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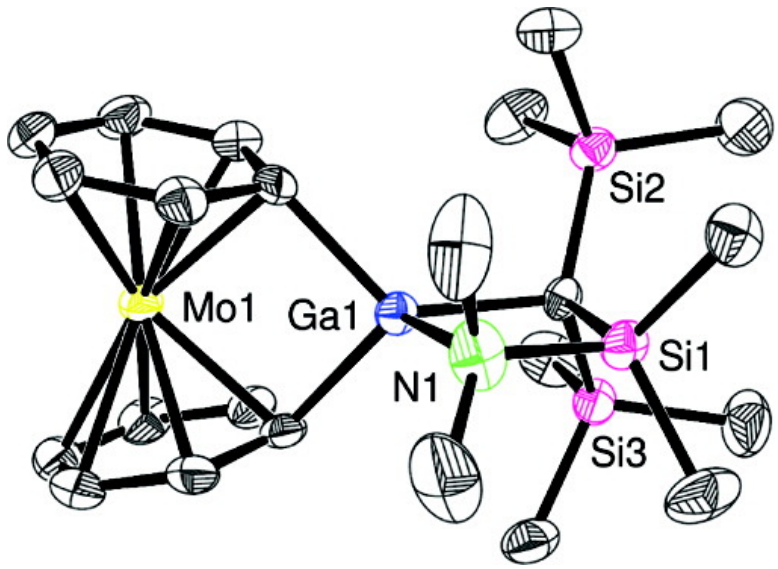

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[1]Molybdarenophanes: Strained Metallarenophanes with Aluminum, Gallium, and Silicon in Bridging Positions

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Abstract: The first [1]molybdarenophanes were synthesized and structurally characterized. The aluminum and gallium compounds [$(Me_2Ntsi)Al(\eta^6\text{-}C_6H_5)_2Mo$] (**2a**) and [$(Me_2Ntsi)Ga(\eta^6\text{-}C_6H_5)_2Mo$] (**2b**) [$Me_2Ntsi = C(SiMe_3)_2(SiMe_2NMe_2)$] were obtained from [$Mo(LiC_6H_5)_2$]·TMEDA and $(Me_2Ntsi)ECl_2$ [E = Al, Ga] in analytical pure form with isolated yields of 74% (**2a**) and 52% (**2b**). The silicon-bridged species [$Ph_2Si(\eta^6\text{-}C_6H_5)_2Mo$] (**2c**) was synthesized from [$Mo(LiC_6H_5)_2$]·TMEDA and Ph_2SiCl_2. Compound **2c** was isolated as a crystalline material in an approximately 90% overall purity, from which a single crystal was used for X-ray analysis. The molecular structures of all three [1]molybdarenophanes **2a**-**c** were determined by single-crystal X-ray analysis. The ring-tilt angle α was found to be 18.28(17), 21.24(10), and 20.23(29)° for **2a**, **2b**, and **2c**, respectively. Variable temperature NMR measurements of **2a** and **2b** (−80 to 80 °C; 500 MHz) showed a dynamic behavior of the gallium species **2b** but not of compound **2a**. The dynamic behavior of **2b** was rationalized by assuming that the Ga−N donor bond breaks, inversion at the nitrogen atom occurs, and a rotation of the Me_2Ntsi ligand takes place followed by a re-formation of the Ga−N bond on the other side of the gallium atom. The analysis of the signals of meta and ortho protons of **2b** gave approximate values of $\Delta G^{\neq}$ of 59.6 and 59.1 kJ mol^{-1}, respectively. Compound **2b** reacted with [$Pt(PEt_3)_3$] to give the ring-open product [$(\eta^6\text{-}C_6H_6)Mo\{\eta^6\text{-}C_6H_5[GaPh(Me_2Ntsi)]\}$] (**3b**). The molecular structure of **3b** was deduced from a single-crystal X-ray determination. The formation of the unexpected platinum-free product **3b** can be rationalized by assuming that benzene reacted with **2b** in a 1:1 ratio. Through a series of ^1H NMR experiments with **2b** it was shown that small amounts of donor molecules (e.g., THF) in benzene are needed to form **3b**; in the absence of a donor molecule, **2b** is thermally stable.

Introduction

Since the discovery that ring-opening polymerization (ROP) of sila[1]ferrocenophanes yield high molecular weight polymers, many new strained[1]metallacyclophanes have been described in the literature (Figure 1).[1,2] Very recently, this area of organometallic chemistry has witnessed important contributions from several research groups. For example, a new class of strained species derived from cycloheptatrienyl−cyclopentadienyl sandwich compounds, [$(\eta^5\text{-}C_7H_7)(\eta^5\text{-}C_5H_5)M$] (M = Ti, Zr, Cr, V), had been prepared during the last 3 years (Figure 1).[3−8] Braunschweig et al. reported on the synthesis of the first strained manganese sandwich, a derivative of the parent compound [$(\eta^6\text{-}C_6H_6)(\eta^5\text{-}C_5H_5)Mn$].[9] The first [1]metallacyclophanes with aluminum and gallium in bridging positions were made accessible by our efforts using trisyl-type ligands with donor abilities at the group 13 element [trisyl stands for tris(trimethylsilyl)methyl, $(Me_3Si)_3C$]. To date, we have characterized [1]ferrocenophanes,[10−12] [1]chromarenophanes,[12] and [1]vanadarenophanes.[12]

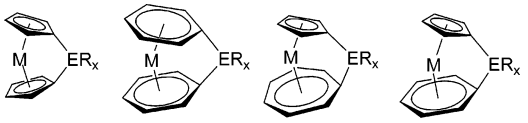

Figure 1. [1]Metallacyclophanes.

The chemistry of strained [1]metallacyclophanes has essentially been restricted to compounds that contain 3d transition

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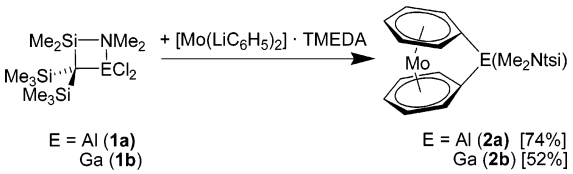
Scheme 1



metals in the sandwich moiety. Besides the zirconium compound mentioned above,[5] [1]ruthenocenophanes are the only strained 4d metal sandwich compounds known today.[13] Surprisingly, even though numerous examples of [1]chromarenophanes are known, not a single [1]molybdarenophane is described in the literature. Bis(benzene)molybdenum was first synthesized by E.O. Fischer et al.[14] Its dilithiation and subsequent reactions with silicon dihalides resulted in sparingly characterized polymeric materials.[15] In the course of the preparation of this manuscript, Braunschweig et al. reported on the dilithiation of $[Mo(C_6H_6)_2]$ and a structural determination of $[Mo(LiC_6H_5)_2(THF)_6]$. However, attempted syntheses of bora- and sila[1]molybdarenophanes were not successful.[16]

Herein, we report on the first successful syntheses of [1]molybdarenophanes, strained organometallic compounds with aluminum, gallium, and silicon in bridging positions.

Results and Discussions

A reaction of freshly prepared $[Mo(LiC_6H_5)_2]$·TMEDA with an intramolecularly coordinated alane or gallane $(Me_2Ntsi)ECl_2$ $[Me_2Ntsi = C(SiMe_3)_2(SiMe_2NMe_2)]$ resulted in [1]molybdarenophanes in moderate isolated yields (Scheme 1).

Both [1]molybdarenophanes **2a** and **2b** show the expected signal pattern for time-averaged C_s symmetric species in their ^1H and ^{13}C NMR spectra. The ^1H NMR spectrum of the alane **2a**, for example, displays two doublets at δ 3.75 and 4.43 (*o*-H) and three pseudotriplets at δ 5.08, 5.16, and 5.57 (*m*-H, *p*-H) with equal signal intensities (25 °C in C_6D_6). At similar conditions, compound **2b** (25 °C in C_7D_8) shows only four instead of the expected five signals: three broad signals at δ 3.52 (*o*-H), 4.05 (*o*-H) and 5.24 (*m*-H), and one well resolved pseudotriplet at δ 5.52 (*p*-H) (Figure 2). A similar sequence of signals for ortho, meta, and para protons was found for the alumina and galla[1]chromarenophanes.[12] A definite proof that the isolated products **2a** and **2b** are indeed strained [1]metallarenophanes comes from their ^{13}C NMR data. The aromatic *ipso*-C atoms resonate at δ 54.4 (**2a**) and 44.5 (**2b**) which is a significant upfield shift compared to that of the unstrained parent bis(benzene)molybdenum (δ 75.7). These shifts are larger than those observed for alumina and galla[1]chromarenophanes equipped with the same stabilizing trisyl-type ligand [δ 62.1 (Al) and 56.6 (Ga) relative to δ 74.8 for $Cr(C_6H_6)_2$].[12] The larger shift is expected as [1]molybdarenophanes should be more highly strained than their chromium analogues.

As mentioned above, the peaks in the proton NMR spectrum of **2b** are broader and not as well resolved as those of **2a** (Figure 2). However, the signals of the gallane **2b** sharpen at lower temperature so that at −10 °C its pattern is similar to that of **2a** (Figure 2). We performed variable temperature NMR measurements of **2a** and **2b** (−80 to 80 °C; 500 MHz). While the alane **2a** does not show coalescences, the signals of meta and ortho protons of **2b** coalescence at 19.0 and 40.1 °C, respectively, resulting in approximate values of $\Delta G^{\neq}$ of 59.6 and 59.1 kJ mol^{-1}.[17] The dynamic behavior can be rationalized by assuming that the E−N donor bond breaks, inversion at the nitrogen atom occurs, and rotation of the Me_2Ntsi ligand takes place followed by a re-formation of the E−N bond on the other side of the bridging atom. This process is fast enough in the case of the gallane **2b** resulting in a time-averaged C_{2v} species at higher temperatures. The fact that compound **2a** does not show coalescence within the accessible temperature range matches the expectation that Al−N donor bonds are stronger than Ga−N donor bonds.

Suitable crystals for X-ray structural determinations of both [1]molybdarenophanes were obtained by crystallization from aromatic solvents. The alane was obtained as **2a**·$^1/_2C_6H_5CH_3$ and the gallane as **2b**·C_6H_6 (Table 1 and Figures 3 and 4). The group 13 element is situated in a spiro position and part of a four-membered ring that deviates only slightly from planarity (rms deviations from planarity are 0.0387 (**2a**) and 0.0330 Å (**2b**)). Aluminum and gallium, respectively, are distorted tetrahedrally coordinated by one N and three C atoms. Whereas Al−C bonds are slightly shorter than the respective Ga−C bonds, the Al−N bond of 2.021(4) Å is significantly shorter than the Ga−N bond of 2.120(3) Å (Figure 3 and 4). Similar sets of bond lengths had been determined for the [1]chromarenophanes and [1]vanadarenophanes.[12] The difference of ca. 0.10 Å between the two E-N bond lengths renders the Ga−N bond much weaker than the Al−N bond, a fact that fits to the observed fluctuating behavior of **2b** in solution.

The extent of strain in metallacyclophanes is usually illustrated by a set of angles (Figure 5). The tilt angles α, which is a measure of the deviation of the two phenyl rings from coplanarity, is the most commonly used parameter to compare different [1]metallacyclophanes. Compounds **2a** and **2b** with tilt angles α of 18.28(17) and 21.24(10)° are expectedly higher tilted than their chromium counterparts [α = 11.81(9) (Al) and 13.24(13)° (Ga)].[12] Dimethylsila[1]ferrocenophane, the most thoroughly investigated [1]metallacyclophane, shows with α = 20.8(5)°[18] a similar distortion as **2a** and **2b**.

For most new [1]metallacyclophanes, silicon-bridged species were the first ones which were explored. On the basis of the promising results we obtained with the synthesis of **2a** and **2b**, we performed initial experiments targeted at silicon-bridged [1]molybdarenophanes. As already mentioned in the introduction, independent from our efforts, Braunschweig and co-worker's targeted these species, but their attempted synthesis of sila[1]molybdarenophanes failed and 1,1′-disubstituted bis(benzene)molybdenum compounds were isolated instead.[16] The authors speculated that the targeted [1]molybdarenophanes were thermally instable, which prevented their isolation; no direct evidence for the formation of these ansa species were found. Following the procedure for the synthesis of **2a-b**, we reacted

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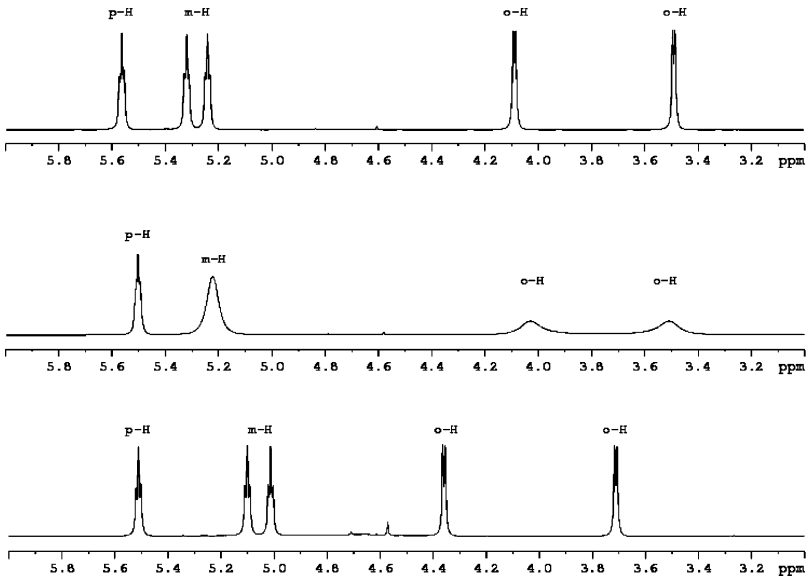

Figure 2. ^{1}H NMR spectra in the region of the arene protons of **2a** at 25 °C (bottom), of **2b** at 25 °C (middle), and **2b** at −10 °C (top) taken in C_7D_8 (small singlet at δ 4.58 (room temp) and 4.61 (−10 °C) is due to $[Mo(C_6H_6)_2]$).

Table 1. Crystal and Structural Refinement Data for Compounds **2a**−**c**, and **3b**

	2a·$^1/_2$toluene	**2b**·benzene	**2c**	**3b**
empirical formula	$C_{53}H_{88}Al_2Mo_2N_2Si_6$	$C_{29}H_{46}GaMoNSi_3$	$C_{24}H_{20}MoSi$	$C_{29}H_{46}GaMoNSi_3$
formula weight	1167.63	658.60	432.43	658.60
wavelength, Å	0.71073	0.71073	0.71073	0.71073
crystal system	triclinic	triclinic	monoclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P21/c$	$P\bar{1}$
Z	1	2	4	2
a, Å	9.0050(4)	9.2069(3)	7.8790(5)	9.2936(5)
b, Å	9.7930(5)	13.3959(4)	18.5687(13)	9.7991(5)
c, Å	17.0803(8)	13.5754(3)	14.5051(9)	17.2637(10)
α, deg	98.873(3)	110.073(2)	90	90.071(4)
β, deg	97.435(2)	90.698(2)	120.590(4)	102.786(3)
γ, deg	96.174(3)	96.944(2)	90	92.141(4)
vol, Å^3	1463.15(12)	1558.49(8)	1826.8(2)	1532.06(14)
d (calcd), mg/m^3	1.325	1.403	1.572	1.428
temp, K	173(2)	173(2)	173(2)	173(2)
abs coefficient, mm^{-1}	0.617	1.400	0.788	1.424
θ range, deg	2.26 to 26.02	2.58 to 27.54	2.81 to 23.25	3.12 to 24.41
refln collected	17573	22845	9175	15565
independent refln	5736 [R(int) = 0.0959]	7144 [R(int) = 0.0607]	2624 [R(int) = 0.1586]	5028 [R(int) = 0.1303]
abs correction	ψ-scan	ψ-scan	none	ψ-scan
ref method	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2
data/restraints/params	5736/99/321	7144/38/296	2624/0/235	5028/0/327
GOF on F^2	1.072	1.041	1.056	1.065
final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0540 w$R2$ = 0.1220	$R1$ = 0.0441 w$R2$ = 0.0986	$R1$ = 0.0633 w$R2$ = 0.1002	$R1$ = 0.0690 w$R2$ = 0.1584
R indices (all data)	$R1$ = 0.0935 w$R2$ = 0.1459	$R1$ = 0.0655 w$R2$ = 0.1107	$R1$ = 0.1169 w$R2$ = 0.1167	$R1$ = 0.1053 w$R2$ = 0.1785
largest diff. peak and hole, e.Å^{-3}	0.717 and −0.819	0.826 and −0.628	0.480 and −0.563	1.317 and −0.943

$[Mo(LiC_6H_5)_2]$·TMEDA with Ph_2SiCl_2. According to the ^{1}H NMR spectrum of the reaction mixture the targeted diphenylsila-[1]molybdarenophane (**2c**) was unequivocally formed among other products. On the basis of the published NMR data for 1,1′-disubstituted bis(benzene)molybdenum compounds,[16] compound **2c** is formed in an approximate 1:1 mixture with $[Mo\{C_6H_5(SiPh_2Cl)\}_2]$. The separation of pure **2c** from this mixture proved to be very difficult. To date, we have successfully crystallized **2c** from benzene, resulting in single crystals suitable for X-ray structural analysis. However, the overall purity of isolated **2c** was estimated to be >90% (see Experimental Section). This first silicon-bridged [1]molybdarenophane (**2c**) was unequivocally identified by ^{1}H and ^{13}C NMR spectroscopy. For example, a large splitting between the resonances of ortho, meta, and para protons at δ 4.04 (d), 4.98 (pst), and 5.46 (pst) (Figure 6), respectively, clearly shows that a strained C_{2v} symmetrical [1]molybdarenophane had been formed.

Via 2D correlated NMR spectroscopy, ^{13}C NMR signals could be assigned to ortho, meta, and para carbon atoms and, more importantly, the signal of the *ipso*-C atom was detected at δ 32.0. The upfield shift of the resonance of the *ipso*-C atom with respect to the unstrained parent bis(benzene)molybdenum (δ 75.7) clearly supports the conclusion from the proton spectra.

To obtain structural details, a single-crystal X-ray analysis of **2c** was undertaken (Table 1 and Figure 7). The silicon atom in **2c** is nearly ideally tetrahedrally surrounded by four carbon

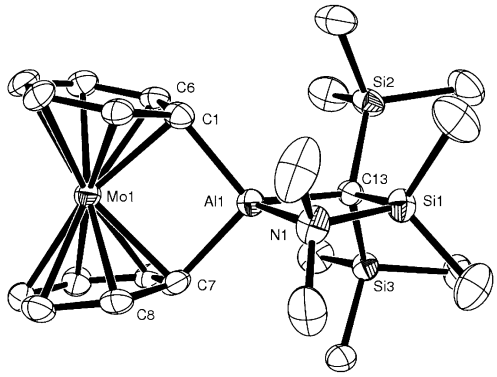

Figure 3. Molecular structure of **2a** with thermal ellipsoids at the 50% probability level. H atoms and $^1/_2$ a molecule of toluene are omitted for clarity. Selected bond lengths [Å] and angles [deg]: Al1−N1 = 2.021(4), Al1−C1 = 2.005(5), Al1−C7 = 2.012(5), Al1−C13 = 2.048(5), C1−Al1−C7 = 98.2(2), C7−Al1−C13 = 125.10(19), C1−Al1−C13 = 122.0(2), C7−Al1−N1 = 111.7(2), C1−Al1−N1 = 113.90(19), C13−Al1−N1 = 86.16(19).

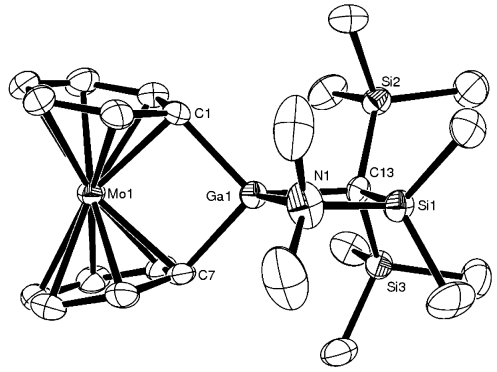

Figure 4. Molecular structure of **2b** with thermal ellipsoids at the 50% probability level. H atoms and one molecule of benzene are omitted for clarity. Selected bond lengths [Å] and angles [deg]: Ga1−N1 = 2.120(3), Ga1−C1 = 2.029(4), Ga1−C7 = 2.023(4), Ga1−C13 = 2.054(3), C1−Ga1−C7 = 93.74(14), C7−Ga1−C13 = 125.85(14), C1−Ga1−C13 = 128.35(14), C7−Ga1−N1 = 114.54(15), C1−Ga1−N1 = 109.96(16), C13−Ga1−N1 = 84.50(14).

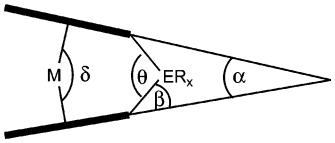

Figure 5. Common angles to describe [1]metallacylophanes. Values for **2a**[2b] in [deg]: α = 18.28(17) [21.24(10)], θ = 98.2(2) [93.74(14)], and δ = 167.31(20) [164.20(17)].

atoms, which can be illustrated by the narrow range of 102.6(4)−111.6(4)° found for the six C−Si−C angles. Expectedly, the θ angle of 102.6(4)° (C1−Si1−C7) is the most distorted C−Si−C angle. The four Si−C bonds are split into a set of two shorter bonds (Si1−C13 = 1.867(8) and Si1−C19 = 1.851(9) Å) and two longer bonds (Si1−C1 = 1.901(9) and Si1−C7 = 1.897(9) Å). Even though the differences between the two sets are small, they are significant and can be rationalized as being a consequence of the strain exerted on the bonds of silicon to the *ipso*-C atoms of the coordinated phenyl rings. In agreement with this interpretation is the fact that the less strained diphenylsila[1]chromarenophane[19] shows a less pronounced difference between the two sets of Si−C bonds (1.882(4)/1.882(4) Å compared to 1868(4)/1.870(5) Å).

The tilt angle α is the most commonly used parameter to illustrate the degree of strain in metallacyclophanes (Figure 5). For the aluminum-bridged [1]molybdarenophanes **2a** the α angle of 18.28(17)° means a 55% (6.5°) increase compared to its chromium analogue [$(Me_2Ntsi)Al(C_6H_5)_2Cr$] (α = 11.81(9)°).[12] Similarly, the gallium species **2b** with α = 21.24(10)° shows an increase of 60% (8.0°) with respect to its chromium counterpart (α = 13.24(13)°).[12] Compound **2c** exhibits a tilt angle α of 20.23(29)° which is only a 40% (5.8°) increase compared to its chromium analogue[19] (α = 14.4°). On the basis of the increases found for **2a** and **2b**, a tilt angle between 22−23° would be expected for compound **2c**.

The interest in novel [1]metallacyclophanes is partly driven by their potential usefulness for ring-opening polymerizations (ROPs). However, the known examples of ROPs of strained metallarenophanes are rare. Manners et al. had shown that thermal or anionic copolymerization of dimethylsila[1]chromarenophane with dimethylsila[1]ferrocenephane can be performed.[20] A few years later, dimethylsila[1]chromarenophane was polymerized using Karstedt's catalyst, but the poor solubility of the resulting polymers prevented a full characterization.[21] To investigate if a metallarenophane is prone to undergo transition-metal mediated ROP, platinum complexes like [Pt(1,5-COD)$_2$][22,23] and [Pt(PEt$_3$)$_3$][23−28] had been used with the intent of isolating a compound in which a PtL$_x$ moiety is inserted into the *ipso*-C bridging-element bond. Compounds of this type have thrown some light on the transition-metal mediated ROP.[23] The first isolatable compound was [Fe(η^5-C$_5$H$_4$)$_2$Pt(PEt$_3$)$_2$SiMe$_2$] obtained from dimethylsila[1]ferrocenophane and [Pt(PEt$_3$)$_3$].[24,25] On this basis, we intended to find out if the new [1]molybdarenophanes might undergo transition-metal mediated polymerizations and we did a series of experiments with the gallium-bridged species **2b**. Surprisingly, compound **2b** reacts with [Pt(PEt$_3$)$_3$] in refluxing benzene to give the new ring-opened product **3b** (Figure 8). As deduced from a single-crystal X-ray analysis, **3b** is a platinum-free species (Table 1 and Figure 8).

Its formation can be rationalized by assuming that benzene reacted with the [1]molybdarenophane **2b** in a 1:1 ratio. We performed a series of NMR experiments to elucidate the role of the platinum complex. ^{1}H NMR experiments with **2b** and [Pt(PEt$_3$)$_3$] in C$_6$H$_6$ and C$_6$D$_6$, respectively, clearly revealed that the nonsubstituted benzene ring of the bis(arene)molybdenum moiety of **3b** exclusively comes from the solvent. From a competing experiment between C$_6$H$_6$ and C$_6$D$_6$, it was shown that both ligands are incorporated into **3b** with the same rate, attesting that C−H activation is not part of a rate determining step. If [Pt(PEt$_3$)$_3$] was not added, the galla[1]molybdarenophane

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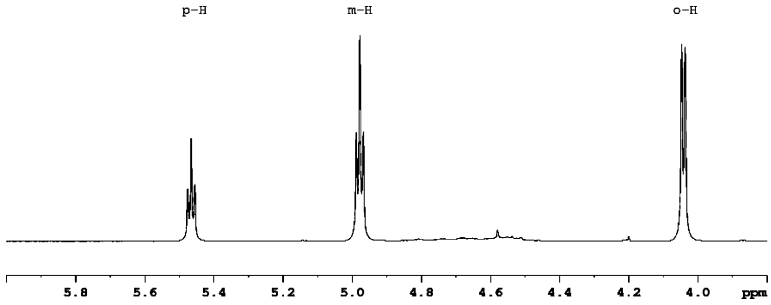

Figure 6. ^{1}H NMR spectrum in the region of the arene protons of **2c** at 25 °C.

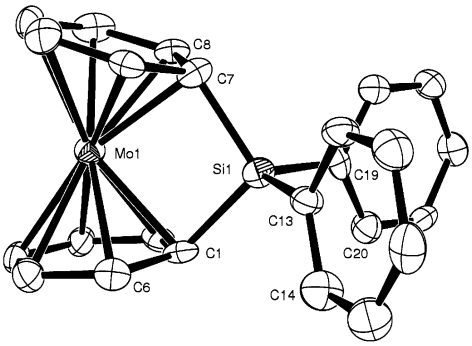

Figure 7. Molecular structure of **2c** with thermal ellipsoids at the 50% probability level. H atoms are omitted for clarity. Selected bond lengths [Å] and angles [deg]: Si1−C1 = 1.901(9), Si1−C7 = 1.897(9), Si1−C13 = 1.867(8), Si1−C19 = 1.851(9), C1−Si1-C7 = 102.6(4), C1−Si1−C13 = 111.3(4), C1−Si1−C19 = 111.0(4), C7−Si1−C13 = 111.6(4), C7−Si1−C19 = 109.3(4), C13−Si1−C19 = 110.8(4), α = 20.23(29), δ = 165.29 (see Figure 5).

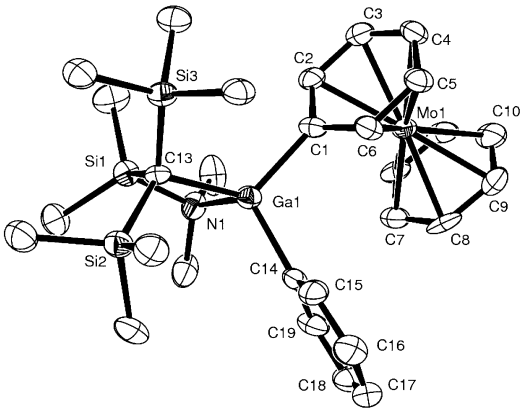

Figure 8. Molecular structure of **3b** with thermal ellipsoids at the 50% probability level. H atoms are omitted for clarity. Selected bond lengths [Å] and angles [deg]: Ga1−N1 = 2.148(6), Ga1−C1 = 2.001(7), Ga1−C14 = 1.994(8), Ga1−C13 = 2.096(7), C1−Ga1−C14 = 109.2(3), C13−Ga1−C14 = 119.9(3), C1−Ga1−C13 = 117.2(3), C14−Ga1−N1 = 112.8(3), C1−Ga1−N1 = 112.2(3), C13−Ga1−N1 = 83.2(3).

2b did not react with benzene at all: the strained species **2b** did not change after heating to 65 °C in C_6D_6 for 7 days. The reaction of [Pt(COD)$_2$] with **2b** gave also product **3b**. On the basis of these findings, we tested if the platinum complex or just free donor ligands are needed for the transformation. NMR experiments of **2b** in C_6D_6 with 0.3−0.5 equiv amounts of PEt$_3$, COD, and THF, respectively, all resulted in the formation of **3b**. However, only in the case of THF did the reaction proceed exclusively from **2b** to **3b**, with no signs of any byproducts. For PEt$_3$ and COD, the ^{1}H NMR spectra revealed the formation of byproducts, which we could not identify so far. For [Mo(C$_6$H$_6$)$_2$] it is known that the benzene ligands are relatively labile and that is what makes the compound a common starting material for half-sandwich complexes.[29,30] However, the substitution of benzene in [Mo(C$_6$H$_6$)$_2$] by other arenes requires forcing thermal conditions (160 °C; 48 h).[31] The respective ligand substitution in the galla[1]molybdarenophane **2b** which yields **3b** is catalyzed by the donor species, and it seems that the reaction occurs at relatively mild conditions because of the high strain of **2b**.

Summary and Conclusion

The first [1]molybdarenophanes with aluminum, gallium, and silicon in bridging positions have been synthesized. Surprisingly the gallium species **2b** with an α tilt angle of 21.24(10)° is significantly higher strained than its aluminum counterpart **2a** (α = 18.28(17)). This is counterintuitive because the slightly smaller Al atom should result in a slightly larger tilt angle α.[32] To date, for all known cases, the tilt angles α are larger for galla- than for alumina[1]metallacyclophanes.[10−12] Compounds **2a** and **2b** follow the same trend but show with 3.0° so far the largest difference; the reasons for the structural differences are unknown. In the presence of donor ligands like PEt$_3$, COD, and THF, respectively, the otherwise thermally robust gallium species **2b** adds one equivalent of benzene to give the unstrained complex **3b**. The reaction with THF proceeds cleanly to give the ring-open product **3b** exclusively, showing that THF acts as a catalyst only. At this point we can only speculate about the mechanism of this catalyzed benzene addition. It seems likely that the σ-donor ligand coordinates to the molybdenum atom and weakens the coordination of the phenyl group so that benzene eventually replaces the σ-donor ligand and the η^6-phenyl group. This is an unprecedented reactivity of a bis(benzene)molybdenum derivative and a similar ring-opening reaction of [1]metallacyclophanes is not reported in the literature. In contrast to many other [1]metallacyclophanes, the gallium compound **2b** does not insert a PtL$_x$ moiety into *E*-C(*ipso*) bonds, which might be due to a steric protection of these bonds by two bulky SiMe$_3$ groups.

The first silicon-bridged [1]molybdarenophane (**2c**) shows with α = 20.23(29)° a smaller angle than expected. Our finding that bis(lithiobenzene)molybdenum and Ph$_2$SiCl$_2$ results in the targeted sila[1]molybdareanophane **2c** is in contrast to a recent

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(32) Al: 1.25 Å and Ga: 1.26 Å (singly bonded, 3-fold-coordinated elements), see: Holleman-Wiberg. *Inorganic Chemistry,* 1st English ed.; Academic Press: San Diego, London, 2001.

report.[16] The authors reported that 1,1′-disubstituted bis(benzene)molybdenum compounds were formed and speculated that the targeted [1]molybdareanophanes were thermally instable and, therefore, could not be obtained. We have proven that the most strained [1]molybdareanophane, the gallium-bridged species **2b**, is thermally robust when heated in benzene. Besides the sensitivity toward donor molecules, all [1]molybdarenophanes are very sensitive toward oxygen. In all cases the highest resolved ^{1}H NMR spectra with the smallest peak width were obtained from freshly synthesized samples. Prolonged handling of the species using Schlenk techniques usually resulted in ^{1}H NMR spectra with unstructured and broad signals for the aromatic protons of the coordinated phenyl groups. In extreme cases, these peaks disappeared in the baseline, while all other signals remained undisturbed. These observations can be rationalized by assuming that small amounts of oxygen result in small amounts of paramagnetic Mo(I) cations. A fast electron exchange between the neutral and oxidized [1]molybdarenophanes spreads, on time average, the paramagnetic impurity evenly over all species so that only the aromatic protons are affected. Electron transfer of this type were found for bis(benzene)-chromium derivatives before.[12,19,33]

Recently, a novel type of ring-opening polymerization, coined photocontrolled ROP, was described.[34,35] Within this method, a ROP of a sila[1]ferrocenophane is initiated by Cp^-, but the polymerization only occurs under irradiation. Photocontrolled ROP is a living polymerization that can be stopped and continued by turning the light off and on, respectively. Photons weaken the Fe−Cp bond allowing the addition of Cp^-. It is the only example of ROP where the ring-opening happens at the transition-metal side of the precursor. On the basis of our findings, it is feasible that one can develop a similar but "dark" version of the photocontrolled ROP for [1]molybdarenophanes with benzene instead of Cp^- as a starter and THF instead of photons as activator.

Experimental Section

General Procedures. All manipulations were carried out using standard Schlenk techniques. Solvents were dried using a Braun solvent purification system and stored under nitrogen over 4 Å molecular sieves. All solvents for NMR spectroscopy were degassed prior to use and stored under nitrogen over 4 Å molecular sieves. $[Mo(LiC_6H_5)_2]\cdot$TMEDA,[15] $AlCl_2[C(SiMe_3)(SiMe_2NMe_2)]$ (**1a**),[36] and $GaCl_2[C(SiMe_3)(SiMe_2NMe_2)]$ (**1b**)[36] were synthesized as described in the literature. $[Pt(PEt_3)_3]$ was prepared from $[Pt(PEt_3)_4]$[37] in situ by heating to 60 °C under high vacuum in an NMR tube. $[Pt(COD)_2]$ was prepared via a modified procedure by substituting potassium in place of lithium.[38] An improved synthesis of $[Mo(C_6H_6)_2]$ with respect to a common method described in reference[39] is reported below. ^{1}H, ^{13}C, and ^{27}Al NMR spectra were recorded on a Bruker 500 MHz Avance at 25 °C, unless noted differently. ^{1}H chemical shifts were referenced to the residual protons of the deuterated solvent (C_6D_6 at δ 7.15; C_7D_8 at δ 2.10); ^{13}C chemical shifts were referenced to C_6D_6 at δ 128.00 and C_7D_8 at δ 20.40. ^{27}Al NMR spectra were referenced to $[Al(acac)_3]$ dissolved in C_6D_6. An unequivocal assignment of signals of the bis(benzene)molybdenum moiety of compound **2c** was done with the help of ^{1}H/^{1}H-COSY, HMQC, and HMBC spectroscopy. Mass spectra were measured on a VG 70SE (m/z > 10% are listed for signals of the most abundant ions). Elemental analyses were performed on a Perkin-Elmer 2400 CHN elemental analyzer using V_2O_5 to promote complete combustion.

Improved Synthesis of $[Mo(C_6H_6)_2]$ (Based on ref 39). $MoCl_5$ (7.4072 g, 27.082 mmol), $AlCl_3$ (18.522 g, 138.91 mmol), Al (1.821 g, 67.44 mmol), mesitylene (1.0 mL), and benzene (70 mL) were set to reflux for 76 h. All volatiles were removed in vacuum and the brown solid was broken up into small pieces and added to N_2 saturated aqueous solution (175 mL) containing KOH (51.090 g, 910.60 mmol) and NaS_2O_4 (11.152 g, 64.051 mmol) over 1 h at −20 to −30 °C. The solution was decanted off and the brown solid was dried on high vacuum. The solid was continually extracted with boiling benzene (150 mL) to give a dark green solution. All volatiles were removed to give a green solid. The solid was washed with hexanes (60 mL) and dried to give a bright green solid (3.2742 g, 48%). ^{1}H NMR (500 MHz): δ 4.58 (s).

Synthesis of $[\{(Me_2NMe_2Si)(Me_3Si)_2C\}Al(\eta^6\text{-}C_6H_5)_2Mo]$ (2a). $[Mo(C_6H_6)_2]$ (0.7830 g, 3.105 mmol), cyclohexane (30 mL), TMEDA (1.875 g, 16.13 mmol), and *n*BuLi (6.0 mL, 2.6 M in hexanes, 15.6 mmol) were added one after the other, and the mixture was heated (2.5 h, 50 °C) during which the slurry changed color from green to dark red. The solution was syringed off, and the remaining red solid was dried in high vacuum to give $[Mo(LiC_6H_5)_2]\cdot$TMEDA (0.811 g, 2.13 mmol). A slurry of this compound in benzene (20 mL, 0 °C) was added to a solution of **1a** (0.770 g, 2.15 mmol) in benzene (10 mL, 0 °C) and stirred for 1 h at room temperature. LiCl was filtered off, followed by concentration of the filtrate to appoximately 5 mL, and crystallization at 6 °C gave green crystals of **2a**$\cdot C_6H_6$ (0.969 g, 74%). ^{1}H NMR (500 MHz, C_6D_6): δ = 0.14 (s, 6H, $SiMe_2$), 0.45 (s, 18 H, $SiMe_3$), 1.97 (s, 6H, NMe_2), 3.75 (d, 2H, o-H), 4.43 (d, 2H, o-H), 5.08 (pst, 2H, m-H), 5.16 (pst, 2H, m-H), 5.57 (pst, 2H, p-H). ^{13}C NMR (C_6D_6): 3.0 ($SiMe_2$), 8.1 ($SiMe_3$), 40.5 (NMe_2), 54.4 (*ipso*-C), 74.4 (o-C), 74.5 (o-C), 82.5 (p-C), 83.1 (m-C), 83.8 (m-C). ^{27}Al NMR (C_6H_6): 148 ($w_{1/2}$ = 1800 Hz). MS (70 eV): m/z (%) 364 (10) $[M^+ - Mo - C_6H_6 - C_6H_5]$, 295 (14), $[M^+ - Mo - C_6H_6 - 2SiMe_3]^+$, 246 (60) $[MH^+ - Mo - Al - C_6H_6 - 2\,C_6H_5 - CH_3]$, 230 (19) $[M^+ - Mo - Al - C_6H_6 - 2\,C_6H_5 - 2\,CH_3]$, 219 (18) $[C_9H_{27}Si_3]^+$, 217 (16) $[C_9H_{25}Si_3]^+$, 203 (42) $[C_8H_{23}Si_3]^+$, 154 (31) $[C_{12}H_{10}]^+$, 129 (30) $[C_5H_{13}Si_2]^+$, 102 (34) $[C_4H_{12}NSi]^+$, 91 (12) $[C_7H_7]^+$, 78 (100) $[C_6H_6]^+$, 73 (35) $[C_3H_9Si]^+$, 58 (19) $[C_2H_6Si]^+$. Anal. Calcd for $C_{29}H_{46}AlMoNSi_3$ (615.8603): C, 56.56; H, 7.53; N, 2.27; Found: C, 55.73; H, 7.35; N, 2.62. Crystals of **2a**$\cdot{}^1/_2C_7H_8$ suitable for X-ray diffraction were grown from toluene at 6 °C.

Synthesis of $[\{(Me_2NMe_2Si)(Me_3Si)_2C\}Ga(\eta^6\text{-}C_6H_5)_2Mo]$ (2b). $[Mo(C_6H_6)_2]$ (0.9116 g, 3.615 mmol), cyclohexane (30 mL), TMEDA (2.180 g, 18.76 mmol), and *n*BuLi (7.0 mL, 2.6 M in hexanes, 18 mmol) were added one after another, and the mixture was heated (2.5 h, 50 °C) during which the slurry changed color from green to dark red. The solution was syringed off and the remaining red solid was dried in high vacuum (0.835 g, 2.20 mmol). A slurry of this compound in benzene (30 mL, 0 °C) was added to a solution of **1b** (0.884 g, 2.20 mmol) in benzene (10 mL, 0 °C). After stirring for 2 h at room temperature, LiCl was filtered off, the filtrate was concentrated (5 mL), and crystallization at 6 °C gave green crystals of **2b**$\cdot C_6H_6$ (0.747 g, 52%). ^{1}H NMR (500 MHz, C_7D_8, −10 °C): δ = 0.19 (s, 6H, $SiMe_2$), 0.45 (s, 18 H, $SiMe_3$), 1.99 (s, 6H, NMe_2), 3.49 (d, 2H, o-H), 4.09 (d, 2H, o-H), 5.23 (pst, 2H, m-H), 5.32 (pst, 2H, m-H), 5.56 (pst., 2H, p-H). ^{13}C NMR (C_7D_8, −10 °C) : 2.8 ($SiMe_2$), 7.3 ($SiMe_3$), 11.7 (CSi_3), 41.2 (NMe_2), 44.5 (*ipso*-C), 73.8 (o-C), 73.9 (o-C), 83.6 (p-C), 84.5

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(m-C), 85.5 (m-C). MS (70 eV): *m/z* (%) 406 (100) [M^+ − Mo − C_6H_6 − C_6H_5], 361 (22) [M^+ − Mo − C_6H_6 − C_6H_5 − $3CH_3$], 292 (13) [M^+ − Mo − Ga − C_6H_6 − C_6H_5 − $3CH_3$], 246 (87) [MH^+ − Mo − Ga − C_6H_6 − 2 C_6H_5 − CH_3], 230 (74) [M^+ − Mo − Ga − C_6H_6 − $2C_6H_5$ − $2CH_3$], 223 (13) $[C_{12}H_{10}Ga]^+$, 217 (35) $[C_9H_{25}Si_3]^+$, 203 (31) $[C_8H_{23}Si_3]^+$, 201 (15) $[C_8H_{21}Si_3]^+$, 187 (25) $[C_7H_{19}Si_3]^+$, 175 (14) $[C_8H_{23}Si_2]^+$, 154 (15) $[C_{12}H_{10}]^+$, 128 (28) $[C_5H_{12}Si_2]^+$, 102 (26) $[C_4H_{12}NSi]^+$, 78 (93) $[C_6H_6]^+$, 73 (31) $[C_3H_9Si]^+$. Anal. Calcd for $C_{29}H_{46}GaMoNSi_3$ (658.6017): C, 52.89; H, 7.04; N, 2.13; Found: C, 52.26; H, 7.10; N, 2.37.

Synthesis of [$Ph_2Si(\eta^6\text{-}C_6H_5)_2Mo$] (2c). [$Mo(C_6H_6)_2$] (1.1062 g, 4.387 mmol), cyclohexane (30 mL), TMEDA (2.589 g, 22.28 mmol), and *n*BuLi (7.8 mL, 2.86 M, 22.3 mmol) were added one after another, and the mixture was heated (2.5 h, 50 °C) during which the slurry changed color from green to dark red. The solution was syringed off, and the remaining red solid was dried in high vacuum (1.383 g, 3.637 mmol). A slurry of this compound in benzene (30 mL, 0 °C) was prepared, and Ph_2SiCl_2 (0.917 g, 3.622 mmol) was added dropwise during 10 min. The solution was warmed to ambient temperature and stirred for 1 h. An ^1H NMR spectrum from an aliquot of the reaction mixture revealed that **2c** had been formed. Crystallization from benzene at 6 °C gave **2c** as a red-brown crystalline solid (0.415 g, app. 23%), from which a single crystal was used for the X-ray structural analysis. However, according to ^1H NMR spectroscopy this crystalline fraction showed an approximate overall purity of 90% (see Supporting Information). ^1H NMR (500 MHz, C_6D_6): $\delta = 4.04$ (d, 4H, o-H), 4.98 (pst, 4H, m-H), 5.46 (pst, 2H, p-H), 7.20 (m, 6H, m-H, p-H), 7.97 (pst, 4H, o-H). ^{13}C NMR (C_6D_6): 32.0 (*ipso*-C), 74.1 (o-C), 85.1 (p-C), 85.6 (m-C), 128.9 (p-C), 130.5 (m-C), 134.4 (*ipso*-C), 134.5 (o-C).

Synthesis of [($\eta^6\text{-}C_6H_6$)Mo{$\eta^6\text{-}C_6H_5$[$GaPh(Me_2Ntsi)$]}] (3b). [$Pt(PEt_3)_4$] (0.3751 g, 0.5618 mmol) was placed in a Schlenk flask and heated to 60 °C under vacuum (10^{-2} Torr) to give [$Pt(PEt_3)_3$] as a red oil.[37] Benzene (5 mL) and **2b** (0.3698 g, 0.5615 mmol) were added. After stirring for 1 h at ambient temperature, the solution was heated to 65 °C for 87 h. The mixture was monitored by ^1H NMR spectroscopy with a gradual disappearance of **2b** and the appearance of new signals. All volatiles were removed and the resulting black solid was extracted with benzene (5 mL). The benzene was removed and the greenish solid was dissolved in a 1:1 mixture of Et_2O and toluene (5 mL) and kept at −30 °C to give green crystals (0.105 g, 28%). ^1H NMR (500 MHz, C_6D_6): $\delta = 0.19$ (br. s, 6 H, $SiMe_2$), 0.35 (s, 18H, $SiMe_3$), 2.22 (s, 6H, NMe_2), 4.47 (s, 6H, Ph), 4.53 (br. d, 2H, o-H), 4.60 (br. s, 2H, m-H), 4.67 (pst, 1H, p-H), 7.21 (pst, 1H, p-H), 7.29 (pst, 2H, m-H), 7.68 (d, 2H, o-H).

^1H NMR Experiments with 2b. [$Pt(PEt_3)_3$] was prepared from [$Pt(PEt_3)_4$][37] in situ by heating to 60 °C under high vacuum in an NMR tube. PEt_3 (1.0 M in THF) was purchased from Aldrich. Samples were prepared in a glovebox and subsequently flame sealed by freezing the samples in liquid nitrogen and evacuating the tubes under high vacuum (10^{-2} mbar). All NMR tubes were heated for prolonged time at an oil bath temperature of 65 °C and monitored by ^1H NMR spectroscopy.

Tube 1: [$Pt(PEt_3)_4$] (37.4 mg, 0.0560 mmol) was weighed into a NMR tube, and the off-white solid was converted to the red oil [$Pt(PEt_3)_3$] by heating the NMR tube to 60 °C under high vacuum. Compound **2b**·C_6H_6 (37.5 mg, 0.0569 mmol) in C_6D_6 (1 mL) was added to the red oil, and the tube was flame sealed. After 1336 h approximately 80% of the starting compound **2b** had been consumed.

Tube 2: PEt_3 (0.016 mL, 1.0 M in THF, 0.016 mmol) was placed in a NMR tube, and THF was removed under reduced pressure. Compound **2b**·C_6H_6 (28.6 mg, 0.0434 mmol) in C_6D_6 (1 mL) was added, and the tube was flame sealed. After 1168 h the starting compound **2b** had been consumed.

Tube 3: **2b**·C_6H_6 (27.1 mg, 0.0411 mmol) was placed in a NMR tube, C_6D_6 (1 mL) was added, and the tube was flame sealed. After 160 h the starting compound **2b** showed no signs of decomposition or transformation. After 832 h 4% of **2b** had been transformed to **3b**.

Tube 4: **2b**·C_6H_6 (26.4 mg, 0.0401 mmol) and [$Pt(PEt_3)_4$] (26.6 mg, 0.0398 mmol) were weighed into an NMR tube, C_6D_6 (1.0 mL) was added, and the tube was flame sealed. After 304 h the starting compound **2b** had been consumed.

Tube 5: [$Pt(COD)_2$] (11.0 mg, 0.027 mmol) was dissolved in C_6D_6 (1.0 mL), compound **2b**·C_6H_6 (15.3 mg, 0.023.2 mmol) was added to the solution, and the tube was flame sealed. After 304 h the starting compound **2b** had been consumed.

Tube 6: **2b**·C_6H_6 (19.4 mg, 0.029 mmol) was placed in a NMR tube and THF (1.2 μL, 0.01 mmol), and C_6D_6 (1.0 mL) were added, followed by flame sealing the tube. After 448 h the starting compound **2b** had been cleanly converted to **3b**.

Tube 7: **2b**·C_6H_6 (25.8 mg, 0.039 mmol) was placed in a NMR tube and COD (2.4 μL, 0.02 mmol) and C_6D_6 (1.0 mL) were added, followed by flame sealing the tube. After 448 h the starting compound **2b** had been consumed.

Tube 8: [$Pt(PEt_3)_4$] (28.3 mg, 0.042 mmol) was converted to [$Pt(PEt_3)_3$] as described above and **2b**·C_6H_6 (28.1 mg, 0.043 mmol) was added. The compounds were dissolved in C_6H_6 (0.50 mL, 5.6 mmol) and C_6D_6 (0.50 mL, 5.6 mmol), and the tube was flame sealed. After 216 h the reaction was stopped because it was determined that no deuterium isotope effect was present.

Crystal Structure Determination. The crystal data of **2a**−**c**, and **3b** were collected at −100 °C on a Nonius Kappa CCD diffractometer, using the COLLECT program.[40] Cell refinement and data reductions used the programs DENZO and SCALEPACK.[41] SIR97[42] was used to solve the structure and SHELXL-97[43] was used to refine the structure. ORTEP-3 for Windows[44] was used for molecular graphics and PLATON[45] was used to prepare material for publication. H atoms were placed in calculated positions with U_{iso} constrained to be 1.2 times U_{eq} of the carrier atom for aromatic protons. U_{iso} is constrained to be 1.5 times U_{eq} for methyl protons. For compound **2a**, a solvent toluene molecule was found disordered around a center of symmetry. It was modeled with a rigid toluene molecule. The temperature factors of the C atoms of the toluene were allowed to refine but were restrained by SIMU, DELU, and ISOR commands in the refinement. For compound **2b**, a solvent benzene molecule was found disordered around a center of symmetry. It was modeled by two rigid benzene molecules with the sum of their occupancies equal to 1.0. The temperature factors of the C atoms of the benzene were allowed to refine, but were restrained by SIMU, DELU, and ISOR commands in the refinement.

Compounds **2c** and **3b** gave crystals of poor quality. The maximum observable diffraction angles were low (23.25° and 24.41°) and the merging *R* values were high (0.159 and 0.13). A full sphere of data was collected in both cases. The presence of a heavy atom (Mo) in both structures contributes strongly to the poor bond precision for the lighter atoms because the Mo atom dominates the scattering. In both structures all non-hydrogen atoms refined anisotropically with no restraints to reasonable positions giving reasonable bond lengths and bond angles, thus clearly establishing the connectivity of the molecules.

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Supporting Information Available: Crystallographic data for **2a**−**c**, and **3b** in CIF file format; ^{1}H and ^{13}C NMR spectra for **2c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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