Intramolecular Carbyne–Isocyanide Coupling to an Alkyne Ligand at a d^4 Tungsten Center

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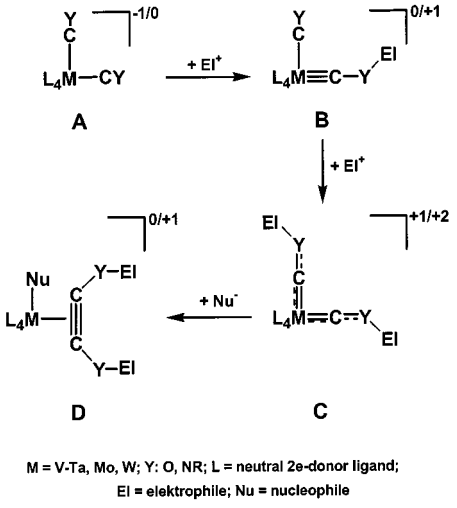
Oxidative decarbonylation of $Cp^*(CO)_2W{\equiv}CNEt_2$ (**1**) with $PhICl_2$ affords the aminocarbyne complex *cis*-$Cp^*(Cl)_2(CO)W{\equiv}CNEt_2$ (**2**), which reacts with *t*BuNC to give the CO substitution product *cis*-$Cp^*(Cl)_2(t\text{BuNC})W{\equiv}CNEt_2$ (**3**) ($Cp^* = C_5Me_5$). Complex **3** undergoes a carbyne–isocyanide coupling reaction with HCl to yield the alkyne complex $Cp^*(Cl)_3W[\eta^2\text{-}t\text{Bu(H)NC}{\equiv}CNEt_2]$ (**4**). In comparison, the reaction of *cis*-$Cp^*(Cl)_2[P(OMe)_3]W{\equiv}CNEt_2$ (**5**) with HCl affords the 16e carbene complex $Cp^*(Cl)_3W{=}C(H)NEt_2$ (**6**) after elimination of $P(OMe)_3$. Complex **5** was obtained from the CO ligand-exchange reaction of **2** with $P(OMe)_3$. Treatment of **6** with *t*BuNC yields the cationic 18e carbene complex $[Cp^*(Cl)_2(t\text{BuNC})_2W{=}C(H)NEt_2]Cl$ (**7**). The mechanism of the C–C coupling reaction of **3** to give **4** is discussed and the crystal structures of **4** and **6** are described.

Introduction

The transition-metal-mediated conversion of carbon monoxide and related C_1 building blocks to organic compounds is a major goal in organometallic chemistry.[1] In this context a class of metal-centered C−C bond-forming reactions involving the coupling of two carbonyl or isocyanide ligands to an alkyne unit has attracted the attention of several research groups (Scheme 1).[2]



Scheme 1. Mechanism of the carbonyl/isocyanide coupling reactions of Group V and VI transition metal complexes; first ionic charge: M = V−Ta, second ionic charge: M = Mo, W

In the first two steps of these reactions successive addition of an electrophile occurs to the O/N atom of the carbonyl/isocyanide ligand leading initially to the carbyne complex **B** and then to the bis-carbyne complex **C**.[3] In the last step a carbyne−carbyne coupling reaction of **C** affords the alkyne complex **D** (Scheme 1).[3g,3k−3m,3o−3q] The carbonyl or isocyanide ligands in **A** and **B** are activated for an electrophilic addition at the heteroatom. This activation occurs upon coordination of these ligands to an octahedral, "electron-rich" d^6 metal center, which is known to form strong metal−carbon triple bonds.[3,4] It was therefore interesting to elucidate whether such ligand-coupling reactions could also occur at transition-metal centers with a different d electron configuration. This has prompted us to carry out the following work reporting on the intramolecular coupling of a carbyne with an isocyanide ligand at a d^4 tungsten center.

Results and Discussion

Starting material for the reactions described below was the W^{II} aminocarbyne complex **2**,[4] which was prepared upon oxidative decarbonylation of **1**[5] with one equivalent of $PhICl_2$ in dichloromethane and isolated as a violet solid in 88% yield (Scheme 2). Complex **2** is readily soluble in CH_2Cl_2 and THF, poorly soluble in Et_2O, insoluble in pentane and decomposes upon heating at 176°C.

Treatment of **2** with *t*BuNC in refluxing toluene yielded the CO substitution product **3**. Complex **3** was isolated in 76% yield as a rose-colored, thermally stable solid, which melts at 105°C (Scheme 2). **3** undergoes a selective and fast carbyne−isocyanide coupling reaction with HCl in diethyl ether to afford the violet W^{IV} alkyne complex **4** in 92% yield (Scheme 2). Complex **4** is thermally stable in the solid state and decomposes upon heating at 157°C.

Complexes **2**−**4** were fully characterized (see Experimental Section). The IR spectra of **2** and **3** in CH_2Cl_2 show an intense absorption for the $\nu(C_{carbyne}{\equiv}N)$ stretching vibration at $\tilde{\nu}$ = 1600 and 1571 cm^{-1}, which indicates the strong π conjugation of the amino group with the tungsten−carbon triple bond.[5] The ^1H- and $^{13}C\{^1H\}$-NMR

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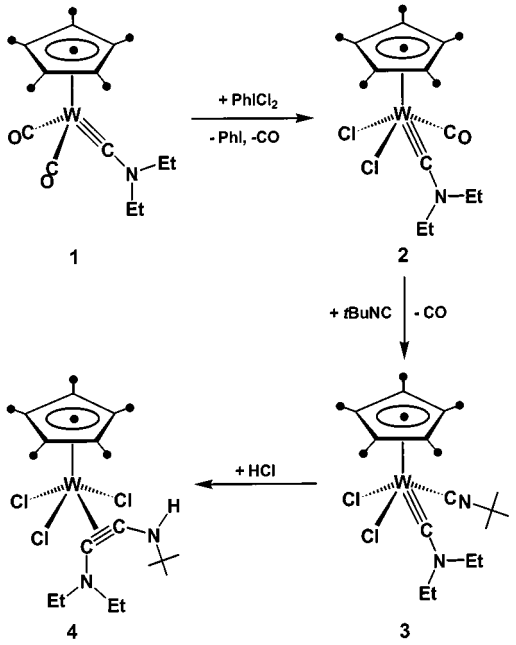


Scheme 2. Syntheses of the complexes **2**, **3** and **4**

spectra of **2** and **3** at 293 K display one set of resonances for the methyl and methylene protons of the aminocarbyne ligand indicating a fast rotation of the diethylamino group around the $C_{carbyne}-N$ bond. The methylene protons of each ethyl group are diastereotopic because of the C_1 symmetry of **2** and **3**. However, they are isochronous by accident and give rise to one quadruplet resonance in the ^{1}H-NMR spectra of **2** and **3** at 293 K. Variable-temperature ^{1}H-NMR spectra (300 MHz) of **2** in CD_2Cl_2 show this complex to be fluxional due to hindered rotation of the amino group about the $C_{carbyne}-N$ bond. The free energy of activation, $\Delta G^{\neq}(T_c)$, for the site exchange of the ethyl groups was calculated at the coalescence temperature T_c of the methyl proton resonances (T_c = 191 K, 300 MHz) to be 39.8 kJ mol^{-1}. The activation barrier is smaller than that of *cis*-Cp(Cl)$_2$(CO)W≡CN*i*Pr$_2$ [$\Delta G^{\neq}$ = 50.5 kJ mol^{-1}] and *cis*-Cp*(Cl)$_2$(CO)W≡CN*i*Pr$_2$ [$\Delta G^{\neq}$ = 47.4 kJ mol^{-1}], but similar to that of *cis*-Cp*(Br)$_2$(CO)W≡CNEt$_2$ [$\Delta G^{\neq}$ = 39.6 kJ mol^{-1}].[5c,6] Further support for the structures of **2** and **3** was given by the ^{13}C{^{1}H}-NMR spectra, which display a carbyne−carbon resonance at low field (**2**: δ = 310.0; **3**: δ = 306.4). This resonance is accompanied by tungsten satellites due to coupling with the ^{183}W nucleus. The ^1J(W,C) coupling constant of 210.0 (**2**) and 223.3 Hz (**3**) is typical of 18e W^{II} aminocarbyne complexes.[4,5c] In comparison, two low-field resonances are observed in the ^{13}C{^{1}H}-NMR spectrum of **4** (δ = 218.5, 219.3) indicating the presence of a 4e-donor alkyne ligand.[3c,3g,3k,7] Furthermore, an intense absorption band is observed in the IR spectrum of **4** in CH_2Cl_2 at 1667 cm^{-1}, which can be assigned to the ν(N=C=C=N) stretching vibration of the diaminoacetylene ligand and suggests an extensive delocalization of the amino-nitrogen lone-pair electrons in the alkyne ligand.[3c,3g,3k] Further evidence for this was given by the NMR spectra of **4** revealing a "frozen" rotation of the diethylamino group about the $C_{alkyne}-N$ bond (see Experimental Section) and the single-crystal X-ray diffraction study of **4**, which shows rather short $C_{alkyne}-N$ bonds [1.301(5) and 1.347(5) Å] and $W-C_{alkyne}$ bonds [2.008(4) and 2.043(4) Å], a long $(C-C)_{alkyne}$ bond of 1.366(6) Å and planar amino groups (Figure 1).[3g,3k,7] Planarity of the amino groups is indicated by the sum of bond angles at the atoms N1 and N2 of 359.3 and 354.6°, respectively. Other features of the molecular structure of **4** are the near orthogonality of the alkyne-ligand plane defined by the atoms W,C6,C7 and the Cp* ring plane (dihedral angle = 80.9°), as well as the *trans* position of the *t*Bu substituent.[8]

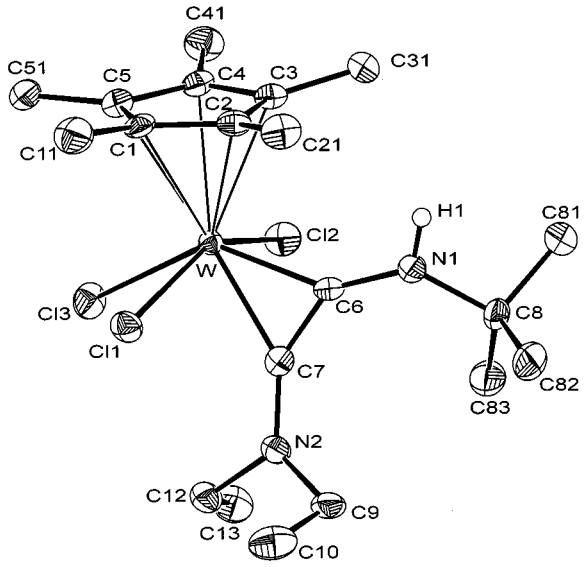
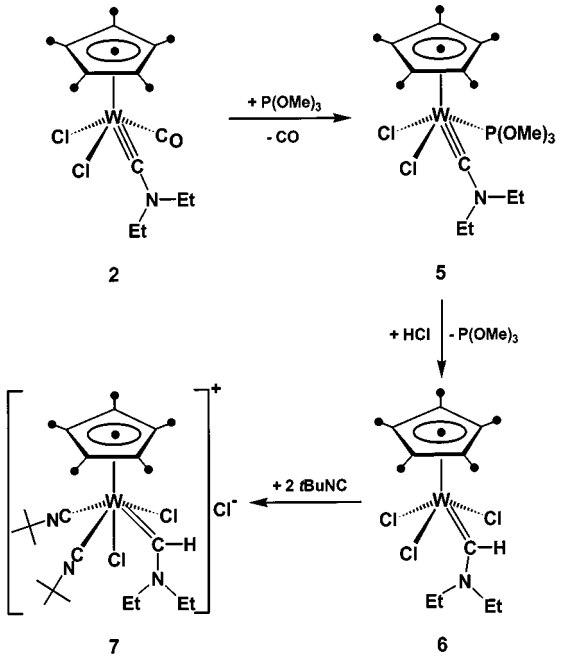


Figure 1. ZORTEP plot of the molecular structure of **4** with the thermal ellipsoids drawn at the 50% probability level; hydrogen atoms are omitted for clarity reasons except that bonded to the nitrogen atom N1; selected bond lengths [Å] and angles [°]: W−C6 2.008(4), W−C7 2.043(4), W−Cl1 2.4457(13), W−Cl2 2.4817(12), W−Cl3 2.4477(12), C6−C7 1.366(6), C6−N1 1.347(5), C7−N2 1.301(5), W−C_g 2.089, (C_g denotes the center of gravity of the Cp* ring), Cl1−W−Cl2 149.04(4), Cl1−W−Cl3 80.92(4), Cl2−W−Cl3 79.21(4), N1−C6−C7 140.5(4), N2−C7−C6 142.4(4), C6−W−C7 39.4(2), W−C6−N1 147.4(3), W−C7−N2 146.8(3), C6−N1−C8 129.4(4), C7−N2−C9 123.5(4), C7−N2−C12 119.5(4), C9−N2−C12 116.3(4)

We were interested to elucidate the mechanism of the acid-promoted carbyne−isocyanide coupling reaction of **3** (Scheme 2) and therefore prepared the aminocarbyne complex **5** from **2** and P(OMe)$_3$ by thermal CO ligand exchange in THF (Scheme 3).

Complex **5** was isolated after purification by column chromatography on silanized silica as an orange solid in 77% yield. It is readily soluble in CH_2Cl_2 and THF, sparingly soluble in Et_2O and decomposes upon heating at 98°C. Treatment of **5** with one equivalent of HCl afforded, after elimination of P(OMe)$_3$, the 16e tungsten(IV) aminocarbene complex **6** as a red, water-sensitive solid in 64% yield (Scheme 3).[4] Complex **6** is very soluble in CH_2Cl_2, sparingly soluble in Et_2O and decomposes upon heating at 135°C.



Scheme 3. Syntheses of the complexes **5**, **6** and **7**

The reaction of complex **6** with *t*BuNC was studied. Addition of the isocyanide to the Lewis acidic tungsten center of **6** would be expected to give the 18e carbene complex $Cp^*(Cl)_3(tBuNC)W{=}C(H)NEt_2$, which would rearrange to afford the alkyne complex **4**, if addition of HCl to the tungsten–carbon triple bond of **3** is the first step of the carbyne–isocyanide coupling reaction of **3** to give **4** (Scheme 2). However, treatment of **6** with *t*BuNC in CH_2Cl_2 afforded the cationic 18e tungsten(IV) aminocarbene complex **7** selectively,[4] which was isolated as a yellow solid in 82% yield (Scheme 3). The outcome of this reaction was independent of the molar ratio of the reactants, half of the starting material **6** being converted into **7**, when only one equivalent of *t*BuNC was used. These results suggest that carbene complex intermediates are not formed during the reaction of **3** with HCl.[3f,3p,9] Instead of this, they indicate a reaction pathway involving protonation of **3** at the isocyanide nitrogen atom followed by spontaneous carbyne–carbyne ligand coupling to afford the alkyne complex **4**. This suggestion is supported by earlier work showing that the 2e-oxidation of W^{II} bis(aminocarbyne) complexes is accompanied by C–C coupling of the carbyne ligands.[3g]

Complexes **5**–**7** were also fully characterized (Experimental Section). The IR spectrum of the aminocarbyne complex **5** in CH_2Cl_2 displays an intense absorption for the $\nu(C_{carbyne}{\equiv}N)$ stretching vibration at 1547 cm^{-1}. This absorption appears at lower wavenumbers than that of **2** and **3** indicating stronger metal–carbyne back bonding.[5] The ^{1}H-NMR spectrum of **5** at 293 K shows one triplet resonance for the methyl protons and two doublets of quadruplets for the diastereotopic methylene protons of the aminocarbyne ligand due to fast rotation of the diethylamino group about the $C_{carbyne}$–N bond and the presence of only the C_1-symmetric *cis* stereoisomer in solution.[5c] The

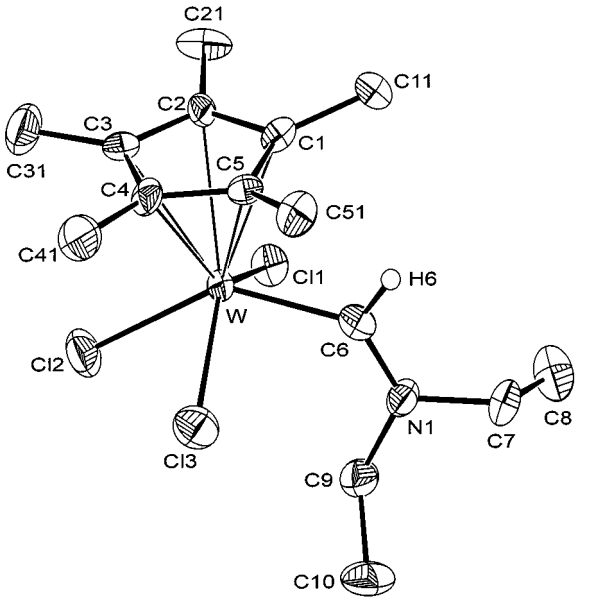


Figure 2. ZORTEP plot of the molecular structure of **6** with the thermal ellipsoids drawn at the 50% probability level; hydrogen atoms are omitted for clarity reasons except that bonded to the carbon atom C6; selected bond lengths [Å] and angles [°]: W–C6 2.065(7), W–Cl1 2.413(2), W–Cl2 2.418(2), W–Cl3 2.382(2), W–C_g 1.979 (C_g denotes the center of gravity of the Cp* ring), C6–N1 1.300(9), Cl1–W–Cl2 81.93(7), Cl1–W–Cl3 133.49(7), Cl2–W–Cl3 81.08(8), Cl1–W–C6 81.8(2), Cl2–W–C6 138.5(3), Cl3–W–C6 83.0(2), W–C6–N1 129.2(6), C6–N1–C7 120.6(7), C6–N1–C9 123.2(6), C7–N1–C9 116.1(6)

$^{13}C\{^1H\}$ spectrum of **5** diplays a doublet resonance for the carbyne–carbon nucleus at $\delta = 306.5$ [^2J(P,C) = 37.8 Hz]. The aminocarbene complexes **6** and **7** are distinguished by an IR absorption band of medium intensity at 1508 and 1579 cm^{-1}, which is assigned to the $\nu(C_{carbene}{\equiv}N)$ stretching vibration. The position of this band indicates the strong π interaction of the amino group with the metal–carbon double bond. This is supported by the temperature-dependent ^{1}H-NMR spectra of **6** (400 MHz) in the range of 233–293 K revealing a hindered rotation of the diethylamino group about the $C_{carbene}$–N bond. The free energy of activation for the site exchange of the inequivalent ethyl groups was found to be 57.3 kJ mol^{-1}. Furthermore, the ^{1}H-NMR spectrum of **7** (400 MHz) in CD_2Cl_2 at 293 K displays two sets of resonances for the methyl and methylene groups indicating that rotation of the diethylamino group around the $C_{carbene}$–N bond is slow on the NMR time scale. The ^{1}H-NMR spectra of **6** and **7** show a singlet resonance at low field (**6**: $\delta = 10.56$; $\delta = 9.95$) for the proton bound to the carbene carbon atom. Accordingly, the carbene carbon resonances of **6** and **7** at $\delta = 248.7$ and 230.9 are split into doublets in the proton-coupled ^{13}C-NMR spectra. The ^1J(C,H) coupling constant of the 16e complex **6** is, at 140.1 Hz, of similar magnitude to that of the 18e complex **7** (144.2 Hz) and excludes any agostic interaction of the C–H bond with the metal center in **6**.[9,10] This is verified by the solid-state structure of **6** showing a W–$C_{carbene}$–N bond angle [W–C6–N1 = 129.2(6)°] in the range found for nondistorted carbene ligands (Figure

2).[10,11] The W−$C_{Carbene}$ bond of 2.065(7) Å is shorter than that of structurally related W^{II} aminocarbene complexes {e.g. [*cis*-Cp*$(CO)_2$(Cl)W=C(H)NEt_2]: W−C = 2.141(3) Å} due to the smaller covalent radius of tungsten(IV). The short $C_{carbene}$−N bond of 1.300(9) Å reflects the double-bond character of this bond in full agreement with the spectroscopic data of **6**. The plane of the aminocarbene ligand passing through the atoms W, C6, and N1 is almost perpendicular to the Cp* ring plane (dihedral angle between the best planes = 88.5°).

Conclusion

The carbyne−isocyanide coupling reaction of *cis*-Cp*$(Cl)_2$(*t*BuNC)W≡$CNEt_2$ (**3**) with HCl to give the alkyne complex Cp*$(Cl)_3$W[η^2-*t*Bu(H)NC≡$CNEt_2$] (**4**) shows that electrophilic activation of C_1 ligands related to carbon monoxide, is also possible at a metal center in high oxidation state and induces C−C bond formation. In comparison, the aminocarbyne complex *cis*-Cp*$(Cl)_2$[$P(OMe)_3$]W≡$CNEt_2$ (**5**) adds HCl to the metal−carbon triple bond to afford the 16e aminocarbene complex Cp*$(Cl)_3$W=C(H)NEt_2 (**6**) after elimination of $P(OMe)_3$. The reaction of **6** with *t*BuNC to give the 18e carbene complex [Cp*$(Cl)_2$(*t*BuNC)W=C(H)NEt_2]Cl (**7**) suggests that electrophilic activation of **3** occurs upon protonation of the isocyanide ligand at the nitrogen atom.

Experimental Section

General: Standard inert-atmosphere techniques were used for all syntheses and sample manipulations. The solvents were dried by standard methods (pentane with CaH_2, diethyl ether, THF and toluene with Na/benzophenone, CH_2Cl_2 with P_2O_5 and Na/Pb alloy) and distilled under argon prior to use. Column chromatography was carried out on a silanized silica support (Merck 7719; 0063−0.200 mm) as the stationary phase in a thermostated column of 15-cm length and 2-cm diameter. The silanized silica was dried in vacuo at 150°C prior to use. Complex **1**,[5b] $PhICl_2$,[12] and *t*BuNC[13] were prepared according to literature procedures. $P(OMe)_3$ was distilled under argon prior to use. All other chemicals were commercially available. − Elemental analyses were obtained from the Central Analytical Group of the Department of Chemistry of the Humboldt-Universität zu Berlin and the Microanalytical Laboratory of the Institute of Inorganic Chemistry of the Technische Universität München. − Solution IR spectra were recorded on a Bruker IFS-55 spectrometer using a NaCl cell. ^{1}H-, $^{13}C\{^1H\}$-, and $^{31}P\{^1H\}$-NMR spectra were recorded on a Bruker AM-300 or a Jeol GX-400 spectrometer in dry, deoxygenated [D_2]dichloromethane. The ^{1}H- and $^{13}C\{^1H\}$-NMR spectra were calibrated against the internal residual proton and natural-abundance ^{13}C resonances of the deuterated solvent ([D_2]dichloromethane, δ_H = 5.32 and δ_C = 53.8) and the $^{31}P\{^1H\}$-NMR spectra against an external 85% H_3PO_4 aqueous solution. − Mass spectra were obtained with a Hewlett−Packard 5995A or a Varian MAT 311 A spectrometer; *m*/*z* values are given relative to the ^{184}W and ^{35}Cl isotopes. − Melting points were determined using a Büchi 530 melting point apparatus and are not corrected. The samples were sealed under argon in capillary tubes and heated with a rate of 1 K min^{-1}. − IR spectra of the heated samples were recorded and compared with those of authentic samples to determine whether the compounds had decomposed.

***cis*-Cp*$(Cl)_2(CO)$W≡$CNEt_2$ (2):** A solution of **1** (0.46 g, 1.00 mmol) in 20 mL of CH_2Cl_2 was cooled to −78°C and treated with a solution of freshly prepared $PhICl_2$ (0.275 g, 1.00 mmol) in 10 mL of CH_2Cl_2. The reaction mixture was allowed to warm to room temperature and stirred for 2 h. Evolution of gas was observed and the color of the solution changed from intense yellow to violet. The complete conversion of **1** to **2** was confirmed by IR spectroscopy in the region of 2200−1500 cm^{-1}. The purple solution was concentrated in vacuo to a few milliliters and a diethyl ether/pentane mixture (1:1) was added to precipitate complex **2**. The supernatant solution was discarded and the residue was washed twice with 10 mL of a diethyl ether/pentane mixture (1:1) and dried in vacuo. Yield 0.44 g (88%), violet, microcrystalline solid, m.p. 176°C (decomp.). − IR (CH_2Cl_2): $\tilde{\nu}$ = 1986 cm^{-1}, vs [ν(CO)], 1600 s [$\nu(C_{carbyne}\cdots N)$]. − ^{1}H NMR (400 MHz, CD_2Cl_2, 293 K): δ = 1.32 [t, ^3J(H,H) = 7.3 Hz, 6 H, $N(CH_2CH_3)_2$], 2.05 (s, 15 H, C_5Me_5), 3.50 [q, ^3J(H,H) = 7.3 Hz, 4 H, $N(CH_2CH_3)_2$]. − $^{13}C\{^1H\}$ NMR: (100.6 MHz, CD_2Cl_2, 293 K): δ = 11.8 (C_5Me_5), 14.9 [$N(CH_2CH_3)_2$], 50.6 [$N(CH_2CH_3)_2$], 109.3 (C_5Me_5), 228.2 [CO, ^1J(W,C) = 135.6 Hz], 310.0 [W≡C, ^1J(W,C) = 210.0 Hz]. − EI-MS (70 eV): *m*/*z* = 473 [M^+ − CO], 444 [M^+ − CO − Et], 389 [M^+ − CO − Et − EtNC]. − $C_{16}H_{25}Cl_2NOW$ (502.14): calcd. C 38.27, H 5.02, Cl 14.12, N 2.79, O 3.19, W 36.61; found C 38.17, H 4.85, Cl 14.52, N 3.05, O 3.75, W 36.99%.

***cis*-Cp*$(Cl)_2$(*t*BuNC)W≡$CNEt_2$ (3):** A suspension of **2** (1.02 g, 2.03 mmol) in 50 mL of toluene was treated at ambient temperature with *t*BuNC (0.253 mL, 2.23 mmol) and then refluxed for 2 h. The color of the solution changed from violet to bright-red. An IR spectrum of the solution was recorded to confirm the complete conversion of **2** to **3**. The solution was then evaporated to dryness, the residue dissolved in a minimum amount of CH_2Cl_2 and the solution treated at −78°C with 10 mL of diethyl ether and 20 mL of pentane to precipitate complex **3**. This procedure was repeated once to afford **3** as a rose-colored, microcrystalline solid. − Yield 0.86 g (76%), m.p. 105°C. − IR (CH_2Cl_2): $\tilde{\nu}$ = 2135 cm^{-1}, vs [ν(*t*BuN≡C)], 1571 s [$\nu(C_{carbyne}\cdots N)$]. IR (toluene): $\tilde{\nu}$ = 2129 cm^{-1}, vs [ν(*t*BuN≡C)], 1577 s [$\nu(C_{carbyne}\cdots N)$]. − ^{1}H NMR (300 MHz, CD_2Cl_2, 293 K): δ = 1.29 [t, ^3J(H,H) = 7.2 Hz, 6 H, $N(CH_2CH_3)_2$], 1.56 (s, 9 H, Me_3C), 1.98 (s, 15 H, C_5Me_5), 3.46 [q, ^3J(H,H) = 7.2 Hz, 4 H, $N(CH_2CH_3)_2$]. − $^{13}C\{^1H\}$ NMR: (75.5 MHz, CD_2Cl_2, 293 K): δ = 11.9 (C_5Me_5), 15.4 [$N(CH_2CH_3)_2$], 31.2 (Me_3C), 49.5 [$N(CH_2CH_3)_2$], 58.5 (Me_3C), 107.2 (C_5Me_5), 166.7 (Me_3CNC), 306.4 [W≡C, ^1J(W,C) = 223.3 Hz]. − $C_{20}H_{34}Cl_2N_2W$ (557.26): calcd. C 43.11, H 6.15, N 5.03; found C 43.32, H 6.35, N 5.13%.

Cp*$(Cl)_3$W[η^2-*t*Bu(H)NC≡$CNEt_2$] (4): A solution of **3** (0.129 g, 0.23 mmol) in 30 mL of diethyl ether was treated at −78°C with a 1 M solution of HCl in diethyl ether (0.23 mL, 0.23 mmol). The reaction mixture was allowed to warm to room temperature and stirred for 1 h. During this time precipititation of a violet solid was observed. The supernatant solution was decanted off and the precipitate washed twice with 10 mL of cold diethyl ether (−78°C) and dried in vacuo. Yield 0.126 g (92%), violet solid, m.p. 157°C (decomp.). − IR (CH_2Cl_2): $\tilde{\nu}$ = 3435 cm^{-1}, m [ν(NH)], 1667 s [$\nu(N\cdots C\cdots C\cdots N)$]. − ^{1}H NMR (300 MHz, CD_2Cl_2, 258 K): δ = 1.22 (t, 3 H, CH_2CH_3), 1.30 (t, 3 H, CH_2CH_3), 1.34 (s, 9 H, CMe_3), 1.97 (s, 15 H, C_5Me_5), 4.01 (q, 2 H, CH_2CH_3), 4.32 (q, 2 H, CH_2CH_3), 5.77 (s, 1H, NH). − $^{13}C\{^1H\}$ NMR (75.5 MHz, CD_2Cl_2, 258 K): δ = 11.0 (C_5Me_5), 15.1 (CH_2CH_3), 15.6 (CH_2CH_3), 31.4 (CMe_3), 51.3 (CH_2CH_3), 51.9 (CH_2CH_3), 58.2 (CMe_3), 117.7 (C_5Me_5), 218.5, 219.3 (C_{alkyne}). − EI-MS (70 eV):

m/z = 557 [M⁺ − Cl], 501 [M⁺ − Cl − $Me_2C{=}CH_2$], 473 [M⁺ − Cl − $Me_2C{=}CH_2$ − CNH_2], 444 [M⁺ − Cl −$Me_2C{=}CH_2$ − CNH_2 − Et], 389 [M⁺ − Cl − $Me_2C{=}CH_2$ − CNH_2 − Et −EtNC], 353 [M⁺ − Cl − $Me_2C{=}CH_2$ − CNH_2 − Et − EtNC − HCl]. − $C_{20}H_{35}Cl_3N_2W$ (593.72): calcd. C 40.46, H 5.94, N 4.72, Cl 17.91; found C 40.32, H 6.12, N 4.75, Cl 17.85%.

***cis*-Cp*(Cl)₂[P(OMe)₃]W≡CNEt₂ (5):** A solution of **2** (0.12 g, 0.24 mmol) in 30 mL of THF was treated with $P(OMe)_3$ (0.034 mL, 0.29 mmol) and refluxed for 5 h. An IR spectrum of the reaction solution was recorded in the region 2200−1500 cm^{-1} to ensure the complete conversion of **2** to **5**. Afterwards the solution was evaporated to dryness and the residue was purified by column chromatography on silanized silica at −20°C. Elution with diethyl ether afforded an orange fraction, which was evaporated to dryness to give **5** as an orange, microcrystalline solid. Yield 0.11 g (77%), m.p. 98°C (decomp.). − IR (CH_2Cl_2): $\tilde{\nu}$ = 1547 cm^{-1}, s [$\nu(C_{carbyne}{\cdots}N)$]. IR (THF): $\tilde{\nu}$ = 1544 cm^{-1}, s [$\nu(C_{carbyne}{\cdots}N)$]. − ^{1}H NMR (400 MHz, CD_2Cl_2, 293 K): δ = 1.26 [t, ^3J(H,H) = 7.3 Hz, 6 H, $N(CH_2CH_3)_2$], 1.96 (s, 15 H, C_5Me_5), 3.38 [dq, ^2J(H,H) = 13.7 Hz, ^3J(H,H) = 7.3 Hz, 2 H, $N(CH_AH_BCH_3)_2$], 3.54 [dq, ^2J(H,H) = 13.7 Hz, ^3J(H,H) = 7.3 Hz, 2 H, $N(CH_AH_BCH_3)_2$], 3.78 [d, ^3J(P,H) = 10.4 Hz, 9 H, OCH_3]. − $^{13}C\{^1H\}$ NMR: (100.6 MHz, CD_2Cl_2, 293 K): δ = 11.8 (C_5Me_5), 15.4 [$N(CH_2CH_3)_2$], 48.2 [d, ^4J(P,C) = 3.4 Hz, $N(CH_2CH_3)_2$], 54.8 [d, ^2J(P,C) = 7.9 Hz, OMe], 108.6 (C_5Me_5), 306.5 [d, ^2J(P,C) = 37.8 Hz, W≡C]. $^{31}P\{^1H\}$ NMR (162.1 MHz, CD_2Cl_2, 293 K): δ = 133.3 [^1J(W,P) = 435.1 Hz]. CI-MS: *m/z* = 473 [M⁺ − $P(OMe)_3$]. − $C_{18}H_{34}Cl_2NO_3PW$ (598.20): calcd. C 36.14, H 5.73, Cl 11.85, N 2.34, W 30.73; found C 36.08, H 5.75, Cl 11.90, N 2.36, W 30.80%.

Cp*(Cl)₃W=C(H)NEt₂ (6): A sample of **5** (0.11 g, 0.18 mmol) was suspended in 40 mL of diethyl ether and treated at −78°C with a 1 M solution of HCl in diethyl ether (0.18 mL, 0.18 mmol). The reaction mixture was warmed to room temperature and stirred for 2.5 h. During this time the color of the suspension changed from orange to red. The resulting red precipitate was then allowed to settle, the supernatant solution was decanted and the precipitate washed three times with 10 mL of cold diethyl ether (−78°C) and dried in vacuo. Yield 0.06 g (64%), red solid, m.p. 135°C (decomp.). − IR (CH_2Cl_2): $\tilde{\nu}$ = 1508 cm^{-1}, m [$\nu(C_{carbene}{\cdots}N)$]. − ^{1}H NMR (400 MHz, CD_2Cl_2, 233 K): δ = 1.24 [t, ^3J(H,H) = 7.3 Hz, 3 H, CH_2CH_3], 1.29 [t, ^3J(H,H) = 7.3 Hz, 3 H, CH_2CH_3], 2.31 (s, 15 H, C_5Me_5), 3.65 [q, ^3J(H,H) = 7.3 Hz, 2 H, CH_2CH_3], 3.81 [q, ^3J(H,H) = 7.3 Hz, 2H, CH_2CH_3], 10.56 (s, 1H, W=C*H*). − ^{13}C NMR (100.6 MHz, CD_2Cl_2, 233 K): 13.5 (C_5Me_5), 16.5 (CH_2CH_3), 16.7 (CH_2CH_3), 50.9 (CH_2CH_3), 54.2 (CH_2CH_3), 107.3 (C_5Me_5), 248.7 [W=*C*, ^1J(W,C) = 103.8 Hz; ^1J(C,H) = 140.1 Hz]. − FD-MS (CH_2Cl_2): *m/z* = 509 [M⁺]. − $C_{15}H_{26}Cl_3NW$ (510.59): calcd. C 35.29, H 5.13, Cl 20.83, N 2.74, W 36.01; found C 34.60, H 5.04, Cl 20.87, N 2.76, W 35.99%.

[Cp*(Cl)₂(*t*BuNC)₂W=C(H)NEt₂]Cl (7): A solution of **6** (0.125 g, 0.24 mmol) in 10 mL of CH_2Cl_2 was treated at room temperature with *t*BuNC (0.058 mL, 0.51 mmol). The color of the solution changed from red over green to orange. After 1 h stirring at room temperature the solution was evaporated to dryness, the residue dissolved in a minimum amount of THF and the product precipitated by addition of diethyl ether. Yield 0.136 g (82%), yellow solid, m.p. 102°C. − IR (CH_2Cl_2): $\tilde{\nu}$ = 2188 cm^{-1}, s, 2132 m [ν(*t*BuN≡C)], 1579 w [$\nu(C_{carbene}{\cdots}N)$]. − ^{1}H NMR (300 MHz, CD_2Cl_2, 293 K): δ = 1.32 [t, 3 H, ^3J(H,H) = 7.3 Hz, CH_2CH_3], 1.40 [t, ^3J(H,H) = 7.3 Hz, 3 H, CH_2CH_3], 1.56 (s, 18 H, 2 × CMe_3), 2.13 (s, 15 H, C_5Me_5), 3.84 (q, ^3J(H,H) = 7.3 Hz, 2 H, CH_2CH_3), 4.15 (m, 2H, CH_2CH_3), 9.95 (s, 1H, W=C*H*). − ^{13}C NMR (75.5 MHz, CD_2Cl_2, 293 K): 11.8 (C_5Me_5), 14.2 (CH_2CH_3), 14.5 (CH_2CH_3), 30.4 (CMe_3), 30.9 (CMe_3), 53.6 (CH_2CH_3), 58.4 (CH_2CH_3), 59.0 (CMe_3), 59.9 (CMe_3), 103.7 (C_5Me_5), 146.4 (*t*BuN*C*), 154.6 (*t*BuN*C*), 230.9 [W=*C*, ^1J(W,C) = 84.4 Hz; ^1J(C,H) = 144.2 Hz]. − $C_{25}H_{44}Cl_3N_3W$ (676.85): calcd. C 44.36, H 6.55, Cl 15.71, N 6.21; found C 44.40, H 6.61, Cl 15.59, N 5.83%.

X-ray Crystal-Structure Determination of 4 and 6: Data collection for **4** was performed on a CAD4-Enraf−Nonius and for **6** on a STOE STADI4 four-circle diffractometer with graphite monochromated Mo-K_α radiation (λ = 0.71073 Å). After data reduction and LP correction the structures were solved with Patterson Methods (SHELXS-86)[14] and subsequent difference-Fourier synthesis (SHELXL-93).[15] Refinement on F^2 was carried out by full-matrix least-squares techniques (SHELXL-93). Non-hydrogen atoms were refined anisotropically, the atoms H1 in **4** and H6 in **6** were refined isotropically. All other hydrogen atoms were calculated using a riding model. Geometrical calculations were performed with PLATON[16] and illustrations with ZORTEP.[17]

Single crystals of **4** were obtained upon diffusion of diethyl ether into a solution of **4** in CH_2Cl_2 at −30°C; $C_{20}H_{35}Cl_3N_2W$ (593.70); crystal dimensions 0.6 × 0.3 × 0.2 mm; orthorhombic, space group $P2_12_12_1$ (Nr. 19), *a* = 9.460(2), *b* = 13.868(4), *c* = 17.056(3) Å, *V* = 2237.7(9) $Å^3$, *Z* = 4, $\rho_{calcd.}$ = 1.762 g cm^{-3}; *T* = 166 K, μ = 5.327 mm^{-1}, *F*(000) = 1176, ω-2Θ scan, 4° ≤ 2Θ ≤ 50°; 2321 total reflections, 2168 unique and 2161 with $I > 2\sigma(I)$, which were used for refinement; empirical absorption correction DIFABS (min. 0.876, max. 1.112);[18] residual electron density, min/max −0.359/0.389 e$Å^{-3}$; refinement of the 239 parameters resulted in R_1 = 0.0142, $wR_2(F^2)$ = 0.0312, GOF = 1.088.

Single crystals of **6** were obtained upon diffusion of diethyl ether into a solution of **6** in CH_2Cl_2 at −30°C; $C_{15}H_{26}Cl_3NW$ (510.57); crystal dimensions 0.5 × 0.4 × 0.3 mm; orthorhombic, space group *Pbca* (Nr. 61), *a* = 12.551(9), *b* = 15.487(10), *c* = 18.663(2) Å, *V* = 3628(4) $Å^3$, *Z* = 8, $\rho_{calcd.}$ = 1.870 g cm^{-3}; *T* = 190 K, μ = 6.553 mm^{-1}, *F*(000) = 1984, ω−2Θ −scan, 4° ≤ 2Θ ≤ 50°; 1984 total reflections, 1754 unique and 1745 with $I > 2\sigma(I)$, which were used for refinement; empirical absorption correction DIFABS (min. 0.906, max. 1.337); residual electron density, min/max −0.722/0.609 e$Å^{-3}$; refinement of the 185 parameters resulted in R_1 = 0.0269, $wR_2(F^2)$ = 0.0586, GOF = 1.134.[19]

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