Designing new free-radical reducing agents: an *ab initio* study of hydrogen atom transfers from some silacyclopentadienes to methyl radical

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Ab initio molecular orbital calculations using the triple-ζ 6-311G** basis set, with (MP2, QCISD) and without (UHF) the inclusion of electron correlation calculate that methyl radicals abstract hydrogen atom from silacyclopentadiene (**3**, R = H), 1-methylsilacyclopentadiene (**3**, R = CH_3) and 1-silylsilacyclopentadiene (**3**, R = SiH_3) *via* transition states (**5**) in which the attacking and leaving radicals adopt collinear (or nearly so) arrangements. Transition states (**5**) which have (overall) Si–C separations of about 3.17–3.19 Å are calculated at MP2/6-311G**; structures (**5**) appear to be sensitive to the nature of the substituent on silicon, with an earlier transition state calculated for the reaction involving the silyl-substituted silane (**3**, R = SiH_3), while the methyl-substituted system (**3**, R = CH_3) is calculated to proceed with a slightly later transition state at the MP2/6-311G** level of theory. Energy barriers ($\Delta E_1^{\ddagger}$) of 35–42 kJ mol^{-1} are calculated for the forward reactions, while the reverse reactions ($\Delta E_2^{\ddagger}$) are calculated to require about 119–124 kJ mol^{-1} at MP2/6-311G**. Inclusion of higher-order correlation correction (QCISD/6-311G**//MP2/6-311G**) has only a marginal effect on the calculated energy barriers.

Introduction

In recent times considerable effort has been directed towards development of silane-based free-radical reagents.[1] Apart from the significant toxicological benefits that silanes have over their more traditional stannane counterparts,[2] silane residues are also removed more easily from reaction mixtures than corresponding tin-based byproducts.[3] Despite these advantages, trialkylsilanes suffer from one major drawback; the Si–H bond strength in most trialkysilanes (*ca.* 460 kJ mol^{-1}),[4] with associated rate constants (k_H) of about 600 M^{-1} s^{-1} for the transfer of hydrogen atom to primary alkyl radicals,[4] leads to poor radical chain propagation. The inability to sustain chain reactions involving the delivery of hydrogen atom as a key chain-propagating step renders most readily available silanes inappropriate for radical based syntheses.[1]

Triphenylsilane is an example of a silane where appropriate substitution accelerates hydrogen atom transfer to alkyl radicals. With a rate constant (k_H) of 5×10^4 M^{-1} s^{-1} (110 °C) for the delivery of hydrogen atom to primary alkyl radicals, triphenylsilane sits at the border of acceptable reactivity and can often be used in radical chain reactions.[1,4]

Tris(trimethylsilyl)silane (TTMSS) (**1**) is another example of a synthetically useful silane.[2] It has been suggested that the silyl radical derived from **1** is stabilised through d-orbital participation of the neighbouring silicon-containing groups;[5] it is presumably this stabilization mechanism which leads to rate constants (k_H) of about 4×10^5 M^{-1} s^{-1} (27 °C) for the delivery of hydrogen atom to primary alkyl radicals.[2] Indeed, TTMSS (**1**) behaves much more like tributyltin hydride ($k_H = 2 \times 10^6$ M^{-1} s^{-1} (25 °C)) than a trialkylsilane in its radical chain propagating properties.[6] This, together with superior chromatographic properties and low toxicity, has lead to this relative newcomer in radical chemistry being widely accepted as the reagent of choice in many free-radical reactions.[1,4]

$(Me_3Si)_3SiH$

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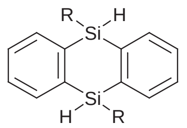

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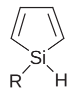

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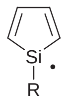

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Apart from some other silanes structurally related to **1**, we are only aware of one other class of silane exhibiting acceptable radical reduction properties. Oba and Nishiyama,[7] as well as Chatgilialoglu and co-workers[8] independently reported that silanes (**2**) based on the 5,10-dihydrosilanthrene ring system react approximately twice as slowly as **1** with alkyl radicals. Chatgilialoglu has suggested that the unexpected reactivity of **2** ($k_H = 2.6 \times 10^5$ M^{-1} s^{-1} (100 °C)) comes about as a result of "either a transannular interaction of the vicinal Si substituent in **2** or by flattening of the radical centre due to ring constraint".[8] Whatever the origin of the radical reactivity of **2**, there is no doubt that **2** would find a place amongst useful radical reagents such as TTMSS (**1**) and tributyltin hydride if it were readily available.

If one considers ways of engineering silanes such that they become more efficient hydrogen atom donors suitable for radical chemistry, clearly, silanes containing substituents at silicon which weaken the Si–H bond through mesomeric and/or inductive effects would appear as prime candidates for preparation and evaluation. Silacyclopentadiene (**3**) appears at first glance to be such a candidate. One might expect significant weakening of the Si–H bond in **3** because the resulting silacyclopentadienyl radical (**4**) should be extensively delocalized or even exhibit some aromatic character.

As part of our continuing interest in the development of new reagents for use in free-radical chemistry, we modelled the radical reactions of silacyclopentadiene (**3**, R = H), 1-methylsilacyclopentadiene (**3**, R = CH_3) and 1-silylsilacyclopentadiene (**3**, R = SiH_3) through the use of *ab initio* molecular orbital theory using the 6-311G** basis set with (MP2, QCISD) and without (SCF) the inclusion of electron correlation. We established previously that these levels of theory provide a good description of hydrogen atom transfer reactions involving trialkylsilanes.[9] These previous data together with our recently published computational study of hydrogen abstractions from stannanes[10] and germanes[9] will provide a comparison for the data presented in this paper and allow an assessment of the synthetic utility of silanes (**3**) to be made.

Table 1 Calculated energy barriers[a] for the forward ($\Delta E_1^\ddagger$) and reverse ($\Delta E_2^\ddagger$) hydrogen abstraction reactions of methyl radical with silacyclopentadiene (**3**, R = H) and transition state imaginary frequency (ν)[b] of structure **5** (R = H)

	$\Delta E_1^\ddagger$	$\Delta E_1^\ddagger$ + ZPE[c]	$\Delta E_2^\ddagger$	$\Delta E_2^\ddagger$ + ZPE[c]	ν
UHF/3-21G$^{(*)}$	81.0	84.9	130.3	114.7	2036i
UHF/6-311G**	90.3	92.9	134.0	121.6	2052i
MP2/6-311G**	41.5	—	119.7	—	—
QCISD/6-311G**[d]	44.1	—	120.7	—	—

[a] Energies in kJ mol^{-1}. [b] Frequencies in cm^{-1}. [c] Zero-point vibrational energy correction. [d] QCISD/6-311G**//MP2/6-311G**.

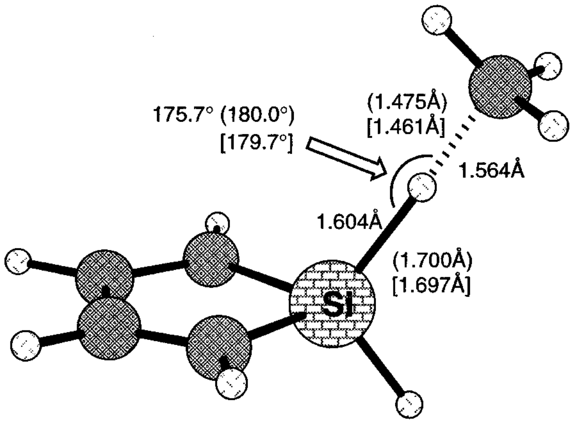
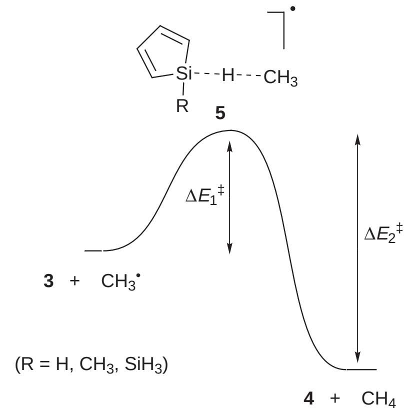
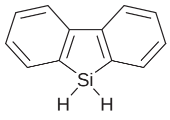


Fig. 1 Important geometrical features of the MP2/6-311G** optimised structure of transition state **5** (R = H). UHF/6-311G** data in parentheses. UHF/3-21G$^{(*)}$ data in square brackets.



Scheme 1



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Methods

All *ab initio* molecular orbital calculations were carried out using the GAUSSIAN94[11] program. Geometry optimisations were performed using standard gradient techniques at the SCF and MP2 levels of theory using RHF and UHF methods for closed and open shell systems, respectively.[12] Further single-point QCISD calculations were performed on the MP2 optimised structures involved in the reaction of **3** (R = H); the remaining QCISD calculations were beyond our resources. When correlated methods were used calculations were performed using the frozen core approximation. Vibrational frequencies were calculated on each SCF-calculated structure in this study. Where appropriate, zero-point vibrational energy (ZPE) corrections have been applied. Values of $<s^2>$ never exceeded 0.81 before annihilation of quartet contamination, indicating little spin contamination in all calculations.

All calculations were performed on Sun SparcStation 10/516, Cray J916, DEC Alphaserver 8400 or DEC Personal Workstation 433au or 600au computers.

Results and discussion

Reaction of silacyclopentadiene with methyl radical

Extensive searching of the C_5H_9Si potential energy surface located structure **5** (R = H) as a stationary point at the UHF/3-21G$^{(*)}$, UHF/6-311G** and MP2/6-311G** levels of theory. Vibrational frequency analysis at each level of theory demonstrated that this structure did indeed correspond to the transition state for the transfer of hydrogen atom from silacyclopentadiene (**3**, R = H) to methyl radical. The MP2/6-311G** optimised structure of **5** (R = H) is displayed in Fig. 1, while the calculated energy barriers for the forward ($\Delta E_1^\ddagger$) and reverse ($\Delta E_2^\ddagger$) reactions (Scheme 1, R = H) are listed in Table 1 together with the calculated (imaginary) frequency associated with the reaction coordinate at each level of theory. Calculated energies of all structures in this study are listed in Table 2.

Inspection of Table 1 reveals that transition state (**5** , R = H) is calculated to lie 81.0, 90.3, 41.5 and 44.1 kJ mol^{-1} above the energy of the reactants at the UHF/3-21G$^{(*)}$, UHF/6-31G**, MP2/6-311G** and QCISD/6-311G**//MP2/6-311G** levels of theory respectively. It is clear from these data that the inclusion of electron correlation is important in describing the potential energy surface for this reaction, but that the transition from MP2 to the higher-order (QCISD) level of correlation has only a minor effect on the calculated activation energy. The reaction is calculated to be significantly exothermic, with reverse energy barriers ($\Delta E_2^\ddagger$) ranging between 119.7 and 134.0 kJ mol^{-1}. As was reported previously by us for reactions involving silanes and alkyl radicals,[9] the reverse barrier ($\Delta E_2^\ddagger$) is calculated to be more strongly affected by the inclusion of zero-point vibrational energy correction than the forward barrier ($\Delta E_1^\ddagger$). These data are to be compared with those in our previous studies in which the reactions of methyl radical with trimethylsilane, trimethylgermane and trimethylstannane are calculated to involve energy barriers of 54.4, 42.2 and 33.0 kJ mol^{-1} respectively at the MP2/DZP † level of theory.[9,10] It would seem, therefore, that silacyclopentadiene might be expected to behave as a more effective radical reagent than a trialkylsilane in radical reduction chemistry.

Inspection of Fig. 1 reveals the near collinear arrangements of attacking and leaving radicals at hydrogen. As expected,[9] MP2/6-311G** calculations, with optimised Si–H$_{\text{TS}}$ and C–H$_{\text{TS}}$ separations of 1.604 and 1.564 Å respectively, calculate an "earlier" transition state in the direction indicated in Scheme 1 than uncorrelated calculations (*cf.* 1.700 and 1.475 Å respectively at UHF/6-311G**). These separations are also to be compared to those calculated for the analogous transition state involved in the reaction of methyl radical with trimethylsilane; MP2/DZP calculations predict Si–H$_{\text{TS}}$ and C–H$_{\text{TS}}$ separations of 1.629 and 1.517 Å respectively, slightly "later" than **5** (R = H) and consistent with the calculated lower activation energy associated with the reaction of **5** (R = H).

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† The double-ζ pseudopotential basis set (DZP) has been shown to provide similar data to that generated using the 6-311G** basis for silicon.[13]

Table 2 Calculated energies[a] of reactants, transition states and products in this study

Structure	HF/3-21G$^{(*)}$	HF/6-311G**	MP2/6-311G**	QCISD/6-311G**[b]
$^{\bullet}CH_3$	−39.34261	−39.57291[c]	−39.70724[c]	−39.72913[c]
CH_4	−39.97688	−40.20901	−40.37923	−40.40160
3 (R = H)	−441.55810	−443.89859	−444.54684	−444.59521
3 (R = CH_3)	−480.39832	−482.95677	−483.75729	—
3 (R = SiH_3)	−730.20364	−734.00198	−734.75205	—
4 (R = H)	−440.94262	−443.28064	−443.90461	−443.95191
4 (R = CH_3)	−479.78113	−482.33745	−483.11478	—
4 (R = SiH_3)	−729.59314	−733.38928	−734.11393	—
5 (R = H)	−480.86988	−483.43712	−484.23825	−484.30754
5 (R = CH_3)	−519.70877	−552.49830	−523.44842	—
5 (R = SiH_3)	−769.51748	−773.54656	−774.44592	—

[a] Energies in Hartrees (1 E_h = 2626 kJ mol^{-1}). [b] QCISD/6-311G**//MP2/6-311G**. [c] Ref. 13.

Table 3 Calculated energy barriers[a] for the forward ($\Delta E_1^{\ddagger}$) and reverse ($\Delta E_2^{\ddagger}$) hydrogen abstraction reactions of methyl radical with 1-methylsilacyclopentadiene (**3**, R = CH_3) and 1-silylsilacyclopentadiene (**3**, R = SiH_3) and transition state imaginary frequency (ν)[b] of structure **5**

R		$\Delta E_1^{\ddagger}$	$\Delta E_1^{\ddagger}$ + ZPE[c]	$\Delta E_2^{\ddagger}$	$\Delta E_2^{\ddagger}$ + ZPE[c]	ν
CH_3	UHF/3-21G$^{(*)}$	84.4	88.6	129.3	113.3	2052i
	UHF/6-311G**	82.4	78.7	126.4	103.3	2082i
	MP2/6-311G**	42.2	—	119.6	—	—
SiH_3	UHF/3-21G$^{(*)}$	74.0	78.2	138.0	119.6	1986i
	UHF/6-311G**	73.7	70.3	135.1	109.3	2007i
	MP2/6-311G**	35.0	—	124.0	—	—

[a] Energies in kJ mol^{-1}. [b] Frequencies in cm^{-1}. [c] Zero-point vibrational energy correction.

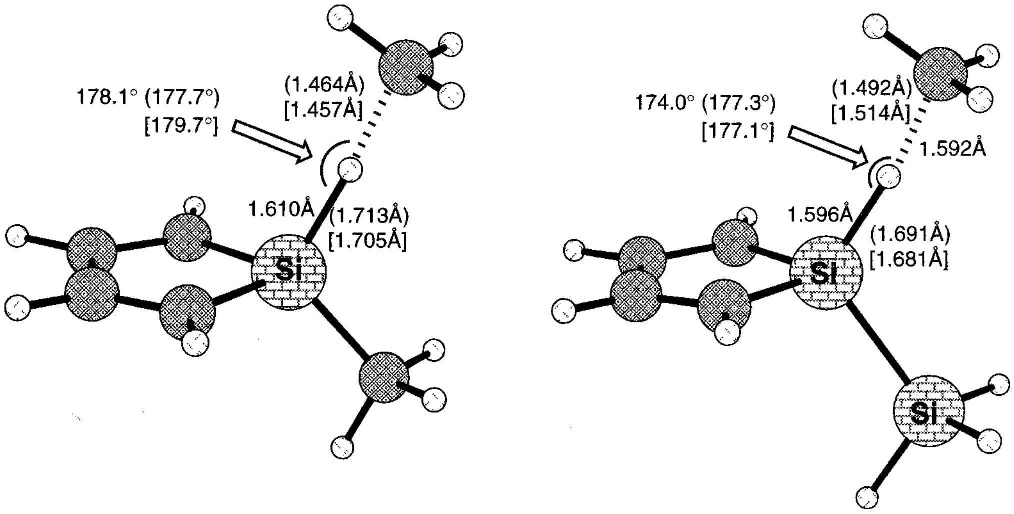

Fig. 2 Important geometrical features of the MP2/6-311G** optimised structures of transition states **5** (R = CH_3, SiH_3). UHF/6-311G** data in parentheses. UHF/3-21G$^{(*)}$ data in square brackets.

Reactions of 1-methylsilacyclopentadiene and 1-silylsilacyclopentadiene with methyl radical

As expected, extensive searching of the $C_6H_{11}Si$ and $C_6H_{11}Si_2$ potential energy surfaces located structures (**5**, R = CH_3, SiH_3) as stationary points at each level of theory on the potential energy surfaces for the reactions of methyl radical with 1-methylsilacyclopentadiene and 1-silylsilacyclopentadiene respectively. Energy barriers for the forward ($\Delta E_1^{\ddagger}$) and reverse ($\Delta E_2^{\ddagger}$) reactions (Scheme 1) are listed in Table 3 together with the (imaginary) frequency corresponding to the reaction coordinate where appropriate, while the optimised geometries of structures **5** (R = CH_3, SiH_3) are displayed in Fig. 2.

Energy barriers ($\Delta E_1^{\ddagger}$) for the forward reaction of between 42.2 (MP2/6-311G**) and 88.6 kJ mol^{-1} (UHF/3-21G$^{(*)}$ +ZPE) are calculated for the reaction involving **3** (R = CH_3), while values of between 35.0 (MP2/6-311G**) and 74.0 kJ mol^{-1} (UHF/3-21G$^{(*)}$ +ZPE) are calculated for the silyl-substituted system (**5**, R = SiH_3). Once again, both reactions are calculated to be significantly exothermic; energy barriers ($\Delta E_2^{\ddagger}$) for the reverse reaction of greater than about 119 kJ mol^{-1} are calculated for both reactions at all levels of theory in this study.

Inspection of Fig. 2 reveals that the MP2/6-311G** optimised structure of transition state (**5**, R = CH_3) is characterised by slightly "later" transition state parameters as that (**5**, R = H) for the unsubstituted system; Si–H_{TS} separations of 1.604 and 1.610 Å are calculated for unsubstituted and substituted transition states respectively, while the corresponding C–H_{TS} distances are calculated to be 1.564 and 1.561 Å respectively. These structural observations are consistent with the calculated slightly lower activation energy ($\Delta E_1^{\ddagger}$) for the reaction involving the unsubstituted silane (**3**, R = H) than the methyl-substituted analogue (**3**, R = CH_3); 41.5 *vs.* 42.2 kJ mol^{-1} at the MP2/6-311G** level of theory. This calculated increase in activation energy on methyl substitution is consistent with our previous calculations; methylsilane is calculated to require 53.8 kJ mol^{-1} to deliver hydrogen atom to methyl radical, as opposed to silane (SiH_4) which is calculated to require only 52.8 kJ.mol-1 at the MP2/DZP level of theory.[9]

Interestingly, 1-silylsilane (**3**, R = SiH_3) is calculated to react with methyl radical with a significantly reduced energy barrier ($\Delta E_1^{\ddagger}$); MP2/6-311G** calculations provide a value of 35.0 kJ mol^{-1} for this barrier, some 6.5 kJ mol^{-1} less energy than that required for the reaction of the parent compound (**3**, R = H). Once again, these calculated energy barriers are consistent with "earlier" transition state parameters (Fig. 2) associated with **5** (R = SiH_3) than either of the other two transition states in this study.

Comparisons of reactivity

The computational data presented in this work suggest the following order of reactivity for the hydrogen transfer reactions to methyl radical of the silanes in this study: **3** (R = SiH_3) > **3** (R = H) > **3** (R = CH_3). All silanes in this study are calculated to be more efficient than trimethylsilane in delivering hydrogen atom to methyl radical, suggesting that the conjugation afforded by the transition states (**5**) and product radicals (**4**) has a slight stabilising influence on these species. By comparison with the data generated in previous calculations, **3** (R = SiH_3), with an MP2/6-311G** calculated $\Delta E_1^{\ddagger}$ of 35.0 kJ mol^{-1} is calculated to deliver hydrogen atom to methyl radical with approximately similar efficiency to $(H_3Si)_3SiH$ which is calculated to require 34.6 kJ mol^{-1} at the MP2/DZP level of theory;[9] the remaining silanes (**3**, R = H, CH_3) are calculated to be significantly less competitive and hence are unlikely to be useful free-radical reagents. These data further reinforce the importance of including silyl substituents on the reacting silicon centre in the design of radical chain-carrying reagents.

Given that the silyl group may in fact underestimate the stabilising influence of the trimethylsilyl substituent in modelling studies,[9,14] and that TTMSS (**1**) is a useful reagent as previously discussed, it seems reasonable to suggest that 1-trimethylsilylsilacyclopentadiene (**3**, R = TMS) is also likely to be a useful reagent. Unfortunately no experimental data exist for free-radical reactions involving the substituted silacyclopentadienes (**3**) in this study or any closely related systems. Consistent with our calculated data, Chatgilialoglu has investigated the free-radical chemistry of 9-silafluorene (**6**) and has demonstrated no appreciable increase in reactivity when compared to diphenylsilane (Ph_2SiH_2).[15]

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