CO})_2\text{CC}(\text{NHMe})_2]^+$	$[\text{Tp}'\text{W}(\text{CO})_2\text{C}$	$\text{C}(\text{NHMe})_2]^+$	$[\text{Tp}'\text{W}(\text{CO})_2\text{C}^+$	$\text{C}(\text{NHMe})_2]$
-1497.02829		-228.012944		-228.27196 (-228.19196)
$[\text{Tp}'\text{W}(\text{CO})_2\text{CCO}]^+$	-1268.79804	CO^+	-1268.56656 (-1268.56437)	CO
-1381.89776		-112.70911		-113.22255 (-113.01292)

Molecular and Electronic Structure of Fragments

The geometry optimized metal containing fragments $[\text{Tp}'\text{W}(\text{CO})_2\text{C}]$ and $[\text{Tp}'\text{W}(\text{CO})_2\text{C}]^+$ differ significantly in structure. The neutral radical species shows more or less parameters, which are similar to that ones in the isolated complex **4a**⁺. In contrast, the cationic species exhibits distinctively shorter W–N bonds to the Tp' ligand reflecting the electron deficiency at the metal leading to an obtuse CO–W–CO angle and deviation of the terminal C atom from the octahedral position avoiding *trans*-position to any ligand. These structure changes are obviously essential in stabilizing the heterolytic bond cleavage.

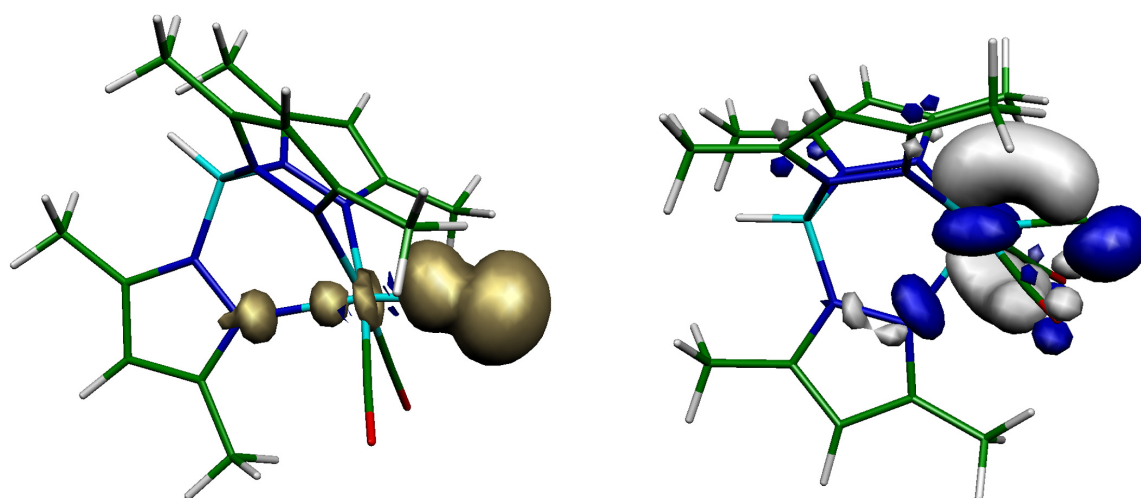
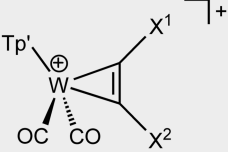
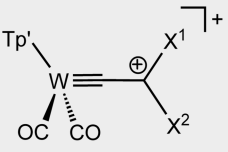
**Figure S2.** Essential structure parameters of geometry optimized fragments $[\text{Tp}'\text{W}(\text{CO})_2\text{C}]$ (left) and $[\text{Tp}'\text{W}(\text{CO})_2\text{C}]^+$ (right).**Figure S3.** Calculated spin density distribution of the $[\text{Tp}'\text{W}(\text{CO})_2\text{C}]$ fragment (cutoff 0.005, left) and LUMO of the $[\text{Tp}'\text{W}(\text{CO})_2\text{C}]^+$ fragment (cutoff 0.05, right).

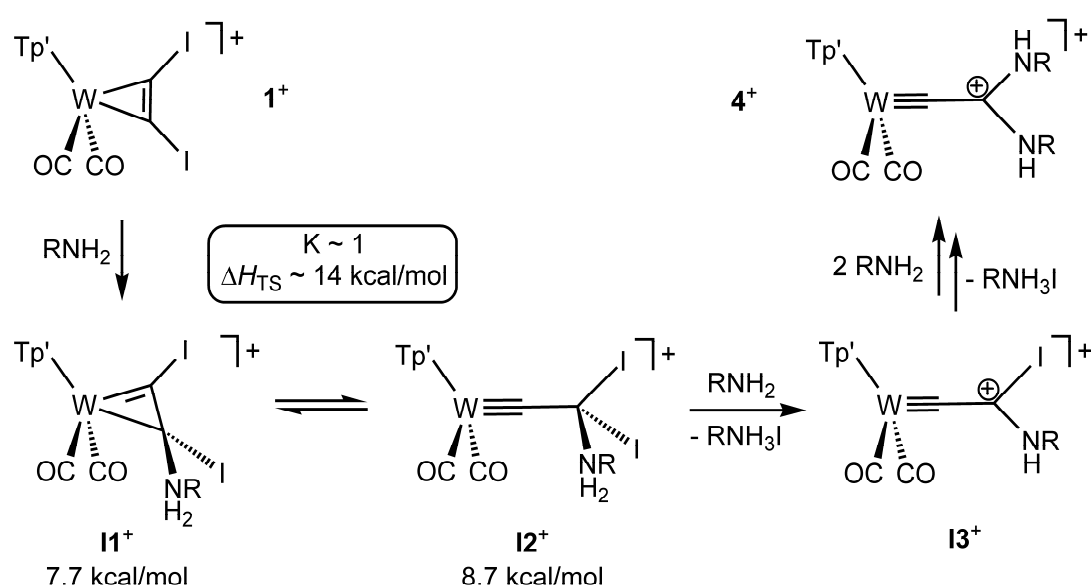
Table S3. Calculated ΔH values for different isomeric η^2 -alkyne and κ^1 -carbyne complexes with variation of substituents from -I to -NHMe.

			
b3lyp lan12dz	$X^1 = X^2 = I$	0	+6.1
	$X^1 = I, X^2 = NHMe$	+1.5	+6.2
	$X^1 = NHMe, X^2 = I$	0	+4.8
	$X^1 = X^2 = NHMe$	0	+1.4
BP86 def2-TZVP	$X^1 = X^2 = I$	0	+7.2
	$X^1 = I, X^2 = NHMe$	+0.6	+5.1
	$X^1 = NHMe, X^2 = I$	0	+5.4
	$X^1 = X^2 = NHMe$	0	+3.2
b3lyp 6-311g(d,p)	$X^1 = X^2 = I$	0	+13.5
	$X^1 = I, X^2 = NHMe$	+1.2	+10.8
	$X^1 = NHMe, X^2 = I$	0	9.8
	$X^1 = X^2 = NHMe$	0	+4.5
b3lyp def2-TZVP	$X^1 = X^2 = H$	0	+18.6
	$X^1 = X^2 = NHMe$	0	+9.0
PBE0 def2-TZVP	$X^1 = X^2 = H$	0	+12.0
	$X^1 = X^2 = NHMe$	0	+3.8

Discussion of Mechanism related Calculations

Addition of neutral methylamine to the W bound C-atom (in proximity to the CO ligands for accessibility reasons) led to realistic minima showing one tetragonal C atom with distinctively longer W–C bonds compared with the respective coordinated alkynes. In parallel studies, minima were identified for both *side-on* and *end-on* isomers (**11**⁺ and **12**⁺, Scheme S1). Remarkably, the differences ΔH for the substitution intermediates between the η^2 -isomer **11**⁺ and the corresponding κ^1 -isomer **12**⁺ with tetragonal C atom in terminal position are non-significant and either slightly negative or positive (–4.2 – +1.0 kcal/mol, depending on the basis set) delivering at least a rationale for the observed rearrangement. Finally, a transition state for the rearrangement step **11**⁺ to **12**⁺ with an activation enthalpy of 13.7 kcal/mol (b3lyp, lan12dz) could be identified. Reasonably, the essential vibration with negative frequency value is dominated by the tumbling movement of the C2 moiety with the heavy iodine atoms as “spectator substituents”. In summary, addition of amine to the complex cation **1**⁺ leads to intermediate **11**⁺ which is moderately higher in enthalpy related to the starting materials. According to the comparable enthalpies **11**⁺ and **12**⁺ are suggested to be at equilibrium in the

subsequent step. Intrinsic elimination of HI from $\mathbf{I2}^+$ is excluded due to the meta-stability of HI. In turn, primary dissociation of iodide is rather unlikely due to the unrealistic increase of complex charge. Finally, deprotonation of $\mathbf{I2}^+$ by further amine (and subsequent or concerted dissociation of iodide) should be favoured in isomer $\mathbf{I2}^+$ because the complex bound ammonium group is much better accessible for additional amine base in the terminal position. This effect seems a reasonable kinetic explanation for the preferred formation of the amidinium carbyne complex $\mathbf{4a-PF}_6$. The assumption of an essential sterical crowd in the *side-on* isomer $\mathbf{I1}^+$ is corroborated by the substitution inertness of the DMAP adduct $\mathbf{3-PF}_6$ under the same reaction conditions used with $\mathbf{1-PF}_6$.



Scheme S1. Reaction mechanism for the formation of the amidinium carbyne complex $\mathbf{4a-PF}_6$ as inferred from DFT calculation results for $\text{Me}^{\text{e}}\mathbf{4a-PF}_6$ ($\text{R} = \text{Me}$).

Table S4. Calculated ΔH values for the substitution intermediates and the transition state.

	$\mathbf{I1}^+$	transition state	$\mathbf{I2}^+$
b3lyp LanI2dz	0	+13.7	-4.2
BP86 def2-TZVP	0	-	+0.5
b3lyp 6-311g(d,p)	0	-	+1.2

Table S5. Cartesian coordinates of the geometry optimized (b3lyp, Lanl2dz) complexes **I1⁺**, **I2⁺** and the respective transition state.

	I1⁺			I2⁺			transition state		
C	-0.558902	-1.960564	1.205306	0.097197	-2.172132	-0.953761	-0.744129	1.846790	-1.351037
C	-0.436723	-1.891234	-1.640558	-0.327521	-1.824251	1.824910	-0.918071	1.957698	1.270108
C	-2.141110	-0.260012	-0.580366	2.663070	0.096090	0.469384	-2.545651	-0.424612	0.328810
C	-1.307899	0.788436	-0.148269	1.264830	-0.183346	0.367817	-1.343825	-0.781994	-0.253149
N	1.991659	-1.759279	-0.051756	-2.621479	-1.495127	0.050545	1.848837	1.879025	0.035802
N	1.349304	0.631673	-1.513276	-1.527751	0.936547	1.366558	1.160632	-0.435505	1.614924
N	1.028477	0.470367	1.506685	-1.182843	0.515373	-1.524915	1.235477	-0.399515	-1.466221
C	2.306539	-3.100709	-0.122707	-3.168918	-2.751576	0.127918	2.086582	3.242937	-0.006771
N	3.197932	-1.071844	0.153746	-3.680664	-0.604041	-0.190033	3.107649	1.250870	0.102472
C	1.169849	1.186057	-2.752989	-1.213710	1.578616	2.533465	0.858201	-0.885543	2.873038
N	2.623773	1.024609	-1.086394	-2.755309	1.451914	0.941118	2.482573	-0.825042	1.364109
C	0.559438	0.854464	2.736014	-0.590314	0.807503	-2.725210	0.969510	-0.800906	-2.750324
N	2.351543	0.915753	1.420235	-2.441146	1.131394	-1.530159	2.537451	-0.820690	-1.171498
C	3.695649	-3.250788	0.046890	-4.562937	-2.658067	-0.060679	3.471619	3.461472	0.049786
B	3.215627	0.477112	0.231445	-3.413564	0.913915	-0.351172	3.212412	-0.304125	0.108852
C	4.232217	-1.963244	0.215605	-4.858134	-1.299169	-0.258550	4.089727	2.196319	0.113172
C	2.310793	1.934314	-3.104084	-2.234195	2.500041	2.847044	1.967843	-1.572234	3.407831
C	3.213668	1.813199	-2.037423	-3.196027	2.396361	1.829217	2.979753	-1.514450	2.437683
C	1.577565	1.560199	3.414804	-1.462142	1.618505	-3.482050	2.089516	-1.496733	-3.254249
C	2.694951	1.578669	2.569702	-2.620562	1.801608	-2.711098	3.065064	-1.486238	-2.245912
H	4.243799	-4.180045	0.045987	-5.268205	-3.474539	-0.055723	3.970205	4.418223	0.044096
H	2.464346	2.487054	-4.017935	-2.273438	3.155114	3.703545	2.033338	-2.038605	4.378794
H	1.508171	1.994159	4.400223	-1.275561	2.016182	-4.467520	2.180166	-1.943247	-4.232311
H	4.331578	0.864412	0.364916	-4.437131	1.485300	-0.552255	4.355945	-0.630143	0.136437
C	-0.054554	1.013588	-3.602609	0.043130	1.336777	3.317786	-0.460701	-0.670301	3.552824
H	-0.302928	-0.047508	-3.743203	0.203743	0.270357	3.512531	-0.949489	0.244927	3.208528
H	-0.910644	1.564736	-3.185352	0.911600	1.748181	2.779530	-1.133305	-1.525189	3.388116
H	0.129347	1.428733	-4.597733	-0.020182	1.851345	4.281214	-0.312118	-0.589384	4.634568
C	-0.795464	0.518483	3.290488	0.765595	0.316731	-3.137967	-0.297380	-0.505799	-3.501943
H	-1.579318	0.513326	2.530481	1.536543	0.588856	-2.410273	-1.192025	-0.668012	-2.895302
H	-0.788207	-0.468103	3.772531	0.786098	-0.773083	-3.256010	-0.316354	0.532977	-3.854422
H	-1.070266	1.250990	4.055855	1.037650	0.760207	-4.100362	-0.357059	-1.153638	-4.381744
C	1.335405	-4.221241	-0.373428	-2.388046	-4.011464	0.377896	1.028853	4.305590	-0.092117
H	0.453586	-4.186184	0.272008	-1.610057	-4.176345	-0.374831	0.436617	4.229314	-1.009771
H	0.992345	-4.237116	-1.414614	-1.911832	-4.015056	1.364812	0.339849	4.280836	0.758709
H	1.839457	-5.173857	-0.185380	-3.067693	-4.867871	0.339908	1.512393	5.286851	-0.093892
W	0.077267	-0.627204	-0.185501	-0.523338	-0.653783	0.212033	0.050677	0.690684	0.051791
C	-3.861355	0.763394	-2.283422	3.214731	-1.438255	2.554885	-3.933033	-0.912586	2.494532
H	-4.151705	0.687863	-3.335699	3.564253	-1.350486	3.587650	-4.311313	-1.761353	3.071346
H	-4.710410	0.533849	-1.640264	2.200494	-1.829545	2.532517	-3.180143	-0.368481	3.061261
H	-3.486637	1.762556	-2.059187	3.881860	-2.083041	1.983190	-4.751835	-0.243036	2.230572
O	-0.827644	-2.618949	-2.499053	-0.177557	-2.508302	2.784901	-1.516715	2.756032	1.917461
O	-0.843823	-2.749496	2.027290	0.493739	-3.056986	-1.628568	-1.201679	2.570383	-2.172124
C	5.664659	-1.568502	0.428545	-6.193584	-0.659463	-0.507597	5.555441	1.882134	0.182721
C	4.047589	2.185018	2.809811	-3.863879	2.571008	-3.052739	4.450801	-2.063591	-2.270327
C	4.587751	2.403446	-1.903425	-4.489918	3.143689	1.680581	4.373508	-2.068890	2.502955
H	4.679184	3.021794	-1.003107	-4.523156	3.718182	0.747269	4.579218	-2.748622	1.667877
H	5.361339	1.627868	-1.853078	-5.352819	2.467106	1.683670	5.129753	-1.275088	2.476994
H	4.800824	3.034835	-2.770696	-4.607539	3.843677	2.512725	4.503847	-2.626951	3.434509
H	5.799129	-1.021860	1.369228	-6.224223	-0.147541	-1.476848	5.882983	1.286665	-0.677640
H	6.290591	-2.464415	0.464968	-6.973431	-1.426199	-0.505963	6.130897	2.811859	0.190291
H	6.034942	-0.929500	-0.382026	-6.442050	0.078181	0.264667	5.806614	1.319341	1.089474
H	4.055985	2.689588	3.780070	-3.744800	3.044601	-4.031347	4.603344	-2.614251	-3.202869
H	4.839465	1.426216	2.818238	-4.745901	1.920787	-3.097933	5.218659	-1.282219	-2.212008
H	4.304580	2.924266	2.041787	-4.069590	3.358225	-2.317771	4.617862	-2.755124	-1.436144
N	-2.749196	-0.244000	-2.019250	3.226221	-0.043601	1.937883	-3.294169	-1.446848	1.219245
H	-1.968340	-0.037016	-2.657099	4.187307	0.329170	1.940877	-4.022170	-1.897258	0.640675
I	-1.570504	2.825582	0.219873	3.060065	2.298542	0.015077	-0.913549	-2.970660	-0.479391
I	-3.835007	-1.070212	0.678666	4.005568	-1.147585	-0.843134	-3.996891	0.989906	-0.407691
H	-3.087091	-1.194979	-2.226742	2.633669	0.577774	2.509997	-2.598486	-2.182174	1.442088

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