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Synthesis and spectroscopic studies of organometallic Mn(I) complexes containing the novel mixed donor ligands 2-$\{MeSeCH_{(2-n)}(SiMe_3)_n\}C_5H_4N$ ($n = 0$–2)

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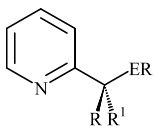
Abstract

Treatment of $MnBr(CO)_5$ with one equivalent of the bidentate ligand, 2-$\{RECH_{(2-n)}(SiMe_3)_n\}C_5H_4N$ (E = S, R = Me, Ph, n = 0; E = Se, R = Me, n = 0, 1, 2) affords the complexes $[MnBr(CO)_3\mathbf{L}]$ as orange powders. The effect of stepwise substitution at the α-carbon of the ligand by a trimethylsilyl group was investigated using $^{77}Se\{^1H\}$- and ^{55}Mn-NMR, and IR spectroscopies. In the case of the pyridyl-selenoether-containing complexes, each additional Me_3Si^- group increases the σ-donating properties of the ligand, in turn reflected in increased Mn → CO backbonding. The solid-state structure of the parent $[MnBr(CO)_3\{2\text{-}(PhSCH_2)C_5H_4N\}]$ showed the molecule to have distorted *fac*-octahedral geometry. All other compounds were assigned the same stereochemistry based on C≡O stretching frequency comparisons.

Keywords: Manganese; Organometallic; Mixed-donor ligands; Synthesis; X-ray structure

1. Introduction

Manganese(I) carbonyl complexes of the type $[MnX(CO)_3\mathbf{L}]$ (X = halide, **L** = bidentate ligand) containing homoleptic bidentate dichalcogenoether ligands have been reported and their behaviour in solution and trends in M–E bonding have been compared using ^{55}Mn-, $^{77}Se\{^1H\}$- and $^{125}Te\{^1H\}$-NMR spectroscopies and infrared spectroscopy [1–4]. Overall, depending on the configuration developed at the chalcogen centre upon coordination to the metal, these compounds can exist as four stereoisomers. These stereoisomers may interconvert via pyramidal inversion at the chalcogen centre, a process which can be observed using NMR spectroscopy. Chemical shifts in NMR spectra also show that as the chalcogen is changed from S → Se → Te, increased shielding is observed as a result of increased **L** → M σ-donation. The large increase in σ-donation from selenium to tellurium is explained by better overlap of the tellurium orbitals with the larger low-valent metal orbitals relative to the lighter chalcogens [4]. Interestingly, a literature search revealed only a small group of manganese carbonyl complexes containing mixed N/S ligands [5]; these complexes contained the N/S donor atoms as part of a gallate ligand. No manganese carbonyl complexes containing mixed N/Se neutral ligands have been reported to the best of our knowledge.



L

Herein we report (i) the preparation and characterisation of a new family of mixed N/Se ligands, 2-$\{MeSeCH_{(2-n)}(SiMe_3)_n\}C_5H_4N$ ($n = 0$ ($\mathbf{L^1}$), 1 ($\mathbf{L^2}$), 2 ($\mathbf{L^3}$)), which differ in respect of stepwise trimethylsilyl

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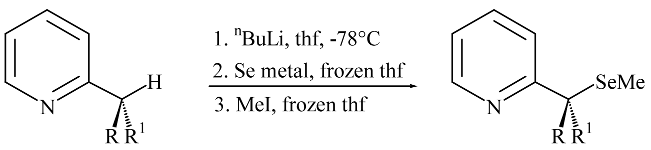
substitution at the α-carbon, and (ii) the synthesis of their manganese(I) tricarbonyl bromide complexes. The mixed donor selenoether manganese compounds reported here represent the first of their kind. We have systematically increased trimethylsilyl substitution at the α-carbon to investigate the effect that additional electron-donating groups on the ligand have on Mn–Se bonding. We have also prepared the manganese(I) tricarbonyl bromide complexes containing the previously prepared related thioether ligands, 2-($RSCH_2$)C_5H_4N (R = Me (**L^4**), Ph (**L^5**)) [6].

2. Results and discussion

2.1. Synthesis and characterisation of mixed N/Se ligands

The synthesis of the pyridyl-selenoether ligands, **L^1**, **L^2** and **L^3**, used a similar approach to that used for diselenoether ligands [7], as shown in Scheme 1. The appropriately α-substituted picoline is deprotonated using ^{n}BuLi at −78 °C to afford the alkyllithium reagent. Addition of this reagent to a frozen mixture of freshly powdered elemental selenium in THF affords the lithium selenolate, which is then quenched with MeI giving the desired ligand. Alternatively, ligand **L^1** can be prepared by the reaction of MeSeLi (prepared in situ from the reaction of elemental selenium and MeLi) and 2-picolylchloride. Ligands **L^1** and **L^2** are colourless oils while **L^3** is a white solid after purification. All three ligands have the characteristic stench associated with selenoether compounds and are assumed to be toxic so that all manipulations involving these compounds were carried out in a well-ventilated fume hood. The compounds are air-stable, although they develop a brown colour over a period of weeks due to the formation of highly coloured impurities not detectable by NMR spectroscopy. Attempts to prepare the analogous tellurium-containing ligand, 2-($MeTeCH_2$)C_5H_4N by the reaction of lithium methylpyridine, elemental tellurium and MeI were unsuccessful. The molecular ion $[M]^+$ was observed for all three selenoether ligands at m/z 187, 259 and 331 for **L^1**, **L^2** and **L^3**, respectively.

^{1}H-NMR spectra of ligands **L^1**–**L^3** exhibit typical resonances between 8.50 and 6.93 ppm associated with the 2-substituted pyridyl rings. The resonance associated with the α-protons of **L^1** can be seen as a singlet at 3.84 ppm. On substitution of a trimethylsilyl group, the methine α-proton singlet of **L^2** shifts upfield to 3.48 ppm due to the shielding effect of the trimethylsilyl group. The singlet associated with the terminal methyl substituent of the selenoether shifts slightly upfield with the addition of the first trimethylsilyl group (1.98 ppm, **L^1**; 1.83 ppm, **L^2**), but remains similar upon the addition of a second trimethylsilyl group (1.85 ppm, **L^3**).



Scheme 1. Preparation of mixed N/Se ligands **L^1** (R = $SiMe_3$, R^1 = H), **L^2** (R = R^1 = H) and **L^3** (R = R^1 = $SiMe_3$).

It has been established that the ^{77}Se-NMR chemical shifts of unsymmetrical organoselenium compounds (RSeR^1) exhibit predictable chemical shift changes with R and R^1, which are additive [8–10]. The chemical shifts of ligands **L^1**–**L^3** (Table 1) are comparable to their predicted chemical shift of 173 ppm, based on δ(MeSe) = 0 from Me_2Se and δ($PhCH_2Se$) = 173 from $PhCH_2SeMe$ [11]. There is a slight upfield shift observed in the ^{77}Se-NMR spectra from **L^1** → **L^2** → **L^3** consistent with increased shielding of the selenium atom upon the stepwise addition of electron-donating trimethylsilyl groups at the α-carbon.

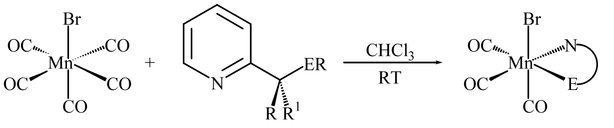
2.2. Synthesis and characterisation of [MnBr(CO)$_3$L] (L = L^1–L^5)

2.2.1. Synthesis of [MnBr(CO)$_3$L] (L = L^1–L^5)

Treatment of $MnBr(CO)_5$ with one equivalent of bidentate N/E ligand in $CHCl_3$ at room temperature in the dark affords the neutral complexes [MnBr(CO)$_3$L] as orange powders (see Scheme 2). The complexes are air- and moisture-stable, though they slowly decompose over a period of months when exposed to sunlight. The solubility of these compounds is very good in halogenated solvents. The complex [MnBr(CO)$_3$**L^3**] (**3**) is also slightly soluble in non-halogenated solvents whereas the other complexes are so less.

Table 1
Selected spectroscopic data for ligands and Mn complexes

	δ ^{77}Se{^{1}H} (ppm)	δ ^{55}Mn (ppm) ($w_{1/2}$ Hz)	ν(C≡O) (cm^{-1})
L^1	168		
L^2	167		
L^3	153		
[MnBr(CO)$_3$L^1] **(1)**	208	48 (2 peaks)	2032, 1951, 1919
	207		
[MnBr(CO)$_3$L^2] **(2)**	281	54 (6300)	2029, 1949, 1917
	217	−25 (sh)	
	203		
[MnBr(CO)$_3$L^3] **(3)**	328	37 (4660)	2028, 1948, 1916
		−77 (6200)	
[MnBr(CO)$_3$L^4] **(4)**	–	51 (2 peaks)	2034, 1955, 1922
[MnBr(CO)$_3$L^5] **(5)**	–	177 (6600)	2034, 1954, 1928



Scheme 2. Preparation of manganese carbonyl complexes [MnBr(CO)$_3$**L**] (**L** = **L**^{1} (**1**), **L**^{2} (**2**), **L**^{3} (**3**), **L**^{4} (**4**), **L**^{5} (**5**)).

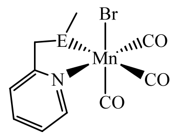
2.2.2. Infrared spectroscopy

The infrared bond-stretching frequencies ν(C$\equiv$O) for complexes **1**–**5** are listed in Table 1. All complexes exhibit three ν(C$\equiv$O) bond stretches in their IR spectra consistent with the formation of *fac*-[MnBr(CO)$_3$**L**] with C_1 symmetry (3A), as confirmed by a single-crystal X-ray diffraction study of [MnBr(CO)$_3$**L**^{5}] (**5**). It has previously been established that the C$\equiv$O bond strengths in complexes of the type [MnBr(CO)$_3$**L**], where **L** is a bidentate dichalcogenoether ligand, are influenced by (i) chelate ring size, (ii) the terminal substituent on the chalcogen centre and (iii) the chalcogen present in the ligand [4]. The C$\equiv$O bond-stretching frequencies of **1**–**3** are similar to the complexes containing diselenoether ligands [2]. A gradual shift to lower wavenumber is observed upon substitution of trimethylsilyl groups on the α-carbon suggesting that the addition of electron-donating groups results in increased backbonding between the manganese centre and the carbonyl groups due to higher electron density on the metal centre imparted by the ligands. Changing the chalcogen centre in the ligand has been seen to have the greatest effect on the strength of C$\equiv$O bonds in organometallic manganese halide complexes containing dichalcogenoether ligands [4]. Changing the chalcogen centre in the mixed donor ligand described here has a much smaller effect on the strength of the C$\equiv$O bond as only a small shift to lower frequency for the highest frequency C$\equiv$O stretch is observed on comparing [MnBr(CO)$_3$**L**^{4}] (**4**) (E = S) (2034 cm^{-1}) and [MnBr(CO)$_3$**L**^{1}] (**1**) (E = Se) (2032 cm^{-1}). Variation of the terminal substituent on the sulfur centre from Me to Ph does not significantly change the C$\equiv$O stretching frequency.

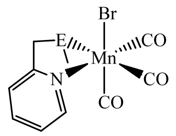
2.2.3. NMR spectroscopy

^{1}H-NMR spectra of all complexes exhibit broad resonances for all protons to the extent that their assignment is not useful, due to the large quadrupolar moment of ^{55}Mn. The ^{13}C{^{1}H}-NMR spectra show well-resolved resonances except for those associated with the CO ligands which are seen as two broad resonances between 215 and 225 ppm as is typically seen in other similar complexes [1–4]. The ^{13}C{^{1}H}-NMR spectra of complex **2** is very complicated due to the number of possible enantiomers.

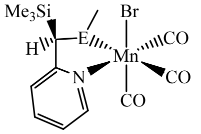
^{77}Se{^{1}H}-NMR chemical shifts for complexes **1**–**3** and ^{55}Mn-NMR chemical shifts for complexes **1**–**5** are listed in Table 1. These spectra are more useful for investigating the behaviour in solution of these compounds. The induced chirality at the chalcogen centre upon coordination of the bidentate ligand to the metal centre results in the possibility of several isomers for complexes **1** and **3**–**5**. These complexes can exist as invertomers **I** and **II** via pyramidal inversion (assuming rapid flipping of the chelate ring [12]). Complex **2**, containing the monosubstituted trimethylsilyl ligand contains two chiral centres, the selenium centre and the α-carbon resulting in four possible invertomers, **III**–**VI**, which differ according to the relative positioning of the Br, SeMe and SiMe$_3$ groups. Not all invertomers, **I**–**VI**, may be observed as the population of each invertomer may differ depending on steric hindrance, for example.



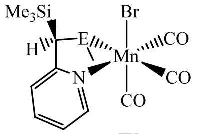
I



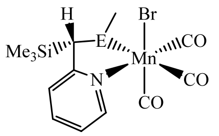
II



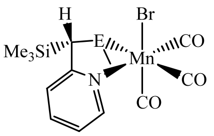
III



IV



V



VI

Complexes [MnBr(CO)$_3$**L**^{1}] and [MnBr(CO)$_3$**L**^{2}] undergo slow pyramidal inversion on 20 °C at the ^{77}Se{^{1}H}-NMR time scale as more than one invertomer is observed in solution. Two resonances are observed for [MnBr(CO)$_3$**L**^{1}] at 208 and 207 ppm in a 7:2 ratio. We propose that the downfield resonance associated with the major invertomer in solution corresponds to invertomer **II** where the methyl substituent of the selenoether and the bromide group are directed away from each other, thus minimising steric interactions within the molecule. For complex **3**, [MnBr(CO)$_3$**L**^{3}], one resonance is observed (328 ppm) which we cannot assign to a particular invertomer. The ^{77}Se-NMR spectrum of **2**, [MnBr(CO)$_3$**L**^{2}], exhibits three resonances at 20 °C at 281, 217 and 203 ppm in a 1:2:3 ratio. We propose that the absence of fourth resonance suggests that invertomer **III** where the trimethylsilyl and methyl substituents of the ligand and bromide group are directed toward the same side of the molecule is not observed at this temperature. For this molecule, we are unable to assign the resonances to each invertomer.

The ^{55}Mn-NMR spectra at 20 °C indicated that all complexes undergo pyramidal inversion, with a number of spectra showing coinciding or broad resonances.

Low-temperature NMR studies (−20 °C) resulted in all complexes, except [MnBr(CO)$_3$**L**^{3}] (**3**) exhibiting very broad spectra (two well-resolved resonances for complex **3** in the range −20 to +30 °C, indicating at least two invertomers are present in the solution). On raising the temperature to 30 °C, we were able to obtain ^{55}Mn-NMR spectra for all complexes on which the following discussion is based. The ^{55}Mn chemical shifts for the complexes containing the mixed donor ligands are generally further downfield compared with those of dichalcogenoether ligands. For example, the chemical shifts for the diselenoether (Se–Se)-containing compounds, [MnBr(CO)$_3$(Se–Se)], are of the range −250 to −500 ppm [2] compared with the chemical shifts of the complexes containing the mixed N/Se ligands reported here which range from 85 to −77 ppm due to the differing donor set. For dithio- and diselenoether ligands, changing methyl substituents for phenyl-chalcogen substituents results in a downfield shift of ~36 ppm in the ^{55}Mn-NMR spectra associated with a shift to lower frequency for the C≡O stretching frequencies in the infrared spectra [1,2]. This trend is also observed for the manganese complexes containing the mixed donor ligands with the ^{55}Mn chemical shift of the phenyl complex shifted downfield by ca. 100 ppm compared to the methyl complex, although there is a little difference in the C≡O stretching frequency region of the infrared spectra for both complexes. The chemical shifts of the complexes containing the selenoether ligands are slightly upfield compared with those of the complexes containing the thioether ligands, a trend which is also observed in complexes containing the homoleptic ligands and indicates that the selenoether ligands have better σ-donating characteristics [2].

2.2.4. Solid-state structure of [MnBr(CO)$_3$L^5] (5)

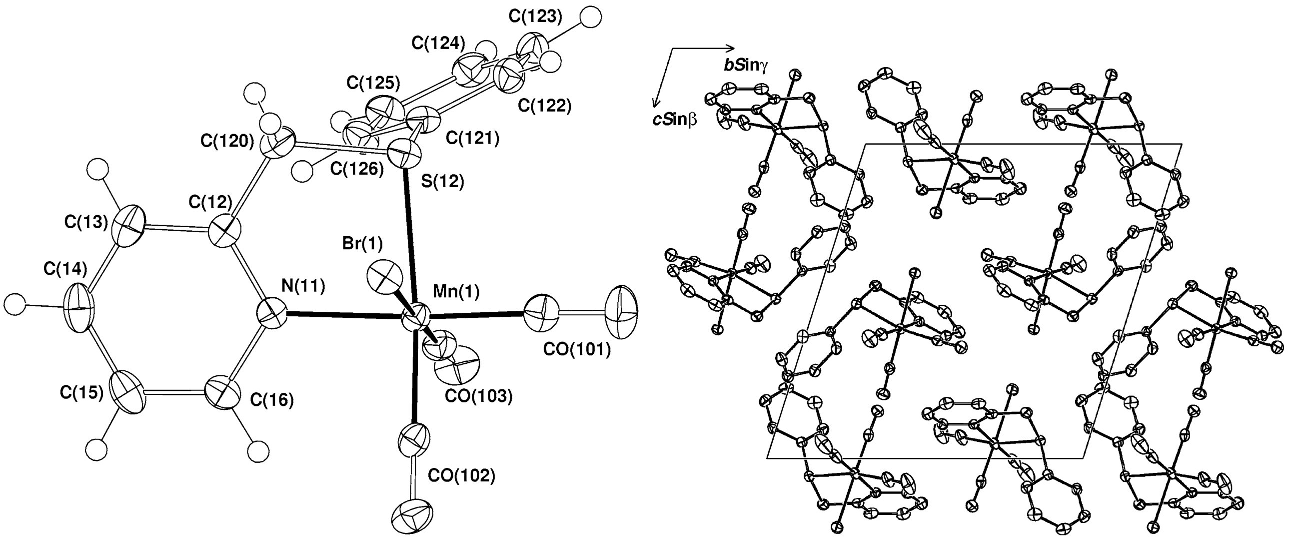
The solid-state structure of [MnBr(CO)$_3$**L**^{5}] (**5**) is shown in Fig. 1. Selected bond distances and angles are given in Table 2. Compound **5** crystallises in the triclinic space group $P\bar{1}$ as orange prisms from the slow evaporation of CH$_2$Cl$_2$. The asymmetric unit comprises two independent molecules, devoid of crystallographic symmetry and of similar conformations with distorted octahedral geometry about the manganese centres. In both molecules, the three CO ligands occupy mutually *fac* coordination sites and the mixed N/S ligand, **L**^{5}, acts as a bidentate ligand with the phenyl group of the sulfur directed away from the bromine atom. These structural features are common to a number of organometallic manganese halide complexes containing bidentate dichalcogenoether ligands [1,2,4] and bidentate nitrogen-containing ligands [13–15]. The crystal packing is of interest (Fig. 1(b)), in respect of the aromatic ring disposition and the pseudo-symmetry of the array.

The M–N bond distances in **5** of 2.083(2) Å (molecule 2, 2.081(2) Å) are similar to those seen in complexes containing homoleptic bidentate N-donor ligands such as MnI(CO)$_3$(bpy) (bpy = 2,2′-dipyridyl) (Mn–N = 2.03(2), 2.05(1) Å) [15] and MnBr(CO)$_3$(N–N) (N–N = *N*,*N*′-dicyclohexylethylenediimine) (Mn–N = 2.050(15), 2.057(14) Å) [14]. The Mn–S bond distance in **5** of 2.3449(6) (2.3467(7) Å) are significantly shorter than those of complexes containing homoleptic bidentate S-donor ligands such as [MnBr(CO)$_3${MeS-(CH$_2$)$_2$SMe}] (Mn–S = 2.3633(9), 2.3698(9) Å) and [MnBr(CO)$_3${PhS(CH$_2$)$_2$SPh}] (Mn–S = 2.362(2) Å) [1]. The difference in Mn-heteroatom bond distances in **5** compared with complexes containing homoleptic ligands may be attributed to ring flexibility and geometric differences in each of the ligands described once coordinated to the manganese centre. The Mn–C bond distances in **5** (1.791(2)–1.823(2) Å) are comparable to those in compounds containing both homoleptic bidentate N- and S-donor ligands, with the Mn–C bond associated with the CO *trans* to the Br slightly longer than those *trans* to N and S, reflecting the *trans*-effect difference of the atoms. The bite angle of the mixed donor ligand is 83.25(5) (83.40(5)°), and is the largest angular distortion of the octahedral geometry about the manganese centre, with larger than ideal bond angles around the metal centre compensating for the smaller than ideal bite angle; despite the similarity of the two molecules, significant differences between them are found, particularly in respect of the angles about the manganese.

3. Experimental

3.1. General

All manipulations were carried out using standard Schlenk techniques under an atmosphere of high-purity argon. Tetrahydrofuran was dried over sodium wire/benzophenone under nitrogen before use. CHCl$_3$ was degassed before use. Mn(CO)$_5$Br [16], 2-[(Me$_3$Si)CH$_2$]C$_5$H$_4$N [17], 2-[(Me$_3$Si)$_2$CH]C$_5$H$_4$N [17] and 2-(PhSCH$_2$)C$_5$H$_4$N [6] were prepared according to the literature procedures. All other reagents were obtained from Aldrich and were used without further purification. ^{1}H- and ^{13}C{^{1}H}-NMR spectra were recorded on a Varian Gemini operating at 200 and 50 MHz, respectively, in deuterated chloroform and referenced to the residual resonances of the solvent (δ 7.24 and 77.0 ppm, respectively). ^{77}Se{^{1}H}- and ^{55}Mn-NMR spectra were recorded on a Varian Unity operating at 76.26 and 99.08 MHz, respectively, using inverse proton decoupling, in deuterated chloroform and referenced to external Ph$_2$Se$_2$ (δ 463 ppm) and aqueous KMnO$_4$ (δ 0 ppm), respectively. Infrared spectra were recorded as CHCl$_3$ solutions on a Bruker IF22 infrared spectrometer. LSIMS mass spectra were recorded on a Kratos



(a) (b)

Fig. 1. Molecular projection of $[\mathrm{MnBr(CO)_3}\mathbf{L}^5]$ (molecule 1; molecule 2 is similar (see Table 2)) showing atom labelling scheme. (b) Unit cell contents projected down *a*.

Analytical Concept ISQ mass spectrometer. Microanalysis (C, H, N) was determined by the Microanalytical Services, Central Science Laboratory, The University of Tasmania.

3.2. Preparation of 2-[MeSeCH$_2$]C$_5$H$_4$N ($\mathbf{L}^1$)

^{n}BuLi (4.0 ml, 1.6 M solution in hexanes) was added dropwise to a solution of 2-picoline (0.59 g, 6.38 mmol) in THF (20 ml) at 78 °C. The reaction was then allowed to warm and was stirred for 3 h. The orange solution was then added to a frozen solution of freshly ground Se (0.50 g, 6.33 mmol) in THF (30 ml). The mixture was allowed to thaw and stirred at room temperature (r.t.) until Se had reacted. The dark red solution was then frozen and MeI (0.40 ml, 6.42 mmol) was added. The reaction was allowed to thaw and stirred at r.t. for 16 h. The reaction was then hydrolysed (50 ml H$_2$O), separated and the aqueous layer extracted with CH$_2$Cl$_2$ (3 × 30 ml). The combined organic extracts were dried over MgSO$_4$. The solvent was removed in vacuo, leaving a brown oil which was purified by distillation to afford $\mathbf{L}^1$ as a colourless oil (0.15 g, 12%). Anal. Found: C, 45.30; H, 4.78; N, 7.26. Calc. for C$_7$H$_9$NSe: C, 45.17; H, 4.87; N, 7.53%. ^{1}H-NMR (200 MHz, CDCl$_3$): δ 1.98 (3H, s, $\mathrm{SeC}H_3$), 3.84 (2H, s, $\mathrm{C}H_2$), 7.12 (1H, d, $^3J_{\mathrm{H-H}} = 5.00$ Hz, $\mathrm{C}_5H_3\mathrm{N}$), 7.62 (1H, d, $^3J_{\mathrm{H-H}} = 6.82$ Hz, $\mathrm{C}_5H_3\mathrm{N}$), 7.62 (1H, td, $^3J_{\mathrm{H-H}} = 7.66$ Hz, $^4J_{\mathrm{H-H}} = 1.76$ Hz, $\mathrm{C}_5H_3\mathrm{N}$), 8.50 (1H, d, $^3J_{\mathrm{H-H}} = 4.08$ Hz, $\mathrm{C}_5H_3\mathrm{N}$) ppm. $^{13}\mathrm{C}\{^1\mathrm{H}\}$-NMR (50 MHz, CDCl$_3$): δ 3.39 ($\mathrm{Se}C\mathrm{H}_3$), 30.39 ($C\mathrm{H}_2$), 122.09, 123.45, 137.19, 149.89, 167.37 ($C_5\mathrm{H}_3\mathrm{N}$), IR (cm^{-1}): 3004(m), 2923(m), 1590(s), 1566(s), 1473(s), 1433(s), 1303(w), 1183(w), 1150(m), 1078(m), 1049(m), 993(m), 921(m), 780(s), 746(s), 617(w), 574(w), 459(m), 421(s). SIMS *m*/*z*: 187 [M]$^+$, 172 [M−Me]$^+$, 92 [M−SeMe]$^+$.

Table 2
Selected bond distances (Å) and angles (°) of $[\mathrm{MnBr(CO)_3}\mathbf{L}^5]$ (**5**)

Bond distances (Å)			
Mn–Br	2.5382(5) (2.5368(5))	Mn–C(x01)	1.812(2) (1.800(2))
Mn–N	2.083(2) (2.081(2))	Mn–C(x02)	1.823(2) (1.804(3))
Mn–S	2.3449(6) (2.3467(7))	Mn–C(x03)	1.791(2) (1.803(2))
Bond angles (°)			
Br–Mn–C(*x*01)	90.20(7) (90.17(9))	C(x01)–Mn–C(x03)	89.2(1) (89.9(1))
Br–Mn–C(*x*02)	87.01(7) (85.78(9))	C(x01)–Mn–N	176.53(8) (176.55(9))
Br–Mn–C(*x*03)	179.42(8) (178.77(6))	C(x01)–Mn–S	93.29(7) (93.47(9))
Br–Mn–N	89.50(5) (90.82(5))	C(x02)–Mn–C(x03)	92.94(9) (93.0(1))
Br–Mn–S	82.36(2) (82.15(2))	C(x02)–Mn–N	93.46(8) (95.65(8))
N–Mn–S	83.25(5) (83.40(5))	C(x02)–Mn–S	168.89(7) (167.88(9))
C(x01)–Mn–C(*x*02)	90.0(1) (87.7(1))	C(x03)–Mn–N	91.08(8) (89.24(8))
		C(x03)–Mn–S	97.72(7) (99.08(7))

Molecule 1 ($x = 1$), molecule 2 ($x = 2$).

3.3. *Preparation of 2-[MeSe(Me$_3$Si)CH]C$_5$H$_4$N (**L^2**)*

Prepared as above using 2-[(Me$_3$Si)$_2$CH]C$_5$H$_4$N to afford **L^4** which was purified by distillation to afford a colourless oil. Anal. Found: C, 46.49; H, 6.81; N, 5.46. Calc. for $C_{10}H_{17}NSeSi$: C, 46.50; H, 6.63; N, 5.42%. ^{1}H-NMR (200 MHz, CDCl$_3$): δ 0.05 (9H, s, Si(C*H*$_3$)$_3$), 1.83 (3H, s, SeC*H*$_3$), 3.46 (1H, s, CH), 6.98 (1H, t, $^3J_{H-H}=$ 5.32 Hz, C$_5$H$_3$N), 7.32 (1H, d, $^3J_{H-H}=7.94$ Hz, C$_5$H$_3$N), 7.53 (1H, t, $^3J_{H-H}=7.80$ Hz, C$_5$H$_3$N), 8.40 (1H, d, $^3J_{H-H}=3.66$ Hz, C$_5$H$_3$N) ppm. ^{13}C{^{1}H}-NMR (50 MHz, CDCl$_3$): δ 1.52 (Si(*C*H$_3$)$_3$), 6.09 (Se*C*H$_3$), 35.45 (*C*H), 120.63, 123.03, 138.74, 149.22, 163.49 (C$_5$H$_3$N), SIMS *m/z*: 259 [M]$^+$, 244 [M−Me]$^+$, 229 [M−2Me]$^+$, 149 [M−SeMe−Me]$^+$, 133 [M−SeMe−2Me]$^+$.

3.4. *Preparation of 2-[MeSeC(Me$_3$Si)$_2$]C$_5$H$_4$N (**L^3**)*

Prepared as above using 2-[(Me$_3$Si)$_2$CH]C$_5$H$_4$N to afford **L^5** which was purified by column chromatography (1:9 ethyl acetate: petroleum spirits) to afford a colourless solid (0.46 g, 22%). Anal. Found: C, 47.52; H, 7.83; N, 4.16. Calc. for $C_{13}H_{25}NSeSi_2$: C, 47.24; H, 7.63; N, 4.24%. ^{1}H-NMR (200 MHz, CDCl$_3$): δ 0.14 (9H, s, Si(C*H*$_3$)$_3$), 1.85 (3H, s, SeC*H*$_3$), 6.93 (1H, d, $^3J_{H-H}=$ 6.66 Hz, C$_5$H$_3$N), 7.58 (1H, td, $^3J_{H-H}=7.4$ Hz, $^4J_{H-H}=$ 1.6 Hz, C$_5$H$_3$N), 7.80 (1H, d, $^3J_{H-H}=8.1$ Hz, C$_5$H$_3$N), 8.43 (1H, d, $^3J_{H-H}=3.8$ Hz, C$_5$H$_3$N) ppm. ^{13}C{^{1}H}-NMR (50 MHz, CDCl$_3$): δ 1.90 (Si(*C*H$_3$)$_3$), 4.58 (Se*C*H$_3$), 119.26, 136.47, 124.14, 148.34, 156.05 (*C*$_5$H$_3$N) ppm. SIMS *m/z*: 331 [M]$^+$, 316 [M−Me]$^+$, 301 [M−2Me]$^+$, 236 [M−SeMe−Me]$^+$, 206 [M−SeMe−3Me]$^+$, 178 [M−SeMe−SiMe$_3$]$^+$, 162 [M−SeMe−SiMe$_3$−Me]$^+$, 148 [M−SeMe−SiMe$_3$−2Me]$^+$.

3.5. *Preparation of [MnBr(CO)$_3$**L^1**] (**1**)*

A solution of **L^1** (150 mg, 0.806 mmol) and MnBr(CO)$_5$ (200 mg, 0.728 mmol) were stirred in CHCl$_3$ (20 ml) for 5 days in the dark. The reaction was monitored by IR. The volume of the solution was reduced in vacuo to ca. 2 ml. Addition of petroleum spirits afforded an orange solid which was collected and washed with petroleum spirits and dried to afford **1** (252 mg, 85%). Anal. Found: C, 29.53; H, 2.21; N, 3.44. Calc. for $C_{10}H_9NBrMnO_3Se$: C, 29.66; H, 2.21; N, 3.46%. ^{13}C{^{1}H}-NMR (100 MHz, CDCl$_3$): δ 12.34 (Se*C*H$_3$), 39.05 (*C*H$_2$), 124.08, 125.73, 138.70, 155.37, 161.11 (*C*$_5$H$_4$N), 221, 223 (*C*O, br)%.

3.6. *Preparation of [MnBr(CO)$_3$**L^2**] (**2**)*

Prepared as above using **L^2** (253 mg, 73%). Anal. Found: C, 32.46; H, 3.51; N, 3.08. Calc. for $C_{13}H_{17}NBrMnO_3SeSi$: C, 32.72; H, 3.59; N, 2.94%. ^{13}C{^{1}H}-NMR (100 MHz, CDCl$_3$): δ −1.16, −0.13, 0.45 (Si(*C*H$_3$)$_3$), 11.40, 13.61, 17.40 (Se*C*H$_3$), 38.55, 39.83, 44.17, 44.63 (*C*H$_2$), 122.00, 122.29, 122.39, 122.94, 123.41, 125.05, 125.21, 136.08, 137.07, 137.78, 138.04, 154.67, 154.80, 155.58, 156.12, 160.55, 164.10, 165.03 (*C*$_5$H$_4$N), 218, 222 (*C*O, br)%.

3.7. *Preparation of [MnBr(CO)$_3$**L^3**] (**3**)*

Prepared as above using **L^3** (258 mg, 64%). Anal. Found: C, 34.99; H, 4.48; N, 2.72. Calc. for $C_{16}H_{25}NBrMnO_3SeSi_2$: C, 34.98; H, 4.59; N, 2.55%. ^{13}C{^{1}H}-NMR (100 MHz, CDCl$_3$): δ 0.7, 12.05, 2.85, 4.41 (Si(*C*H$_3$)$_3$), 14.42 (Se*C*H$_3$), 43.06 (*C*H$_2$), 121.93, 124.56, 136.59, 157.26, 166.78 (*C*$_5$H$_4$N), 218, 222 (*C*O, br)%.

3.8. *Preparation of [MnBr(CO)$_3$**L^4**] (**4**)*

Prepared as above using **L^4** (229 mg, 88%). Anal. Found: C, 33.26; H, 2.25; N, 3.95; S, 8.81. Calc. for $C_{10}H_9NBrMnO_3S$: C, 33.54; H, 2.53; N, 3.91; S, 8.95%. ^{13}C{^{1}H}-NMR (100 MHz, CDCl$_3$): δ 22.92(S*C*H$_3$), 46.37(*C*H$_2$), 124.20, 124.70, 138.69, 154.71, 159.95 (*C*$_5$H$_4$N), 219, 221 (*C*O, br)%.

3.9. *Preparation of [MnBr(CO)$_3$**L^5**] (**5**)*

Prepared as above using **L^5** (282 mg, 92%). Anal. Found: C, 42.69; H, 2.64; N, 3.41; S, 7.42. Calc. for $C_{15}H_{11}NBrMnO_3S$: C, 42.88; H, 2.64; N, 3.33; S, 7.63%. ^{13}C{^{1}H}-NMR (100 MHz, CDCl$_3$): δ 46.88 (*C*H$_2$), 124.25 (*C*$_5$H$_4$N), 124.60 (*C*$_5$H$_4$N), 128.32 (*C*$_6$H$_5$), 129.96 (*C*$_6$H$_5$), 130.23 (*C*$_6$H$_5$), 135.59 (*C*$_6$H$_5$), 139.42 (*C*$_5$H$_4$N), 154.88 (*C*$_5$H$_4$N), 160.75 (*C*$_5$H$_4$N), 220, 221 (*C*O, br)%.

3.10. *X-ray crystallography*

Orange plates of **5** (specimen: 0.24 mm × 0.20 mm × 0.09 mm) were grown by slow evaporation of a solution of the complex in CHCl$_3$. A full sphere of CCD area-detector diffractometer data was measured (Bruker AXS, ω-scans, $2\theta_{max}=75°$; monochromatic Mo−K$_\alpha$ radiation, $\lambda=0.7107_3$ Å; *T* ca. 153 K). 32 970 total reflections merged to 16 360 unique after "empirical"/multi-scan absorption correction (proprietary software), 10 165 with $F>4\sigma(F)$ being used in the full-matrix least-squares refinements; anisotropic thermal parameter forms were refined for the non-hydrogen atoms, $(x, y, z, U_{iso})_H$ also being refined. Conventional R, R_w (weights: $(\sigma(F)+0.0004F^2)^{-1}$) on $|F|$ at convergence were 0.036 and 0.037. Neutral atom complex scattering factors were employed within the context of the XTAL 3.7 program system [18]. Pertinent results are given above and in the tables and figures, the latter showing 50% probability amplitude–displacement ellipsoids for the non-hydrogen atoms, hydrogen atoms having arbitrary radii of 0.1 Å.

Crystal data for $C_{15}H_{11}BrMnNO_3S$, $M = 420.2$, triclinic, space group $P\bar{1}$, $a = 8.731(2)$ Å, $b = 13.646(2)$ Å, $c = 14.107(2)$ Å, $\alpha = 106.614(4)^\circ$, $\beta = 94.659(4)^\circ$, $\gamma = 97.889(4)^\circ$, $V = 1582$ Å^3. $D_c(Z = 4) = 1.76_3$ g cm^{-3}, μ(Mo–K$_\alpha$) = 3.5 mm^{-1}, $T_{min/max} = 0.65$. $|\Delta\rho_{max}| = 0.9(1)$ e Å^3.

4. Conclusions

We have successfully prepared a new group of organometallic manganese bromide complexes containing mixed nitrogen-chalcogenoether ligands, the compounds containing the mixed pyridyl/selenoether ligands being the first of their type. We have established that the bonding properties seen in analogous complexes containing dichalcogenoether ligands are reflected in the compounds reported here containing the mixed donor ligands. That is, on changing the Group 16 donor atom from sulfur to selenium, more electron density is transferred to the metal centre as can be seen in the weakening of the C = O bond. ^{77}Se{^{1}H}- and ^{55}Mn-NMR spectroscopies show that in solution, a number of invertomers can exist for each compound. The stepwise addition of electron-donating trimethylsilyl groups to the α-carbon of the ligand 2-{$MeSeCH_{2-n}(Si(SiMe_3)_n$}$C_5H_4N$ also results in increased electron density at the metal centre, resulting in increased M → CO backbonding, suggesting these ligands can be modified at this position to influence the electron density at the metal centre and thus the lability of the ligand at the chalcogen atom. This may have important implications in catalysis where the mechanism of the catalytic cycle relies on one donor to be labile for ease of decoordination.

5. Supplementary material

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 201714 for compound **5**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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References

[1] J. Connolly, G.W. Goodban, G. Reid, A.M.Z. Slawin, J. Chem. Soc. Dalton Trans. (1998) 2225.

[2] J. Connolly, M.K. Davies, G. Reid, J. Chem. Soc. Dalton Trans. (1998) 3833.

[3] M.K. Davies, M.C. Durrant, W. Levason, G. Reid, R.L. Richards, J. Chem. Soc. Dalton Trans. (1999) 1077.

[4] W. Levason, S.D. Orchard, G. Reid, Organometallics 18 (1999) 1275.

[5] (a) B.M. Louis, S.J. Retting, A. Storr, J. Trotter, Can. J. Chem. 63 (1985) 2261;
(b) S.J. Retting, A. Storr, J. Trotter, Can. J. Chem. 59 (1981) 2391.

[6] (a) L. Canovese, F. Visentin, P. Uguagliati, G. Chessa, A. Pesce, J. Organomet. Chem. 566 (1998) 61;
(b) L. Canovesse, F. Visentin, P. Uguagliati, G. Chessa, V. Lucchini, G. Bandoli, Inorg. Chim. Acta 275–276 (1998) 385.

[7] J.E. Drake, P.T. Hemmings, J. Chem. Soc. Dalton Trans. (1976) 1730.

[8] W. McFarlane, R.J. Wood, J. Chem. Soc. Dalton Trans. (1972) 1397.

[9] D.H. O'Brien, N. Dereu, C.K. Huang, K.J. Irgolic, F.F. Knapp, Jr., Organometallics 2 (1983) 305.

[10] D.J. Gulliver, E.G. Hope, W. Levason, S.G. Murray, D.M. Potter, G.L. Marshall, J. Chem. Soc. Perkin Trans. II (1984) 429.

[11] C. Rodger, N. Sheppard, H.C.E. MaFarlane, W. McFarlane, in: R.K. Harris, B.E. Mann (Eds.), NMR and the Periodic Table, Academic Press, London, 1978.

[12] B.W. Skelton, V.-A. Tolhurst, A.H. White, A.M. Williams, A.J. Wilson, B.F. Yates, Unpublished results.

[13] G. Schmidt, H. Paulus, R. van Eldik, H. Elias, Inorg. Chem. 27 (1988) 3211.

[14] A.J. Graham, D. Akrigg, B. Sheldrick, Cryst. Struct. Commun. 6 (1977) 571.

[15] G.J. Stor, D.J. Stufkens, P. Vernooijs, E.J. Baerends, J. Fraanje, K. Goubitz, Inorg. Chem. 34 (1995) 1588.

[16] M.H. Quick, R.J. Angelici, Inorg. Synth. 19 (1979) 160.

[17] R.I. Papasergio, B.W. Skelton, P. Twiss, A.H. White, C.L. Raston, J. Chem. Soc. Dalton Trans. (1990) 1161.

[18] S.R. Hall, D.J. du Boulay, R. Olthof-Hazekamp (Eds.), The XTAL 3.7 System, University of Western Australia, 2000.