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Dilithiation of Bis(benzene)molybdenum and Subsequent Isolation of a Molybdenum-Containing Paracyclophane

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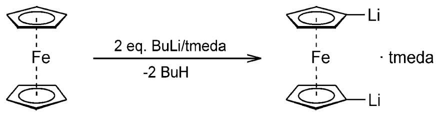
Abstract: The homoleptic sandwich complex bis(benzene)molybdenum, $[Mo(\eta^6\text{-}C_6H_6)_2]$, was successfully dilithiated by employing an excess of BuLi in the presence of *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (up to 6 equiv each) at slightly elevated temperatures furnishing the highly reactive, ring metalated species $[Mo(\eta^6\text{-}C_6H_5Li)_2]\cdot$tmeda in high yields. Alternatively, this compound was synthesized upon prolonged sonication with 5 equiv of ^{t}BuLi/tmeda without heating. An X-ray crystal structure determination revealed a symmetrical, dimeric composition in the solid state, i.e., a formula of $[Mo(\eta^6\text{-}C_6H_5Li)_2]_2\cdot(thf)_6$, where the six-membered rings are connected by two pairs of bridging lithium atoms. The synthesis of an elusive ansa-bridged complex failed in the case of a [1]bora and a [1]sila bridge due to the thermal lability of the resulting compounds. Instead, reverse addition of the dilithio precursor to an excess of the appropriate element dihalide facilitated the isolation of several unstrained, 1,1′-disubstituted derivatives, namely, $[Mo\{\eta^6\text{-}C_6H_5(BN(SiMe_3)_2X)\}_2]$ (X = Cl, Br) and $[Mo\{\eta^6\text{-}C_6H_5(Si^iPr_2Cl)\}_2]$, respectively. However, the incorporation of a less congesting [2]sila bridge was accomplished. In addition to the formation of $[Mo\{(\eta^6\text{-}C_6H_5)_2Si_2Me_4\}]$, a molybdenum-containing paracylophane complex was isolated and characterized by means of crystal structure analysis. The ancillary formation of 1 equiv of bis(benzene)molybdenum strongly suggests that this species is generated by deprotonation of the ansa-bridged complex by the dilithiated precursor and subsequent reaction with a second equivalent of the disilane.

Introduction

The discoveries and structural elucidation of the first sandwich compounds, ferrocene, $[Fe(\eta^5\text{-}C_5H_5)_2]$,[1] and bis(benzene)chromium, $[Cr(\eta^6\text{-}C_6H_6)_2]$,[2] are rightly regarded as landmark moments in organometallic chemistry. A host of interesting chemical compounds and applications have stemmed from the initial discoveries, which challenged traditional notions of connectivity and enthroned the cyclopentadienyl ring as the preeminent ligand in transition and f element metal chemistry. Selective metalation of metallocenes and bisarene transition metal complexes is a perennial area of related research, in which 1,1′-dilithiation of ferrocene by BuLi and *N*,*N*,*N*′,*N*′-tetramethylethylendiamine (tmeda) was an early and important achievement (Scheme 1).[3] Such dimetalated derivatives have found widespread application in the synthesis of ring-substituted metallocenes, in particular for ansa-bridged type systems,[4] which have proven to be facile precursors for various metal-based materials.[5]



Scheme 1. Metalation of Ferrocene Using BuLi/tmeda

Recently, the regioselective tetrametalation of ferrocene and its higher homologues,[6] the synergic monodeprotonation of bis(benzene)chromium,[7] as well as the selective dimetalation of ferrocene[8] were reported by Mulvey and co-workers, accomplished by the enhanced basicity of mixed alkali metal−magnesium amide bases. In addition, pentafluorophenylcopper

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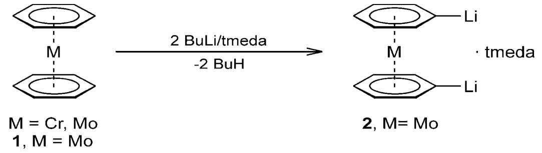
Scheme 2. Metalation of Group 6 Bis(benzene) Sandwich Complexes



$[C_6F_5Cu]_4$ has been successfully employed in the selective synthesis of mono- and dimetalated ferrocenylcopper complexes.[9] While ferrocene and its derivatives, by virtue of the precursor's air stability and comparative ease of synthesis, dominate this field of chemistry, the reactivity of the isoelectronic group 6 bisarenes, of which $[Cr(\eta^6\text{-}C_6H_6)_2]$ is the prime example, is still the subject of considerable inquiry. $[Cr(\eta^6\text{-}C_6H_6)_2]$ can be 1,1′-dilithiated in a similar fashion to ferrocene, viz., by treatment with BuLi and in the presence of a coordinating amine such as tmeda at slightly elevated temperatures (Scheme 2).[10] With regard to $[Mo(\eta^6\text{-}C_6H_6)_2]$ (**1**) and $[W(\eta^6\text{-}C_6H_6)_2]$,[11] only the former can be synthesized in reasonable quantity and is susceptible to lithiation reactions following Scheme 2 at elevated temperatures.[12] To date, no unequivocally characterized, dimetalated derivative of $[Cr(\eta^6\text{-}C_6H_6)_2]$ or $[Mo(\eta^6\text{-}C_6H_6)_2]$ (**1**) has been reported, though both dilithiates have been employed in further syntheses. The corresponding chemistry of the isoelectronic, mixed ring metallocenes $[M(\eta^7\text{-}C_7H_7)(\eta^5\text{-}C_5H_5)]$ (M = Ti,[13] V,[13,14] Cr[4i,15]) is also pertinent to mention in this regard, although a dilithiated example has again eluded structural characterization. At the same time, while ansa-bridged derivatives of $[Cr(\eta^6\text{-}C_6H_6)_2]$[4c,16] and $[Cr(\eta^7\text{-}C_7H_7)(\eta^5\text{-}C_5H_5)]$[4i,15] have been prepared and structurally characterized, for instance, $[Cr(\eta^6\text{-}C_6H_5)_2BN(SiMe_3)_2]$[16d] and $[Cr(\eta^7\text{-}C_7H_6)(\eta^5\text{-}C_5H_4)SiMe_2]$,[15] scant few higher homologues of Mo or W have been reported, and none at all have been unequivocally characterized.

Here, the complete characterization of the dimetalated derivative $[Mo(\eta^6\text{-}C_6H_5Li)_2]$, as its various tmeda (**2**) and thf (**3**) solvates, is reported, along with structural data for $[Mo(\eta^6\text{-}C_6H_5Li)_2]_2\cdot(thf)_6$ (**3**). This highly reactive species is converted to several structurally characterized 1,1′-disubstituted derivatives via salt elimination reactions with appropriate element dihalides. In addition, the isolation of an elusive ansa-bridged derivative has been accomplished, as well as the full characterization of a molybdenum-containing paracyclophane complex.

Results and Discussion

As shown in Scheme 2, treatment of bis(benzene)molybdenum (**1**) with BuLi and tmeda in aliphatic solvents such as heptane gives excellent yields of the dilithiated derivative **2**. The alkyl lithium reagent has to be present in excess (up to 6 equiv), and for complete conversion the temperature must be maintained at 55−60 °C for a prolonged period (12−24 h). Alternatively, prolonged sonication in an ultrasonic bath of the starting material with ^{t}BuLi/tmeda (5 equiv each) in hexanes can access the dilithiated material without heating. The presence of tmeda in concert with BuLi is known to be essential to effect deprotonation of the arene rings; alternative bases such as MeLi, ^{t}BuLi, or BuK formed in situ were ineffective without the addition of the ancillary base. The pale brown, pyrophoric product may be recovered on a Schlenk frit and washed clean of the excess BuLi and tmeda with pentane. Compound **2** is thermally stable under an inert atmosphere, and ^{1}H NMR spectroscopy in thf-d_8 indicates the presence of three multiplets due to the ortho, meta, and para protons of the benzene ring. However, dissolving in thf causes the replacement of the tmeda ligand by coordinating thf molecules, and free tmeda was detected. The integration ratio of the signals suggests the incorporation of one tmeda molecule per arene complex, i.e., a formula of **2**·tmeda. ^{13}C NMR spectroscopy after prolonged acquisition times reveals the expected four carbon resonances of the arene rings, with the ipso-C−Li resonances shifted downfield to $\delta = 106.4$ ppm with respect to the CH carbon atoms. In addition, this signal is significantly broadened by the quadrupolar momentum conferred by the ^{7}Li nucleus. While **2**·tmeda is totally insoluble in aliphatic and aromatic solvents, recrystallization from thf/benzene/pentane mixtures gives deep brown-orange crystals that were formulated as $\mathbf{2}\cdot(thf)_3$ on the basis of ^{1}H NMR spectroscopy. To confirm the selectivity of the dimetalation, the molecular structure of the dilithiated precursor (**3**) was determined by crystal structure analysis (Figure 1).

In the solid state, **3** exhibits a symmetrical dimeric structure, in which both molecules are connected by two pairs of bridging lithium atoms bound to the ipso carbons of each C_6H_5 moiety. The unsaturated lithium centers are stabilized by the coordination of the thf oxygen atoms, whereas two distinct lithium environments can be distinguished; Li1 and Li1_a are stabilized by two thf molecules and Li2 and Li2_a are coordinated by one

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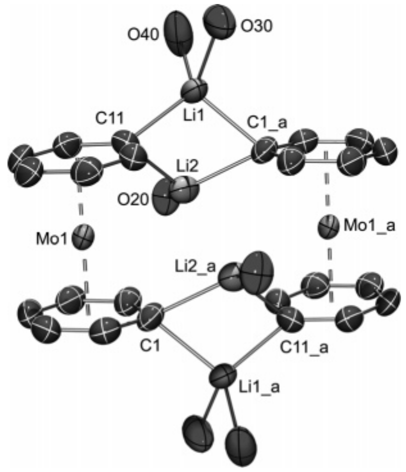
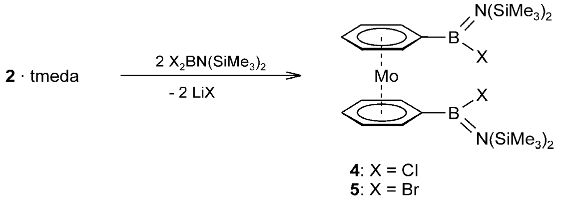


Figure 1. Molecular structure of the $[Mo(\eta^6\text{-}C_6H_5Li)_2)]_2(thf)_6$ (**3**) solvate. For clarity, only the oxygen atoms of the thf molecules are shown. Symmetry related positions ($-x$, $-y$, $-z$) are labeled with _a. Selected distances (angstroms) and angles (deg): Li1−Li2 2.355(10), Li2−Li2_a 3.156(15), Li1−C11 2.191(9), Li1−C1_a 2.149(9), Li2−C11 2.190(9), Li2−C1_a 2.186(9), Li1−O30 1.964(10), Li1−O40 1.943(16), Li2−O20 1.959(8), Mo1−C_{aryl} 2.249(5)−2.377(5) [ave 2.282(5)], Mo1−X_{Ph1} 1.787, Mo1−X_{Ph2} 1.794, C11−Li−C1_a 106.7(4), C11−Li2−C1_a 105.5(4), X_{Ph1}−Mo1−X_{Ph2} 178.9 (X_{Ph1} = centroid of the C_6H_5 ring C1 to C6, X_{Ph2} = centroid of the C_6H_5 ring C11 to C16, respectively).

thf molecule, respectively. The thf molecules show extensive disorder, thus requiring a combination of constraints and restraints in the refinement, and as a consequence, the structural parameters within these moieties are excluded from the following discussion. As expected for a tetra-coordination, the bridging lithium atoms Li1 and Li1_a display a distorted tetrahedral environment. In contrast, the coordination sphere of the unsaturated, three-coordinate lithium atoms Li2 and Li2_a deviates significantly from an expected trigonal planar geometry (Σ = 336°) and is best described as a trigonal pyramidal arrangement, which is presumably adopted for steric reasons. The lithium ···lithium separation distances within the two bridging units [Li1−Li2 2.355(10) Å] differ perspicuously from that found between these two moieties [Li2−Li2_a 3.156(15) Å]. The former is comparable to that found in cyclohexyllithium [2.397 Å][17] and might suggest a stabilizing lithium−lithium interaction. However, according to earlier investigations on alkyllithium reagents[18] or the related dilithiated ferrocene derivative $[Fe(\eta^5\text{-}C_5H_4Li)_2]$·pmdta,[19] this type of stabilization is weak at best. The Li−C bond distances [2.149(9)−2.191(8) Å],[19,20] as well as the Li−O bond lengths [1.943(16)−1.964(10) Å],[21] lie within previously reported ranges. The structural parameters of the bis(benzene)molybdenum units are in agreement with the anticipated attributes of an unstrained 1,1′-disubstituted sandwich molecule. The molybdenum CH carbon bond distances are found within a range of 2.249(5) and 2.283(5) Å, though the molybdenum ipso carbon bonds are significantly elongated for both six-membered rings [2.371(4) and 2.377(4) Å]. As expected, the aromatic rings are arranged almost parallel with an angle between the planes of the C_6H_5 moieties of 3.9(3)°, and the angle δ, defined by the ring centroids and the metal center, indicates an almost linear arrangement (178.9°).

Scheme 3. Syntheses of **4** and **5** via Salt Elimination Reaction



Given the availability of gram quantities of **2**·tmeda the obvious course was to treat **2** with a series of element dihalides and attempt the isolation of the elusive ansa-bridged species. In fact, treatment of **2** with 1 equiv of a range of aminoboranes, X_2BNR_2 (X = Cl, Br; R = ^{i}Pr, $SiMe_3$) gave only the 1,1′-disubstituted bis(benzene)molybdenum derivatives, $[Mo\{\eta^6\text{-}C_6H_5(BNR_2X)\}_2]$, in low yields (Scheme 3). Yields were notably improved by reverse addition of a slurry of **2**·tmeda to 2.5 equiv of the aminoborane in heptane or pentane, and hence, these experiments were sufficiently reproducible to allow the isolation and structural characterization of $[Mo\{\eta^6\text{-}C_6H_5(BN(SiMe_3)_2Cl)\}_2]$ (**4**) and $[Mo\{\eta^6\text{-}C_6H_5(BN(SiMe_3)_2Br)\}_2]$ (**5**). While the aromatic protons of the C_6H_6 rings in bis(benzene)-molybdenum give rise to only one resonance signal in the ^{1}H and ^{13}C NMR spectra, the introduction of two substituents on the arene rings in **4** and **5** results in the expected splitting pattern for time-averaged C_s symmetric species in solution. Both compounds feature two distinct pseudotriplets for the meta [δ = 4.67 (**4**) and 4.67 ppm (**5**)] and para protons [δ = 4.90 (**4**) and 4.91 ppm (**5**)], as well as a pseudodoublet for the ortho protons [δ = 4.95 (**4**) and 4.95 ppm (**5**)] with a relative intensity of 4:2:4. Accordingly, three carbon resonances are observed in the ^{13}C NMR spectra of **4** and **5**, whereas the ipso carbons bearing the boryl substituents are not observed at room temperature, a fact that can be assigned to the quadrupolar momentum of the boron nuclei.[22] It should be noted here that the isolated material from the synthesis of **5** always contained small amounts of LiBr·tmeda, which could not be removed even after several recrystallization steps. However, the NMR spectroscopic data are in excellent agreement with the results reported for the corresponding disubstituted ansa complexes of bis(benzene)chromium.[16d]

To gain more detailed insight into the structural properties of **4** and **5**, the molecular structures were determined by single-crystal X-ray diffraction analyses (Figures 2 and 3). Both molecules crystallize in the triclinic space group $P\bar{1}$ with two independent molecules in the asymmetric unit, whereas, in each case, the structural parameters of both moieties differ only marginally. Hence, for simplicity reasons only one of each molecular structure is discussed below. The structural parameters are unremarkable and can be compared to those found for the related silyl-substituted complex $[Mo\{\eta^6\text{-}C_6H_5(SiMe_2H)\}_2]$.[12] As expected, the unstrained character of **4** and **5** is demonstrated by the linear alignment of the metal centers and the ring centroids [δ = 180.0°], as well as the consummately parallel

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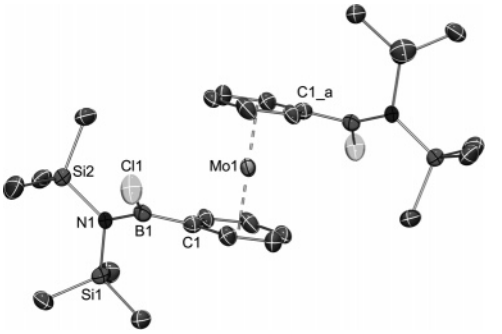


Figure 2. Molecular structure of **4**. Symmetry related positions (−*x*, −*y*, −*z*) are labeled with _a. Only one molecule of the asymmetric unit is shown for clarity. Selected distances (angstroms) and angles (deg): Mo1−C1 2.294(5), Mo1−C2 2.265(5), Mo1−C3 2.293(5), Mo1−C4 2.273(5), Mo1−C5 2.268(6), Mo1−C6 2.263(5), C1−B1 1.551(8), B1−Cl1 1.815(6), B1−N1 1.420(8), N1−Si1 1.770(4), N1−Si2 1.768(4), Mo1−X_{Ph} 1.783, N1−B1−C1 125.7(5), N1−B1−Cl1 118.6(4), C1−B1−Cl1 115.7(4), X_{Ph}−Mo1−X_{Ph_a} 180.0 (X_{Ph} = centroid of the C_6H_5 ring).

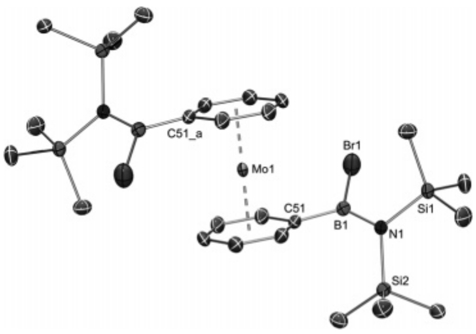
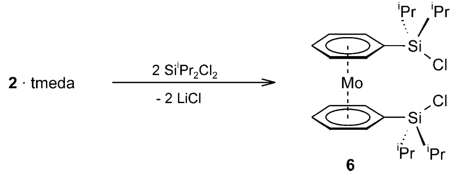


Figure 3. Molecular structure of **5**. Symmetry related positions (−*x*, −*y*, −*z*) are labeled with _a. Only one molecule of the asymmetric unit is shown for clarity. Selected distances (angstroms) and angles (deg): Mo1−C51 2.287(3), Mo1−C52 2.263(4), Mo1−C53 2.283(4), Mo1−C54 2.289(4), Mo1−C55 2.284(4), Mo1−C56 2.269(4), C51−B1 1.550(5), B1−Br1 1.968(4), B1−N1 1.416(5), N1−Si1 1.773(3), N1−Si2 1.777(3), Mo1−X_{Ph} 1.783, N1−B1−C51 125.6(2), N1−B1−Br1 119.1(3), C51−B1−Br1 115.4(3), X_{Ph}−Mo1−X_{Ph_a} 180.0 (X_{Ph} = centroid of the C_6H_5 ring).

arrangement of the aromatic ring moieties; the angle between the least-squared planes of the six-membered rings amounts to exactly 0.0° in both **4** and **5**. For steric reasons, the boryl substituents are found in trans positions, and as a consequence, the benzene rings adopt an eclipsed conformation. The boron−nitrogen bond distances [**4**: 1.420(8), **5**: 1.416(5) Å] are in agreement with the presence of B═N double bonds, which is further supported by the trigonal planar geometry of the boron environments [**4**: $\Sigma = 360°$, **5**: $\Sigma = 360°$].

While an ansa-bridge in respect of boron might be considered unlikely, given the short B−C bond length, no such restriction should apply to a silicon ansa-bridge. In fact, however, after numerous attempts, no such silicon-bridged ansa complex could be isolated. This result was also observed in ethereal solvents, i.e., thf and Et_2O, the use of which was prevented in the case of the aforementioned boron halide reagents due to the likelihood of ether cleavage. While a 1,1′-disubstituted product could be obtained in poor yields for $Si^iPr_2Cl_2$, i.e., $[Mo\{\eta^6\text{-}C_6H_5(Si^iPr_2Cl)\}_2]$ (**6**), no tractable material could be obtained with $SiMe_2Cl_2$, $SiPh_2Cl_2$, $Si^iPrMeCl_2$ or $SiMe_2(O_3SCF_3)_2$, despite numerous attempts under different conditions. In line with the reaction of **2**·tmeda and $Si^iPrMeCl_2$, however, analysis of the reaction mixture by GC/MS gave a peak at $m/z = 240$, which is attributable to the free ligand $Si^iPrMePh_2$. On the basis of this result, it appears plausible that the ansa-bridged complex has been formed, but thermal instability prevented its isolation. The reaction mixtures also routinely showed the presence of neutral $[Mo(\eta^6\text{-}C_6H_6)_2]$ (**1**), whose presence in a strictly anhydrous medium argues that the dimetalated precursor is a potent reductant and acted to reduce the added element dihalides to unknown species. However, the yields of the 1,1′-disubstituted derivative **6** have been essentially improved following a protocol in analogy to the syntheses of **4** and **5**, i.e., by reverse addition of **2**·tmeda to an excess of the dichlorosilane (Scheme 4).

Scheme 4. Synthesis of **6** by Reaction of **2**·tmeda and $Si^iPr_2Cl_2$



The NMR spectroscopic data of **6** are in full agreement with those of the 1,1′-diborylated complexes **4** and **5** and with the presence of an unstrained sandwich derivative in general. The ^1H NMR spectrum exhibits the expected splitting pattern for the signal resonances of the ortho [$\delta = 4.62$ ppm], meta [$\delta = 4.71$ ppm], and para protons [$\delta = 4.84$ ppm] with a relative ratio of 4:4:2. In contrast to the aforementioned complexes **4** and **5**, the ^{13}C NMR spectrum shows four distinct resonances for the chemically nonequivalent carbon atoms of the six-membered rings; consequently, the ipso carbons bearing the silyl substituents can easily be detected in this case. To confirm the formation of an unstrained 1,1′-disubstituted derivative, a crystal structure analysis of **6** was carried out (Figure 4).

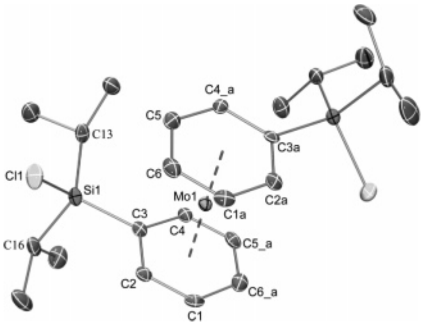


Figure 4. Molecular structure of **6**. Symmetry related positions (−*x* + 2, −*x* + *y* + 1, −*z* + 1/3) are labeled with _a. Selected distances (angstroms) and angles (deg): Mo1−C1 2.263(4), Mo1−C2 2.278(4), Mo1−C3 2.291(4), Mo1−C4 2.278(4), Mo1−C5 2.270(4), Mo1−C6 2.284(5), C3−Si1 1.861(4), C13−Si1 1.877(4), C16−Si1 1.868(4), Si1−Cl1 2.077(1), Mo1−X_{Ph1} 1.780, Mo1−X_{Ph2} 1.780, C3−Si1−C13 113.3(2), C3−Si1−C16 111.0(2), C13−Si1−C16 110.4(2), C3−Si1−Cl1 107.6(1), C13−Si1−Cl1 107.8(1), C16−Si1−Cl1 106.5(1), X_{Ph1}−Mo1−X_{Ph2} 176.8 (X_{Ph1} = centroid of the C_6H_5 ring C1 to C6_a, X_{Ph2} = centroid of the C_6H_5 ring C1_a to C6, respectively).

The structural parameters of **6** are unremarkable with respect to the crystal structures of **4**, **5**, and $[Mo\{\eta^6\text{-}C_6H_5(SiMe_2H)\}_2]$,[12] save that the silyl substituents do not adopt an anti arrangement due to crystal packing effects; the angle between them amounts to 123.5°. However, both rings are virtually planar and can be considered as η^6 coordinated. The separation distances between the molybdenum atom and the centroids [1.780 Å] lie within the expected range and are almost identical to those found in **4** and **5** [both 1.783 Å], respectively. As anticipated, the silicon

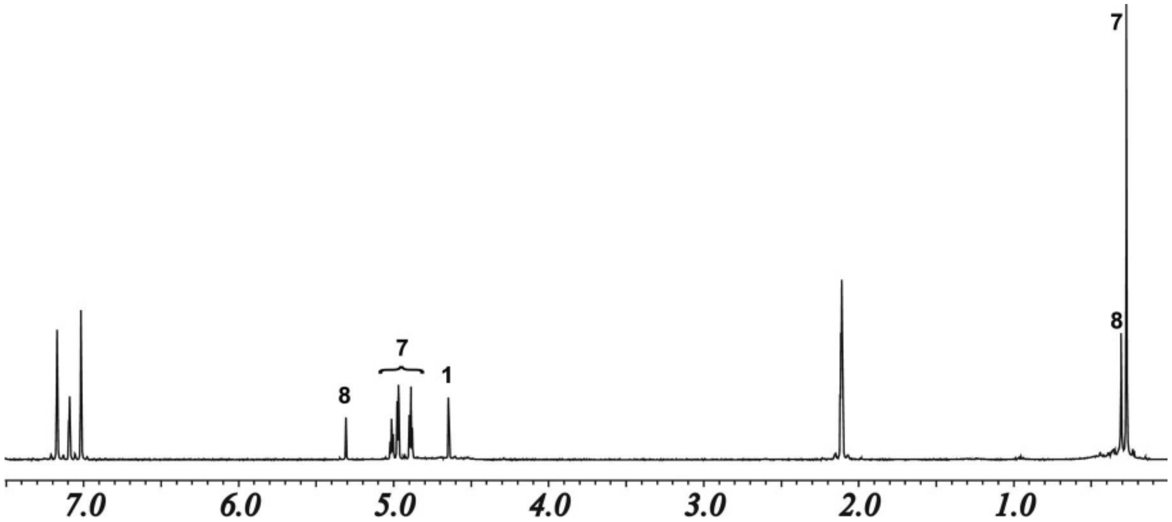
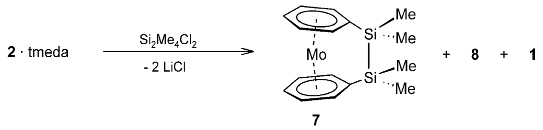


Figure 5. ^{1}H NMR spectrum of the isolated solid comprising **7**, **8**, and **1** in a ratio of 8:1:1 in toluene-d_8 at −60 °C.

centers display a distorted tetrahedral environment that differs only marginally from the ideal geometry.

The utilization of dichlorotetramethyldisilane $Si_2Me_4Cl_2$, which undoubtedly should confer less molecular strain upon the anticipated [2]sila derivative of bis(benzene)molybdenum (**7**) in comparison to its hypothetical [1]bora and [1]sila congeners, and therefore should make its isolation more likely, has led to a surprising result. Reaction of the dilithio precursor **2**·tmeda with $Si_2Me_4Cl_2$ afforded after workup an orange powder that turned out to be a mixture of three different compounds (Scheme 5). The ^{1}H NMR spectrum exhibits signals for the carbocyclic hydrogen atoms which can be unambiguously assigned to the desired ansa-bridged complex **7** [$\delta = 4.89$ ppm (m, 4H); 4.97 ppm (m, 4H); 5.01 ppm (m, 2H)] as the main product but shows additional singlets at $\delta = 4.65$ ppm and $\delta = 5.31$ ppm in a relative ratio of 4:3 (Figure 5). In addition, the aromatic carbon atoms of **7** give rise to four resonance signals in the ^{13}C NMR spectrum [between 77.3 and 80.3 ppm], whereas three ancillary signals were observed at $\delta = 75.2$, 81.1, and 84.6 ppm. According to two-dimensional ^{1}H,^{13}C-HMQC NMR experiments, the former resonance is associated with the singlet at 4.65 ppm in the ^{1}H NMR spectrum and the latter one with that at 5.31 ppm. The remaining resonance proved to be a quaternary aromatic carbon atom, evidenced by ^{13}C DEPT 135 NMR spectroscopy, that display a cross-peak with the singlet at 5.31 ppm in the two-dimensional long-range ^{1}H,^{13}C-HMBC NMR spectrum. Accessorily, the ^{29}Si NMR spectrum comprises two distinct resonances with chemical shifts of $\delta = -14.8$ and -17.3 ppm, respectively, indicating similar chemical environments of the silicon nuclei. Even the [2]sila derivative **7** is thermally unstable and decomposes within 10 h in benzene solutions to yield the free ligand $Ph(Me)_2Si{-}Si(Me)_2Ph$ and black molybdenum metal. However, in the solid state, **7** can be stored for several months at room temperature under an inert atmosphere.

Scheme 5. Synthesis of the ansa-Bridged Derivative **7**



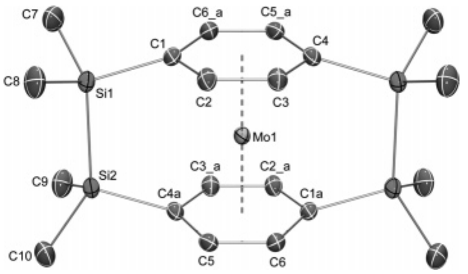


Figure 6. Molecular structure of **8**. Symmetry related positions ($-x$, $-y + 2$, $-z$) are labeled with _a. Selected distances (angstroms) and angles (deg): Mo1−C1 2.264(1), Mo1−C2 2.268(1), Mo1−C5 2.267(1), Mo1−C4 2.264(1), Mo1−C5 2.270(1), Mo1−C6 2.269(1), Si1−Si2 2.381(1), C1−Si1 1.895(1), C4_a−Si2 1.897(1), Si1−C7 1.876(2), Si1−C8 1.874(2), Si2−C9 1.871(2), Si2−C10 1.876(2), Mo1−X_{Ph} 1.761, C1−Si1−Si2 106.6(1), C4_a−Si2−Si1 106.4(1), C1−Si1−Si2−C4_a −0.5(1), X_{Ph}−Mo1−X_{Ph_a} 180.0 (X_{Ph} = centroid of the C_6H_5 ring).

One of the additional compounds (^{1}H, 4.65 ppm; ^{13}C, 75.2 ppm) formed in the course of this reaction can be unambiguously identified as bis(benzene)molybdenum (**1**) by comparison of the chemical shifts with a corresponding pure sample. However, the identity of the other remained unclear until its composition has been revealed by a single-crystal X-ray diffraction study, due to its preeminent crystallization properties. The molecular structure of the isolated paracyclophane **8** is depicted in Figure 6 and represents along with its lighter congeners of chromium, namely, $[Cr(\eta^6\text{-}C_6H_4Si_2Me_4)_2]$[23] and $[Cr(\eta^6\text{-}C_6H_4C_2H_4)_2]$,[24] the only known paracyclophane complex derived from the benzene perimeter.

The structural parameters of **8** show several differences in comparison to the unstrained 1,1′-disubstituted derivatives **4**, **5**, and **6**, which are related to the rigid ligand framework. Hence, the distance between the centroids of the six-membered rings is slightly contracted to a value of 3.522 Å [cf., **4** and **5**, 3.566 Å; **6**, 3.560 Å] and the molybdenum carbon bond lengths [between 2.264(1) and 2.270(1) Å] are found in a closer interval than in **4**, **5**, and **6** [between 2.261(4) and 2.294(5) Å]. However, these alterations are much less pronounced than expected for such a paracyclophane species. The silicon−silicon bond

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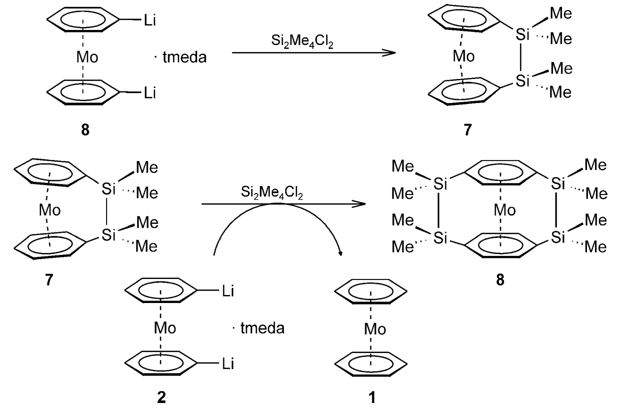
Scheme 6. Proposed Mechanism for the Formation of the Paracyclophane Derivative **8**



distance [2.381(1) Å], as well as the torsion angle C1−Si1−Si2−C4_a [−0.5(1)°], are comparable to the values found in the corresponding chromium derivative [2.361 Å and 0.22°, respectively].[23] In addition, the silicon centers display an almost ideal tetrahedral environment, whereas the largest discrepancy is found for the ipso carbon−Si−Si angles [C1−Si1−Si2 106.6(1)° and C4_a−Si2−Si1 106.4(1)°]; consequently, these data suggest a minor molecular ring strain present in **8** than in the chromium congener [102.7 and 102.9°].[23] As anticipated for such a structural motif, the planes of the arene rings are disposed parallel to each other, and a perfect linear arrangement of the metal center and the ring centroids is observed. With the structural composition of **8** in mind, all observed signal resonances of the NMR spectroscopic experiments can be completely assigned to the ansa-bridged derivative **7**, the paracyclophane species **8**, and bis(benzene)molybdenum (**1**). Additionally, the integration of the resonances for **8** (8 protons) and **1** (12 protons) in the ^{1}H NMR spectrum, which was found to be 3:4, results in a relative ratio of 1:1 of these compounds in the reaction mixture.

The formation of **8** in concert with the appearance of bis(benzene)molybdenum during the synthesis of **7** can be explained by the enhanced reactivity of the ansa-bridged complex **7** toward deprotonation, which can be accomplished by the reactive precursor **2**·tmeda; i.e., **2** can also act as a strong base in this reaction (Scheme 6). Thus, once the [2]silametalloarenophane **7** has formed, the arene rings are regioselectively dimetalated in the para position to yield a highly reactive, dilithiated intermediate in small concentrations, which, on its part, is converted to the paracyclophane **8** by salt elimination reaction with another equivalent of $Si_2Me_4Cl_2$. Given the fact that the reaction generates **8** and bis(benzene)molybdenum (**1**) in a ratio of 1:1, the proposed mechanism appears plausible, although, the reactive intermediate has been neither isolated nor observed spectroscopically in any case. However, the proposed mechanism is supported by the following aspects: (1) substituted ferrocenes, for instance, $[Fe(\eta^5\text{-}C_5H_4SiMe_3)_2]$,[25] $[Fe(\eta^5\text{-}C_5H_4Cl)_2]$,[26] or $[Fe(\eta^5\text{-}C_5H_4CH_2NMe_2)(\eta^5\text{-}C_5H_5)]$,[27] are prone to deprotonation under conditions similar to, or even milder than, those for the metalation of the parent ferrocene; (2) a regioselective dilithiation of **8** is in agreement with previous results obtained for the metalation of substituted ferrocenes, which yields 1,2-disubstituted complexes for donor-substituted ferrocenes such as $[Fe(\eta^5\text{-}C_5H_4CH_2NMe_2)(\eta^5\text{-}C_5H_5)]$[27] or 1,3-disubstituted derivatives for different functionalized ferrocenes such as $[Fe(\eta^5\text{-}C_5H_4X)_2]$ (X = $SiMe_3$, ^{t}Bu).[25,28] It should be noted that all attempts to prepare **8** selectively by tetrametalation of bis(benzene)molybdenum and subsequent reaction with 2 equiv of $Si_2Me_4Cl_2$, or by deprotonation of the ansa-bridged species **7** with BuLi/tmeda followed by treatment with the disilane, were unsuccessful to date.

Summary and Conclusions

In this paper, the derivatization of metallocenes via metalation and subsequent salt elimination reaction with element dihalides has been extended to bis(benzene)molybdenum. The use of conventional bases such as BuLi and tmeda has allowed for the isolation and full characterization of $[Mo(\eta^6\text{-}C_6H_5Li)_2]$·tmeda, including a crystal structure analysis of its thf solvate, i.e., $[Mo(\eta^6\text{-}C_6H_5Li)_2]_2\cdot(thf)_6$ (**3**). Structural characterization of metalated sandwich complexes is still a challenging area due to the high reactivity of these compounds, and hence, the solution of the molecular structure of **3** contributes to the understanding of the fundamentals that determine the conformation of this class of organometallic compounds. The surprising feature of the molybdenum chemistry was the thermal stability of the dilithiated derivative on the one hand and the difficulties of converting this reactive material to the appropriate ansa-bridged bis(benzene)molybdenum derivatives on the other hand. The introduction of a [1]bora and a [1]sila bridge was prevented by the thermal lability of the resulting products. Instead, the 1,1′-disubstituted derivatives were exclusively formed, whereas the 1,1′-diboryl- and the 1,1′-disilyl-substituted complexes **4**, **5**, and **6** were isolated and characterized by means of X-ray diffraction. The utilization of the larger disilane bridge led to the isolation of the first ansa-bridged bis(benzene)molybdenum derivative, $[Mo\{(\eta^6\text{-}C_6H_5)_2Si_2Me_4\}]$ (**7**), as well as the structural characterization of the unexpected paracyclophane complex **8**, $[Mo(\eta^6\text{-}C_6H_4Si_2Me_4)_2]$. The formation of **8** was explained by the enhanced reactivity of **7** toward deprotonation by dimetalated bis(benzene)molybdenum and subsequent reaction with a second equivalent of the disilane.

Experimental Section

General remarks: All manipulations were performed under an inert atmosphere of dry argon using standard Schlenk techniques or in a glovebox. Solvents were dried according to standard procedures and stored under argon over molecular sieves. Deuterated solvents were distilled from potassium over a glass bridge and subjected to several freeze−pump−thaw cycles. $[Mo(\eta^6\text{-}C_6H_6)_2]$,[29] $Cl_2BN(SiMe_3)_2$,[30] and $Br_2BN(SiMe_3)_2$[31] were prepared according to known methods. All dichlorosilanes were obtained from Aldrich and distilled from magnesium turnings before use. BuLi and ^{t}BuLi were purchased from Acros as 1.6 mol L^{-1} and 1.5 mol L^{-1} solutions in hexanes or pentane, respectively. The tmeda was dried over K and distilled under argon prior to use. The NMR spectra were recorded on a Bruker Avance 200 (^{1}H, 200.13 MHz), a Bruker DRX 300 (^{7}Li, 116.64 MHz), and on a

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Bruker AV 500 (^{1}H, 500.13 MHz; ^{11}B, 160.46 MHz, ^{13}C, 125.76 MHz, ^{29}Si, 99.36 MHz) FT-NMR spectrometer. ^{1}H and ^{13}C{^{1}H} NMR spectra were referenced to external TMS via the residual protio of the solvent (^{1}H) or the solvent itself (^{13}C). ^{7}Li{^{1}H} NMR spectra were referenced to external LiCl, ^{11}B{^{1}H} NMR spectra to $BF_3 \cdot OEt_2$, and ^{29}Si{^{1}H} NMR spectra to external TMS. Microanalyses for C, H, and N were performed on a Leco CHNS-932 elemental analyzer.

[Mo(η^6-$C_6H_5Li)_2$]·tmeda, 2: Method A. BuLi (26.17 mL, 65.43 mmol, 5.5 equiv) was added to a mixture of [Mo(η^6-$C_6H_6)_2$] (3.00 g, 11.90 mmol) (**1**), tmeda (7.60 g, 65.43 mmol, 5.5 equiv), and heptane (75 mL) via syringe, and the resulting suspension was heated to 55 °C over a period of 20 h, while the color of the suspension changed from green to dark brown. The resulting precipitate was collected by filtration, washed several times with pentane (3 × 10 mL), and dried in vacuo to yield **2**·tmeda as a pyrophoric pale brown powder (3.79 g, 9.97 mmol, 84%).

Method B. To a suspension of [Mo(η^6-$C_6H_6)_2$] (1.00 g, 3.96 mmol) (**1**) and tmeda (2.53 g, 21.81 mmol, 5.5 equiv) in pentane (40 mL) was added ^{t}BuLi (21.81 mmol, 14.54 mL) via syringe at 0 °C. After warming to room temperature the green suspension was sonicated over a period of 12 h accompanied by the formation of a brown precipitate and a color change to dark brown. The solid product was collected by filtration, washed with pentane (3 × 10 mL), and dried in vacuo. **2**·tmeda was isolated as a pale brown powder (1.32 g, 3.47 mmol, 87%). ^{1}H NMR (500 MHz, thf-d_8, 297 K): $\delta = 2.16$ (s, 12H, N(CH_3)$_2$), 2.30 (s, 4H, N(CH_2)$_2$N), 4.10 (m, 4H, C_6H_5), 4.41 (m, 6H, C_6H_5). ^{7}Li{^{1}H} NMR (117 MHz, thf-d_8, 297 K): $\delta = 1.6$. ^{13}C{^{1}H} NMR (126 MHz, thf-d_8, 297 K): $\delta = 46.7$ (N($CH_3)_2$), 59.3 (N($CH_2)_2$N), 69.1, 77.1, 84.9 (C_6H_5), 106.4 (*ipso*-C_6H_5). Anal. Calcd for $C_{18}H_{26}Li_2N_2Mo$ (380.23): C, 56.86; H, 6.89; N, 7.37. Found: C, 56.48; H, 7.12; N, 7.23.

[Mo(η^6-$C_6H_5Li)_2]_2$·(thf)$_6$, 3. The recrystallization of **2**·tmeda in thf/benzene/pentane at −35 °C yielded orange-brown crystals of the **3** that were suitable for crystal structure analysis. ^{1}H NMR (200 MHz, thf-d_8, 297 K): $\delta = 1.70$ (m, 12H, (CH_2)$_2$), 3.60 (s, 12H, O(CH_2)$_2$), 4.06 (m, 4H, C_6H_5), 4.39 (m, 6H, C_6H_5).

[Mo{η^6-C_6H_5(BN(SiMe$_3$)$_2$Cl}$_2$], 4. A suspension of **2**·tmeda (0.75 g, 1.97 mmol) in pentane (30 mL) was added rapidly to a well-stirred solution of $Cl_2BN(SiMe_3)_2$ (1.19 g, 4.93 mmol, 2.5 equiv) in pentane (20 mL) at room temperature. Upon stirring for 18 h the color of the slurry changed from dark brown to deep red. Insoluble materials were removed by filtration, and the red filtrate was concentrated to about 10 mL in volume. Cooling to −60 °C afforded **4** as a dark orange, microcrystalline solid, which was obtained analytically pure after washing with cold pentane (3 × 3 mL, −100 °C) and drying in vacuo (0.45 g, 0.68 mmol, 34%). X-ray quality crystals were grown from saturated heptane solutions at −25 °C. ^{1}H NMR (500 MHz, C_6D_6, 297 K): $\delta = 0.32$ (s, 36H, Si(CH_3)$_3$), 4.67 (m, 4H, *m*-C_6H_5), 4.90 (m, 2H, *p*-C_6H_5), 4.95 (m, 4H, *o*-C_6H_5). ^{11}B{^{1}H} NMR (160 MHz, C_6D_6, 297 K): $\delta = 47.1$. ^{13}C{^{1}H} NMR (126 MHz, C_6D_6, 297 K): $\delta = 4.29$ (Si($CH_3)_3$), 77.4, 81.3, 83.9 (C_6H_5). Anal. Calcd for $C_{24}H_{46}B_2Cl_2N_2MoSi_4$ (663.44): C, 43.45; H, 6.99; N, 4.22. Found: C, 43.62; H, 6.61; N, 4.33.

[Mo{η^6-C_6H_5(BN(SiMe$_3$)$_2$Br}$_2$], 5. In a procedure analogous to the preparation of **4**, employing **2**·tmeda (0.27 g, 0.71 mmol) in pentane (20 mL) and $Br_2BN(SiMe_3)_2$ (0.59 g, 1.78 mmol, 2.5 equiv) in pentane (10 mL), afforded **5** (0.23 g, 0.31 mmol, 44%) as dark red crystals after crystallization and drying in vacuo. The product always contained traces of LiBr·tmeda, which could not be removed even after several recrystallization steps. ^{1}H NMR (500 MHz, C_6D_6, 297 K): $\delta = 0.32$ (s, 36H, Si(CH_3)$_3$), 4.67 (m, 4H, *m*-C_6H_5), 4.91 (m, 2H, *p*-C_6H_5), 4.95 (m, 4H, *o*-C_6H_5). ^{11}B{^{1}H} NMR (160 MHz, C_6D_6, 297 K): $\delta = 46.6$. ^{13}C{^{1}H} NMR (126 MHz, C_6D_6, 297 K): $\delta = 2.87$ (Si($CH_3)_3$), 76.2, 81.3, 83.4 (C_6H_5). Correct elemental analysis could not be obtained due to LiBr·tmeda impurities.

[Mo{η^6-C_6H_5(Si^{i}Pr$_2$Cl)}$_2$], 6. A slurry of **2**·tmeda (0.49 g, 1.28 mmol) in heptane (20 mL) was added over a period of 10 min to a well-stirred solution of $Cl_2Si^iPr_2$ (0.71 g, 3.84 mmol, 3.0 equiv) in heptane (20 mL) at −78 °C. The brown mixture was allowed to warm to room temperature and was stirred for an additional 3 h. After the solid had settled, the solution was filtered into another flask by a filter canula and the brown filtrate was concentrated to about 10 mL in volume to yield orange-brown crystals of **6** (0.26 g, 0.47 mmol, 37%), which were subsequently washed with cold pentane (3 × 5 mL, −100 °C) and dried in vacuo. ^{1}H NMR (500 MHz, C_6D_6, 297 K): $\delta = 1.10$ (m, 24H, CH(CH_3)$_2$), 1.19 (m, 4H, CH(CH$_3$)$_2$), 4.62 (m, 4H, *o*-C_6H_5), 4.71 (m, 4H, *m*-C_6H_5), 4.84 (m, 2H, *p*-C_6H_5). ^{13}C{^{1}H} NMR (126 MHz, C_6D_6, 297 K): $\delta = 15.2$ (CH($CH_3)_2$), 17.8 (CH(CH$_3$)$_2$), 74.6 (*ipso*-C_6H_5), 75.9, 78.9, 81.1 (C_6H_5). Anal. Calcd for $C_{24}H_{38}Cl_2MoSi_2$ (549.57): C, 52.45; H, 6.96. Found: C, 52.62; H, 6.61.

[Mo{(η^6-$C_6H_5)_2Si_2Me_4$}], 7 and [Mo(η^6-$C_6H_4Si_2Me_4)_2$], 8. A solution of $Si_2Me_4Cl_2$ (0.29 g, 1.33 mmol) in heptane (10 mL) was added dropwise over a period of 1 h to a slurry of **2**·tmeda (0.51 g, 1.33 mmol) in heptane (30 mL) at −78 °C. The reaction mixture was kept for additional 3 h at −78 °C and then slowly warmed to room temperature, while the color of the suspension changed from dark brown to deep red and a white precipitate deposited. Insoluble materials were removed by filtration, and the red filtrate was concentrated to about 10 mL. Storage at −30 °C yielded an orange solid (0.23 g, 0.63 mmol, 47%), which was isolated as a powder after washing with cold pentane (3 × 5 mL, −100 °C) and drying in vacuo. According to ^{1}H NMR spectroscopy the product contained a mixture of the ansa complex **7**, the paracyclophane species **8**, and bis(benzene)molybdenum (**1**) in a ratio of about 8:1:1. **7**: ^{1}H NMR (500 MHz, C_7D_8, 213 K): $\delta = 0.27$ (s, 12H, CH_3), 4.89 (m, 4H, *m*-C_6H_5), 4.97 (m, 4H, *o*-C_6H_5), 5.01 (m, 2H, *p*-C_6H_5). ^{13}C{^{1}H} NMR (126 MHz, C_7D_8, 213 K): $\delta = -2.0$ (CH_3), 77.3 (*ipso*-C_6H_5), 78.1, 79.9, 80.3 (C_6H_5). ^{29}Si{^{1}H} NMR (99 MHz, C_7D_8, 213 K): $\delta = -14.8$. **8**: ^{1}H NMR (500 MHz, C_7D_8, 213 K): $\delta = 0.31$ (s, 24H, CH_3), 5.31 (s, 8H, C_6H_4). ^{13}C{^{1}H} NMR (126 MHz, C_7D_8, 213 K): $\delta = -1.4$ (CH_3), 81.1 (*ipso*-C_6H_4), 84.6 (C_6H_4). ^{29}Si{^{1}H} NMR (99 MHz, C_7D_8, 213 K): $\delta = -17.3$. **1**: ^{1}H NMR (500 MHz, C_7D_8, 213 K): $\delta = 4.65$ (s, C_6H_6). ^{13}C{^{1}H} NMR (126 MHz, C_7D_8, 213 K): $\delta = 75.2$ (C_6H_6).

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre. Copies of the data [**2**, **4**−**6**, **8**: CCDC 631647−631651] can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by e-mailing data_request@ccdc.cam.ac.uk, or by contacting the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB 1EZ, UK; fax +44 1223 336033.

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Supporting Information Available: Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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