Synthesis, derivatization, and structural characterization of [Mn($CNC_6H_3Me_2$-2,6)$_5$]$^-$, a five-coordinate isonitrilate complex containing Mn^{-I}

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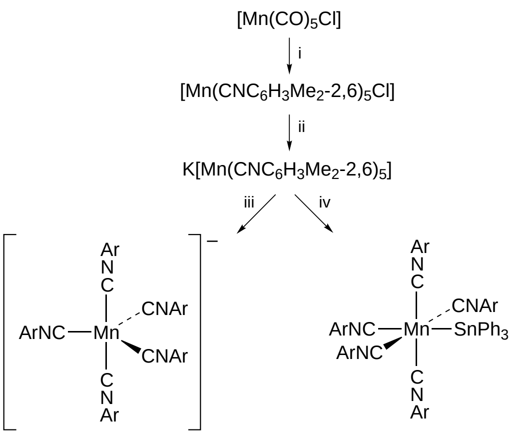
Naphthalenide reduction of [Mn($CNC_6H_3Me_2$-2,6)$_5$Cl] forms solutions of trigonal-bipyramidal [Mn($CNC_6H_3Me_2$-2,6)$_5$]$^-$, as established by an X-ray diffraction study of a [K(18-C-6)(dme)]$^+$ salt and derivatization with $SnClPh_3$ to give [Mn($CNC_6H_3Me_2$-2,6)$_5$($SnPh_3$)].

Our recent syntheses of the first isonitrilates (homoleptic isonitrile complexes of metals in negative oxidation states) generated complexes of Co^{-I} {[Co($CNC_6H_3Me_2$-2,6)$_4$]$^-$}[1] and of Ru^{-II} {[Ru($CNC_6H_3Me_2$-2,6)$_4$]$^{2-}$ and [Ru($CNBu^t$)$_4$]$^{2-}$}.[2] The existence of these complexes established that isonitrilates could be prepared with several different metals, with metals in oxidation states as low as −ii, and with both alkyl and aryl substituents on the ligands. It remained unclear, however, whether isonitrilates could be prepared in geometries other than tetrahedral; the cobalt(−i) and ruthenium(−ii) complexes are all four coordinate, and a tetrahedral geometry has been established crystallographically[1] for [Co($CNC_6H_3Me_2$-2,6)$_4$]$^-$ and is consistent with IR data in the ruthenium(−ii) case,[2] as would be anticipated on the basis of the d^{10} configurations of the metals and by analogy with the isoelectronic carbonylmetalates [Co(CO)$_4$]$^{-}$[3] and [Fe(CO)$_4$]$^{2-}$.[4] Structurally characterized homoleptic carbonylmetalates are known in five[5,6] and six coordinate[7,8] geometries, but the established propensity of isonitrile ligands to couple in higher coordinate environments[9] left open whether isonitrilates would be accessible in similar geometries despite the close analogies between isonitriles and CO.[10] We have now examined the synthesis of five coordinate manganese(−i) isonitrilates, and we wish to report the synthesis of the trigonal-bipyramidal isonitrilate [Mn($CNC_6H_3Me_2$-2,6)$_5$]$^-$ **1**$^-$ and its structural characterization as a [K(18-crown-6)(dme)]$^+$ salt (dme = dimethoxyethane), together with evidence that **1**$^-$ can react as a metal centred nucleophile with simple electrophiles (Scheme 1).



Scheme 1 *Reagents and conditions*: i, $CNC_6H_3Me_2$-2,6; ii, 2 K(Naph); iii, 18-C-6, dme; iv, $SnClPh_3$

We recently reported that cobalt(−i) isonitrilates can be prepared by naphthalenide reduction of any of a range of cobalt(0), cobalt(i) and cobalt(ii) precursors which contain an adequate number of isonitrile ligands,[1] and this led us to approach the synthesis of [Mn($CNC_6H_3Me_2$-2,6)$_5$]$^-$ by reduction of [Mn(CNC_6H_3Me-2,6)$_5$Cl] **2**.[11] Dropwise addition of 2 equiv. of a 0.4 m potassium naphthalenide [K(Naph)] solution[12] to an orange thf solution of **2** at −78 °C gave a blood-red solution. The sharp ν_{CN} bands of **2** at 2062s and 2008(sh) cm^{-1} were replaced by two broad ν_{CN} absorptions at 1920s and 1710m cm^{-1} indicating complete consumption of **2** and formation of a more reduced isonitrile complex. These solutions are extremely air sensitive, changing from blood red to cherry red in seconds, and are also thermally unstable, undergoing a similar colour change in a few days at room temperature.

Initial attempts to isolate the reduction product were unsuccessful, but it was readily established that this solution is an effective source of [Mn($CNC_6H_3Me_2$-2,6)$_5$]$^-$ by addition of $SnClPh_3$ (1 equiv. in thf) at −78 °C. The solution became clear and yellow in colour, and IR spectra indicated complete consumption of the anion and formation of a new species with higher energy ν_{CN} bands at 2135m, 2064(sh) and 1998s cm^{-1}. The solvent was removed under reduced pressure and the product was purified by slow diffusive mixing of a pentane layer into a concentrated toluene solution to give crystals of [Mn($CNC_6H_3Me_2$-2,6)$_5$($SnPh_3$)] **3**† in 88% yield.

Isolation of a crystalline salt of [Mn($CNC_6H_3Me_2$-2,6)$_5$]$^-$ from the reduction of [Mn($CNC_6H_3Me_2$-2,6)$_5$Cl] required that samples be maintained at or below −30 °C, and began with filtration of a freshly prepared solution through a bed of Celite 545 into a flask containing 1 equiv. of neat 18-crown-6 (18-C-6). After 1 h the solvent was removed under reduced pressure and the mixture was washed with pentane to give a red–brown solid from which red–black crystals of [K(18-C-6]**1**† could be obtained in 53% yield by crystallization from a saturated dme solution following addition of a layer of pentane. This material does not entirely redissolve in dme; this behaviour is reminiscent of that of alkali-metal salts of [M(CO)$_5$]$^{2-}$ (M = Cr, Mo, W) in the solid state at room temperature.[6]

Crystals suitable for X-ray diffraction studies were grown from a freshly prepared sample of [K(18-C-6)]**1** by dissolving it in a minimal volume of dme and cooling the unfiltered solution to −30 °C overnight. A low-temperature diffraction study‡ established that these crystals contain [K(18-C-6)(dme)]**1**, a dme solvate of [K(18-C-6)]**1**, but this material is not stable in the solid state at room temperature and crystals do not diffract well if stored for more than few days.

In this salt of **1**$^-$ the bis-chelate dme and the 18-C-6 ligand are both coordinated to the K$^+$ counter ion, effectively blocking K$^+$– Mn$^-$ contact ion pairing in the solid state, and allowing the [Mn($CNC_6H_3Me_2$-2,6)$_5$]$^-$ anion (Fig. 1) to adopt a geometry close to the trigonal bipyramid anticipated by analogy with the established structures of five coordinate carbonylmetalates[5,6] and of the isoelectronic d^8 homoleptic isonitrile complex [Fe($CNBu^t$)$_5$].[13] The C(1) and C(5) isonitriles are in the axial positions, but there are some irregularities in the coordination

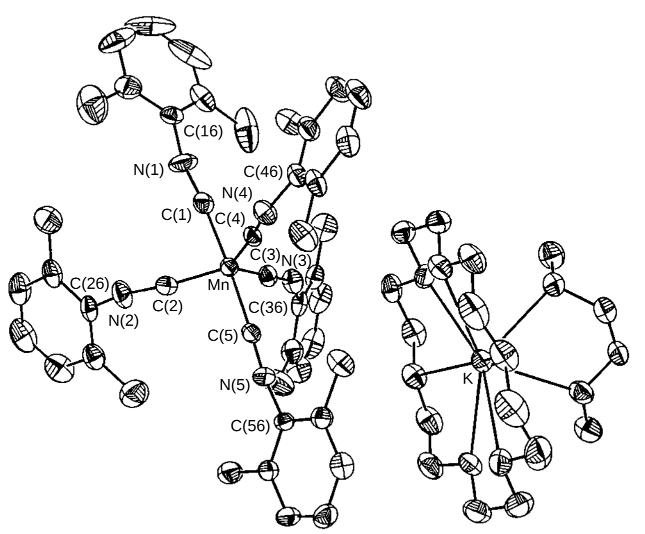


Fig. 1 Molecular structure of [K(18-C-6)(dme)][Mn(CNC$_6$H$_3$Me$_2$-2,6)$_5$] ([K(18-C-6)(dme)]**1**; 35% probability ellipsoids; hydrogen atoms omitted for clarity). Selected bond lengths (Å) and angles (°): Mn–C(1) 1.847(6), Mn–C(2) 1.724(6), Mn–C(3) 1.837(6), Mn–C(4) 1.806(6), Mn–C(5) 1.869(6), C(1)–N(1) 1.195(7), C(2)–N(2) 1.185(7), C(3)–N(3) 1.225(7), C(4)–N(4) 1.219(7), C(5)–N(5) 1.184(6) Å; C(1)–Mn–C(5) 174.4(3), C(2)–Mn–C(4) 123.7(3), C(2)–Mn–C(3) 111.9(3), C(3)–Mn–C(4) 124.3(2), C(1)–Mn–C(2) 82.9(3), C(1)–Mn–C(3) 98.1(3), C(1)–Mn–C(4) 85.3(2), C(2)–Mn–C(5) 94.2(2), C(3)–Mn–C(5) 87.4(2), C(4)–Mn–C(5) 92.4(2), C(1)–N(1)–C(16) 163.2(7), C(2)–N(2)–C(26) 143.3(6), C(3)–N(3)–C(36) 149.2(6), C(4)–N(4)–C(46) 149.2(5), C(5)–N(5)–C(56) 163.4(6)°.

sphere. The C(2) isonitrile in particular has Mn–C and C≡N bonds which are 0.097 Å ($>15\sigma$) and 0.04 Å ($>5\sigma$) shorter, respectively, than the average C≡N bonds in the other two equatorial isonitriles; we ascribe this shortening to distortions induced by van der Waals interactions between neighbouring [Mn(CNC$_6$H$_3$Me$_2$-2,6)$_5$]$^-$ ions, consistent with the 2.95 and 2.72 Å distances between the hydrogen atoms on the *para* carbon and one *meta* carbon of the C(2) isonitrile and the aryl plane of the C(3) isonitrile ligand. It is interesting that the axial isonitriles are less bent at nitrogen (both 163°) than the equatorial isonitriles (av. 147°, range 143–149°); a similar pattern in metric parameters for [Fe(CNBu^t)$_5$] was ascribed to more effective back bonding from the low-valent Fe(0) metal centre to the equatorial isonitrile ligands.[13]

Our results establish that isonitrilates can be prepared in five coordinate environments, and that a d^8 example adopts a trigonal bipyramidal geometry. The successful synthesis of [Mn(CNC$_6$H$_3$Me$_2$-2,6)$_5$]$^-$ represents a significant addition to the small number of complexes accepted to contain manganese in the $-$i oxidation state,[14] and its derivatization with SnClPh$_3$ also suggests that **1**$^-$ may prove a valuable intermediate which will allow access to an isonitrile chemistry of Mn comparable to the carbonyl chemistry of Mn accessible from the isoelectronic carbonylmetalate [Mn(CO)$_5$]$^-$.[15]

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Footnotes

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† **3**: IR ν_{CN}; 2135m, 2064(sh). 1998s cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$, 300 MHz): δ 7.60–7.57 (m, 5 H, *p*-H of C$_6$H$_3$), 6.99–6.87 (m, 25 H, *m*-H of CNC$_6$H$_3$Me$_2$ and SnPh$_3$), 2.42 (s, 6 H, CH$_3$ of CNC$_6$H$_3$Me$_2$ *trans* to SnPh$_3$), 2.16 (s, 24 H, CH$_3$ of CNC$_6$H$_3$Me$_2$ *cis* to SnPh$_3$).

[K(18-C-6)]**1**: IR ν_{CN}: 1920s, 1710m cm^{-1}. ^{1}H NMR (CD$_3$CN, 300 MHz): δ 6.92 (d, 7.2 Hz, 10 H, *m*-H of CNC$_6$H$_3$Me$_2$), 6.73 (t, 7.2 Hz, 1 H, *p*-H of CNC$_6$H$_3$Me$_2$), 3.53 (s, 24 H, C$_{12}$H$_{24}$O$_6$), 2.37 (s, 30 H, CH$_3$ of CNC$_6$H$_3$Me$_2$). The instability of the compound has precluded satisfactory combustion analysis, but the 18-C-6 : isonitrile ratio is confirmed by ^{1}H NMR spectra. These spectra also establish that there is negligible dme in crystals prepared in this manner.

‡ *Crystal data*: [K(18-C-6)(dme)]**1**: triclinic, space group $P\bar{1}$, Z = 2, a = 11.825(5), b = 12.623(6), c = 22.663(2) Å, α = 99.12(4), β = 101.17(4), γ = 112.47(4)°, U = 2964(2) Å^3, T = 213(2) K. Of the 9842 reflections measured in the range $3.62 < 2\theta < 50.56°$ range, 9376 unique reflections were used in the structure solution by direct methods. Refinement on F^2 converged at R = 0.0705 R_w = 0.1958 (all data), with GOF = 1.037.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/392.

References

1 P. A. Leach, S. J. Geib, J. A. Corella, G. F. Warnock and N. J. Cooper, *J. Am. Chem. Soc.*, 1994, **116**, 8566.

2 J. A. Corella, R. L. Thompson and N. J. Cooper, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 83.

3 P. Z. Klüfers, *Z. Kristallogr.*, 1984, **167**, 253; D. P. Schussler, W. R. Robinson and W. F. Edgell, *Inorg. Chem.*, 1974, **13**, 153.

4 H. B. Chin and R. Bau, *J. Am. Chem. Soc.*, 1976, **98**, 2434; R. G. Teller, R. G. Finke, J. P. Collman, H. B. Chin and R. Bau, *J. Am. Chem. Soc.*, 1977, **99**, 1104.

5 [Mn(CO)$_5$]$^-$: B. A. Frenz and J. A. Ibers, *Inorg. Chem.*, 1972, **11**, 1109; M. Heberhold, F. Wehrmann, D. Neugebauer and G. Huttner, *J. Organomet. Chem.*, 1978, **152**, 329; B. Balbach, S. Baral, H. Biersack, W. A. Herrmann, J. A. Labinger, W. R. Scheidt, F. J. Timmers and M. L. Ziegler, *Organometallics*, 1992, **11**, 35; H. Ben Laarab, B. Chaudret, F. Dahan, J. Devillers, R. Poilblanc and S. Sabo-Etienne, *New J. Chem.*, 1990, **14**, 321; W. Petz and F. Weller, *Z. Naturforsch., Teil B*, 1991, **46**, 297.

6 [W(CO)$_5$]$^{2-}$: J. M. Maher, R. P. Beatty and N. J. Cooper, *Organometallics*, 1985, **4**, 1354.

7 [M(CO)$_6$]$^-$ (M = V, Nb or Ta): R. D. Wilson and R. Bau, *J. Am. Chem. Soc.*, 1974, **96**, 7601; L. D. Silverman, P. W. R. Corfield and S. J. Lippard, *Inorg. Chem.*, 1981, **20**, 3106; F. Calderazzo, U. Englert, G. Pampaloni, G. Prelizzi and R. Zamboni, *Inorg. Chem.*, 1983, **22**, 1865; F. Calderazzo, G. Pampaloni, D. Vitali and R. Zanazzi, *J. Chem. Soc., Dalton Trans.*, 1982, 1993.

8 [M(CO)$_6$]$^{2-}$ (M = Ti, Zr or Hf): J. E. Ellis and K.-M. Chi, *J. Am. Chem. Soc.*, 1990, **112**, 6022.

9 E. M. Carnahan, J. D. Protasiewicz and S. J. Lippard, *Acc. Chem. Res.*, 1993, **26**, 90.

10 L. Malatesta, *Prog. Inorg. Chem.*, 1959, **1**, 283; L. Malatesta and F. Bonati, *Isocyanide Complexes of Transition Metals*, Wiley, New York, 1969; P. M. Treichel, *Adv. Organomet. Chem.*, 1973, **11**, 21; Y. Yamamoto, *Coord. Chem. Rev.*, 1980, **32**, 193; E. Singleton and M. E. Oosthuizen, *Adv. Organomet. Chem.*, 1983, **22**, 209.

11 Prepared by a procedure analogous to that used to prepare the corresponding CNPh complex: K. K. Joshi, P. L. Pauson and W. H. Stubbs, *J. Organomet. Chem.*, 1963, **1**, 51; P. M. Treichel, G. E. Dirreen and H. J. Mueh, *J. Organomet. Chem.*, 1972, **44**, 339.

12 J. M. Maher, R. P. Beatty, G. R. Lee and N. J. Cooper, *Organometallic Syntheses*; ed. R. B. King and J. J. Eisch, Elsevier, Amsterdam, 1986, vol. 3, p. 35.

13 J. M. Bassett, M. Green, J. A. K. Howard and F. G. A. Stone, *J. Chem. Soc., Chem. Commun.*, 1977, 853; J. M. Bassett, D. E. Berry, G. K. Barker, M. Green and J. A. K. Howard, *J. Chem. Soc., Dalton Trans.*, 1979, 1003.

14 There are few accepted examples other than [Mn(CO)$_5$]$^-$ and [Mn(NO)$_2$(CN)$_2$]$^{3-}$ (H. von Behrens, E. Linder and H. Schindler, *Z. Anorg. Allg. Chem.*, 1969, **365**, 119): B. Chiswell, E. D. McKenzie and L. F. Lindoy, in *Comprehensive Coordination Chemistry*, ed. G. Wilkinson, R. D. Gillard and J. A. McCleverty, Pergamon, Oxford, 1987, vol. 4, ch. 41.

15 P. M. Treichel, in *Comprehensive Organometallic Chemistry II*, ed. E. W. Abel, F. G. A. Stone and G. Wilkinson, Pergamon, Oxford, 1995, vol. 6, section 1.3; P. M. Treichel, in *Comprehensive Organometallic Chemistry*, ed. G. Wilkinson, F. G. A. Stone and E. W. Abel, Pergamon, Oxford, 1982, vol. 4, section 29.2.

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