Neutral isonitrile adducts of alkali and alkaline earth metals‡

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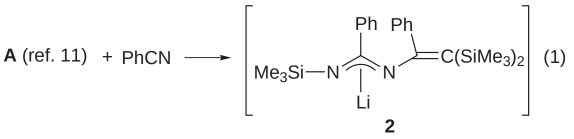
Isonitriles are shown to form stable neutral adducts with some group 1 and 2 metal complexes; the synthesis and structures of $[\overline{\mathrm{Li\{N(R)C(Ph)N}}\mathrm{C(Ph){=}CR_2\}(CNPh)}]_2$, $[\mathrm{LiNR_2(CNPh)}]_2$, $[\mathrm{Mg(CHR_2)_2(CNC_6H_3Me_2\text{-}2,6)_2}]$ and $[\mathrm{Mg(CHR_2)(\mu\text{-}Br)(CNBu^t)}]_2$ are described ($R = SiMe_3$).

Nitriles and isonitriles are important in transition metal chemistry and nitriles also in the coordination chemistry of main group elements.[1] In contrast, isonitrile adducts of main group elements are rare. They include early reports on labile adducts of trialkyl- or triaryl-boranes,[2] $[\mathrm{AlPh_3\{CN(\mathit{c}\text{-}C_6H_{11})\}}]$[3] and polyhedral boranes.[4] Recently, X-ray structures of $[\mathrm{Al(C_5H_5)_3(CNBu^t)}]$,[5] the labile $[\mathrm{BPh_3\{CNC_6H_4(OSiMe_3)\text{-}4\}}]$[6] and $[\overline{\mathrm{B(C_6F_5)(CNAr)\{N(Bu^t)B(C_6F_5)N(Bu^t)C}}\mathrm{{=}NAr\}}]$[7] have been published; and spectroscopic evidence has been provided for the labile $[\mathrm{SiR^1R^2(CNR^3)}]$ [$R^1 = \mathrm{C_6H_2\{CH(SiMe_3)_2\}_3}$-2,4,6; $R^2 = \mathrm{C_6H_2Me_3}$-2,4,6; and $R^3 = R^2$, $\mathrm{Pr^i}$ or $\mathrm{C_6H_2Bu^t_3}$-2,4,6][8] and the 1 : 1 adducts of $\mathrm{LiCH(SiMe_3)_2}$ and $[\overline{\mathrm{Li\{N(Bu^t)C(SiMe_3)C(H)C(SiMe_3)NBu^t}}\mathrm{\}(CNR')}]$ ($R' = \mathrm{Bu^t}$ or $\mathrm{C_6H_3Me_2}$-2,6).[9] Boche and coworkers have described the anionic isonitrile complex $[\mathrm{Li(CNPh_2)\{(-)\text{-}sparteine\}(thf)_2}]$ ($\mathrm{thf = OC_4H_8}$).[10] We now report the first thermally stable and structurally authenticated complexes of lithium and magnesium in which an isonitrile acts as a neutral ligand.

Addition of an isonitrile R′NC to $\mathrm{Li\{N(R)C(Ph){=}CR_2\}(thf)}$ **A**[11] yielded (Scheme 1, step i) the enamide **1a** ($R' = c\text{-}\mathrm{C_6H_{11}}$) or **1b** ($R' = \mathrm{C_6H_3Me_2}$-2,6), while **A** with PhCN gave [eqn. (1)] the 1,3-diazaallyl **2** which with PhNC gave (Scheme 1, step ii) the dimeric 1 : 1 adduct **3** ($R = \mathrm{SiMe_3}$).

Walborsky and Ronman have shown that treatment of an isonitrile R′NC with a lithium alkyl or a Grignard reagent derived from an alkyl halide R″Hal gave the metallo-aldimine, which was a convenient source of various organic compounds (*e.g.* see ref. 12). Surprisingly, we now find that the new Grignard reagent $[\mathrm{Mg(\mu\text{-}Br)(CHR_2)(OEt_2)}]_2$ **4** with an isonitrile R′NC simply gave (Scheme 1, step iii) the 1 : 1 adduct $[\mathrm{Mg(\mu\text{-}Br)(CHR_2)(CNR')}]_2$ ($R' = \mathrm{Bu^t}$ **5a** or $\mathrm{C_6H_3Me_2}$-2,6 **5b**). Even when heated, the latter did not undergo an isomerisation to yield the insertion product, a magnesio-aldimine. Likewise, $\mathrm{Mg(CHR_2)_2}$[13] and R′NC gave (Scheme 1, step iv) the thermally stable adduct $[\mathrm{Mg(CHR_2)_2(CNR')_2}]$ ($R' = \mathrm{Bu^t}$ **6a** or $\mathrm{C_6H_3Me_2}$-2,6 **6b**). These results are all the more unexpected since $\mathrm{LiCHR_2}$ readily underwent insertion reactions with the same isonitriles.[9] On the other hand, we now show that the isoelectronic $\mathrm{LiNR_2}$ and PhNC gave (Scheme 1, step v) the adduct $[\mathrm{LiNR_2(CNPh)}]_2$ **7**, whereas[14] $\mathrm{LiNR_2}$ + PhCN readily yielded the benzamidinate insertion product $[\overline{\mathrm{Li\{N(R)C(Ph)N}}\mathrm{R\}}]_2$.



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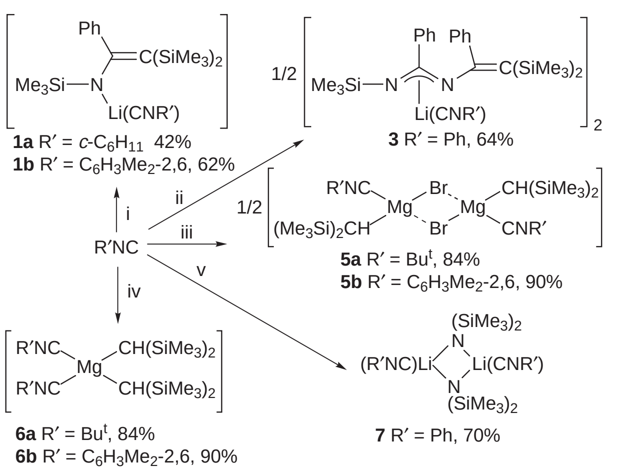

Scheme 1 Synthesis of the isonitrile adducts **1**–**7**. *Reagents and conditions*: i, **A**, $\mathrm{Et_2O}$; ii, **2**, $\mathrm{Et_2O}$; iii, $[\mathrm{Mg(\mu\text{-}Br)\{CH(SiMe_3)_2\}(OEt_2)}]_2$ **4**, PhMe; iv, $\mathrm{Mg[CH(SiMe_3)_2]_2}$, PhMe; v, $\mathrm{Li[N(SiMe_3)_2]}$, $\mathrm{C_5H_{12}}$. Reagents were mixed at −78 °C or −35 °C; the mixture was then brought to *ca.* 25 °C.

The new, pale yellow (**5**) or colourless, highly air-sensitive, readily hydrocarbon-soluble, crystalline solids **1**–**7** gave satisfactory analyses and NMR and IR spectra. Their formulation as isonitrile adducts (rather than insertion products) is consistent with the low frequency shift ($\Delta\delta$) of the $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR spectral signal [$\delta(\mathrm{R'NC})$] and the increase ($\Delta\nu$) in the NC stretching mode $\nu(\mathrm{R'N{\equiv}C})$ for each of **1**–**7** compared with the value in the free ligand R′NC, Table 1. The trends in $\Delta\delta[^{13}\mathrm{C}\{^1\mathrm{H}\}]$ and $\Delta\nu(\mathrm{NC})$ for $(\mathrm{R'NC})\mathrm{ML}_n$ (**1**–**7**) indicate, in valence bond terms, that (*i*) the triply bonded canonical form is more significant in the complex ($\mathrm{R'N^+{\equiv}C^-ML}_n \leftrightarrow \mathrm{R'N{=}C{=}ML}_n$) than in the free ligand ($\mathrm{R'N^+{\equiv}C^-} \leftrightarrow \mathrm{R'N{=}C{:}}$), and (*ii*) the largest values for $\Delta\delta[^{13}\mathrm{C}\{^1\mathrm{H}\}]$ and $\Delta\nu(\mathrm{NC})$ are found for the strongest Lewis acid ML_n in accord with the inequality sequence $\mathrm{Mg(Br)CHR_2} > \mathrm{Mg(CHR_2)_2} > \mathrm{Li(NR_2)} > \mathrm{Li[N(R)C(Ph){=}CR_2]}$. A cumulene-type canonical form for an isonitrile-transition metal complex is significant when M can participate in $d_\pi \rightarrow \pi^*$ bonding, as in the d^8 $[\mathrm{Ni(CNAr)_4}]^{2+}$ [$\Delta\nu(\mathrm{NC})$ negative], in contrast to, *e.g.* the d^2 $[\mathrm{Mo[CN]_4(CNMe)_4}]$, having $\Delta\nu(\mathrm{NC})$ positive.[1]

The X-ray molecular structures of complexes **3** and **6b** are shown in Figs. 1 and 2; those of **5a** and **7** will appear in a full paper.§ In each, the M–C–NR′ and C–N–R′ vectors are close to linear, and the short R′N–C distances are consistent with NC being a triple bond. The trends in the latter (d_{NC}, Table 1) are consistent with the above inequality sequence. The centrosym-

Table 1 Some important structural and spectroscopic data for compounds **1**–**7** and the isonitriles R′NC

	Property				
Compound	$\delta(^{13}\mathrm{C_{NC}})$	$\Delta\delta(^{13}\mathrm{C})$	ν_{NC}/ cm^{-1}	$\Delta\nu_{\mathrm{NC}}$	d_{NC}/Å
7	156.4	10.7	2170	43	1.148(5) (av.)
3	166.3	0.8	2165	38	1.157(4)
PhNC	167.1		2127		—
5b	135.8	35.0	2191	76	—
6b	156.4	14.4	2173	58	1.14(1) (av.)
1b	163.6	7.2	—	—	—
$2,6\text{-}\mathrm{Me_2C_6H_3NC}$	170.8		2115		—
5a	135.4	20.6	2216	76	1.07(2)
6a	141.8	14.2	2201	58	—
$\mathrm{Bu^tNC}$	154.0		2136		—

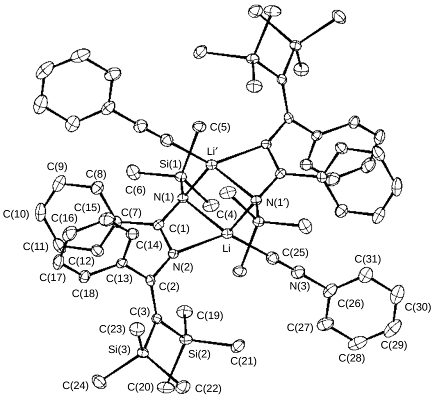

Fig. 1 Molecular structure of **3** with selected bond distances (Å) and angles (°): Li–N(1) 2.174(5), Li–N(2) 2.035(5), Li–N(1′) 2.115(5), Li–C(25) 2.178(6), N(3)–C(25) 1.157(4); N(3)–C(25)–Li 171.4(3), C(25)–N(3)–C(26) 176.0(3)

metric dimer **3** (Fig. 1), having a planar [LiN(1)Li′N(1)′] ring, has a ladder-like structure similar to that of [Li{N(R)C(C_6H_4Me-4)NR}(thf)$]_2$.[14] The shortest metal contact is to N(2) [2.035(5) Å] while the distances Li–N(1) 2.174(5), Li–N(1)′ 2.115(5) and Li–C(25) 2.178(6) Å are significantly longer. Compound **7** is also a dimer, but in contrast to **3**, the Li atoms are only three-coordinate with essentially symmetrical bridging NR_2 groups. The coordination sphere around Li is completed by the neutral isonitrile ligand with a slightly longer Li–C bond than in **3**. The overall geometry is therefore closely related to [{Li(μ-NR_2)L$\}_2$] (*e.g.* L = OEt_2[15*a*] or NCBu^t[15*b*]). Compound **6b** (Fig. 2) is monomeric with a distorted tetrahedral environment at Mg and fairly standard Mg–C σ-bond distances[13] of 2.148(7) and 2.138(9) Å, while the contacts to the neutral isonitrile ligands [2.31(1) Å] are much longer. The Grignard complex **5a** is unusual in that while it is a centrosymmetric dimer in the solid, the two monomeric MgBr(CHR_2) units are only weakly bound, the [Mg(μ-Br)$]_2$ moiety being unsymetrical: Mg–Br 2.561(5), Mg···Br 2.927(5) Å. The former distance is unexceptional, being close to those found (2.56–2.58 Å) in the symmetrical dimers [Mg(μ-Br)(Et)L$]_2$ (L = OEt_2[16*a*] or NEt_3[16*b*]) **B** and [Mg(μ-Br)(CHR_2)(OEt_2)$]_2$ **4** (details will be published in the full paper). This contrast between the structures of **4** and **5a** is consistent with the suggestion that the Mg–CNR′ bond is strong. This is further evident by the exceptionally short Mg–CHR_2 distance of 1.89(1) Å; *cf.* 2.114(7) and 2.125(6) Å in **4** or of 2.094(11)–2.18 Å in **B**,[16] which are close to the Mg–CNR′ bond lengths of 2.12(2) Å in **5a**. The angles at N [179(2)°] and C [174(2)°] of **5a** are close to linear.

It is noteworthy that in each of **1**–**7**, the isonitrile ligand is firmly bound to the metal as shown not only by the thermal stability but also that, in at least some of the cases, R′NC displaces Et_2O or thf from a precursor metal substrate (Scheme 1). Such complexes may have opened a new chapter in main group metal coordination chemistry.

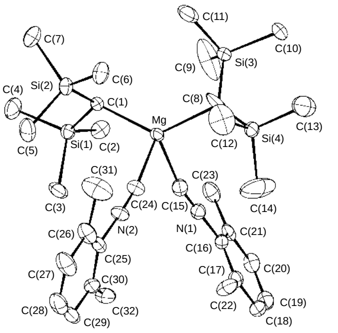

Fig. 2 Molecular structure of **6b** with selected bond distances (Å) and angles (°): Mg–C(1) 2.148(7), Mg–C(8) 2.138(9), Mg–C(15) 2.307(10), Mg–C(24) 2.306(9), N(1)–C(15) 1.140(10), N(1)–C(15)–Mg 168.02(7), C(15)–N(1)–C(16) 177.2(8)

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Notes and References

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‡ No reprints available.

§ *Crystallographic data* for **3**/**7**/**6b**/**5a**: $C_{62}H_{84}Li_2N_6Si_6$/$C_{26}H_{46}Li_2N_4Si_4$/$C_{32}H_{56}MgN_2Si_4$/$C_{24}H_{56}Br_2MgN_2Si_4$, M = 1095.8/540.9/605.5/693.5 all monoclinic, space group $P2_1/n$/$C2/c$/$P2_1$/$P2_1/c$, a = 11.401(2)/12.991(7)/10.310(6)/11.053(3), b = 23.979(5)/12.508(4)/11.925(8)/15.155(4), c = 11.956(2)/21.727(3)/16.316(6)/13.144(5) Å, β = 90.18(1)/106.84(3)/104.25(4)/113.52(2), U = 3269(1)/3379(2)/1944(2)/2019(1) Å^3, Z = 2/4/2/2, D_c = 1.11/1.06/1.03/1.14 Mg m^{-3}, F(000) = 1176/1168/660/728, λ(Mo-Kα) = 0.710 73 Å, μ = 0.17/0.20/0.19/2.17 mm^{-1}. Data were collected at 173(2) K on a Enraf Nonius CAD4 diffractometer in the ω–2θ mode for the range of $2 < \theta < 25°$ (**3**, **6b**) or $2 < \theta < 30°$ (**7**, **5a**). The structure was solved by direct methods (SHELXS86) and refined with full matrix least squares on all F^2 (SHELXL93). All non-hydrogen atoms were anisotropic, and hydrogen atoms were included in the riding mode with U_{iso}(H) = 1.2 U_{eq}(C) or 1.5 U_{eq} for Me groups. Final residuals for 5748/5120/3593/3546 independent reflections were R_1 = 0.080/0.079/0.100/0.228, wR_2 = 0.142/0.121/0.195/0.289 and for the 4093/3391/2688/1565 with $I > 2\sigma(I)$, R_1 = 0.049/0.046/0.068/0.103, wR_2 = 0.116/0.106/0.168/0.226. **7** is disordered across a crystallographic twofold rotation axis with the N, Si and Li atoms ordered, but with two alternative positions for the PhNC groups and two slightly different positions for each of the methyl groups. CCDC 182/862.

1 E. Singleton and H. E. Oosthuizen, *Adv. Organomet. Chem.*, 1983, **22**, 209; B. N. Storhoff and H. C. Lewis, *Coord. Chem. Rev.*, 1977, **23**, 1; H. Endres, in *Comprehensive Coordination Chemistry*, ed. G. Wilkinson, R. D. Gillard and J. A. McCleverty, Pergamon, Oxford, 1987, vol. 2, p. 261.
2 J. Casanova and R. E. Schuster, *Tetrahedron Lett.*, 1964, 405; J. Casanova, H. R. Kiefer, D. Kuwada and A. H. Boulton, *ibid.*, 1965, 703; G. Hesse and H. Witte, *Liebigs Ann. Chem.*, 1965, **687**, 1; G. Hesse, H. Witte and G. Bittner, *ibid*, p. 9; W. P. Fehlhammer, H. Hoffmeister, H. Stolzenberg and B. Boyadjiev, *Z. Naturforsch., Teil B*, 1989, **44**, 419.
3 G. Hesse, H. Witte and P. Mischke, *Angew. Chem., Int. Ed. Engl.*, 1965, **4**, 355.
4 *E.g.* A. Arafat, J. Baer, J. C. Huffman and L. J. Todd, *Inorg. Chem.*, 1986, **25**, 3757.
5 J. D. Fisher, M.-Y. Wei, R. Willett and P. J. Shapiro, *Organometallics*, 1994, **13**, 3324.
6 M. Tamm, T. Lügger and F. E. Hahn, *Organometallics*, 1996, **15**, 1251.
7 C. Klöfkorn, M. Schmidt, T. Spaniol, T. Wagner, O. Costisor and P. Paetzold, *Chem. Ber.*, 1995, **128**, 1037.
8 N. Takeda, H. Suzuki, N. Tokitoh and R. Okazaki, *J. Am. Chem. Soc.*, 1997, **119**, 1456.
9 P. B. Hitchcock, M. F. Lappert and M. Layh, *Chem. Commun.*, 1998, 201.
10 B. Ledig, M. Marsch, K. Harms and G. Boche, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 79.
11 P. B. Hitchcock, J. Hu, M. F. Lappert, M. Layh and J. Severn, *Chem. Commun.*, 1997, 1189; P. B. Hitchcock, M. F. Lappert and M. Layh, *Inorg. Chim. Acta*, 1998, **269**, 181.
12 H. M. Walborsky and P. Ronman, *J. Org. Chem.*, 1978, **43**, 731 and references therein.
13 P. B. Hitchcock, J. A. K. Howard, W.-P. Leung and S. F. Mason, *J. Chem. Soc., Chem. Commun.*, 1990, 847.
14 D. Stalke, M. Wedler and F. T. Edelmann, *J. Organomet. Chem.*, 1992, **431**, C1; and references therein.
15 (*a*) M. F. Lappert, M. J. Slade, A. Singh, J. L. Atwood, R. D. Rogers and A. Shakir, *J. Am. Chem. Soc.*, 1983, **105**, 302; (*b*) G. Boche, I. Langlotz, M. Marsch, K. Harms and G. Frenking, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 1171.
16 (*a*) A. L. Spek, P. Voorbergen, G. Schat, C. Blomberg and F. Bickelhaupt, *J. Organomet. Chem.*, 1974, **77**, 147; (*b*) J. Toney and G. D. Stucky, *Chem. Commun.*, 1967, 1168.

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