Organocalcium-mediated nucleophilic alkylation of benzene

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The electrophilic aromatic substitution of a C-H bond of benzene is one of the archetypal transformations of organic chemistry. In contrast, the electron rich π-system of benzene is highly resistant to reactions with electron rich and negatively charged organic nucleophiles. Here, we report that this previously insurmountable electronic repulsion may be overcome though the use of sufficiently potent organocalcium nucleophiles. Calcium *n*-alkyl derivatives, synthesized by reaction of ethene, but-1-ene and hex-1-ene with a dimeric calcium hydride, react with protio and deutero benzene at 60 °C through nucleophilic substitution of an aromatic C-D/H bond. These reactions produce the *n*-alkyl benzenes with regeneration of the calcium hydride. Density functional theory calculations implicate an unstabilized Meisenheimer complex in the C-H activation transition state.

One Sentence Summary: Aliphatic *n*-alkyl calcium compounds effect the alkylation of benzene by nucleophilic substitution of a single sp^2 C-H bond.

The Friedel–Crafts (F-C) reaction has been one of the cornerstones of organic and industrial synthetic chemistry for 140 years (*1*, *2*). In its most fundamental manifestation, one of the hydrogen atoms of benzene is replaced by the alkyl component of an alkyl halide, R–Hal (Fig. 1A, Hal = Cl, Br, I). Typically, a Lewis acid catalyst such as $FeCl_3$ or $AlCl_3$ binds the halide to transform the alkyl carbon into a positively charged carbenium ion, which is a sufficiently electron poor (electrophilic) target for the comparatively electron rich (nucleophilic) aromatic π-system of benzene to attack (*3*). This process

generates a new C-C bond via a Wheland intermediate in which the resultant positive charge is stabilized through its delocalization around the remaining five carbon atoms (*4*). Substitution is then effected through loss of a proton and the generation of the relevant hydrogen halide.

Despite its importance, F-C alkylation suffers from some serious limitations. Alkylbenzenes are generally more reactive to electrophilic substitution than benzene itself and F-C conditions commonly result in over-alkylation (*5*). Primary carbenium ions are also prone to rearrangement to more stable secondary or tertiary carbenium ions such that, for example, F-C alkylation of benzene with *n*-propyl electrophiles provides primarily *iso*-propylbenzene (cumene) (*5*, *6*).

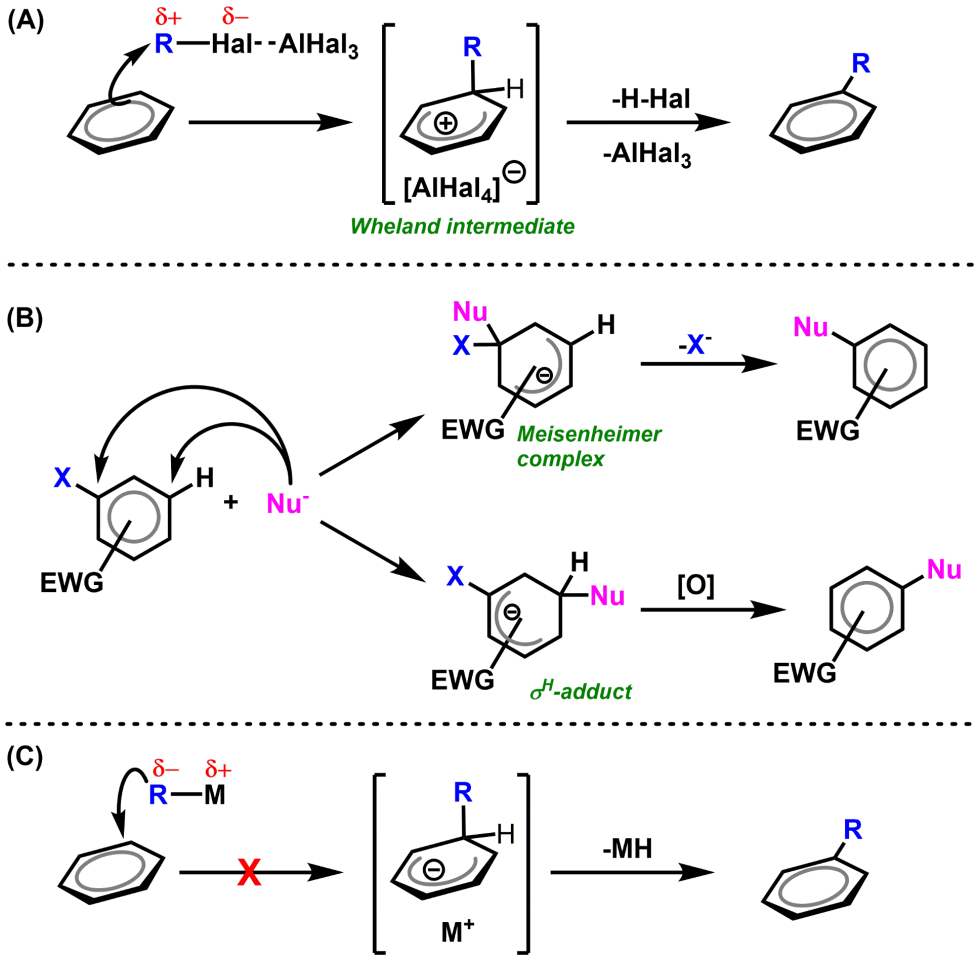
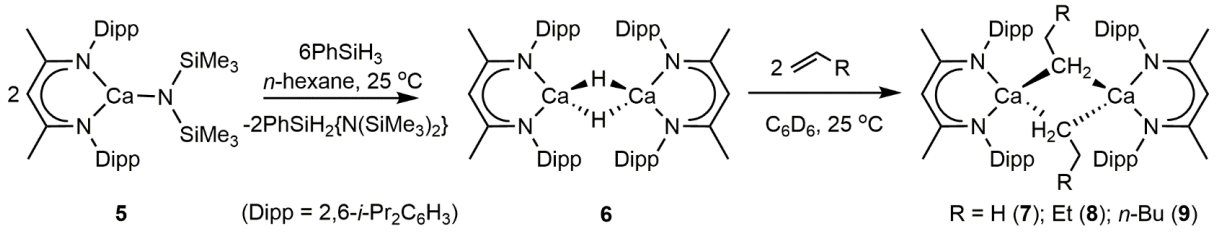


Fig. 1: Distinct aromatic alkylation mechanisms. (A) electrophilic aromatic substitution: Friedel-Crafts alkylation of benzene via Wheland intermediate; (B) nucleophilic aromatic substitution of electron poor arenes via Meisenheimer or σ^H-adduct intermediates; (C) direct nucleophilic aromatic substitution of benzene.

These issues may be potentially circumvented through the alternative pathway of nucleophilic aromatic substitution. The substitution of a C-H bond in unsubstituted benzene by an organic nucleophile, however, is very much more disfavored. The electron rich π-system, which renders benzene so susceptible to attack by electrophiles, tends to repel approaching nucleophiles while the 6π-electron system is significantly destabilized through the formal addition of two extra electrons. Although these factors may be overcome through the installation of sufficiently powerful electron-withdrawing substituents (e.g. nitro, NO_2^-), whereupon nucleophilic attack provides Meisenheimer or σ^H-adduct intermediates (Fig. 1B) (*7*), the departure of the hydride anion invariably requires the addition of a potent external oxidant (*8, 9*). The direct nucleophilic alkylation of benzene (Fig. 1C) has not been achieved, therefore, primarily for the lack of a sufficiently potent alkyl nucleophile.

We have a long standing interest in the development and use of highly polar organometallic derivatives of the heavier alkaline earth (AE = Ca, Sr, Ba) elements as reagents and catalysts (*10, 11*). The electropositive character of these elements and the resultant polarization of the [AE]-X bonding (X = e.g. H, CR_3, NR_2) provide systems which display a high degree of charge separation (i.e. $[AE]^+ X^-$) and which, as a result, are extremely nucleophilic sources of X. A relevant case in point is provided by the reactivity of 1-alkenes with molecular calcium hydrides, a variety of which have now been described (*12-19*). $[(BDI)Ca(THF)H]_2$ (**1**; BDI = $CH[C(CH_3)N\text{-}Dipp]_2$, Dipp = 2,6-diisopropylphenyl) (*12*, *13*) and $[Ca_2H_2(Me_4TACD)_2][BAr_4]_2$ (Me_4TACD = 1,4,7,10-tetramethyl-1,4,7,10-tetraazacyclododecane; Ar = C_6H_4-4-*t*-Bu (**2**) or C_6H_3-3,5-Me_2 (**3**)) (*16*) are active catalysts for the hydrogenation of alkenes. The catalysis by **1**, however, was restricted to substrates with more activated terminal C=C multiple bonds, while its stoichiometric reactivity with alkenes was limited to 1,1-diphenylethene. The resultant 1,1-diphenylethyl derivative, $[(BDI)CaC(CH_3)Ph_2(THF)]$ (**4**) was indefinitely stable in arene solvents (*14*). In contrast, the cationic hydridocalcium derivatives, **2** and **3**, catalyzed the hydrogenation of even 1-hexene and 1-octene (*16*). In neither case, however, could the implied *n*-alkylcalcium intermediates be observed. These latter compounds were, thus, deduced to be unstable toward β-hydride elimination and the regeneration of the cationic hydrides. In this contribution, we show that use of a THF-free version of compound **1** also facilitates reactions with non-activated (*n*-aliphatic) terminal alkenes. The

resultant calcium primary *n*-alkyls are stable and are able to effect the direct nucleophilic substitution of benzene at moderately elevated temperatures.



5 (Dipp = 2,6-*i*-$Pr_2C_6H_3$) **6** R = H (**7**); Et (**8**); *n*-Bu (**9**)

Fig. 2: Synthesis of compounds **6** – **9**.

The reaction of [(BDI)CaN(SiMe$_3$)$_2$] (**5**) (*20*) with phenylsilane has very recently been reported to result in inevitable dismutation of [(BDI)CaH]$_2$ (**6**) to [(BDI)$_2$Ca] and a fine insoluble white powder which was presumed to be CaH_2 (*15*). In our hands, room temperature reaction of a threefold excess of $PhSiH_3$ with compound **5** performed in hexane provides good yields (>70%) of compound **6**, which crystallizes readily from a saturated toluene solution at –35 °C (Fig. 2). Analysis of compound **6** by NMR spectroscopy provided data indicative of a single BDI ligand environment and a singlet resonance observed in the ^{1}H NMR spectrum at δ 4.27 ppm, which was assigned to the hydridic Ca-*H* proton (Fig. S1). This latter chemical shift resembles the analogous hydride resonances arising from compound **1** (δ 4.45 ppm) (*12*) and other previously reported bridged calcium hydrides (*15*-*19*). These data suggest that **6** adopts a comparable bridged dimeric structure in solution, a supposition which was subsequently confirmed in the solid state by a single crystal x-ray diffraction analysis (Fig. 3A).

Although there have been recent notable advances in the synthesis of calcium σ–aryl derivatives (*21*-*23*), the successful isolation of well-defined calcium σ–alkyls has been historically dependent upon the use of highly sterically demanding and kinetically stabilizing organic anions (*24*–*32*). The synthesis of compound **6** prompted us to study its reactivity with less bulky terminal alkenes in an attempt to synthesize the corresponding calcium *n*-alkyl derivatives. Compound **6** was, thus, treated with 1 atmosphere of the gaseous alkenes ethene and but-1-ene and with three molar equivalents of hex-1-ene at room temperature in d_6-benzene to provide the respective ethyl (**7**), *n*-butyl (**8**) and *n*-hexyl (**9**) calcium compounds (Fig. 2). Monitoring by ^{1}H NMR spectroscopy indicated that the reaction to generate the

ethyl derivative (**6**) appeared to be less discriminating than those of its longer chain homologs and resulted in the production of additional reaction products (*vide infra*). Although this onward reactivity precluded the isolation of a pure bulk sample of compound **7**, all three reactions resulted in the disappearance of the ^{1}H NMR hydride resonance of compound **6** over a period of 48 hours at room temperature. In each case, the simultaneous generation of β-diketiminato calcium ethyl (**7**), *n*-butyl (**8**) and *n*-hexyl (**9**) derivatives was clearly evidenced through the appearance of upfield (δ –0.7 to –0.8 ppm) α-methylene ^{1}H NMR resonances as quartet (**7**) and triplet (**8**, **9**) signals, respectively. In each case, a similar resonance was also observed to persist at ca. 0.3 ppm higher field throughout the course of the reactions but to disappear on complete consumption of the hydride starting material (*vide infra*). The solid-state constitutions of compounds **7** – **9** were confirmed by x-ray diffraction analysis (Figs. 3B (**7**), S20 (**8**) and S29 (**9**)), which demonstrated that each compound crystallizes as a centrosymmetric dimer. Although initial attempts to synthesize calcium analogs of magnesium Grignard reagents were described more than 100 years ago (*33*, *34*), and the structures of a number of σ-bonded aryl (*21*-*23*), benzyl (*35*-*39*) and trimethylsilylmethyl (*21*-*32*) derivatives have been described, aliphatic *n*-alkylcalcium compounds have not been previously crystallographically characterized. All three compounds display asymmetric calcium-to-α-methylene bond lengths (ca. 2.49, 2.58 Å), allowing discrimination between the formal intra- and intermolecular Ca-C bonds. Despite the bridging nature of these interactions, the shorter distance is, in each case, closely comparable to the terminal Ca-C interactions observed in several trimethylsilyl-substituted calcium methyl derivatives, for example $[Ca\{CH(SiMe_3)_2\}_2(THF)_2]$ (2.4930(18) Å) (*26*), and are significantly shorter than the Ca-C bonds typically observed in the various benzylcalcium compounds that have been reported (ca. 2.58 Å) (*35*-*39*). The structures of **7** - **9** also display close contacts (ca. 2.8 Å) between the calcium centers and the carbons of the methyl (**7**) or β-methylene (**8**, **9**) units of each *n*-alkyl chain.

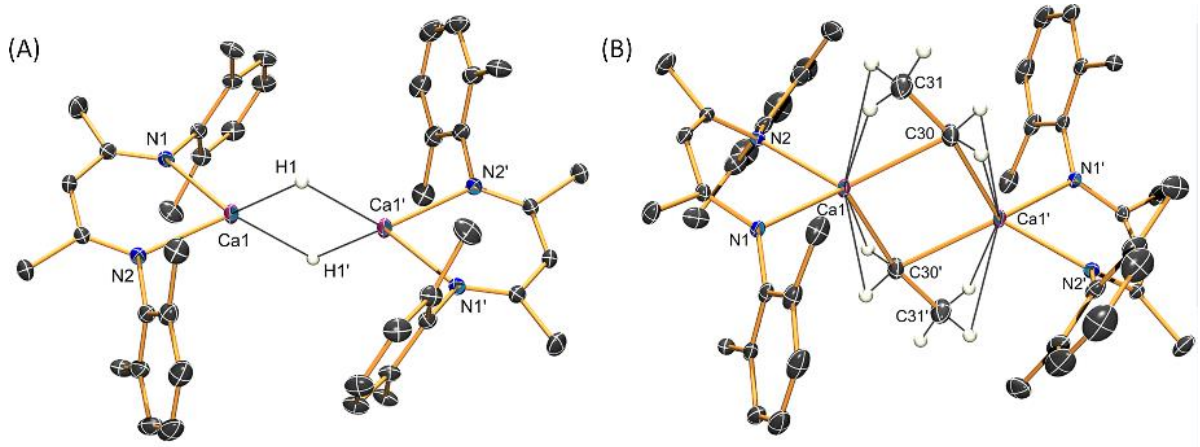


Fig. 3: ORTEP representations (25% probability ellipsoids) of (A) compound **6**; (B) compound **7**; In each case, hydrogen atoms, except for H1 and H1' (**6**), those attached to C30 and C31 (**7**), *iso*-propyl methyl groups and co-crystallized solvent molecules have been omitted for clarity. Selected bond lengths (Å) and angles (°): (**6**) Ca1-N1 2.3097(12), Ca1-N2 2.3222(12), N1-Ca1-N2 79.24(4); (**7**) Ca1-Ca1' 3.3401(6), Ca1-N1 2.3432(12), Ca1-N2 2.3336(13), Ca1 C30' 2.4847(19), Ca1-C30 2.5733(19), Ca-C31 2.840(2); N1-Ca1-Ca1' 136.97(3), N1-Ca1-C30 122.64(6), N1-Ca1-C30' 115.09(6), N1-Ca1-C31' 101.84(6). Symmetry operations to generate equivalent atoms (**6**) ' –*x*, 1–*y*, 1–*z*; (**7**) ' 1-*x*, 1-*y*, -*z*.

The formation of compound **9** was studied by density functional theory (DFT, B3PW91) calculations. This analysis (Fig. S55) indicated that the exothermic (ΔH = –18.4 kcal mol^{-1}) reaction takes place with the retention of the dimeric structure of compound **6**. The rate determining step is a classical highly polarized Ca-H/C=C insertion, which, consistent with the necessary room temperature conditions, occurs via an accessible barrier of 19.6 kcal mol^{-1}. The π component of the C=C bond is almost fully broken during the assembly of the highly polarized transition state ($TS_{\mathbf{BC}}$ in Fig. S55), which induces partial charges of –0.6 and –0.2 on the C1 and C2 carbon atoms of the hexene molecule, respectively. Hex-1-ene insertion into the dimeric calcium hydride was also found to take place sequentially via the formation of a dicalcium alkyl-hydrido complex (Fig. S55, **C**). On this basis, we suggest that the higher field methylene ^{1}H NMR resonances observed during the formation of compounds **7** – **9** arise from the intermediacy of the relevant ethyl-, *n*-butyl- and *n*-hexylhydrido-dicalcium intermediates.

In an attempt to optimize the synthesis of compound **7**, the reaction of ethene with compound **6** was repeated in d_{12}-cyclohexane. Although this procedure resulted in a similar rate and level of consumption of the calcium hydride, monitoring of the solution by ^{1}H NMR spectroscopy revealed that compound **7** displayed significantly enhanced stability in the aliphatic solvent. Comparison with the corresponding spectrum of the reaction performed in d_6-benzene highlighted that the generation and subsequent disappearance of compound **7** was accompanied by the formation of a further predominant compound, which was characterized by the appearance of a quartet signal at δ 2.45 ppm. Subsequent trap-to-trap distillation and analysis of the volatiles by NMR spectroscopy identified this compound as d_5-ethylbenzene (Figs. S30 – S33). This observation prompted us to study the stability of the isolable longer chain analogues, compounds **8** and **9**, in d_6-benzene, which revealed that these *n*-alkylcalcium complexes display a remarkable capacity to effect the nucleophilic alkylation of benzene (Fig. 4A).

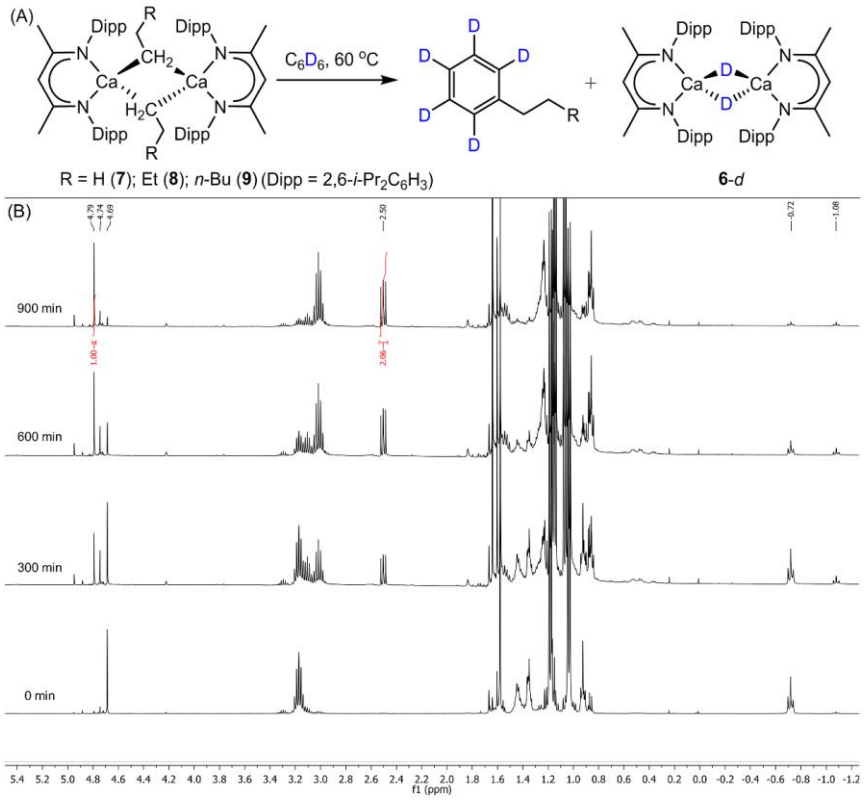


Fig. 4: (A) Nucleophilic C-D activation of C_6D_6 by **7** – **9** to provide the alkylated d_5-benzene products and **6**-*d*. (B) Stacked ^{1}H NMR spectra of a 30 mg sample of compound **9** in 0.55 mL of C_6D_6 heated to 60 °C after 0, 300, 600 and 900 minutes. The signal at 4.79 ppm corresponds to the BDI methine of **6**-*d*. As the reaction proceeds an intermediate proposed to be [{(BDI)Ca}$_2$(D)*n*-hexyl] displays resonances

at δ 4.74 and –1.08 ppm. This compound appears and maintains a steady state concentration until completion of the reaction. The methine at δ 4.69 ppm and multiplet at δ –0.72 ppm correspond to compound **9**. Concurrent formation of d_5-*n*-hexylbenzene is indicated by the increase in intensity of the multiplet at 2.50 ppm arising from the α-CH_2 of *n*-hexylbenzene. This latter resonance displays a 2:1 ratio by relative integration with the methine signal at δ 4.69 ppm at the completion of the reaction.

Samples of compounds **8** and **9** were heated in C_6D_6 at 60 °C and monitored over a 16 hour period by ^{1}H NMR spectroscopy. These reactions resulted in the respective stoichiometric production of d_5-*n*-butylbenzene (Fig. S41) and d_5-*n*-hexylbenzene (Fig. 4B), which were identified by 2D NMR spectroscopy and mass spectrometry as the sole organic products of the reactions (Figs. S34 – S42 and Figs S43 – S50). During both reactions, the ^{1}H NMR resonances associated with compounds **8** and **9** were observed to decrease in intensity concurrently with the generation of the alkylated benzenes and to be replaced by a single BDI-containing calcium product. Although the BDI ligand resonances associated with this latter compound were identical to those of **6**, no Ca-*H* signal could be observed in the ^{1}H NMR spectra. Rather, a resonance at δ 4.30 ppm, which was detected in the corresponding ^{2}H NMR spectra, led to its identification as $[(BDI)CaD]_2$ (**6**-*d*), a supposition which was subsequently confirmed through a further x-ray diffraction analysis performed on single crystals (see fig S54) isolated from a typical reaction performed with compound **9**. Monitoring of the transformation of **9** at 60 °C suggested that this reaction was half order in [**9**] (Fig. S51). Further NMR scale reactions performed in protio-benzene with a minimum amount of C_6D_6 as an internal locking source demonstrated that this reactivity could be extended to the synthesis of the non-deuterated alkylbenzenes, which were formed through the activation of a single C(sp^2)-H bond and the generation of compound **6** (Figs. S52, S53).

To provide further insight into the nature of these processes, the reaction of compound **9** with benzene was assessed by DFT (B3PW91) calculations (Fig. 5). Consistent with the half order dependence of the reaction on [**9**], the dimeric calcium alkyl must first dissociate to a monomeric form (**G**). As implied by the reaction temperature (60 °C), this process is substantially endothermic (ΔH = +23.2 kcal mol^{-1}). The resultant coordinatively unsaturated calcium center interacts via an η^6 contact

with the aromatic electron density of a molecule of benzene (**H**). The subsequent barrier toward the nucleophilic attack of the *n*-hexyl α-methylene carbon on a benzene C(sp^2)-H bond via $TS_{\mathbf{HI}}$ is negligible. At this transition state, the *n*-hexyl group acts as a charge-separated external nucleophile and attacks the benzene molecule at a C-H bond from the opposite face to that engaged with the calcium center. This process enforces an interaction between calcium and the hydrogen bonded to the now four-coordinate carbon, such that the negative charge (−0.9) is relocalized on the remaining five carbon atoms of the benzene ring, in a manner which is analogous to a non-stabilized Meisenheimer complex. While the maximum negative charges are located at the *ortho*, *ortho*' and *para* positions, a positive charge is found on the newly four-coordinate carbon (+1.2), and the reactive hydrogen accumulates a charge (−0.3) consistent with incipient hydridic character prior to the C-H bond breaking process. The overall reaction, therefore, is not a classical sigma bond metathesis in which both Ca-C bond breaking and Ca-H bond formation ensue simultaneously, but is best described as an effective nucleophilic (S_N2) displacement of hydride from the benzene C-H bond (*40*). The breaking of the benzene C-H bond results in the generation of a further π complex of the as-formed calcium hydride and *n*-hexylbenzene (**I**), while arene dissociation and dimerization of the monomeric hydride ensures the overall exothermicity of the reaction (ΔH = −30.1 kcal mol^{-1}). The reaction is, thus, heavily dependent upon a sequence of monomer-dimer equilibria of both the initial calcium *n*-hexyl and ultimate calcium hydride species. In support of this latter hypothesis further examination of the *in situ* ^{1}H NMR spectra recorded during the experimental monitoring of the reactions between compounds **8** and **9** and C_6D_6 revealed an additional upfield triplet resonance at ca. δ −1.1 ppm which persisted in low but steady state concentrations until the complete consumption of the calcium *n*-alkyl derivatives and which we ascribe to the presence of dimeric hydrido(*n*-alkyl)dicalcium derivative analogous to species **C** shown in Fig. S55.

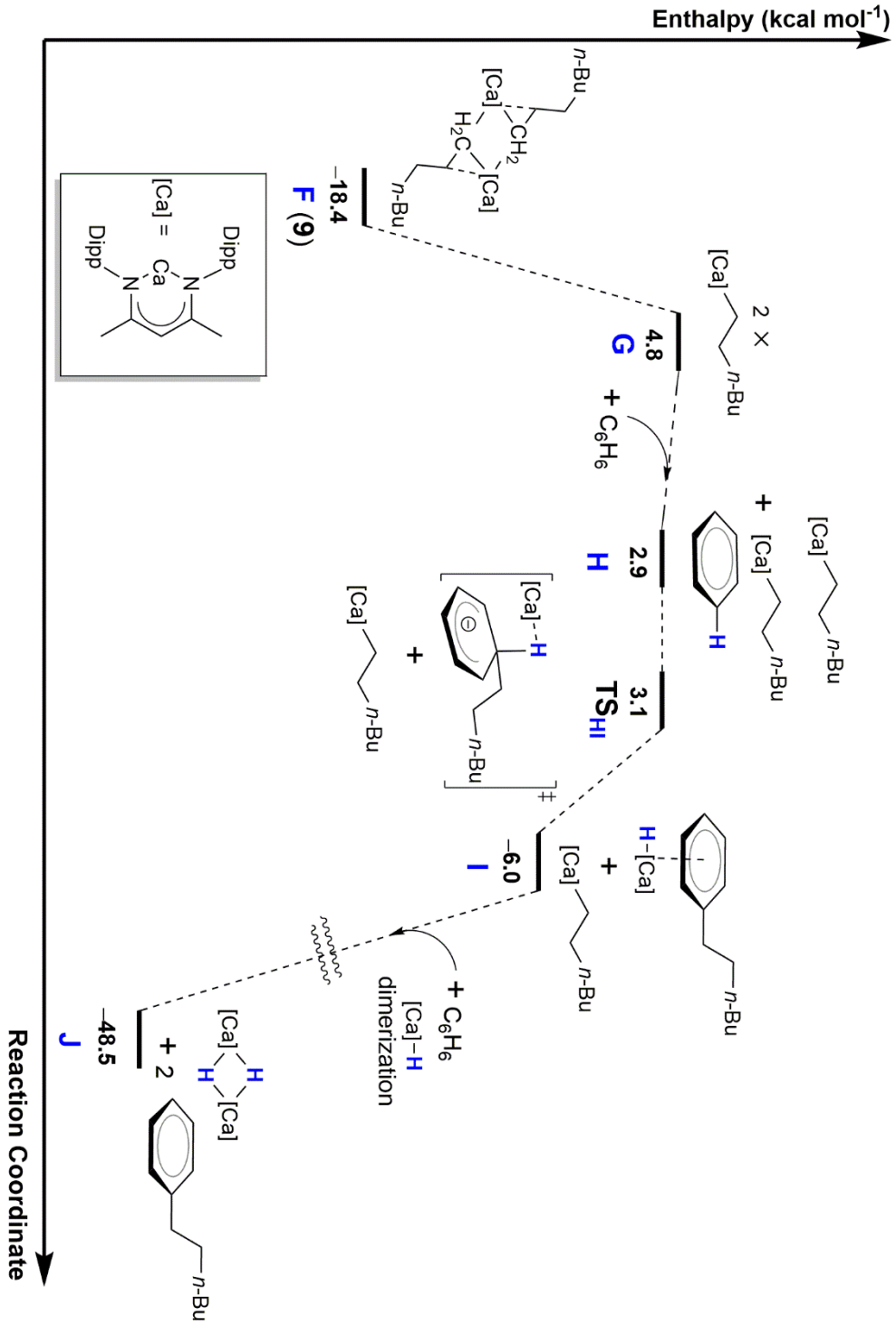


Fig. 5: Computed (DFT, B3PW91) energy profile for the reaction between compound **9** and benzene.

The reactions of compounds **7** – **9** with benzene show that nucleophilic alkylation of benzene may be achieved through the use of sufficiently potent alkylcalcium nucleophiles. This reactivity also achieves

the net hydroarylation of terminal alkenes. The simultaneous re-formation of the calcium hydride (**6**), therefore, indicates that this chemistry holds the potential for elaboration to catalysis.

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Supplementary Materials

Materials and Methods

Figs. S1 – S56

Table S1

Data S1

Data S2

References (*42-51*)