

## Adducts of Group 4B Organometallic Radicals with Quinones and Aromatic Ketones: an Electron Resonance Investigation

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The e.s.r. spectra of free radicals obtained by addition of silyl, germyl, and stannyl radicals to acenaphthoquinone, 9,10-phenanthroquinone, a number of *para*-quinones, benzophenone, and fluorenone have been investigated over a range of temperatures. A number of the adducts exhibit line-width alternation in their e.s.r. spectra. Activation parameters are reported for intramolecular migration of triphenylgermyl, tri-*n*-butylgermyl, and tri-*n*-butylstannyl groups between the two oxygen atoms of acenaphthoquinone. This is the first measurement of an activation barrier for an adduct of a tin-centred radical.

In a recent communication<sup>1</sup> we have described temperature-dependent variations in the e.s.r. spectra of adducts of silyl and germyl radicals with benzil. The nature of the linewidth variations, which were attributed to migration of the organometallic moiety between the two carbonyl groups, is similar to the well documented effects of intramolecular cation transfer in radical ion-pairs. The interpretation of results for  $\alpha$ -diketones such as benzyl and biacetyl is complicated by the possibility of *cis-trans* isomerism; we have therefore extended our investigations to acenaphthoquinone and 9,10-phenan-

throquinone which have the carbonyl groups in a fixed conformation.

Earlier attempts to prepare radical adducts of these *ortho*-quinones were unsuccessful,<sup>2</sup> probably because of their limited solubility in di-*t*-butyl peroxide employed as an initiator in the photolytic production of the organometallic radicals. However, we have found that excellent spectra of the adduct radicals can be produced by simply melting a mixture of the *ortho*-quinone with the appropriate silane, germane, or ditin compound. A similar method was used to prepare the triphenylsilyl

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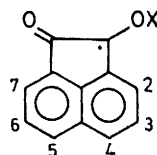
<sup>1</sup> A. Alberti and A. Hudson, *Chem. Phys. Letters*, 1977, **48**, 331.

<sup>2</sup> N. P. C. Simmons, B.Sc. by Thesis dissertation, University of Sussex, 1975.

adduct of benzil and we refer to our previous work<sup>1</sup> for details of the experimental procedure. We also report the reactions of silyl, germyl, and stannyl radicals with 9,10-anthraquinone, 1,4-naphthoquinone, *p*-benzoquinone, toluquinone, 2,5-di-*t*-butyl-*p*-benzoquinone, benzophenone, and fluorenone.

## RESULTS

**Acenaphthoquinone.**—The e.s.r. spectrum obtained from a melt of triphenylsilane and acenaphthoquinone in the range 200–250 °C consisted of a triplet of doublets of triplets.



(1)

We assign it to the adduct (I; X = SiPh<sub>3</sub>) with the coupling constants in Table 1. Essentially identical spectra

TABLE 1  
Hyperfine coupling constants (G) for adducts with acenaphthoquinone

MR <sub>3</sub>	<i>a</i> <sub>2</sub>	<i>a</i> <sub>3</sub>	<i>a</i> <sub>4</sub>	<i>a</i> <sub>5</sub>	<i>a</i> <sub>6</sub>	<i>a</i> <sub>7</sub>
SiPh <sub>3</sub>	4.00	1.02	4.00	0.22	0.00	0.22
GeBu <sup>n</sup> <sub>3</sub> (i) *	3.32	0.80	3.20	0.18	0.20	0.18
(ii)	1.84	0.50	1.77	1.77	0.50	1.84
GePh <sub>3</sub> (i)	3.53	0.86	3.34	0.18	0.19	0.18
(ii)	1.92	0.55	1.82	1.82	0.55	1.92
SnMe <sub>3</sub>	1.47	0.42	1.55	1.55	0.42	1.47
					( <i>a</i> <sup>117,119</sup> Sn = 3.12)	
SnBu <sup>n</sup> <sub>3</sub> (i)	2.57	0.60	2.49	0.37	0.19	0.50
(ii)	1.47	0.42	1.55	1.55	0.42	1.47
SnBu <sup>n</sup> <sub>3</sub> † (i)	2.18	0.52	2.02	0.35	0.10	0.45
(ii)	1.36	0.36	1.44	1.44	0.36	1.36
SnPh <sub>3</sub>	1.42	0.40	1.60	1.60	0.40	1.42

\* (i) Slow exchange, and (ii) fast exchange. † In THF-HMPMA (1 : 1).

were obtained with a number of other silanes. Our assignment of the coupling constants is supported by McLachlan spin-density calculations although the overall agreement with experiment is not particularly good. Fraenkel and Dehl<sup>3</sup> experienced similar difficulties in their study of the acenaphthoquinone radical anion.

No temperature dependence was apparent in the spectra of the silyl adducts, even at 250 °C, but a marked alternation in linewidths was apparent when germanium was substituted for silicon. The tri-*n*-butylgermyl adduct was studied in the range 150–256 °C and the triphenylgermyl adduct in the range 60–260 °C. At the lowest temperatures the spectra were similar in appearance to those of the silicon adducts although with smaller coupling constants. However, at elevated temperatures the spectra tended towards a quintet of triplets with the *m*<sub>l</sub> = ±1 lines so broadened as to be almost undetectable. This behaviour is consistent with an intramolecular migration of the germyl group between the two oxygen atoms. It proved possible to simulate the spectra using the modified Bloch equations and activation parameters for both germanium radicals are given in Table 2.

\* Hexametapol = hexamethylphosphoramide.

<sup>3</sup> R. Dehl and G. K. Frankel, *J. Chem. Phys.*, 1963, **39**, 1793.

The high-temperature spectra observed on addition of trimethyl-, tri-*n*-butyl, and triphenyl-stannyl to acenaphthoquinone were different from those obtained with silicon

TABLE 2

Kinetic parameters for intramolecular exchange of germyl and stannyl groups in adducts with acenaphthoquinone

MR <sub>3</sub>	<i>E</i> <sub>a</sub> / kJ mol <sup>-1</sup>	log <i>A</i>	$\Delta H^\ddagger$ / kJ mol <sup>-1</sup>	$\Delta S^\ddagger$ / J mol <sup>-1</sup> K <sup>-1</sup>
GeBu <sup>n</sup> <sub>3</sub>	40.4	11.1	36.3	-44.8
GePh <sub>3</sub>	32.6	11.1	28.6	-44.4
SnBu <sup>n</sup> <sub>3</sub> <sup>a</sup>	31.9	14.0	29.4	15.8
SnBu <sup>n</sup> <sub>3</sub> <sup>b</sup>	38.1	14.5	35.3	24.4

<sup>a</sup> In THF. <sup>b</sup> In THF-HMPMA (10 : 1).

or germanium; they are similar to the radical anion-alkali metal ion-pairs reported by Warhurst and Wilde.<sup>4</sup> The

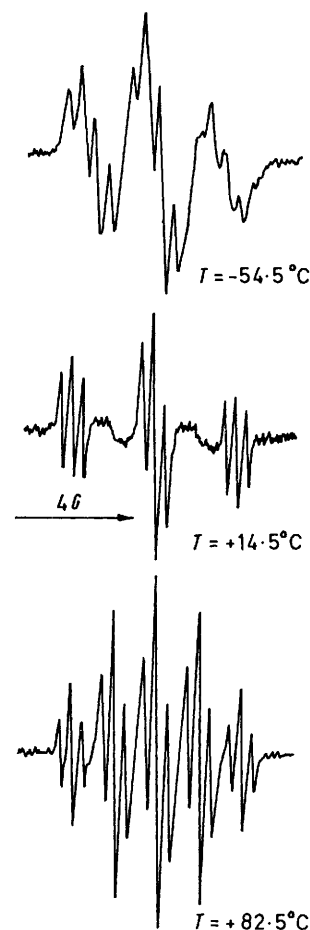


FIGURE 1 The e.s.r. spectrum of the acenaphthoquinone adduct with tri-*n*-butylstannyl radicals

spin distribution is consistent with the full molecular symmetry and there is no hint of linewidth alternation. The spectra obtained from the three tin compounds were similar apart from the <sup>117</sup>Sn and <sup>119</sup>Sn hyperfine satellites which were only observed for the methyl compound.

No linewidth variations were apparent in the high temperature melts and in an attempt to obtain spectra at lower temperatures we carried out measurements on the butyl and phenyl compounds in tetrahydrofuran (THF) and in a 10 : 1 mixture of THF and hexametapol\* (HMPMA). We were

<sup>4</sup> E. Warhurst and A. M. Wilde, *Trans. Faraday Soc.*, 1969, **65**, 1413.

then able to observe linewidth alternation, and, in the case of the tri-*n*-butylstannyl adduct, to obtain activation parameters (Table 2) in both solvent mixtures. The temperature dependence of the e.s.r. spectrum of the acenaphthoquinone-tri-*n*-butylstannyl adduct is shown in Figure 1. Line broadening was also observed in the triphenylstannyl adduct but we were unable to reach the slow exchange limit and it was not possible to perform a computer simulation. We deduce however that the barrier is lower for the triphenylstannyl adduct than for tri-*n*-butylstannyl. Lower barriers were found for the triphenylsilyl and triphenylgermyl adducts of benzil compared with trialkylsilyl and trialkylgermyl compounds.

**9,10-Phenanthroquinone.**—This compound underwent a thermal reaction with triphenylsilane in the range 50–80 °C to give a well resolved e.s.r. spectrum (Figure 2) which

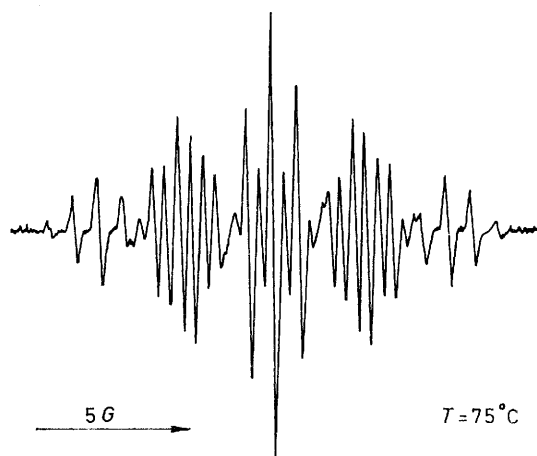


FIGURE 2 The adduct formed by triphenylsilyl radicals and 9,10-phenanthroquinone

could be analysed in terms of interaction with two sets of two equivalent protons and a small coupling to four equivalent protons (Table 3). A similar spectrum was obtained over the range 0–80 °C by photolysing a solution of the reactants in benzene containing some di-*t*-butyl peroxide; no linewidth alternation was apparent down to 0 °C.

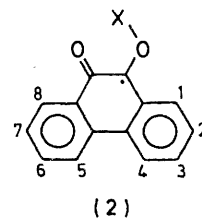
The e.s.r. spectrum of the triphenylgermane adduct (2; X = GePh<sub>3</sub>) studied in the melt (80–160 °C) and in hexane containing a little di-*t*-butyl peroxide (–60 to 70 °C), showed marked differences from the triphenylsilane adduct. Firstly the hyperfine couplings were much smaller and secondly strong linewidth alternation was apparent as the temperature was varied. However, the system was still in the intermediate exchange region at –60 °C and it was not possible to obtain Arrhenius parameters. McLachlan spin-density calculations assign the largest triplet splitting to a time average of positions 1 and 8.

In contrast the tri-*n*-butylstannyl adduct studied either by mixing the reactants (40–100 °C) or in hexane (–40 to 100 °C) showed no temperature dependence. The signals were considerably enhanced by a short period of u.v. irradiation and <sup>117</sup>Sn and <sup>119</sup>Sn satellites were readily detectable. Triphenylstannyl radicals gave similar results but with a smaller metal hyperfine interaction. Semi-

<sup>5</sup> A. Hudson, R. A. Jackson, and N. P. C. Simmons, *J.C.S. Perkin II*, 1977, 1633.

<sup>6</sup> J. Cooper, A. Hudson, and R. A. Jackson, *J.C.S. Perkin II*, 1973, 1933.

empirical m.o. calculations suggest that in this case the largest coupling arises from protons 3 and 6.



**para-Quinones.**—The results of our experiments with 9,10-anthraquinone, 1,4-naphthoquinone, and three *p*-benzoquinones are summarised in Table 3. The general features are well exemplified by the 9,10-anthraquinone adducts. Unsymmetrical species are observed for all the Group 4B elements with no evidence to suggest migration of the organometallic group between the two oxygen atoms, even though it was possible to record some of the spectra at temperatures as high as 240 °C. Delocalisation of the unpaired electron, as evidenced by the proton hyperfine couplings, decreases in the order Sn < Ge < Si in agreement with earlier work.<sup>5,6</sup> The spin distribution is close to that found in the well known hydrogen atom adducts of the quinones. The coupling constants for a number of these radicals which are formed on photolysis of the quinone in a hydrogen atom donating solvent such as isopropyl alcohol, are included in Table 3. Only the H atom adduct was observed when we attempted to add Ph<sub>3</sub>Si radicals to *p*-benzoquinone. Usual behaviour was also apparent in the reactions of hexabutyliditin with *p*-benzoquinone and 1,4-naphthoquinone.

In general a superposition of two spectra was obtained. Below about 60 °C the e.s.r. spectra were mainly attributable to the radical anion whereas at higher temperatures the main species was an unsymmetrical adduct. The addition of hexametapol to the system gave cleaner spectra of the adducts. In the *p*-benzoquinone-hexabutyliditin system the superposition of the quintet spectrum of the semiquinone and a triplet with twice the hyperfine coupling gives rise to an unusual pattern of line intensities which in earlier work<sup>6</sup> was taken as an indication of linewidth alternation. However, the higher temperatures used in the present work rule out the possibility that the apparent linewidth variations were due to an intramolecular exchange of the SnBu<sub>3</sub> group. The radical anion might arise from decomposition of the adduct or by direct electron transfer from the stannyl radical to the quinone.

**Aromatic Ketones.**—Benzophenone and fluorenone gave strong, well-resolved spectra of the expected adducts with silyl, germyl, and stannyl radicals. The triphenylsilyl adduct of benzophenone formed in a melt of the ketone and the silane has been reported previously.<sup>7</sup> The behaviour of these systems is similar to that already discussed for the *para*-quinones with a reduction in splitting on going from Si to Sn and a spin distribution close to that found<sup>8</sup> in the H atom adducts.

#### DISCUSSION

The interpretation of our results for acenaphthoquinone is straightforward; this compound behaves very

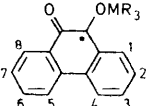
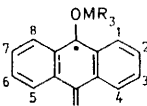
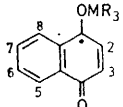
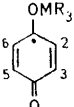
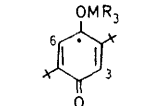
<sup>7</sup> A. R. McIntosh and J. K. S. Wan, *Canad. J. Chem.*, 1971, **49**, 817; *Mol. Phys.*, 1971, **22**, 183.

<sup>8</sup> R. Wilson, *J. Chem. Soc. (B)*, 1968, 84, 1581; R. S. Davidson and R. Wilson, *ibid.*, 1970, 71.

much like benzil. The e.s.r. spectrum obtained with silyl radicals is attributed to an unsymmetrical adduct (I), whereas with germyl and stannyl radicals we observe a dynamic equilibrium between equivalent conformers. The activation energies for migration of the organo-metallic group are higher for acenaphthoquinone than

with a low barrier to interconversion. Previous work with  $\alpha$ -diketones<sup>6,9</sup> has not distinguished between these possibilities because the e.s.r. spectra were only observed in the fast exchange region. The higher barriers found for acenaphthoquinone have enabled us to establish for the first time that stannyl adducts of  $\alpha$ -diketones can

TABLE 3

MR <sub>3</sub>	<i>a</i> <sub>1</sub>	<i>a</i> <sub>2</sub>	<i>a</i> <sub>3</sub>	<i>a</i> <sub>4</sub>	<i>a</i> <sub>5</sub>	<i>a</i> <sub>6</sub>	<i>a</i> <sub>7</sub>	<i>a</i> <sub>8</sub>	<i>a</i> <sub>M</sub>
	Ph <sub>3</sub> Si	3.06	0.84	2.69	0.84	0.84	2.69	0.84	3.06
	Bz <sub>3</sub> Si	3.07	0.90	2.69	0.90	0.90	2.69	0.90	3.07
	Hex <sub>3</sub> Si	3.10	0.90	2.70	0.90	0.90	2.70	0.90	3.10
	Ph <sub>3</sub> Ge	1.86	0.41	1.79	0.41	0.41	1.79	0.41	1.86
	But <sub>3</sub> Sn	1.68	0.34	1.76	0.34	0.34	1.76	0.34	1.68
	Ph <sub>3</sub> Sn	1.58	0.35	1.62	0.35	0.35	1.62	0.35	1.58
	Ph <sub>3</sub> Si	2.86	0.88	3.21	0.88	0.88	3.21	0.88	2.86
	Ph <sub>3</sub> Ge	2.70	0.86	3.10	0.86	0.86	3.10	0.86	2.70
	But <sub>3</sub> Sn	2.50	0.82	3.00	0.82	0.82	3.00	0.82	2.50
	Ph <sub>3</sub> Sn	2.34	0.74	2.68	0.74	0.74	2.68	0.74	2.34
	Ph <sub>3</sub> Si		1.52	8.45		0.64	2.14	0.64	2.14
	Ph <sub>3</sub> Ge		1.16	8.05		0.51	1.86	0.54	1.98
	H*		1.59	7.20		0.20	1.78	0.20	1.78
	But <sub>3</sub> Sn †		0.25	6.59		0.25	1.30	0.25	1.58
	But <sub>3</sub> Sn ‡		3.37	3.37		0.61	0.61	0.61	0.61
	Ph <sub>3</sub> Si §		0.70	5.75		5.75	0.70		1.55 (H)
	Ph <sub>3</sub> Ge		0.88	5.85		5.85	0.88		
	H		0.85	5.64		5.64	0.85		1.43
	But <sub>3</sub> Sn ‡		2.38	2.38		2.38	2.38		(T ≤ 60 °C)
	But <sub>3</sub> Sn			4.90		4.90			(T ≥ 80 °C)
	But <sub>3</sub> Sn †		0.28	4.55		4.55	0.28		(T > 80 °C)
	Ph <sub>3</sub> Si		1.11	6.20		6.20	1.55		
	Ph <sub>3</sub> Ge		0.68	(CH <sub>3</sub> ) 5.79		5.79	1.20		
	H			(CH <sub>3</sub> ) 5.15		5.15	0.68		1.77
	But <sub>3</sub> Sn †			(CH <sub>3</sub> ) 4.20		4.73	0.48		
	Ph <sub>3</sub> Si			(CH <sub>3</sub> ) 4.68			1.12		
	Ph <sub>3</sub> Ge			4.38			0.85		
	But <sub>3</sub> Sn			3.55					
	Ph <sub>3</sub> Si	3.53	0.80	3.81	0.80	0.80	3.81	0.80	3.53
	Ph <sub>3</sub> Ge	3.40	0.80	3.72	0.80	0.80	3.72	0.80	3.40
	H	3.26	0.74	3.66	0.74	0.74	3.66	0.74	3.26
	But <sub>3</sub> Sn	3.21	0.76	3.65	0.76	0.76	3.65	0.76	3.21
		( <i>a</i> <sub>o</sub> , 4 H)		( <i>a</i> <sub>m</sub> , 4 H)		( <i>a</i> <sub>p</sub> , 2 H)			
	Ph <sub>3</sub> Si		3.20		1.25		3.55		
	Ph <sub>3</sub> Ge		3.16		1.22		3.55		
	But <sub>3</sub> Sn		3.12		1.20		3.55		
	H		3.21		1.23		3.64		2.91

\* In isopropyl alcohol. † In THF-HMPTA (10 : 1). ‡ Radical anion. § Hydrogen adduct.

for benzil (32.6 for GePh<sub>3</sub> and 40.4 GeBu<sub>3</sub> compared with 15.5 and 29.2 kJ mol<sup>-1</sup> respectively), and this accounts for our failure to observe line broadening in the silyl adducts. In the case of benzil the silyl adducts had activation energies some 10 kJ mol<sup>-1</sup> higher than the corresponding germyl species.

As mentioned above, the stannyl radical adducts exhibit e.s.r. spectra which at high temperatures resemble those reported<sup>4</sup> for alkali metal ion-pairs of acenaphthoquinone radical anion. The spectra could arise from a symmetrical structure with the trialkyltin group chelated between the two oxygen atoms, or from rapid exchange between unsymmetrical structures

exist as rapidly interconverting species in which the organometallic group oscillates between the two oxygen atoms.

The behaviour of acenaphthoquinone as a  $\alpha$ -diketone is supported by its crystal structure;<sup>10</sup> the value of 153 pm found for the bond joining the two carbonyl groups is typical of that found for  $\alpha$ -diketones like biacetyl. The similarity between the results for benzil and acenaphthoquinone suggests that the stannyl adducts of benzil have a *cis*-conformation. One major difference between the

<sup>9</sup> B. Schroeder, W. P. Neumann, and H. Hillgarter, *Chem. Ber.*, 1974, **107**, 3494.

<sup>10</sup> T. C. W. Mak and J. Trotter, *Acta Cryst.*, 1963, **16**, 811.

results for benzil and acenaphthoquinone lies in the magnitude of the tin satellite splitting from  $^{117}\text{Sn}$  and  $^{119}\text{Sn}$  in natural abundance. For benzil, satellites were detectable with  $\text{SnMe}_3$  \* (8.49, 8.85 G),  $\text{SnBu}^n_3$  (8.8, 9.2 G), and  $\text{SnPh}_3$  (5.21, 5.46 G) but for acenaphthoquinone only  $\text{SnMe}_3$  gave a measurable coupling (3.1 G).

We attribute this sensitivity of the tin coupling to conformational changes induced by variation in size of the substituent groups and by different degrees of steric hindrance around the carbonyl groups in the various  $\alpha$ -diketones. Like all  $\beta$ -couplings the tin splittings are expected to be sensitive to out of plane rotations, in this case about the C-O bond.

A direct comparison of the activation energies for  $\text{GeR}_3$  and  $\text{SnR}_3$  adducts (Table 2) is complicated by the presence of solvent effects. Whereas the germyl results were obtained in melts of the quinone and the germane, it was necessary to add a solvent in order to reach the lower temperatures necessary for observation of the slow exchange limit with the tin adducts.

The absolute values of the activation energies quoted in Table 2 should be treated with circumspection. Although excellent linear Arrhenius plots with low standard deviations ( $<1 \text{ kJ mol}^{-1}$  for  $E_a$ ) were obtained for all four determinations, the high  $\log A$  values for the Sn adducts suggest larger absolute errors. The most probable source of error lies in the measurement of temperature, although the latter was measured <sup>1</sup> before and after recording each spectrum.

The large solvent effect on the coupling constants and activation energy found with hexamethylphosphoramide was a chance observation made during a search for a solvent system in which it was possible to reach the slow exchange limit. The marked effects of HMPTA on our systems are worthy of further investigation.

The interaction of germyl and stannyl radicals with 9,10-phenanthroquinone follows the pattern found for acenaphthoquinone. The observation of line broadening with  $\text{GePh}_3$  establishes the fluxional nature of the germyl adduct; the similar hyperfine splittings of the stannyl adducts indicate analogous structures. The

\* The hyperfine coupling constants for the  $\text{SnMe}_3$  adducts of benzil reported by Schroeder *et al.*<sup>9</sup> are incorrect. We find  $a_o = a_p = 1.1$ ,  $a_m = 0.47$ ,  $a(^{117}\text{Sn}) = 8.49$ ,  $a(^{119}\text{Sn}) = 8.85 \text{ G}$ .

activation energies for migration of the  $\text{MR}_3$  group are lower than in acenaphthoquinone, possibly because the oxygen atoms are closer together. The nature of the species obtained with silyl radicals poses more of a problem. The e.s.r. spectrum (Figure 2) corresponds to a symmetrical spin distribution in the aromatic moiety with much larger coupling constants than the Ge and Sn adducts. This species is thus out of line with all the other systems reported in Table 3. The available evidence is consistent with a symmetrical structure in which a five-co-ordinate silicon atom bridges both oxygen atoms. This would involve a change from the double minimum found in the potential energy surfaces for the other adducts to a single minimum. In the absence of observable line broadening it is not of course possible to rule out fast exchange with a low barrier to interconversion but the change in hyperfine couplings suggests a significant difference in structure compared with the germyl adduct.

*Conclusion.*—By extending the range of compounds studied and by recording e.s.r. spectra over a wider range of temperatures, we have been able to produce a more coherent picture of the interaction of Group 4B radicals with  $\alpha$ -diketones and quinones than hitherto. The variation in behaviour between silicon and tin is attributable to decreasing activation energies for intramolecular exchange of the organometallic group rather than to a different reaction pathway as at one time seemed possible. This trend is consistent with the known decrease in strength of the metal-oxygen bond on descending the group.<sup>11</sup> The tendency for migration also depends on the distance between the two oxygen atoms (no exchange was found in *para*-quinones) and on the ability of the rest of the system to delocalise the unpaired electron (silyl and germyl groups migrate in benzil but not in biacetyl).

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<sup>11</sup> M. F. Lappert, J. B. Pedley, J. Simpson, and T. R. Spalding, *J. Organometallic Chem.*, 1971, **29**, 195.