pyridine)$_2$]$^{2+}$ exhibits very different behavior.[15] Results from ligand isomerization studies suggest that intraligand states, ^{3}IL, are formed only upon photolysis directly into the ligand $^3(\pi \rightarrow \pi^*)$ absorption. Photolysis into the lower energy MLCT absorption results in a cis:trans ratio reasonably close to the thermodynamic ratio, implying the ^{1}MLCT manifold does not sensitize the ^{3}IL state, which yields nearly equal amounts of cis and trans isomers. In [(dmb)$_2$Ru(dstyb)]$^{2+}$, MLCT irradiation results in an intersystem crossing efficiency into the ^{3}IL state of 0.7. The difference in behavior between styrylpyridine and dstyb complexes may simply reflect the fact that the ^{3}IL state of dstyb (14 150 cm^{-1}) is lower than that of styrylpyridine (17 500 cm^{-1}). Another difference between the styrylpyridine complex and the dstyb complexes is that the lowest MLCT absorption in [(bpy)$_2$Ru(4-styrylpyridine)$_2$]$^{2+}$ is Ru(dπ) $\rightarrow$ bpy(π^*) whereas for both dstyb complexes the transition is Ru(dπ) $\rightarrow$ dstyb(π^*). We are currently examining other complexes that will address this question more directly.

Many of the complexes prepared as potential sensitizers for multielectron redox reactions employ bridging ligands having extended conjugation similar to that of dstyb. The presence of low-energy, nonluminescent ^{3}IL states, as in complexes of dstyb, coupled with low yields for population of ^{3}MLCT states, can serve to decrease the efficiency of reactions of this type.

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Reactions of Triplet Carbonyl Compounds and Nitro Derivatives with Silanes

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Abstract: The photoinduced reactions of aromatic and aliphatic carbonyl compounds and nitro derivatives with tetramethylsilane, hexamethyldisilane, and tetrakis(trimethylsilyl)silane were investigated by EPR spectroscopy. The photoreaction of benzophenone with the three silanes was also studied by time-resolved optical techniques. Triplet ketones and quinones reacted with $Me_3SiSiMe_3$ and with $(Me_3Si)_4Si$ by a radical-like displacement mechanism. Homolytic substitution was also observed by reacting photoexcited nitro compounds with the same silanes. The nature of the radical adducts being formed suggests that this reaction is likely to proceed, at least for some of the investigated compounds, via a partial or complete electron transfer (ET). Corroborating evidence for the latter process was sought in polarographic, cyclic voltammetric, and controlled-potential coulometric experiments.

Group IVB organometallic compounds can undergo homolytic substitution reactions, S_H2, at the metal atom. These processes take place more readily when the heavier elements of the group, such as tin and lead, are involved;[1-3] examples have also been reported of homolytic displacement at silicon and germanium brought about by halogen atoms.[2] Generally, metal-to-metal bonds are more easily cleaved via an S_H2 mechanism than metal-to-carbon bonds,[2] this being in agreement with the different bond strengths involved, i.e., 80.5 (Me_3Si–$SiMe_3$), 89.4 (Me_3Si–Me),[4] 73 (Ge–Ge), 76 (Ge–Me), 56 (Sn–Sn), and 65 kcal/mol (Sn–Me).[5]

The capability of bringing about homolytic displacement reactions is not a peculiarity of free radicals and is also exhibited by other species containing unpaired electrons such as triplet-state molecules. Indeed, we have shown in previous papers that the reaction of triplet diphenylcarbene with sulfides, disulfides, diselenides,[6] some tervalent phosphorus compounds,[7] and group IVB organometallic derivatives containing metal–metal bonds[8] is analogous to the familiar homolytic substitution process, S_H2. Also triplet carbonyl compounds have been shown to give homolytic displacements, in particular at phosphorus[7] and boron[9] derivatives.

We report here the results of an investigation on the photochemical reactions between a number of carbonyl and nitro derivatives with some silanes. This study has been carried out by using electron paramagnetic resonance spectroscopy (EPR) to identify the radicals formed, electrochemical techniques to determine redox potentials, and time-resolved optical techniques to measure the rate of quenching of a representative triplet ketone, i.e., benzophenone, by several silanes.

Results and Discussion

The silicon-containing compounds that have been used are tetramethylsilane and two derivatives containing the silicon–silicon bond, i.e., hexamethyldisilane and tetrakis(trimethylsilyl)silane.

Carbonyl Compounds. EPR Measurements. The reactions of triplet ketones with group IVB metal hydrides have been exten-

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(1) Ingold, K. U.; Roberts, B. P. *Free Radical Substitution Reactions*; Wiley-Interscience; New York, 1971.

(2) Sakurai, H. In *Free Radicals*; Kochi, J. K., Ed.; Wiley: New York, 1973; Vo. 2, p 741.

(3) Davies, A. G. *J. Organomet. Chem.* **1980**, *200*, 87.

(4) Walsh, R. *Acc. Chem. Res.* **1981**, *14*, 246.

(5) Jackson, R. A. *J. Organomet. Chem.* **1979**, *166*, 17.

(6) Alberti, A.; Griller, D.; Nazran, A. S.; Pedulli, G. F. *J. Am. Chem. Soc.* **1986**, *108*, 3024.

(7) Alberti, A.; Griller, D.; Nazran, A. S.; Pedulli, G. F. *J. Org. Chem.* **1986**, *51*, 3959.

(8) Alberti, A.; Pedulli, G. F. *Gazz. Chim. Ital.*, submitted for publication.

(9) (a) Davies, A. G.; Roberts, B. P.; Scaiano, J. C. *J. Chem. Soc. B* **1971**, 2171. (b) Alberti, A.; Pedulli, G. F. *J. Organomet. Chem.* **1985**, *297*, 13.

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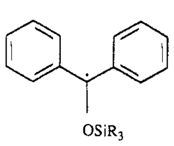
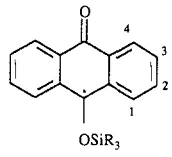
sively investigated and shown to proceed by abstraction of the hydrogen linked to the metal atom; accurate values of the rate constants for these reactions have also been reported.[10] The analogous reactions with group IVB derivatives lacking a metal–hydrogen bond have been studied only for tin compounds, and it has been shown that ketone triplets behave similarly to alkoxyl radicals in inducing homolytic substitution at the metal center.[3] The lack of reports for silicon derivatives prompted us to study the photochemical reactions of some ketones and quinones with tetramethylsilane (Me_4Si) and with the two polysilanes $Me_3SiSiMe_3$ and $(Me_3Si)_4Si$.

The three silanes were first reacted within the EPR cavity with photolytically produced *tert*-butoxyl radicals in deoxygenated di-*tert*-butyl peroxide. They were found to give spectra of $Me_3SiCH_2^\bullet$ (a(2 H) = 20.9, a(9 H) = 0.40 G, g = 2.0025),[11] $Me_3SiSiMe_2CH_2^\bullet$ (a(2 H) = 20.2, a(6 H) = 0.24 G, g = 2.0026),[11] and $(Me_3Si)_3SiMe_2CH_2^\bullet$ (a(2 H) = 20.08 G, g = 2.0026), respectively, as already reported in the literature. Since no EPR spectra of $Me_3Si^\bullet$ or $(Me_3Si)_3Si^\bullet$ radicals were observed with the two polysilanes, it is deduced that *tert*-butoxyl radicals react essentially by abstracting hydrogen from the methyl groups.

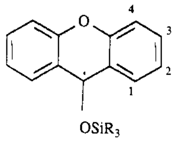
When the silanes were photolytically reacted with benzophenone in *tert*-butylbenzene, none of the above silyl-substituted methyl radicals were detected; EPR spectra typical of α-substituted diphenylmethyl radicals were instead observed, the nature of the substituent varying with the silane. With tetramethylsilane the observed radical was identified as $Ph_2\dot{C}{-}OH$ on the basis of the aryl proton hyperfine splitting (hfs) constants and of the marked temperature dependence of the a(OH) coupling (2.45 G at 253 K, 3.03 G at 428 K), this demonstrating that hydrogen abstraction represents, in this case, the most important reaction pathway. $Ph_2\dot{C}{-}OSiMe_3$ (**1a**) was the only detectable species when $Me_3SiSiMe_3$ was photoreacted with benzophenone between 253 and 373 K; the intensity of the EPR signals was stronger at higher temperature. With $(Me_3Si)_4Si$ two superimposed spectra were detected, one being due to $Ph_2\dot{C}{-}OSiMe_3$ (**1a**) and the other to $Ph_2\dot{C}{-}OSi(SiMe_3)_3$ (**1b**). An unambiguous identification of the latter was achieved by generating the authentic adduct by photolysis of benzophenone and $(Me_3Si)_3SiH$ in the presence of di-*tert*-butyl peroxide.



(**1a**,b)



(**2a**,b)



(**3a**,b)

a: R=Me

b: R=$SiMe_3$

An analogous behavior was exhibited by other carbonyl compounds such as anthraquinone and xanthone, which afforded the spectra of the Me_3Si adducts when photoreacted with $Me_3SiSiMe_3$ and of both the Me_3Si and $(Me_3Si)_3Si$ adducts when reacted with $(Me_4Si)_4Si$. These two adducts were generally characterized by slightly different EPR parameters (Table I) so that distinct lines from both radicals could be resolved, especially at high magnetic field. Spectra of silyl adducts were also observed with fluorenone and benzo[1,2-*b*;5,4-*b*′]dithiophene-4,8-dione, for which the spectral parameters of the various species were not determined.

The formation of the silyl radical adducts to carbonyl compounds can be explained by a homolytic substitution reaction, S_H2, at one of the silicon atoms of the silanes by the triplet ketone or quinone (eq 1–5).

Table I. EPR Parameters for Radicals **1–6** in *tert*-Butylbenzene and **7–9** in Toluene

radical	hyperfine splitting constants (a_H/G)	g	T/K
1a	3.16 (H_o), 1.21 (H_m), 3.52 (H_p)	2.0028_5	348
1b	3.22 (H_o), 1.26 (H_m), 3.59 (H_p)	2.0027_8	
2a	2.71 ($H_{1,8}$), 0.87 ($H_{2,4,5,7}$), 3.13 ($H_{3,6}$)	2.0036	338
2b	2.83 ($H_{1,8}$), 0.90 ($H_{2,4,5,7}$), 3.23 ($H_{3,6}$)	2.0035_1	
3a	3.62 ($H_{1,8}$), 0.95 ($H_{2,7}$), 3.92 ($H_{3,6}$), 0.64 ($H_{4,5}$)	2.0029_5	383
3b	3.60 ($H_{1,8}$), 0.96 ($H_{2,7}$), 3.93 ($H_{3,6}$), 0.63 ($H_{4,5}$)	2.0029_2	
4	8.37 (3 H), 0.13 (9 H)	2.0033_6	325
5	7.96 (3 H), 1.09 (3 H)	2.0034_2	325
6	7.84 (3 H), 0.95 (3 H)	2.0034_2	325
7	6.77 (1 H)	2.0041	193
8	1.04 (2 H)	2.0046	193
9	0.99 (2 H)	2.0046	213

$$^3Ar_2C{=}O + Me_3SiSiMe_3 \rightarrow Ar_2\dot{C}{-}OSiMe_3 + Me_3Si^\bullet \quad (1)$$

$$Me_3Si^\bullet + Ar_2C{=}O \rightarrow Ar_2\dot{C}{-}OSiMe_3 \quad (2)$$

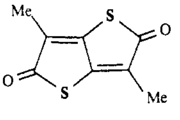
$$^3Ar_2C{=}O + (Me_3Si)_4Si \rightarrow Ar_2\dot{C}{-}OSiMe_3 + (Me_3Si)_3Si^\bullet \quad (3)$$

$$\rightarrow Ar_2\dot{C}{-}OSi(SiMe_3)_3 + Me_3Si^\bullet \quad (4)$$

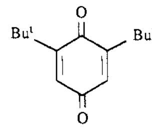
$$(Me_3Si)_3Si^\bullet + Ar_2C{=}O \rightarrow Ar_2\dot{C}{-}OSi(SiMe_3)_3 \quad (5)$$

Thus, displacement was observed only when the relatively weak silicon–silicon bond was present, while with Me_4Si, which contains the stronger carbon–silicon bonds, hydrogen abstraction seems the only accessible process. However, it should be pointed out that also with polysilanes we cannot exclude that displacement is accompanied by hydrogen abstraction since $Ph_2\dot{C}{-}OH$ or related radicals originating from the latter process are much less persistent than the silyl adducts.

From the reaction scheme of eq 1–5 it is apparent that $(Me_3Si)_4Si$ can react with the ketones in two different ways, depending on which of the two radicals $(Me_3Si)_3Si^\bullet$ (eq 3) or $Me_3Si^\bullet$ (eq 4) is displaced. With the substrates we have been dealing so far, no discrimination between the two routes is possible since they lead eventually to the same radical adducts. Compounds potentially capable of providing more detailed information on the mechanism of the S_H2 displacement are instead 3,6-dimethylthieno[3,2-*b*]thiophene-2,5-dione (DMTD) and 2,6-di-*tert*-butyl-*p*-benzoquinone (DBQ), for which we have recently reported that addition of $Et_3Si^\bullet$ and $Ph_3Si^\bullet$ radicals occurs with a high regioselectivity at a ring carbon atom and only to a minor extent to the carbonyl oxygen.[12a] The determination of the relative ratio of the isomeric radical adducts in the photoreaction of these two diones with $Me_3SiSiMe_3$ and $(Me_3Si)_4Si$ could therefore provide more insight into the preferred reaction pathway. Since, however, the regioselectivity of attack of the $Me_3Si^\bullet$ and $(Me_3Si)_3Si^\bullet$ radicals was not known, DMTD and DBQ were first reacted with Me_3SiH and $(Me_3Si)_3SiH$ in the presence of di-*tert*-butyl peroxide.



DMTD



DBQ

Trimethylsilyl radicals, $Me_3Si^\bullet$, proved to add both to the heterocyclic ring and to the carbonyl oxygen of DMTD (see Figure 1a) according to eq 6 and 7, while tris(trimethylsilyl)silyl radicals, $(Me_3Si)_3Si^\bullet$, only added to the oxygen atom (eq 8 and 9). The percents of radicals **4** and **5** were determined from the relative intensities of their EPR spectra, while the assignment of the spectra

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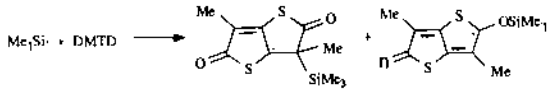
(10) Chatgilialoglu, C.; Scaiano, J. C.; Ingold, K. U. *Organometallics* **1982**, *1*, 466.

(11) Krusic, P. J.; Kochi, J. K. *J. Am. Chem. Soc.* **1969**, *91*, 6161. Hudson, A.; Hussain, H. A. *J. Chem. Soc. B* **1969**, 793.

(12) (a) Alberti, A.; Chatgilialoglu, C.; Pedulli, G. F.; Zanirato, P. *J. Am. Chem. Soc.* **1986**, *108*, 4993. (b) Alberti, A.; Hudson, A.; Pedulli, G. F.; McGimpsey, W. G.; Wan, J. K. S. *Can. J. Chem.* **1985**, *63*, 917–921.

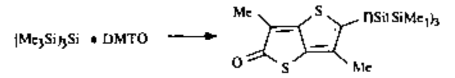
$$\mathrm{Me_3SiH + BuO \longrightarrow Me_3Si + BuOH} \qquad (6)$$



(7)

4 (80%) 5 (20%)

$$\mathrm{(Me_3Si)_3SiH + BuO \longrightarrow (Me_3Si)_3Si + BuOH} \qquad (8)$$

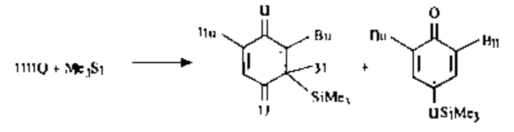


(9)

6 (100%)

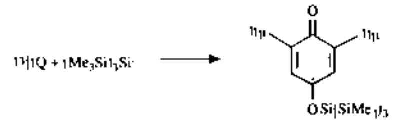
was based on the fact that the unpaired electron is coupled with the protons of both methyl groups (ca. 8 and 1 G, respectively) in the oxygen adduct but with those of only a methyl group (ca. 8 G) in the ring adduct, as previously found in the analogous radicals resulting from addition of Ph$_3$Si$^\bullet$, Et$_3$Si$^\bullet$,[12a] and phosphorus-centered radicals[12b] to DMTD.

Similarly, when Me$_3$Si$^\bullet$ radicals were reacted with 2,6-di-*tert*-butyl-*p*-benzoquinone at low temperature (<230 K), the adducts to the ring (7) and to the carbonyl oxygen (8) were obtained in a 4:1 ratio, while with (Me$_3$Si)$_3$Si$^\bullet$ radicals, only the oxygen adduct 9 was observed.



(10)

7 (80%) 8 (20%)



(11)

9 (100%)

DMTD was thereafter photoreacted with hexamethyldisilane and with tetrakis(trimethylsilyl)silane. In the former case both radicals 4 and 5 were still observed but their relative amounts, i.e., 20% and 80%, determined by computer simulation of the EPR spectra, were very different from those in the previous reaction (see Figure 1b). This result is interpreted in terms of displacement of trimethylsilyl radicals by triplet DMTD with concurrent formation of radical 5, which now becomes the dominant species. The displaced Me$_3$Si$^\bullet$ radicals may subsequently add either to the ring carbon or to the carbonyl oxygen of DMTD to afford 4 and 5.

The photoreaction of DMTD with tetrakis(trimethylsilyl)silane afforded the three radical adducts 4, 5, and 6 in the approximate ratio 1:2:3. The formation of the ring adduct 4 indicates that, along with the more predictable displacement of (Me$_3$Si)$_3$Si$^\bullet$ (eq 12), displacement of Me$_3$Si$^\bullet$ also takes place (eq 14).

$$\mathrm{^3DMTD + (Me_3Si)_4Si \rightarrow 5 + (Me_3Si)_3Si^\bullet} \qquad (12)$$

$$\mathrm{(Me_3Si)_3Si^\bullet + DMTD \rightarrow 6} \qquad (13)$$

$$\mathrm{^3DMTD + (Me_3Si)_4Si \rightarrow 6 + Me_3Si^\bullet} \qquad (14)$$

$$\mathrm{Me_3Si^\bullet + DMTD \rightarrow 4 + 5} \qquad (15)$$

The relative weight of reactions 12 and 14 was determined from the ratio of the isomeric adducts as 3:2, under the assumption that all the displaced silyl radicals are scavenged by DMTD.

When Me$_3$SiSiMe$_3$ was photoreacted with DBQ, radicals 7 and 8 were formed in approximately equal amounts, consistent with the proposed homolytic substitution process. The displacement of trimethylsilyl radicals from Me$_3$SiSiMe$_3$ by the same photoreacted quinone was recently confirmed by using the CIDEP technique.[13]

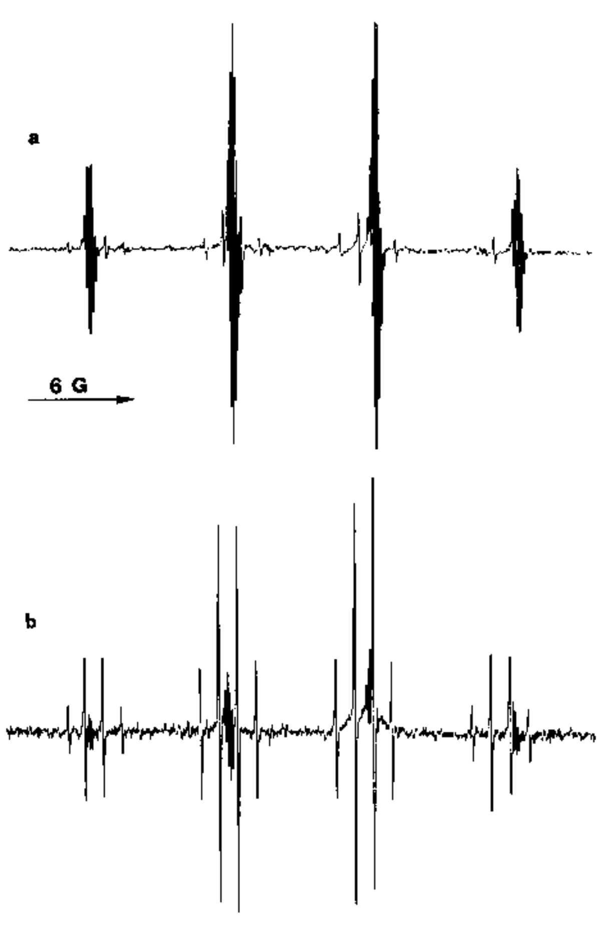
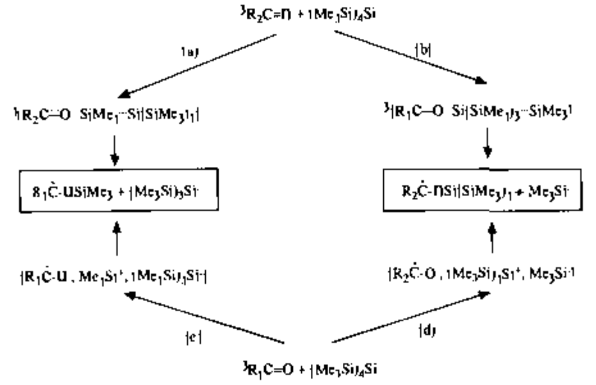


Figure 1. EPR spectra of radicals 4 and 5 obtained by photolyzing at 325 K benzene solutions of (a) DMTD, Me$_3$SiH, and di-*tert*-butyl peroxide and (b) DMTD and Me$_3$SiSiMe$_3$.

Scheme 1



With (Me$_3$Si)$_4$Si and DBQ, a doublet spectrum due to 7 was detected together with a superimposition of the two triplets from 8 and 9, the overall triplet signal being 3 times more intense than the doublet. Again, with tetrakis(trimethylsilyl)silane displacement of Me$_3$Si$^\bullet$ radicals takes place as indicated by the observation of radical 7, along with that of (Me$_3$Si)$_3$Si$^\bullet$.

The above results seem to leave little doubt that photoexcited carbonyl compounds are capable of bringing about radical displacements at silicon atoms of polysilanes in a fashion that is akin to the familiar S$_H$2 homolytic substitution reaction. The collected data also allow some mechanistic considerations to be made. The

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[13] Craw, M. T.; Alberti, A.; Depew, M. C.; Wan, J. K. S. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 3675.

initial step of the process may be direct attack of the carbonyl oxygen of the triplet ketone or quinone to a silicon atom of the silane to give a biradical intermediate or transition state or may involve a partial or complete electron transfer from the silane to the triplet-state molecule.[14] These two different pathways are exemplified in Scheme I for tetrakis(trimethylsilyl)silane.

The reactions between ketones and both polysilanes or those between the diones and hexamethyldisilane do not provide mechanistic information, since the nature and the relative amounts of the radicals being formed are predicted to be independent of the actual reaction pathway. Some reasonable hypothesis, based on the different regioselectivity of addition of $Me_3Si^•$ and $(Me_3Si)_3Si^•$ to DMTD and DBQ, can instead by made from the composition of the radical mixtures obtained by reacting $(Me_3Si)_4Si$ with these diones. Very important in this respect was the detection of radicals **4** and **7**, whose formation implies the displacement of $Me_3Si^•$ radicals from $(Me_3Si)_4Si$. If the reaction proceeds by direct attack of the triplet quinone to the silane, this should occur at the highly hindered central silicon atom (route b of Scheme I), which seems very unlikely on steric grounds. Instead, electron transfer followed by fragmentation of the resulting cation to give $(Me_3Si)_3Si^+$ and $Me_3Si^•$, according to route d of Scheme I, would nicely account for the formation of radicals **4** from DMTD and **7** from DBQ.

Among carbonyl derivatives, electron transfer should be more difficult for aliphatic than for aromatic ketones or for quinones that exhibit higher electron affinities. To check if electron-transfer-mediated displacement may also take place with more unfavorable substrates, we photoreacted acetone (2.5 M) with hexamethyldisilane and tetrakis(trimethylsilyl)silane in benzene or *tert*-butylbenzene. In the temperature range 240–330 K no EPR signals were detected despite the fact that acetone is a scavenger of silyl radicals.[15] This indicates that the displacement reaction does not occur. The photoreaction was repeated at 243 K in acetonitrile and in neat acetone. In both cases EPR signals due to the silyl adducts to acetone were observed, the spectrum being that of the rapidly decaying $Me_2\dot{C}{-}OSiMe_3$ radical (a(6 H) = 20.4 G, g = 2.0031) with $Me_3SiSiMe_3$ and that of the much more persistent $Me_2\dot{C}{-}OSi(SiMe_3)_3$ radical (a(6 H) = 19.92, $a(^{29}Si)$ = 18.66 G, g = 2.0032) with $(Me_3Si)_4Si$. It is worth pointing out that we could not observe signals arising from $(Me_3Si)_3Si^•$ at any temperature, although it is well-known that this particular radical, because of its low rate of addition to acetone, is readily detectable below 300 K when produced from the corresponding hydride.[15,16]

The failure to detect displacement of $(Me_3Si)_3Si^•$ radicals along with the dependence on solvent polarity of the reactivity of photoexcited acetone is more easily rationalized by admitting that $Me_2\dot{C}{-}OSi(SiMe_3)_3$ radicals are formed via an ET process as outlined in route d of Scheme I, rather than by direct attack on the silane as in route b.

Time-Resolved Optical Techniques. In order to gain deeper insight into the different behavior exhibited by the three silanes toward triplet ketones, we examined their efficiency as quenchers of the triplet state of benzophenone. Measurements were carried out at 293 K in degassed benzene solutions by using a concentration of $Ph_2C{=}O$ of ca. 2×10^{-3} M; in the absence of quencher the lifetime of triplet benzophenone was 5.0–6.0 μs. In the presence of the silanes the decrease of the emission lifetime followed a linear Stern–Volmer equation (16), as typically shown in Figure 2, from which the values of k_q could be obtained as 2.8×10^4, 3.9×10^5, and 2.6×10^6 M^{-1} s^{-1} for Me_4Si, $Me_3SiSiMe_3$, and $(Me_3Si)_4Si$, respectively.

$$1/\tau - 1/\tau_0 = k_q[Q] \qquad (16)$$

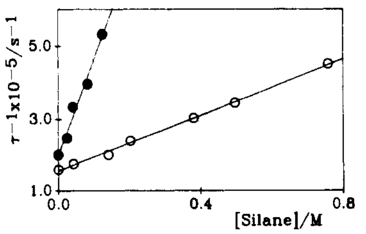

Figure 2. Stern–Volmer plots for the quenching of triplet benzophenone (2×10^{-3} M in benzene) by $Me_3SiSiMe_3$ (○) and $(Me_3Si)_4Si$ (●) at 293 K.

In comparing the k_q values for the last two compounds with the rate constants for hydrogen abstraction by *tert*-butoxyl radicals measured for the same derivatives, i.e., 1.7×10^6 and 7.8×10^6 M^{-1} s^{-1},[17] one can note that they are similar despite the fact that the EPR experiments lead to the detection of different radical species. It should, however, be pointed out that the EPR observation of only one radical does not necessarily imply the occurrence of a single chemical process, and therefore we cannot exclude that hydrogen abstraction from the polysilanes is a reaction concurrent with radical displacement. Product studies for the photoreaction between benzophenone and the polysilanes could, in principle, provide information on the relative importance of the displacement and of the hydrogen abstraction reaction. Disappointingly, they proved to be impracticable because the conversion of the reactants was found to be very low even in samples irradiated for several hours.

The increase of the quenching rate constants in the series Me_4Si, $Me_3SiSiMe_3$, and $(Me_3Si)_4Si$, which are characterized by ionization potentials of 10.30,[18] 8.69, and 8.24 eV,[19] respectively, might suggest that this is due to the increasing rate of electron transfer. However, we should not forget that also the ease of hydrogen abstraction should increase along the same series.[17]

We have also determined the rate constant, k_q, for the quenching of triplet benzophenone by hexamethyldisilane and tetrakis(trimethylsilyl)silane in acetonitrile, where, due to the higher dielectric constant, the electron-transfer process is expected to be accelerated with respect to benzene solutions. The values obtained, i.e., 3.9×10^5 and 3.1×10^6 M^{-1} s^{-1} for $M_3SiSiMe_3$ and $(Me_3Si)_4Si$, respectively, were practically identical with those measured in benzene. The lack of dependence of k_q on solvent polarity may be interpreted by admitting either that in the S_H2 homolytic substitution reaction by photoexcited benzophenone the ET mechanism plays a negligible role or that displacement is only a concurrent pathway, hydrogen abstraction being the more important route of reaction.

Electrochemistry. In order to ascertain the thermodynamic feasibility of the ET reaction between polysilanes and triplet carbonyl compounds, we carried out electrochemical investigations on DBQ, DMTD, $Me_3SiSiMe_3$, and $(Me_3Si)_4Si$ to obtain information on standard reduction potentials of the carbonyl compounds and standard oxidation potentials of the silanes. The value relative to the couple $DBQ/DBQ^{•-}$, although already known,[20] was remeasured to ensure identical scaling.

For both DBQ and DMTD the cyclic voltammetric curves (Figure 3) show two reduction peaks which, according to the usual criteria, appear to be due to one-electron diffusion-controlled reversible processes.

The half-wave potentials, $E_{1/2}$, deduced by adding 29 mV to the peak potentials, E_p, are −0.730 and −0.810 ± 0.003 V for the first wave and −1.370 and −1.385 ± 0.003 V for the second wave for DBQ and DMTD, respectively. The value of −0.730 V was identical with that reported in the literature.[20] Within the usual assumption that the ratios of activity and diffusion coefficients are nearly unit, the $E_{1/2}$ values can be considered equal to $E°$.

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(14) Fukuzumi, S.; Kochi, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 2141, 2654. Fukuzumi, S.; Wong, C. L.; Kochi, J. K. *Ibid.* **1980**, *102*, 2928. Klingler, R. J.; Kochi, J. K. *Ibid.* **1980**, *102*, 4790.

(15) Cooper, J.; Hudson, A.; Jackson, R. A. *J. Chem. Soc., Perkin Trans. 2* **1973**, 1933.

(16) We have confirmed these results by photoreacting $(Me_3Si)_3SiH$ with acetone at several temperatures.

(17) Chatgilialoglu, C.; Rossini, S. *Bull. Chim. Soc. Fr.* **1988**, 297.

(18) Pitt, C. G.; Boch, H. *Chem. Commun.* **1972**, 28.

(19) Bock, H.; Ensslin, W. *Angew. Chem., Int. Ed. Engl.* **1970**, *10*, 404.

(20) Ryba, O.; Pilãr, J.; Petranek, J. *Collect. Czech. Chem. Commun.* **1968**, *33*, 26.

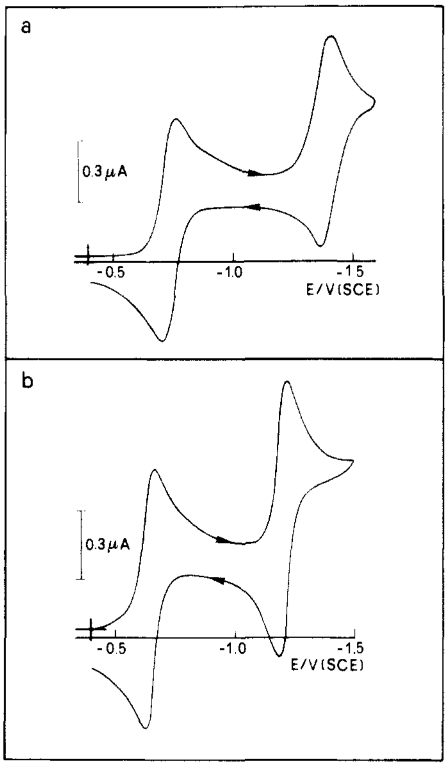

Figure 3. Cyclic voltammetric curves at 298 K for 5 × 10^{-4} M ACN solutions of (a) DBQ and (b) DMTD in 0.1 M TEATFB. Working electrode; hanging mercury drop electrode. Sweep rate: 0.4 V/s.

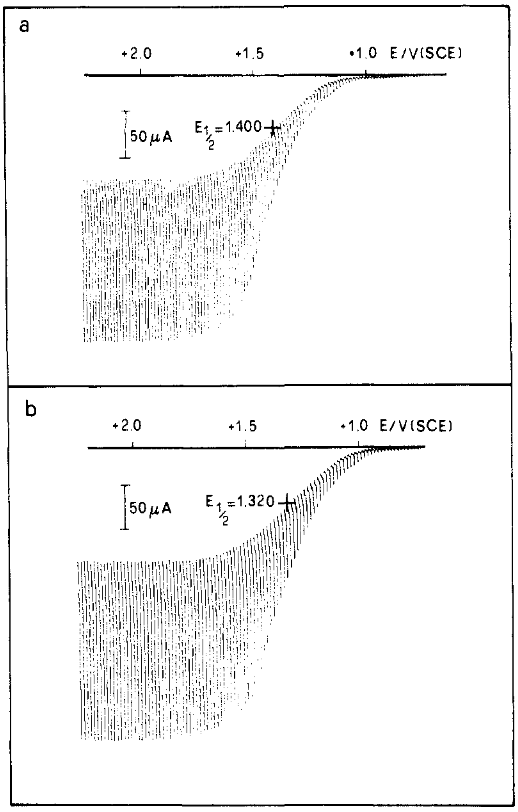

Figure 4. Voltammetric curves recorded at 298 K with a platinum electrode with periodic renewal of the diffusion layer for 5 × 10^{-4} M ACN solutions of (a) $Me_3SiSiMe_3$ and (b) $(Me_3Si)_4Si$ in 0.1 M TEATFB. Renewal time: 3 s.

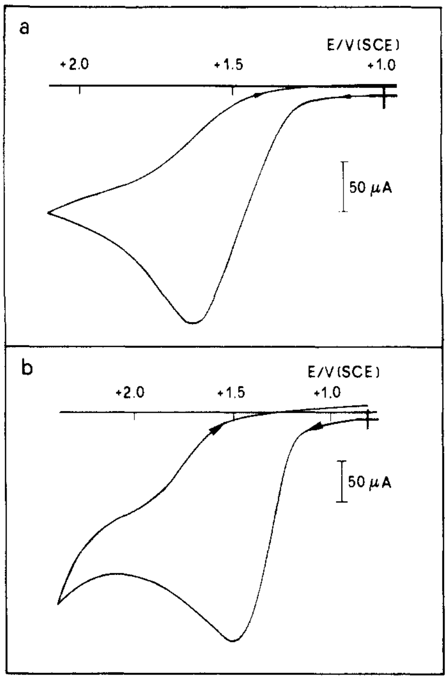

Figure 5. Cyclic voltammetric curves at 298 K for 5 × 10^{-4} M ACN solutions of (a) $Me_3SiSiMe_3$ and (b) $(Me_3Si)_4Si$. Working electrode: platinum. Sweep rate: 0.4 V/s.

The $E_{1/2}$ values for the two polysilanes determined from the volatmmetric curves recorded with a Pt electrode with periodic renewal of the diffusion layer[21] were +1.400 and +1.320 ± 0.005 V (see Figure 4) for $Me_3SiSiMe_3$ and $(Me_3Si)_4Si$, respectively. These values indicate that tetrakis(trimethylsilyl)silane is more easily oxidizable than hexamethyldisilane, in agreement with what is expected on the basis of ionization potentials of the two compounds (8.24 and 8.69 eV, respectively).[19] For these compounds, however, the $E_{1/2}$'s cannot be considered coincident with E° since the process is irreversible as indicated by the absence of the reverse cathodic peak in the cyclic voltammetric curves (see Figure 5). This behavior is observed even at temperatures as low as −40 °C and at sweep rates up to 250 V/s. Furthermore, for both polysilanes, the ratio between peak current, i_p, and the square root of the sweep rate v is constant over the investigated scan rate range (0.1–500 V/s), both peak potentials, E_p, and i_p vary linearly with log v, and the difference between E_p and half-peak potential, $E_{p/2}$, is independent of v. In particular, values of $E_p - E_{p/2} = 170$ and 180 mV, $\Delta E_p/\Delta \log v = 100$ and 115 mV/log v, and $\Delta E_p/\Delta \log i_p = 195$ and 225 mV/log i_p, were obtained for $Me_3SiSiMe_3$ and $(Me_3Si)_4Si$, respectively. All these results indicate that irreversibility of the peak is due to the intrinsic slowness of the first electron transfer, similarly to what was previously found for analogous alkylmetals.[14] The values of the average transfer coefficient, α, deduced from $E_p - E_{p/2}$, $\Delta E_p/\Delta \log v$, and $\Delta E_p/\Delta \log i_p$, within the context of Butler–Volmer kinetics,[22] were practically coincident and equal to 0.28 and 0.27 ± 0.01 for Me_3SiSiM_3 and $(Me_3Si)_4Si$, respectively. The controlled-potential coulometry at a platinum gauze electrode of 5 × 10^{-4} M solutions of the silanes afforded two electrons per molecule of alkylmetal.

The oxidation mechanism, exemplified in eq 17–19 for $Me_3SiSiMe_3$, accounts for all the experimental observations collected.

$$Me_3SiSiMe_3 \xrightarrow{\text{slow}} Me_3Si^{\bullet} + Me_3Si^{+} + e^{-} \qquad (17)$$

$$Me_3Si^{\bullet} \xrightarrow{\text{fast}} Me_3Si^{+} + e^{-} \qquad (18)$$

$$Me_3SiSiMe_3 \rightarrow 2\ Me_3Si^{+} + 2e^{-} \qquad (19)$$

The slow release of the first electron is most likely concerted with the Si–Si bond cleavage as inferred from the low value of α.[23] At these potentials, the ensuing radical is quickly oxidized

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(21) Farnia, G.; Roffia, S. *J. Electroanal. Chem.* **1981**, *122*, 347.

(22) Matsuda, H.; Ayabe, Y. Z. *Z. Elektrochem.* **1955**, *59*, 494.

Table II. Redox Potentials ($E_{1/2}$/V) in ACN vs SCE, Triplet-State Energies (E_T/eV), and Calculated Free Energy Changes[a] ($\Delta G°$/(kcal mol^{-1})) for the ET Reactions in ACN

compd	E_{Ox}	E_{Red}	E_T	$\Delta G°$	
				Me_6Si_2	$(Me_3Si)_4Si$
Me_6Si_2	+1.40				
$(Me_3Si)_4Si$	+1.32				
DBQ		−0.73	~2.3[b,c]	−3.9	−5.8
DMTD		−0.81			
AQ[d]		−0.82[e]	2.69[f]	−10.8	−12.7
Ph_2CO		−1.68[b]	3.00[b]	+1.8	0
Me_2CO		−2.84[g]	3.4[f]	+19.4	+17.5
$PhNO_2$		1.15[b]	2.60[b]	−1.1	−3.0

[a] The reported $\Delta G°$'s are upper values (see text). [b] Reference 24. [c] Value for *p*-benzoquinone. [d] AQ = 9,10-anthraquinone. [e] Reference 27, in DMF. [f] Reference 28, p 352. [g] Reference 26.

at the electrode to the corresponding cation, in agreement with the overall two-electron character of the process.

From the characteristics of the irreversible electrochemical process and on the basis of the above considerations, it can be inferred that $E°$ must be more negative than the observed $E_{1/2}$ even by as much as 0.8–1.0 V.

Thermodynamics of the ET Process. The free energy change, $\Delta G°$, of a photoinduced ET reaction between an electron donor, D, and an electron acceptor, A, can be evaluated by the Rehm–Weller equation (20).[24,25]

$$\Delta G° = 23.06[E°_{Ox}(D) - E°_{Red}(A) - \Delta E_{exc} + \Delta E_{coul}] \qquad (20)$$

In eq 20 $E°_{Ox}(D)$ is the oxidation potential of the donor, $E°_{Red}(A)$ is the reduction potential of the acceptor, ΔE_{exc} is the energy of the electronically excited compound, and ΔE_{coul} is the Coulombic interaction energy for the two radical ions formed in the ET process. The importance of the last term decreases with increasing dielectric constant of the solvent and is practically negligible in acetonitrile.

In the present case $E°_{Ox}$ is the standard potential of the rate-determining redox step (eq 17) relative to the dissociative oxidation of the silane, while $E°_{red}$ and ΔE_{exc} refer to the carbonyl compound.

Table II collects the $E_{1/2}$ and ΔE_{exc} values for some of the compounds examined in the present work. As already pointed out, the half-wave reduction potentials of the carbonyl derivatives may be considered coincident with the $E°_{Red}$ with the exception of acetone,[26] while the oxidation potentials of the silanes represent the upper limit for $E°_{Ox}$, the actual values being possibly lower by as much as 0.8–1.0 V, i.e., 18–23 kcal/mol. On the other hand, the photolytic experiments were performed in benzene, where Coulombic interactions should also be taken into account; this would lead to an increase in the calculated free energy change of approximately 6–10 kcal/mol. This means that the $\Delta G°$ values for the ET reaction can only be approximately estimated from eq 5 by using the data of Table II. Nevertheless, these estimates may be indicative of the feasibility of the electron-transfer reaction and therefore they are reported in the last column of Table II.

From these data it is evident that electron transfer may be a possible pathway for the quenching of triplet quinones by silanes, because of the exoergonicity expected for this process, provided that the intrinsic kinetic barrier is not too high. On the other hand, the involvement of ET becomes questionable with benzophenone and even more so with acetone, whose reactions were estimated to be thermoneutral and endoergonic, respectively.

Table III. EPR Parameters for the Silyloxy Nitroxide $RN(\dot{O})OSi(SiMe_3)_3$

R	a_N/G	a_{other}/G	*g*
Me	29.33	9.01 (3 H), 1.41 (3 ^{29}Si)	2.0053
t-Bu	29.13		2.0052
Ph	15.02	3.14 (2 H_o), 1.08 (2 H_m), 3.29 (H_p)	2.0047
$4\text{-}NO_2C_6H_4$	12.40	3.10 (2 H_o), 1.03 (2 H_m), 0.95 (N)	2.0049
$3\text{-}NO_2C_6H_4$	14.01	3.16 (3 H), 1.08 (1 H), 0.24 (N)	2.0048
$3,5\text{-}(NO_2)_2C_6H_3$	12.95	3.23 (2 H_o), 3.31 (H_p), 0.23 (2 N)	2.0048

Nitro Compounds. Another class of compounds having readily accessible triplet states and high electron affinities are nitro derivatives, which should also be capable of giving displacement reactions when photoreacted with polysilanes. We have chosen $MeNO_2$, *t*-$BuNO_2$, nitrobenzene, *m*-dinitro- and *p*-dinitrobenzene, and 1,3,5-trinitrobenzene. All these compounds when photoreacted with Me_3SiH or $(Me_3Si)_3SiH$ afford strong EPR spectra due to the silyloxy nitroxides $RN(\dot{O})OSiMe_3$ and $RN(\dot{O})OSi(SiMe_3)_3$ formed by addition of the silyl radicals to a nitro group. The two series of nitroxides showed very similar EPR spectra, which in most cases differed only in the line width. The spectral parameters of the as yet unreported $RN(\dot{O})OSi(SiMe_3)_3$ radicals are collected in Table III.

The photochemical reactions of the four nitroarenes with $Me_3SiSiMe_3$ and $(Me_3Si)_4Si$ in benzene at room temperature afforded the EPR spectra of silyloxy nitroxides, although with the latter silane it was impossible to ascertain the nature of the entering group (Me_3Si or $(Me_3Si)_3Si$) since the spectra of the resulting radicals can hardly be distinguished. The photoreaction of *t*-$BuNO_2$ with both polysilanes led to the appearance of the spectrum of *t*-$Bu_2NO^•$ only, while with $MeNO_2$ and $(Me_3Si)_4Si$ a weak spectrum of $MeN(\dot{O})OSi(SiMe_3)_3$ was observed. No EPR signals were detected when nitromethane was reacted with $Me_3SiSiMe_3$.

It seems therefore that also nitro derivatives can bring about homolytic displacements at the silicon atom of polysilanes. Nevertheless, despite their rather high electron affinities, nitro compounds appear to be less efficient than carbonyl derivatives in promoting this reaction, as can be inferred from the relatively low intensity of the EPR spectra of the resulting nitroxide radicals. This, perhaps, might be the result of a short lifetime of the triplet state of nitro compounds. Thermodynamic estimates of the free energy change for the electron-transfer reactions involving nitrobenzene (Table II) suggest that, at least for nitroarenes, the occurrence of this process cannot be ruled out.

Conclusions

We have shown that an S_H2 homolytic substitution reaction at the silicon atom of polysilanes can be brought about by carbonyl and nitro compounds photoexcited in their triplet state. This reaction may proceed either by direct displacement (route a or b of Scheme I) or via an electron-transfer process leading to the cleavage of the silicon–silicon bond (route c or d of Scheme I). With quinones, the latter mechanism seems most likely in view of the fact that $Me_3Si^•$ radicals are displaced from $(Me_3Si)_4Si$ along with $(Me_3Si)_3Si^•$ and is also consistent with thermodynamic estimates that predict this reaction to be exoergonic.

For benzophenone the available data appear less conclusive; in fact (i) no information about the mechanism can be obtained from EPR measurements, (ii) the thermodynamic calculations estimating the ET reaction to be thermoneutral are not incompatible with the ET process, and (iii) the lack of solvent dependence of the rate constant for the quenching of the triplet benzophenone seems to point against the involvement of electron transfer. In this respect the results are even more dubious for acetone since, while the ET reaction is estimated to be endoergonic, formation of radical adducts is only observed in polar solvents. Moreover, the EPR results for the photoreaction of neat acetone with $(Me_3Si)_4Si$ are hardly explainable without admitting the occurrence of electron transfer. It is, perhaps, possible that under these conditions the reactive species is singlet acetone, which is char-

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(23) Savéant, J. M. *Bull. Chim. Soc. Fr.* **1988**, 225.

(24) Kavarnos, G. J.; Turro, N. J. *Chem. Rev.* **1986**, *86*, 401.

(25) Mattay, J. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 825.

(26) Albisson, A.; Mousset, G.; Simonet, J. *C. R. Acad. Sci., Ser. C* **1971**, *272*, 646.

(27) House, H. O.; Koepsell, D. G.; Kampbell, W. J. *J. Org. Chem.* **1972**, *37*, 1003.

(28) Turro, N. J. *Modern Molecular Photochemistry*; Benjamin/Cummings: Menlo Park, CA, 1978.

acterized by an energy 0.3 eV higher than that of triplet acetone.

Experimental Section

Benzo[1,2-*b*;5,4-*b*′]dithiophene-4,5-dione[29] and 3,6-dimethylthieno-[3,2-*b*]thiophene-2,5-dione[30] were obtained as described in the literature. Tetrakis(trimethylsilyl)silane and tris(trimethylsilyl)silane were prepared by reaction of trichlorosilane with trimethylchlorosilane[31] and were purified by distillation. All other chemicals were commercially available and used as purchased unless otherwise specified.

Phosphorescence Lifetime Measurements. The commercial silanes and benzene were of high purity and were therefore used as received. Benzophenone was recrystallized three times from ethanol. All the solutions were freshly prepared and sealed under vacuum after repeated freeze–pump–thaw cycles in a 1-cm fluorescence cell. The concentration of benzophenone was adjusted in all the experiments to ca. 2.0×10^{-3} M. The actual concentrations of the highly volatile tetramethylsilane (TMS) were determined by careful NMR integrations of the peaks due to TMS and benzene of portions of the solutions used for the phosphorescence experiments.

Phosphorescence lifetime measurements were carried out by using a N_2 laser (Lambda Physik M100A, $\lambda_{exc} = 337.1$ nm, fwhm ca. 4.0 ns, peak power 1 MW) as exciting source. The light emitted after the laser pulse was detected at right angle with respect to the exciting beam. The sample emission was filtered by a 5-cm cell filled with chlorine at a pressure of 2 atm and a cutoff filter at 400 nm and then collected by a Bausch and Lomb high-intensity monochromator centered at 450 nm. The transient signals monitored by an R955 Hamamatsu photomultiplier were stored by an R7912 transient digitizer equipped with a 7A26 vertical amplifier or by a Tektronix 468 digital storage oscilloscope interfaced to a PDP 11/23 microcomputer. Data reduction and treatment were carried out by a standard computer program, and the obtained curves fitted a monoexponential decay. Lifetime values (τ) used for the k_q determination were obtained by averaging data of three independent runs. The scattering in the τ values was ±5%. Quenching rate constants were determined from Stern–Volmer plots of the emission lifetimes. All the experiments were performed at room temperature (ca. 293 K).

EPR Measurements. EPR spectra were recorded with a Bruker ER 200D spectrometer equipped with standard devices for field calibration, *g* factor determination, and temperature control. Radicals were generated by photolysis of nitrogen-purged benzene or *tert*-butylbenzene solutions containing the appropriate triplet precursor and a silane. Typical concentrations of the samples were ca. 0.1 M carbonyl or nitro compound, 0.1–0.2 M $(Me_3Si)_4Si$ or metal hydride, and 0.5–1 M $Me_3SiSiMe_3$ or Me_4Si.

The light from the photolysis source, a 1-kW high-pressure mercury lamp focused within the EPR cavity, was used unfiltered. The EPR spectra were usually recorded at room temperature unless otherwise specified. The silyl adducts with benzophenone or other aromatic ketones afforded stronger spectra at higher temperatures due to the shifting to the left of the radical–dimer equilibrium.[32] High-quality spectra of these radicals were obtained from solutions irradiated for several minutes at room temperature and then heated in the dark at 370–390 K.

Electrochemistry. All electrochemical measurements were made in acetonitrile used as received, utilizing 0.1 M $(C_2H_5)_4NBF_4$ (TEATBF) as supporting electrolyte. Experiments were performed at 25 ± 0.1 °C, unless otherwise stated, by using a conventional three-electrode cell. For temperatures above 0 °C, a saturated calomel electrode (SCE), separated from the test solution by a 0.1 M TEATBF solution in ACN, sandwiched between two fritted disks, was used as reference electrode and all potentials are referred to it. For temperatures below 0 °C a silver quasi-reference electrode was used instead of SCE. Mercury and platinum electrodes, respectively, were used as working electrodes in the case of ketones and of silanes.

Polarographic, cyclic voltammetric, and controlled-potential coulometric experiments were carried out with an AMEL 552 potentiostat, a 568 programmable function generator, a 731 integrator, an 836 *x*/*y* recorder, and a Nicolet 3091 digital oscilloscope. The minimization of the effect of uncompensated resistance in cyclic voltammetry was achieved with a positive-feedback network of the potentiostat.

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[29] McDowell, D. W. H.; Wisowaty, J. C. *J. Org. Chem.* **1972**, *37*, 1712.

[30] Martelli, G.; Testaferri, L.; Tiecco, M.; Zanirato, P. *J. Org. Chem.* **1975**, *40*, 3384.

[31] Burger, H.; Kilian, W. *J. Organomet. Chem.* **1969**, *18*, 299.

[32] Ziebarth, M.; Neumann, W. P. *Liebigs Ann. Chem.* **1975**, 2279.