Metal–metal bond cleavage of carbene complexes by halogens: The crystal and molecular structures of *ax*-[Mn₂(CO)₉{C(OEt)2-thienyl}], [Mn(CO)₄(I)-{C(OEt)2-thienyl}] and *eq*-[Mn₂(CO)₉{C(NH₂)2-thienyl}]

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Dedicated to Professor Helgard G. Raubenheimer.

Abstract

The metal–metal bond in [M₂(CO)₉{C(OEt)R}] (M = Mn (**1**), Re (**2**), R = 2-thienyl (**a**), 2-bithienyl (**b**)) is readily cleaved with halogens to afford *cis*-[M(CO)₄(X){C(OEt)R}] (M = Mn (**3**), X = I; M = Re (**4**), X = Br). In the binuclear manganese complex, the carbene ligand is found in an axial position due to steric reasons, whereas the electronically favoured equatorial position is found for the carbene ligands in the corresponding rhenium complexes and in [Mn₂(CO)₉{C(NH₂)thienyl}] (**5a**), containing a sterically less demanding NH₂-substituent.
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1. Introduction

The chemistry of group 7 transition metals carbonyl complexes containing Fischer carbene and halogen ligands, [M(CO)₄(carbene)X] (M = Mn, Re; X = halogens), has been neglected due to difficulties associated with the synthesis of such compounds [1]. On the other hand, group 7 transition metal carbene complexes with cyclopentadienyl ligands are readily accessible from MCp(CO)₃ and organolithium reagents [2]. Also, binuclear monocarbene complexes [M₂(CO)₉(carbene)] (M = Mn, Re) are obtainable from M₂(CO)₁₀ and organolithium precursors [3]. The King compound,

[Mn₂(CO)₉($\overline{COCH_2CH_2CH_2}$)], that was initially assigned an incorrect structure without a carbene ligand, [Mn₂-(CO)₁₀(CH₂)₃] [4], sparked interest in the challenges associated with the synthesis of [M(CO)₄(carbene)X] (M = Mn, Re; X = halogens) complexes. The isolation of binuclear monocarbene complexes of group 7 transition metals, [Mn₂(CO)₉{C(OR)R}], (R = alkane) prepared from Na[Mn(CO)₅] and 1,3-dihaloalkanes was reinvestigated and resulted in detailed mechanistic studies of the reactions of Na[M(CO)₅] (M = Mn, Re) with dihaloalkanes [5]. By using different dihaloalkanes, a number of complexes similar to the King compound containing a cyclic carbene ligand were synthesized and characterized [6]. In a few instances, with more sophisticated chloro precursors, cationic mononuclear carbene complexes [Mn(CO)₃(L)₂(carbene)]⁺ (L = phosphine or

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CO) could be obtained, which after subsequent treatment with halides, afforded the desired neutral halo-carbene complexes [M(CO)$_4$(carbene)X] [7]. However, the complexes [Mn(CO)$_3$(L)$_2$(carbene)]$^+$ (L = a phosphine ligand or CO) could be afforded by employing the alkylation of [Mn(CO)$_3$(L)$_2${C(O)R}] with the strong alkylating agent MeOSO$_2$F [8]. A major contribution to the carbene chemistry of group 7 transition metals came from the group of Angelici [9,10] on the reaction of strained 3-membered heterocyclic substrates with M(CO)$_5$X (M = Mn, Re; X = Br, Cl). The reactions of aziridine and oxirane with these reagents afforded 5-membered cyclic aminooxy and dioxy carbene compounds. The reaction could also be applied to M$_2$-(CO)$_{10}$ (M = Mn, Re) for oxirane [9]. Largely unnoticed in later work, the cleavage of the metal–metal bond of the dioxy carbene complexes by bromine, was also reported [9]. Nevertheless, very few examples exists where the ligand in [M(CO)$_4${carbene}X] (M = Mn, Re; X = halogen) complexes is not a cyclic alkoxy carbene. Complexes of group 7 transition metals [M(CO)$_4${C(R)R′}X] (M = Mn, Re; R = H, alkoxy, etc., R′ = aryl; X = halogen) are attractive alternative precursors to existing carbene complexes with potential catalytic properties.

Reaction of the lithiated [(η^5-thiophene)Cr(CO)$_3$] or the analogous lithiated [(η^6-benzene)Cr(CO)$_3$ with [Mn(CO)$_5$Br] involved attack either on the metal centre or on a carbonyl ligand with elimination of bromide and yielded for the thiophene precursor the binuclear complexes [{η^1,η^5-thienyl-Mn(CO)$_5$}Cr(CO)$_3$] and [{η^1,η^5-thienyl-C(O)Mn(CO)$_5$}Cr(CO)$_3$] (Scheme 1) [11,12]. By contrast, the corresponding reaction with [Re(CO)$_5$Br] involved attack on a carbonyl ligand without the elimination of bromide. Subsequent alkylation of the latter with [Et$_3$OBF$_4$] yielded the binuclear carbene complex, [{η^1,η^5-thienyl-C(OEt)Re(CO)$_4$Br}Cr(CO)$_3$] (Scheme 1).

This prompted us to investigate the reaction of [Re(CO)$_5$Br] with lithiated thiophene to assess the role, if any, of the Cr(CO)$_3$-fragment. Although not reacting smoothly, it was possible, after subsequent alkylation with [Et$_3$OBF$_4$], to isolate and characterize the mono-carbene dirhenium nonacarbonyl complex, [Re$_2$(CO)$_9$-{C(OEt)thienyl}]. This reaction showed that it was possible to eliminate a bromide from [Re(CO)$_5$X] during a Fischer carbene synthesis-procedure (Li-thienyl/Et$_3$OBF$_4$) and replace it with the isolobal fragment Re(CO)$_5$ to give [Re$_2$(CO)$_9${C(OEt)thienyl}]. In contrast, reactions of lithiated thiophene with [Mn(CO)$_5$Br] afforded a number of unstable compounds that could not be characterized unambiguously. We envisaged that the reverse reaction of cleaving metal–metal bonds in carbene complexes of group 7 transition metals with halogens could be applied more generally, provided the carbene ligand is not affected by the oxidant. The metal–metal bond in [M$_2$(CO)$_{10}$] (M = Mn, Re) is easily cleaved reductively by sodium affording the anionic sodium salt, Na[M(CO)$_5$] [13] or oxidatively with halogens to give neutral metal carbonyl halides, [M(CO)$_5$X] (M = Mn, Re; X = halogens) [14]. The reductive cleavage of the Mn–Mn bond of [Mn$_2$(CO)$_9$-{C(OR)Me}] with sodium in THF was attempted by Fischer and co-workers, but only Mn$_2$(CO)$_{10}$ and Na[Mn(CO)$_5$] were observed to have formed [3a]. Oxidation of the metal results either in the loss of the carbene ligand or the coordination of the products of the oxidizing agent to the metal. Biscarbene complexes of group 6 transition metals are readily oxidized by trace amounts of oxygen to give monocarbene-ester products [15] while diaminocarbene complexes of tungsten could be oxidized with I$_2$ to yield [W(CO)$_4$(I)$_2$(carbene)] [16].

2. Results and discussion

2.1. Synthesis of dinuclear carbene complexes

In a typical experiment (Scheme 2), the bimetallic carbene complexes 1a, 1b, 2a and 2b were prepared by reacting the bimetallic decacarbonyl precursors with lithiated thiophene or 2,2′-bithiophene in THF at −78 °C [17]. After removing the THF under reduced pressure, the residue was dissolved in dichloromethane and alkylated by Et$_3$OBF$_4$ at −30 °C. Purification of the product to remove unreacted metal decacarbonyl was achieved by column chromatography. The bimetallic monocarbene complexes were isolated in yields ranging

Scheme 1.

M = Mn (**1**, **3**), Re (**2**, **4**), R = H (**a**), thienyl (**b**); Y = I (Mn); Br (Re); L = CO
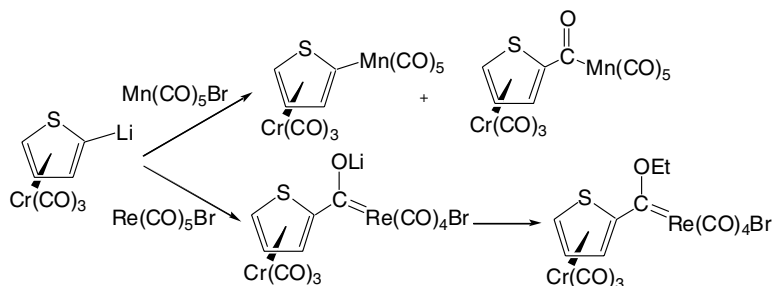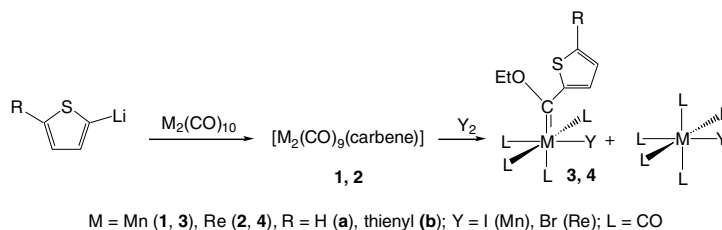
Scheme 2.

from 63–75%. IR spectroscopy, ^{1}H and ^{13}C NMR spectroscopy (Table 1) and mass spectrometry corroborated the single crystal X-ray structure of **1a** (Fig. 1).

Slow decomposition of products with time was observed in the ^{1}H NMR spectra of **1a** and **1b**, but spectra of high resolution could be obtained in either CDCl$_3$ or d$_6$-acetone. The carbonyl resonances in the ^{13}C NMR spectra were broadened in some instances. Whereas the infrared data in the carbonyl region for the rhenium complexes **2a** and **2b** displayed the typical 9 or 8-band pattern for equatorially substituted bimetal nonacarbonyl complexes (C_s symmetry), the corresponding manganese complexes **1a** and **1b** gave a 5-band pattern associated with the carbene ligand in an axial position (C_{4v} symmetry) [18]. A search of the Cambridge Structural Database revealed that **1a** is the second axially substituted carbene complex of manganese nonacarbonyl to be structurally characterized. The only other

Table 1
Spectral data of complexes **1**–**5**

| Complex	IR[a] (ν/cm^{-1} in hexane)	^{1}H NMR (δ/ppm and J/Hz in CDCl$_3$)	^{13}C NMR (δ/ppm in CDCl$_3$)
1a	2090 (m), 2010 (m), 1996 (vs), 1975(m), 1946 (m)	8.35 (dd, 4.1, 0.8, H3), 7.42 (dd, 4.9, 4.1, H4), 8.07 (dd, 5.0, 0.8, H5), MnCOEt: 5.32 (q, 7.0) 1.80 (t, 7.0)	306.5 (C1, carbene), 224.6 (Mn(CO)$_5$, trans), 208.9 (Mn(CO)$_5$, cis), 155.4 (C2), 133.9, 128.9 (C3, C4), 138.9 (C5), MnCOEt: 74.6, 15.1
1b	2089 (m), 2009 (m), 1996 (vs), 1975 (m), 1945 (m)	8.33 (d, 4.4, H3), 7.61 (d, 4.4, H4), 7.65 (dd, 3.6, 0.8, H7), 7.23 (dd, 5.0, 3.6, H8), 7.76 (d, 4.1, H9), MnCOEt: 5.31 (q, 7.0) 1.79 (t, 7.0)	309.9 (C1, carbene), 222.7 (Mn(CO)$_5$, trans), 211.0 (Mn(CO)$_5$, cis), 162.1 (C2), 140.9, 134.4, 128.8, 127.8, 126.6, 125.3 (C3, C4, C6, C7, C8, C9), 146.8 (C5) MnCOEt: 74.4, 15.5
2a	2103 (w), 2071 (w), 2042 (m), 2015 (vs), 2002 (s), 1994 (s), 1977 (s), 1955 (m), 1945 (w)	7.65 (d, 4.4 H3), 7.11 (dd, 4.7, 4.4, H4), 7.65 (d, 4.7, H5), ReCOEt: 4.51 (q, 7.0) 1.58 (t, 7.0)	294.8 (C1, carbene), 192.8 (Re(CO)$_5$), 157.9 (C2), 132.5, 127.6 (C3, C4), 132.8 (C5), ReCOEt: 77.3, 14.6
2b	2102 (w), 2041 (m), 2017 (s), 2001 (vs), 1994 (vs), 1977 (w), 1972 (w), 1954 (m), 1944 (w)	7.73 (d, 4.1, H3), 7.18 (d, 4.1, H4), 7.35 (d, 4.4, H7), 7.05 (dd, 4.4, 1.3, H8), 7.35 (d, 1.3, H9), ReCOEt: 4.54 (q, 7.0) 1.60 (t, 7.0)	289.8 (C1, carbene), 196.0 (Re(CO)$_5$ trans), 181.4 (Re(CO)$_5$ cis), 155.9(C2), 136.2, 128.4, 128.0 127.0, 125.9, 124.1 (C3, C4, C6, C7, C8, C9), 145.6 (C5), ReCOEt: 77.4, 14.6
3a	2078 (m), 2024 (s), 2000 (vs), 1963 (s)	8.74 (dd, 4.1, 1.1, H3), 7.49 (dd, 4.9, 4.1, H4), 8.29 (dd, 4.9, 1.1 H5), MnCOEt: 5.67 (q, 7.0) 1.72 (t, 7.0)	296.4 (C1, carbene), 211.9 (Mn(CO)$_4$), 144.9 (C2), 138.0, 129.4 (C3, C4), 143.6 (C5), MnCOEt: 79.6, 14.9
3b	2078 (m), 2024 (s), 2000 (vs), 1963 (s)	8.53 (H3), 7.72 (H4), 7.80 (H7), 7.49 (H8), 7.90 (H9), MnCOEt: 5.53 (q) 2.02 (t)	n.o.(C1, carbene), n.o. (Mn(CO)$_4$), 162.3(C2), 134.4, 133.5, 131.3, 127.3, 125.6, 124.4 (C3, C4, C6, C7, C8, C9), 134.6(C5), MnCOEt: 76.2, 14.7
4a	2071 (s), 2015 (s), 2004 (s), 1977 (s)	7.98 (dd, 4.9, 1.0, H3), 7.19 (dd, 4.5, 4.2, H4), 7.79 (dd, 4.1, 1.0 H5), ReCOEt: 4.78 (q, 7.0) 1.68 (t, 7.0)	260.4 (C1, carbene), 211.9 (Re(CO)$_4$), 137.3 (C2), 134.7, 128.5 (C3, C4), 138.3 (C5), ReCOEt: 77.2, 14.5
4b	2042 (m), 2000 (vs), 1995 (vs), 1956 (m)	8.50 (d, 4.4, H3), 7.36 (d, 4.4, H4), 7.45 (dd, 5.2, 1.0 H7), 7.09 (dd, 3.6, 5.2, H8), 7.48 (dd, 3.6, 1.0, H9), ReCOEt: 5.28 (q, 7.0) 1.66 (t, 7.0)	268.0 (C1, carbene), 185.6 (Re(CO)$_4$), 152.8 (C2), 150.8 (C5), 135.7 (C6), 148.6, 128.8, 127.6, 125.7 (C3, C4, C7,C8), 131.7 (C9), ReCOEt: 78.8, 15.1
5a	2083 (m), 2013 (vs), 1987 (vs), 1979 (s), 1969 (m), 1936 (s), N–H stretch: 3453 (w), 3328 (w)	7.79 (H3), 7.23 (H4), 7.58 (H5), NH$_2$: 9.76 (s)	267.6 (C1, carbene), 225.9 (Mn(CO)$_5$, trans), 222.1 (Mn(CO)$_5$, cis), 154.3 (C2), 130.1 (C3), 129.6 (C4), 131.8 (C5)

[a] Carbonyl region.
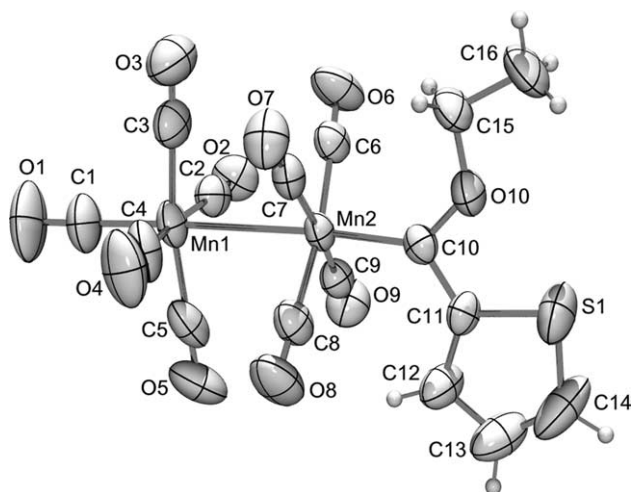
Fig. 1. ORTEP [20] + POV-Ray [21] plot of the geometry of **1a**. Displacement ellipsoids are set at 50% probability.

example has the unusual carbene ligand, =C(NMe₂)-OAl₂(NMe₂)₅ [19]. Most eq-[Mn₂(CO)₉(carbene)] complexes studied crystallographically have cyclic carbene ligands that are less bulky compared to carbene complexes with two separate substituents [6]. We concluded that, although the equatorial position is the electronically favoured position for the carbene ligand (i.e. *trans* to a carbonyl ligand), steric effects can force the carbene ligand to occupy an axial position.

Complex **1a** crystallizes in the monoclinic system, space group $P2_1/c$ with four molecules in the unit cell. The coordination environment of each manganese atom is approximately octahedral with the two sets of the equatorial carbonyl ligands being staggered. The carbene ligand is in the axial position and is therefore *trans* to the metal–metal bond. The thienyl ring is close to being coplanar with the plane of the bonding geometry about the carbene carbon. The dihedral angle between the least-squares planes through (S1, C11, C12, C13 and C14) and through (C10, C11, O10 and Mn2) is 7.6(9)°. The plane of the carbene carbon, thienyl ring and oxygen atom is approximately perpendicular to the equatorial plane of carbonyl ligands (C10–Mn2–CO (91–96°)) and is in an intermediate position between the carbonyl ligands around Mn2, as is evident from the torsion angles of 45.5(10)° and −44.9(10)° for C6–Mn2–C10–O10 and C7–Mn2–C10–O10, respectively. Some disorder of the ethoxy-thien-2-yl-methylidene ligand was observed with a minor component rotated approximately 180° about the Mn–C(carbene) bond with respect to the orientation of the major component, such that the C11A, C12A and C13A atoms of the thienyl ring of the minor component nearly coincide with the O10, C15 and C16 atoms, respectively, of the ethoxy group of the major component (O10A, C15A and C16A also nearly coincide with C11, C12 and C13, respectively). Fig. 1 shows the major orientation

(88.2(4)%). The carbene ligand is in the *trans*-configuration about the C–O bond (C11–C10–O10–C15 177.2(8)°). The metal–carbon(carbonyl) bond distance *trans* to the Mn–Mn bond is significantly shorter than the mean distances of the Mn–C(carbonyl) bond lengths in the equatorial planes (Table 2) to compensate for the weaker π-acceptor properties of the carbene carbon compared to a carbonyl carbon on the other side of the metal-metal bond. The Mn1–Mn2 distance of **1a** is longer, and the *trans* Mn–C(carbonyl) distance is shorter than the corresponding Mn–Mn (2.9038(6) Å) and *trans* Mn–C(carbonyl) (1.811(3) Å) distances reported for [Mn₂(CO)₁₀] [22]. The Mn–C(carbene), Mn–Mn and M–C(carbonyl) distances are similar to the corresponding distances in the dimanganese nonacarbonyl carbene complex, eq-[Mn₂(CO)₉{C(OEt)Ph}], where the carbene ligand is *cis* to the metal–metal bond and the carbene substituents are in the *cis*-configuration about the carbene C–O bond. The Mn–C(carbene)–C angles are identical in the two structures, however, the other bond angles about the carbene carbon are significantly different with Mn–C(carbene)–O 119.4(3)° and C–C(carbene)–O 115.5(3)° in [Mn₂(CO)₉{C(OEt)Ph}] [23]. The large Mn2–C10–O10 angle in **1a** (131.1(6)°) can be ascribed to the steric interactions between the CH₂ of the ethyl group and the adjacent equatorial carbonyl ligands.

2.2. Halogen cleavage of the dinuclear carbene complexes

The bimetallic carbene complexes were dissolved in a small volume hexane and a stoichiometric amount of bromine, also dissolved in a minimum volume of hexane, was added dropwise under vigorous stirring. A red-orange precipitate immediately started forming and stirring was continued until the solution became clear. The solvent and unreacted bromine were removed under reduced pressure and the products were purified by column chromatography on silica gel. In a typical experiment for rhenium with bithiophene, 41% of **4b** and 45% [Re(CO)₅Br] could be isolated. The analogous reaction with manganese did not proceed so well and only 21% **3b** and 41% [Mn(CO)₅Br] were isolated. By changing the solvent to CS₂, a solvent generally used to cleave Mn₂(CO)₁₀ [12a], only reactions leading to the decomposition of the complex and elimination of the carbene ligand with the formation of [Mn₂(CO)₁₀] were observed. Replacing the bromine with iodine and using the minimum amount of hexane as solvent, gave 43% **3b** after purification on aluminium oxide 90. Presently we are investigating methods of synthesis of the corresponding bimetallic biscarbene complexes, [{M(CO)₄(carbene)}₂] (M = Mn, Re), hoping to double the yields of [M(CO)₄(carbene)X] (M = Mn, Re; X = I or Br) after cleaving the metal–metal bond. In spite of starting with equatorially coordinated dirhenium carbene

Table 2
Selected bond lengths and angles of **1a**, **3a** and **5a**

1a		3a		5a	
Bond lengths (Å)					
Mn1–C1	1.798(7)	Mn1–C1	1.949(10)	Mn1–C1	1.820(4)
Mean Mn1–Cx (x = 2,3,4,5)	1.841(9)	Mean Mn1–Cx (x = 2,4)	1.857(6)	Mean Mn1–Cx (x = 2,3,4,5)	1.843(4)
Mn1–Mn2	2.9238(14)			Mn1–Mn2	2.9280(6)
Mean Mn2–Cx (x = 6,7,8,9)	1.833(7)			Mean Mn2–Cx (x = 7,9)	1.845(3)
Mn2–C10	1.933(7)	Mn1–C5	1.986(8)	Mn2–C10	2.019(3)
C10–O10	1.312(7)	C5–O5	1.318(8)	C10–N1	1.464(4)
C10–C11	1.470(11)	C5–C6	1.437(9)	C10–C11	1.315(4)
C11–C12	1.384(10)	C6–C7	1.411(10)	C11–C12	1.496(4)
C12–C13	1.390(12)	C7–C8	1.414(13)	C12–C13	1.431(5)
C13–C14	1.313(19)	C8–C9	1.364(15)	C13–C14	1.321(7)
		Mn1–C3	1.784(6)	Mn2–C6	1.790(3)
		Mn1–I1	2.709(1)	Mn2–C8	1.836(3)
Bond angles (°)					
Mn2–C10–O10	131.1(6)	Mn1–C5–O5	132.8(6)	Mn2–C10–N1	125.7(2)
O10–C10–C11	103.8(5)	O5–C5–C6	105.2(6)	N1–C10–C11	109.8(3)
C11–C10–Mn2	125.1(6)	C6–C5–Mn1	122.0(6)	C11–C10–Mn2	124.4(2)

complexes and axially coordinated dimanganese carbene complexes, the cleaved product is always *cis*-[M(CO)₄(carbene)X]. Substitution kinetics of carbonyl ligands in [Mn(CO)₅halides] revealed that rates increased with decreasing atomic number for the halides [24] and competitive rates for dimerisation vary in the same order with greater rates for Mn compared to Re for a particular halide [25]. Based on these results we concluded that the bromo-carbene complex of manganese was less stable in the reaction medium compared to the analogous iodo-carbene complex of manganese. Compositions of products were established by spectroscopic methods and mass spectrometry and final confirmation of the structures came from a single crystal X-ray diffraction study of **3a** (Fig. 2).

Complex **3a** crystallizes in the tetragonal system, space group $I4_1/a$ with 16 molecules in the unit cell. The coordination of the manganese atom is octahedral and a *cis*-arrangement of non-carbonyl ligands, already deduced from the infrared spectra of the molecule, is confirmed. The thienyl ring is again close to being coplanar with the plane of the bonding geometry about the carbene carbon. The dihedral angle between the least-squares planes through (S1, C6, C7, C8 and C9) and through (C5, C6, O5 and Mn1) is 8.0(6)°. The plane of the carbene carbon, thienyl ring and oxygen atom is again approximately perpendicular to the equatorial plane of ligands (C5–Mn1–CO 90–93°, C5–Mn1–I1 95.4(3)°) and is approximately positioned intermediately between the equatorial ligands around Mn1, as is evident from the torsion angles of −38.9(7)° and 51.4(7)° for C2–Mn1–C5–O5 and I1–Mn1–C5–O5, respectively. The same disorder of the ethoxy-thien-2-yl-methylidene ligand as that described for **1a** was also observed in **3a**. Fig. 2 shows the major orientation (85.9(5)%). The carbene ligand is again in

the *trans*-configuration about the C–O bond (C(6)–C(5)–O(5)–C(10) −173.8(6)°) – as expected when the thienyl ring is close to being coplanar with the plane of the bonding geometry about the carbene carbon as this prevents a *cis*-configuration being adopted. The metal carbon bond distance *trans* to the iodide ligand is significantly shorter than the Mn–CO distances opposite carbonyl ligands, reflecting the poor π-acceptor properties of an iodide ligand. The Mn–carbon distances observed for the carbene and the carbonyl ligand *trans* to the carbene are almost the same corresponding to a very long metal–carbon(carbonyl) bond.
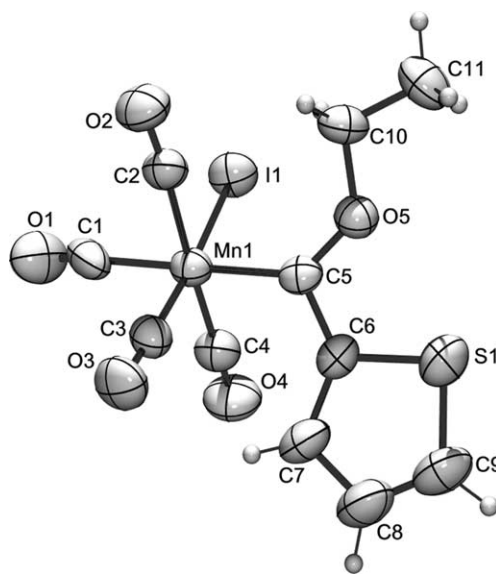

Fig. 2. ORTEP [20] + POV-Ray [21] plot of the geometry of **3a**. Displacement ellipsoids are set at 50% probability.

2.3. Reaction of the dimanganese carbene complex (1a) with ammonia

A slow stream of ammonia was bubbled through a solution of **1a** dissolved in ether. The colour of the solution changed quickly from red to orange. After TLC confirmed that all the ethoxy carbene had been converted, the solvent was removed and the amino carbene complex, **5a**, was purified by column chromatography on aluminium oxide 90. The bimetallic carbene complex formed quantitatively and its composition was confirmed by NMR and IR spectroscopy. Surprisingly, the infrared data in the carbonyl region for the amino carbene displayed the pattern for an equatorially substituted bimetallic nonacarbonyl complex and not the 5-band pattern observed for the ethoxy precursor **1a** [18]. The single crystal X-ray structure of **5a** (Fig. 3) [17] corroborated these observations. In the ^{1}H NMR spectrum, the thiophene and amine protons are duplicated in a major and minor isomer. We suspect that in solution, a mixture of the equatorial and axial isomers exists. It is unclear which set of signals belongs to which isomer. The N–H stretch vibrations in the infrared spectrum of **5a** are at 3453 and 3328 cm^{-1} and two of the bands in the carbonyl region of the spectrum are very strong displaying band overlap. See Scheme 3.

Complex **5a** crystallizes in the monoclinic system, space group $P2_1/c$ with four molecules in the unit cell. The average Mn–CO and Mn–Mn bond lengths are very similar to that of **1a**, although the Mn–C(carbene) bond length for **5a** (2.019(3) Å) is significantly longer than the corresponding distance in **1a** (1.933(7) Å). A very short C(carbene)–N bond length (1.315(4) Å) indicates double bond character and implies a high degree of electron
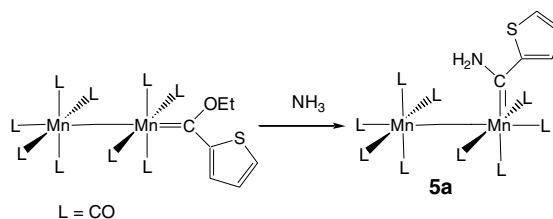
Scheme 3.

donation from the nitrogen lone pair to the electrophilic carbene carbon [26]. This is also evident from the chemical shift of the carbene carbon atom at 268 ppm compared to 307 ppm for **1a**. In contrast to **1a** and **3a**, the thienyl ring is not close to being coplanar with the plane of the bonding geometry about the carbene carbon. The dihedral angle between the least-squares planes through (S1, C11, C12, C13 and C14) and through (C10, C11, N1 and Mn2) is 39.7(1)°. A deviation out of the plane is necessary to fit the thienyl S between the two closest carbonyl ligands C6–O6 and C7–O7. Unlike the previous two structures, no disorder was observed in the carbene ligand as the spatial similarity between the nearly coplanar ethoxy group and thienyl ring in the carbene ligand in both **1a** and **3a** is not present in the carbene ligand of **5a**. The small NH$_2$-group can be accommodated adjacent to the carbonyl ligands C2–O2, C3–O3 and C9–O9 in the equatorial plane. In **1a**, with the carbene ligand adopting a *trans*-configuration about the C–O bond, the ethoxy group is probably too bulky to be accommodated and the carbene ligand is forced to occupy the axial position. On the other hand, the ethoxy carbene ligand is a better π-acceptor ligand compared to the amino carbene and one could argue that the carbene position is affected by the π-accepting ability of the two types of carbene ligands. This is supported by the Mn–C(carbene) bond distances since the ligand *trans* to the Mn–Mn metal bond represents the best site for the strongest π-acceptor ligand in [Mn$_2$(CO)$_9$(carbene)] complexes. However, the more bulky amino substituent NHEt in [Mn$_2$(CO)$_9${C(NHEt)thienyl}] again displayed the 5-band pattern in the carbonyl region of the infrared spectrum of this compound, typical for an axial substituted carbene ligand [27]. The Mn–Mn bond in **5a** can be cleaved with iodine in a manner similar to that of complexes **1a,b** [27].

In conclusion, we have made use of the fact that metal–metal bonds of carbene complexes can be cleaved oxidatively by halogens without affecting the carbene ligand. The products represent a novel class of carbonyl complexes that display both a halogen and a carbene ligand with potential application in organic synthesis and catalysis. These complexes are ideal to study electronic and steric factors in the conformations of [M(CO)$_9$(carbene)] complexes. Studies on the mechanistic detail of axial to equatorial conversions of the carbene ligand
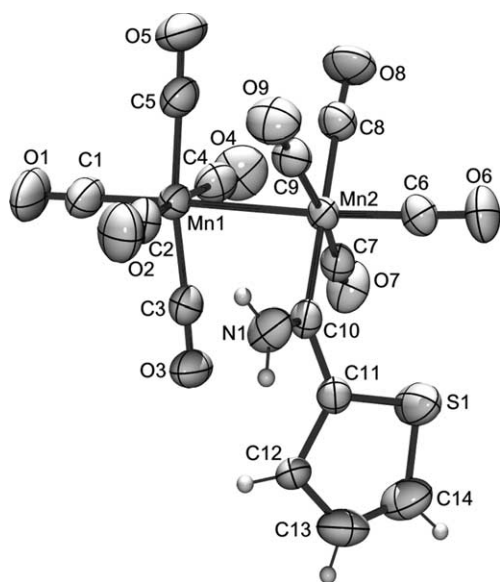

Fig. 3. ORTEP [20] + POV-Ray [21] plot of the geometry of **5a**. Displacement ellipsoids are set at 50% probability.

during aminolysis in binuclear complexes as well as the use of other cleaving reagents to break metal–metal bonds in carbene complexes of group 7 transition metals, are currently underway. We plan to further extend this approach to include other transition metal carbene complexes such as dicobalt and diiron carbonyl complexes.

3. Experimental

3.1. General remarks

All reactions were performed in an inert atmosphere of either nitrogen or argon with dry solvents by using standard Schlenk and vacuum-line techniques. Column chromatography was carried out under a nitrogen atmosphere using silica gel (particle size 0.063–0.200 nm) and aluminium oxide 90 as stationary phase. Solvents were dried and distilled under an atmosphere of nitrogen before use. Diethyl ether, tetrahydrofuran and hexane were distilled from sodium metal, with benzophenone as indicator in the case of the etheral solvents. Dichloromethane was distilled from phosphorus pentoxide. All other reagents were purchased from commercial suppliers and used without further purification. All NMR spectra were recorded in degassed deuterated chloroform on a Bruker ARX-300 spectrometer. Chemical shifts were referenced to chloroform. ^{1}H and ^{13}C NMR spectra were measured at 300.133 and 75.469 MHz, respectively. Infrared spectra were recorded on a Perkin–Elmer Spectrum RX1 FT-IR spectrophotometer with a NaCl cell using hexane as solvent. FAB-MS spectra were recorded on a VG 70SEQ Mass Spectrometer with the resolution for FAB = 1000 in a field of 8 kV. Nitrobenzyl alcohol was used as solvent. Melting points were recorded on a hot stage Gallenkamp melting point apparatus and are uncorrected.

3.2. Synthesis

3.2.1. Preparation of ax-[Mn₂(CO)₉{C(OEt)2-thienyl}] (1a)

Thiophene (2.2 mmol, 0.185 g, 0.175 mL), was stirred while adding BuLi (2.2 mmol, 1.6M, 1.4 mL) in 40mL THF at −30 °C under an inert N$_2$ atmosphere. Stirring was continued for 30 minutes. Yellow Mn$_2$(CO)$_{10}$ (2 mmol, 0.78 g) was added to the reaction mixture at −78°C, resulting in a colour change of the reaction mixture to orange-red while stirring for 1 h. Stirring was then continued for an additional 30 min at room temperature. THF solvent was evaporated under reduced pressure. Et$_3$OBF$_4$ (2.2 mmol, 0.42 g) in dichloromethane was added to the reaction mixture at −30 °C and stirred until reaction completion. LiBF$_4$ salts were removed by filtering, and reaction products were purified

on aluminium oxide 90 using 4:1 hexane/dichloromethane as eluent. Product **1a** ax-[Mn$_2$(CO)$_9${C(OEt)2-thienyl}] (1.24 mmol, 0.62 g, 62% yield) was obtained.

Complexes **1b**, **2a** and **2b** were prepared in a similar fashion. However, the rhenium complexes were purified using silica gel 60 column chromatography. The reaction solutions were adsorbed directly onto silica gel 60, and eluting with hexane isolated the products. It was found that for the Mn complexes, adsorption onto aluminium oxide 90 afforded better yields. Column chromatography performed at low temperatures (−20 °C) lead to a further increase in yields. Product **1a** was recrystallized from dichloromethane/hexane mixtures.

1a: Orange solid; m.p.: 103–106 °C. Anal. Calc. for Mn$_2$C$_{16}$H$_8$O$_{10}$S (502.18): C, 38.27; H, 1.61. Found: C, 38.51; H, 1.74%. MS (EI): m/z 502 [M$^+$].

1b: Orange solid; m.p.: 103–106 °C. Anal. Calc. for Mn$_2$C$_{20}$H$_{10}$O$_{10}$S$_2$ (584.30): C, 41.11; H, 1.73. Found: C. 41.56; H, 1.81. Yield: 0.43 g (74%). MS (EI): m/z 584 [M$^+$].

2a: Orange solid; m.p.: 112–113 °C. Anal. Calc. for Re$_2$C$_{16}$H$_8$O$_{10}$S (764.72): C, 25.13; H, 1.06. Found: C, 25.55; H, 1.17%. Yield: 0.49 g (64%). MS (EI): m/z 764 [M$^+$].

2b: Orange solid; m.p.: 117–119 °C. Anal. Calc. for Re$_2$C$_{20}$H$_{10}$O$_{10}$S$_2$ (846.84): C, 28.36; H, 1.19. Found: C, 28.54; H, 1.23%. Yield: 0.65 g (77%). MS (EI): m/z 847 [M$^+$].

3.2.2. Preparation of [Mn(CO)₄(I){C(OEt)2-thienyl}] (3a)

To a minimum volume of hexane solvent was added **3a** (1 mmol, 0.50 g) and I$_2$ (1 mmol, 0.26 g) while stirring at room temperature under an inert N$_2$ atmosphere until reaction was complete. The unreacted I$_2$ was separated on a aluminium oxide 90 column with a hexane eluent. Products **3a** [Mn(CO)$_4$(I){C(OEt)2-thienyl}] (0.43 mmol, 0.185 g, 43% yield) and [Mn(CO)$_5$I] (0.48 mmol, 0.155 g, 48%) were obtained. Complexes **3b**, **4a** and **4b** were prepared in a similar fashion. For the rhenium complexes a solution of Br$_2$ (1.1 mmol, 0.18 g) in hexane was used and unreacted Br$_2$ was removed during the removal of solvent under reduced pressure. Again, the rhenium complexes were purified using silica gel 60 column chromatography. Product **3a** was recrystallized from dichloromethane/hexane mixtures.

3a: Orange solid; m.p.: 103–106 °C. Anal. Calc. for MnC$_{11}$H$_8$O$_5$SI (434.09): C, 30.43; H, 1.86. Found: C, 30.81; H, 1.98. MS (EI): m/z 434 [M$^+$].

3b: Orange solid; m.p.: 103–106 °C. Anal. Calc. for MnC$_{15}$H$_{10}$O$_5$S$_2$I (516.21): C, 34.90; H, 1.96. Found: C, 35.08; H, 2.08%. Yield: 0.16 g (37%). MS (EI): m/z 516 [M$^+$].

4a: Orange solid; m.p.: 117–119 °C. Anal. Calc. for ReC$_{11}$H$_8$O$_5$SBr (518.36): C, 25.49; H, 1.56. Found: C, 25.66; H, 1.67%. Yield: 0.20 g (39%). MS (EI): m/z

Table 3
Crystal data and structure refinement of **1a**, **3a** and **5a**

	1a	**3a**	**5a**
Colour	Red	Dark-red	Orange
Habit	Rectangular prism	Irregular fragment	Hexagonal prism
Crystal size (mm^3)	$0.40 \times 0.30 \times 0.18$	$0.58 \times 0.54 \times 0.42$	$0.32 \times 0.28 \times 0.20$
Chemical formula	$C_{16}H_8Mn_2O_{10}S$	$C_{11}H_8IO_5MnS$	$C_{16}H_8Mn_2NO_{10}S$
Formula weight	502.16	434.07	473.13
Wavelength (Å)	0.71073	0.71073	0.71073
Unit cell dimensions			
a (Å)	7.920(4)	21.438(8)	14.4298(8)
b (Å)	22.236(11)		9.1653(5)
c (Å)	11.548(5)	12.895(10)	14.7785(8)
β (°)	95.591(7)		113.7790(10)
Volume ($Å^3$)	2024.0(16)	5926(5)	1788.58(17)
Crystal system	Monoclinic	Tetragonal	Monoclinic
Space group	$P2_1/c$	$I4_1/a$	$P2_1/n$
Z	4	16	4
Absorption coefficient (mm^{-1})	1.400	3.125	1.576
Theta range for data collection (°)	2.55–26.30	2.65–26.43	2.68–26.54
Index ranges	$-5 \leqslant h \leqslant 9$;	$-25 \leqslant h \leqslant 21$;	$-13 \leqslant h \leqslant 17$;
	$-24 \leqslant k \leqslant 27$;	$-20 \leqslant k \leqslant 25$;	$-11 \leqslant k \leqslant 11$;
	$-10 \leqslant l \leqslant 3$	$-15 \leqslant l \leqslant 10$	$-14 \leqslant l \leqslant 17$
Reflections measured	6741	11926	9351
Unique reflections [R_{int}]	3324 [0.0390]	2678 [0.0339]	3345 [0.0260]
Completeness to theta = 25.0°	0.893	0.931	0.992
Absorption correction [28]	Multi-scan	Multi-scan	Multi-scan
Minimum and maximum transmission	0.476 and 0.777	0.188 and 0.269	0.549 and 0.730
Refinement method [29]	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
$R_1 = \Sigma\|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\|$ for $F_o > 4\sigma(F_o)$	0.0582	0.0409	0.0397
$wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$	0.1431	0.1147	0.1263

518 [M^+]. On heating, the orange solid darkens around 118 °C with the formation of $Re_2(CO)_{10}$ as a white crystalline material on the outside and leaving a dark residue in the middle.

4b: Orange solid; m.p.: 117–119 °C. Anal. Calc. for $ReC_{15}H_{10}O_5S_2Br$ (600.48): C, 30.00; H, 1.68. Found: C, 30.26; H, 1.77%. Yield: 0.25 g (41%). MS (EI): *m/z* 518 [M^+].

3.2.3. Preparation of eq-[$Mn_2(CO)_9\{C(NH_2)2$-thienyl\}] (5a)

1a (2 mmol, 1.00 g) was dissolved in diethyl ether at room temperature, and a slow stream of NH_3 was bubbled through the reaction solution until the color of the reaction mixture changed from red to orange. After evaporation of the solvent under reduced pressure and purification on aluminium oxide 90, product **5a** eq-[$Mn_2(CO)_9\{C(NH_2)2$-thienyl\}] (1.80 mmol, 0.84 g, 89%) was obtained. The product was recrystallized from dichloromethane/hexane mixtures.

5a: Red solid; m.p.: 103–106 °C. Anal. Calc. for $Mn_2C_{14}H_5O_9SN$ (473.14): C, 35.54; H, 1.07. Found: C, 35.81; H, 1.16%. MS (EI): *m/z* 473 [M^+].

3.3. X-ray crystallography

Data were collected at 20 °C by means of a combination of phi and omega scans on a Bruker (SIEMENS)

P4 diffractometer, fitted with a 1 K CCCD detector, using graphite-monochromated, Mo Kα radiation. In the structure refinements all hydrogen atoms were added in calculated positions and treated as riding on the atom to which they are attached. All non-hydrogen atoms (except those refined as rigid groups) were refined with anisotropic displacement parameters, all isotropic displacement parameters for hydrogen atoms were calculated as $X \times U_{eq}$ of the atom to which they are attached, $X = 1.5$ for the methyl hydrogens and 1.2 for all other hydrogens. In structures **1a** and **3a** the carbene ligand showed some disorder with a minor component (11.8(4)% and 14.1(5)%, respectively) rotated approximately 180° about the Mn–C(carbene) bond with respect to the major component. The parameters for the major orientations were refined freely. The minor orientations were refined as rigid bodies with geometries derived from those of the major orientations. Site occupation factors for the major and minor orientations were refined but constrained to sum to 1.0. Crystal data and other experimental procedures and refinement parameters are given in Table 3.

4. Supplementary material

Crystallographic data (excluding structure factors) for the structures reported in this paper have been

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