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Coordination and reactivity of functionalized fullerenes, open-cage fullerenes, and endohedral metallofullerenes by organometallic complexes☆

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ABSTRACT

Fullerene adducts, open-cage fullerenes, and endohedral fullerenes represent the fundamental research topics of modified fullerenes. Recently, attachment of metal fragments to the fullerene cages, and investigating their properties and reactivity, becomes an important area within fullerene chemistry. This article provides a brief review of some selected recent advances in organometallic reactions of modified fullerenes with a focus on the work in the author's group.

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Introduction

The discovery of fullerenes in 1985 marked the beginning of a new field of chemical research [1]. Fullerene molecules possess an outer surface available for chemical modification and an inner space available for the encapsulation of a variety of chemical entities [2]. Thereafter the fullerene adducts, open-cage fullerenes, and endohedral fullerenes represent the fundamental research

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topics of modified fullerenes [3,4]. Insight into the coordination behavior of fullerenes was first provided by Fagan and co-workers [5]. Because the π-orbitals within a hexagon of the C_{60} framework are tilted away from the center of the ring, the C_{60} hexagons behave more like a cyclohexatriene unit [6]. Complexation of transition metals to the fullerene core proceeds similar to the well-established reactions of electron-deficient olefins in a *dihapto* manner to one or more π-bonds [7–13].

One of the most fascinating aspects pertaining to organometallic chemists concerns the C–H bond activation and C–C bond formation of organic substrates at transition-metal centers [14–17], because these processes hold the promise of leading to efficient and catalytic methods for the selective conversion of hydrocarbon feedstocks into functionalized organic compounds [18–22]. Investigation of the reactivity of fullerene-bound organometallic compounds also becomes an attractive research topic. Herein I present our recent studies concerning the reactions of organometallic complexes with C_{60}, phosphine-functionalized fullerenes, open-cage fullerenes, and endohedral metallofullerenes.

C_{60}-induced ligand activation reactions of orgnometallic complexes

Steric effects are very important in organometallic chemistry. It is well established that the steric bulk of a particular ligand can influence the bonding, stability, and reactivity of a complex [23]. The cone angle of C_{60} in an η^2-bonding fashion is about 130° (Fig. 1), which is between that measured for *t*-butyl (126°) and η^5-C_5H_5 (136°) groups [24]. Obviously, coordination of such bulky C_{60} molecule should affect the structure and reactivity of the metal complexes and might induce some activation reactions of the ancillary ligands.

Polyalkyne complexes of the type $W(RC{\equiv}CR')_3(CO)$ [25] have attracted much attention owing to their unique structure and mode of bonding [26–28]. We previously described the stepwise alkyne–alkyne coupling reactions with $W(PhC{\equiv}CPh)_3(L)$ (L = CO, NCMe) to lead to the tungstenocene complex $W(\eta^5\text{-}C_5Ph_5)_2$ (Scheme 1) [29–32]. Comparably, the reaction of $W(PhC{\equiv}CPh)_3(CO)$ and C_{60} in refluxing *o*-dichlorobenzene produces $W(CO)(\eta^2\text{-}C_2Ph_2)(\eta^2\text{-}C_{60})(\eta^4\text{-}C_4Ph_4)$ (**1**), $W(\equiv CPh)(CO)(\eta^2\text{-}C_{60})(\eta^5\text{-}C_5Ph_5)$ (**2**), and $W(CO)_2(\eta^5,\eta^3\text{-}C_5Ph_4(o\text{-}C_6H_4)CHPh)$ (**3**) (Scheme 2) [33]. Compound **1** is obtained from [2 + 2] cyclization of two diphenylacetylene ligands, apparently induced by the coordination of C_{60}. Compound **2** contains an η^5-Cp ring and a terminal benzylidyne moiety (≡CPh) from [2 + 2 + 1] cyclization and scission reactions of the three alkyne ligands. Thermolysis of **2** gives **3** by insertion of the benzylidyne group into the C–H bond of one phenyl ring to generate an η^3-benzylic ligand. In contrast, treating $W(PhC{\equiv}CPh)_3(NCMe)$ with C_{60} in refluxing chlorobenzene affords $W(\eta^3\text{-}NC(Me)C_{60})(\eta^4,\eta^2\text{-}C_6Ph_6)$ (**4**) and $W(\equiv CPh)(NCMe)(\eta^2\text{-}C_{60})(\eta^3,\eta^2\text{-}C_5Ph_5)$ (**5**) (Scheme 3) [34]. Compound **4** contains a hexaphenylbenzene ring from cyclization of the three alkyne ligands, and the acetonitrile group is inserted into one 6:5-ring junction on the C_{60} cage to give a ring-opened fulleroid motif. It is noteworthy that the C_6Ph_6 ring is bent by 24° to display an η^4-butadiene+η^2-olefin bonding fashion, likely due to steric repulsions between the phenyl groups and the fullerene ligand. The cyclopentadienyl ring of **5** is not planar but displaying an allylic distortion.

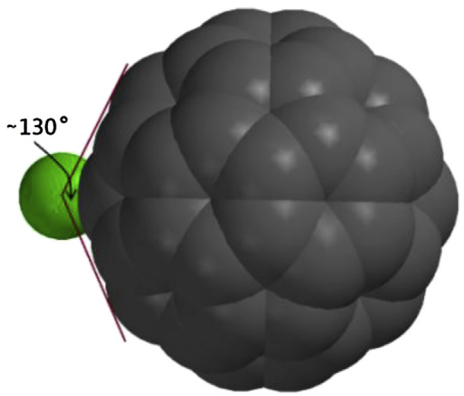

Fig. 1. Estimated cone angle for the η^2-C_{60} ligand.

Complexes bearing M≡C triple bonds are important catalysts for alkyne–metathesis reactions [35–37]. Compound **5** contains a terminal benzylidyne ligand and reveals an unusual thermal reactivity that involves activation of all ligands to give C_6Ph_6, $WCl(NC(Me)C_{60})(\eta^6\text{-}C_5Ph_4(o\text{-}C_6H_4)CPh)$ (**6**), and $WCl(\eta^3\text{-}CCl_2Ph)(\eta^5\text{-}C_5Ph_5)$ (**7**) (Scheme 4) [38]. Formation of C_6Ph_6 is interesting, presumably from insertion of the CPh moiety into the C_5Ph_5 ring. In compound **6** the CPh ligand is coupled with one phenyl ring to form a benzylidene species. It is noteworthy that compound **7** is formally a 17-electron paramagnetic species, of which the phenyldichloromethyl moiety acts as an η^3-allylic type ligand to donate five electrons to the tungsten center.

The complexes $M(CO)_2(\eta^3\text{-}PCHO)_2$ (M = Mo, W; PCHO = $PPh_2(o\text{-}C_6H_4CHO)$) bear two aldehyde groups in a unique π-bonding fashion [39,40]. Reaction of C_{60} and $Mo(CO)_2(\eta^3\text{-}PCHO)_2$ in refluxing chlorobenzene leads to coupling of the two aldehyde groups and eliminating two oxygen atoms to generate the trans-alkene complex $Mo(CO)_2(\eta^4\text{-}(PPh_2(o\text{-}C_6H_4)CH)_2)(\eta^2\text{-}C_{60})$ (**8**) (Scheme 5) [41], which mimics the organic McMurry reaction [42].

Coordination of arene molecule to a transition metal in an η^6-mode is common [43–45]. However, due to the surface curvature, the η^6-bonding mode of fullerenes to a single metal atom (or ion) is difficult to form. Instead, reaction of C_{60} with $M_3(CO)_{12}$ (M = Ru, Os) produces $M_3(CO)_9(\eta^2,\eta^2,\eta^2\text{-}C_{60})$ [46,47], and reaction of $C_{60}Me_5H$ with $Ru_3(CO)_{12}$ produces $Ru_3(CO)_9(\eta^2,\eta^2,\eta^2\text{-}C_{60}Me_5H)$ [48]. In these complexes, one hexagon of fullerene caps the triangular face of the metal cluster. In contrast, the reaction of $Os_3(CO)_{12}$ and C_{60} in the presence of benzonitrile affords $Os_3(CO)_9(\eta^2,\eta^2,\eta^2\text{-}C_{60})$ (**9**), $Os_3(CO)_5(\mu\text{-}NCHPh)(\mu_3,\eta^5\text{-}NCPhC_{60}C(C_6H_4)N)(\eta^2,\eta^2\text{-}C_{60})$ (**10**), and $Os_3(CO)_4(NCPh)(\mu\text{-}NCHPh)(\mu_3,\eta^5\text{-}NCPhC_{60}C(C_6H_4)N)(\eta^2,\eta^2\text{-}C_{60})$ (**11**) (Scheme 6) [49]. In compounds **10** and **11**, 1,4-addtion of two benzonitrile molecules to the C_{60} cage occurs to generate an unprecedented fullerodiketimide ligand, while the other C_{60} is bonded to the Os_3 cluster in an uncommon η^2:η^2-fashion.

It is shown that the coordinated fullerene molecule can induce coupling of the ancillary ligands surrounding the metal center, or react with the ligands to generate a new fullerene derivative. This may provide an attractive strategy for activation of small organic substrates and for functionalization of fullerenes.

Preparation and reactions of fullerophosphines with organometallic complexes

With the development of an extensive organic chemistry of fullerenes, it is now possible to construct a variety of modified fullerenes that incorporate metal-binding group into their structures [50–52]. The syntheses of such fullerene-containing ligands offer the potential to exploit the chemical reactivity, redox and electron-acceptor characteristics, photochemical behavior, and novel structural features that a fullerene group provides [53–56].

The phosphine-functionalized fullerene $(PPh_2)C_{60}H$ (**12**) is prepared by addition of a phosphide nucleophile to C_{60} and subsequent protonation of the resulting anion [57]. Reaction of **12** and

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