Group IVB Organometal Derivatives of Pyridine. Part II.[1] The Reaction with Bis(trimethylsilyl)mercury; Organometal-substituted *N*-Trimethylsilylpyridyl Free Radicals [2]

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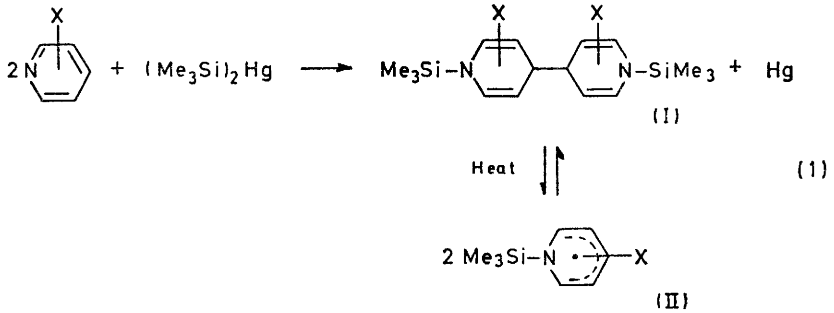
Bis(trimethylsilyl)mercury reacts with 3- and 4-trialkylmetal derivatives of pyridine (the metal can be silicon, germanium, tin, or lead) to give organometal-substituted *NN'*-bis(trimethylsilyl)tetrahydro-4,4'- or -2,2'-bipyridyls (I); no reaction occurs with 2-trialkylmetal derivatives of pyridine. The mechanism of the reaction is discussed. The bipyridyls (I) are either partially dissociated at room temperature or dissociate on warming to give stable pyridyl free radicals (II), the e.s.r. parameters of which are presented and discussed. The values of the metal hyperfine-splitting constants indicate that the trialkylmetal group stabilises the radicals merely by virtue of its bulk. No reaction was observed between the metallopyridines and bis(trimethylgermyl)mercury.

Reaction of bis(trimethylsilyl)mercury with pyridine and derivatives thereof [3] gives *NN'*-bis(trimethylsilyl)-tetrahydro-4,4'-bipyridyls (I); when warmed these dissociate reversibly to give pyridyl radicals (II):



(X = H, 2-Me, 3-Me, 4-Me, 3-CN, 4-CN, 3-CO_2Me, 4-CO_2Me, 4-COMe)

However, at the beginning of the work reported here the mechanism of the reaction was still uncertain. We therefore decided to use the trialkylmetal-substituted pyridines in order to attempt to cast further light on the reaction mechanism. We also wished to study the influence of the trialkylmetal substituent on the stability of the *N*-silylpyridyl radicals of type (II), using the metal hyperfine-splitting constants of the spin-$\frac{1}{2}$ isotopes (^{29}Si, ^{73}Ge, ^{117}Sn, ^{119}Sn, ^{207}Pb) to measure the amount of spin delocalisation on to the metal centre.

RESULTS AND DISCUSSION

The reactions of $(Me_3Si)_2Hg$ with 14 pyridine derivatives (1)—(14) were studied; Table 1 shows the compounds studied and the reaction times and conditions. Compounds (1)—(4) showed no reaction, either when heated at 80 °C in benzene or on photolysis of the reaction mixture in benzene with a daylight lamp (Philips HPL 125). Compounds (5)—(13) reacted (in some cases exothermically) according to equation (1), where X = MR_3; in each case the corresponding products of type (I) and (I') were observed and characterised. The reaction of (14) with $(Me_3Si)_2Hg$ was exothermic, but did not lead to the required products; even when the reaction was carried out at –20 °C and followed by ^1H n.m.r. spectroscopy, compounds of type (I) and (I') were not observed.

The reactions were carried out as follows: the pyridine derivative was added to a benzene solution of $(Me_3Si)_2Hg$ (molar ratio 2 : 1). In some cases (see Table 1) an exothermic reaction occurred, in others the reaction mixture was photolysed with a daylight lamp until no further mercury separated. It now seems certain that under these latter reaction conditions free trimethylsilyl radicals can be produced; however, for reasons outlined below, it seems unlikely that such free radicals are involved in the reactions studied in this work. Becker and

TABLE 1

Reaction of $(Me_3Si)_2Hg$ with compounds RC_5H_4N: reaction conditions, type, and melting point of product

R (Compound no.)	Amount reacted (mmol)	Reaction t/h (θ_c/°C)	Product type	M.p. (θ_c/°C)
3-Me_3Si (5)	4.5	2.5 (30) [a]	(I)	Oil
3-Me_3Ge (6)	5.0	4 (30) [a]	(I)	Oil
3-Me_3Sn (7)	5.0	3 (30) [a]	(I)	*b*
3-Bu_3Sn (8)	5.0	3 (30) [a]	(I)	Oil
3-Bu_3Pb (9)	10.0	3 (30) [a]	(I)	Oil
4-Me_3C (10)	20.0	12 (30) [a]	(I')	83—88
4-Me_3Si (11)	5.1	2 (30) [a]	(I')	88—94
4-Me_3Ge (12)	3.6	1 (30) [a]	(I')	85—93
4-Me_3Sn (13)	3.0	Exotherm.	(I') [c]	*d*
4-Bu_3Pb(14)	2.0	Exotherm.		

[a] With irradiation (daylight lamp). [b] (±)-Form m.p. 59—65 °C (recryst. from hexane), *meso*-form oil. [c] Plus other products. [d] Product not isolated.

Compounds (1)—(4) as follows: R = 2-Me_3Si (1), 2-Me_3Ge (2), 2-Me_3Sn (3), 2-Bu_3Pb (4).

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[1] Part I, T. N. Mitchell, *Org. Magnetic Resonance*, 1975, **7**, 610.

[2] T. N. Mitchell, Abstracts First International Conference on the Organic Chemistry of Germanium, Tin and Lead, Marseilles, 1974.

[3] (*a*) H. P. Becker and W. P. Neumann, *J. Organometallic Chem.*, 1972, **37**, 57; (*b*) R. Kordowski, Diplomarbeit Universität Dortmund 1972; (*c*) B. Schroeder, W. P. Neumann, J. Hollaender, and H. P. Becker, *Angew. Chem.*, 1972, **84**, 894; (*d*) S. V. Ponomarev, H. P. Becker, and W. P. Neumann, *Annalen*, 1975, 1895. (*e*) K. Reuter and W. P. Neumann, unpublished data.

Neumann[3a] carried out their reactions between 20 and 90 °C; under these conditions free trimethylsilyl radicals are certainly not produced, but the mechanism proposed by these authors now seems less probable. Schroeder[4] observed that 2,6-dimethylpyridine does not react with $(Me_3Si)_2Hg$; this suggests that steric factors play a role in determining the reactivity of the pyridine derivative. The failure of compounds (1)—(4) to react lends support to this suggestion, and contrasts with their ability to form weak complexes with trimethyltin bromide in solution, as evidenced by the values of ^1J(Sn–C) and ^2J(Sn–CH_3). Though we have not made a systematic study of such complexes, Table 2 contains some coupling-constant values. These clearly show that complexes are formed in solution; the values are, as expected, higher in each case when the substituent is in the 3-position, since the steric hindrance is much lower than when a 2-substituent is present. 2,6-Dimethylpyridine does not form a complex with Me_3SnCl.[5] A trimethylsilyl radical is much less bulky than trimethyltin bromide, and should, therefore, be able readily to interact with the pyridine nitrogen even in compounds (1)—(4). Further pieces of evidence against a free-radical mechanism are firstly that the reactions of pyridine and its derivatives with $(Me_3Si)_2Hg$ are virtually quantitative[3a,4] and secondly that the velocity of the reaction is greatly increased when the basicity of the pyridine nitrogen is increased. Literature values show that compound (3) is much more basic than either (1) or (2),[6] and though we have as yet been unable to obtain pK_a values for the complete series of metal-substituted pyridines, ^{13}C n.m.r. data lend support to the suggestion that the $+I$ effect of the R_3M group increases in the series $Me_3Si < Me_3Ge < Me_3Sn < Bu_3Pb$.[1] The tetrahydrobipyridyls (I) obtained from 3-substituted pyridines contain two asymmetric carbon atoms, and can therefore exist in the (+)-, (−)-, and *meso*-forms. ^{1}H N.m.r. investigation of the reaction products from the reaction of $(Me_3Si)_2Hg$ with compounds (5)—(9) showed that the primary product of the reaction was in each case a 1 : 1 mixture of the (±)-(racemic) and *meso*-forms of (I). (Table 3 shows the ^{1}H n.m.r. data of the product mixtures.)

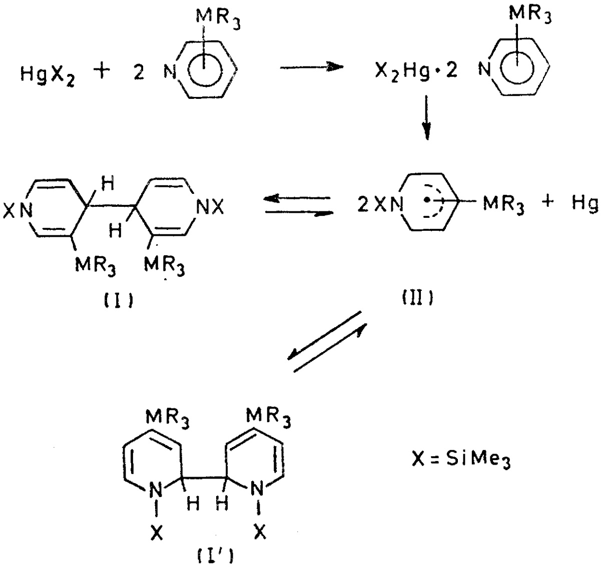
TABLE 2

Values of ^1J(Sn-C) and ^2J(Sn-CH_3) for trimethyltin bromide dissolved in various pyridine derivatives

Solvent	^1J(Sn–C) [a] Hz	^2J(Sn–CH_3) [b] Hz
	382	58.5
Pyridine	472 [c]	
2-Methylpyridine	451	61.0
3-Methylpyridine	502	68.0
2,6-Dimethylpyridine		58.5
2-Trimethylsilylpyridine		62.0
3-Trimethylsilylpyridine		68.0
2-Trimethylstannylpyridine	404	61.5
3-Trimethylstannylpyridine	476	68.0

[a] At *ca.* 45 °C. [b] At 37 °C. [c] For Me_3SnCl in pyridine. The solubility of Me_3SnBr in pyridine is too low to permit measurement.

When such a product is further photolysed or heated to 100—130 °C, the intensity of the resonances due to the racemic mixture decreases while the resonances due to the *meso*-form become stronger. Molecular models indicate that the *meso*-form is less hindered and, therefore, presumably thermodynamically more stable; it appears that in the course of the reaction radicals of type (II) are formed, the dimerisation of which produces a statistical product distribution. Becker[7] did not observe the formation of such a mixture when β-picoline reacted with $(Me_3Si)_2Hg$, apparently because the reaction temperature used was too high; photolysis of these reactants does however give the expected 1 : 1 (±)- and *meso*-product mixture. We wish tentatively to suggest the following scheme for the reaction of $(Me_3Si)_2Hg$ with pyridine and its derivatives:



It is well known that mercury can increase its co-ordination number to four, and Schaaf and Oliver[8] have shown that $(Me_3Si)_2Hg$ forms 1 : 1 and 1 : 2 complexes with trimethylsilyl-lithium. We suggest that the complex involves N→Hg co-ordination, and that 2,6-dimethylpyridine and compounds (1)—(4) cannot form such a complex. We cannot however exclude the possibility of N→Si co-ordination, and we can say little about the lifetime of the complex, which could merely be a transient one of the charge-transfer type; since we were unable to detect such a complex by means of ^{1}H n.m.r. spectroscopy, its lifetime must be relatively short.

Radicals of type (II) are theoretically capable of dimerisation *via* the 2-, 4-, and 6-position of the heterocyclic ring. When the trialkylmetal substituent is in the 3-position, only dimerisation *via* the 4-position is ob-

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[4] B. Schroeder, Dissertation Universität Dortmund 1973.

[5] T. L. Bolles and R. S. Drago, *J. Amer. Chem. Soc.*, 1966, **88**, 5730.

[6] D. G. Anderson, J. R. Chipperfield, and D. E. Webster, *J. Organometallic Chem.*, 1968, **12**, 323.

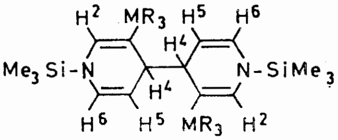
[7] H. P. Becker, Dissertation Universität Dortmund 1971.

[8] T. F. Schaaf and J. P. Oliver, *J. Amer. Chem. Soc.*, 1969, **91**, 4327.

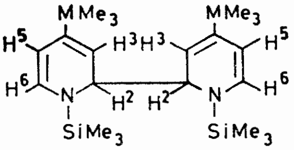
served; the product obtained from $(Me_3Si)_2Hg$ and 3-tributylplumbylpyridine is partially dissociated into free radicals at room temperature. When the trialkylmetal group is in the 4-position, only products (I′) which are dimerised *via* the 2-position were isolated; the reaction does not however proceed cleanly, the major product being formed in 70—80% yield. It can be obtained in a pure state by careful recrystallisation from acetone, and in each case [M = C, Si, or Ge: compounds (10)—(12)] melts over a range of several degrees, but at roughly the same temperature (see Table 1). E.s.r. spectroscopy shows that products (I′) are partially dissociated at, or slightly above, room temperature into radicals (II), since even 2,2′-dimerisation yields a sterically crowded product; this can also exist in (+)-, (−)-, or *meso*-forms, since the bridgehead carbon is asymmetric, but only one isomer was observed, which molecular models suggest to be the *meso*-isomer. The product mixture from (13) (4-trimethylstannylpyridine) also contains free radicals of type (II); however, the proton n.m.r. spectrum shows it to consist of several components, as yet unidentified apart from the tetrahydrobipyridyl, which are thermally labile, decomposing fairly rapidly at 75 °C in a concentrated benzene solution.

TABLE 3

Proton n.m.r. chemical shifts for organometal-substituted *NN′*-bis(trimethylsilyl)tetrahydro-4,4′- and -2,2′-dipyridyls



MR_3	(±) or meso-form	$\tau(H^2)$	$\tau(H^4)$	$\tau(H^5)$	$\tau(H^6)$	τ (MMe_3)	τ $(SiMe_3)$
CH_3	(±)	3.88	6.67	5.20	3.80	*a*	9.97
	meso		6.48				
$SiMe_3$	(±)	3.53	6.80	5.00	3.87	9.70	9.90
	meso		6.58			9.73	9.93
$GeMe_3$	(±)	3.69	6.75	5.07	3.80	9.79	9.93
	meso		6.55				9.94
$SnMe_3$	(±)	3.67 [b]	6.68	5.02	3.78	9.72 [c]	9.93
	meso		6.48			9.77 [c]	9.95
$PbBu_3$	(±)	3.75	6.68	5.01	3.85		9.87
	meso						9.93



MMe_3	$\tau(H^2)$	$\tau(H^3)$	$\tau(H^5)$	$\tau(H^6)$	τ (MMe_3)	τ $(SiMe_3)$
CMe_3	5.80	4.85	4.45	3.67	8.78	9.85
$SiMe_3$	5.77	4.45	4.38	3.63	9.78	9.88
$GeMe_3$	5.73	4.55	4.42	3.65	9.68	9.88

[a] $\tau(CH_3)$ 8.10 (±), 8.25 (*meso*). [b] $^2J(^{119}Sn{-}H)$ 56.0 Hz. [c] $^2J(^{119}Sn{-}H)$ 53.0 Hz. Spectra recorded using C_6D_6 as solvent; τ-values given are for infinite dilution.

Table 3 shows the ^1H n.m.r. chemical shifts of the bipyridyls (I) and (I′); these will be discussed in a forthcoming paper, which will include ^{13}C n.m.r. data which, we hope, will help to clarify the structures of the products from (14). It should be remembered that the heterocyclic rings in (I) and (I′) are flexible and not necessarily planar, and molecular models show that free rotation about the bond joining the rings is not possible. The ^1H n.m.r. splitting patterns of the bridgehead proton (H^4) are different in the (±)- and *meso*-forms. The small (1.5 Hz) additional doublet splitting in the H^4 resonance of the (±)-form is apparently not due to inter-ring coupling, since it would then correspond to a sterically improbable inter-proton dihedral angle of *ca.* 90°; it may be due to differences of ring geometry in the two forms.

Table 4 contains the e.s.r. parameters of the pyridyl free radicals (II); for comparison those of the corresponding picolinyls [3c,4] are included. It will be seen that the spin-density distribution in the *N*-trimethylsilyl-3-trialkylmetalpyridyl radicals (16)—(20) is basically similar to that in the corresponding picolinyl radical (15). Replacement of Me by Me_3Si causes an increase in all except the H^6 and nitrogen splitting constants, while variations of the attached metal cause appreciable changes in all the splitting constants. Variation of the alkyl groups attached to the metals causes almost no change in the spectra, however: the radicals obtained from (*a*) $(Me_3Si)_2Hg$ and 3-tributylstannyl-pyridine and (*b*) $(Et_3Si)_2Hg$ and 3-trimethylstannylpyridine are almost exactly identical with radical (17). No ^{29}Si coupling was observed in these radicals; the small values of the metal (Sn, Pb) splitting constants in radicals (18)—(20) show that the metal plays practically no electronic role in stabilising the radicals (16)—(20).

The e.s.r. parameters of the three *N*-trimethylsilyl-4-trialkylmetalpyridyl radicals studied [(23)—(25)], together with the corresponding derivative obtained from 4-t-butylpyridine and $(Me_3Si)_2Hg$ (22) are also contained in Table 4. These radicals are characterised by a higher value of a_N and a lower value of a_{H^3,H^5} than observed in the corresponding picolinyl radical (21). Radicals (22) and (23) show a small (0.25 G) coupling to the methyl protons of the 4-t-butyl and 4-trimethylsilyl group; the corresponding couplings in (24) and (25) were too small to be detected.

Selection of appropriate *Q*-values for π spin-density calculations was somewhat difficult. In the light of recent work [9,10] it seems that the *Q*-values used by Schroeder *et al.*[3c,4] (Q^H_{CH} −22.5 G, $Q^H_{CCH_3}$ 28 G, Q^N_{NSi} 32 G) cannot be applied to the *N*-silylpyridyl system. Rakowsky and Dohrmann [10] studied the closely related *N*-hydropyridyl and *N*-hydropicolinyl radicals, and calculated the following *Q*-values: Q^H_{CH} −27.7 G, $Q^H_{CCH_3}$ 31 G, $Q^N_{N(C_2H)}$ 9.6 G, and Q^N_{CN} 8.5 G. We did not have sufficient data to calculate $Q^N_{N(C_2H)}$ and Q^N_{CN} for our system; application of the above Q^H_{CH} and $Q^H_{CCH_3}$ values to the *N*-silyl-β- and -γ-picolinyls and use of a McConnell relation to calculate

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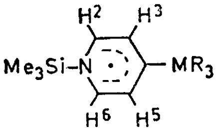
[9] H. Zeldes and R. Livingston, *J. Phys. Chem.*, 1972, **76**, 3348.

[10] Th. Rakowsky and J. K. Dohrmann, *Ber. Bunsengesellschaft Phys. Chem.*, 1975, **79**, 18.

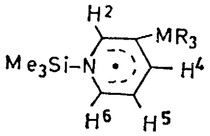
$Q^{\mathrm{N}}_{\mathrm{NSi}}$ produced values of 16.5 and 14.3 G respectively. However, since replacement of CH_3 in the *N*-silyl-β-picolinyl by Me_3Si causes an increase in almost all proton hyperfine-splitting constants (by up to 33%), $Q^{\mathrm{H}}_{\mathrm{CH}}$ may well be somewhat larger than −27.7 G for radicals (16)—(20); $Q^{\mathrm{N}}_{\mathrm{NSi}}$ is, however, probably not larger than 16.5 G in this series, and is of approximately this magnitude in radicals (22)—(25). The π-spin densities shown in Table 4 were [except for radical (21)] calculated using $Q^{\mathrm{H}}_{\mathrm{CH}}$ − 28 G, $Q^{\mathrm{N}}_{\mathrm{NSi}}$ 16.5 G.

TABLE 4

E.s.r. parameters of *N*-trimethylsilyl-3- and -4-trialkylmetalpyridyls; hyperfine splitting constants *a* in G and π-spin densities ρ



MR_3		H^2	H^4	H^5	H^6	N	M	*g*-Factor	θ_c/°C
CH_3 (15) *	*a*	6.52	11.03	1.23	5.90	4.16		2.004 0	118
	ρ	0.233	0.394	−0.044	0.211	0.252			
$SiMe_3$ (16)	*a*	6.92	12.00	1.64	5.72	4.15	‡		160
	ρ	0.247	0.428	−0.059	0.204	0.252			
$GeMe_3$ (17)	*a*	6.63	11.95	1.50	6.15	4.25	‡		140
	ρ	0.237	0.427	−0.054	0.220	0.258			
$SnMe_3$ (18)	*a*	6.30	12.00	1.45	6.30	4.25	8.50	2.004 2	100
	ρ	0.225	0.428	−0.051	0.225	0.258			
$SnBu_3$ (19)	*a*	6.29	12.00	1.43	6.32	4.25	8.50		120
	ρ	0.225	0.428	−0.051	0.226	0.258			
$PbBu_3$ (20)	*a*	6.28	12.00	1.30	6.50	4.32	12.00	2.004 4	100
	ρ	0.224	0.428	−0.046	0.323	0.262			



MR_3		H^2	H^3	H^5	H^6	N	CH_3	M	*g*-Factor	θ_c/°C
CH_3 (21) *	*a*	6.24	1.57	1.57	6.24	3.86	12.30		2.003 9	90
	ρ †	0.223	−0.056	−0.056	0.223	0.270				
CMe_3 (22)	*a*	6.50	1.52	1.52	6.50	4.10	0.25		2.003 5	100
	ρ	0.232	−0.054	−0.054	0.232	0.248				
$SiMe_3$ (23) §	*a*	6.00	1.03	1.03	6.00	4.30	0.25	8.90	2.003 3	40 ¶
	ρ	0.214	−0.037	−0.037	0.214	0.261				
$GeMe_3$ (24) §	*a*	6.15	0.95	0.95	6.15	4.30	‡	4.16	2.003 1	60
	ρ	0.220	−0.034	−0.034	0.220	0.261				
$SnMe_3$ (25) §	*a*	6.13	0.95	0.95	6.13	4.30	‡	72.0/ 75.25	2.002 7	60
	ρ	0.219	−0.034	−0.034	0.219	0.261				

* *a*- and *g*-Values from ref. 3*c*. † Calculated using $Q^{\mathrm{H}}_{\mathrm{CH}}$ −28 G, $Q^{\mathrm{N}}_{\mathrm{NSi}}$ 14.3 G. All other values calculated using $Q^{\mathrm{H}}_{\mathrm{CH}}$ −28 G, $Q^{\mathrm{N}}_{\mathrm{NSi}}$ 16.5 G. ‡ Not observed. § $a(^{29}Si{-}N)$ 8.90 G. ¶ Probe irradiated with high-pressure mercury lamp. Signal intensity decreased in 10 min by 50% on removing light source. For signs of splitting constants see ref. 10.

Radicals (23)—(25) show coupling with the spin-½ metal nuclei; the intensity of the ^{29}Si coupling in (23), together with the facts that (*a*) the satellites in (22) are very weak, and (*b*) small satellites with $a = 8.9$ G are visible in (24) and (25), suggest that the coupling with the ^{29}Si nuclei of the *N*-trimethylsilyl group is in each case 8.9 G. The metal couplings in the formally related radicals $CH_3\dot{C}HSiEt_3$ and $\cdot CH_2SnMe_3$ are 15.2 G[11] and 137 G[12] respectively; the smaller values ($a_{\mathrm{Sn\text{-}119}}$ 75.25 G) in radicals (23) and (25) are, however, not unexpected in view of the different geometry and the large spin delocalisation in the latter. The metal coupling constants in the corresponding $Me_3M\cdot$ free radicals are much larger: (23) a_{Si} 8.9 G, $Me_3Si\cdot$ 181 G;[13] (24) a_{Ge} 4.16 G, $Me_3Ge\cdot$ 84.7 G;[14] (25) $a_{\mathrm{Sn\text{-}119}}$ 75.25 G, $Me_3Sn\cdot$ 1 611 G.[15] In each case the quotient of the two a_{metal} values is 0.048 ± 0.001; this means that the π-spin density at the metal centres in radicals (23)—(25) is somewhat less than 0.048, which indicates that the 4-trimethylmetal substituents also stabilise the pyridyl radicals almost only by virtue of their bulk. The radical-dimer product mixtures are stable for periods of at least a year when stored in an argon atmosphere at room temperature.

The *g*-factors of a number of the radicals were deter-

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[11] P. J. Krusic and J. K. Kochi, *J. Amer. Chem. Soc.*, 1969, **91**, 6161.

[12] A. Hudson and A. Hussain, *J. Chem. Soc.* (*B*), 1969, 793.

[13] S. W. Bennett, C. Eaborn, A. Hudson, R. A. Jackson, and K. D. J. Root, *J. Chem. Soc.* (*A*), 1970, 348; S. W. Bennett, C. Eaborn, A. Hudson, A. Hussain, and R. A. Jackson, *J. Organometallic Chem.*, 1969, **16**, P36.

[14] R. V. Lloyd and M. T. Rogers, *J. Amer .Chem. Soc.*, 1973, **95**, 2459.

[15] J. E. Bennett and J. A. Howard, *Chem. Phys. Letters*, 1972, **15**, 322.

mined (see Table 4); with one exception [radical (25), $g = 2.002\,7$] the values are higher than that (2.002 9) observed for the parent *N*-hydropyridyl and *N*-hydropicolinyl radicals.[10] This difference of 0.000 8—0.001 1 between corresponding *N*-hydro- and *N*-trimethylsilyl-radicals must be due to interaction between the *N*-trimethylsilyl group and the heteroaromatic nucleus. The metal substituents in the 3-position [values determined only for radicals (18) and (20)] cause little variation in the *g*-factor compared with the value for the 3-methyl substituent; this is not unexpected, as it is clear from the values of a_{metal} that little interaction between the metal and the pyridyl nucleus occurs.

The *g*-factor variation in the 4-substituted pyridyls is much larger; as in radicals of the type $\cdot CH_2MMe_3$,[16] the *g*-factor decreases on going from M = C to M = Sn. This behaviour has been interpreted in terms of *d*-orbital participation by the metals.

In many cases the reactions of bis(trimethylsilyl)- and bis(trimethylgermyl)-mercury with a given substrate are similar or identical. We therefore expected to be able to prepare compounds analogous to (I) and (II) by treating pyridine and derivatives thereof with $(Me_3Ge)_2Hg$. However, we observed no reaction when this compound was treated with pyridine or a trialkylmetal-substituted pyridine, either on heating or on irradiating the mixture; this was particularly surprising in view of a report [17] that pyridine reacts with bis(trimethylgermyl)cadmium to give a product of the expected type. Work in progress in these laboratories suggests that $(Me_3Ge)_2Hg$ reacts only with pyridine derivatives which contain an electron-withdrawing substituent; for example compounds RC_5H_4N have been found to react, where R = 3-CN, 4-CN, 3-CO_2Me, 4-CO_2Me, 4-$CONEt_2$.[3e] Reactions of $(Me_3Ge)_2Hg$ with substituted phosphabenzenes have also successfully been carried out.[3e]

EXPERIMENTAL

Since bis(trimethylsilyl)mercury and the *N*-silylated reaction products are air-sensitive, all manipulations were carried out in an argon atmosphere.

^1H N.m.r. spectra were recorded on a Varian A-60D or Perkin-Elmer R24 spectrometer and e.s.r. spectra using a Varian E-6 spectrometer.

Reaction mixtures were irradiated with a daylight lamp (Philips HPL 125), using benzene as solvent.

Trialkylmetal derivatives of pyridine [1] and bis(trimethylsilyl)mercury were prepared as described previously.

Reaction times and conditions are to be found in Table 1. Three preparations will be described; others were carried out similarly.

(a) *Reaction of* $(Me_3Si)_2Hg$ *with 3-Trimethylstannylpyridine*.—A mixture of 3-trimethylstannylpyridine (1.21 g, 5 mmol) and $(Me_3Si)_2Hg$ (4.0 ml benzene solution, 2.5 mmol) was irradiated for 3 h with a daylight lamp, after which time mercury (0.49 g, 98%) had separated. The ^1H n.m.r. data of the product mixture were as given in Table 3. Removal of solvent left NN′-*bis(trimethylsilyl)-3,3′-bis(trimethylstannyl)tetrahydro-4,4′-bipyridyl* as a yellow semi-solid. This was heated for *ca.* 5 min at 130 °C and redissolved in benzene; the ^1H n.m.r. spectrum showed a decrease in intensity of the peaks at 6.72, 9.83, and 9.93 [ascribed to the (±)-form]. Further heating or irradiation caused these peaks to disappear completely.

In a second experiment, the product mixture was treated with n-hexane (5 ml) and cooled to *ca.* −60 °C; a light-yellow crystalline solid (0.3 g, m.p. 59—65 °C) separated. The ^1H n.m.r. spectrum of this solid in benzene showed only the peaks due to the thermally labile (±)-form (Found: C, 41.05; H, 6.5; N, 4.0. $C_{22}H_{44}N_2Si_2Sn_2$ requires C, 41.41; H, 6.95; N, 4.4%).

(b) *Reaction of* $(Me_3Si)_2Hg$ *with 4-t-Butylpyridine*.—A mixture of 4-t-butylpyridine (2.7 g, 20 mmol) and $(Me_3Si)_2Hg$ (12.0 ml benzene solution, 10 mmol) was irradiated for 12 h with a daylight lamp; mercury (1.93 g, 96%) was recovered. Removal of solvent left a yellow semi-solid; this was purified by washing rapidly with cold acetone, to leave NN′-*bis(trimethylsilyl)-4,4′-di-t-butyltetrahydro-2,2′-bipyridyl* as a colourless crystalline solid, m.p. 83—88 °C (2.2 g, 70%). The ^1H n.m.r. data of the solid (in benzene) are given in Table 3 (Found: C, 65.95; H, 10.5; N, 6.7. $C_{22}H_{44}N_2Si_2$ requires C, 66.28; H, 10.75; N, 6.92%). A benzene solution of the solid gave a well-resolved e.s.r. signal (for data see Table 4) at room temperature.

(c) *Reaction of* $(Me_3Si)_2Hg$ *with 4-Trimethylstannylpyridine*.—4-Trimethylstannylpyridine (0.8 g, 3 mmol) was added to $(Me_3Si)_2Hg$ (2 ml benzene solution, 1.5 mmol); the mixture became slightly warm and developed an orange colour. Mercury (0.28 g, 93%) separated during 30 min, and the solution gave a well-resolved e.s.r. spectrum at room temperature during as well as after this period. The signal intensity increased, as usual, on warming the sample. The ^1H n.m.r. spectrum was extremely complex, indicating the presence of a number of products; signals due to the expected bipyridyl were not visible. The experiment was repeated at 0 °C in the n.m.r. spectrometer, toluene being used as solvent; again, a complex mixture of products was formed, the spectrum undergoing several changes when the sample was heated to 70 °C.

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