The Syntheses and Crystal Structures† of Two Iminolithium Adducts: $(Ph_2C{=}NLi{\cdot}NC_5H_5)_4$, a Tetrameric Pseudo-cubane formed by stacking Two $(LiN)_2$ Four-membered Rings, and $[Bu^t{}_2C{=}NLi{\cdot}OP(NMe_2)_3]_2$, a Dimer prevented sterically from Stacking

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The syntheses and crystal structures of two iminolithium adducts $[Bu^t{}_2C{=}NLi{\cdot}OP(NMe_2)_3]_2$ (**1**) $[OP(NMe_2)_3$ = hexamethylphosphoramide (hmpa)] and $(Ph_2C{=}NLi{\cdot}NC_5H_5)_4$ (**2**) (NC_5H_5 = pyridine) are described. Adduct (**1**) contains a centrosymmetric planar $(LiN)_2$ ring, with Li–N distances of 1.923(6) and 1.948(6) Å, and a ring angle at nitrogen of 75.4(3)°. Unexpectedly, the $C_2C{=}N$ skeletal planes of its imino ligands are twisted 58.6(6)° with respect to the $(LiN)_2$ ring plane, apparently to accommodate the bulky hmpa ligands, so preventing the $(LiN)_2$ rings from stacking to form an $(LiN)_4$ cubane structure. In contrast, adduct (**2**), with sterically compatible $Ph_2C{=}N$ and NC_5H_5 ligands, has an $(LiN)_4$ cubane structure with three distinct categories of metal–nitrogen distance (averaging 2.03, 2.08, and 2.16 Å respectively) and ligand orientations that support an interpretation of this cubane in terms of two stacked $(LiN)_2$ four-membered ring systems.

In recent papers[1–3] we have outlined ring-stacking and ring-laddering principles by which one can rationalise numerous aspects of the structural chemistry of lithium. For example, the hexameric molecules $(RR'C{=}NLi)_6$ ($R = R' = Bu^t$ or Me_2N; $R = Ph$, $R' = Bu^t$ or Me_2N) found in certain crystalline iminolithium compounds may conveniently be regarded as stacked pairs of cyclic trimers $(RR'C{=}NLi)_3$.[1,2] The stacking, facilitated by the orientation of the substituents R and R′ [whose primary atoms need to be coplanar with the trimers' $(LiN)_3$ rings, Figure 1(*a*)], raises the metal co-ordination number from two in the trimer to three (with respect to nitrogen atoms) in the hexamer, and converts half of the two-centre two-electron bonds in each trimer into three-centre two-electron bonds within and between trimers [Figure 1(*b*)]. Stacking of four-membered $(LiX)_2$ rings as well as six-membered $(LiX)_3$ ones (X = C or O) is also common in organolithium and lithium alkoxide chemistry,[4] and appears likely to occur elsewhere unless prevented by the bulk of substituents or by their orientation, as in the case of lithium amides $(RR'NLi)_n$ (n = 2–4), Figure 1(*c*) (n = 3). Nevertheless the tendency of lithium to acquire a higher co-ordination number than two encourages such amides to associate laterally, generating $(LiN)_n$ ladders, as in the pyrrolidinyl-lithium complex $\{[H_2\overline{C(CH_2)_3N}Li]_3{\cdot}Me_2N(CH_2CH_2NMe_2)_2\}_2$.[3]

Here, we describe two iminolithium complexes whose structures (previously reported[5,6] in a preliminary form) shed further light on these principles. These are the hexamethylphosphoramide (hmpa) adduct $[Bu^t{}_2C{=}NLi{\cdot}OP(NMe_2)_3]_2$, (**1**),[5] and the pyridine adduct $(Ph_2C{=}NLi{\cdot}NC_5H_5)_4$, (**2**).[6] The $(LiN)_2$ four-membered ring structure of the former is prevented from stacking by the bulk of the substituents, while the latter's $(LiN)_4$ cubane core provides an unprecedented example of the stacking of two four-membered $(LiN)_2$ rings.

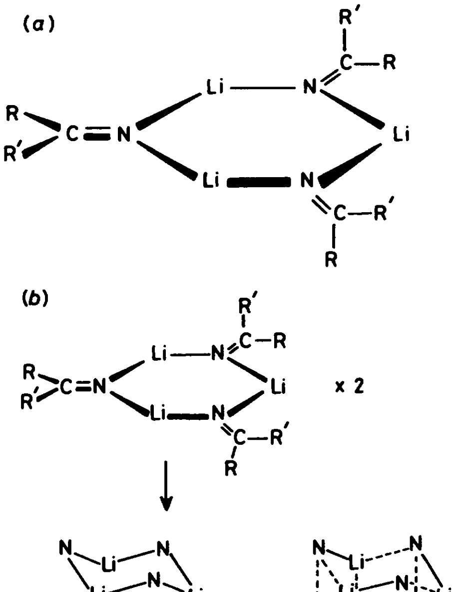

Figure 1. Ligand orientations in iminolithium trimers, (*a*), which allow stacking to form hexamers, (*b*), whereas those in amidolithium trimers, (*c*), prevent stacking

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† Tetra-μ₃-diphenylmethyleneamido-*cyclo*-tetrakis(pyridinelithium) and di-μ-di-t-butylmethyleneamido-bis(hexamethylphosphoramide lithium).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

Table 1. Atomic co-ordinates ($\times 10^4$) for compound (**1**)

Atom	*x*	*y*	*z*
Li	4 298(6)	4 672(5)	5 577(5)
N(1)	4 368(3)	3 549(2)	3 820(2)
C(11)	3 732(3)	2 370(3)	2 916(3)
C(12)	2 765(3)	2 176(3)	1 575(3)
C(13)	2 890(6)	1 002(5)	349(3)
C(14)	1 143(4)	1 992(6)	1 546(5)
C(15)	3 237(5)	3 483(4)	1 503(4)
C(16)	3 870(4)	1 063(3)	3 058(4)
C(17)	5 067(7)	477(5)	2 448(6)
C(18)	4 445(8)	1 523(6)	4 499(5)
C(19)	2 437(7)	−92(5)	2 465(6)
O	2 744(3)	4 336(2)	6 210(2)
P	1 873(1)	4 108(1)	6 991(1)
N(2)	2 220(4)	2 968(3)	7 432(3)
C(21)	3 774(6)	3 195(5)	8 128(5)
C(22)	1 423(8)	1 555(5)	6 750(7)
N(3)	2 216(4)	5 521(3)	8 344(3)
C(31)	2 584(5)	6 862(4)	8 383(5)
C(32)	1 899(7)	5 583(5)	9 521(4)
N(4)	102(3)	3 566(3)	6 187(3)
C(41)	−1 032(7)	3 550(8)	6 838(9)
C(42)	−426(8)	2 990(9)	4 846(6)

Results and Discussion

The metal atoms in the hexameric molecules $(RR'C{=}NLi)_6$ ($R = R' = Bu^t$ or Me_2N; $R = Ph$, $R' = Bu^t$ or Me_2N), being formally involved in three bonds apiece, are in principle co-ordinatively unsaturated. The metal atoms in the cyclic trimers $(RR'C{=}NLi)_3$ of which they are effectively composed would be involved in only two bonds apiece, and be even more co-ordinatively unsaturated. It was therefore expected that these compounds would show some evidence of Lewis acidity, possibly accompanied by deaggregation of the hexamers into trimers or even smaller units. Surprisingly, the hexameric iminolithium species were recovered intact after treatment with various proportions of various bases, including Et_2O, pyridine, $Me_2NCH_2CH_2NMe_2$, and $MeN(CH_2CH_2NMe_2)_2$.[7] However, treatment of $(Bu^t_2C{=}NLi)_6$ with a molar equivalent of $OP(NMe_2)_3$ in hexane–pentane afforded a 1:1 adduct $[Bu^t_2C{=}NLi{\cdot}OP(NMe_2)_3]_2$ (**1**), as highly air- and moisture-sensitive deep yellow crystals. These have been shown by an *X*-ray crystallographic study to contain centrosymmetric molecules, based on $(LiN)_2$ four-membered rings, illustrated in Figure 2. Tables 1 and 2 give atomic co-ordinates and selected interatomic distances and angles, respectively.

The cleavage of the hexamer $(Bu^t_2C{=}NLi)_6$ [effectively a stacked pair of trimers $(Bu^t_2C{=}NLi)_3$] into the co-ordinated dimers of (**1**) appears at first sight surprising. It becomes intelligible if one considers the relative merits of the co-ordination sites offered to Lewis bases (L) by dimers $(R_2C{=}NLi)_2$ on the one hand and trimers $(R_2C{=}NLi)_3$ on the other. The former provide more room for Lewis bases (in that they have a larger 'co-ordination arc,' θ, at lithium) and require less bond-angle modification on co-ordination [Figure 3(*a*)] than the latter [Figure 3(*b*)]. In fact, complexed iminolithium (or, indeed, amidolithium) trimers are unknown. For example, the compound $[(Me_3Si)_2NLi]_n$ is dimeric ($n = 2$) in the gas phase,[8] with a ring angle at lithium, NLiN, of *ca.* 100°, trimeric ($n = 3$) in the crystal,[9] NLiN 148°, but again dimeric as the diethyl ether adduct $[(Me_3Si)_2NLi{\cdot}OEt_2]_2$,[10,11] NLiN 105°. Similarly, the benzylamido compound $[(PhCH_2)_2NLi]_n$, trimeric ($n = 3$) in the crystal, with ring angles at Li of *ca.* 144°, co-ordinates to Et_2O and $OP(NMe_2)_3$ to give dimers ($n = 2$) in which the average ring angle is *ca.* 103°.[12] In compound (**1**), the ring angle at Li is 104.6°.

Table 2. Selected bond lengths (Å) and angles (°) for (**1**)

Li–N(1)	1.948(6)	Li–N(1')	1.923(6)
Li–O	1.858(7)	N(1)–C(11)	1.233(3)
O–P	1.449(3)		
O–Li–N(1)	125.1(2)	N(1)–Li–N(1')	104.6(3)
O–Li–N(1')	125.9(3)	Li–N(1)–Li'	75.4(3)
Li–N(1)–C(11)	136.5(3)	Li'–N(1)–C(11)	147.9(3)
Li–O–P	163.9(3)		

Symmetry operator for primed atoms: $1 - x, 1 - y, 1 - z$.

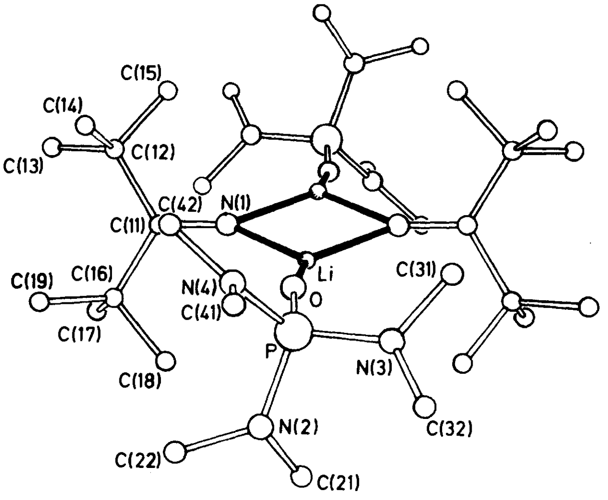

Figure 2. Centrosymmetric molecular structure of the cyclic dimer (**1**), $[Bu^t_2C{=}NLi{\cdot}OP(NMe_2)_3]_2$

Although, as just argued, dimers $(R_2C{=}NLi)_2$ offer more space in which to accommodate Lewis bases co-ordinating to the metal atoms than do trimers $(R_2C{=}NLi)_3$, it is apparent from Figure 2 that (**1**) is a very crowded molecule. Of particular significance are the orientations of the imino ligands with respect to the $(LiN)_2$ ring plane. Ideally, for maximum lithium–nitrogen bond energy, the $C_2C{=}N$ skeleton of the imino residue $R_2C{=}N$ should lie in the $(LiN)_2$ ring plane in iminolithium dimers $(R_2C{=}NLi)_2$ or their adducts $(R_2C{=}NLi{\cdot}L)_2$ [Figure 3(*a*); see also Figure 1(*a*) for iminolithium trimers]. In compound (**1**), however, the $C_2C{=}N$ planes of the imino ligands are orientated at 58.6° with respect to the $(LiN)_2$ ring plane, which orientation, while precluding stacking of two such four-membered rings, allows room for the hexamethylphosphoramide ligands (for which a cone angle of *ca.* 138° is expected) to co-ordinate to the metal atoms through their oxygen atoms, with near-linear POLi arrangements (163.9°) lying in the $(LiN)_2$ ring plane. Evidently the strength of the oxygen to lithium bonds is sufficient to offset not only the loss of Li–N bonding resulting from the distortion from planarity, but also the loss of C–H$\cdots$Li interactions that would be expected in an unco-ordinated dimer $(Bu^t_2C{=}NLi)_2$.

Recent molecular orbital (m.o.) calculations[13,14] have given some indication of the energy losses involved. *Ab initio* calculations at the 6-31G level[13] on the model dimer $(H_2C{=}NLi)_2$ showed the all-planar form to be 17.0 kcal mol^{-1} more stable than the perpendicular one; MNDO calculations[14] gave a much smaller energy difference of 6.8 kcal mol^{-1}. In contrast, for the model amidolithium dimer $(H_2NLi)_2$, the perpendicular form is the more stable (*ca.* 26 kcal mol^{-1} by *ab initio*,[15] 22 kcal mol^{-1} by MNDO[14]).

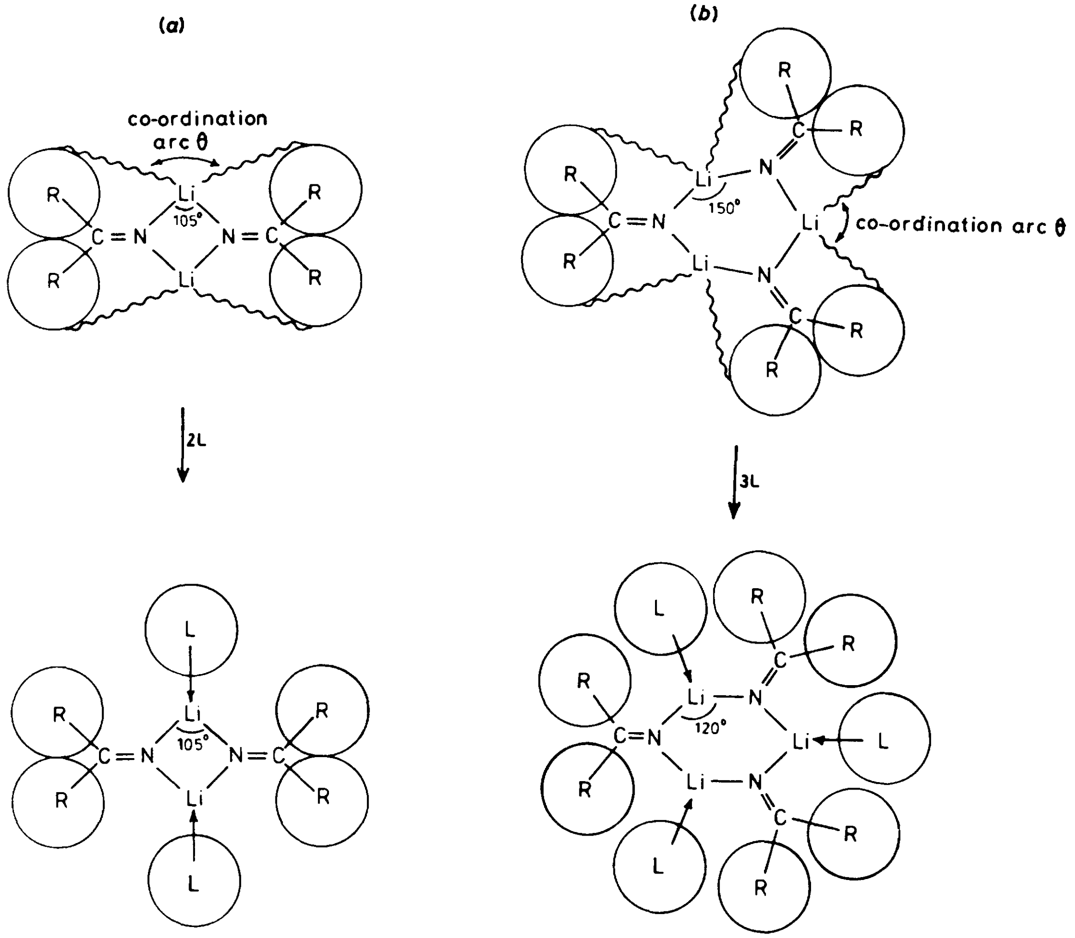

Figure 3. Iminolithium dimers $(R_2C{=}NLi)_2$, (*a*), provide more room (larger co-ordination arc θ) to accommodate ligands L than do trimers $(R_2C{=}NLi)_3$, (*b*)

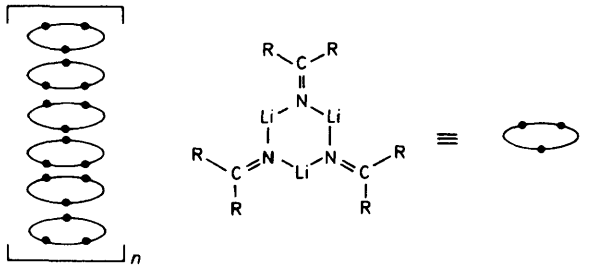

Figure 4. Extended stacking of trimers $(R_2C{=}NLi)_3$ believed to occur in the structures of certain diaryl iminolithium compounds $[(aryl)_2C{=}NLi]_{3n}$

Interestingly, despite the extent to which the imino ligands in compound (**1**) are twisted away from their preferred orientations, the lithium–nitrogen bond lengths reveal no significant bond weakening. Indeed at 1.923(6) and 1.948(6) Å they are as short as any yet found in organonitrogen–lithium ring systems. Formally single Li–N bonds tend to have lengths in the range 1.94—2.02 Å, depending on the co-ordination numbers of the atoms involved, though examples outside these limits are known. The amidolithium complex $[(PhCH_2)_2NLi{\cdot}OP(NMe_2)_3]_2$,[12] for example, has N–Li bonds of length 2.01 Å, connecting atoms of co-ordination numbers four and three respectively, while the monomeric lithioanilide complex $2,4,6\text{-}Bu^t_3C_6H_2NHLi{\cdot}Me_2NCH_2CH_2NMe_2$, in which the lithium and nitrogen atoms are both three-co-ordinate, has an (anilide)nitrogen–lithium bond of length 1.90 Å.[8] In the *ab initio* optimised all-planar model compound $(H_2C{=}NLi)_2$, containing two-co-ordinate metal atoms, the calculated Li–N bond distance is 1.92 Å.[2,13]

While iminolithium compounds $(RR'C{=}NLi)_n$ with no aryl substituents (*e.g.* R = R' = Bu^t or Me$_2$N), or with only one aryl substituent (*e.g.* R = Ph, R' = Bu^t or Me$_2$N), dissolve readily in aromatic solvents, from which they crystallise as hexamers $(RR'C{=}NLi)_6$, all the diaryl iminolithium compounds so far reported (*e.g.* R = R' = Ph or *p*-MeC$_6$H$_4$; R = Ph, R' = *p*-MeC$_6$H$_4$ or *p*-ClC$_6$H$_4$)[7,16,17] are amorphous powders, insoluble in non-donor solvents. For example, $(Ph_2C{=}NLi)_n$ itself is a yellow powder which decomposes at 262—264 °C {contrast $[Ph(Me_2N)C{=}NLi]_6$ which decomposes at 129—131 °C} and which is insoluble in hexane, benzene, or toluene.[7,16] The lower solubility and amorphous nature of the diaryl imino compounds are believed to reflect more highly associated structures composed of extended stacks of cyclic trimers (Figure 4). Though stacks incorporating more than two cyclic trimers [as in the hexamers $(RR'C{=}NLi)_6$] have yet to be characterised in the solid phase for any iminolithium compounds, higher oligomers than hexamers are thought to be present in solutions of some of the compounds known to be hexameric in the crystal, judging by their n.m.r. spectra.[18] Furthermore, more extensive stacking of $(RR'C{=}NLi)_3$ rings

Table 3. Atomic co-ordinates (× 10^4) for compound (**2**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Li(1)	5 551(4)	2 328(4)	7 979(2)	Li(3)	3 158(3)	3 413(2)	7 826(2)
N(111)	6 264(2)	2 064(2)	7 062(1)	N(311)	3 549(2)	3 476(2)	6 822(1)
C(112)	7 257(2)	1 605(2)	6 706(1)	C(312)	2 775(2)	4 146(2)	6 475(1)
C(121)	8 450(2)	1 315(2)	6 913(1)	C(321)	2 266(2)	5 466(2)	6 455(1)
C(122)	9 308(2)	1 565(2)	6 545(1)	C(322)	1 969(2)	6 144(2)	5 909(1)
C(123)	10 363(2)	1 321(2)	6 764(1)	C(323)	1 598(3)	7 324(2)	5 901(2)
C(124)	10 582(3)	804(3)	7 344(2)	C(324)	1 505(3)	7 848(3)	6 429(2)
C(125)	9 753(3)	534(3)	7 706(1)	C(325)	1 785(3)	7 203(2)	6 971(2)
C(126)	8 682(2)	804(2)	7 499(1)	C(326)	2 174(3)	6 021(2)	6 979(1)
C(131)	7 376(2)	1 261(2)	6 043(1)	C(331)	2 292(2)	3 691(2)	6 047(1)
C(132)	6 416(2)	1 835(2)	5 709(1)	C(332)	3 048(2)	2 621(2)	5 785(1)
C(133)	6 466(3)	1 484(3)	5 124(1)	C(333)	2 645(3)	2 144(3)	5 403(1)
C(134)	7 479(3)	551(3)	4 864(1)	C(334)	1 472(4)	2 733(3)	5 283(1)
C(135)	8 449(3)	−25(3)	5 180(1)	C(335)	705(3)	3 775(3)	5 545(1)
C(136)	8 396(2)	328(2)	5 767(1)	C(336)	1 106(2)	4 264(2)	5 925(1)
N(141)	6 430(2)	2 213(2)	8 721(1)	N(341)	1 275(2)	4 070(2)	7 947(1)
C(142)	6 991(3)	2 839(3)	8 693(2)	C(342)	417(3)	4 949(3)	8 265(1)
C(143)	7 534(3)	2 889(3)	9 180(2)	C(343)	−789(3)	5 282(3)	8 299(2)
C(144)	7 494(3)	2 258(4)	9 702(2)	C(344)	−1 130(3)	4 676(3)	7 989(2)
C(145)	6 943(4)	1 602(4)	9 739(2)	C(345)	−265(3)	3 776(3)	7 652(2)
C(146)	6 411(3)	1 621(3)	9 247(1)	C(346)	916(2)	3 495(2)	7 650(1)
Li(2)	4 830(4)	3 824(4)	7 074(2)	Li(4)	4 776(4)	1 841(3)	7 034(2)
N(211)	4 203(2)	4 145(2)	7 995(1)	N(411)	4 286(2)	1 723(2)	8 034(1)
C(212)	3 917(2)	4 888(2)	8 397(1)	C(412)	4 307(2)	870(2)	8 376(1)
C(221)	4 564(2)	5 591(2)	8 419(1)	C(421)	5 455(2)	−106(2)	8 585(1)
C(222)	4 926(2)	6 066(2)	7 885(1)	C(422)	5 462(2)	−593(2)	9 189(1)
C(223)	5 569(2)	6 669(2)	7 908(1)	C(423)	6 527(3)	−1 378(3)	9 403(2)
C(224)	5 843(2)	6 793(2)	8 458(2)	C(424)	7 588(3)	−1 709(3)	9 014(2)
C(225)	5 487(3)	6 337(3)	8 992(2)	C(425)	7 609(3)	−1 272(3)	8 405(2)
C(226)	4 828(3)	5 748(3)	8 978(1)	C(426)	6 540(2)	−466(2)	8 198(1)
C(231)	2 886(2)	5 158(2)	8 918(1)	C(431)	3 195(2)	731(2)	8 621(1)
C(232)	2 787(3)	4 296(3)	9 311(1)	C(432)	3 183(2)	−303(2)	8 559(1)
C(233)	1 846(4)	4 550(4)	9 784(2)	C(433)	2 142(3)	−410(3)	8 762(1)
C(234)	967(3)	5 657(3)	9 877(1)	C(434)	1 127(3)	491(3)	9 040(1)
C(235)	1 010(3)	6 534(3)	9 489(1)	C(435)	1 132(3)	1 516(3)	9 103(1)
C(236)	1 978(2)	6 286(2)	9 017(1)	C(436)	2 152(2)	1 629(2)	8 891(1)
N(241)	5 652(2)	4 635(2)	6 452(1)	N(441)	4 925(2)	302(2)	6 726(1)
C(242)	6 680(3)	4 496(2)	6 586(1)	C(442)	3 966(2)	150(2)	6 878(1)
C(243)	7 398(3)	4 892(3)	6 207(2)	C(443)	3 888(3)	−796(3)	6 735(2)
C(244)	7 045(3)	5 444(2)	5 655(1)	C(444)	4 858(3)	−1 634(3)	6 412(1)
C(245)	6 000(3)	5 592(2)	5 500(1)	C(445)	5 878(3)	−1 525(3)	6 250(2)
C(246)	5 328(3)	5 178(2)	5 909(1)	C(446)	5 873(3)	−537(3)	6 415(2)

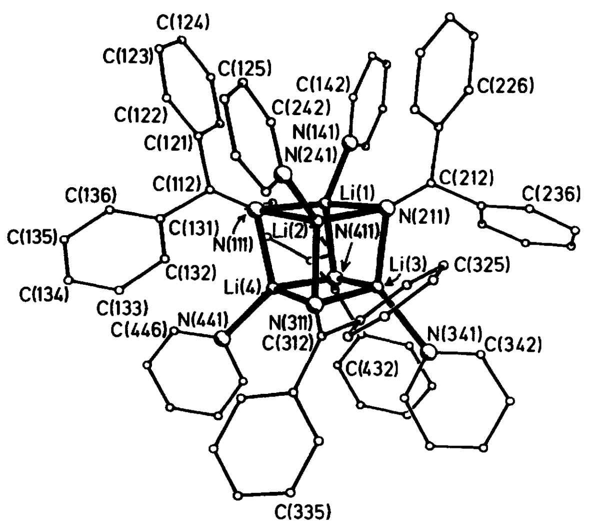

Figure 5. Cubane-type molecular structure of the tetrameric pyridine adduct (**2**), $(Ph_2C{=}NLi{\cdot}NC_5H_5)_4$

beyond two such, while increasing lithium's co-ordination number (with respect to nitrogen) from three in hexamers to four in the inner rings of the higher oligomer, would presumably weaken individual Li–N bonds, including those between constituent rings. This might explain therefore why diaryl imino compounds dissolve in various donor solvents from which they can be recovered as crystalline oligomeric adducts. For example, $(Ph_2C{=}NLi)_n$ gives such adducts when treated with the Lewis bases tetrahydrofuran,[16] pyridine,[6,7,16] hexamethylphosphoramide,[7,19] and 1,4-diazabicyclo[2.2.2]octane.[7] The first of these to be structurally characterised, the tetrameric pyridine adduct, $(Ph_2C{=}NLi{\cdot}NC_5H_5)_4$ (**2**), has a Li_4N_4 cubane-type structure, various aspects of which are shown in Figures 5—8.

The view of the molecule shown in Figure 5 emphasises the skeletal geometry in which two interpenetrating Li_4 and N_4 tetrahedra (the latter being the larger) generate a distorted Li_4N_4 cubane core in which the bond angles at lithium and nitrogen lie in the ranges 94—105 and 75—83° respectively (atomic co-ordinates and selected interatomic distances and angles are given in Tables 3 and 4 respectively). The C=N bond lengths in the imino ligands (1.260—1.264 Å) are normal for

Table 4. Selected bond lengths (Å) and angles (°) for compound (**2**)

Li(1)–N(111)	2.035(4)	Li(2)–N(111)	2.152(4)
Li(1)–N(211)	2.171(4)	Li(2)–N(211)	2.034(5)
Li(1)–N(411)	2.096(6)	Li(2)–N(311)	2.067(6)
Li(3)–N(211)	2.079(6)	Li(4)–N(111)	2.068(6)
Li(3)–N(311)	2.154(5)	Li(4)–N(311)	2.019(4)
Li(3)–N(411)	2.034(4)	Li(4)–N(411)	2.165(5)
Li(1)–N(141)	2.075(5)	Li(2)–N(241)	2.076(6)
Li(3)–N(341)	2.104(5)	Li(4)–N(441)	2.114(6)
N(111)–C(112)	1.263(3)	N(211)–C(212)	1.260(4)
N(311)–C(312)	1.264(3)	N(411)–C(412)	1.264(3)
N(111)–Li(1)–N(141)	127.4(2)	N(111)–Li(1)–N(211)	104.0(2)
N(141)–Li(1)–N(211)	101.2(2)	N(111)–Li(1)–N(411)	100.1(2)
N(141)–Li(1)–N(411)	123.4(2)	N(211)–Li(1)–N(411)	94.1(2)
N(111)–Li(2)–N(211)	104.7(2)	N(111)–Li(2)–N(241)	100.6(2)
N(211)–Li(2)–N(241)	127.3(3)	N(111)–Li(2)–N(311)	96.9(2)
N(211)–Li(2)–N(311)	100.6(2)	N(241)–Li(2)–N(311)	121.4(2)
N(211)–Li(3)–N(311)	96.4(2)	N(211)–Li(3)–N(341)	130.9(2)
N(311)–Li(3)–N(341)	100.8(2)	N(211)–Li(3)–N(411)	98.8(2)
N(311)–Li(3)–N(411)	101.7(2)	N(341)–Li(3)–N(411)	121.7(3)
N(111)–Li(4)–N(311)	101.2(2)	N(111)–Li(4)–N(411)	96.8(2)
N(311)–Li(4)–N(411)	101.9(2)	N(111)–Li(4)–N(441)	122.5(2)
N(311)–Li(4)–N(441)	125.9(3)	N(411)–Li(4)–N(441)	102.8(2)
Li(1)–N(111)–C(112)	142.1(2)	Li(1)–N(111)–Li(2)	75.7(2)
C(112)–N(111)–Li(2)	130.0(2)	Li(1)–N(111)–Li(4)	82.0(2)
C(112)–N(111)–Li(4)	126.1(2)	Li(2)–N(111)–Li(4)	77.8(2)
Li(1)–N(211)–Li(2)	75.3(2)	Li(1)–N(211)–C(212)	129.4(2)
Li(2)–N(211)–C(212)	142.0(3)	Li(1)–N(211)–Li(3)	80.5(2)
Li(2)–N(211)–Li(3)	81.4(2)	C(212)–N(211)–Li(3)	126.2(2)
Li(2)–N(311)–Li(3)	78.8(2)	Li(2)–N(311)–C(312)	123.7(2)
Li(3)–N(311)–C(312)	123.2(2)	Li(2)–N(311)–Li(4)	80.8(2)
Li(3)–N(311)–Li(4)	78.3(2)	C(312)–N(311)–Li(4)	148.0(2)
Li(1)–N(411)–Li(3)	83.3(2)	Li(1)–N(411)–Li(4)	78.3(2)
Li(3)–N(411)–Li(4)	77.7(2)	Li(1)–N(411)–C(412)	124.5(2)
Li(3)–N(411)–C(412)	141.2(2)	Li(4)–N(411)–C(412)	129.7(2)

carbon–nitrogen double bonds, so the triply bridging role played by each imino ligand over a face of the tetrahedral Li$_4$ core is clearly achieved with no reduction of the carbon–nitrogen bond order. Rather, each imino ligand evidently acts as a source of just three electrons for skeletal bonding, so the Li$_4$N$_4$ core is held together by a total of 16 electrons, *i.e.* eight pairs, which is still twice as many electrons as are usually associated with the skeletal bonding in structurally analogous organolithium compounds like (EtLi)$_4$,[20] (MeLi)$_4$·2Me$_2$NCH$_2$CH$_2$NMe$_2$,[21] (PhLi·OEt$_2$)$_4$,[22] and (PhC≡CLi)$_4$·2Me$_2$N(CH$_2$)$_6$NMe$_2$.[23] [Compound (**2**) is incidentally the first Li$_4$N$_4$ cubane species to have been structurally characterised, although a similar skeleton was deduced for (LiNCS)$_4$ from its vibrational spectra in ether and amine solutions.[24]]

The manner in which the eight skeletal electron pairs hold the Li$_4$N$_4$ skeleton of (**2**) together can readily be inferred from an examination of the metal–nitrogen distances and imino ligand planes. The twelve Li–N edges of the Li$_4$N$_4$ 'cube' have lengths that fall into three well defined, distinct categories, four short [Li(1)–N(111), Li(2)–N(211), Li(3)–N(411), and Li(4)–N(311), mean 2.03 Å], four long [Li(1)–N(211), Li(2)–N(111), Li(3)–N(311), and Li(4)–N(411), mean 2.16 Å], and the remainder of intermediate length (2.08 Å). From Figure 6 we can see that the short Li–N bonds are arranged alternately about two opposite faces of the cube, those defined by atoms Li(1), N(111), Li(2), and N(211) on the one hand and Li(3), N(411), Li(4), and N(311) on the other. The intermediate-length Li–N bonds link these faces to each other.

Our interpretation of these edge lengths is that the Li$_4$N$_4$ cubane structure of (**2**) can be regarded as resulting from the stacking of one (Ph$_2$C=NLi·NC$_5$H$_5$)$_2$ dimer on top of another, aligned so as to superimpose the metal atoms of one dimer over two of the Li–N bonds in the other dimer. Bonds eclipsed by metal atoms are formally converted from two- into three-centre bonds, and are accordingly lengthened from *ca.* 2.03 to *ca.* 2.16 Å. Bonds not so eclipsed retain a length (*ca.* 2.03 Å) appropriate for two-centre bonds. The links between the two original (LiN)$_2$ rings, all of which are formally involved in three-centre bonds, are of intermediate length (Figure 6).

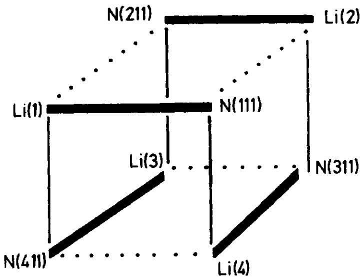

Figure 6. The Li$_4$N$_4$ skeleton of compound (**2**), showing the three types of Li • • • N cube edges

Support for this interpretation of the skeletal bonding is provided by the orientations of the bridging imino groups, illustrated in Figures 7 and 8. Figure 7(*a*)—(*c*) shows views of the complete molecule from the three possible directions linking Li$_2$N$_2$ face centres of the Li$_4$N$_4$ cube. It is immediately apparent that, whereas the views in 7(*b*) and 7(*c*), looking from above the Li(2)Li(4) and Li(2)Li(3) faces respectively, are similar, the view from above the face containing atoms Li(1) and Li(2) is unique. It is this direction that was identified above, purely on the grounds of the Li–N distances, as the stacking direction, looking through one (LiN)$_2$ ring dimer down towards the other, whereas views 7(*b*) and 7(*c*) are both perpendicular to the stacking direction.

The precise alignment of each μ_3-Ph$_2$C=N group with respect to the three metal atoms it bridges, not easily seen from Figure 7, is shown in Figure 8 in the form of the view down each ligand C=N bond on to the bridged Li$_3$ triangle uncluttered by other atoms or groups. If the imino ligands are treated as anions Ph$_2$C=N$^-$, they have two lone pairs of electrons on the nitrogen atom available for co-ordination to the metal atoms. These lone pairs lie in the C$_2$C=N skeletal plane of the ligand, so their orientations are eclipsed, in Figure 8, by the bonds from the azomethine carbon atom to the phenyl groups. A metal atom that is eclipsed, or nearly eclipsed, by these bonds in Figure 8 is therefore suitably located to form a two-centre two-electron LiN bond to the azomethine nitrogen atom, while pairs of metal atoms that straddle the ligand plane are suitably located to be involved in three-centre Li$_2$N bonds.

The ligand alignments in Figure 8 show a consistent pattern. In each case, the metal atom uppermost is that which forms the longest Li–N bond. Significantly, this metal atom is also the one furthest from the ligand C$_2$C=N plane. The remaining two metal atoms in each triangle, the basal pair, are located close to the ligand plane, which is however tilted slightly in a manner to favour bonding to one metal atom. For the ligands bonding through atoms N(111), N(311), and N(411), the metal atom most nearly eclipsed forms the shortest (two-centre) Li–N bond. Only one ligand, that bonding through atom N(211), deviates slightly from this pattern, by forming an intermediate-length Li–N bond (2.08 Å) to the metal atom most nearly eclipsed. For the structural and bonding pattern we have outlined to be complete, this one imino ligand would need to be rotated some 20° anticlockwise about its C=N bond.

Finally, it is interesting to compare the stacking of $(\mathrm{LiN})_2$ rings in compound (**2**) with the stacking of $(\mathrm{LiN})_3$ rings in hexamers such as $[\mathrm{Ph(Me_2N)C{=}NLi}]_6$. Both require the conversion of alternate two-centre Li–N bonds in the parent ring into three-centre $\mathrm{Li_2N}$ bonds within and between the rings. However, the actual bond lengths, and their sequences, differ. If we classify the Li–N links as (*a*) two-centre bonds within a parent ring, (*b*) three-centre links within a parent ring, and (*c*) three-centre links between rings, then their average lengths in $[\mathrm{Ph(Me_2N)C{=}NLi}]_6$ are 1.97, 2.01, and 2.06 Å respectively; *cf.* 2.03, 2.16, and 2.08 Å respectively in (**2**). The greater lengths of the bonds in compound (**2**) may be related to the presence of the *exo*-pyridine ligands, which raise the metal co-ordination numbers relative to those in the hexamer. However, the different sequences, (*a*) < (*b*) < (*c*) for the hexamer and (*a*) < (*c*) < (*b*) for (**2**), suggest that the ring association is stronger in (**2**) than in the hexamer, though at the expense of the residual three-centre bonding within the rings. Again, the reason for these differences in the bond lengths can be traced to different imino ligand orientations. Those in compound (**2**), as already outlined (Figure 8) favour bonding to one metal of the original ring and then a metal of the other ring, leaving the bonding to the second adjacent metal of the original ring relatively weak, whereas in the hexamer $[\mathrm{Ph(Me_2N)C{=}NLi}]_6$ bonding to the second ring atom is favoured relative to that to the other ring. In turn, the reason for these differences in ligand orientations is presumably the need in (**2**) to accommodate the pyridine ligands not present in the hexamer. The way the flat pyridine ligands can be accommodated between the similarly flat rings of the $\mathrm{Ph_2C{=}N}$ ligands in (**2**) is illustrated by Figures 5 and 7.

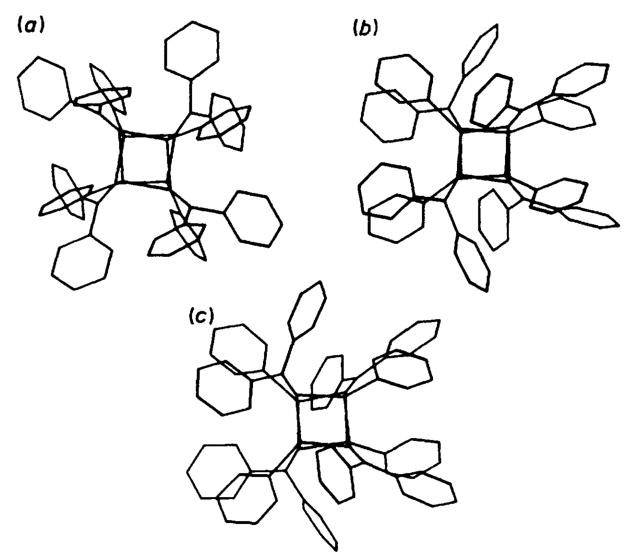

Figure 7. The ligand orientations in compound (**2**), when viewed through the face containing lithium atoms (*a*) (1) and (2), (*b*) (2) and (4), and (*c*) (2) and (3)

Experimental

Standard inert-atmosphere techniques were used for the preparation and characterisation of compounds (**1**) and (**2**). Analytical values were determined using a Perkin-Elmer 240 elemental analyser (C, H, and N) and a 360 Perkin-Elmer atomic absorption spectrometer (Li).

Synthesis of $(\mathrm{Bu^t{}_2C{=}NLi{\cdot}hmpa})_2$, (**1**).—A pentane solution of t-butyl-lithium (7.1 cm^3 of a 1.40 mol dm^{-3} solution, 10 mmol) was added to a chilled hexane solution of t-butyl cyanide (0.83 g, 10 mmol). Warming to room temperature gave a pale yellow solution of $(\mathrm{Bu^t{}_2C{=}NLi})_6$.[1,2] Addition of hmpa (1.79 g, 10 mmol) caused a deepening of the yellow colour and, on stirring, the precipitation of a yellow solid. This redissolved on treatment with a few drops of toluene and, after filtration, cooling of the solution to 0 °C produced fine yellow crystals of complex (**1**); yield 90%, m.p. 128—130 °C (Found: C, 55.2; H, 10.8; Li, 2.1; N, 16.8; P, 10.4. $\mathrm{C_{15}H_{36}LiN_4OP}$ requires C, 55.2; H, 11.0; Li, 2.2; N, 17.2; P, 9.5%).

Synthesis of $(\mathrm{Ph_2C{=}NLi{\cdot}NC_5H_5})_4$, (**2**).—A solution of benzonitrile (1.03 g, 10 mmol) in hexane (5 cm^3) was added by syringe to a frozen solution of phenyl-lithium (5.0 cm^3 of a 2.0 mol dm^{-3} solution in diethyl ether–benzene, 10 mmol). Warming to room temperature produced a deep red solution [of $(\mathrm{Ph_2C{=}NLi})_n$ or

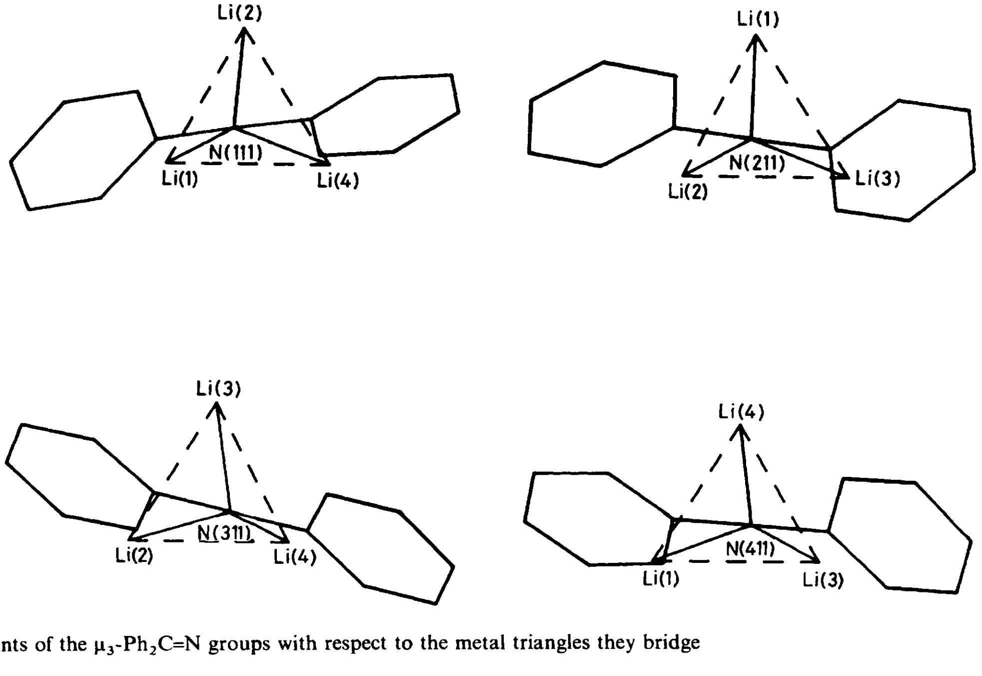

Figure 8. Alignments of the μ_3-$\mathrm{Ph_2C{=}N}$ groups with respect to the metal triangles they bridge

its diethyl ether complex].[16] Addition of pyridine (0.79 g, 10 mmol) caused precipitation of a red powder which redissolved when treated with warm toluene (2 cm^3). Cooling to room temperature afforded deep red rhomboid crystals of (**2**); yield 88%, m.p. 108—110 °C (Found: C, 79.7; H, 5.7; Li, 2.9; N, 10.0. $C_{18}H_{15}LiN_2$ requires C, 81.2; H, 5.6; Li, 2.6; N, 10.5%).

Crystal-structure Determinations.—Crystals of complexes (**1**) and (**2**) suitable for *X*-ray analysis were transferred in a nitrogen-filled glove-box to glass Lindemann capillary tubes which were then sealed prior to data collection. All *X*-ray diffraction computer programs used in this study were written by W. C. and Professor G. M. Sheldrick. Calculations were performed on a Data General Eclipse S/250 computer.

Crystal data for compound (**1**). $C_{30}H_{72}Li_2N_8O_2P_2$, $M = 652.78$, triclinic, $a = 9.505(1)$, $b = 11.128(2)$, $c = 12.015(3)$ Å, $\alpha = 115.95(1)$, $\beta = 101.91(1)$, $\gamma = 98.22(2)°$, $U = 1\,078.1$ Å^3 (from 2θ values of 40 reflections centred at $\pm\omega$), $T = 291$ K, Mo-K_α radiation, $\lambda = 0.710\,69$ Å, space group $P\bar{1}$, $F(000) = 360$, $Z = 1$ dimer, $D_c = 1.005$ g cm^{-3}. Yellow crystal, $0.4 \times 0.4 \times 0.8$ mm, $\mu = 1.29$ cm^{-1}.

Data collection and processing. Stoe-Siemens AED diffractometer, ω—θ scan mode with on-line profile fitting,[25] $2\theta_{max.} = 50°$, no absorption or extinction corrections, no significant variation in standard reflection intensities. 3 798 Reflections (no equivalents), 2 719 with $F > 4\sigma(F)$.

Structure analysis and refinement. Direct methods and difference syntheses, blocked-cascade refinement on F, $w^{-1} = \sigma^2(F) + 0.0018\,F^2$ optimised automatically, rigid Me groups with C–H 0.96 Å, H–C–H 109.5°, $U_{iso}(H) = 1.2U_{eq.}(C)$, anisotropic thermal parameters for other atoms. Final $R = 0.070$, $R' = (\Sigma w\Delta^2/\Sigma wF_o^2)^{\frac{1}{2}} = 0.102$, max. (shift/e.s.d.) = 0.004, mean = 0.001, max. peak in final difference synthesis = 0.25 e Å^{-3}, scattering factors from ref. 26. Programs: SHELXTL,[27] diffractometer control program by W. C.

Crystal data for compound (**2**). $C_{72}H_{60}Li_4N_8$, $M = 1\,065.1$, triclinic, $a = 12.764(3)$, $b = 13.134(2)$, $c = 21.750(3)$ Å, $\alpha = 83.47(2)$, $\beta = 79.82(2)$, $\gamma = 61.30(2)°$, $U = 3\,146.2$ Å^3 (from 24 reflections), $T = 291$ K, Mo-K_α radiation, $\lambda = 0.710\,69$ Å, space group $P\bar{1}$, $F(000) = 1\,120$, $Z = 2$ tetramers, $D_c = 1.124$ g cm^{-3}. Red crystal, $0.58 \times 0.54 \times 0.80$ mm, $\mu = 0.61$ cm^{-1}.

Data collection and processing. As for (**1**), $2\theta_{max.} = 45°$, 8 194 reflections, 6 210 with $F > 3\sigma(F)$.

Structural analysis and refinement. As for (**1**), $w^{-1} = \sigma^2(F) + 0.00056\,F^2$, H atoms on external bisectors of ring angles, C–H 0.96 Å, $U_{iso}(H) = 1.2U_{eq.}(C)$. Final $R = 0.056$, $R' = 0.059$, max. (shift/e.s.d.) = 0.005, mean = 0.001, max. difference peak = 0.16 e Å^{-3}.

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References

1 D. Barr, W. Clegg, R. E. Mulvey, R. Snaith, and K. Wade, *J. Chem. Soc., Chem. Commun.*, 1986, 295.
2 D. R. Armstrong, D. Barr, R. Snaith, W. Clegg, R. E. Mulvey, K. Wade, and D. Reed, *J. Chem. Soc., Dalton Trans.*, 1987, 1071.
3 D. R. Armstrong, D. Barr, W. Clegg, R. E. Mulvey, D. Reed, R. Snaith, and K. Wade, *J. Chem. Soc., Chem. Commun.*, 1986, 869.
4 See, for a review, W. Setzer and P. v. R. Schleyer, *Adv. Organomet. Chem.*, 1985, **24**, 353.
5 D. Barr, W. Clegg, R. E. Mulvey, D. Reed, and R. Snaith, *Angew. Chem., Int. Ed. Engl.*, 1985, **24**, 328.
6 D. Barr, W. Clegg, R. E. Mulvey, and R. Snaith, *J. Chem. Soc., Chem. Commun.*, 1984, 79.
7 R. E. Mulvey, Ph.D. Thesis, University of Strathclyde, 1984.
8 T. Fjeldberg, P. B. Hitchcock, M. F. Lappert, and A. J. Thorne, *J. Chem. Soc., Chem. Commun.*, 1984, 822.
9 R. D. Rogers, J. L. Atwood, and R. Grüning, *J. Organomet. Chem.*, 1978, **157**, 229.
10 M. F. Lappert, M. J. Slade, A. Singh, J. L. Atwood, R. D. Rogers, and R. Shakir, *J. Am. Chem. Soc.*, 1983, **105**, 302.
11 L. M. Engelhardt, A. S. May, C. L. Raston, and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1983, 1671.
12 D. Barr, W. Clegg, R. E. Mulvey, and R. Snaith, *J. Chem. Soc., Chem. Commun.*, 1984, 285.
13 D. R. Armstrong and G. T. Walker, *J. Mol. Struct.*, 1986, **137**, 235.
14 J. Kaneti, P. v. R. Schleyer, T. Clark, A. J. Kos, G. W. Spitznagel, J. G. Andrade, and J. B. Moffat, *J. Am. Chem. Soc.*, 1986, **108**, 1481.
15 A-M. Sapse, E. Kaufmann, P. v. R. Schleyer, and R. Gleiter, *Inorg. Chem.*, 1984, **23**, 1569.
16 I. Pattison, K. Wade, and B. K. Wyatt, *J. Chem. Soc. A*, 1968, 837.
17 L-H. Chan and E. G. Rochow, *J. Organomet. Chem.*, 1967, **9**, 231.
18 D. Barr, R. Snaith, R. E. Mulvey, K. Wade, and D. Reed, *Magn. Reson. Chem.*, 1986, **24**, 713.
19 D. Barr, W. Clegg, R. E. Mulvey, and R. Snaith, *J. Chem. Soc., Chem. Commun.*, 1984, 226.
20 H. Dietrich, *J. Organomet. Chem.*, 1981, **205**, 291.
21 D. Thönnes and E. Weiss, *Chem. Ber.*, 1978, **111**, 3157.
22 H. Hope and P. P. Power, *J. Am. Chem. Soc.*, 1983, **105**, 5320.
23 B. Schubert and E. Weiss, *Angew. Chem., Int. Ed. Engl.*, 1983, **22**, 496.
24 M.Chabanel, M. Luçon, and D. Paoli, *J. Phys. Chem.*, 1981, **85**, 1058.
25 W. Clegg, *Acta Crystallogr., Sect. A*, 1981, **37**, 22.
26 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4, pp. 99, 149.
27 G. M. Sheldrick, SHELXTL: an integrated system for solving, refining, and displaying crystal structures from diffraction data, University of Göttingen, 1978.

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