α-Lithium Alkyls of α-Trimethylsilyl-*p*-xylenes and the Synthesis of *p*-$C_6H_4(CH_2SnMe_3)_2$ from a New Di-Grignard Reagent: Crystal Structure of $[\{Li(Me_2NCH_2CH_2NMe_2)\}_2\{p\text{-}C_6H_4(CHSiMe_3)_2\}]$ †

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Metallation of the *p*-xylene compounds *p*-$C_6H_4(CHRR')(CHR''R''')$ (R,R',R'',R''' = H or $SiMe_3$) with $[LiBu^n(tmen)]$ (tmen = *NNN'N'*-tetramethylethylenediamine) or $[LiBu^n(pmdien)]$ (pmdien = *NNN'N''N''*-pentamethyldiethylenetriamine) occurs selectively at the benzylic carbon atom(s) (C_α) in a manner dependent on the degree of substitution and the tertiary amine. Four of the organolithium complexes generated have been isolated as crystalline solids and the molecular structure of one, $[\{Li(tmen)\}_2\{p\text{-}C_6H_4(CHSiMe_3)_2\}]$, has been determined from single-crystal *X*-ray diffraction data. The *p*-xylenediyl moiety is planar with the trimethylsilyl groups *trans* to each other, being related by an inversion centre. There is evidence of a dominant *p*-quinodimethanide bonding contribution, with each lithium, on opposite sides of the $C_8H_6Si_2$ plane, interacting unsymmetrically with both C_α and its adjacent ring-carbon atom [$Li-C_\alpha$ 2.10(1) and $Li-C_\beta$ 2.38(1) Å]. A high-yield synthesis of a di-Grignard reagent derived from 1,4-bis(chloromethyl)benzene in thf (tetrahydrofuran) which yields a compound of composition $[Mg_{1.5}Cl(thf)_2(C_8H_8)]_n$ after *ca.* 1 h is described. The utility of this compound is illustrated by the synthesis of *p*-$C_6H_4(CH_2SnMe_3)_2$ from $SnMe_3Cl$.

The utility of $LiBu^n$, activated with tmen (*NNN'N'*-tetramethylethylenediamine), as a metallating agent in synthesis is well established. More recently, the tridentate tertiary amine pmdien (*NNN'N''N''*-pentamethyldiethylenetriamine) has been employed which maintains the selectivity of metallation and with which there is an increase in reactivity;[1] moreover, one can dispense with the necessity to use the more reactive lithium alkyls, $LiBu^s$ and $LiBu^t$, which have limited shelf life. For example, metallation of $SiMe_4$ with $[LiBu^n(tmen)]$ yields only *ca.* 40% of the desired lithiation product,[2] whereas $[LiBu^n(pmdien)]$ affords almost quantitative formation of $[Li(CH_2SiMe_3)(pmdien)]$.[3]

α-Metallation products of α-trimethylsilylated *o*-xylenes, using $[LiBu^nL]$ (L = tmen or pmdien)[1] and 1,8-$(Me_3SiCH_2)_2C_{10}H_6$ [4] and $(2\text{-}RCH_2C_6H_4)_2$ (R = H or $SiMe_3$)[5] using $[LiBu^n(tmen)]$, are all crystalline, a feature allowing the use of exact stoicheiometric ratios of highly pure starting materials in subsequent reactions. Several such complexes have been structurally characterised and show unusual bonding configurations for organolithium compounds. Herein we report the results of metallation reactions of various α-trimethylsilylated *p*-xylenes using $[LiBu^nL]$ (L = tmen or pmdien), and the crystal structure of one lithium alkyl thus obtained, $[\{Li(tmen)\}_2\{p\text{-}C_6H_4(CHSiMe_3)_2\}]$. Novel reactions in the *o*-xylene system may be a consequence of the close proximity of the benzylic carbon atoms. In the *p*-xylene case this constraint is removed but electronic variations, in principle, should be similar and thus the present study is likely to resolve the factors controlling such reactions.

Synthesis of *p*-xylene dilithium derivatives was also of interest in the development of suitable reagents for the synthesis of bimetallic *p*-xylenediyl $[p\text{-}C_6H_4(CH_2)_2]$ metal alkyls. A di-Grignard reagent of 1,4-bis(chloromethyl)benzene has been developed for the same reason and is reported herein. To our knowledge, the only *p*-xylenediyl metal alkyl complexes known are $[p\text{-}\{Ni(PR_3)_nCH_2\}_2C_6H_4]$, R = Ph, $n = 2$ and R = cyclohexyl, $n = 1$, both prepared by oxidative-addition reactions,[6a] and *p*-$C_6H_4(CH_2SnMe_3)_2$ prepared by a Grignard *in situ* trapping reaction.[6b]

Results and Discussion

Organolithium species derived from metallation of α-trimethylsilyl-*p*-xylenes using $LiBu^n$ activated with tmen or pmdien are shown in Schemes 1 and 2; all were prepared in hexane. Without the presence of a tertiary amine little or no reaction was evident after several hours at room temperature. The crystalline lithium alkyls isolated are derived exclusively from α-metallation. They are extremely air sensitive, being characterised by ^1H and ^{13}C n.m.r., a crystal structure determination for compound (2), and by derivatization with $SiMe_3Cl$ to yield air-stable compounds. As with the *o*-xylene system, there is enhanced reactivity of $[LiBu^n(pmdien)]$ compared with $[LiBu^n(tmen)]$ as demonstrated by the relative optimum reaction times of the order of minutes and hours respectively.

Compound (8) was reported previously.[1] An earlier paper describes the metallation of *p*-xylene with $[LiBu^n(tmen)]$ yielding a mixture of benzyl-lithium species.[7] In the same paper formation of (8) in high yield was established, although 4 and 2 equivalents respectively of $LiBu^n$ and pmdien were used. A feature of our work and that on the *o*-xylene system[1] is the use of stoicheiometric quantities of metallating agent; the formation of compound (8) in high yield requires only 1 equivalent of $[LiBu^n(pmdien)]$. In contrast to the use of pmdien selectively to lithiate *p*-xylene, the metallation of toluene, in high yield, is effective using tmen.[8] To our knowledge, the synthesis, n.m.r. data, and m.p. of the compound $[Li(CH_2Ph)(tmen)]$ have not been reported and accordingly they are included in this paper.

Access to the series of compounds $R_xCH_{3-x}C_6H_4CH_{3-y}R_y\text{-}p$ [R = $SiMe_3$, for $x = y = 1$, (1); $x = y = 2$, (3); $x = 1$, $y = 0$, (9); $x = 2$, $y = 0$, (11); and $x = 2$, $y = 1$, (6)] is possible by using either tmen or pmdien in the metallation experiment followed by quenching with $SiMe_3Cl$ in hexane (Schemes 1 and 2). *p*-Xylene requires pmdien (see above) whereas for its derivative, (9), tmen is effective, yielding (10), the product consistent with established relative thermodynamic acidities.[1,3] Incorporation of a second $SiMe_3$ group on the

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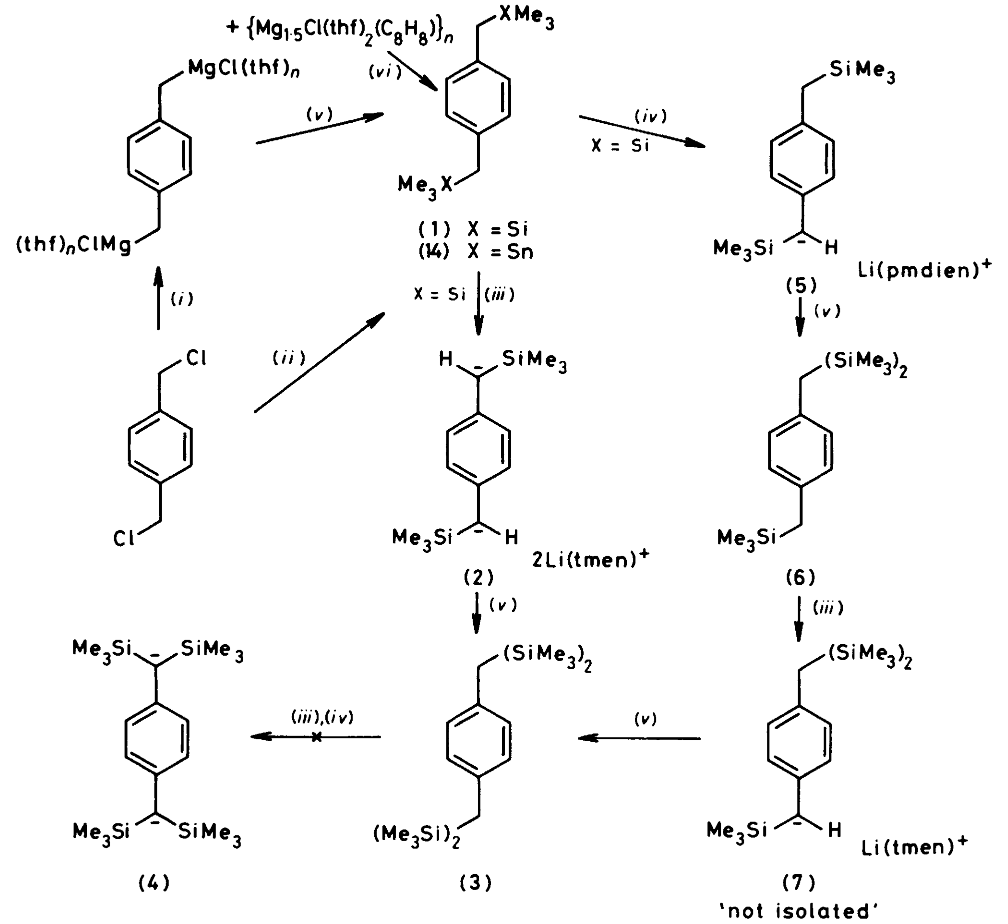
† α,α'-Bis[(*NNN'N'*-tetramethylethylenediamine)lithio]-α,α'-bis(trimethylsilyl)-*p*-xylene.

Supplementary data available (No. SUP 23928, 7 pp.): thermal parameters, H-atom co-ordinates, structure factors. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.

Non-S.I. unit employed: mmHg ≈ 133 Pa.



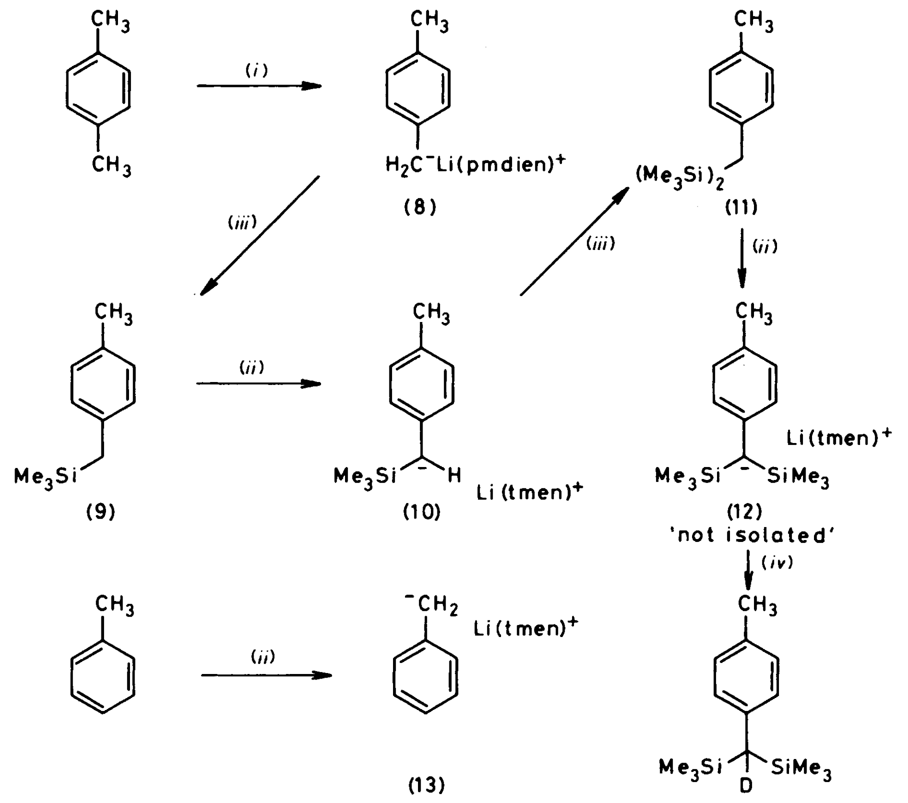
Scheme 1. (*i*) Mg–thf; (*ii*) Mg–thf–SiMe$_3$Cl (or SnMe$_3$Cl); (*iii*) [LiBu^n(tmen)] in hexane; (*iv*) [LiBu^n(pmdien)] in hexane; (*v*) SiMe$_3$Cl; (*vi*) SnMe$_3$Cl

same carbon results in metallation at the tertiary carbon centre. However, the product, (12), could not be isolated for either reagent and the position of metallation was established by quenching the reaction mixtures with DCl–D$_2$O and from g.c.–m.s. and ^{1}H n.m.r. data of the products. Although the tertiary carbon proton is expected to be the most acidic, metallation of the related compound $(Me_3Si)_3CH$ using [LiBu^n(tmen)] affords a CH_3Si lithiated species, a result that has been explained in terms of a steric effect. The use of $(LiMe)_4$ in OEt$_2$–thf (tetrahydrofuran) for lithiation of $(Me_3Si)_3CH$ does, however, yield the analogous product to (12), *viz.* '$(Me_3Si)_3CLi$'.[9]

Metallation of the *o*-isomer of (11) does not yield a tertiary carbon-centre lithiated species, possibly a consequence of steric crowding by the adjacent methyl-ring substituent. The product is a CH_3Si lithiated species which rearranges in benzene at 50 °C to [{Li(pmdien)}{*o*-$C_6H_4(CHSiMe_3)_2$}] *via* a proposed methylarene lithiated species that undergoes an anionic 1,4-silyl migration. Similar rearrangements have been noted in the lithiation of 9,9-bis(trimethylsilyl)-9,10-dihydroanthracene[10] and MeC_6H_4-*o*-$C_6H_4[CH(SiMe_3)_2]$-2,[5] respectively 1,4- and 1,6-silyl migrations, and are thought to arise *via* the silyl group shifting intramolecularly through a five-co-ordinate intermediate.[11] For the 1,6-migration this is conceivable by a torsion about the biphenyl axis, allowing the benzylic carbon atoms to approach each other.[5] Silyl migration on metallation of compound (11) is not evident. It would be unfavourable as an intramolecular process and in addition would require methylarene lithiation at some stage. It is likely, however, that methylarene proton abstraction does occur as the initial step on metallation of (11) since the compound bearing two tertiary carbon centres, (3), is resistant to metallation at these centres. Nevertheless, lithiation of compound (6) yields secondary rather than tertiary carbon metallation, as demonstrated by the isolation of (3) in high yield on quenching the reaction with SiMe$_3$Cl, and the formation of a secondary carbon deuterium-labelled derivative of (6) with DCl–D$_2$O. Unfortunately (7) could not be isolated as a crystalline solid, possibly a consequence of the three trimethylsilyl groups imparting high solubility in hexane.

Compound (6) is accessible *via* selective monolithiation of 1,4-bis(trimethylsilylmethyl)benzene, (1), using [LiBu^n(pmdien)] and subsequent quenching with SiMe$_3$Cl; the alternative metallating agent [LiBu^n(tmen)] yielded a mixture of the dilithiated complex, (2), and unreacted (1). We have investigated the metallation of (1) and its *o*-isomeric compound with two equivalents of [LiBu^n(pmdien)] and find that both compounds yield a *ca.* 1 : 1 mixture of tris- and tetrakis(trimethylsilyl)xylenes on quenching the reaction mixtures with SiMe$_3$Cl, indicating that steric control of metallation in the *o*-isomer is minimal.

Both organolithium tertiary amine reagents failed to yield the *p*-quinodimethanide dianion, (4), a result consistent with the behaviour of (6). Unlike the tetrakis(trimethylsilyl) derivative of *o*-xylene, the likelihood of forming the dianion (4) using other metallating reagents is not unreasonable. Accordingly several reagents have been investigated, *viz.* LiMe in OEt$_2$–thf, n-butyl(1,4-diazabicyclo[2.2.2]octane)-

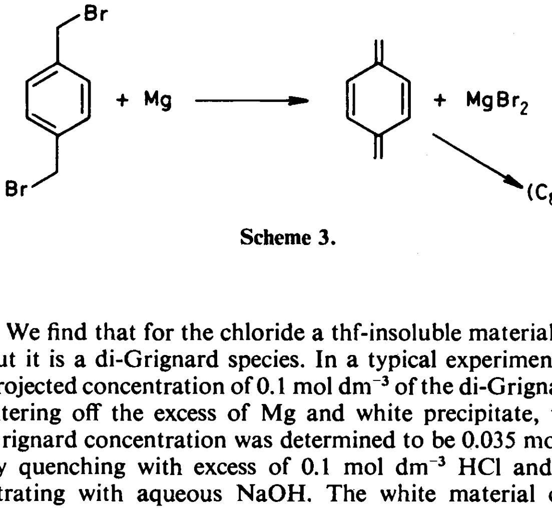


Scheme 2. (*i*) [LiBu^n(pmdien)] in hexane; (*ii*) [LiBu^n(tmen)] in hexane; (*iii*) $SiMe_3Cl$; (*iv*) $DCl-D_2O$

lithium in hexane, Li, K, KH, or NaH in thf, and Lochmann's base (LiBu^n–KOBu^t). However, quenching reaction mixtures with $SiMe_3Cl$ yielded traces of the pentakis compound and no hexakis. The latter has been prepared in low yield (6%) *via* a Grignard *in situ* reaction involving $SiMe_3Cl$.[12]

p-Xylene and (9) are resistant to dimetallation with the reagents and conditions employed, as for *o*-xylene and its mono(trimethylsilyl) derivative.[1] Polymethylnaphthalenes behave in a similar manner towards the reagent [LiBu^n(tmen)].[13] In a recent study on the metallation of 2,3-dimethylnaphthalene the product was found to be mono-α-metallated and surprisingly the $SiMe_3Cl$ derivative is a ring-silylated compound (in the 1-position).[14] Both the *o*- and *p*-xylenediyl dianion species, *o*- and *p*-$C_6H_4(CH_2)_2^{2-}$, have been prepared by LiBu^n–KOBu^t metallation of the xylenes,[15] and the reaction of 6 equivalents of LiBu^n–$KOCMe_2CH_2Me$ with 1-methyl-2- or -4-methylenecyclohexane.[16] In addition, [$Na(CH_2CH_2CH_2CH_2Me)$(tmen)] yields the *o*-xylenediyl dianion but not that of the *p*-isomer; [17] this may be related to the greater stability of the *o*-dianion.[15] The utility of the reactions involving LiBu^n and potassium alkoxides has been demonstrated by the formation of compound (1).[15,16]

The di-Grignard of 1,4-bis(chloromethyl)benzene is accessible under rather critical conditions of high dilution, thf as the solvent, temperature, and the choice of halide, chloride rather than bromide, as for the corresponding 1,2 di-Grignard reagent.[18] Moreover, these conditions are applicable to the synthesis of the di-Grignard of (*o*-$ClCH_2C_6H_4)_2$.[19] However, they appear not to be general conditions for preparing previously inaccessible bis(halogenomethyl)aryl Grignards since for 1,8-$(ClCH_2)_2C_{10}H_6$ formation of an oligomeric material, $(C_{12}H_{10})_n$, predominates.[4] 1,4-Bis(bromomethyl)benzene gives a polymer thought to arise by elimination of $MgBr_2$ with concomitant formation of highly reactive *p*-quinodimethane (Scheme 3).[20]



Scheme 3.

We find that for the chloride a thf-insoluble material forms but it is a di-Grignard species. In a typical experiment for a projected concentration of 0.1 mol dm^{-3} of the di-Grignard, on filtering off the excess of Mg and white precipitate, the di-Grignard concentration was determined to be 0.035 mol dm^{-3} by quenching with excess of 0.1 mol dm^{-3} HCl and back-titrating with aqueous NaOH. The white material can be separated from the excess of magnesium, albeit with difficulty. It reacts with $SiMe_3Cl$ to afford (1) as the exclusive trimethylsilyl derivative. Therefore the active Grignard species is based on $C_8H_8^{2-}$ rather than some higher oligomer, for example $(CH_2C_6H_4CH_2^{-}\text{-}p)_2$. [It is noteworthy that intramolecular elimination is the prevalent competing reaction for 1,8-$(BrCH_2)_2C_{10}H_6$[4] and (*o*-$BrCH_2C_6H_4)_2$,[19] while it is intermolecular for 1,8-$(ClCH_2)_2C_{10}H_6$.[4]] Moreover, chloride analysis and the Grignard activity are in agreement with a stoicheiometry $Mg_{1.5}Cl(thf)_2(C_8H_8)$. The *o*-isomeric di-Grignard solutions at concentrations greater than *ca.* 0.1 mol dm^{-3} yield a completely $MgCl_2$-free compound, a macrometallocycle, [{$Mg(thf)_2(C_8H_8)$}$_3$] in which the *o*-xylenediyl ligands bridge successive magnesium centres.[18] The loss of half a $MgCl_2$ unit for $C_8H_8^{2-}$ in the present case and the low solubility of it in thf suggests the product is oligomeric and likely

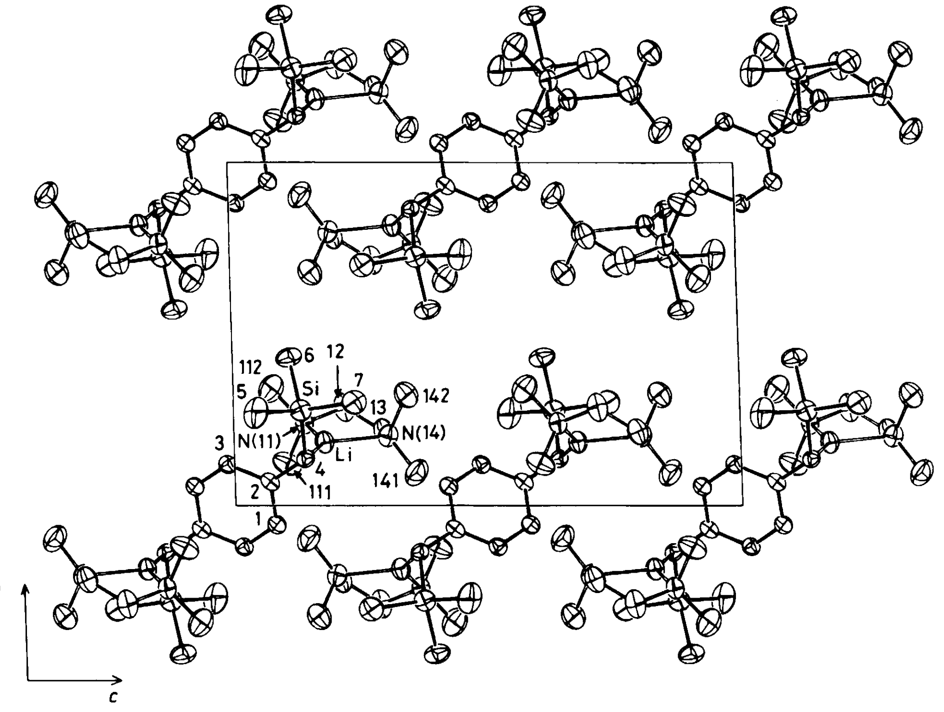


Figure 1. Unit-cell contents of compound (2) projected down *b*; 20% thermal ellipsoids are shown for the non-hydrogen atoms

to possess similar bridging $C_8H_8^{2-}$ species. Quenching the Grignard solution prior to formation of the white precipitate, which usually occurs 1 h after addition of the dichloro-compound, yields (1) in *ca.* 80% yield. This is consistent with the formation of a di-Grignard species which is subsequently unstable with respect to formation of solid $Mg_{1.5}Cl(thf)_2(C_8H_8)$ and a soluble $C_8H_8^{2-}$-containing species, possibly $Mg_{2.5}Cl_3(thf)_nC_8H_8$. These are not in equilibrium since the filtered solution remains clear indefinitely.

The utility of the white solid as an alternative source of *p*-xylenediyl dianion is demonstrated by the formation of a bimetallic complex, (14), with $SnMe_3Cl$. Other *p*-xylenediyl reagents are complexes of Li, Na, and K which are expected to be stronger reducing agents than those of the magnesium reagents. Of the three isomeric xylenediyl dianions, the *p*-isomer is the strongest reducing species.[21]

Compound (1) was also prepared by an *in situ* Grignard reaction (Scheme 1) using the chloride rather than the bromide which has been used previously but with no yield quoted.[22] Previous syntheses of compounds (11) and (3), *in situ* Grignard and potassium alkyl reactions respectively, gave low yields, 13 and 15% respectively.[12] Jousseaume *et al.*[6b] have recently reported the synthesis of the tin complex, (14), *via* an *in situ* Grignard trapping reaction.

Crystal Structure of Compound (2).—As is usual with compounds of this type, the structure determination at room temperature is of modest precision because of high thermal motion and high light-atom content (Figures 1 and 2, Tables 1 and 2). Nevertheless, beyond establishing the stoicheiometry to be that given above, some further features of interest emerge.

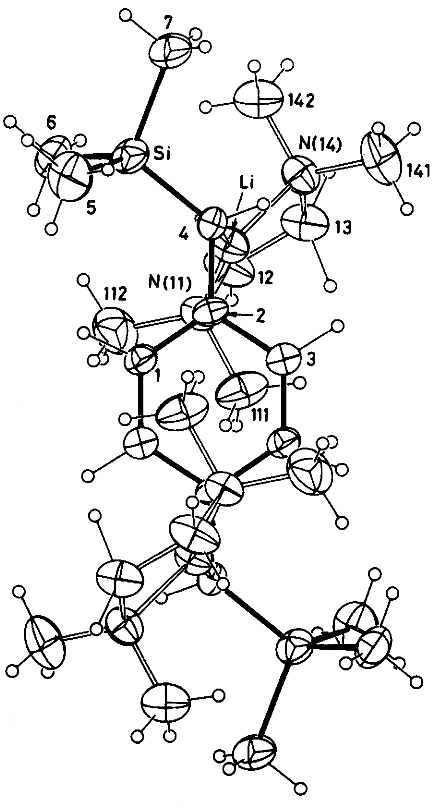


Figure 2. A single molecule of complex (2). Hydrogen atoms have an arbitrary radius of 0.1 Å

The geometry of the aromatic fragment of the structure shows evidence of a dominant *p*-quinodimethanide contribution to the bonding description: C(1)–C(2), 1.443(9) Å, is well above the usual aromatic C–C distance of 1.4$_0$ Å, while C(2)–C(3) is comparable being 1.402(9) Å; C(1)–C(3′) is much shorter being 1.376(10) Å. C(2)–C(4), 1.458(9) Å, lies well below the normal C(aromatic)–C_{sp^3} distance of 1.4$_9$ Å, and C(4)–Si [1.802(8) Å] is shorter than the mean of Si–C(5, 6, 7) (1.88$_3$ Å), presumably a consequence of $Si_{d\pi}$–$C_{p\pi}$ bonding. C(1), C(2), C(3), C(4), together with their inversion

Table 1. Non-hydrogen-atom co-ordinates for compound (2)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
C(1)	−0.055 7(7)	0.014 2(6)	0.079 4(5)	C(111)	0.122 0(8)	−0.266 9(8)	0.103 0(6)
C(2)	0.068 8(6)	0.070 1(6)	0.068 5(4)	C(112)	0.339 0(10)	−0.217 1(9)	0.075 0(6)
C(3)	0.119 5(7)	0.048 9(6)	−0.013 9(4)	N(11)	0.239 3(5)	−0.210 1(5)	0.139 4(3)
C(4)	0.135 8(7)	0.133 8(7)	0.139 8(4)	C(12)	0.285 1(11)	−0.266 5(8)	0.218 4(6)
Si	0.275 7(2)	0.229 3(2)	0.132 6(2)	C(13)	0.214 7(10)	−0.230 5(8)	0.296 5(6)
C(5)	0.268 5(9)	0.346 3(8)	0.044 3(6)	N(14)	0.202 7(5)	−0.098 6(5)	0.304 2(4)
C(6)	0.430 0(7)	0.143 5(8)	0.111 5(6)	C(141)	0.095 5(9)	−0.066 6(9)	0.358 3(6)
C(7)	0.300 0(8)	0.311 0(7)	0.238 7(6)	C(142)	0.321 7(9)	−0.046 5(8)	0.341 7(5)
Li	0.184 2(13)	−0.041 4(11)	0.177 8(8)				

Table 2. Non-hydrogen molecular geometry for compound (2): distances (Å), angles (°) *

C(1)–C(2)	1.443(9)	Si–C(5)	1.880(9)	Li–N(11)	2.06(1)	C(12)–C(13)	1.48(1)
C(1)–C(3′)	1.376(10)	Si–C(6)	1.894(8)	Li–N(14)	2.04(1)	C(13)–N(14)	1.48(1)
C(2)–C(3)	1.402(9)	Si–C(7)	1.874(9)	N(11)–C(111)	1.46(1)	N(14)–C(141)	1.45(1)
C(2)–C(4)	1.458(9)	C(2)–Li	2.38(1)	N(11)–C(112)	1.45(1)	N(14)–C(142)	1.46(1)
C(4)–Si	1.802(8)	C(4)–Li	2.10(1)	N(11)–C(12)	1.43(1)		

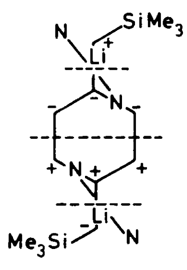
C(3′)–C(1)–C(2)	123.0(6)	C(5)–Si–C(6)	104.1(4)	C(111)–N(11)–C(112)	108.2(6)
C(1′)–C(3)–C(2)	124.1(6)	C(5)–Si–C(7)	106.6(4)	N(11)–C(12)–C(13)	114.1(8)
C(1)–C(2)–C(3)	112.9(6)	C(6)–Si–C(7)	107.8(4)	C(12)–C(13)–N(14)	112.3(7)
C(1)–C(2)–C(4)	121.8(6)	N(11)–Li–N(14)	88.0(5)	C(13)–N(14)–Li	104.0(6)
C(3)–C(2)–C(4)	125.2(6)	Li–N(11)–C(12)	104.4(6)	C(13)–N(14)–C(141)	110.9(7)
C(2)–C(4)–Si	127.2(5)	Li–N(11)–C(111)	105.9(6)	C(13)–N(14)–C(142)	110.9(6)
C(4)–Si–C(5)	116.3(4)	Li–N(11)–C(112)	116.8(6)	Li–N(14)–C(141)	114.5(6)
C(4)–Si–C(6)	112.9(4)	C(12)–N(11)–C(111)	112.2(6)	Li–N(14)–C(142)	107.5(6)
C(4)–Si–C(7)	108.7(4)	C(12)–N(11)–C(112)	109.3(7)	C(141)–N(14)–C(142)	108.9(6)

* Primes denote atoms at $\bar{x}$, $\bar{y}$, $\bar{z}$.

images, define a good plane (σ 0.016 Å, χ^2 36.7) from which the silicon atom deviates by 0.30 Å and C(5), C(6), and C(7) by 1.86, −1.09, and 0.45 Å respectively; the lithium-atom deviation is −2.06 Å. The trimethylsilyl hydrogen atoms show no contacts within the van der Waals distance to H(1), so that the enlargement of the angle Si–C(4)–C(2) is probably not attributable to contacts of this type.

The lithium atom lies equidistant from N(11) and N(14) [2.06(1) and 2.04(1) Å], with the LiN_2 plane approximately normal to the aromatic ring plane (dihedral angle 79.3°); the lithium–nitrogen distances are as short as any hitherto observed [*cf.*, [{Li(tmen)}$_2${*o*-C_6H_4(CHSiMe$_3$)$_2$}],[1] 2.07(1) and 2.08(1) Å for Li(2)]. Deviations of the methyl and methylene carbon atoms from the LiN_2 plane are: C(111), −1.34; C(112), 0.96; C(12) 0.27; C(13) −0.31; C(141) −0.95; C(142), 1.34 Å.

In relation to the aromatic system, Li lies 2.10(1) and 2.38(1) Å from C(4) and C(2) respectively, indicating interaction with both of these atoms, *via* the π system between them, with a preference for C(4). The Li–C(4) distance is unusually short in the context of the approach of the lithium atom pseudo-normal to the aromatic ring plane and suggests that the conventional 'contact ion pair' structure of lithium benzyl tertiary amine complexes may be an inappropriate description of the present structure. On the other hand, the geometry about C(4) is nearly coplanar with the aromatic ring, precluding a description in terms of a conventional covalent bond, which would dictate the further requirement of a tetrahedral substituent at C(4), at variance with the observed C(2)–C(4)–Si angle of 127.2(5)°. The present situation may be compared with that found in [Li(pmdien){*o*-$C_6H_4CH_3$-(CHSiMe$_3$)}][1] wherein the same angle is 124.0(4)°, the Li–C distance 2.26(1) Å, and the deviation of the lithium atom from the aromatic ring plane 2.10 Å. In [{Li(tmen)}$_2${*o*-C_6H_4-(CHSiMe$_3$)$_2$}], Si–C–C is 130°, with the lithium atom equidistant from the two carbon atoms [range 2.32(2)—2.41(2) Å; mean distance to the centre of gravity of the C–C bonds, 2.2_7 Å], but in that compound the C–C bonds are approached by a pair of lithium atoms on either side of the aromatic ring plane, the mean lithium deviation from the plane being 1.85 Å. By contrast, we find that in [Li{CH(SiMe$_3$)$_2$}(pmdien)], where the lithium atom lies 0.96 Å out of the Si–C–Si plane, Li–C is 2.13(5) Å and Si–C–Si is 124(2).° The Li–C–Si angles are 117(2) and 112(2)°, and this compound, by comparison with the structure of [Li(thf)(tmen){C(Ph)SCH$_2$CH$_2$CH$_2$S}],[23] was considered covalent or at least polarised covalent.



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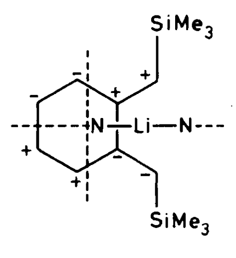

(II)

In lithium aryl (and benzyl) complexes, of the contact ion pair type, the lithium resides over a node in the highest occupied molecular orbital (h.o.m.o.) of the organic anion.[24] In the present structure a node between C(3) and C(4) is implied, and is predicted for the *p*-xylenediyl dianion, (I).[25] For a substituted dianion the order of energy levels is not expected to alter, although the energies may do so by virtue of empty d_{Si} orbital participation in bonding. Maximum sp^3_{Li} or p_{Li} orbital overlap is postulated for the LiN_2 plane to be normal to the C(3)–C(4) vector.[24] In compound (2) the normal to the LiN_2 plane and the C(3)–C(4) vector subtend an angle of 80.1°; the departure from 90° may be a consequence of otherwise unfavourable non-bonding interactions between the bulky $SiMe_3$ group and the methyl substituents of tmen. The structure of the o-$C_6H_4(\bar{C}HSiMe_3)_2$ complex also satisfies the nodal arrangement of the h.o.m.o.[25] and has the LiN_2 plane ideally orientated, (II).[1]

Experimental

General Procedures.—Owing to the air-sensitivity of all the lithium complexes, $SiMe_3Cl$, and the Grignard reagent, manipulations were carried out under a dry and oxygen-free argon atmosphere or *in vacuo* using standard Schlenk techniques. Solvents were dried over and distilled from $LiAlH_4$ (pentane and thf), CaH_2 (hexane), or sodium metal (diethyl ether).

Materials.—Compounds (1)[22] and (8)[1] were prepared according to the literature. 1,4-Bis(chloromethyl)benzene was recrystallized from hexane, and tmen and pmdien were purified by distillation over KOH under a dinitrogen atmosphere.

Physical and Analytical Measurements.—Elemental (C and H) analyses of the organolithium derivatives were performed by the Australian Mineral Development Laboratories, Melbourne. Hydrogen-1 and carbon-13 n.m.r. and mass spectra were recorded on Hitachi–Perkin-Elmer R-24B (60 MHz), Brüker WP-80, CH 7, or HP-5986 spectrometers respectively.

Preparations.—$[\{Li(tmen)\}_2\{p$-$C_6H_4(CHSiMe_3)_2\}]$ (2). To an ice-cooled solution of compound (1) (2.0 g, 8.0 mmol) and $LiBu^n$ in hexane (10 cm^3, 1.7 mol cm^{-3}, 17 mmol) was added tmen (2.5 cm^3, 16.7 mmol) and the resulting red solution was stored at room temperature overnight, yielding dark red crystals of *compound* (2). These were filtered off, washed with cold (*ca.* −20 °C) pentane (2 × 5 cm^3), and dried *in vacuo*. Yield 3.44 g (87%), m.p. 160 °C. N.m.r. (C_6D_6): ^1H (60 Mz), δ 0.20 (s, 18 H), 1.20 (s, 2 H), 1.50 (s, 8 H), 1.61 (s, 24 H), 6.25, and 6.48 (m, 4 H); ^{13}C (^1H decoupled), δ 4.05 $[(CH_3)_3Si]$, 31.94 (CHSi), 45.72 (CH_2N), 57.17 $[(CH_3)_2N]$, 141.32, and 122.98 (C_6H_4).

p-$C_6H_4\{CH(SiMe_3)_2\}_2$ (3). To an ice-cooled hexane solution of (2) (3.4 g, 6.9 mmol in 50 cm^3) was added $SiMe_3Cl$ (2.0 cm^3, 16 mmol). The mixture was then stirred for 2 h at room temperature whereupon concentrated HCl (20 cm^3) was added and the hexane solution separated, washed with water (50 cm^3), and dried over $MgSO_4$ for 2 h. Removal of solvent *in vacuo* afforded white crystals of *compound* (3), which were either recrystallized from methanol or sublimed *in vacuo* (0.1 mmHg) at 110 °C. Yield 2.30 g (85%), m.p. 112 °C (Found: C, 60.6; H, 10.7. Calc. for $C_{20}H_{42}Si_4$: C, 60.8; H, 10.7%). N.m.r. ($CDCl_3$): ^1H (60 MHz), δ −0.05 (s, 36 H), 1.40 (s, 2 H), 6.70 (m 4 H,); ^{13}C (^1H decoupled), δ 0.38 (Me_3Si), 28.79 (CH), 137.76, and 128.77 (C_6H_4). Mass spectrum: *m/e* 394, $[P]^+$; 321, $[P - Me_3Si]^+$; and 235, $[P - CH(SiMe_3)_2]^+$.

$[Li(pmdien)(p$-$Me_3SiCH_2C_6H_4CHSiMe_3)]$ (5). To an ice-cooled solution of compound (1) (1.0 g, 4 mmol) and pmdien (0.70 g, 4 mmol) was added $LiBu^n$ in hexane (5 cm^3, 1.7 mol dm^{-3}, 8.5 mmol). The yellow solution was stored at room temperature for 18 h. Yellow crystals of *compound* (5) were isolated similarly to (2). Yield 1.60 g (93%), m.p. 141 °C. N.m.r. (C_6D_6): ^1H (60 MHz), δ 0.03 (s, 2 H), 0.14 (s, 9 H), 0.44 (s, 9 H), 1.57 (s, 1 H), 1.76 (s, 8 H), 1.91 (s, 12 H), 1.98 (s, 3 H), 6.49, 6.68, and 6.89 (m, 4 H); ^{13}C (^1H decoupled), δ −1.53 (Me_3Si), 3.31 (Me_3Si), 25.57 (CH_2), 37.45 (CHLi), 45.78 $[(CH_3)_2N]$, 53.81 (CH_2N), 57.46 (CH_2N), 120.71, 126.80, 128.74, and 155.61 (C_6H_4).

p-$Me_3SiCH_2C_6H_4CH(SiMe_3)_2$ (6). The procedure was as for the synthesis of compound (3), with the product being purified by distillation (b.p. 78 °C, 0.2 mmHg). The yield of compound (6) from (5) (1.5 g) was 0.84 g (75%) (Found: C, 63.6; H, 11.0. Calc. for $C_{17}H_{34}Si_3$: C, 63.25; H, 10.65%). N.m.r. ($CDCl_3$): ^1H (80 MHz), δ 0.12 (s, 9 H), 0.15 (s, 18 H), 1.53 (s, 1 H), 2.12 (s, 2 H), and 6.85 (m, 4 H); ^{13}C (^1H decoupled), δ −1.68 (Me_3Si), 0.43 (Me_3Si), 26.39 (CH_2), 28.90 (CH), 135.25, 138.50, 128.08, and 128.88 (C_6H_4). Mass spectrum: *m/e* 322.2, $[P]^+$; 249, $[P - Me_3Si]^+$; and 235, $[P - CH_2SiMe_3]^+$.

Compound (3) *from* (6). To a solution of compound (6) (1.0 g, 3.1 mmol) and $LiBu^n$ in hexane (2.0 cm^3, 1.7 mol dm^{-3}, 3.4 mmol) at 0 °C was added tmen (0.5 cm^3, 3.3 mmol). After 2 h at room temperature the yellow solution was added slowly to a hexane solution of $SiMe_3Cl$ (0.5 cm^3, 3.9 mmol in 20 cm^3). The mixture was then stirred at room temperature for 1 h, after which the product was isolated as described above. Yield 1.04 g (85%).

p-$MeC_6H_4CH_2SiMe_3$ (9). The procedure was as for the synthesis of compound (6) from (5). Yield 75%, b.p. 165 °C (Found: C, 74.05; H, 10.1. Calc. for $C_{11}H_{18}Si$: C, 74.1; H, 10.15%). N.m.r. ($CDCl_3$): ^1H (60 MHz), δ −0.07 (s, 9 H), 2.00 (s, 2 H), 2.25 (s, 3 H), and 6.90 (m, 4 H); ^{13}C (^1H decoupled), δ 1.67 (Me_3Si), 21.10 (CH_3), 26.68 (CH_2), 128.31, 129.22, 133.27, and 137.31 (C_6H_4). Mass spectrum *m/e* 178, $[P]^+$; 163, $[P - CH_3]^+$; and 105, $[P - SiMe_3]^+$.

$[Li(tmen)(p$-$MeC_6H_4CHSiMe_3)]$ (10). To an ice-cooled solution of compound (9) (1.25 g, 7.0 mmol) and $LiBu^n$ in hexane (4.5 cm^3, 1.7 mol dm^{-3}, 7.7 mmol) was added tmen (1.2 cm^3, 8 mmol). The yellow solution was stored at room temperature for 18 h during which massive yellow crystals of *compound* (10) precipitated. These were filtered off, washed with cold (*ca.* −20 °C) pentane (2 × 5 cm^3), and dried *in vacuo* (1.84 g, 87%), m.p. 92—94 °C. N.m.r. (C_6D_6): ^1H (60 MHz), δ 0.4 (s, 9 H), 1.32 (s, 1 H), 1.55 (s, 4 H), 1.80 (s, 12 H), 2.25 (s, 3 H), and 6.70 (m, 4 H); ^{13}C (^1H decoupled), δ 2.74 (Me_3Si), 20.68 (CH_3), 38.90 (CHLi), 45.39 $[(CH_3)_2N]$, 56.20 (CH_2N), 117.13, 118.89, 130.62, and 153.96 (C_6H_4).

p-$MeC_6H_4CH(SiMe_3)_2$ (11). The procedure was as for the synthesis of compound (6) from (5). The product was purified by distillation (b.p. 138 °C, 18—20 mmHg). Yield 62% (Found: C, 67.1; H, 10.45. Calc. for $C_{14}H_{26}Si_2$: C, 67.1; H, 10.75%). N.m.r.: ^1H (60 MHz, $CDCl_3$), δ 0.02 (s, 18 H), 1.42 (s, H), 2.27 (s, 3 H), and 6.86 (m, 4 H); ^{13}C (^1H decoupled, C_6D_6), 0.55 (Me_3Si), 21.16 (CH_3), 29.19 (CH), 129.22, 129.00, 132.81, and 140.04 (C_6H_4). Mass spectrum: *m/e* 250, $[P]^+$; 235, $[P - CH_3]^+$; and 162, $[C_6H_4CH(SiMe_3)]^+$.

Magnesium reagents of 1,4-*bis*(*chloromethyl*)*benzene*. To a suspension of magnesium powder (1.80 g, 74 mmol) in thf (20 cm^3) preactivated with $BrCH_2CH_2Br$ was added slowly over 3 h a solution of 1,4-bis(chloromethyl)benzene (4.38 g, 25 mmol) in thf (230 cm^3). The solution became pale green and, after the addition was completed, the mixture was stirred for 18 h at room temperature. The white suspension which formed was collected after the excess of Mg had settled out, yield 3.5 g (44%). The concentration of the clear filtered solution was 0.035 mol dm^{-3} (35% yield). Chloride and C_8H_8 analysis on the white solid: 12.55 and 33.4% respectively. Calc. for $Mg_{1.5}Cl(thf)_2(C_8H_8)$: Cl, 11.05; C_8H_8, 32.55%.

p-$C_6H_4(CH_2SnMe_3)_2$ (14). To a suspension of $[Mg_{1.5}Cl(thf)_2(C_8H_8)]_n$ (1.05 g, 3.3 mmol) in diethyl ether (50 cm^3) was added $SnMe_3Cl$ (1.20 g, 6 mmol). After stirring at room temperature for 1 h, the solution was filtered and water (30 cm^3) added. Concentration of the ether solution (*ca.* 10 cm^3) afforded the white crystalline product, yield 0.68 g (52%), m.p. 61 °C (Found: C, 39.15; H, 6.00. Calc. for $C_{14}H_{26}Sn_2$: C, 38.95; H, 6.05%). N.m.r. ($CDCl_3$): ^1H (60 MHz), δ 0.04 (s, 18 H), [*J*(Sn–H) = 26], 2.28 (s, 4 H) [*J*(Sn–H) = 30 Hz], and 6.80 (s, 4 H); ^{13}C (^1H decoupled), δ −9.93 (CH_3Sn)

[J(Sn–C) = 158.50], 19.74 (CH_2Sn) [J(Sn–C) = 141.85 Hz], 127.17, and 137.76 (C_6H_4). Mass spectrum: m/e 430, $[P]^+$; 415, $[P - CH_3]^+$; 267, $[P - SnMe_3]^+$; and 104, $[C_6H_4(CH_2)_2]^+$.

[Li(CH_2Ph)(tmen)] (13). This was prepared by variation of the above procedures. Yield 87%, m.p. 48—49 °C. N.m.r. (C_6D_6): ^1H, δ 1.85 (s, 4 H), 1.98 (s, 12 H), 2.23 (s, 2 H), 6.0, and 7.0 (m, 5 H); ^{13}C (^1H decoupled), δ 36.90 (CH_2Li), 45.44 [$(CH_3)_2N$], 56.60 (CH_2N), 105.85, 115.82, 126.75, 129.20, 129.65, and 157.44 (C_6H_5).

Crystallography.—Crystal data. $C_{26}H_{56}Li_2N_4Si_2$, M = 494.8, Monoclinic, space group $P2_1/c$ (C_{2h}^5, no. 14), a = 10.313(7), b = 11.176(9), c = 15.32(2) Å, β = 91.80(8)°, U = 1 765(2) Å^3, Z = 2, D_c = 0.93 g cm^{-3}, monochromatic Mo-K_α radiation, λ = 0.710 69 Å, μ_{Mo} = 1.1 cm^{-1}. Specimen: 0.15 × 0.12 × 0.45 mm (capillary).

Structure determination. A unique data set was measured within the limit $2\theta_{max.}$ = 40° using a Syntex $P2_1$ four-circle diffractometer in conventional 2θ—θ scan mode. 1 659 Independent reflections were obtained, 780 with $I > 3\sigma(I)$ being considered 'observed' and used in the basically 9 × 9 block-diagonal least-squares refinement without absorption correction after solution of the structure by direct methods. Anisotropic thermal parameters were refined for the non-hydrogen atoms; $(x, y, z, U)_H$ were constrained at estimated values, except for the aromatic and methylene hydrogens for which (x, y, z) were refined. Residuals at convergence were R 0.057 and R' 0.064, reflection weights being $[\sigma^2(F_o) + 0.0005(F_o)^2]^{-1}$. Neutral atom scattering factors were used, those for the non-hydrogen atoms being corrected for anomalous dispersion (f', f'').[26] Computation used the X-RAY 76 program[27] system implemented on a Perkin-Elmer 3240 computer by S. R. Hall. Non-hydrogen-atom labelling is shown in Figures 1 and 2; hydrogen-atom labelling follows that of the parent atom, suffixed A, B, and C for distinguishing purposes.

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References

1 M. F. Lappert, C. L. Raston, B. W. Skelton, and A. H. White, *J. Chem. Soc., Chem. Commun.*, 1982, 14.

2 D. J. Peterson, *J. Organomet. Chem.*, 1967, **9**, 373.

3 M. F. Lappert, L. M. Engelhardt, C. L. Raston, and A. H. White, *J. Chem. Soc., Chem. Commun.*, 1982, 1323.

4 L. M. Engelhardt, R. I. Papasergio, C. L. Raston, and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1984, 311.

5 L. M. Engelhardt, W-P. Leung, C. L. Raston, P. Twiss, and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1984, 321.

6 (*a*) B. Hipler, E. Uhlig, and J. Vogel, *J. Organomet. Chem.*, 1981, **218**, C1; E. Uhlig, *ibid.*, 1980, **199**, C27; (*b*) B. Jousseaume, J. G. Duboudin, and M. Petraud, *ibid.*, 1982, **238**, 171.

7 J. Klein, A. Medlik, and A. Y. Meyer, *Tetrahedron*, 1976, **32**, 51.

8 A. W. Langer, 'Polyamine-chelated Alkali Metal Compounds,' American Chemical Society, Washington, 1974, p. 32.

9 O. W. Steward and J. S. Johnson, *J. Organomet. Chem.*, 1973, **55**, 209.

10 M. Daney, R. Lapouyade, B. Labrande, and H. Bouas-Laurent, *Tetrahedron Lett.*, 1980, **21**, 153.

11 J. J. Eisch and M-R. Tsai, *J. Organomet. Chem.*, 1982, **225**, 5.

12 H. Bock, W. Kaim, and H. E. Rohwer, *Chem. Ber.*, 1978, **111**, 3573.

13 E. Dunkelblum and H. Hart, *J. Org. Chem.*, 1979, **44**, 3482.

14 R. H. Mitchell, T. W. Dingle, and R. V. Williams, *J. Org. Chem.*, 1983, **48**, 903.

15 R. B. Bates, B. A. Hess, C. A. Ogle, and L. J. Schaad, *J. Am. Chem. Soc.*, 1981, **103**, 5052.

16 D. Wilhelm, T. Clark, T. Friedl, and P. von Rague Schleyer, *Chem. Ber.*, 1983, **116**, 751.

17 G. B. Trimitsis, A. Tuncay, R. D. Beyer, and K. J. Ketterman, *J. Org. Chem.*, 1973, **38**, 1491.

18 M. F. Lappert, T. R. Martin, C. L. Raston, B. W. Skelton, and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1982, 1959.

19 W-P. Leung and C. L. Raston, *J. Organomet. Chem.*, 1982, **240**, C1.

20 I. T. Millar and H. Heaney, *Q. Rev., Chem. Soc.*, 1957, **11**, 109.

21 F. G. Bordwell and A. H. Clemens, *J. Org. Chem.*, 1981, **46**, 1035.

22 H. Bock and H. Alt, *J. Am. Chem. Soc.*, 1970, **92**, 1569.

23 R. Amstutz, J. D. Dunitz, and D. Seebac, *Angew. Chem., Int. Ed. Engl.*, 1981, **20**, 465.

24 M. E. O'Neill and K. Wade, in 'Comprehensive Organometallic Chemistry,' eds. G. Wilkinson, F. G. A. Stone, and E. W. Abel, Pergamon Press, Oxford, 1982, vol. 1, ch. 1.

25 C. R. Flynn and J. Michl, *J. Am. Chem. Soc.*, 1974, **96**, 3280.

26 'International Tables for X-Ray Crystallography,' eds. J. A. Ibers and W. C. Hamilton, Kynoch Press, Birmingham, 1974, vol. 4.

27 'The X-Ray System,' Version of March 1976, Technical Report TR-446, ed. J. M. Stewart, Computer Science Center, University of Maryland, U.S.A.

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