Organometallics **1999,** *18,* 4234−4236

Reaction of Bis(1-substituted-1-boratabenzene)bis(trimethylphosphine)zirconium(II) with 1,3-Diynes

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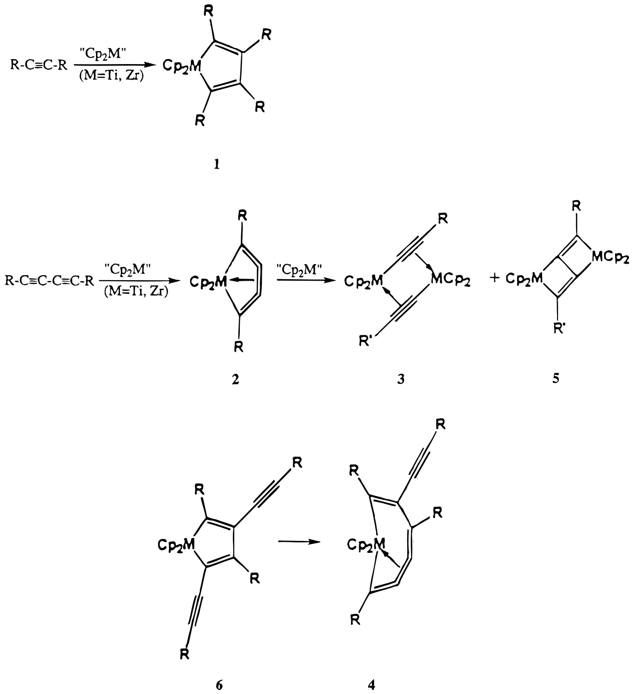
Received July 12, 1999

Summary: 1,4-Diphenyl-1,3-butadiyne readily displaces PMe_3 from bis(N,N-diisopropyl-1-amino-1-boratabenzene)bis(trimethylphosphine)zirconium(II) to afford a 1:1 adduct which contains a 2,5-diphenyl-1-zirconacyclopenta-2,3,4-triene unit.

The reactions of $Cp_2Zr(II)$ derivatives with monoacetylenes usually afford zirconacyclopentadienes **1** (Scheme 1).[1−5] This reaction has proven useful for the synthesis of carbocyclic[6] and heterocyclic[6,7] compounds. On the other hand, the analogous reactions of $Cp_2Zr(II)$ compounds with 1,3-diynes are more complex. Depending upon conditions of the reaction and diyne substituents, products of type **2**,[8] **3**,[8,9] and **4**[8,10] have been obtained. Closely related reactions of titanocenes with 1,3-diynes are even more complex, affording additional products of type **5**,[11] **6**,[12] and others.[13] It has been suggested that these reactions proceed initially to afford the normal addition products **2** and **6**.[13,14] Subsequent addition of Cp_2M to **2** affords **3** and **5**, while **6** may rearrange to form **4**.[10]

Since 1-substituted-1-boratabenzenes are anionic 6π-electron ligands that form many Cp-like complexes,[15,16] we have undertaken a comparative study of boratabenzene−zirconium coordination chemistry.[17] We recently reported that bis(1-phenylboratabenzene)bis(trimethylphosphine)zirconium(II) (**8**) reacted with acetylene to give adduct **10** in place of the expected zirconacycle **9**.[18,19] We proposed that **9** was formed first followed by transfer of the C_4H_4 unit to one of the boratabenzene rings. We now wish to report that **8** reacts with 1,3-diynes to give zirconacycles **11** (Scheme 2).

Scheme 1



Results and Discussion

The treatment of 1 equiv of 1,4-diphenyl-1,3-butadiyne with **8a** in hexane at 25 °C led to immediate reaction that afforded 86% of the orange crystalline 1:1 adduct

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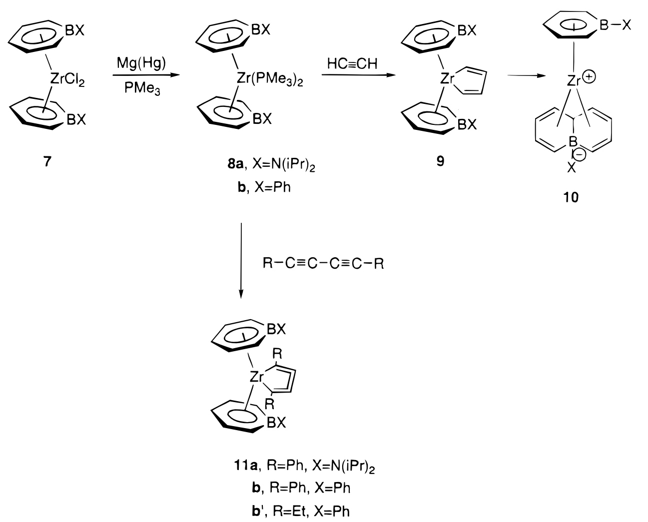
10.1021/om990532s CCC: $15.00
Publication on Web 09/10/1999

Scheme 2



11a. In the same manner the bis(1-phenyl-1-boratabenzene)zirconium derivative **8b** gave adduct **11b** in 76% yield. Similarly, the reaction of **8b** with 3,5-octadiyne afforded **11b′** as an orange oil. However the more stericly hindered 1,4-bis(trimethylsilyl)-1,3-butadiyne failed to react with **8a** or **8b** under identical conditions. The NMR spectra of these 1:1 adducts are highly symmetrical and are consistent with the assignment as metallacumulenes **11**.

To confirm this assignment, we have obtained a crystal structure for **11a**. The molecular structure of **11a** illustrated in Figure 1 shows that the compound has the anticipated 1-zirconacyclopenta-2,3,4-triene unit, which closely resembles the same unit in **2**. Selected bond distances and angles are listed in Table 1. The C−C bond lengths of the zirconacyclopentatriene unit are all similar and are consistent with those of a cumulene. In particular the central (C(31)−C(32)) distance (1.325(8) Å) is double bond like. The atoms Zr, C(30), C(31), C(32), and C(33) are coplanar (±0.02 Å). However the cumulene carbon atoms deviate markedly from linearity, which is indicative of considerable bond angle strain. The constituent p-orbitals of the central C(31)−C(32) double bond must lie in the ring plane and are probably coordinated to Zr.[14,20] The short C−Zr distances (2.273(7), 2.304(7) Å) are consistent with such bonding. This in-plane coordination must be essential for the stability of **11**, as well as **2** and **4**, since small ring cyclic cumulenes are very labile.[21]

The geometry of the diisopropylaminoboratabenzene rings of **11a** are virtually identical to that found for **7a**[22] and similar Zr(IV)[23] derivatives. As has been previously discussed for **7a**,[22] the Zr atom of **11a** is slip distorted away from the B atoms so that the B−Zr distances (2.917(8), 2.965(8) Å) are too long for effective bonding. Thus the Zr atoms are η^5-bound by the ring carbon atoms. It should be noted that the B−Zr distances (2.830(3) Å (av)) of the Zr(II) derivative **8a** are shorter, which suggests η^6-coordination to Zr.[18] Thus the structure of **11a** is more consistent with assignment as a Zr(IV) derivative.

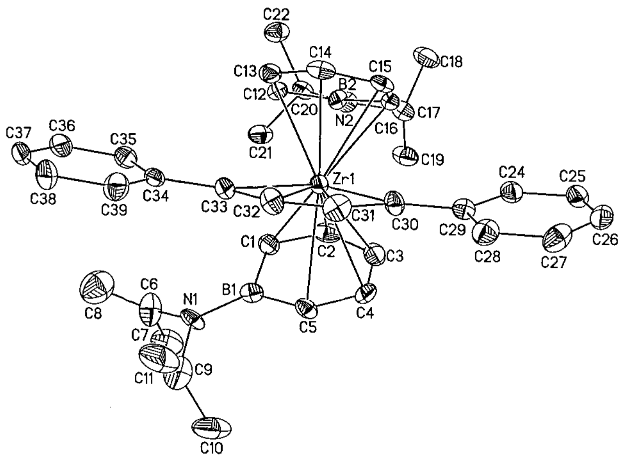


Figure 1. Molecular structure and atom labeling for **11a**.

Table 1. Selected Bond Distances (Å) and Angles (deg) for 11a

Zr(1)−C(32)	2.273(7)	B(1)−C(1)	1.526(10)
Zr(1)−C(31)	2.304(7)	B(1)−C(5)	1.534(9)
Zr(1)−C(30)	2.308(6)	B(2)−C(12)	1.519(9)
Zr(1)−C(33)	2.313(6)	B(2)−C(16)	1.524(8)
Zr(1)−C(3)	2.501(6)	C(1)−C(2)	1.400(9)
Zr(1)−C(14)	2.521(5)	C(2)−C(3)	1.381(10)
Zr(1)−C(2)	2.535(6)	C(3)−C(4)	1.415(10)
Zr(1)−C(15)	2.551(6)	C(4)−C(5)	1.378(9)
Zr(1)−C(4)	2.591(6)	C(12)−C(13)	1.393(8)
Zr(1)−C(13)	2.606(6)	C(13)−C(14)	1.392(9)
Zr(1)−C(1)	2.651(6)	C(14)−C(15)	1.412(8)
Zr(1)−C(16)	2.682(6)	C(15)−C(16)	1.392(8)
Zr(1)−C(5)	2.685(6)	C(29)−C(30)	1.455(8)
Zr(1)−C(12)	2.711(7)	C(30)−C(31)	1.289(8)
Zr(1)−B(2)	2.917(8)	C(31)−C(32)	1.325(8)
Zr(1)−B(1)	2.965(8)	C(32)−C(33)	1.300(8)
N(1)−B(1)	1.429(9)	C(33)−C(34)	1.466(8)
N(2)−B(2)	1.446(8)		
C(31)−C(30)−C(29)	135.2(7)	C(33)−C(32)−C(31)	149.7(8)
C(30)−C(31)−C(32)	145.8(7)	C(32)−C(33)−C(34)	136.5(7)

In summary bis(boratabenzene)bis(trimethylphosphine)zirconium(II) (**8**) reacts with 1,3-diynes to give stable zirconacyclopentatrienes **11**. Adducts analogous to **3**−**6** have not been detected. This simpler reaction of **8** relative to those of Cp$_2$Zr(II) derivatives may be a consequence of the greater steric bulk of the boratabenzene ligand relative to Cp. The more hindered **8** would be expected to favor coordination by only a single diyne leading to **11**, while **11** may be protected from further attack by the bulky boratabenzene groups. It is also likely that the in-plane Zr coordination of the central double bond of the triene unit of **11** would prevent rearrangement to products analogous to **10**.

Experimental Section

General Remarks. All reactions were carried out under an atmosphere of nitrogen. Solvents were dried by using standard procedures. The mass spectra were determined by using a VG-70-S spectrometer, while the NMR spectra were obtained by using either a Bruker WH-400, WH-360, or AM-300 spectrometer. The ^{1}H NMR and ^{13}C NMR spectra were calibrated by using signals from the solvents referenced to

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$SiMe_4$. The ^{11}B NMR spectra were referenced to external BF_3-OEt_2. The combustion analyses were determined by the Analytical Services Department of the Department of Chemistry, University of Michigan.

Bis(*N*,*N*-diisopropyl-1-aminoboratabenzene)(1,4-diphenyl-1,3-butadiyne)zirconium (11a). A solution of **8a** (0.11 g, 0.18 mmol) in 10 mL of hexane was treated with a solution of 1,4-diphenyl-1,3-butadiyne (0.04 g, 0.19 mmol) in 5 mL of hexane at 25 °C. The color changed to orange immediately. After 30 min the solvent was removed under reduced pressure, leaving a residue, which was extracted with pentane. On cooling, the extract afforded 0.1 g (86%) of **11a** as orange crystals, mp 135 °C (dec).

^1H NMR (C_6D_6, 360 MHz): δ 0.87 (d, J = 6.7 Hz, CH_3); 1.07 (d, J = 6.7 Hz, CH_3); 3.50 (m, NCH), 4.53 (t, J = 6.6 Hz, $H\gamma$); 5.08 (d, J = 10.8 Hz, $H\alpha$) 6.75 (dd, J = 10.8, 6.6 Hz, $H\beta$), 7.19 (t, J = 7.6 Hz, Ph(p)), 7.34 (t, J = 7.6 Hz, Ph(m)); 8.18 (d, J = 7.6 Hz, Ph(o)).^{13}C NMR (C_6D_6, 90.56 MHz): δ 22.7 (Me), 23.9 (Me), 46.4 (NCH), 94.3 ($C\gamma$), 105.7 ($C\alpha$), 108.3 (Ph *C*), 128.6 (Ph (p)), 129.3 (Ph (m)), 131.9 ($C\beta$), 134.3 (Ph (o)), 181.4 (PhC *C*). ^{11}B NMR (C_6D_6, 115.5 MHz): δ 39.2.

Anal. Calcd for $C_{38}H_{48}B_2N_2Zr$: C, 70.67; H, 7.50; N, 4.34. Found: C, 70.50; H, 7.43; N, 4.13.

Bis(1-phenylboratabenzene)(1,4-diphenyl-1,3-butadiyne)zirconium (11b). 11b was prepared from **8b** in the same manner as **11a**. The product was isolated in 76% yield as orange crystals, mp 74 °C.

^1H NMR (C_6D_6, 360 MHz): δ 4.96 (t, J = 6.98 Hz, $H\gamma$); 5.92 (d, J = 11.1 Hz, $H\alpha$); 6.64 (dd, J = 11.1, 6.6 Hz, $H\beta$); 7.19 (m, BPh (J = 7.2 Hz), CPh (J = 7.3 Hz)). 7.28 (m, CPh (m), BPh-(m)); 7.70 (d, J = 7.3 Hz, CPh(o)), 7.90 (d, J = 7.2 Hz, BPh (o)). ^{13}C NMR (C_6D_6, 90.6 MHz): δ 100.9 (Ph*C*); 104.2 ($C\gamma$); 117.1 ($C\alpha$); 128.4 (CPh (p)); 128.7 (CPh (m)); 129.0 (BPh (p)); 129.7 (BPh (p)), 132.3 (CPh (o)); 133.3 ($C\beta$); 134.5 (BPh(o)), 178.4 (PhC*C*). ^{11}B NMR (C_6D_6, 115.5 MHz): δ 34.4. HRMS-(EI): Calcd for $C_{38}H_{30}{}^{11}B_2{}^{90}Zr$: 598.1581; found 598.1606.

Bis(1-phenylboratabenzene)(3,5-octadiyne)zirconium (11b′). 11b′ was prepared from **8b** and 3,5-octadiyne in the same manner as above. The product was isolated as an orange oil in 55% yield.

^1H NMR (C_6D_6, 360 MHz): δ 1.20 (t, J = 7.3 Hz, Me), 2.63 (q, J = 7.3 Hz, CH_2), 5.31 (t, J = 7.35 Hz, $H\gamma$), 5.53 (d, J = 10.9 Hz, $H\alpha$), 6.38 (dd, J = 10.9, 7.4 Hz, $H\beta$). ^{13}C NMR (C_6D_6, 90.56 Hz): δ 18.5 (Me), 28.0 (CH_2), 102.2 ($C\gamma$), 117.5 ($C\alpha$), 128.5 (Ph(p)), 129.0 (Ph(m)), 131.6 (Ph(o)), 133.4 ($C\beta$), 180.5 (*C* Ph). ^{11}B NMR (C_6D_6, 115.5 MHz): δ 32.9. HRMS(EI): Calcd for $C_{30}H_{30}{}^{11}B_2{}^{90}Zr$: 502.1581; found 502.1588.

Table 2. Crystal Data and Structure Refinement for 11a[a]

empirical formula	$C_{38}H_{50}B_2N_2Zr$
fw	647.64
temperature	178(2) K
wavelength	0.71073 Å
crystal system	monoclinic
space group	$P2(1)/c$
unit cell dimens	$a = 11.737(2)$ Å $b = 18.208(3)$ Å, $\beta = 96.210(10)°$ $c = 15.938(2)$ Å
volume, Z	3386.1(9) Å^3, 4
density (calcd)	1.270 Mg/m^3
abs coeff	0.353 mm^{-1}
$F(000)$	1368
crystal size	0.10 × 0.20 × 0.24 mm
θ range for data collection	2.54−26.01°
limiting indices	$-5 \le h \le 14$, $-22 \le k \le 22$, $-19 \le l \le 19$
no. of reflns collected	8155
no. of indep reflns	6643 [R(int) = 0.0715]
abs corr	none
refinement method	full-matrix least-squares on F^2
no. of data/restraints/params	6625/0/488
goodness-of-fit on F^2	0.738
final R indices [$I > 2\sigma(I)$]	R1 = 0.0640, wR2 = 0.1166
R indices (all data)	R1 = 0.1693, wR2 = 0.1431
extinction coeff	0.0005(2)
largest diff peak and hole	0.735 and −1.122 e Å^{-3}

[a] One of the N-iPr groups is disordered over two positions each at 50% occupancy.

X-ray Structure Determination. Crystals of **11a** suitable for X-ray diffraction were obtained by recrystallization from hexane. Crystallographic data are collected in Table 2. An ORTEP drawing of **11a** showing the numbering scheme used in refinement are presented in Figure 1. Additional crystallographic data are available in the Supporting Information.

Acknowledgment. We are grateful to the National Science Foundation for the partial support of this research.

Supporting Information Available: Tables of bond distances, angles, positional parameters, aniosotropic thermal parameters, and hydrogen atom coordinates of **11a**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM990532S