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Organometallic Chemistry at the Edge of Polycyclic Aromatic Carbon Compounds: Cp$_2$Zr(1,9-anthracendiyl)

Paul R. Sharp

Department of Chemistry
University of Missouri-Columbia
Columbia, Missouri 65211

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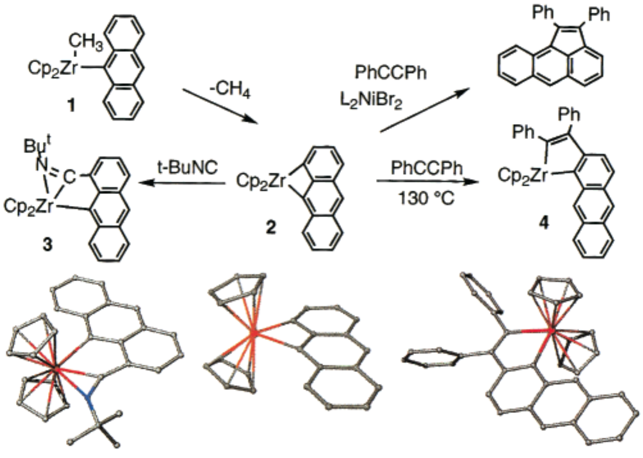
Polycyclic aromatic carbon compounds,[1] including fullerenes and carbon nanotubes,[2] are a fascinating and potentially useful class of compounds. Although many such compounds have been prepared there is still a great need for the development of facile and selective syntheses and derivatization techniques. Transition metal organometallic chemistry offers much in this area. However, most transition metal organometallic chemistry with polycyclic aromatic carbon compounds involves metal coordination to the π-face of the polycyclic.[3] In contrast, complexes with transition metals multiply coordinated to the edge of polycyclic aromatic carbon compound are rare.[4,5] Zirconocene chemistry at the edge of the anthracene system is reported herein as a first step in the development of this potentially rich and useful chemistry (Scheme 1).

Following procedures developed for the synthesis of zirconocene benzyne complexes,[6] Cp$_2$ZrMeCl was treated with 9-lithioanthracene in diethyl ether. A smooth reaction occurs yielding yellow Cp$_2$ZrMe(9-anthracenyl) (**1**).[7] Complex **1** is unstable and slowly eliminates methane at 25 °C producing the orange four-membered metallacycle complex Cp$_2$Zr(1,9-anthracendiyl) (**2**)[8] in an 80% yield. (Complex **1** is usually not isolated but allowed to decompose to **2** in the reaction mixture.) An X-ray crystal structure determination confirmed the identity of **2** establishing abstraction of a *peri*-hydrogen (γ-hydrogen) by the departing methyl group. The structure is similar to that observed for Cp$_2$Ti(1,8-naphthadiyl) prepared from Cp$_2$TiCl$_2$ and 1,8-magnesionaphthalene and represents only the second report of these types of four-membered metallacycles.[5] The reaction chemistry of such complexes has not previously been investigated and proves to be extensive for **2** (Scheme 1).

Scheme 1



Addition of *t*-BuNC to a yellow toluene solution of **2** rapidly gives the red insertion product Cp$_2$Zr(η^3-NC(t-Bu)C$_{14}$H$_8$) (**3**)[9] in a 91% yield. NMR data and an X-ray structure determination indicate a regioselective insertion into the more exposed Zr−C bond of **2** at the 1-position. A rapid reaction of **2** with CO gives an insoluble red powder that probably has a similar structure but the product was not further characterized.

Yellow solutions of **2** react with PhCCPh in toulene or benzene at 130 °C (24 h) yielding a red-orange product (83% yield) that was thought to be a six-membered zirconacycle insertion product. However, an X-ray crystal structure determination revealed the unexpected formation of the five-membered zirconacycle **4** (Scheme 1) where derivatization of the anthracene unit is no longer at the 1,9-positions but at the 1,2-positions.[10] Kinetic experiments revealed that the reaction is zero order in alkyne and first order in **2** suggesting that **2** undergoes a rearrangement prior to reaction with the alkyne. A likely rearrangement product consistent with the formation of **4** is the anthracyne complex **5** (Scheme 2). Zirconocene aryne complexes are known to insert alkynes. Formation of **5** is supported by the observation of a ^{31}P NMR signal (−3.9 ppm) in the region expected for an aryne PMe$_3$ adduct[11] when **2** is heated at 130 °C in the presence of PMe$_3$. The PMe$_3$ adduct of **5** cannot be isolated as it decomposes at these temperatures. A possible rearrangement pathway is addition of a solvent C−H bond across the Zr−C(9) bond of **2** (Scheme

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[7] Data for **1**: ^{1}H NMR (250 MHz, C$_6$D$_6$) δ 8.16 (s, 1H), 8.03−7.91 (m, 2H), 7.56−7.22 (m, 6H), 5.79 (s, 10H), 0.46 (s, 3H).

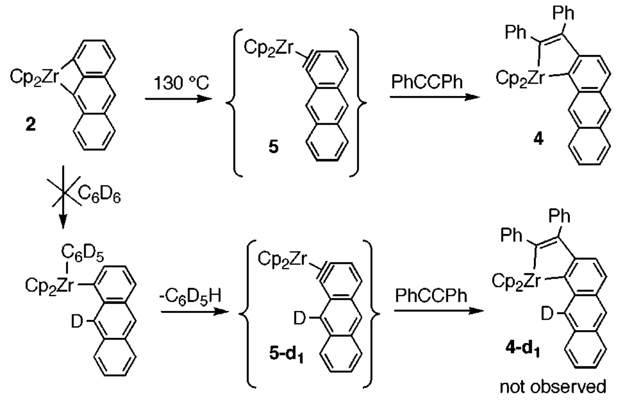
[8] Data for **2**: ^{1}H NMR (250 MHz, C$_6$D$_6$) δ 8.25 (s, 1H), 8.04 (d of m, $J = 8$ Hz, 1H), 7.95−7.90 (m, 3H), 7.58−7.44 (m, 3H), 5.66 (s, 10H). ^{13}C NMR (C$_6$D$_6$) δ 194.7, 190.2 (Zr−C), 138.1, 133.1, 129.7, 128.7 (C), 135.0, 131.7, 129.9, 127.1, 127.0, 126.1, 126.0, 124.7 (CH), 110.8 (Cp). X-ray (Bruker Smart CCD, 173 K): monoclinic, $P2_1/n$, $a = 11.3333(9)$ Å, $b = 12.5274(10)$ Å, $c = 24.280(2)$ Å, $\beta = 90.6420(10)°$, 7578 data, $R1 = 0.0272$.

[9] Data for **3**. ^{1}H NMR (250 MHz, C$_6$D$_6$) δ 8.31 (s, 1H), 8.24 (d, $J = 8.7$ Hz, 1H), 8.15 (d, $J = 8$ Hz, 1H), 8.09 (d, $J = 8$ Hz, 1H), 7.66−7.37 (m, 4H), 5.49 (s, 10H), 1.29 (s, 9H). X-ray (Bruker Smart CCD, 173 K): monoclinic, $P2_1/n$, $a = 13.1333(8)$ Å, $b = 12.1886(8)$ Å, $c = 14.3921(9)$ Å, $\beta = 104.2580(10)°$, 4880 data, $R1 = 0.0293$.

[10] Data for **4**. ^{1}H NMR (250 MHz, C$_6$D$_6$) δ 8.18 (s, 1H), 7.89 (m, 2H), 7.65 (d, $J = 8.8$ Hz, 1H), 7.44 (d, $J = 8.8$ Hz, 1H), 7.37−7.01 (m, 10H), 6.83−6.78 (m, 3H), 6.10 (s, 10H). ^{13}C NMR (C$_6$D$_6$) δ 196.4, 185.4 (Zr−C), 148.8, 142.9, 142.2, 141.8, 141.0, 132.4, 131.9, 131.7 (C), 131.2, 129.1, 128.8, 128.7, 128.39, 128.36, 127.8, 127.1, 127.0, 126.6, 126.1, 125.4, 125.1, 123.6 (CH), 112.7 (Cp). X-ray (Bruker Smart CCD, 173 K): triclinic, $P\bar{1}$, $a = 7.8828(6)$ Å, $b = 15.7871(12)$ Å, $c = 21.9477(17)$ Å, $\alpha = 90.3980(10)°$, $\beta = 92.1130(10)°$, $\gamma = 90.7430(10)°$, 11711 data, $R1 = 0.0403$.

10.1021/ja005512s CCC: $19.00

Scheme 2



2).[12] However, the ^{1}H NMR spectrum of **4** prepared in C_6D_6 is identical with that of **4** prepared in toluene indicating that **4-*d*$_1$** does not form.

A recent report[13] of alkyne cycloaddition reactions of the low reactivity five-membered zirconacycles by transmetalation with Ni(II) inspired an examination of the reaction of **2** with $(Ph_3P)_2NiBr_2$ in the presence of PhCCPh. A rapid reaction ensues and the resulting mixture contains $(Ph_3P)_2Ni(\eta^2\text{-PhCCPh})$,[14] Cp_2ZrBr_2, and deep red diphenylaceanthrylene.[15] The aceanthrylene is readily isolated from the reaction mixture in a 70% yield. As with the five-membered system this process most likely occurs by metallacycle transfer[16] to Ni(II) followed by cycloaddition of the nickelacycle with the alkyne. The formation of the five-membered aceanthrylene ring is notable since five-membered rings are crucial for the development of curvature in polycyclic aromatic carbon compounds.[17]

In summary, derivatization at the edge of anthracene at the 1- and 9-positions has been achieved by metalation and hydrogen abstraction. The reaction chemistry of the resulting four-membered zirconacycle demonstrates insertion chemistry and a novel rearrangement process resulting in derivatization at the 1- and 2-positions of anthracene. Growth of the aromatic ring system and formation of a new five-membered-ring polycyclic aromatic has been accomplished by transfer of the four-membered metallacycle to Ni(II) followed by cycloaddition with an alkyne. Application of this chemistry to larger polycyclic aromatic carbon systems is currently underway.

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