

Supplementary Information for

C₆₀-induced alkyne-alkyne coupling and alkyne scission reactions of tungsten tris(diphenylacetylene) complex

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Experimental

General Methods.

All manipulations were carried out under an atmosphere of purified dinitrogen with standard Schlenk techniques. Solvents were dried over appropriate reagents under dinitrogen and distilled immediately before use. Preparative thin-layer chromatographic (TLC) plates were prepared from silica gel (Merck). ¹H and ¹³C spectra were obtained on a Varian Unity INOVA-500 spectrometer at 500 and 125.7 MHz, respectively. Matrix-assisted laser desorption ionization (MALDI) mass spectra were recorded on a Bruker Microflex-LT mass spectrometer. Elemental analyses were performed at the National Science Council Regional Instrumentation Center at National Chen-Kung University, Tainan, Taiwan.

Preparation and Characterization of compound 2 and 3.

C₆₀ (180 mg, 0.25 mmol) and W(NCMe)(η^2 -PhC≡CPh)₃ (**1**) (180 mg, 0.24 mmol) were placed in an oven-dried 100 mL Schlenk flask, equipped with a condenser, under a dinitrogen atmosphere. Chlorobenzene (30 mL) was introduced into the flask via a syringe and the solution was heated to reflux for 8 min, resulting in a solution color change from purple to

deep green. The flask was immediately put into an ice bath to cool down the reaction mixture. The volatile materials were removed under vacuum, and the residue was subjected to TLC, eluting with carbon disulfide. Isolation of the material forming the first purple band recovered C₆₀ (61 mg, 34%). Isolation of the material forming the second green band gave dark green crystals of W(η^3 -NC(Me)C₆₀)(η^4, η^2 -C₆Ph₆) (**2**, 107 mg, 0.072 mmol, 44% based on the C₆₀ consumed) after crystallization from CH₂Cl₂/CS₂/*n*-hexane at -20° C. Isolation of the material forming the third green band gave dark green crystals of W($\equiv$ CPh)(NCMe)(η^2 -C₆₀)(η^3, η^2 -C₅Ph₅) (**3**, 31 mg, 0.021 mmol, 13%) after crystallization from CS₂/*n*-hexane at 0° C.

Compound 2: MS (MALDI): *m/z* 1479 (M⁺, ¹⁸⁴W). Anal.Calcd for C₁₀₄H₃₃NW: C, 84.39; H, 2.25; N, 0.95. Found: C, 84.10; H, 2.09; N, 0.91. ¹H NMR (CD₂Cl₂+CS₂, 23 °C): δ 7.19 (d, J_{H-H} = 7 H, 12H, Ph), 6.92–6.85 (m, 18H, Ph), 2.54 (s, 3H, CH₃). ¹³C{¹H} NMR (CD₂Cl₂+CS₂, 23 °C): δ 166.3, 157.7, 151.6, 147.9, 146.8, 146.6, 146.2, 146.1, 146.0, 145.9, 145.3, 145.2, 145.1, 144.8, 144.4, 144.1, 144.0, 143.9, 143.8, 143.7, 143.5, 143.3, 142.7, 142.4, 142.3, 141.7, 139.7, 139.4, 139.3, 138.6, 137.0 (C₆₀), 136.5, 134.7, 127.7, 127.5 (Ph), 114.8 (C₆Ph₆), 95.9 (η^2 -C₆₀), 83.5 (C-N), 25.9 (CH₃).

Compound 3: MS (MALDI): *m/z* 1438 (M⁺ – MeCN, ¹⁸⁴W). Anal.Calcd for C₁₀₄H₃₃NW: C, 84.39; H, 2.25; N, 0.95. Found: C, 84.77; H, 2.30; N, 0.88. ¹H NMR (CD₂Cl₂, 23 °C): δ 7.41–7.06 (m, 30H, Ph), 2.19 (s, 3H, CH₃). ¹³C{¹H} NMR (CD₂Cl₂, 23 °C): δ 291.4 (W $\equiv$ C), 172.8, 171.2, 165.9, 163.6, 150.0, 149.7, 149.3, 149.0, 148.5, 147.9, 147.2, 146.4, 146.3, 146.1, 146.0, 145.9, 145.8, 145.7, 145.5, 145.4, 145.3, 145.2, 145.1, 145.0, 144.9, 144.8, 144.7, 144.6, 144.4, 144.3, 144.2, 143.9, 143.8, 143.5, 143.4, 143.2, 143.1, 143.0, 142.9, 142.8, 142.7, 142.6, 142.5, 142.4, 142.1, 142.0, 141.9, 141.2, 139.9, 138.1, 137.6, 137.0 (C₆₀), 135.2, 134.2, 133.9, 133.5, 130.6, 128.1, 128.0, 127.9, 127.6 (Ph, C $\equiv$ N), 118.8 (C₅Ph₅), 101.2, 91.1 (η^2 -C₆₀), 4.97 (CH₃).

Structure Determination for **2** and **3**.

The crystals of **2** and **3** found suitable for X-ray analysis were each mount in a thin-walled glass capillary and aligned on the Nonius Kappa CCD diffractometer, with graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å). The θ range for data collection is 2.12 to 25.02° for **2** and 0.88 to 25.03° for **3**. Of the 22544 and 21999 reflections collected, 893 and 1338 reflections were independent for **2** and **3**, respectively. All data were corrected for Lorentz and polarization effects and for the effects of absorption. The structure was solved by the direct method and refined by least-square cycles. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. All calculations were performed using the SHELXTL-97 package.