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Synthesis of dimanganese nonacarbonyl cyclic carbene complexes and molecular structures of two of them

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Discussion and Conclusion

Siloles react as 4e-donor-like conjugated dienes toward metal phosphine fragments, giving rise to five-coordinate 18e complexes with cobalt and tetracoordinated 16e complexes with rhodium as expected. Complexes were obtained in good yield. Thus, through their butadiene fragment, the siloles mimic the reaction of cyclopentadiene.

The essential interactions between silole and the $[Co(PMe_3)_3]^+$ and $[Rh(PR_3)_2]^+$ fragments are emphasized in Chart I. Only the orbitals involved in the bonding are represented. The important valence orbitals of d^8 ML_3 and ML_2 groups are reasonably well-known.[15] They are decomposed into three levels of low energy ($1e + 1a_1$) in ML_3 (C_{3v} symmetry) and $1a_1$, $1b_2$, and $1a_1$ in ML_2 (C_{2v} symmetry) and an upper set of three levels, pointing away from the cobalt, toward the silole. The major difference between the two fragments is the energy of the d_{xz} set, which is significantly stabilized in the ML_2 fragment and consequently less involved in the bonding. The silole presents to the metal three π orbitals: π^1, π^2, π^3. They clearly interact with the metal in a manner similar to that for butadiene, as shown by the X-ray structures of the analogous $[(butadiene)Co(PMe_3)_3]^+$ and $[(silole)Co(PMe_3)_3]^+$[2,6] complexes, the silicon atom being bent away from cobalt after complexation.

Thus, qualitatively, on the basis of symmetry considerations, the basic patterns of interaction between the silole and the cobalt and rhodium fragments are very much alike. The two empty metal orbitals are destabilized by interaction with the filled π^1 and π^2 silole orbitals, giving rise to a two-electron stabilizing interaction. In $[Co(PMe_3)_3]^+$, the π^3 empty silole orbital is also well suited to interact with the filled metal d orbital and thus increase the strength of the bonding by the back-donation d (Co) → π (silole). However, in $[Rh(PR_3)_2]^+$ the corresponding filled d orbital is of higher energy and is thus less suited to match the silole π^3 level and consequently to give extra stabilization by back-bonding. This is in accord with the higher stability of the cobalt complex compared to that of the rhodium one toward silole dissociation or phosphine substitution. As a consequence, an increase in the Co–silole interaction would strengthen the M–silole bond and weaken the C–C bond. This is in accord with the NMR data.

Moreover, the lack of empty metal d orbitals in the *xy* plane indicates why there is no coordination of the allyl substituent on Si with the cobalt or rhodium center.

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Registry No. 1, 82763-95-9; 2, 98749-91-8; 3, 118512-97-3; 4, 118512-99-5; 6, 129176-16-5; 7, 129176-18-7; 8, 129176-20-1; 9, 129176-22-3; 10, 129176-24-5; 11, 129176-26-7; 12, 129176-28-9; $CoBr(PMe_3)_3$, 53432-07-8; $[Rh(COD)(PPh_3)_2]PF_6$, 35238-97-2; $[Rh(THF)_2(H_2)(PPh_3)_2]PF_6$, 129176-30-3.

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Synthesis of Dimanganese Nonacarbonyl Cyclic Carbene Complexes and Molecular Structures of Two of Them

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Summary: The reactions of $Br(CH_2)_3Br$, $BrCH_2CH_2CH(CH_3)Br$, $Br(CH_2)_4Br$, and $BrCH_2CH_2CH_2CH(CH_3)Br$ with $Na[Mn(CO)_5]$ yield the dimanganese cyclic carbene complexes $[(CO)_5MnMn(CO)_4L]$ (where L = $\overline{CCH_2CH_2CH_2O}$, $\overline{CCH_2CH_2CH(CH_3)O}$, $\overline{CCH_2CH_2CH_2CH_2O}$, and $\overline{CCH_2CH_2CH_2CH(CH_3)O}$, respectively). The structures of the first two of these complexes have been determined by X-ray crystallography, and this confirms that the cyclic carbene ligand occupies an equatorial position. IR, ^1H and ^{13}C NMR, and mass spectra are reported and discussed for these carbene complexes.

Binuclear metal complexes containing carbene or μ-hydrocarbyl ligands are of considerable current interest.[1,2] This is partly due to the proposed intermediacy of such species in a variety of catalytic reactions.[3-5]

The reaction of $Br(CH_2)_3Br$ with several metal carbonyl anions was first reported several years ago.[6-8] The orange product of the reaction of $Na[Mn(CO)_5]$ with $Br(CH_2)_3Br$ was originally reported by King to be a μ-1,3-propanediyl compound,[7] with a novel structure to account for the ^1H NMR data. Some years later, Casey,[9] using ^1H NMR data and deuterium-exchange experiments, put forward very convincing evidence that King's orange manganese compound was *not* the propanediyl compound $[(CO)_5MnCH_2CH_2CH_2Mn(CO)_5]$ but an isomer of this, namely the cyclic carbene complex $[(CO)_5MnMn(CO)_4(\overline{CCH_2CH_2CH_2O})]$, and explained the mechanism of its formation. Surprisingly, the structure of King's orange dimanganese compound has never been confirmed. We now report the structure of this compound and the related compound

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$[(CO)_5MnMn(CO)_4(CCH_2CH_2CH(CH_3)O)]$. We propose a mechanism for the formation of these compounds as well as new spectroscopic data for them and the related six-membered-ring carbene complexes $[(CO)_5MnMn(CO)_4(CCH_2CH_2CH_2CH_2O)]$ and $[(CO)_5MnMn(CO)_4(CCH_2CH_2CH_2CH(CH_3)O)]$.

Experimental Section

All reactions 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]

Preparation of *eq*-$[(CO)_5MnMn(CO)_4(CCH_2CH_2CH_2O)]$ (1). A tetrahydrofuran solution of $Na[Mn(CO)_5]$ (10.88 mmol) was added dropwise with stirring to 1,3-dibromopropane (1.108 g; 5.49 mmol), and the reaction mixture was stirred at room temperature for 18 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 band was compound 1. The product was recrystallized from hexane at −15 °C to give orange crystals of 1 (0.883 g; 38% yield), mp 68–69 °C. Anal. Calcd for $C_{13}H_6Mn_2O_{10}$: C, 36.14; H, 1.40. Found: C, 36.15; H, 1.6. IR (ν(CO), hexane): 2089 (mw), 2024 (s), 2008 (mw), 1999 (s), 1987 (s), 1971 (m), 1957 (m), 1951 (m) cm^{-1}. IR spectra of compounds 1–4 were run as HCBD (HCBD is hexachlorobutadiene) mulls in the region 1500–800 cm^{-1}; the spectra of 1 and 2 are identical with those obtained by King.[7]

Preparation of *eq*-$[(CO)_5MnMn(CO)_4(CCH_2CH_2CH(CH_3)O$ (2). The preparation was carried out in a manner analogous to that for 1. $Na[Mn(CO)_5]$ (10.88 mmol) reacted with 1,3-dibromobutane (1.108 g; 5.74 mmol) to give orange crystals of 2 (0.859 g; 35% yield), mp 72–73 °C. Anal. Calcd for $C_{14}H_8Mn_2O_{10}$: C, 37.69; H, 1.81. Found: C, 37.9; H, 1.9. IR (ν(CO), hexane): 2089 (mw), 2023 (s), 2007 (mw), 1999 (s), 1987 (s), 1970 (m), 1956 (m), 1950 (m) cm^{-1}.

Preparation of *eq*-$[(CO)_5MnMn(CO)_4(CCH_2CH_2CH_2CH_2O)]$ (3). The preparation was carried out in a manner analogous to that for 1. $Na[Mn(CO)_5]$ (10.88 mmol) reacted with 1,4-dibromobutane (1.182 g; 5.47 mmol) to give orange crystals of 3 (0.556 g; 23% yield), mp 95–98 °C. Anal. Calcd for $C_{14}H_8Mn_2O_{10}$: C, 37.69; H, 1.81. Found: C, 37.6; H, 1.8. IR (ν(CO), hexane): 2088 (mw), 2022 (s), 2009 (m), 1996 (s), 1985 (s), 1969 (m), 1954 (mw(, 1948 (m) cm^{-1}. IR (HCBD mull in region 1500–800 cm^{-1}): 1470 (w), 1461 (w), 1443 (w), 1418 (w), 1379 (m), 1335 (mw), 1290 (w), 1250 (s), 1140 (m), 1081 (mw), 1070 (m), 1040 (s), 914 (w), 901 (vw), 881 (w), 872 (mw) cm^{-1}.

Preparation of *eq*-$[(CO)_5MnMn(CO)_4(CCH_2CH_2CH_2CH(CH_3)O)]$ (4). The preparation was carried out in a manner analogous to that for 1. $Na[Mn(CO)5]$ (13.73 mmol) reactd with 1,4-dibromopentane (1.571 g; 6.83 mmol) to give orange crystals of 4 (0.724 g; 23% yield), mp 54–56 °C. Anal. Calcd for $C_{15}H_{10}Mn_2O_{10}$: C, 39.16; H, 2.19. Found: C, 39.14; H, 2.25. IR (ν(CO), hexane): 2087 (mw), 2021 (s), 2006 (m), 1996 (s), 1985 (s), 1968 (m), 1953 (mw), 1947 (m) cm^{-1}. IR (HBCD mull in region 1500–800 cm^{-1}): 1454 (w), 1444 (w), 1385 (mw), 1364 (w), 1351 (w), 1310 (mw), 1258 (m), 1249 (m), 1143 (w), 1069 (m), 1042 (w), 1010 (w), 950 (m), 884 (w) cm^{-1}.

Table I. Crystal and X-ray Diffraction Data

	1	2
formula	$C_{13}H_6O_{10}Mn_2$	$C_{14}H_8O_{10}Mn_2$
cryst color	orange	orange
cryst habit	plates	plates
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/n$
a, Å	8.902 (6)	8.342 (1)
b, Å	12.796 (6)	13.444 (3)
c, Å	15.428 (5)	16.494 (2)
α, deg	107.21 (3)	90
β, deg	97.30 (5)	104.50 (1)
γ, deg	91.01 (5)	90
V, Å^3	1662 (1)	1790.9 (5)
Z	4	4
D(calcd), g cm^{-3}	1.73	1.65
cryst dimens, mm	0.50 × 0.53 × 0.56	0.47 × 0.53 × 0.56
temp, °C	room temp	room temp
μ(Mo Kα), cm^{-1}	15.06	14.01
radiatn	graphite-monochromated Mo Kα (λ = 0.71069 Å)	
scan mode	$\omega/2\theta$	$\omega/2\theta$
scan width, deg	0.90 + 0.35 tan θ	0.90 + 0.35 tan θ
aperture width, mm	4	4
stability of std refln, %	1.3	1.3
2θ range, deg	1–25	1–25
abs cor factor	0.927–0.999	0.867–0.999
no. of collected data	6088	3401
no. of unique data	5453	2953
no. of unique data with $I > 2\sigma(I)$	4873	2718
range in h	−10 to +10	−9 to +9
range in k	−15 to +15	0–16
range in l	0–18	0–19
R_{int}	0.017	0.022
no. of variables	486	246
weighting scheme	$1/[\sigma^2(F_o) + 0.001539F_o]$	$1/[\sigma^2(F_o) + 0.000219F_o]$
final residual, e Å^{-3}	0.43	0.51
R	0.034	0.034
R_w	0.041	0.039
S	1.2	4.2

Crystallographic Studies. Suitable crystals of 1 and 2 were obtained by slow crystallization of the compounds from hexane solutions at 0 °C. Lattice parameters were determined by the least-squares fitting of the setting angles of 25 reflections with $16° \leq \theta \leq 17°$, automatically centered on a CAD4 diffractometer. Three intensity control reflections were monitored after every 1 h of data collection: 1,1,11, 381, −7,2,3 (1); −3,5,11, −2,10,3, 622 (2). An empirical absorption correction[11] was applied to each set of data. The structures were solved by direct methods. Least-squares anisotropic refinement (based on F) of the positions of the non-hydrogen atoms and constrained isotropic refinement of the hydrogen atom positions (with C–H = 0.96 Å) were straightforward with the exception of the atomic positions for the $(CH_2)_3O$ moiety in the carbene ring of molecule II in compound 1. At the end of the straightforward refinement the bond lengths in this carbene ring did not look sensible. Two difference maps computed for compound 1 after isotropic refinement of the structure without the carbene ring atoms (i) in molecule 1 and (ii) in molecule II were inspected. Electron densities (e Å^{-3}) observed were 9.05, 8.52, 8.09, 8.14, and 12.35 for the positions of C(1A) to O(5A) and 8.74, 7.91, 5.76, 4.55, and 8.86 for the corresponding atomic positions in molecule II. These values and the presence of additional electron density maxima in the vicinity of C(A2), C(A3), and C(A4) confirmed the suspicion that this carbene ring was disordered. The refinement of the atomic positions of the carbene ring for molecule II in compound 1 was completed as follows: (i) the bond lengths in both models were constrained to have the same values as corresponding bond lengths in molecule I; (ii) all hydrogen atoms were placed in fixed calculated positions; (iii) the site occupation factors were refined.

The ratio of occupancy of the model containing C(A2), C(A3), C(A4), and O(A5) to that containing O(B2), C(B3), C(B4), and C(B5) is 0.754:(1−0.754). The positions of C(A2) and O(B2) are virtually superimposed, as is also the case for the positions of O(A5) and C(B5); i.e., unequal occupation of the set of positions by enantiomers is found.

Complex neutral-atom scattering factors were used for hydrogen[12] and for all other atom types[13]; dispersion corrections were

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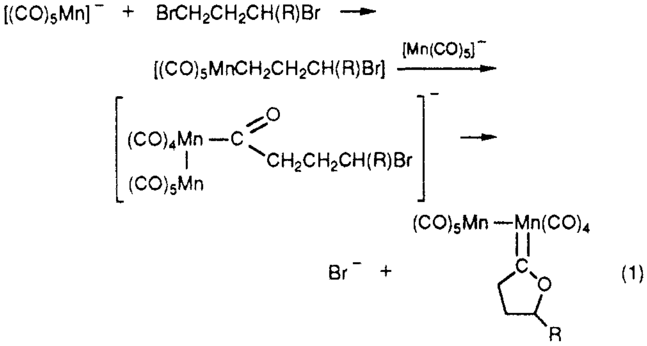
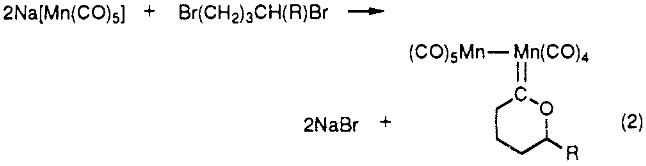
from ref 14. Computer programs used are as follows: SHELX76;[15] SHELX86;[16] PLUTO;[17] PARST.[18] All calculations were performed at the Computer Centre of the University of Cape Town on a Univac 1100/81 computer. Further details of the data collection, structure solution, and refinement are given in Table I.

Results and Discussion

Synthesis and Characterization of Compounds 1–4. The compounds 1–4 were synthesized by the reactions of THF solutions of $Na[Mn(CO)_5]$ with the appropriate dibromoalkanes, as shown in eq 1 for the five-membered-ring complexes and eq 2 for the six-membered-ring complexes.



1, R = H
2, R = CH$_3$



3, R = H
4, R = CH$_3$

This preparative method is similar to that used by King.[7] The product of eq 1 has previously been shown by Casey[9] to be the cyclic carbene complex 1. The reaction of $Na[Mn(CO)_5]$ with 1,3-dibromobutane was previously carried out by King;[7] we now reformulate the product of this reaction as the cyclic carbene complex 2 (eq 1). We observe selective formation of only one isomer of 2. Thus, the methyl group of 1,3-dibromobutane directs the attack of the first $[Mn(CO)_5]^-$ as shown in eq 1. The reaction of $Na[Mn(CO)_5]$ with 1,4-dibromobutane was also reported by King.[7] We now reformulate this orange product on spectroscopic evidence as the six-membered-ring carbene complex 3 (see eq 2). The reaction of $Na[Mn(CO)_5]$ with 1,4-dibromopentane had not previously been reported; we isolate only one isomer and assign the formulation 4 on spectroscopic evidence.

The compounds 1–4 are all orange crystalline solids, with 1 and 2 being more thermally stable than 3 and 4; we also find that the methyl derivatives are less stable than the unsubstituted compounds.[19] The compounds 1–4 all show eight ν(CO) bands in their IR spectra, consistent with the compounds all being of the type *eq*-$[Mn_2(CO)_9L]$. IR spectra for compounds 1–4 were recorded in HCBD mulls between 1500 and 800 cm^{-1} (where ν(C–O–) may be expected) and are identical with the results obtained by King.[7] The spectra in this region for 1–4 and for related compounds[20] are complex. The mass spectra of the compounds 1–4 are similar, and all show parent molecular ions with the predominant fragmentation pathway being the sequential loss of CO groups from the parent ion, indicating that the carbene ligand is bonded to the manganese atom more strongly than the other ligands, including the second magnanese atom. This is in agreement with the literature.[21]

Table II. ^{1}H and ^{13}C NMR Data[a,b]

compd	^{1}H NMR	^{13}C NMR[c]
1	4.87 (t, 2 H, OCH_2); 3.68 (t, 2 H, MnCCH_2); 1.97 (q, 2 H, OCH$_2$CH_2)	338.1 (Mn=*C*); 85.1 (O*C*H$_2$); 55.1 (Mn*C*CH$_2$); 21.6 (OCH$_2$*C*H$_2$)
2	5.13 (qu, 1 H, OCH(CH$_3$)); 3.85 (m, 2 H, MnCCH_2); 2.12 (m, 2 H, OCH(CH$_3$)CH_2); 1.54 (d, 3 H, CH_3)	336.4 (Mn=*C*); 95.6 (O*C*H(CH$_3$)); 58.7 (Mn*C*CH$_2$); 28.9 (*C*H$_3$); 20.2 (OCH$_2$*C*H$_2$)
3	4.61 (t, 2 H, OCH_2); 3.51 (t, 2 H, MnCCH_2); 1.80 (m, 4 H, OCH$_2$CH_2CH_2)	351.3 (Mn=*C*); 76.4 (O*C*H$_2$); 51.2 (Mn*C*CH$_2$); 21.8 (MnCCH$_2$*C*H$_2$); 17.1 (OCH$_2$*C*H$_2$)
4	3.60 (m, 1 H, OCH(CH$_3$)); 3.43 (t, 2 H, MnCCH_2); 2.54 (m, 2 H, OCH(CH$_3$)CH_2); 1.02 (m, 2 H, MnCCH$_2$CH_2); 0.91 (m, 3 H, CH_3)	349.9 (Mn=*C*); 83.7 (O*C*H(CH$_3$)); 50.9 (Mn*C*CH$_2$); 27.9 (*C*H$_3$); 19.8 (MnCCH$_2$*C*H$_2$); 16.3 (MnCCH$_2$CH$_2$*C*H$_2$)

[a] Compounds 1–3 were recorded as CDCl$_3$ solutions, and compound 4 was recorded as a C$_6$D$_6$ solution. [b] Chemical shifts are reported relative to tetramethylsilane (δ 0.00 ppm) as a reference standard: m = multiplet; d = doublet; t = triplet; q = quintet; qu = quartet. [c] Broad, weak peaks were observed for all the compounds in the region 217–220 ppm due to CO groups.

Discussion of NMR Data for Compounds 1–4. The ^{1}H and ^{13}C NMR spectra of compounds 1–4 are given in Table II. The ^{1}H NMR data and assignments for compound 1 agree well with those reported by Casey.[9] The ^{13}C NMR spectrum of 1 has not been reported previously and is now given. Some discussion of the ^{1}H NMR spectra of 2 and 3 has been given previously,[7] but this was based on the assumption that the compounds were the alkanediyl compounds $[(CO)_5MnCH_2CH_2CH(CH_3)Mn(CO)_5]$ and $[(CO)_5Mn(CH_2)_4Mn(CO)_5]$. Also, the butanediyl compound $[(CO)_5Mn(CH_2)_4Mn(CO)_5]$ has been prepared by the decarbonylation of $[(CO)_5MnC(O)(CH_2)_4C(O)Mn(CO)_5]$[22] and shows the expected ^{1}H NMR spectrum of two multiplets at δ 1.70 and 1.09.

Some interesting trends are observed in the ^{13}C NMR data (Table II) when the nature of the carbene ligand is changed. The most significant shifts are for the two carbon atoms adjacent to the ring oxygen atom. Thus, the chemical shift of the carbene carbon atom increases when the ring size is increased from five to six but decreases when the substituent on the other carbon atom adjacent

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Table III. Bond Lengths (Å) for Compounds 1 and 2

	1 (I)	1 (II)	2
Mn(1)-Mn(2)	2.903 (1)	2.914 (1)	2.903 (1)
Mn(1)-C(1A)	1.948 (3)	1.952 (3)	1.948 (3)
Mn(1)-C(1)	1.779 (4)	1.792 (4)	1.787 (3)
Mn(1)-C(2)	1.851 (4)	1.853 (3)	1.838 (3)
Mn(1)-C(3)	1.838 (3)	1.844 (3)	1.836 (3)
Mn(1)-C(4)	1.827 (3)	1.846 (3)	1.855 (3)
Mn(2)-C(5)	1.846 (3)	1.851 (3)	1.845 (3)
Mn(2)-C(6)	1.836 (3)	1.851 (3)	1.837 (3)
Mn(2)-C(7)	1.851 (4)	1.822 (3)	1.833 (4)
Mn(2)-C(8)	1.830 (3)	1.842 (3)	1.852 (3)
Mn(2)-C(9)	1.808 (4)	1.805 (4)	1.804 (3)
C(1)-O(1)	1.151 (5)	1.147 (5)	1.147 (4)
C(2)-O(2)	1.130 (5)	1.125 (4)	1.137 (4)
C(3)-O(3)	1.149 (4)	1.129 (4)	1.140 (5)
C(4)-O(4)	1.135 (4)	1.132 (4)	1.124 (4)
C(5)-O(5)	1.130 (4)	1.131 (4)	1.133 (4)
C(6)-O(6)	1.131 (4)	1.130 (4)	1.128 (4)
C(7)-O(7)	1.125 (5)	1.150 (4)	1.134 (4)
C(8)-O(8)	1.142 (4)	1.126 (4)	1.134 (4)
C(9)-O(9)	1.142 (5)	1.133 (6)	1.133 (4)

to the oxygen atom is changed from H to CH_3. The chemical shift of the other carbon atom adjacent to the oxygen atom decreases when the ring size changes from five to six and increases when the substituent on it changes from H to CH_3.

Molecular Structures of 1 and 2. These results confirm Casey's proposal that King's orange complex, originally formulated as $[(CO)_5Mn(CH_2)_3Mn(CO)_5]$, is an equatorially substituted dimanganese cyclic carbene complex. The structure of **2** is very similar to that of **1**. The methyl substituent on **2** is shown to be on the carbon atom next to the ring oxygen atom, as suggested by NMR results. Views of a molecule of **1** and a molecule of **2** are shown in Figures 1 and 2.

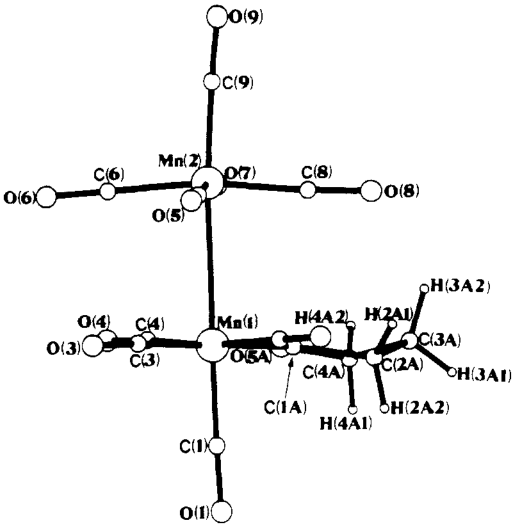

Figure 1. View of the structure of compound 1 (molecule I).

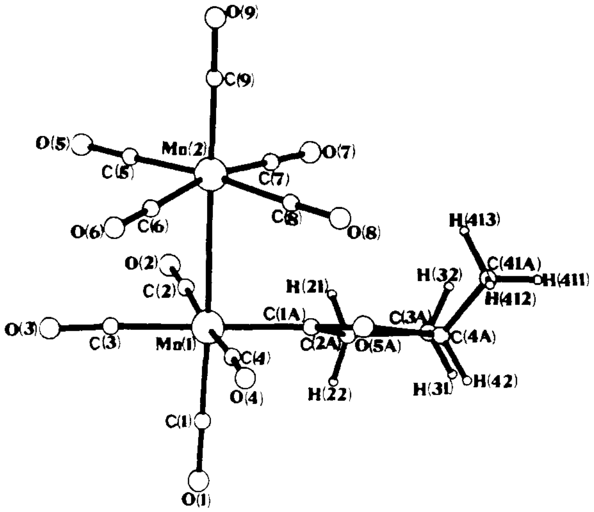

Figure 2. View of the structure of compound 2.

The metal atoms are approximately octahedrally coordinated with one position occupied by the second manganese atom. The equatorial CO groups adopt a staggered configuration, thereby minimizing their steric interactions. The results of only a few single-crystal X-ray diffraction studies of similar compounds of the type $Mn_2(CO)_9L$ have been reported.[23-28] In **1** and **2** the Mn-Mn bond lengths of 2.903 (1), 2.914 (1) Å and of 2.903 (1) Å respectively fall within the range of previously reported distances. The

Table IV. Bond Lengths (Å), Bond Angles (deg), and Torsion Angles (deg) for the Carbene Ring in Compounds 1, 2, 5,[a] and 6[b]

	1 (I)	1 (II)	2	5	6
C(1A)-C(2A)	1.498 (4)	1.498 (6)	1.504 (5)	1.53 (3)	1.45 (1)
C(2A)-C(3A)	1.503 (4)	1.500 (10)	1.463 (8)	1.50 (4)	1.51 (2)
C(3A)-C(4A)	1.481 (5)	1.481 (11)	1.481 (7)	1.49 (4)	1.45 (2)
C(4A)-O(5A)	1.475 (3)	1.481 (6)	1.486 (5)	1.49 (3)	1.45 (2)
O(5A)-C(1A)	1.312 (3)	1.309 (4)	1.299 (3)	1.33 (3)	1.34 (1)
C(4A)-C(41A)			1.452 (6)		

	1 (I)	1 (II)	2	5	6
Mn(1)-C(1A)-C(2A)	129.5 (2)	127.2 (4)	128.6 (2)	130 (1)	128.2 (6)
Mn(1)-C(1A)-O(5A)	122.4 (2)	123.7 (4)	123.3 (2)	124 (1)	123.7 (6)
O(5A)-C(1A)-C(2A)	107.5 (3)	108.7 (5)	107.9 (2)	106 (2)	108.1 (7)
C(1A)-C(2A)-C(3A)	105.1 (3)	106.8 (5)	106.6 (4)	107 (2)	105.2 (8)
C(2A)-C(3A)-C(4A)	102.9 (3)	105.5 (6)	107.1 (5)	104 (2)	103.1 (10)
C(3A)-C(4A)-O(5A)	103.8 (3)	105.7 (6)	103.5 (4)	104 (2)	105.2 (10)
C(4A)-O(5A)-C(1A)	112.7 (3)	113.0 (4)	114.1 (2)	113 (2)	111.2 (8)
C(3A)-C(4A)-C(41A)			118.0 (5)		
O(5A)-C(4A)-C(41A)			108.2 (4)		
Mn(2)-Mn(1)-C(1A)	92.2 (1)	92.2 (1)	92.7 (1)		
Mn(2)-Mn(1)-C(1A)-C(2A)	100.3 (3)	-94.5 (5)	117.9 (3)		
Mn(2)-Mn(1)-C(1A)-O(5A)	-89.3 (3)	93.4 (4)	69.0 (2)		
Mn(1)-C(1A)-O(5A)-C(4A)	171.2 (3)	177.7 (4)	173.2 (2)		
Mn(1)-C(1A)-C(2A)-C(3A)	172.0 (3)	174.0 (5)	178.7 (3)		
C(2A)-C(3A)-C(4A)-O(5A)	26.9 (4)	4.9 (6)	-9.0 (5)		

[a] Data from ref 29. [b] Data from ref 30.

Mn-Mn-$(CO)_{eq}$ angles are all acute in contrast to the Mn-Mn-C(ring) angle of 92.2 (1), 92.2 (1)° and of 92.7 (1)°. Final bond lengths for the $Mn_2(CO)_9$ moiety are listed in Table III. The Mn-$(CO)_{ax}$ bond lengths are shorter than the Mn-$(CO)_{eq}$ bond distances; corresponding values for $Mn_2(CO)_{10}$ are 1.811 (3) and 1.856 (7) Å.[24] In a comparison of the structures of **1** and **2**, it appears that the presence of the methyl substituent has little effect, although the methyl group in **2** points toward the second manganese atom, not away from it, as might have been expected on steric grounds. The carbene ring is approximately perpendicular to the Mn-Mn bond direction in **1** but is twisted somewhat further out of this plane in **2**. This configuration may occur to maximize the π back-bonding and may not be a consequence of the cyclic carbene ligands, since it is also observed in *eq*-$[Mn_2(CO)_9(C(OCH_3)Ph)]$.[25] Bond lengths and angles for the Mn-carbene fragments are given in Table IV together with similar values for the Mo-cyclic carbene fragments in $[Cp^*MoI(CO)_2(\overline{CCH_2CH_2CH_2O})]$ ($Cp^* = \eta^5\text{-}C_5Me_5$) (**5**)[29] and $[CpMoI(CO)_2(\overline{CCH_2CH_2CH_2O})]$ ($Cp = \eta^5\text{-}C_5H_5$) (**6**).[30] The Mn-C(carbene) bond lengths in **1** and **2** of 1.948 (3), 1.952 (3) Å and of 1.948 (3) Å agree with the corresponding distance of 1.950 (5) Å found in the acyclic Fischer-type carbene complex *eq*-$[(CO)_5MnMn(CO)_4(C(OCH_3)Ph)]$,[25] suggesting delocalization of electron density over Mn-C(carbene)-O in all of these complexes.

Thus, the nature of the products from the reactions of $Na[Mn(CO)_5]$ with dibromoalkanes depends on the nature of the dibromoalkane. X-ray crystal structure determinations are underway on the six-membered-ring carbene complexes $[(CO)_5MnMn(CO)_4(\overline{CCH_2CH_2CH_2CH_2O})]$ and $[(CO)_5MnMn(CO)_4(\overline{CCH_2CH_2CH_2CH(CH_3)O})]$.[19]

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Supplementary Material Available: A listing of mass spectral data for **1**–**4** and listings of fractional atomic coordinates and temperature factors for **1** and **2** (6 pages); listings of observed and calculated structure factors for **1** and **2** (36 pages). Ordering information is given on any current masthead page.

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Redox Behavior of Nickel Acylate Complexes

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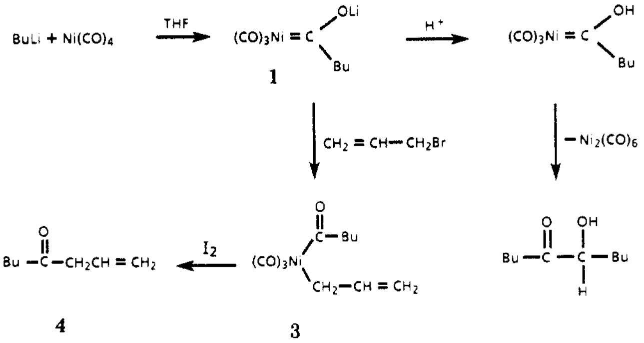
Summary: **The cyclic voltammetry and bulk oxidation with ferrocenium ion and molecular iodine of three nickel complexes were studied. The results are most consistent with both Cp_2Fe^+ and I_2 acting as single-electron oxidants.**

Recently, we have been investigating the reactivity of the monomeric nickel acylate complex **1**, generated from the reaction of butyllithium and nickel tetracarbonyl in tetrahydrofuran, with a variety of acids and electrophiles.[2]



When the acylate complex is treated with water, a mineral acid, or a ketone that has a pK_a less than 17, an acyloin derivative is formed. When acylate complex **1** is treated with allyl bromide, a stable acyl(allyl)nickel complex, **3**, is formed. This complex converts to a ketone upon oxidation with iodine (I_2).[3,4]

In addition, the I_2 oxidation of nickel acylate complex **1** itself has been investigated.[2] This reaction generates a variety of acyl coupling products, which appear to be due to radical coupling reactions; however, the exact mechanism of formation of these products is unknown.

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(4) Many oxidation-induced reductive eliminations of iron complexes have been reported, although the role of the metal-centered radical generally has not been elucidated. See for example: (a) Yamamoto, A.; Morifuji, K.; Ikeda, S.; Saito, T.; Uchida, Y.; Misono, A. *J. Am. Chem. Soc.* **1968**, *90*, 1878. (b) Liebeskind, L. S.; Welker, M. E.; Fengl, R. W. *Ibid.* **1986**, *108*, 6328.

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