mixture. The oligomeric product **18** is most probably the insoluble residue of the reaction mixture; its further characterization is in progress. The formation of **18** would be of a certain importance since it is likely a functionalized CO oligomer derivative.

The formation of hydrocarbons RH (**8**) and R–R after the protolysis of the reaction mixtures results from the presence of unchanged R–M bonds. It should be noted that (at least formally) reductive elimination of the R–R species in the protolytic cleavage of tetrabenzyl–transition-metal derivatives has been reported by one of us.[27]

There is a distinct difference in the behavior of tetra-1-norbornyl derivatives **1f** and **1g** with respect to arylmethyl compounds **1a–e**. In the case of **1f** no reaction with CO has been observed within several days. This finding is in agreement with the observation[20] that other polar molecules, such as hydrogen halides or alcohols, react with the sterically shielded titanium atom in **1f** only very slowly or not at all. By contrast, the sterically less hindered Zr derivative **1g** reacts readily with CO and the product of the primary reaction (ketone **4g**) could be detected. The dinorbornyl ketone seems, however, to be too bulky to attack **1g** while, however, reaction products (Scheme III) of the alkyl–acyl intermediate **3g** with **1g** (i.e. alcohol **14** and ketone **17**) could be detected.

It can be concluded that tetraorganyls of Ti, Zr, and Hf react readily with CO if the metal is not too shielded sterically. The primary reactions lead to the formation of symmetrical ketones. Subsequent reactions of these ketones and acyl metal type intermediates with the starting tetraorganyls provide secondary alcohols, asymmetric ketones, and trisubstituted ethylene derivatives. The reactions deduced from distribution of the organic products resemble more the reactivity of main-group organometallics (especially Li[22]) than that of late-transition-metal organyls.[1,25f,28] This difference should be attributed mostly to (i) the high number of alkyl groups in the R_4M compounds, (ii) the oxophilic nature[2c,f,3c,4b,e,j,25f] of the group IVB (4) transition metals, and (iii) the well-documented possibility of the formation of M–O–C–M moieties in the CO-derived chemistry of these metals.[2a,b,4j,30]

Acknowledgment. We thank Dr. J. Scholz and Dipl. Chem. D. Schenke (Merseburg, GDR) for help in the preparation of the starting materials and to Mrs. E. Fekete (Veszprêm, Hungary) for assistance in performing the analyses.

Registry No. **1a**, 17520-19-3; **1b**, 31406-67-4; **1c**, 34074-41-4; **1d**, 34074-40-3; **1e**, 108815-98-1; **1f**, 110241-91-3; **1g**, 110241-90-2; **4** (R = $PhCH_2$), 102-04-5; **4** (R = NaphMe), 51042-38-7; **4** (R = Nor), 110223-83-1; **9** (R = $PhCH_2$, Ar = Ph), 50485-27-3; **9** (R = NaphMe, Ar = Naph), 110223-84-2; **10**, 119-61-9; **12**, 58-72-0; **14** (R = $PhCH_2$), 5381-92-0; **14** (R = NaphMe), 110223-87-5; **14** (R = Nor), 110223-88-6; **17** (R = $PhCH_2$), 50485-28-4; **17** (R = NaphMe), 110223-85-3; **17** (R = Nor), 110223-86-4; CO, 630-08-0.

Supplementary Material Available: Table III, mass spectral data of the organic products (3 pages). Ordering information is given on any current masthead page.

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(30) (a) Manriquez, J. M.; McAlister, D. R.; Sanner, R. D.; Bercaw, J. E. *J. Am. Chem. Soc.* **1976**, *98*, 6733. (b) Fachinetti, G.; Floriani, C.; Roselli, A.; Pucci, S. *J. Chem. Soc., Chem. Commun.* **1978**, 269. (c) Gell, K. I.; Williams, G. M.; Schwartz, J. *J. Chem. Soc., Chem. Commun.* **1980** 550. (d) Erker, G.; Kropp, K. *Chem. Ber.* **1982**, *115*, 2437. (e) Erker, G.; Kropp, K; Krüger, C.; Chiang, A.-P. *Chem. Ber.* **1982**, *115*, 2447.

Activation of C–H Bonds of Aromatic Rings Using Calcium Atoms[1]

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Calcium atoms inserted into C–H bonds of aromatic rings in benzene, alkylbenzenes, phenyltrimethylsilane, and xylenes to give the corresponding arylcalcium hydrides. Arylcalcium hydrides reacted with trimethylchlorosilane to give aryltrimethylsilanes and the reduced product (trimethylsilane). Trimethylsilyl-substituted positions on aromatic rings of the aromatic compounds reflected the spin densities on the aromatic rings in the aromatic compound anion radicals. The aromatic compound anion radicals generated by the reactions of calcium atoms with aromatic compound vapors were also detected by ESR. Arylcalcium hydrides reacted with various organic substances to give aryl-substituted substrates and reduced substrates.

Introduction

The study of a metal–vapor reaction has been of considerable interest in organometallic chemistry and organic synthesis during the last few decades.[2] With these methods, it is proving feasible to synthesize organometallic compounds which would be difficult, if not impossible, to

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(1) Preliminary results of this study see: Mochida, K.; Takeuchi, H.; Hiraga, Y.; Ogawa, H. *Chem. Lett.* **1984**, 1989.

(2) For example: (a) Blackborow, J. R. *Metal Vapor Synthesis in Organometallic Chemistry*; Springer-Verlag: New York, 1979. Klabunde, K. J. *Chemistry of Free Atoms and Particles*; Academic: New York, 1980. Klabunde, K. J. *Reactive Intermediates*; Abramovitch, R. A., Ed.; Plenum: New York, 1980, Chapter 2.

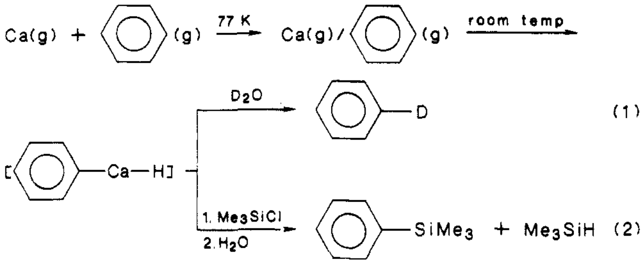
prepare by other methods and to study their reactive intermediates.

Activation of the C–H bond by metal atoms (or clusters) is especially an area of intense research activity.[2,3] In studying the reaction of calcium atoms in the condensed phase, we have found that calcium atoms insert into the C–H bonds of aromatic rings in aromatic compounds.

In this paper, we first describe the formation and mechanism of arylcalcium hydrides produced from the reactions of calcium atoms with aromatic compound vapors since they appear to be unique in the literature of organic compounds.

Results and Discussion

Activation of the C–H Bonds of the Phenyl Ring Using Calcium Atoms. Calcium atoms were generated by evaporation from a tungsten filament using essentially the same apparatus and conditions as have been described in the literature (ca. 900 °C, 5×10^{-3} Torr, 1 Torr = 133.322 Pa).[1,4–8] Calcium metal was evaporated at a rate of ca. 20 mg min^{-1} while an excess of benzene was cocondensed on the walls of a quartz reaction flask containing the crucible and a perforated inlet tube through which benzene was introduced. The reaction flask was immersed in liquid nitrogen during the calcium evaporation. The color of cocondensation product of calcium atoms and benzene vapor at 77 K is green. After the calcium evaporation and introduction of benzene was completed, the reaction flask was warmed to room temperature. The cocondensation product of calcium atoms and benzene vapor turns black. The excess benzene was pumped off, leaving a black solid that was very reactive and decomposed rapidly in the atmosphere. The black solid produced from the cocondensation of calcium atoms with benzene can be safely assigned to a new organometallic compound, phenylcalcium hydride, for the following reasons. (1) The black solid was dissolved in a dried tetrahydrofuran (THF) under an argon atmosphere, and the ^{1}H NMR spectrum was recorded immediately afterward. The ^{1}H NMR spectrum of the black solid consisted of a singlet at δ 0.2 (ca. 1 H) and a multiplet at δ 7.4 (ca. 5 H). Nicol and Waugham have reported that ^{1}H NMR spectrum of CaH_2 exhibits a singlet at δ -4.5 ± 3.0.[9] Perhaps a difference in the C–H chemical shifts between PhCaH and CaH_2 compounds may be due to a shielding effect of the phenyl ring of PhCaH. (2) The black solid reacted with D_2O and trimethylchlorosilane (Me_3SiCl) in THF at room temperature under an argon atmosphere for 1 h to give benzene-d_1, phenyltrimethylsilane (6.1%), and trimethylsilane (8.1%), respectively (eq 1 and 2). Other products could not be detected. Thus, this black solid (phenylcalcium hydride) is a mild agent for both phenylation and reduction as shown in eq 2. Phenylcalcium halides are known to react easily with Me_3SiCl and to produce phenyltrimethylsilane.[7] Although organometal hydrides and metal complex hydrides have been known to be reducing agents, there is no report on reduction of organic halides with organocalcium hydrides. (3) The cocondensation product formed by the reaction of calcium atoms with benzene-d_6 vapor also reacted with Me_3SiCl under the same conditions as eq 2 to give (phenyl-d_5)trimethylsilane (6.0%) and trimethyldeuteriosilane (7.5%). These deuteriated products were identified with a GC-MS spectrometer.



The yields of phenyltrimethylsilane and trimethylsilane are low. The yields of these products formed by the reaction of calcium atoms and benzene vapor with Me_3SiCl were determined on the basis of the calcium metal consumed by supposing that the calcium metal except for the calcium metal that remained in the crucible completely reacted with the benzene vapor. Therefore, by taking into consideration that phenylcalcium hydride includes the unreacted calcium metal, the yields of products may be underestimated. In fact, the yields of products are high ($\sim$85%) on the basis of the amount of benzene consumed. Unreacted benzene was removed by pumping, and the amount of benzene that reacted was calculated by GLC with an internal standard method.

Reactions of Calcium Atom, Substituted Benzene Vapor Products (ArCaH) with Trimethylchlorosilane. In order to gain evidence for the mechanism of insertion into C–H bonds of the aromatic rings with calcium atoms, the reaction products (ArCaH) formed by the reactions of calcium atoms with substituted benzene vapors were treated with Me_3SiCl. These results are summarized in Table I. As shown in Table I, the reaction products of calcium atoms and toluene, ethylbenzene, isopropylbenzene, and *tert*-butylbenzene vapors when treated with Me_3SiCl gave *m*-(trimethylsilyl)-substituted alkylbenzenes and trimethylsilane as main products. *o*- and *p*-(trimethylsilyl)-substituted alkylbenzenes were also formed as minor products. The yields of *o*-(trimethylsilyl)-substituted products decreased upon extending the length of alkyl side chains, whereas paraproducts increased. On the other hand, the reaction products of calcium atoms and phenyltrimethylsilane vapor when treated with Me_3SiCl gave *p*-bis(trimethylsilyl)benzene and trimethylsilane mainly. *m*-Bis(trimethylsilyl)benzene was formed as a minor product. Calcium atoms and *o*-, *m*-, and *p*-xylene vapor products reacted with Me_3SiCl to give trimethylsilyl-substituted xylenes, (trimethylsilyl)methyltoluenes, and trimethylsilane.

Spectroscopic data for anion radicals of alkylbenzenes, phenyltrimethylsilane, and xylenes used in this study have been extensively studied by ESR.[10–12] It appears that the position of calcium atom attack may be influenced by unpaired spin density. If this is true, we suggest that the reaction sequence may be (1) electron transfer to form a Ca^+ $\text{arene}^{\bullet-}$ and (2) attack of the Ca^+ on the most electron-rich site. Thus, selective insertion of calcium atoms into C–H bonds may depend upon spin densities on the aromatic compound anion radicals.

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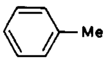
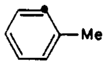
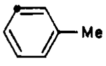
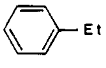
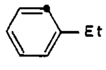
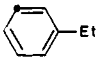
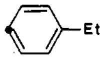
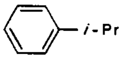
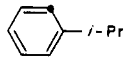
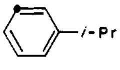
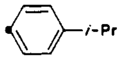
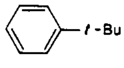
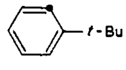
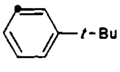
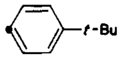
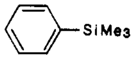
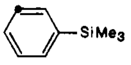
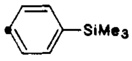
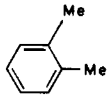
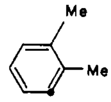
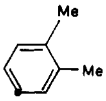
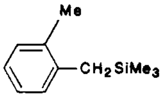
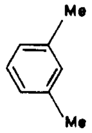
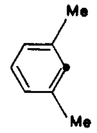
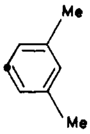
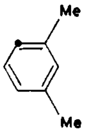
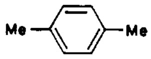
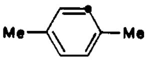
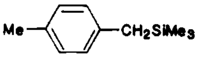
Table I. Reactions of Calcium Atom, Substituted Benzene Vapor Products with Trimethylchlorosilane[a]

compd	products (yield/%[b])			
	 (2.6)	 (7.2)		Me_3SiH (14.0)
	 (2.5)	 (15.7)	 (trace)	Me_3SiH (18.0)
	 (2.3)	 (15.9)	 (0.3)	Me_3SiH (16.7)
	 (trace)	 (16.0)	 (2.2)	Me_3SiH (17.6)
		 (2.2)	 (12.8)	Me_3SiH (12.0)
	 (2.7)	 (2.7)	 (1.8)	Me_3SiH (21.0)
	 (1.5)	 (9.5)	 (1.1)	Me_3SiH (21.0)
	 (23.9)	 (4.5)		Me_3SiH (37.0)

[a] Reactions were performed at room temperature for 1 h. [b] Yields of products were based on the calcium metal consumed. ● = Me_3Si group on aromatic rings.

C–H bonds of arenes are activated by calcium atoms rather than by clusters since the colors of the cocondensation products of calcium atoms and arene vapors at 77 K are green to blue, probably due to charge-transfer complexes or anion radicals of arenes; depending upon the arenes used, activation of C–H bonds of arenes could proceed only in such cases under these reaction conditions. However, activation of C–H bonds by clusters are not always undeniable.[13]

ESR Measurements. In order to observe directly the anion radicals of aromatic compounds as reactive intermediates as mentioned above, ESR studies on the cocondensation products of calcium atoms and substituted benzene vapors were carried out.[14] Calcium atom matrix ESR measurements were performed on the degassed solutions at cryogenetic temperture in the solid matrix. The calcium atom matrix ESR apparatus and measurements were published elsewhere.[14]

The ESR spectra of the cocondensation products were poorly resolved probably because of the high concentrations of reaction intermediates or matrix conditions. However, these ESR signals could safely be assigned to anion radicals of the corresponding substituted benzenes by comparison with the reported ESR data and by computer simulations. As a typical example, Figure 1 shows the ESR spectrum of the product formed by the reaction of calcium atoms with benzene vapor (a_H = 0.35 mT and line width = 0.39 mT).

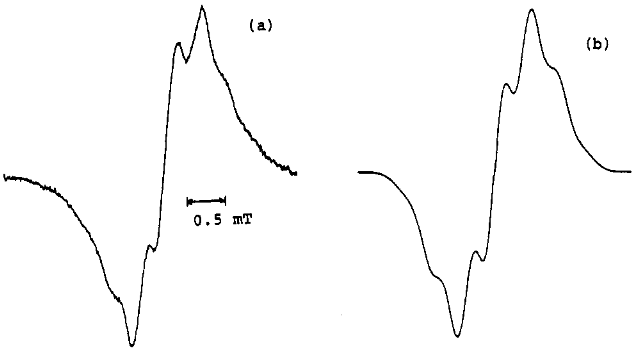


Figure 1. (a) The observed ESR spectrum of the calcium atom, benzene vapor product at −60 °C. (b) Computer-simulated spectrum using Lorentzian line shape and a line width of 0.39 mT.

In this ESR experiment, anion radicals of substituted benzenes were confirmed by ESR to be reactive intermediates.

Reactions of the Calcium Atom, Benzene Vapor Product PhCaH with Organic Substrates. Phenylcalcium hydride produced by the reaction of calcium atoms with benzene vapor are expected to act as both phenylcalcium halides and metal hydrides. So, we carried out reactions of the calcium atom, benzene vapor product PhCaH with organic halides, carbonyl compounds, nitriles, and esters. The reactions in THF proceeded smoothly at

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(13) We thank the reviewers for the constructive criticism on this point.

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Table II. Reactions of the Calcium Atom, Benzene Vapor Product PhCaH with Organic Substrates[a]

run	substrate	products (rel ratio)	yield/%[b]
	Ar–X	ArC_6H_5/ArH	
1	o-MeC_6H_4F	o-$MeC_6H_4C_6H_5/MeC_6H_5$ (7/93)	10.7
2	m-MeC_6H_4F	m-$MeC_6H_4C_6H_5/MeC_6H_5$ (27/73)	15.3
3	p-MeC_6H_4F	p-$MeC_6H_4C_6H_5/MeC_6H_5$ (6/94)	19.8
4	o-MeC_6H_4Cl	o-$MeC_6H_4C_6H_5/MeC_6H_5$ (0/100)	16.0
5	m-MeC_6H_4Cl	m-$MeC_6H_4C_6H_5/MeC_6H_5$ (10/90)	26.9, 90.0[c]
6	p-MeC_6H_4Cl	p-$MeC_6H_4C_6H_5/MeC_6H_5$ (6/94)	15.7
7	m-MeC_6H_4Br	m-$MeC_6H_4C_6H_5/MeC_6H_5$ (10/90)	8.1
	R–X	RC_6H_5/RH	
8	EtBr	EtC_6H_5/EtH (100/0)	4.9
9	n-BuBr	n-BuC_6H_5/n-BuH (50/50)	4.0
10	t-BuCl	t-BuC_6H_5/t-BuH (76/24)	21.4
11	Me_3SiCl	$Me_3SiC_6H_5/Me_3SiH$ (43/57)	14.2, 85.0[c]
12[d]	Me_3SiCl	$Me_3SiC_6D_5/Me_3SiD$ (45/55)	14.5
13	Et_3SiCl	$Et_3SiC_6H_5/Et_3SiH$ (40/60)	8.0
14[d]	Et_oSiCl	$Et_3SiC_6D_5/Et_3SiD$ (40/60)	7.0
	RR′CO	$RR'C_6H_5COH/RR'CHOH$	
15	Me_2CO	$Me_2C_6H_5COH/Me_2CHOH$ (75/25)	14.5, 100[c]
16	MeEtCO	$MeEtC_6H_5COH/MeEtCHOH$ (60/40)	18.4, 100[c]
17[d]	MeEtCO	$MeEtC_6D_5COH/MeEtCDOH$ (60/30)[e]	17.0
18	Et_2CO	$Et_2C_6H_5COH/Et_2CHOH$ (45/55)	29.3
19	C_6H_5CHO	$(C_6H_5)_2CHOH/C_6H_5CH_2OH$ (23/77)	30.0
20[d]	C_6H_5CHO	$C_6H_5(C_6D_5)CHOH/C_6H_5CH_2OH$ (20/80)[f]	25.0
	R–CN	C_6H_5COR	
21	MeCN	C_6H_5COMe (100)	6.2
22	EtCN	C_6H_5COEt (100)	5.6
23	C_6H_5CN	$C_6H_5COC_6H_5$ (100)	3.2
	RCOOR′	C_6H_5COR	
24	HCO_2Me	C_6H_5CHO (100)	4.4
25	HCO_2Et	C_6H_5CHO (100)	5.9
26	$MeCO_2Me$	C_6H_5COMe (100)	3.0
27	$MeCO_2Et$	C_6H_5COMe (100)	6.4

[a] Reactions were performed at room temperature for 1 h. [b] Yields of products were based on the calcium metal consumed on the assumption that calcium atom, benzene vapor products reacted with organic substrates to give reduced and phenyl-substituted products individually. [c] Yields of products were based on the amount of benzene consumed. [d] Calcium atom, benzene-d_6 vapor product was used. [e] MeEtCHOH was also formed. [f] No C_6H_5CHDOH was formed.

room temperature under an argon atmosphere. These results are summarized in Table II. The calcium atom, benzene vapor product reacted with tolyl halides to give toluene predominantly and methylbiphenyl as the minor product (runs 1–7). The yields of the products shown in Table II were almost constant regardless of the nature of the halogen and the position of the methyl group on the phenyl group. The reactions of a calcium atom, benzene vapor product with alkyl halides or chlorosilanes gave alkylbenzenes and alkanes or phenylsilanes and hydrosilanes, respectively (runs 8–14). The relative ratios of alkylbenzenes to alkanes and phenylsilanes to hydrosilanes except for ethyl bromide are almost same. With ethyl bromide, a calcium atom, benzene vapor product gave ethylbenzene exclusively. The reactions of a calcium atom, benzene-d_6 vapor product with chlorosilanes gave (phenyl-d_5)silanes and deuteriosilanes (runs 12 and 14). Above 90% of the hydrosilanes contained deuterium in these reactions.

A calcium atom, benzene vapor product also reacted with carbonyl compounds to give two kinds of alcohol as expected (runs 15–20). The reaction of a calcium atom, benzene-d_6 vapor product with 2-butanone gave 2-methyl-2-(phenyl-d_5)propanol and deuteriated 2-butanol (run 17). About 75% of 2-butanol contained deuterium. With benzaldehyde, a calcium atom, benzene vapor product gave diphenylmethanol and benzyl alcohol (runs 19 and 20). Benzyl alcohol did not contain any deuterium from the reaction of a calcium atom, benzene-d_6 product with benzaldehyde. Benzyl alcohol may be formed by proton abstraction from unreacted benzaldehyde with the intermediate ketyl.

A calcium atom, benzene vapor product reacted with nitriles to give the corresponding ketones (runs 21–23). With esters, a calcium atom, benzene vapor product also gave the corresponding ketones (runs 24–27). The expected alcohol could not be detected.

Although the yields of products are low, a calcium atom, benzene vapor product (PhCaH) is a very useful reagent for phenylation and reduction.

Conclusions

Calcium atoms first inserted into C–H bonds of aromatic rings to give the corresponding arylcalcium hydrides. The arylcalcium hydrides formed were very useful reagents in organic synthesis.

Experimental Section

^1H NMR spectra were recorded on a Varian FT 80A, with tetramethylsilane as an internal standard. GC–MS spectra were obtained on a JEOL JMS-DX 303 mass spectrometer. Infrared spectra were recorded on a Hitachi 260-10 spectrometer. Gas chromatographyl was performed on a Shimazu GC-6A and 8A with 2-m 20% SE-30 and 2-m 30% Apiezon L columns.

Materials. Calcium metal (granules, 99% pure, Wako chemical), organic halides, and other chemicals were commerically available. THF and aromatic compounds were distilled from benzophenone ketyl immediately prior to use. o-$MeC_6H_4SiMe_3$ (bp 95 °C (25 mmHg)),[15] m-$MeC_6H_4SiMe_3$ (bp 92–94 °C (25 mmHg)),[16] o-$EtC_6H_4SiMe_3$ (bp 95–100 °C (23 mmHg)),[17] m-$EtC_6H_4SiMe_3$ (bp 94–96 °C (22 mmHg)),[18] p-$EtC_6H_4SiMe_3$ (bp 96–100 °C (22 mmHg)),[17] m-$Me_2CHC_6H_4SiMe_3$ (bp 95 °C (15 mmHg)),[18] p-$Me_2CHC_6H_4SiMe_3$ (bp 126–130 °C (40 mmHg)),[19]

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o-$\mathrm{Me_3CC_6H_4SiMe_3}$ (bp 85 °C (6 mmHg)),[20] *m*-$\mathrm{Me_3CC_6H_4SiMe_3}$ (bp 84–87 °C (5 mmHg)),[18] *p*-$\mathrm{Me_3CC_6H_4SiMe_3}$ (mp 77–79 °C),[19] 1,3-$\mathrm{(Me_3Si)_2C_6H_4}$ (bp 112–114 °C (22 mmHg)),[16] 1,4-$\mathrm{(Me_3Si)_2C_6H_4}$ (bp 135 °C 20 mmHg)),[21] *o*-$\mathrm{MeC_6H_4CH_2SiMe_3}$ (bp 90–100 °C 14 mmH)),[22] *p*-$\mathrm{MeC_6H_4CH_2SiMe_3}$ (bp 50–60 °C (3 mmHg)),[23] (2,3-$\mathrm{Me_2C_6H_3)SiMe_3}$ (bp 75–86 °C (3 mmHg)),[24] (2,4-$\mathrm{Me_2C_6H_3)SiMe_3}$ (bp 75–82 °C (3 mmHg)),[24] and (2,5-$\mathrm{Me_2C_6H_3)SiMe_3}$ (bp 93–96 °C 15 mmHg))[24] were prepared as described in the cited references.

o-$\mathrm{Me_2CHC_6H_4SiMe_3}$ was isolated from the reaction products of Ca atoms and cumene vapor with $\mathrm{Me_3SiCl}$ by a preparative gas chromatography (5-m 30% Apiezon L column) and identified with ^{1}H NMR, IR, and GC–MASS spectroscopy: ^{1}H NMR ($\mathrm{CDCl_3}$) 0.24 (s, 9 H), 1.27 (d, 6 H), 2.70 spm (sept, 1 h), 7.1 (s, 4 H); IR (neat) 1250 cm^{-1}; M$^+$ 192.

Reaction of Calcium Atoms with Benzene Vapor. Calcium atoms were produced by using essentially the same apparatus and conditions as described in literatures.[4–8] Calcium metal (0.3 g, 7.5 mmol) was vaporized at a temperature of 900–1000 °C by using a resistively heated, alumina-coated tungsten spiral crucible at 4.0–5.0 V, 15 A, which was connected to copper electrodes, in vacuo (ca. 5×10^{-3} Torr, 1 Torr = 133.322 Pa) at a rate of ca. 20 mg min^{-1}. During vaporization of the calcium metal, benzene (8 mL, 90 mmol) was cocondensed on the walls of a quartz reaction flask containing the tungsten crucible and a perforated inlet tube through which benzene was introduced as vapor. The crucible was maintained at 900–1000 °C and the reaction flask immersed in liquid nitrogen during calcium vaporization and introduction of benzene. The initial product at 77 K was a green solid. After calcium vaporization and introduction of benzene were completed, the reaction flask was warmed to room temperature. The excess benzene was pumped off, leaving a black solid. The black solid thus prepared was very sensitive to oxygen and moisture.

Reactions of Calcium Atoms and Substituted Benzene Vapors with Trimethylchlorosilane. As a typical example, the reaction of calcium atoms and benzene vapor with trimethylchlorosilane is described. A calcium atom, benzene vapor product at 77 K was prepared as described above. The reaction vessel was allowed to warm to 0 °C, and then, an excess of trimethylchlorosilane was introduced as a vapor into the reaction flask. The reaction flask containing calcium atoms and benzene vapor with trimethylchlorosilane was warmed to room temperature and left to stand for 1 h. After removal of the reaction flask from a vacuum line, the reaction mixture was hydrolyzed with water slowly. The organic layer was extracted with ether. Phenyltrimethylsilane (6.1%) and trimethylsilane (8.1%) were formed. The yields of products were based on the calcium metal consumed. All products were isolated by preparative GLC and identified by comparing their IR, NMR, and GC-MS spectra and retention times on GLC with those of authentic samples.

ESR Measurements. As a typical experiment, the reaction of calcium atoms with benzene vapor is described. Calcium metal (0.15 g, 3.7 mmol) was vaporized at a temperature of ca. 900 °C by using a filament of tungsten in vacuo (ca. 5×10^{-3} Torr) at a rate of ca. 20 mg min^{-1}. During the vaporization of calcium metal, benzene (4 mL, 45 mmol) was introduced as a vapor. The calcium atom, benzene vapor product cocondensed on the stainless-steel drum filled with liquid nitrogen. The product of calcium atoms and benzene vapor at 77 K was transferred to the ESR tube by using a scratching bar. ESR spectra were taken on a Varian E-109 E spectrometer at low temperatures. The details of the calcium atom matrix ESR apparatus and measurements were published elsewhere.[14]

Reactions of the Calcium Atom, Benzene Vapor Product PhCaH with Organic Substrates. As a typical example, the reaction of a calcium atom, benzene vapor product with acetone is described. A calcium atom, benzene vapor product at 77 K was prepared as described above. After warmup to 0 °C, it turned black. The excess benzene was pumped off, leaving a black solid. The vessel was filled with argon, and then the product was isolated from the vacuum pump. The calcium atom, benzene vapor product PhCaH was weighed in an argon-filled glovebox. The calcium atom, benzene vapor product containing unreacted calcium metals was transferred to two-necked 50-mL flask equipped with a serum cap and a reflux condenser. Then, THF (20 mL) and acetone (2 g, 34 mmol) were syringed in. The reaction mixture was stirred at room temperature for 1 h under argon. After hydrolysis of the reaction mixture with water, the organic layer was extracted with ether. 1-Methyl-1-phenylethanol (10.9%) and 2-propanol (3.6%) were produced on the basis of calcium metal consumed. All products were isolated by preparative GLC and identified by comparing their IR, NMR, and GC–MS and their retention times on GLC with those of authentic samples.

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Registry No. $\mathrm{MeC_6H_5}$, 108-88-3; $\mathrm{EtC_6H_5}$, 100-41-4; i-$\mathrm{PrC_6H_5}$, 98-82-8; t-$\mathrm{BuC_6H_5}$, 98-06-6; $\mathrm{Me_3SiC_6H_5}$, 768-32-1; *o*-$\mathrm{MeC_6H_4Me}$, 95-47-6; *m*-$\mathrm{MeC_6H_4Me}$, 108-38-3; *p*-$\mathrm{MeC_6H_4Me}$, 106-42-3; $\mathrm{C_6H_6}$, 71-43-2; *o*-$\mathrm{MeC_6H_4F}$, 95-52-3; *m*-$\mathrm{MeC_6H_4F}$, 352-70-5; *p*–$\mathrm{MeC_6H_4F}$, 352-32-9; *o*-$\mathrm{MeC_6H_4Cl}$, 95-49-8; *m*-$\mathrm{MeC_6H_4Cl}$, 108-41-8; *p*-$\mathrm{MeC_6H_4Cl}$, 106-43-4; *m*-$\mathrm{MeC_6H_4Br}$, 591-17-3; EtBr, 74-96-4; *n*-BuBr, 109-65-9; *t*-BuCl, 507-20-0; $\mathrm{Et_3SiCl}$, 994-30-9; $\mathrm{Me_2CO}$, 67-64-1; MeEtCO, 78-93-3; $\mathrm{Et_2CO}$, 96-22-0; $\mathrm{C_6H_5CHO}$, 100-52-7; MeCN, 75-05-8; EtCN, 107-12-0; $\mathrm{C_6H_5CN}$, 100-47-0; $\mathrm{HCO_2Me}$, 107-31-3; $\mathrm{HCO_2Et}$, 109-94-4; $\mathrm{MeCO_2Me}$, 79-20-9; $\mathrm{MeCO_2Et}$, 141-78-6; *o*-$\mathrm{Me_3SiC_6H_4Me}$, 7450-03-5; *m*-$\mathrm{Me_3SiC_6H_4Me}$, 3728-44-7; $\mathrm{Me_3SiH}$, 993-07-7; *o*-$\mathrm{Me_3SiC_6H_4Et}$, 17988-52-2; *m*-$\mathrm{Me_3SiC_6H_4Et}$, 17988-51-1; *o*-$\mathrm{Me_3SiC_6H_4Pr}$-i, 110271-39-1; *m*-$\mathrm{Me_3SiC_6H_4Pr}$-i, 18027-96-8; *m*-$\mathrm{Me_3SiC_6H_4Bu}$-t, 18412-67-4; *p*-$\mathrm{Me_3SiC_6H_4Bu}$-t, 18412-68-5; *m*-$\mathrm{Me_3SiC_6H_4SiMe_3}$, 2060-89-1; *p*-$\mathrm{Me_3SiC_6H_4SiMe_3}$, 13183-70-5; *o*-$\mathrm{Me_3SiCH_2C_6H_4Me}$, 4225-37-0; *p*-$\mathrm{Me_3SiCH_2C_6H_4Me}$, 7450-04-6; *o*-$\mathrm{MeC_6H_4C_6H_5}$, 643-58-3; *m*-$\mathrm{MeC_6H_4C_6H_5}$, 643-93-6; *p*-$\mathrm{MeC_6H_4C_6H_5}$, 644-08-6; *n*-$\mathrm{BuC_6H_5}$, 104-51-8; *n*-BuH, 106-97-8; *t*-BuH, 75-28-5; $\mathrm{Me_3SiC_6D_5}$, 95450-75-2; $\mathrm{Me_3SiD}$, 18026-91-0; $\mathrm{Et_3SiC_6H_5}$, 2987-77-1; $\mathrm{Et_3SiH}$, 617-86-7; $\mathrm{Et_3SiC_6D_5}$, 95450-76-3; $\mathrm{Et_3SiD}$, 1631-33-0; $\mathrm{Me_2C_6H_5COH}$, 617-94-7; $\mathrm{Me_2CHOH}$, 67-63-0; $\mathrm{MeEtC_6H_5COH}$, 1565-75-9; MeEtCHOH, 78-92-2; $\mathrm{MeEtC_6D_5COH}$, 95450-77-4; MeEtCDOH, 19403-02-2; $\mathrm{Et_2C_6H_5COH}$, 1565-71-5; $\mathrm{Et_2CHOH}$, 584-02-1; $\mathrm{(C_6H_5)_2CHOH}$, 91-01-0; $\mathrm{C_6H_5CH_2OH}$, 100-51-6; $\mathrm{C_6H_5(C_6D_5)CHOH}$, 95450-78-5; $\mathrm{C_6H_5COMe}$, 98-86-2; $\mathrm{C_6H_5COEt}$, 93-55-0; $\mathrm{C_6H_5COC_6H_5}$, 119-61-9; PhCaH, 110271-40-4; $\mathrm{Me_3SiCl}$, 75-77-4; calcium, 7440-70-2; 2,3-dimethyl-1-(trimethylsilyl)benzene, 17961-79-4; 3,4-dimethyl-1-(trimethylsilyl)benzene, 17988-43-1; 2,6-dimethyl-1-(trimethylsilyl)benzene, 17961-82-9; 3,5-dimethyl-1-(trimethylsilyl)benzene, 17961-83-0; 2,4-dimethyl-1-(trimethylsilyl)benzene, 17961-80-7; 2,5-dimethyl-1-(trimethylsilyl)benzene, 17961-81-8.

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