Structure Elucidation

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# Unusual Thermal Reactivity of [W(≡CPh)(NCMe)($\eta^2$-$C_{60}$)($\eta^5$-$C_5Ph_5$)] in Chlorobenzene Involving Activation of All Ligands**

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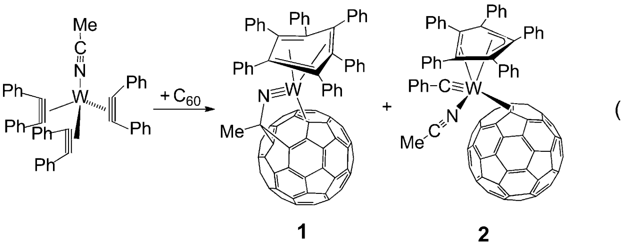
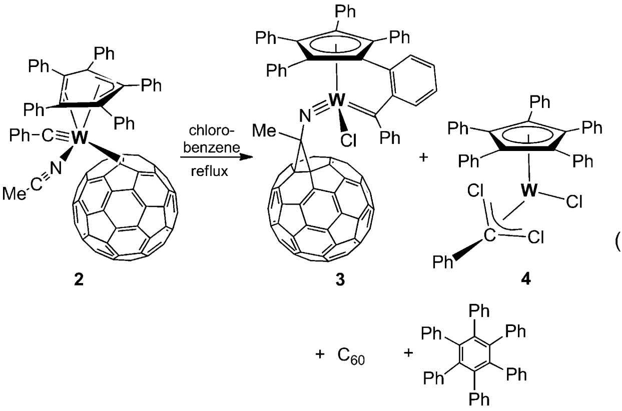
*In memory of Yasushi Mizobe*

One of the most fascinating aspects pertaining to organometallic chemistry concerns the C–H bond activation and C–C bond formation of organic substrates at transition-metal centers,[1] because these processes hold the promise of leading to efficient and catalytic methods for the selective conversion of hydrocarbon feedstocks into functionalized organic compounds.[2] In particular, complexes containing metal–carbon multiple bonds (alkylidenes and alkylidynes) are important and undergo numerous reactions, several of which are useful in alkyne/alkene metathesis[3] and cyclization reactions,[4] as well as in the synthesis of complicated organic molecules.[5] Recently, the availability of gram quantities of the fullerene $C_{60}$ has facilitated the study of the reactivity of this intriguing molecule.[6,7] Subsequent work has been extensive, and many attempts have been made to coordinate fullerenes to metals,[8] and to incorporate metal-binding groups into their structures.[9] Investigation of the reactivity of fullerene-bound organometallic compounds also becomes an attractive research topic.[10] It was recently described that $C_{60}$ induced alkyne–alkyne coupling and alkyne scission reactions of [W(NCMe)($C_2Ph_2$)$_3$] to produce [W($\eta^3$-NCMe$C_{60}$)($\eta^6$-$C_6Ph_6$)] (**1**) and [W(≡CPh)(NCMe)($\eta^2$-$C_{60}$)($\eta^5$-$C_5Ph_5$)] (**2**) [Eq. (1)].[11] Compound **2** contains a terminal benzylidyne moiety and might be able to undergo additional ligand activation/insertion reactions. Presented herein are results concerning the thermal reactivity of **2**, which leads to quite striking products.



(1)

A chlorobenzene solution of compound **2** was heated to reflux under dinitrogen to result in a change in the color of the solution from dark green to brown. The products were separated by thin-layer chromatography (TLC; silica gel) to afford $C_{60}$ (67 %), [WCl(NC(Me)$C_{60}$)($\eta^6$-$C_5Ph_4$(*o*-$C_6H_4$)CPh)] (**3**; 25 %), [WCl($\eta^3$-$CCl_2Ph$)($\eta^5$-$C_5Ph_5$)] (**4**; 18 %), and $C_6Ph_6$ (35 %) [Eq. (2)]. For comparison, thermolysis of **2** was carried out in refluxing xylene to yield $C_{60}$ (75 %), $C_6Ph_6$ (42 %), and a new olive-colored complex, which was characterized as [WH(NC(Me)$C_{60}$)($\eta^6$-$C_5Ph_4$(*o*-$C_6H_4$)CPh)] (**5**; 25 %), and converted into **3** in refluxing chlorobenzene. Two reaction routes, depicted in Scheme 1, can be proposed. Apparently, thermal reaction of **2** is dominated by dissociation of the labile acetonitrile and the weakly coordinated $C_{60}$ ligands, thus likely generating the reactive species [W(≡CPh)($\eta^5$-$C_5Ph_5$)] (**A**), which can either abstract three chlorine atoms from the solvent to yield **4**, or have the benzylidyne ligand inserted into the cyclopentadienyl ring to release hexaphenylbenzene. In contrast, C–H bond activation of one periphery phenyl group on the tungsten atom, with concomitant [1+2] cycloaddition of the acetonitrile ligand to one 6:6-ring junction of $C_{60}$, would generate **B**, which would then undergo benzylidyne insertion to afford **5**. Subsequent H/Cl atom exchange from **5** to **3** probably involves oxidative addition of one Ph–Cl bond and reductive elimination of a benzene molecule.



(2)

Compound **3** forms an air-stable, dark-brown solid. The MALDI mass spectrum shows the molecular ion peak at *m*/*z* 1513, and the isotope distribution matches the calculated pattern for the compound containing one chlorine atom. Crystals of **3** suitable for an X-ray diffraction study were grown from toluene/$CS_2$/*n*-hexane (1:1:1) at room temperature. An ORTEP diagram of **3** is depicted in Figure 1, where the tungsten atom is linked to an imido, a benzylidene, and an

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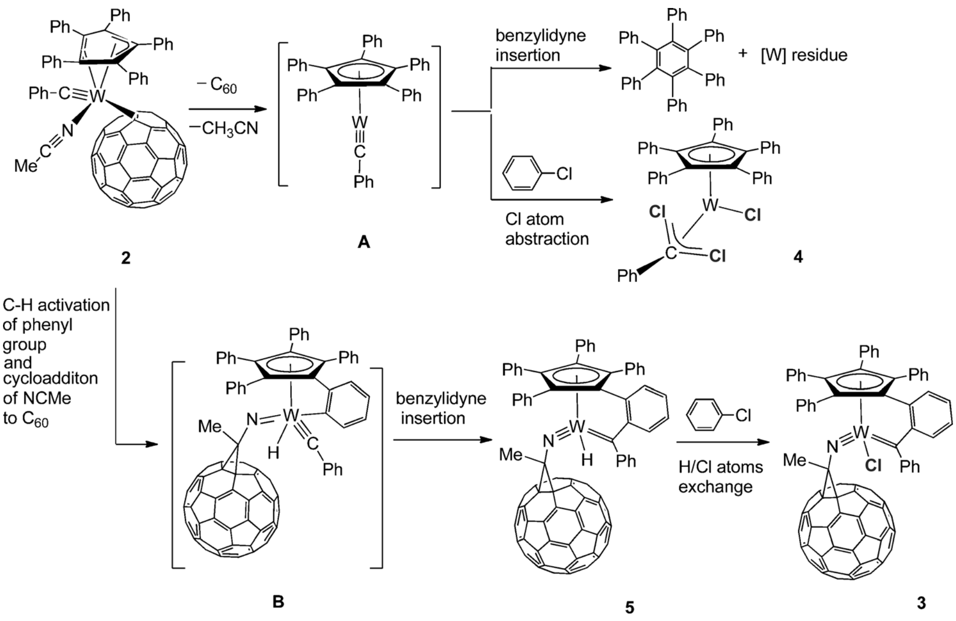

***Scheme 1.*** Proposed pathways for the thermal reaction of **2**.

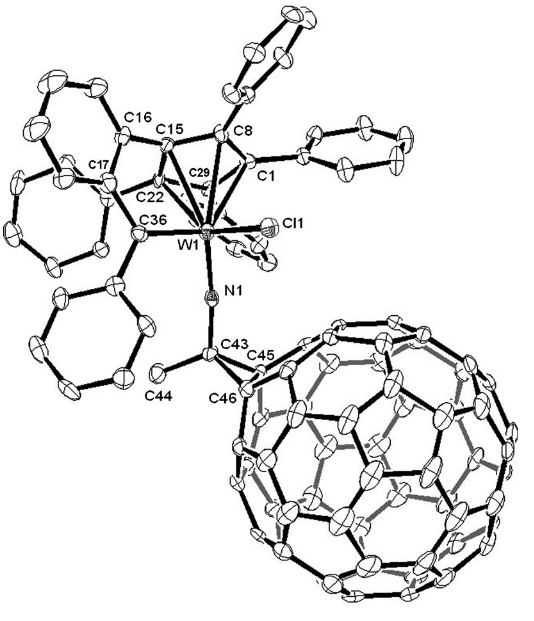

***Figure 1.*** Molecular structure of **3**. Thermal ellipsoids shown at 30% probability. Selected bond distances [Å]: C1–W1 2.449(7), C8–W1 2.506(7), C15–W1 2.432(7), C22–W1 2.351(8), C29–W1 2.370(7), C36–W1 2.003(8), N1–W1 1.747(6), Cl1–W1 2.367(2), C1–C8 1.44(1), C1–C29 1.46(1), C8–C15 1.401(9), C15–C22 1.46(1), C22–C29 1.454(9), C43–C44 1.51(1), C43–C45 1.54(1), C43–C46 1.55(1), C45–C46 1.64(1), N1–C43 1.435(9). Selected bond angles [°]: C36-W1-N1 100.4(3), C36-W1-Cl1 96.3(2), Cl1-W1-N1 101.3(2), W1-N1-C43 173.3(5), N1-C43-C44 115.7(6), N1-C43-C45 114.6(6), N1-C43-C46 114.7(6).

$\eta^5$-$C_5Ph_5$ group, as well as a chlorine atom. The cyclopentadienyl ring is coordinated to the tungsten atom asymmetrically, with the C-W bond lengths varying from 2.351(8) Å for C22-W1 through 2.506(7) Å for C8-W1 (average 2.422 Å), and the C-C bond lengths within the ring are in the range of 1.401(9)–1.46(1) Å. It is interesting that the *ortho* C–H bond of one phenyl group is activated and coupled with the benzylidyne carbon atom to generate a benzylidene species with the W1-C36 double bond distance of 2.003(8) Å, which is lengthened by approximately 0.2 Å compared to that of the W≡C distance in **2** (1.78(1) Å).[11] Moreover, the $C_{60}$ molecule is not ligated to the tungsten atom, but to one 6:6-ring junction undergoing a [1+2] cycloaddition with the acetonitrile ligand to yield an imido moiety. The distances C43-C44 1.51(1) Å, C43-C45 1.54(1) Å, and C43-C46 1.55(1) Å are typical C–C single bond lengths, whereas the C45-C46 distance (1.64(1) Å) is substantially longer, likely due to the ring strains. We note that the acetonitrile ligand is inserted into one 6:5-ring junction in **1** to give a ring-opened fulleroid structure.[11] One chlorine atom is bonded to tungsten with Cl1-W1 2.367(2) Å, and is presumably abstracted from the chlorobenzene solvent. Furthermore, for the complex to satisfy the 18-electron rule, the resulting imido RN group is best considered as a four-electron donor, thus giving rise to a formal N≡W bond.[12] This feature is supported by the short N1-W1 distance of 1.747(6) Å, whereas the N–W single bond distance is 2.17(3) Å for $[W(NCMe)(C_2Ph_2)_3]$.[13] A related conversion of nitriles into imidos through azavinylidenes in tungsten carbonyl complexes was previously reported.[14]

The $^{13}C\{^1H\}$ NMR spectrum of **3** displays a downfield resonance at $\delta = 272.4$ ppm for the benzylidene carbon atom. Because of the chirality at the pseudo-tetrahedral tungsten atom and the rigidity of the complex, signals at $\delta = 124.3$, 124.0, 119.5, 118.9, and 116.7 ppm were recorded for the five cyclopentadienyl ring carbon atoms, signals at $\delta = 82.3$, 80.7, and 68.6 ppm for the three cyclopropanyl carbon atoms, and signals within the range of $\delta = 163.6$–135.9 ppm for the rest of the remaining fifty carbon resonances on the $C_{60}$ core (with some signals being coincident).

Compound **5** is isomeric to **1** and **2**, with the ESI mass spectrum showing the molecular ion peaks around $m/z$ 1477. The $^1H$ and $^{13}C\{^1H\}$ NMR spectra of **5** bear a close resemblance to **3**, except that a far downfield $^1H$ signal at $\delta = 9.16$ ppm with $^{183}W$ satellites ($^1J$(W-H) = 159 Hz) is recorded, and is assigned to the H-W resonance. These spectral data indicate a similar coordination environment for the tungsten atom of **3** and **5**. Although hydride signals are most commonly found upfield of $Me_4Si$ (TMS),[15] this is not always the case. For example, a hydride resonance at $\delta = 20.4$ ppm has been reported for $[W_2H(\mu\text{-}C_4Me_4)(\mu\text{-}CPh)(O\textit{i}Pr)_4]$,[16] and at $\delta = 10.8$ ppm with $^1J$(W-H) = 115 Hz for [TpWH(CO)(PhC≡CMe)].[17]

Compound **4** forms an air-stable, greenish brown crystalline solid. The ESI mass spectrum displays the molecular ion peaks around $m/z$ 823, and the isotope distribution matches the calculated pattern. Crystals of $\mathbf{4}{\cdot}CS_2$ suitable for an X-ray diffraction study were grown from $CS_2$/$n$-hexane (1:1) at −20 °C. The Cl2 and C36–C42 atoms are disordered at their sites, and are shown with 65 % occupancy for **4** in Figure 2 a.

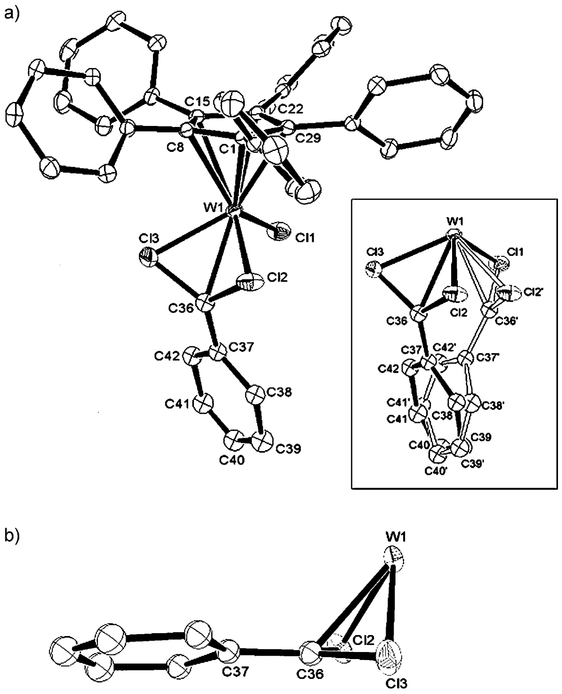

***Figure 2.*** a) Molecular structure of $\mathbf{4}{\cdot}CS_2$. Thermal ellipsoids shown at 30 % probability. The hydrogen atoms and crystal solvent have been artificially omitted. The phenyldichloromethyl group is disordered at two sites (inset), and the ORTEP diagram displays the atoms with 65 % occupancy; b) Skeleton of the $[PhCCl_2W]$ unit, showing an $\eta^3$-allyl-type bonding structure. Selected bond distances [Å]: C1–W1 2.446(4), C8–W1 2.433(4), C15–W1 2.368(4), C22–W1 2.390(4), C29–W1 2.395(4), C36–W1 2.252(7), Cl1–W1 2.194(1), Cl2–W1 2.274(2), Cl3–W1 2.266(1), C36–Cl2 1.739(7), C36–Cl3 1.701(7), C1–C8 1.420(6), C1–C29 1.447(6), C8–C15 1.441(6), C15–C22 1.430(6), C22–C29 1.441(6). Selected bond angles [°]: C36-W1-Cl1 91.6(2), C36-W1-Cl2 45.2(2), C36-W1-Cl3 44.2(2), Cl1-W1-Cl2 109.78(6), Cl1-W1-Cl3 108.72(5), Cl2-W1-Cl3 78.33(7), W1-C36-C37 130.5(5).

Overall, the tungsten atom is linked to an $\eta^5$-$C_5Ph_5$ group, a chlorine atom, and a phenyldichloromethyl species. The carbon atoms of the Cp ring are bonded to the tungsten atom asymmetrically, such that the C–W lengths vary from 2.368(4) Å (C15-W1) through 2.446(4) Å (C1-W1), with an average length of 2.407 Å, and the C–C lengths within the ring are in the range of 1.420(6)–1.447(6) Å. The most striking feature of **4** is the phenyldichloromethyl moiety acting as an $\eta^3$ ligand to bind the tungsten atom, with C36-W1 2.252(7) Å, Cl2-W1 2.274(2), and Cl3-W1 2.266(1) Å. Since the C37, C36, Cl2, and Cl3 are essentially coplanar (Figure 2 b) with the bond angles C37-C36-Cl2 122.6(5)°, C37-C36-Cl3 124.4(5)°, and Cl2-C36-Cl3 113.0(4)°, which sum to 360°, this structure can be viewed to have a π-allyl bonding character.[18]

Compound **4** is formally a 17-electron species by counting the neutral $\eta^5$-$C_5Ph_5$ and the $\eta^3$-$CCl_2Ph$ ligand as a five-electron donor and the chlorine atom as a one-electron donor, thus suggesting that it is paramagnetic. This was confirmed by employing a variation of the Evans NMR method[19] which revealed a magnetic moment indicative of one unpaired electron ($\mu_{\text{eff}} = 1.66$ BM). The observed air-stability of this paramagnetic mononuclear complex can be attributed to protection by the bulky $C_5Ph_5$ ligand and the electronic stabilization by three π-donating chlorine atoms.

In summary, an unusual thermal reactivity of **2** has been revealed, and it involves C–H bond activation and C–C bond formation within the ligands, and chlorine atom abstraction from the solvent. The [1+2] cycloaddition of acetonitrile to one 6:6-ring junction of $C_{60}$, and the benzylidyne insertion into the cyclopentadienyl ring are novel. Mostly, the air-stable, 17-electron compound **4** bearing an $\eta^3$-$CCl_2Ph$ structure is unprecedented and unique. Finally, this work suggests that chlorobenzene, which has been widely used for the reactions of organometallic compounds and fullerenes because of solubility and temperature concerns, might not be an innocent solvent.[20]

## *Experimental Section*

Details on the reaction procedures, characterization data, and structural determination for the new compounds are given in the Supporting Information. CCDC 837439 for **3** and 837438for **4** contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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