A comparison of some complexes of the type *eq*-$[Mn_2(CO)_9L]$, where L is a cyclic carbene ligand with a five- or six-membered ring and the molecular structures of two complexes containing six-membered carbene rings

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(Received September 7, 1992; revised November 30, 1992)

Abstract

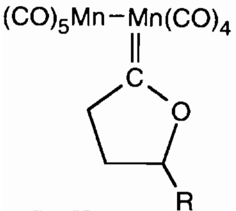
Two new five-membered ring cyclic carbene complexes *eq*-$[Mn_2(CO)_9L]$ (where $L = \overline{CCH_2CH(CH_3)CH_2O}$ or $\overline{CC(CH_3)_2CH_2CH_2O}$) have been prepared and characterized. Thermal analysis and $^1H/^2D$ exchange experiments are compared for several five- and six-membered ring cyclic carbene complexes of the type *eq*-$[Mn_2(CO)_9L]$. The X-ray crystal structures of the six-membered ring carbene complexes *eq*-$[Mn_2(CO)_9L]$ (where $L = \overline{CCH_2CH_2CH_2CH_2O}$ and $\overline{CCH_2CH_2CH_2CH(CH_3)O}$) have been determined and are compared with the known structures of the related five-membered ring complexes.

Introduction

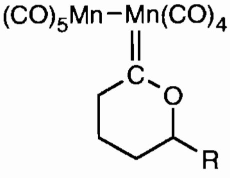
Transition metal carbene complexes are useful precursors in synthetic chemistry [1] and their involvement in catalytic reactions [2–4] has resulted in intense interest in this area [5–8].

We recently reported the preparation of several dimanganese complexes containing cyclic carbene ligands and the molecular structures of two of them containing the oxacyclopentylidene ligand (compounds **1** and **2**) [9].

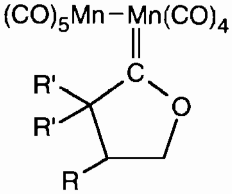
Although there have been many reports of cyclic carbene complexes with five-membered rings, there are very few known with six-membered rings, and to our knowledge there are no structures reported for this type of ligand. We carried out this present study to determine whether an increase in ring size of the cyclic carbene ligand would have any effect on the properties, both physical and chemical, of these carbene complexes.



1, R = H
2, R = CH_3



3, R = H
4, R = CH_3



5, R' = H; R = CH_3
6, R' = CH_3; R = H

Experimental

All syntheses were carried out in Schlenk tubes under an atmosphere of nitrogen. The sodium salt $Na[Mn(CO)_5]$ was prepared by the previously published procedure of sodium amalgam reduction of $[Mn_2(CO)_{10}]$ in tetrahydrofuran solution [10]. Deuterium exchange experiments were monitored by ^1H NMR on a Varian EM360A 60 MHz instrument. The results were analyzed using a linear regression program; error values were typically in the region of 5%. The differential scanning calorimetry was performed on a Perkin-Elmer Series 7 DSC instrument using a heating rate of 10 °C min^{-1}, under a N_2 flow of 40 ml min^{-1}. The dimanganese nonacarbonyl cyclic carbene compounds **1–4** were prepared as previously described [9].

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0020-1693/93/$6.00

Preparation of eq-$[(CO)_5MnMn(CO)_4(\overline{CCH_2CH(CH_3)CH_2O})]$ *(5)*

A tetrahydrofuran solution of Na[Mn(CO$_5$] (10.11 mmol) was added dropwise with stirring to 1-bromo-3-chloro-2-methylpropane (0.875 g; 5.103 mmol) and the reaction mixture was heated at reflux for 2 h. The solvent was then removed under reduced pressure to give an orange oil which was extracted with hexane. Chromatography on a short alumina column (2 cm × 7 cm) with hexane as eluent separated two yellow bands. The first yellow band was $[Mn_2(CO)_{10}]$ and the second yellow band was compound **5**. The product was recrystallized from hexane at -15 °C to give orange crystals of **5** (0.618 g; 27% yield) m.p. 79–80 °C. *Anal.* Calc. for $C_{14}H_8Mn_2O_{10}$: C, 37.69; H, 1.81. Found: C, 37.8; H, 1.9%. IR (ν(CO), hexane): 2089(w), 2024(s), 2008(m), 1998(s), 1987(s), 1971(m), 1957(w), 1950(w) cm^{-1}.

Preparation of eq-$[(CO)_5MnMn(CO)_4(\overline{CC(CH_3)_2CH_2CH_2O})]$ *(6)*

1.225 g of **1** (2.835 mmol) were reduced by sodium amalgam in tetrahydrofuran. 1.007 g methyl iodide (7.095 mmol) were added dropwise with stirring and the reaction mixture was stirred at room temperature for 20 h. The solvent was then removed under reduced pressure to give an orange oil which was extracted with hexane. Chromatography on a short alumina column (2 cm × 8 cm) with hexane as eluent gave two yellow bands. The first yellow band was **1** and the second band was compound **6**. The product was recrystallized from hexane at -15 °C to give orange crystals of **6** (0.222 g; 18% yield) m.p. 80–82 °C. *Anal.* Calc. for $C_{15}H_{10}Mn_2O_{10}$: C, 39.16; H, 2.19. Found: C, 39.2; H, 2.1%. IR (ν(CO), hexane): 2089(m), 2020(s), 2014(m), 1994(s, broad), 1971(m), 1955(m), 1945(m) cm^{-1}.

Crystallographic studies

Suitable crystals of **3** and **4** were obtained by slow crystallization of the compounds from hexane solutions at 0 °C. Cell parameters were determined by the least-squares fitting of the setting angles of 24 reflections with $16 \leqslant \theta \leqslant 17°$, automatically centred on a CAD4 diffractometer. During data collection, the intensities of 3 reference reflections were monitored every 1 h and recentering was checked after every 100 measured reflections. Data were corrected for Lorentz–polarization effects and an empirical absorption correction was applied [11]. The structures were solved by direct methods and refined by full-matrix least-squares techniques (SHELX [12]). High temperature factors in the ring atoms indicate conformational flexibility and associated disorder in the carbene ring, with the disorder in **3** being greater than in **4**. The disorder appears to be of the type observed in other similar transition metal carbene complexes [6]. This is suspected mainly because in **3** the C(25)–C(29) bond is uncharacteristically short; a fact which can be explained if the positions C(29) and O(25) are each assumed to be composites of carbon and oxygen electron density. This situation arises through rotation of the Mn(2)–C(25) bond by 180°. The α-carbon and oxygen positions were thus modelled as 50:50 C:O mixtures. The space group being $P2_1/c$, however, did not allow any further resolution of the two rotamers. All hydrogen atoms were placed in calculated positions. Detailed mapping of the ring electron density in **3** showed that the observed positions for C(26), C(27) and C(28) are fairly well defined, with only slight blurring around the mean positions. This is to be expected since the observed half-chair ring conformation has a pseudo-C_2 axis aligned with the Mn(2)–C(25) axis. Complex neutral atom scattering factors were taken from ref. 13 and dispersion corrections from ref. 14. Computer programs used are as follows: SHELX 76 [15]; SHELX 86 [12]; PLUTO [16]; PARST [17]. All calculations were performed at the University of Cape Town on a Univac 1100/81 computer. Further details of the data collection, structure solution and refinement are given in Table 1.

Kinetic studies

Typically, *c*. 130 mg of carbene complex were dissolved in 0.500 ml of acetone-d_6 and a ^1H NMR spectrum was run. Then 0.100 ml of deuterium oxide was added and the solution was immediately placed in a thermostatted water bath at 40.0 °C. The NMR tube was then withdrawn periodically, the solution was frozen until the ^1H NMR spectra were run. The disappearance of the peak due to the protons attached to the α-carbon atom of the carbene ring was monitored. A plot of $\ln(I_t/I_0)$ versus time t (I_t = integration at time = t, I_0 = integration at time = 0) gave a straight line of slope k_{obs}, the rate constant for the deuterium exchange reaction (the results were analyzed by linear regression). The reactions were followed for approximately three half-lives.

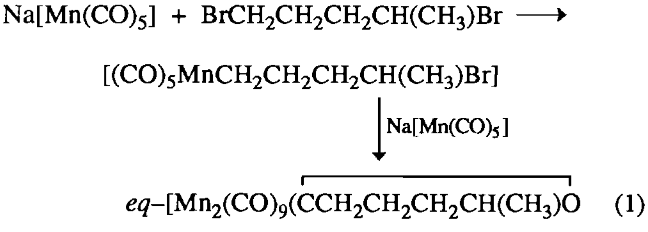
Results and discussion

Synthesis and characterization of compounds 1–6

Compounds **1**–**4** were synthesized by known procedures involving the reactions of THF solutions of $Na[Mn(CO)_5]$ with the appropriate dibromoalkanes as shown in eqn. (1) for compound **4**.

TABLE 1. Crystal and X-ray diffraction data

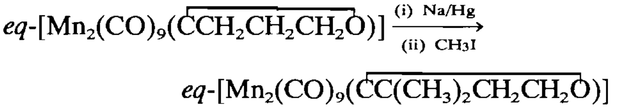
	3	4
Formula	$C_{14}H_8O_{10}Mn_2$	$C_{15}H_{10}O_{10}Mn_2$
Crystal colour	orange	orange
Crystal habit	plates	plates
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/n$
a (Å)	9.669(2)	10.495(1)
b (Å)	11.828(2)	11.724(1)
c (Å)	16.027(2)	15.832(1)
α (°)	90	90
β (°)	105.36(2)	106.19(1)
γ (°)	90	90
V (Å^3)	1761.0(6)	1871.0(6)
Z	4	4
D_{calc} (g cm^{-3})	1.68	1.63
Crystal dimensions (mm)	0.30×0.40×0.50	0.19×0.31×0.41
Temperature	r.t.	r.t.
μ(Mo Kα) (cm^{-1})	14.196	13.434
Radiation	graphite monochromated Mo Kα (λ=0.71069 Å)	
Scan mode	ω–2θ	ω–2θ
Stability of standard reflections (%)	2.6	2.8
2θ Range (°)	1–25	1–25
No. collected data	3860	3596
No. unique data	2489	2860
No. unique data with $I > 2\sigma(I)$	1829	2350
Weighting scheme	$(\sigma^2F)^{-1}$	$(\sigma^2F)^{-1}$
R	0.042	0.056
R_w	0.038	0.053
S	2.31	6.08



$$Na[Mn(CO)_5] + BrCH_2CH_2CH_2CH(CH_3)Br \longrightarrow [(CO)_5MnCH_2CH_2CH_2CH(CH_3)Br] \xrightarrow{Na[Mn(CO)_5]} eq\text{-}[Mn_2(CO)_9(\overline{CCH_2CH_2CH_2CH(CH_3)O} \quad (1)$$

4

Compound **5** was similarly prepared by the reaction of a THF solution of $Na[Mn(CO)_5]$ with 1-bromo-3-chloro-2-methylpropane. Compound **6** was prepared by exchange of the two acidic α-hydrogens on the carbene ring for two methyl groups.



$$eq\text{-}[Mn_2(CO)_9(\overline{CCH_2CH_2CH_2O})] \xrightarrow[\text{(ii) } CH_3I]{\text{(i) Na/Hg}} eq\text{-}[Mn_2(CO)_9(\overline{CC(CH_3)_2CH_2CH_2O})]$$

6

It is interesting to note that the methyl group of the substituted dihaloalkane directs the attack of the first $[Mn(CO)_5]^-$ moiety, i.e. the regioselectivity observed in this alkylation reaction probably reflects the different reactivity of the two halide functions (primary versus secondary). Compounds **1**–**6** are all orange crystalline solids. They all show eight ν(CO) bands in their IR spectra (the broad band at 1994 cm^{-1} for compound **6** is a combination of two unresolved bands) consistent with the compounds all being of the type *eq*-$[Mn_2(CO)_9L]$ rather than *ax*-$[Mn_2(CO)_9L]$. The mass spectra of compounds **1**–**6** are similar and all show parent molecular ions with the predominant fragmentation pathway being sequential loss of CO groups from the parent ion, indicating that the carbene ligand may be bonded to the manganese atom more strongly than the other ligands, including the second manganese atom. The conclusion that the carbene ligand is bound to the metal more firmly than the other ligands is in agreement with conclusions reached by other workers [18].

Discussion of NMR data

The ^1H and ^{13}C NMR data for compounds **5** and **6** are given in Table 2. A general discussion of the NMR data for compounds **1**–**4** has been given previously [9]. Compound **5**, however, gave a very interesting ^1H NMR spectrum, differing from the others in its complexity. A doublet at 1.07 ppm is observed, as expected, for the substituent methyl group. A very complex signal at 2.46 ppm is observed for the lone proton attached to the same carbon atom as the methyl group. (One would expect this signal to be complex because there are a total of seven other protons on adjacent carbon atoms to engage in first-order coupling with this proton). A quartet of doublets, centred at 3.57 ppm, is observed for the protons attached to the α-carbon atom of the

TABLE 2. ^1H and ^{13}C NMR data[a]

Compound	^1H	^{13}C
5	4.70 (d of tr, 2H, OCH_2) 3.57 (qu of d, 2H, $MnCCH_2$) 2.46 (m, 1H, $OCH_2CH(CH_3)$) 1.07 (d, 3H, CH_3)	339.6 (Mn=C) 90.6 (OCH_2) 65.9 ($MnCCH_2$) 30.0 (CH_3) 17.6 ($OCH_2CH(CH_3)$)
6	4.78 (tr, 2H, OCH_2) 1.80 (m, 2H, OCH_2CH_2) 1.41 (s, 3H, CH_3) 1.38 (s, 3H, CH_3)	349.0 (Mn=C) 81.7 (OCH_2) 66.5 ($MnCC(CH_3)_2$) 36.7 (OCH_2CH_2) 25.3 (CH_3) 25.1 (CH_3)

[a] Recorded as $CDCl_3$ solutions. Chemical shifts are reported relative to tetramethylsilane (δ 0.00 ppm) as a reference standard: m = multiplet; s = singlet; d = doublet; tr = triplet; qu = quartet. Broad, weak peaks were observed in the region 217–222 ppm due to the CO groups.

carbene ring. These protons are inequivalent and couple to each other and then to the lone proton on the adjacent atom, i.e. an ABX spin system that appears as a quartet of doublets. Similarly, a doublet of triplets, centred at 4.70 ppm, is observed for the $-OCH_2-$ protons; here the vicinal and geminal coupling constants have similar values.

Molecular structures of 3 and 4

The crystal structures confirm the proposal that the six-membered cyclic carbene ligands occupy equatorial positions on one of the manganese atoms. Apart from ring details, the structures do not differ significantly from the related dimanganese carbene structures previously reported by us [9]. Bond lengths are given in Table 3(a) and bond angles and torsion angles for the carbene ring are given in Table 4. Views of a molecule of **3** and a molecule of **4** are given in Figs. 1 and 2, respectively. As shown in Figs. 1 and 2, the carbene ring exists in a twist conformation, the conformational restriction being the sp^2 hybridized atom C(25). The out-of-plane bending for the ring appears to be confined to C(27) and C(28); presumably this is in order to maximize orbital overlap. Both rings bend away from the other manganese atom in order to minimize unfavourable steric interactions. The carbene rings in both **3** and **4** are twisted out of the plane of the Mn–Mn bond direction; this configuration may occur to maximize the π-backbonding and may not be a consequence of the cyclic carbene ligand since it is also observed in *eq*-$[Mn_2(CO)_9\{C(OCH_3)Ph\}]$ [19]. The Mn(2)–C(25) bond length is longer for the six-membered ring complexes than for the five-membered ring complexes, indicating greater electron delocalization in the six-membered rings and less electron delocalization over the Mn(2)–C(25) bond than for the five-membered rings. The equatorial CO groups adopt the usual staggered conformation, thereby minimizing their steric interactions.

TABLE 3. Bond lengths (Å) for compounds 3 and 4 (a) and for the carbene ring in compounds 1 and 2 (data from ref. 9) (b)

	3	4
(a)		
Mn(1)–Mn(2)	2.892(2)	2.898(2)
Mn(1)–C(11)	1.849(9)	1.864(7)
Mn(1)–C(12)	1.807(8)	1.785(8)
Mn(1)–C(13)	1.865(8)	1.806(8)
Mn(1)–C(14)	1.850(9)	1.887(9)
Mn(1)–C(15)	1.870(8)	1.820(8)
Mn(2)–C(21)	1.843(7)	1.833(7)
Mn(2)–C(24)	1.780(8)	1.782(8)
Mn(2)–C(23)	1.836(8)	1.876(8)
Mn(2)–C(22)	1.853(8)	1.851(7)
Mn(2)–C(25)	1.971(7)	1.982(7)
C(11)–O(11)	1.120(11)	1.116(9)
C(12)–O(12)	1.152(9)	1.114(9)
C(13)–O(13)	1.123(10)	1.158(11)
C(14)–O(14)	1.123(11)	1.109(10)
C(15)–O(15)	1.123(10)	1.157(10)
C(21)–O(21)	1.126(10)	1.145(9)
C(24)–O(24)	1.147(10)	1.152(10)
C(23)–O(23)	1.147(9)	1.122(10)
C(22)–O(22)	1.153(9)	1.138(9)
C(25)–O(25)	1.384(11)	1.299(7)
C(25)–C(29)	1.396(12)	1.493(11)
O(25)–C(26)	1.468(14)	1.497(10)
C(26)–C(62)		1.460(11)
C(26)–C(27)	1.405(20)	1.355(12)
C(27)–C(28)	1.476(25)	1.464(14)
C(28)–C(29)	1.461(14)	1.391(15)
	1	**2**
(b)		
Mn(2)–C(25)	1.948(3)	1.948(3)
C(25)–O(25)	1.312(3)	1.299(3)
O(25)–C(26)	1.475(3)	1.486(5)
C(26)–C(62)		1.452(6)
C(26)–C(27)	1.485(5)	1.481(7)
C(27)–C(28)	1.503(4)	1.463(8)
C(28)–C(25)	1.498(4)	1.504(5)

TABLE 4. Bond angles (°) and torsion angles (°) for the carbene ring in compounds 3 and 4

	3	4
Mn(2)–C(25)–C(29)	125.3(6)	126.4(5)
Mn(2)–C(25)–O(25)	118.5(5)	118.5(5)
O(25)–C(25)–C(29)	116.1(7)	115.0(6)
C(25)–O(25)–C(26)	120.7(8)	120.1(6)
O(25)–C(26)–C(27)	109.2(12)	112.3(7)
O(25)–C(26)–C(62)		104.9(7)
C(62)–C(26)–C(27)		123.8(8)
C(26)–C(27)–C(28)	111.4(14)	117.5(8)
C(27)–C(28)–C(29)	116.8(11)	115.0(9)
C(25)–C(29)–C(28)	118.0(9)	116.6(8)
Mn(1)–Mn(2)–C(25)	93.9(2)	94.5(2)
Mn(1)–Mn(2)–C(25)–O(25)	-93.7(6)	-71.9(5)
Mn(1)–Mn(2)–C(25)–C(29)	90.7(7)	112.1(6)
Mn(2)–C(25)–C(29)–C(28)	147.9(9)	139.7(8)
Mn(2)–C(25)–O(25)–C(26)	-175.0(8)	-177.2(5)
O(25)–C(25)–C(29)–C(28)	-27.8(12)	-36.4(11)
C(29)–C(25)–O(25)–C(26)	1.0(12)	-0.8(9)
C(25)–O(25)–C(26)–C(62)		176.7(6)
C(25)–O(25)–C(26)–C(27)	42.5(15)	39.8(10)
O(25)–C(26)–C(27)–C(28)	-56.8(16)	-41.6(12)
C(62)–C(26)–C(27)–C(28)		-169.3(10)
C(26)–C(27)–C(28)–C(29)	32.9(19)	7.0(15)
C(27)–C(28)–C(29)–C(25)	11.0(17)	33.3(13)

Kinetic studies

Deuterium exchange studies were carried out in 1:5 $D_2O:(CD_3)_2CO$ (with no added catalyst) at 40.0 °C and were interpreted on the basis of the following scheme:

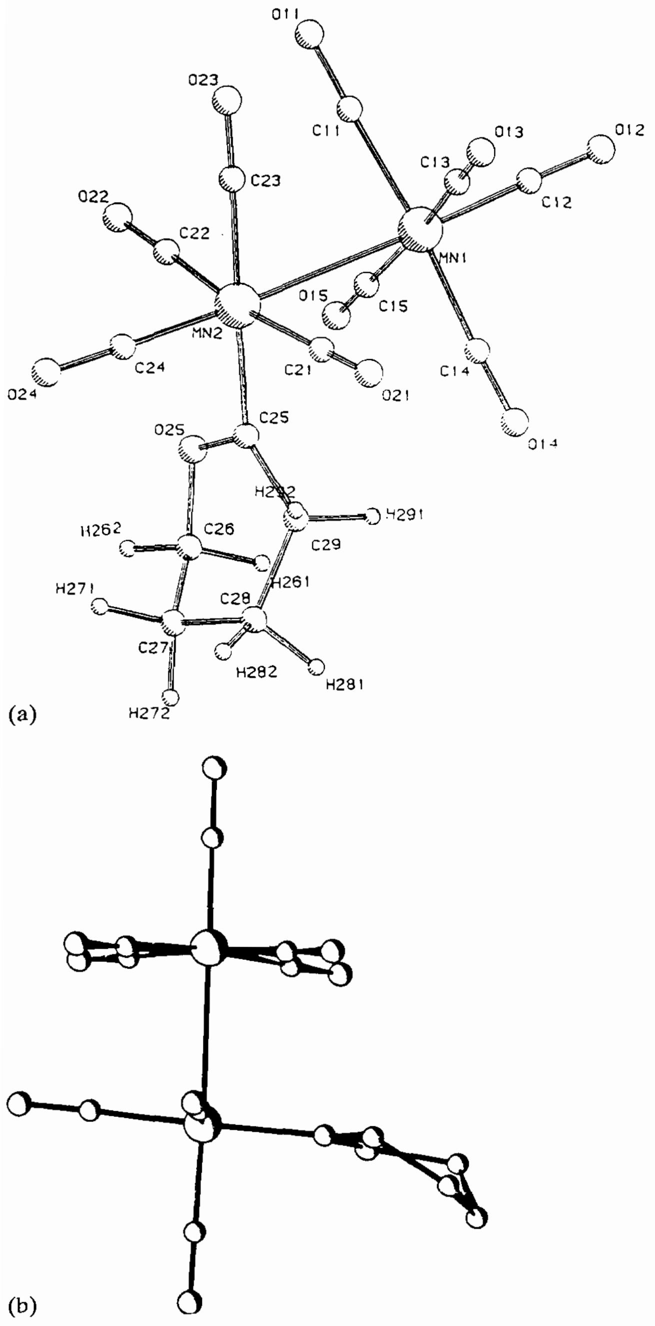


Fig. 1. (a) View of the structure of compound 3 and (b) showing puckering in the carbene ring.

$$X\text{-}H+\tfrac{1}{2}D_2O \longrightarrow X\text{-}D+\tfrac{1}{2}H_2O \qquad (3)$$

(X = carbene complex)

The reaction is irreversible and the rate data are therefore assessed only in terms of the forward reaction. Under the pseudo-first order conditions imposed by a very large concentration of D_2O relative to the carbene complex, the rate is given by:

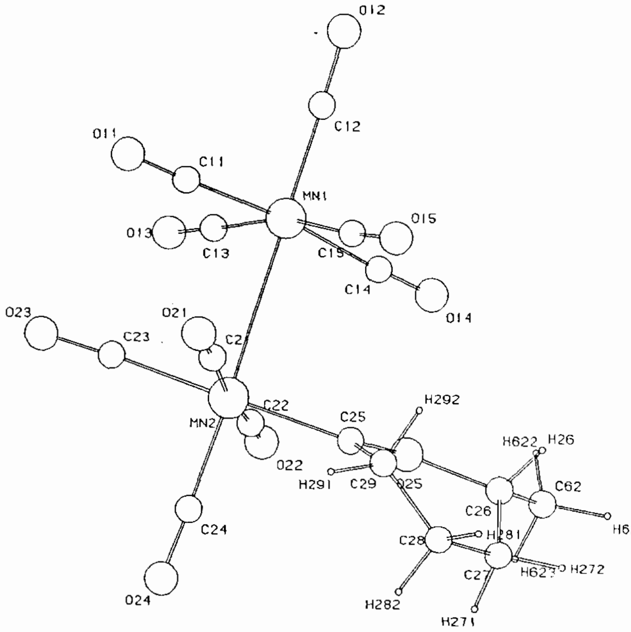


Fig. 2. View of the structure of compound 4.

TABLE 5. Results of deuterium exchange

Compound	k_{obs} (S^{-1})	$t_{1/2}$[a] (min)
1	5.476×10^{-4}	21.09
3	1.110×10^{-3}	10.41

[a] Given by $\dfrac{\ln 2}{k_{obs}}$.

$$\frac{-\mathrm{d}[XH]}{\mathrm{d}t}=k_{OBS}[XH]$$

Only the carbene complexes with unsubstituted rings (**1** and **3**) underwent deuterium exchange. The results are given in Table 5. No exchange reaction occurred for compounds **2**, **4**, **5** or **6**. This shows how the electron-donating effect of the substituent methyl group can be transmitted through the ring to positions several carbon atoms away which lends credence to the proposal that there is a considerable amount of electron delocalization in these carbene rings. This is further borne out by the relatively short carbon–carbon bond lengths (in between a double and a single bond length) in the carbene rings of **1**, **2**, **3** and **4** (see Table 3(a) and (b)). Compound **3** reacts approximately twice as fast as compound **1**, indicating that the α-CH_2 protons in the six-membered ring are more acidic than those in the five-membered ring. The half-life for the deuterium exchange reaction in **1** (21 min) is in good agreement with the value of 23 min obtained by Casey for the same reaction [20].

TABLE 6. Melting ranges and DSC results for compounds **1**–**6**

Compound	Melting range (°C)[a]	T_i (°C)[b]	T_{max} (°C)[c]	ΔH endo[d] (kJ mol^{-1})
1	68–69	62	68	19.49
2	72–73	62	74	21.71
3	98–101	93	103	23.08
4	56–58	46	61	22.88
5	79–80	74	79	24.01
6	80–82	73	83	25.30

[a]Determined on a Kofler hot stage microscope. [b]Temperature corresponding to onset of peak. [c]Temperature corresponding to peak maximum. [d]Calculated by Perkin-Elmer Series DSC7 machine (in Jg^{-1}).

Thermal analysis

Differential scanning calorimetry

The DSC traces for **1**–**6** were recorded over the range 30–480 °C. All traces show a sharp endothermic peak in temperature ranges which coincide with their melting ranges measured using a Kofler hot stage microscope, so these endotherms can be attributed to melting of the crystalline samples. The peak temperatures, T_{max}, are taken as the melting points of the compounds. Table 6 lists the onset and peak temperatures, T_i and T_{max}, for the thermograms of each sample compound, and ΔH endo, the enthalpies of melting.

Thermogravimetry

The TGAs of compounds **1**–**6** all show only one very sharp loss in mass over the temperature range 130–200 °C corresponding to elimination of $Mn_2(CO)_{10}$ (which was not unexpected, since compounds **1**–**6** all decompose to $Mn_2(CO)_{10}$ at high temperatures [21]). No peak was observed for the loss of the carbene ligand, which implies that it is bonded very strongly to the rest of the molecule. Thus, compounds **1**–**6** all show similar thermal behaviour and high thermal stability.

Acknowledgements

We thank Mr N. Hendricks for assistance with the ^{1}H NMR rate studies, Miss R. Mohammed for performing the DSC and TGA experiments, Dr Anne Irving for helpful discussions and the University of Cape Town and the FRD for financial support.

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