Supporting Information

The Triple-Bond Metathesis of Aryldiazonium Salts: A Prospect for Dinitrogen Cleavage
Aaron D. Lackner and Alois Fürster†

anie_201506546_sm_miscellaneous_information.pdf
Figure S-1. Structure of the tungsten alkylidyne ate-complex 5; co-crystallized CH$_2$Cl$_2$ is not shown for clarity; color code: W = green, O = red, Si = blue, K = yellow; CCDC- 1412622

Figure S-2. Structure of the tungsten ate-complex 6a (co-crystallized CH$_2$Cl$_2$ is not shown for clarity); color code: W = green, O = red, Si = blue, K = yellow, N = cyan; CCDC- 1412623
Figure S-3. Structure of the tungsten ate-complex 6b (co-crystallized CH₂Cl₂ is not shown for clarity); color code: W = green, O = red, Si = blue, K = yellow, N = cyan; CCDC- 1412652

Figure S-4. Structure of the tungsten nitride ate-complex 7-EtCN in the solid state; color code: W = green, O = red, Si = blue, K = yellow, N = cyan; CCDC- 1412624
Figure S-5. Structure of the metathesis product 9b in the solid state; the disorder of the tert-butyl group over two positions is not shown for clarity; color code: W = green, O = red, Si = blue, K = yellow, N = cyan; CCDC-1412625

Figure S-6. Structure of the metathesis product 10 in the solid state, showing the two independent molecules in the unit cell and the co-crystallized CH₂Cl₂; color code: Mo = orange, O = red, Si = blue, K = yellow, N = cyan; CCDC-1412626
Figure S-7. Structure of one of the two independent molecules of 10 in the unit cell (depicted in Figure S-6); color code: Mo = orange, O = red, Si = blue, K = yellow, N = cyan; CCDC-1412626

X-ray Crystal Structure Analysis of Complex 5: C_{164}H_{142}Cl_{8}K_{10}O_{8}Si_{8}W_{2}, M_r = 3226.99 g · mol⁻¹, orange prism, crystal size 0.25 x 0.12 x 0.08 mm, monoclinic, space group P2₁/n, a = 13.6369(15) Å, b = 20.0740(18) Å, c = 27.376(2) Å, β = 99.771(10)°, V = 7385.3(12) Å³, T = 100 K, Z = 2, D_c = 1.451 g · cm⁻³, λ = 0.71073 Å, μ(Mo-Kα) = 1.882 mm⁻¹, Empirical absorption correction (T_{min} = 0.72, T_{max} = 0.88), Bruker AXS Enraf-Nonius KappaCCD diffractometer, 2.70 < θ < 27.50°, 65707 measured reflections, 16948 independent reflections, 15249 reflections with I > 2σ(I), Structure solved by direct methods and refined by full-matrix least-squares against F² to R₁ = 0.067 [I > 2σ(I)], wR₂ = 0.171, 872 parameters, H atoms riding, S = 1.308, residual electron density 4.5 / -3.2 e Å⁻³. CCDC-1412622.

X-ray Crystal Structure Analysis of Complex 6a: C_{93}H_{77}Cl_{2}K_{2}N_{2}O_{5}Si_{4}W, M_r = 1708.78 g · mol⁻¹, red plate, crystal size 0.27 x 0.15 x 0.05 mm, monoclinic, space group P2₁/c, a = 16.348(2) Å, b = 25.430(3) Å, c = 19.302(3) Å, β = 92.892(2)°, V = 8014.4(18) Å³, T = 100 K, Z = 4, D_c = 1.416 g · cm⁻³, λ = 0.71073 Å, μ(Mo-Kα) = 1.675 mm⁻¹, Empirical absorption correction (T_{min} = 0.70, T_{max} = 0.93), Bruker-AXS Kappa Mach3 APEX-II diffractometer, 1.48 < θ < 30.51°, 227218 measured reflections, 24478 independent reflections, 21038 reflections with I > 2σ(I), Structure solved by direct methods and refined by full-matrix least-squares against F² to R₁ = 0.023 [I > 2σ(I)], wR₂ = 0.055, 983 parameters, H atoms riding, S = 1.019, residual electron density 1.2 / -1.3 e Å⁻³. CCDC-1412623.
X-ray Crystal Structure Analysis of Complex 6b: C_{80} H_{67} O_{3} Si_{4} W \cdot C_{36} H_{24} K N_{6} \cdot 1.5 C_{2} H_{2} Cl_{2}, M_r = 1562.78 \text{ g} \cdot \text{mol}^{-1}, \text{ orange prism, crystal size 0.24 x 0.21 x 0.14 mm, triclinic, space group P1, a = 14.7528(17) Å, b = 17.1029(10) Å, c = 20.776(6) Å, α = 87.485(6)^°, β = 78.533(11)^°, γ = 82.209(8)^°, V = 5089.3(15) Å}^3, T = 100 K, Z = 2, D_{calc} = 1.378 \text{ g} \cdot \text{cm}^{-3}, λ = 0.71073 Å, μ(Mo-Kα) = 1.360 mm^{-1}, \text{ Empirical absorption correction (T_{min} = 0.60, T_{max} = 0.74), Bruker AXS Enraf-Nonius KappaCCD diffractometer, 2.62 < θ < 33.09^°, 151511 measured reflections, 38556 independent reflections, 34270 reflections with I > 2σ(I), Structure solved by direct methods and refined by full-matrix least-squares against F^2 to R_1 = 0.100 [I > 2σ(I)], wR_2 = 0.293, 1250 parameters, H atoms riding, S = 1.098, residual electron density 4.0 / -3.1 e Å^{-3}. \text{CCDC-1412652.}

X-ray Crystal Structure Analysis of Complex 7-EtCN: C_{75} H_{65} K N_{2} O_{4} Si_{4} W, M_r = 1393.60 \text{ g} \cdot \text{mol}^{-1}, \text{ colorless prism, crystal size 0.12 x 0.08 x 0.05 mm, monoclinic, space group P2_1/c, a = 18.6289(19) Å, b = 14.2871(12) Å, c = 25.032(7) Å, β = 101.306(18)^°, V = 6533(2) Å}^3, T = 100 K, Z = 4, D_{calc} = 1.417 \text{ g} \cdot \text{cm}^{-3}, λ = 0.71073 Å, μ(Mo-Kα) = 1.957 mm^{-1}, \text{ Empirical absorption correction (T_{min} = 0.80, T_{max} = 0.90), Bruker AXS Enraf-Nonius KappaCCD diffractometer, 2.599 < θ < 33.221^°, 143201 measured reflections, 24867 independent reflections, 20217 reflections with I > 2σ(I), Structure solved by direct methods and refined by full-matrix least-squares against F^2 to R_1 = 0.042 [I > 2σ(I)], wR_2 = 0.118, 785 parameters, H atoms riding, S = 1.169, residual electron density 3.1 / -2.9 e Å^{-3}. \text{CCDC-1412624.}

X-ray Crystal Structure Analysis of Complex 9b: C_{91} H_{82} Cl_{2} N_{2} O_{5} Si_{4} W, M_r = 1650.69 \text{ g} \cdot \text{mol}^{-1}, \text{ yellow plate, crystal size 0.08 x 0.07 x 0.02 mm, orthorhombic, space group Pbca, a = 15.9596(14) Å, b = 20.994(3) Å, c = c = 46.933(7) Å, V = 15725(3) Å}^3, T = 100 K, Z = 8, D_{calc} = 1.394 \text{ g} \cdot \text{cm}^{-3}, λ = 0.71073 Å, μ(Mo-Kα) = 1.653 mm^{-1}, \text{ Empirical absorption correction (T_{min} = 0.85, T_{max} = 0.96), Bruker AXS Enraf-Nonius KappaCCD diffractometer, 2.663 < θ < 30.361^°, 252053 measured reflections, 23664 independent reflections, 11117 reflections with I > 2σ(I), Structure solved by direct methods and refined by full-matrix least-squares against F^2 to R_1 = 0.067 [I > 2σ(I)], wR_2 = 0.169, 947 parameters, H atoms riding, S = 1.016, residual electron density 4.1 / -2.5 e Å^{-3}. \text{CCDC-1412625.}

X-ray Crystal Structure Analysis of Complex 10: C_{91} H_{82} Cl_{2} Mo N_{2} O_{5} Si_{4} M_r = 1562.78 \text{ g} \cdot \text{mol}^{-1}, \text{ colorless plate, crystal size 0.14 x 0.11 x 0.06 mm, monoclinic, space group P2_1/c, a = 47.070(8) Å, b = 15.847(2) Å, c = 21.004(3) Å, β = 90.897(10)^°, V = 15666(4) Å}^3, T = 100 K, Z = 8, D_{calc} = 1.325 \text{ g} \cdot \text{cm}^{-3}, λ = 0.71073 Å, μ(Mo-Kα) = 0.352 mm^{-1}, \text{ Empirical absorption correction (T_{min} = 0.96, T_{max} = 0.98), Bruker AXS Enraf-Nonius KappaCCD diffractometer, 2.607 < θ < 27.103^°, 199841 measured reflections, 33915 independent reflections, 23568 reflections with I > 2σ(I), Structure solved by direct methods and refined by full-matrix least-squares against F^2 to R_1 = 0.100 [I > 2σ(I)], wR_2 = 0.293, 1889 parameters, H atoms riding, twinning law and batch scale factor [1 0 0 0 -1 0 0 0 -1] and 0.097(1), S = 1.828, residual electron density 2.5 / -1.1 e Å^{-3}. \text{CCDC-1412626.}
General. Unless stated otherwise, all reactions were carried out under Ar in flame-dried glassware. The solvents were purified by distillation over the indicated drying agents and were transferred under Ar: Et$_2$O (Mg/anthracene), CH$_2$Cl$_2$, pentane, toluene (Na/K); propionitrile, 1,2-dimethoxyethane (CaH$_2$), pyridine were dried by an adsorption solvent purification system based on molecular sieves. 1,10-phenanthroline was dried by sublimation. Celite was dried overnight at 120 °C under high vacuum. Flash column chromatography: Merck silica gel 60 (40–63 μm) with HPLC grade solvents. NMR: Spectra were recorded on Bruker DPX 300, AV400, AV500 or AVIII 600 spectrometer in the solvents indicated; chemical shifts (δ) are given in ppm relative to TMS, coupling constants (J) in Hz. The solvent signals were used as references and the chemical shifts converted to the TMS scale (CDCl$_3$: δ$_C$ = 77.16 ppm; residual CHCl$_3$ in CDCl$_3$: δ$_H$ = 7.26 ppm; CD$_2$Cl$_2$: δ$_C$ = 54.00 ppm; residual CHDC$l_2$: δ$_H$ = 5.32 ppm; [D$_6$]-acetone: δ$_C$ = 206.26 ppm; residual [D$_6$]-acetone: δ$_H$ = 2.05 ppm); [D$_6$]-DMSO: δ$_C$ = 39.52 ppm; residual [D$_5$]-DMSO: δ$_H$ = 2.50 ppm); IR: Spectrum One (Perkin-Elmer) spectrometer, wavenumbers (ν) in cm$^{-1}$; High resolution mass spectrometry: Bruker APEX III FT-MS (7 T magnet) or MAT 95 (Finnigan).

The Mo-alkylidyne ate complex 2 and neutral Mo-alkylidyne complex 3 were prepared according to the literature.

Upon indication of decomposition (color change, irreproducible yields) the aryldiazonium salts were repurified by dissolution into acetone and precipitation with diethyl ether.

Starting metal complexes

**Note:** The complexes carrying Ph$_3$SiO-ligands contained ≤10% of silanolate impurities even after recrystallization; fully satisfactory elemental analyses were therefore not obtained. The NMR spectra, however, confirm an acceptable purity of the bulk material.

![Diagram](attachment:image.png)

To a solution of 4-iodoanisole (4.68 g, 20.0 mmol) in Et$_2$O, stirring at −78 °C, was added a solution of nBuLi in pentane (1.6 M, 12.5 mL, 20.0 mmol) over 2 min. After stirring 20 min at this temperature, the mixture was warmed to 0 °C, then added by addition funnel to a refluxing mixture of W(CO)$_6$ (7.04 g, 20 mmol) in

---

Et₂O (200 mL) over 5 min. Upon addition of the generated aryllithium reagent, the refluxing mixture became dark orange in color. Stirring was continued at reflux temperature for 45 min; the mixture was then cooled to ambient temperature and was concentrated to dryness under vacuum. To the resultant thick orange paste was added a solution of Me₄NBr (4.62 g, 30 mmol) in H₂O (50 mL). The mixture was stirred 30 min, then the precipitate was collected by filtration, washing alternately with H₂O and Et₂O (2 x 40 mL each), then dried under vacuum, leaving the desired product S-1 as a bright orange solid (9.31 g, 87% yield).

To a solution of Fischer carbene S-1 (4.56 g, 8.47 mmol), stirring in CH₂Cl₂ at −78 °C, was added by cannula a solution of oxalyl bromide (820 µL, 8.73 mmol) in CH₂Cl₂ (5 mL) held at −78 °C. After stirring at this temperature for 15 min, the violet solution was allowed to warm until it reached an internal temperature of around −20 °C, at which point it had become dark yellow in color. The reaction mixture was cooled again to −78 °C, then filtered at −78 °C through Celite using a jacketed filter into a receiving flask held at −78 °C and containing 1,2-dimethoxyethane (4.54 mL, 44.0 mmol). To the resulting orange solution was added dropwise through an addition funnel a solution of Br₂ (450 ul, 8.73 mmol) in CH₂Cl₂ (5 mL). After 15 min stirring at −78 °C, the reaction mixture was warmed to ambient temperature, then filtered through Celite. The brown-green filtrate was concentrated until persistent green precipitate was observed. Pentane (300 mL) was added by addition funnel over 1 h, resulting in the formation of more green precipitate. The precipitate was collected by filtration and dried under vacuum to give the desired alkylidyne 1b as a green solid (4.40 g, 82% yield).

To a solution of complex 1b (2.27 g, 3.59 mmol) in toluene (50 mL), stirring at 0 °C, was added a solution of Ph₃SiOK (5.64 g, 17.9 mmol) in toluene (50 mL) over 10 min. The mixture was warmed to ambient temperature and stirred an additional 2 h, then filtered through Celite. The filtrate was concentrated and dried under vacuum to give the desired alkylidyne 5 as a pink solid (2.98 g, 58% yield).
To a solution of 5 (120 mg, 0.0831 mmol) in CH₂Cl₂ (10 mL) was added 1,10-phenanthroline (15.0 mg, 0.0831 mol). The reaction mixture was stirred for 3 h at ambient temperature. Pentane (50 mL) was added, the resulting precipitate was collected by filtration, dissolved in a minimum of CH₂Cl₂ (2 mL) and reprecipitated with pentane (10 mL). The precipitate was collected by filtration and dried under vacuum to give the phenanthroline adduct 6a as an orange solid (121 mg, 90% yield).

To a mixture of the tungsten alkylidyne 5 (1.12 g, 0.727 mmol) in toluene (5 mL) was added propionitrile (270 µL, 3.75 mmol). The pink reaction mixture quickly became homogeneous and was heated to 60 °C with stirring for 3 h, by which point the mixture had become yellow in color. The mixture was cooled to ambient temperature and concentrated to dryness under high vacuum. The residue was taken up in 3:1 Et₂O/CH₂Cl₂ (40 mL) and insoluble material filtered off through Celite. The filtrate was concentrated to dryness, the residue was redissolved in a minimum of CH₂Cl₂ (5 mL), and the product was precipitated by addition of pentane (~150 mL). Recrystallization by slow diffusion of pentane into a concentrated solution of the material in CH₂Cl₂ furnished single crystals of the propionitrile adduct 7·EtCN suitable for X-ray diffraction. As the EtCN ligand in 7·EtCN, however, is labile and can be removed in high vacuum, the material was spectroscopically characterized as the EtCN-free complex 7 after it had been dried in high vacuum; yellow powder (680 mg, 70% yield). ¹H NMR (400 MHz, CD₂Cl₂) δ 7.45 – 7.37 (m, 24H), 7.26 – 7.22 (m, 12H), 7.06 – 6.97 (m, 24H) ppm; ¹³C NMR (101 MHz, CD₂Cl₂) δ 138.3, 136.5, 129.5, 127.9 ppm.

General procedure for the preparation of aryldiazonium salts

Note: Though the tetrafluoroborate salts of aryldiazoniums are typically nonexplosive, care should nonetheless be taken to avoid potential detonation from friction or from impact of the dry compounds.

Performed open to atmosphere: To a aqueous solution of HBF₄ (48% w/w, 3.2 mL, 25 mmol), stirring vigorously at 0 °C, was added aniline (10 mmol), and precipitation was observed. tert-Butyl methyl ether was added until the biphasic mixture was free of heterogeneity (~5 mL). An aqueous solution of NaNO₂ (696 mg, 10.1 mmol in 3 mL H₂O) was then added dropwise over 2 min and the reaction
was stirred at 0 °C for an additional 20 min. The mixture was allowed to warm to ambient temperature and stirred an additional 30 min, by which point the crude product had precipitated. The precipitate was collected by filtration, washing with cold H2O (2 x 3 mL) and tert-butyl methyl ether (2 x 10 mL). The solid material was then dissolved in acetone, and precipitated by addition of tert-butyl methyl ether. The aryldiazonium was isolated by filtration and dried under vacuum.

The product 8a was isolated as a colorless solid (1.53 g, 80% yield). 1H NMR (300 MHz, Acetone-d6) δ 8.92 – 8.81 (m, 2H), 8.40 (ddt, J = 8.0, 7.4, 1.2 Hz, 1H), 8.16 – 8.05 (m, 2H) ppm; 13C NMR (75 MHz, Acetone-d6) δ 142.2, 133.6, 132.4, 116.4 ppm; IR (film): ν = 3107, 2294, 1570, 1462, 1311, 1290, 1173, 1025, 989, 943, 755, 665, 530, 522, 453 cm⁻¹. HRMS (ESI+) m/z: calcd for C6H5N2: 105.0447; found: 105.0448.

The procedure was modified, employing 15N-labeled aniline and 15N-labeled sodium nitrite on a 2.0 mmol scale. The product 15N2-8a was isolated as a colorless solid (205 mg, 53% yield). 1H NMR (400 MHz, Acetone-d6) δ 8.86 – 8.77 (m, 2H), 8.37 (tt, J = 7.8, 1.3 Hz, 1H), 8.08 (tt, J = 7.8, 1.3 Hz, 2H) ppm; 13C NMR (101 MHz, Acetone-d6) δ 142.0, 133.4 (d, J = 2.2 Hz), 132.2 (d, J = 3.2 Hz), 116.2 (dd, J = 9.9, 5.7 Hz) ppm; 15N NMR (61 MHz, Acetone-d6) δ -66.2, -148.9 ppm; IR (film): ν = 3107, 2217, 1570, 1461, 1311, 1290, 1173, 1027, 990, 944, 756, 665, 522, 446 cm⁻¹. HRMS (ESI+) m/z: calcd for C6H5N2: 107.0388; found: 107.0392.

The reaction was run on a 6.88 mmol scale, and the product 8b was isolated as a colorless solid (798 mg, 47% yield). 1H NMR (300 MHz, CDCl3) δ 8.60 – 8.53 (m, 2H), 7.86 – 7.79 (m, 2H), 1.36 (s, 9H) ppm; 13C NMR (75 MHz, CDCl3) δ 167.3, 132.9, 129.1, 110.6, 36.9, 30.6 ppm; IR (film): ν = 3016, 2966, 2273, 1574, 1480, 1417, 1373, 1269, 1036, 841, 768, 721, 619, 543, 520 cm⁻¹. HRMS (ESI+) m/z: calcd for C10H13N2: 161.1073; found: 161.1073.

The product 8c was isolated as a colorless solid (1.31 g, 59% yield). 1H NMR (400 MHz, Acetone-d6) δ 8.84 – 8.76 (m, 2H), 7.60 – 7.53 (m, 2H), 4.18 (d, J = 0.8 Hz, 3H) ppm; 13C NMR (101 MHz, Acetone-d6) δ 142.0, 133.0, 118.4, 103.7, 36.9, 30.6 ppm; IR (film): ν = 3119, 2685, 2250, 1580, 1568, 1493, 1442, 1343, 1288, 1197, 1099, 1033, 841, 807, 685, 522, 498 cm⁻¹. HRMS (ESI+) m/z: calcd for C7H7N2O: 135.0553; found: 135.0553.

The product 8d was isolated as a colorless solid (820 mg, 39% yield). 1H NMR (300 MHz, Acetone-d6) δ 9.02 – 8.90 (m, 2H), 7.93 – 7.82 (m, 2H) ppm; 13C NMR (101 MHz, Acetone-d6) δ 170.3 (d, J = 268.8 Hz), 138.0 (d, J = 12.3 Hz), 120.5 (d, J = 25.6 Hz), 112.1 (d, J = 3.0 Hz) ppm; 19F NMR (282 MHz, Acetone-d6) δ –86.9 ppm; IR (film): ν = 3115, 2294, 1932, 1579, 1484, 1431, 1250, 1167, 1012, 850, 836, 685, 525 cm⁻¹. HRMS (ESI+) m/z: calcd for C4H4N2F: 123.0353; found: 123.0355.
The product **8e** was isolated as a tan solid (1.36 g, 50% yield). $^1$H NMR (300 MHz, Acetone-$d_6$) $\delta$ 8.94 (d, $J = 8.0$ Hz, 1H), 8.36 (d, $J = 8.0$ Hz, 1H), 8.31 (app t, $J = 8.0$ Hz, 1H), 8.09 (app t, $J = 8.0$ Hz, 1H) ppm; $^{13}$C NMR (101 MHz, Acetone-$d_6$) $\delta$ 143.2, 136.3, 136.2, 131.3, 125.3, 118.7 ppm; IR (film): $\tilde{\nu}$ = 3096, 2288, 1562, 1468, 1302, 1269, 1051, 1033, 772, 656 cm$^{-1}$. HRMS (ESI+) $m/z$: calcd for C$_6$H$_4$N$_2$Br: 182.9552; found: 182.9553.

The product **8f** was isolated as a pale yellow solid (2.01 g, 57% yield). $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 8.29 (d, $J = 8.2$ Hz, 2H), 8.07 (t, $J = 8.2$ Hz, 1H) ppm; $^{13}$C NMR (101 MHz, DMSO-$d_6$) $\delta$ 142.5, 134.4, 126.7, 121.2 ppm; IR (film): $\tilde{\nu}$ = 3105, 3076, 2276, 1556, 1545, 1446, 1284, 1221, 1157, 1022, 802, 739, 521, 405 cm$^{-1}$. HRMS (ESI+) $m/z$: calcd for C$_6$H$_3$N$_2$Br$_2$: 260.8658; found: 260.8659.

The reaction was run on a 4.10 mmol scale, and the product **8g** was isolated as a colorless solid (771 mg, 70% yield). $^1$H NMR (400 MHz, Acetone-$d_6$) $\delta$ 8.92 (dd, $J = 8.4$, 1.3 Hz, 1H), 8.43 (app td, $J = 7.8$, 1.3 Hz, 1H), 8.11 (dd, $J = 7.8$, 1.2 Hz, 1H), 8.06 (ddd, $J = 8.4$, 7.8, 1.2 Hz, 1H), 7.92 – 7.86 (m, 2H), 7.74 – 7.69 (m, 3H) ppm; $^{13}$C NMR (101 MHz, Acetone-$d_6$) $\delta$ 146.4, 142.4, 134.7, 133.9, 133.2, 131.9, 131.3, 130.7, 129.5, 114.7 ppm; IR (film): $\tilde{\nu}$ = 3103, 2267, 1590, 1557, 1471, 1293, 1030, 785, 759, 718, 705, 520, 496, 456 cm$^{-1}$. HRMS (ESI+) $m/z$: calcd for C$_{12}$H$_9$N$_2$: 181.0760; found: 181.0761.

The procedure was modified, employing $^{15}$N-labeled sodium nitrite, and the reaction was run on a 1.87 mmol scale, and the product **$^{15}$N-8g** was isolated as a colorless solid (375 mg, 74% yield). $^1$H NMR (400 MHz, Acetone-$d_6$) $\delta$ 8.95 (dd, $J = 8.4$, 1.3 Hz, 1H), 8.45 (app td, $J = 7.8$, 1.3 Hz, 1H), 8.13 (dd, $J = 7.8$, 1.2 Hz, 1H), 8.08 (ddd, $J = 8.4$, 7.8, 1.2 Hz, 1H), 7.93 – 7.87 (m, 2H), 7.76 – 7.69 (m, 3H) ppm; $^{13}$C NMR (101 MHz, Acetone-$d_6$) $\delta$ 146.5, 142.6, 134.9, 134.0, 133.3, 132.1, 131.5, 130.8, 129.7, 114.9 ppm; IR (film): $\tilde{\nu}$ = 3103, 2234, 1591, 1557, 1471, 1293, 1031, 784, 759, 718, 705, 520, 495, 455 cm$^{-1}$. HRMS (ESI+) $m/z$: calcd for C$_{12}$H$_9$N$^{15}$N: 182.0731; found: 182.0732.

**Synthesis of imido complexes**

To aryldiazonium **8a** (18.8 mg, 0.098 mmol) in CH$_2$Cl$_2$ (2 mL) stirring at 0 °C was added dropwise a solution of the tungsten alkylidyne **5** (142 mg, 0.098 mmol) in CH$_2$Cl$_2$ (2 mL) over 2 min. Upon contact, the reaction mixture immediately became purple in color, and the color dissipated to the original pink color within seconds. The mixture was warmed to ambient temperature and stirred 1 h, by which time it had become yellow in color. The reaction mixture was filtered through Celite, the filtrate was concentrated to dryness, the residue was redissolved in a minimum of CH$_2$Cl$_2$ and the product precipitated with pentane. The precipitate was collected by
filtration, giving 9a as a yellow solid (127 mg, 86% yield, by NMR contains ~10% impurity). H NMR (400 MHz, CD₂Cl₂) δ 7.24-7.14 (m, 41H), 7.10 (t, J = 8.0 Hz, 2H), 6.94 (d, J = 8.0 Hz, 2H), 6.85-6.80 (m, 24 H), 6.34 (d, J = 8.0 Hz, 2H), 3.88 (s, 3H) ppm; C NMR (75 MHz, CD₂Cl₂) δ 164.5, 153.3, 137.6, 136.4, 136.1, 135.8, 129.5, 129.0, 127.8, 127.5, 117.6, 115.5, 101.7, 56.3 ppm.

To aryldiazonium 8a (10.8 mg, 0.0557 mmol) in CH₂Cl₂ (2 mL) stirring at 0 °C was added dropwise a solution of the tungsten alkylidyne 5 (80.4 mg, 0.0557 mmol) in CH₂Cl₂ (2 mL) over 2 min. Upon contact, the reaction mixture immediately became purple in color. The reaction mixture was warmed to ambient temperature and stirred 1 h, by which time it had become yellow in color. The reaction mixture was filtered through Celite, the filtrate was concentrated to dryness, the residue was redissolved in a minimum of CH₂Cl₂ and the product precipitated with pentane. The precipitate was collected by filtration, giving 9a as a yellow solid (65 mg, 77% yield). H NMR (600 MHz, CD₂Cl₂) δ 7.22-7.16 (m, 38H), 7.11 (t, J = 7.2 Hz, 2H), 6.95 (m, 2H), 6.85-6.80 (m, 25 H), 6.35 (d, J = 8.4 Hz, 2H), 3.90 (s, 3H) ppm; C NMR (151 MHz, CD₂Cl₂) δ 164.3, 153.1 (J_C-W,C_N = 38.0, 10.7 Hz) 137.5, 136.1, 134.7, 129.2, 128.9, 127.6, 127.3 (J_C-N = 2.0 Hz), 127.3, 117.5 (J_C-N = 25 Hz), 115.3, 101.6, 44.3 ppm; N NMR (61 MHz, CD₂Cl₂) δ −0.6 (J_W-N = 135 Hz), −145.0 ppm.

To aryldiazonium 8b (37.8 mg, 0.152 mmol) in CH₂Cl₂ (3 mL) stirring at 0 °C was added dropwise a solution of the tungsten alkylidyne 5 (220 mg, 0.152 mmol) in CH₂Cl₂ (3 mL) over 2 min. Upon contact, the reaction mixture immediately became purple in color. The reaction mixture was warmed to ambient temperature and stirred 1 h, by which time it had become yellow in color. The reaction mixture was filtered through Celite, the filtrate was concentrated to dryness, the residue was redissolved in a minimum of CH₂Cl₂ and the product precipitated with pentane. The precipitate was collected by filtration, giving 9b as a yellow solid (200 mg, 84% yield). X-ray quality single crystals were grown by layered diffusion with CH₂Cl₂ and pentane. H NMR (400 MHz, CD₂Cl₂) δ 7.27 (d, J = 12.0 Hz, 2H), 7.24-7.15 (m, 36H), 7.10 (d, J = 12.0 Hz), 6.94 (d, J = 8.0 Hz, 2H), 6.88-6.81 (m, 24H), 6.31 (d, J = 8.0 Hz, 2H), 3.89 (s, 3H), 1.30 (s, 9H) ppm; C NMR (101 MHz, CD₂Cl₂) δ 164.4, 151.2, 150.9, 134.7, 129.2, 128.9, 127.6, 127.3 (J_C-N = 2.0 Hz), 127.3, 117.5 (J_C-N = 25 Hz), 115.3, 101.9, 56.3, 34.7, 31.8 ppm.

To aryldiazonium 8b (35.5 mg, 0.143 mmol) in CH₂Cl₂ (3 mL) stirring at 0 °C was added dropwise a solution of the molybdenum alkylidyne 2 (194 mg, 0.143 mmol) in CH₂Cl₂ (3 mL) over 2 min. Upon contact, the reaction mixture immediately became purple in color. The reaction mixture was warmed to ambient temperature and stirred 1 h, by which time it had become orange/brown in color. The mixture was filtered through Celite, the filtrate was concentrated to dryness, the residue was redissolved in a minimum of CH₂Cl₂ and the product precipitated with pentane.
The precipitate was collected by filtration, giving 10 as an orange solid (172 mg, 81% yield). X-ray quality single crystals were grown by layered diffusion with CH₂Cl₂ and pentane. ¹H NMR (400 MHz, CD₂Cl₂) δ 7.30 (d, J = 7 Hz, 2H), 7.23-7.17 (m, 24H), 6.96 (d, J = 9 Hz, 2H), 6.92 (d, J = 7 Hz, 2H), 6.90-6.83 (m, 24H), 6.45 (d, J = 9 Hz, 2H), 3.86 (s, 3H), 1.37 (s, 9H) ppm; ¹³C NMR (101 MHz, CD₂Cl₂) δ 163.8, 153.6, 153.5, 137.6, 136.3, 134.7, 129.5, 128.1, 127.8, 124.9, 118.5, 115.2, 103.1, 56.2, 35.2, 31.4 ppm.

To aryldiazonium 8c (21.5 mg, 0.097 mmol) in CH₂Cl₂ (3 mL) stirring at 0 °C was added dropwise a solution of the tungsten alkylidyne 5 (140 mg, 0.097 mmol) in CH₂Cl₂ (3 mL) over 2 min. Upon contact, the reaction mixture immediately became purple in color. The reaction mixture was warmed to ambient temperature and stirred 1 h, by which time it had become orange in color. Pyridine (39 ul, 0.485 mmol) was then added and the reaction mixture was stirred an additional 30 min. The reaction mixture was filtered through Celite, the filtrate was concentrated to dryness, the residue was redissolved in a minimum of CH₂Cl₂ and the product precipitated by addition of pentane and cooling to −20 °C. The precipitate was collected by filtration, washing with 10 mL cold 1:1 pentane/Et₂O, giving 11c as a yellow solid (118 mg, 82% yield). ¹H NMR (300 MHz, CD₂Cl₂) δ 8.88 (s, 2H), 7.58 (t, J = 7 Hz, 1H), 7.25-7.16 (m, 12H), 7.12-7.03 (m, 24H), 6.93 (t, J = 7 Hz, 2H), 6.85 (t, J = 8 Hz, 24H), 6.62 (d, J = 9 Hz, 2H), 6.42 (d, J = 9 Hz, 2H), 3.81 (s, 3H) ppm; ¹³C NMR (75 MHz, CD₂Cl₂) δ 159.3, 151.2, 147.1, 137.8, 136.7, 135.5, 131.6, 129.5, 127.8, 124.0, 112.6, 56.0 ppm.

To aryldiazonium 8d (25.0 mg, 0.119 mmol) in CH₂Cl₂ (3 mL) stirring at 0 °C was added dropwise a solution of the tungsten alkylidyne 5 (172 mg, 0.119 mmol) in CH₂Cl₂ (3 mL) over 2 min. Upon contact, the reaction mixture immediately became purple in color. The reaction mixture was warmed to ambient temperature and stirred 1 h, by which time it had become yellow in color. Pyridine (48 ul, 0.590 mmol) was then added and the reaction mixture was stirred an additional 30 min. The mixture was filtered through Celite, the filtrate was concentrated to dryness, the residue was redissolved in a minimum of CH₂Cl₂ and the product precipitated by addition of pentane and cooling to −20 °C. The precipitate was collected by filtration, washing with 10 mL cold 1:1 pentane/Et₂O, giving 11d as a yellow solid (124 mg, 71% yield). ¹H NMR (400 MHz, CD₂Cl₂) δ 8.88 (br s, 2H), 7.65-7.55 (m, 1H), 7.25-7.15 (m, 12H), 7.12-7.00 (m, 24H), 6.95-6.87 (m, 2H), 6.88-6.73 (m, 26H), 6.42-6.35 (m, 2H) ppm; ¹³C NMR (75 MHz, CD₂Cl₂) δ 151.3, 149.6, 138.8, 137.6, 136.7, 131.6 (d, J = 8 Hz), 129.6, 127.9, 124.1, 114.4 (d, J = 23 Hz) ppm (carbon at para position not observed); ¹⁹F NMR (282 MHz, CD₂Cl₂) δ −113.70.
To aryldiazonium 8e (11.9 mg, 0.0439 mmol) in CH₂Cl₂ (1 mL) stirring at 0 °C was added dropwise a solution of the tungsten alkylidyne 5 (63.4 mg, 0.0439 mmol) in CH₂Cl₂ (1 mL) over 2 min. The mixture was warmed to ambient temperature (remained deep purple for ~20 min) and stirred 1 h, by which time it had become yellow in color. To the reaction mixture containing complex 9e was added drops of H₂O and stirring was continued for 30 min. The mixture was concentrated to dryness and the residue purified by flash column chromatography on SiO₂ (1:1 to 3:1 benzene/hexanes), giving 2-bromoaniline (5.5 mg, 73% yield) and 4-methoxybenzonitrile (3.0 mg, 51% yield). ¹H NMR spectra were in good agreement with the literature data.²,³

To aryldiazonium 8g (28.1 mg, 0.0803 mmol) in CH₂Cl₂ (2 mL) stirring at 0 °C was added dropwise a solution of the tungsten alkylidyne 5 (116 mg, 0.803 mmol) in CH₂Cl₂ (2 mL) over 2 min. The mixture was warmed to ambient temperature and stirred 1 h, by which time it had become dark yellow in color. To the reaction mixture containing complex 9g was added drops of H₂O and stirring was continued for an additional 30 min. The mixture was concentrated to dryness and the residue purified by flash column chromatography on SiO₂ (1:1 to 3:1 benzene/hexanes), giving 2,6-dibromoaniline (12.0 mg, 60% yield) and 4-methoxybenzonitrile (6.0 mg, 56% yield). ¹H NMR spectra were in good agreement with the literature data.²,⁴

To aryldiazonium 8g (21.9 mg, 0.0817 mmol) in CH₂Cl₂ (3 mL) stirring at 0 °C was added dropwise a solution of the tungsten alkylidyne 5 (118 mg, 0.0817 mmol) in CH₂Cl₂ (1 mL) over 2 min. The reaction mixture was warmed to ambient temperature and stirred 3 h, by which time it had become orange in color. To the reaction mixture containing complex 9g was added drops of H₂O and stirring continued for an additional 30 min. The mixture was concentrated to dryness and the residue purified by flash column chromatography on SiO₂ (1:1 benzene/hexanes to separate from PH₃SiOH, then 9:1 hexanes/tert-butyl methyl ether), giving 2-aminobiphenyl (7.0 mg, 51% yield)

---
and 4-methoxybenzonitrile (10.0 mg, 92% yield). \(^1\)H NMR spectra were in good agreement with the literature data.\(^2,5\)

### Reaction of the tungsten nitride complex 7 with aryldiazonium 8b

To aryldiazonium 8b (13.9 mg, 0.0560 mmol) in DCM (2 mL) stirring at −20 °C was added dropwise a solution of the tungsten nitride 7 (75.0 mg, 0.560 mmol) in CH\(_2\)Cl\(_2\) (2 mL) over 2 min. The reaction mixture was warmed to ambient temperature and stirred 2 h, by which time it had become brown in color. To the reaction mixture was added drops of H\(_2\)O and the reaction mixture was stirred an additional 30 min. The reaction mixture was concentrated to dryness and purified by flash column chromatography on SiO\(_2\) (4:1 hexanes/tert-butyl methyl ether), giving 4-tert-butylaniline 12b (6.0 mg, 72% yield). \(^1\)H NMR spectra were in good agreement with the literature values.\(^2,6,7\)

---


\(^7\) GC/MS and IR inspection of the crude material suggest that small amounts of (tert-butyl)phenyl azide are also present; studies into this interesting side reaction are underway.
Low temperature $^{13}$C NMR of showing a carbene formed on reaction of $^{15}$N-8g with 5