Synthesis of d^2 Tungsten Arene Complexes and Their Reaction with Diphenylacetylene

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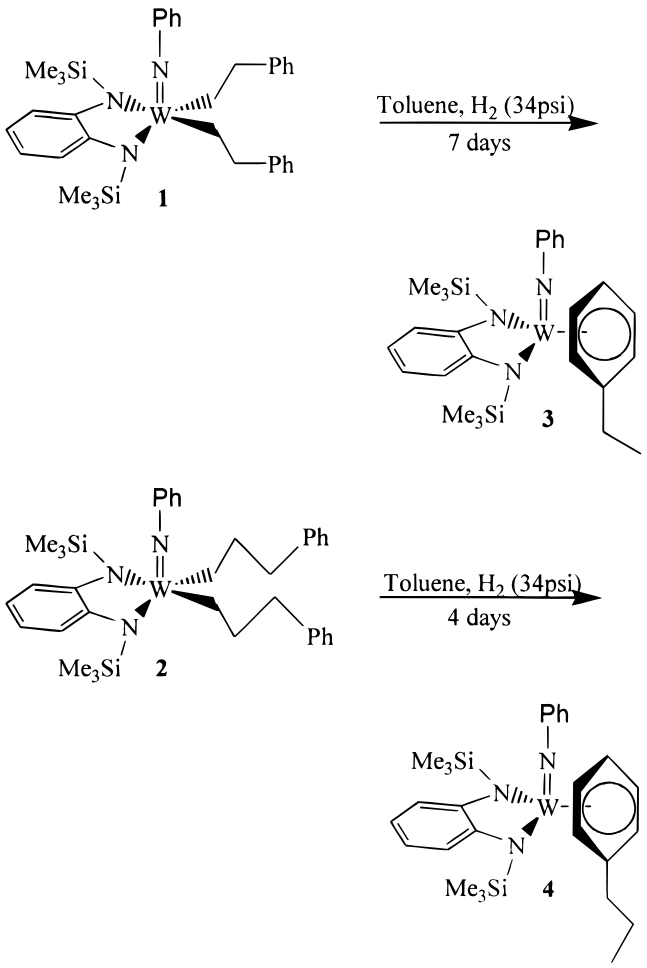
*Summary: The synthesis of the d^2 arene complexes [W(NPh)(η^6-arene)(o-($Me_3SiN)_2C_6H_4$)] (arene = C_6H_5Et (**3**), C_6H_5Pr (**4**)) by the room-temperature hydrogenolysis of the dialkyl complexes [W(NPh)(o-($Me_3SiN)_2C_6H_4$)($R)_2$] (R = CH_2CH_2Ph (**1**), $CH_2CH_2CH_2Ph$ (**2**)) is described. The ethylbenzene complex **3** reacts with diphenylacetylene, giving the metallacyclopent-3-ene complex **5**.*

The chemistry of metal complexes containing six-membered π-arene ligands has been thoroughly developed since Fischer and Hafner first characterized Cr(η^6-benzene)$_2$.[1] Stable arene complexes have now been characterized for virtually all of the transition metals.[2] Although most early examples were limited to compounds containing metals in low oxidation states,[3] more recently d^0 metal arenes have become more common.[4] Surprisingly, examples of d^2 arene complexes have been limited to [Zr(η^6-C_6H_5Me)($PMe_3)_2Cl_2$][5] and [Ti(η^6-C_6H_6)-($AlCl_3)_2Cl_2$],[6] formed from the reduction of the appropriate metal halide in the presence of an arene, and [Ta-(η^6-C_6Me_6)($OAr)_2$Cl],[7] formed from the metal-mediated cyclotrimerization of 2-butyne. Following earlier work from our group on the reactivity of β-hydrogen-containing W(VI) dialkyl complexes of the type [W(NPh)(*o*-(Me_3-$SiN)_2C_6H_4)R_2$] (where R = CH_2CH_3, CH_2CMe_3)[8] with H_2,[9] we report the synthesis of d^2 tungsten arene complexes with the general formula [W(NPh)(η^6-arene)-(*o*-($Me_3SiN)_2C_6H_4$)] (arene = $CH_3CH_2C_6H_5$, CH_3CH_2-$CH_2C_6H_5$) and their reaction with diphenylacetylene.

Scheme 1



Room-temperature hydrogenolysis (34 psi, H_2) of a toluene solution of [W(NPh)(*o*-($Me_3SiN)_2C_6H_4$)(CH_2-$CH_2C_6H_5)_2$] (**1**) or [W(NPh)(*o*-($Me_3SiN)_2C_6H_4$)(CH_2CH_2-$CH_2C_6H_5)_2$] (**2**) (Scheme 1) results in a slow color change from orange to dark purple over several days. From this solution, the d^2 arene complexes [W(NPh)(η^6-ethylbenzene)(*o*-($Me_3SiN)_2C_6H_4$)] (**3**) and [W(NPh)(η^6-propylbenzene)(*o*-($Me_3SiN)_2C_6H_4$)] (**4**) (Scheme 1) can be isolated as dark purple solids. Compounds **3** and **4** are indefi-

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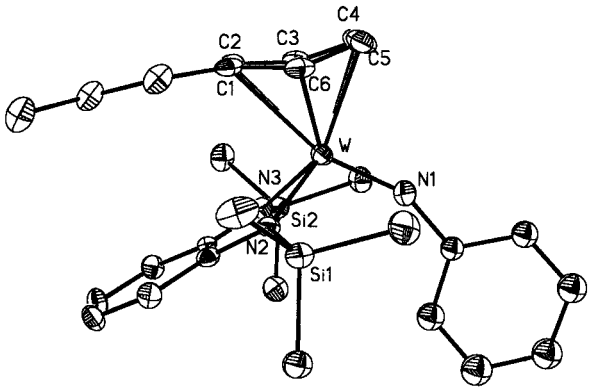
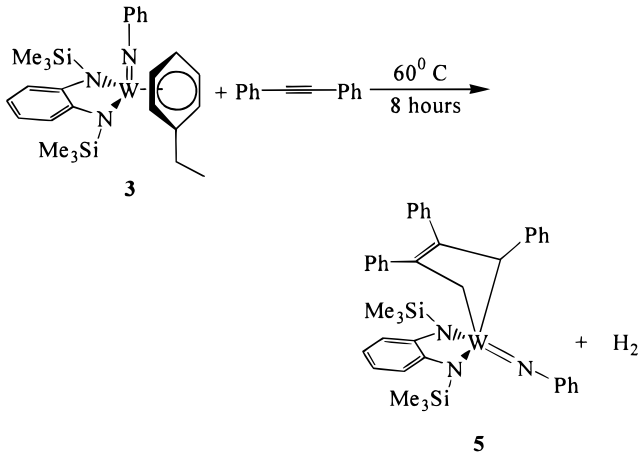


Figure 1. Molecular structure of W(NPh)(η^4-propylbenzene)(*o*-$(Me_3SiN)_2C_6H_4$) (**4**), showing 40% thermal ellipsoids and the atom-labeling scheme. The silylmethyl hydrogen atoms have been removed for clarity. Selected bond distances (Å): W−N(1), 1.762(4); W−N(2), 2.057(4); W−N(3), 2.056(4); W−C(1), 2.533(5); W−C(2), 2.503(5); W−C(3), 2.251(5); W−C(4), 2.363(5); W−C(5), 2.382(5); W−C(6), 2.267(5); C(1)−C(2), 1.371(6); C(2)−C(3), 1.459(7); C(3)−C(4), 1.416(7); C(4)−C(5), 1.372(7); C(5)−C(6), 1.434(7); C(6)−C(1), 1.459(7). Selected bond angles (deg): W−N(1)−C(7), 155.2(6); N(1)−W−N(2), 102.50(16), N(1)−W−N(3), 103.44(16); N(3)−W−N(2), 77.66(14).

Scheme 2



nitely stable at room temperature in the solid state when stored under an inert atmosphere. In addition, solutions of both **3** and **4** display surprising stability toward arene−arene exchange reactions which have been observed to readily occur for analogous molybdenum arene complexes,[10] suggesting a more robust interaction between tungsten and the arene ring. The new π-bound arene ring is clearly indicated in the ^{1}H NMR spectra of **3** and **4**. The aromatic resonances of the coordinated ring display typical upfield chemical shifts (δ 4.27 (t), 4.65 (d), 4.73 (t) for **3** and δ 4.29 (t), 4.68 (d), 4.74 (t) for **4**) associated with arene complexes due to the depletion of π-electron density from the ring upon coordination to the metal center.[2]

Single crystals of **4** suitable for an X-ray diffraction study were obtained through slow evaporation of a concentrated C_6D_6 solution of **4**.[11] The crystal structure of **4** shows that the arene ring is coordinated in an η^4 fashion. The W−C distances of four of the ring carbons, 3 (2.251 Å), 4 (2.363 Å), 5 (2.382 Å), and 6 (2.267 Å),

(10) Ortiz, C. G.; Boncella, J. M. Unpublished results.

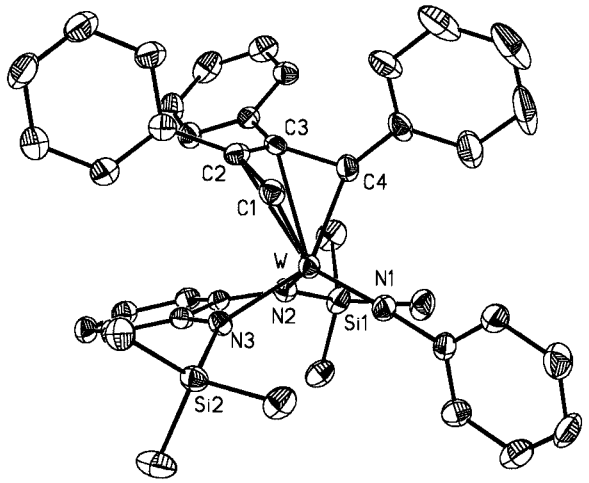


Figure 2. Molecular structure of the W metallacyclopent-3-ene complex **5**, showing 40% thermal ellipsoids and the atom-labeling scheme. All hydrogen atoms have been removed for clarity, except those of the metallacycle. Selected bond distances (Å): W−N(1), 1.745(3); W−N(2), 2.034(3); W−N(3), 2.037(3); W−C(1), 2.162(4); W−C(2), 2.589(4); W−C(3), 2.582(3); W−C(4), 2.204(4); C(1)−C(2), 1.497(5); C(2)−C(3), 1.364(5); C(3)−C(4), 1.495(5). Selected bond angles (deg): W−N(1)−C(24), 176.2(3); C(1)−W−C(4), 76.97(15); N(2)−W−N(3), 79.43(12).

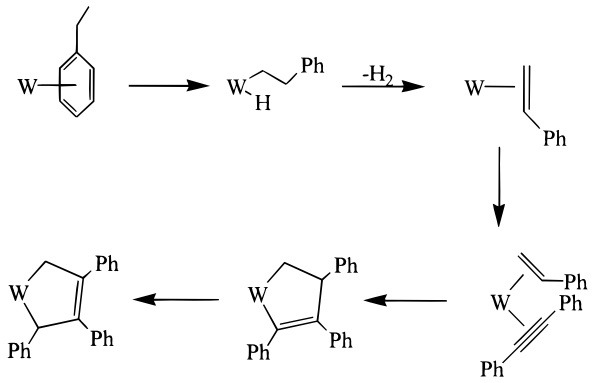
are significantly shorter than those for ring carbons 1 (2.533 Å) and 2 (2.503 Å) (Figure 1). As a result, a considerable distortion from planarity of the coordinated arene ring is observed (the angle between the planes formed by C2−C1−C6−C5 and C2−C3−C4−C5 is 20.4°). Furthermore, the short ring C−C distances for C4−C5 (1.372 Å) and C1−C2 (1.371 Å), consistent with C−C double bonds, coupled with the fold of the arene ring indicate that there is a significant disruption of aromaticity upon coordination. Overall, the interaction of the arene ring with the tungsten center in **4** is similar to the ($\sigma_2\pi$) bonding extreme of a 1,3-butadiene−metal interaction.[12] Despite the inherent stability of the coordinated arene ring in **3** and **4**, compound **3** was found to undergo a unique coupling reaction with diphenylacetylene.

Thermolysis (60 °C) for 12 h of a toluene solution containing equimolar amounts of **3** and PhC≡CPh afforded the W(VI) metallacyclopent-3-ene species [*o*-$(Me_3SiN)_2C_6H_4$)(NPh)W$\overline{CH_2C(Ph)=C(Ph)CHPh}$] (**5**) in 54% yield (Scheme 2). The ^{1}H NMR of **5** displays two doublet resonances (2.58 and 2.81 ppm, ^2J = 10.8 Hz) and a singlet resonance (4.77 ppm, ^2J(W−H) = 4.8 Hz), for the α-CH_2 and α-CH protons of the metallacycle, respectively. In the $^{13}C\{^1H\}$ NMR spectrum the two carbons bonded to the metal center resonate at δ 57.74 ppm as a triplet with $^1J(^{13}C-^1H)$ = 143.0 Hz and 73.72 ppm as a doublet with $^1J(^{13}C-^1H)$ = 137.36 Hz.[13] An X-ray diffraction study of a single crystal of **5** grown by slow evaporation of a pentane solution of **5** (Figure 2) confirmed the metallacyclopent-3-ene structure which was deduced from the spectroscopic data.[14]

(11) Crystal data for **4**: $C_{27}H_{39}N_3Si_2W$, M_r = 645.64, monoclinic, $P2_1/n$, dark red-purple, a = 12.1874(5) Å, b = 15.6037(7) Å, c = 14.5968(6) Å, α = 90°, β = 94.317(1)°, γ = 90°, 173(2) K, Z = 4, R = 0.0371 with GOF = 0.961 on F^2.

(12) Maslowsky, E. *J. Chem. Educ.* **1992**, *70*, 980.

Scheme 3



It has been shown that early-transition-metal complexes facilitate the metal-mediated [2 + 2] cycloaddition of alkynes and olefins to generate metallacyclopentenes.[15] The formation of **5** appears to proceed by initial C−H bond activation of the coordinated ethylbenzene in **3**, followed by reductive elimination of H_2 (Scheme 3). The intermediate η^2-styrene complex then undergoes the expected cycloaddition with PhC≡CPh followed by rearrangement[16] to generate **5**. Support for the proposed formation of the η^2-styrene intermediate through loss of H_2 comes from reactions of the mixed-dialkyl tungsten complex [W(NPh)(*o*-$(Me_3SiN)_2C_6H_6$)-($CH_2CH_2C_6H_5$)(Me)] with PhC≡CPh, in which **5** is formed in high yield.[17]

We are currently investigating the scope of this type of chemistry with several different mixed-dialkyl systems and a variety of unsaturated substrates. Our interest in the initial coupling of coordinated ethylbenzene with PhC≡CPh focuses on the observed loss of H_2. Further studies into the mechanism for this process and the possible generality of the dehydrogenation of the arene side chain are currently in progress.

Acknowledgment. We wish to acknowledge the National Science Foundation (Grant No. CHE-9523279) for the support of this work. K.A.A. wishes to acknowledge the National Science Foundation and the University of Florida for funding of the purchase of the X-ray equipment.

Supporting Information Available: Figures giving 300 MHz ^{1}H NMR spectra of **2**−**5** and tables of crystal data, structure solution and refinement, atomic coordinates, bond lengths and angles, and anisotropic thermal parameters for **4** and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) The $^1J(^{13}C-^1H)$ coupling constants measured for the α-carbons of **5** (143 and 137 Hz) are similar to those for strongly $\sigma_2\pi$-bound group 4 and 5 butadiene complexes (138−150 Hz):[13a−c] (a) Yasuda, H.; Tatsumi, K.; Nakamura, A. *Acc. Chem. Res.* **1985**, *18*, 120. (b) Kruger, C.; Muller, G.; Erker, G.; Dorf, U.; Engel, K. *Organometallics* **1985**, *4*, 215. (c) Yasuda, H.; Tatsumi, K.; Okamoto, T.; Mashima, K.; Lee, K.; Nakamura, A.; Kai, Y.; Kanehisa, N.; Kasai, N. *J. Am. Chem. Soc.* **1985**, *107*, 2410.

(14) Crystal data for **5**: $C_{40}H_{46}N_3Si_2W$, $M_r = 808.83$, monoclinic, $P2_1/n$, dark red-brown, $a = 18.4684(8)$ Å, $b = 20.4038(9)$ Å, $c = 20.9892(9)$ Å, $\alpha = 90°$, $\beta = 109.780(1)°$, $\gamma = 90°$, 173(2) K, $Z = 8$, $R = 0.0328$ with GOF = 1.072 on F^2.

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(16) Reaction of an analogous Mo styrene complex with PhC≡CPh at room temperature initially (after 2 h) yields a metallacyclopent-2-ene. Over a period of 2 days this product is slowly converted to a metallacyclopent-3-ene analogous to **5**, suggesting the final step in the formation of **5** is rearrangement of the metallacyclopent-2-ene.

(17) Thermolysis (70 °C) of a toluene solution of the mixed-dialkyl complex [W(NPh)(*o*-$(Me_3SiN)_2C_6H_6$)($CH_2CH_2C_6H_5$)(Me)] yields an η^2-styrene complex with the liberation of CH_4. In agreement with the proposed mechanism for the formation of **5**, thermolysis of [W(NPh)-(*o*-$(Me_3SiN)_2C_6H_6$)($CH_2CH_2C_6H_5$)(Me)] in the presence of 1 equiv of PhC≡CPh produces **5** in good yield.