A novel metal-chain extension reaction: synthesis of $(X)[Os(CO)_3(CN\text{-}t\text{-}Bu)]_nMn(CO)_5$ (X = Cl, Br, I; *n* = 1, 2, 3)

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Abstract: Complexes of formula $(X)[Os(CO)_3(CN\text{-}t\text{-}Bu)]_nMn(CO)_5$ (X = Cl, Br, I; n = 1, 2, 3) have been prepared by the reaction of $Os(CO)_4(CN\text{-}t\text{-}Bu)$ with $Mn(CO)_5(X)$ in hexane at room temperature. The characterization of the complexes included the crystal structures of compounds with X = I, n = 1, 3 and X = Cl, Br, n = 2 (**2ClA** and **2BrB**). The trinuclear products were isolated as two isomers. The major isomer (**2XA**) has an isocyanide ligand attached to each osmium atom, whereas the minor isomer (**2XB**) has both of these ligands bound to the terminal Os atom. The structures contain Os_nMn chains with unbridged Os—Mn bonds (range of lengths are 2.870(1)–2.9245(8) Å) and for compounds with n = 2 or 3 Os—Os bonds (range of lengths are 2.8812(4)–2.8928(5) Å). The mechanism of formation is believed to involve replacement of a CO ligand with the $18e^-$ ligand $Os(CO)_4(CN\text{-}t\text{-}Bu)$ at the metal with the coordinated halide, followed by a rearrangement in which the halide ligand migrates to the donor Os atom with concomitant migration in the reverse direction of a carbonyl ligand. The preparation of $(OC)_4(t\text{-}BuNC)OsMn(CO)_4(Cl)$ with an Os–Mn dative bond is also reported along with the $(OC)_4(t\text{-}BuNC)OsRe(CO)_4(X)$ analogues.

Key words: manganese–osmium, rhenium–osmium, dinuclear, metal chain, dative metal–metal bond.

Résumé : On a préparé des complexes de formule $(X)[Os(CO)_3(CN\text{-}t\text{-}Bu)]_nMn(CO)_5$ (X = Cl, Br, I; n = 1, 2, 3) par réaction du $Os(CO)_4(CNB\text{-}t\text{-}Bu)$ avec du $Mn(CO)_5(X)$, dans l'hexane, à la température ambiante. La caractérisation des complexes a impliqué la détermination des structures cristallines des composés pour lesquels X = I avec n = 1 ou 3 et X = Cl ou Br et n = 2 (**2ClA** et **2BrB**). On a isolé deux formes isomères des produits trinucléaires. L'isomère principal (**2XA**) comprend un ligand isocyanure attaché à chaque atome d'osmium alors que, dans l'isomère minoritaire (**2XB**), chacun de ces deux ligands est attaché à l'atome d'osmium terminal. Les structures comportent des chaînes Os_nMn dans lesquelles on retrouve des liaisons Os—Mn qui ne sont pas pontées (longueurs des liaisons allant de 2,870(1) à 2,9245(8) Å) et, dans les cas où n est égal à 2 ou 3, on rencontre aussi des liaisons Os—Os (longueurs des liaisons allant de 2,8812(4) à 2,8928(5) Å). On croit que le mécanisme de formation implique premièrement le remplacement, au niveau du métal coordiné à l'halogène, d'un ligand CO par le ligand à $18e^-$ $Os(CO)_4(CN\text{-}t\text{-}Bu)$, suivi d'un réarrangement dans lequel le ligand halogène migre vers l'atome d'osmium donneur avec une migration concomitante d'un ligand carbonyle dans la direction inverse. On rapporte aussi la préparation du $(OC)_4(t\text{-}BuNC)OsMn(CO)_4(Cl)$ comportant une Os–Mn liaison dative ainsi que celles de ses analogues $(OC)_4(t\text{-}BuNC)OsRe(CO)_4(X)$.

Mots clés : manganèse–osmium, rhénium–osmium, dinucléaire, chaîne de métaux, liaison dative métal–métal.

[Traduit par la Rédaction]

Introduction

Much of the past work from this laboratory has described complexes in which an 18-electron organometallic compound acts as a 2-electron donor ligand to a 16-electron organometallic fragment in much the same way as a conventional ligand such as PPh_3 (1–7). Typical examples of molecules of this type are $(OC)_5OsOs(CO)_3(GeCl_3)(Cl)$ (1), $(L)(OC)_4OsM(CO)_5$ (M = Cr, Mo, W; L = PR_3 (2), CN-*t*-Bu (3)), and $(R_3P)(OC)_4M'Ru(CO)_3(SiCl_3)_2$ (M′ = Ru, Os, but not Fe) (4). These complexes contain an unbridged dative bond between two transition metal atoms and are rare (8); complexes with dative metal–metal bonds supported by bridging ligands are, however, more common (9). There has also been renewed interest in complexes with unbridged dative bonds between a transition metal and a main-group metal (10).

In some of our earliest studies, it was observed that isomerization often occurred for complexes with unbridged dative metal–metal bonds that also contained a halide or (especially) a hydride ligand coordinated to the acceptor metal atom (11, 12). The isomerization involved migration of the halide (or hydride) ligand to the donor atom with

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concomitant migration of a carbonyl ligand to the acceptor atom (Scheme 1; in this and other schemes presented here the carbonyl ligands not involved in the isomerization have been omitted.) If the halogen ligand is considered a one-electron donor ligand, then the isomerization process results in the conversion of the dative metal–metal bond to a nondative bond.

It is well-known that the presence of a halide ligand in a metal-carbonyl complex often labilizes the carbonyls to ligand substitution (13, 14). The possibility, therefore, exists for further substitution–isomerization reactions on the binuclear compound to yield complexes with extended metal chains. Several previous attempts to exploit this strategy to the synthesis of polynuclear compounds were unsuccessful. Here we report the partial realization of the method in the synthesis of (X)[Os(CO)$_3$(CN-*t*-Bu)]$_n$Mn(CO)$_5$ (X = Cl, Br, I; *n* = 1, 2, 3) complexes that contain chains of up to four metal atoms. The tetranuclear complex has been the subject of a communication (15).

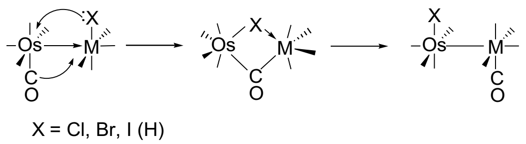
Experimental

Unless otherwise stated, manipulations of starting materials and products were carried out under a nitrogen atmosphere with the use of standard Schlenk techniques. Hydrocarbon solvents were heated to reflux over potassium, distilled, and stored over molecular sieves before use. Dichloromethane was dried in a similar manner except that P_2O_5 was employed as the drying agent. The precursory compounds Mn(CO)$_5$(X) (X = Cl, Br, I) (16), [Re(μ-X)(CO)$_4$]$_2$ (17), and Os(CO)$_4$(CN-*t*-Bu) (3) were prepared by literature procedures. The reaction vessels were Carius tubes of volumes between 25–50 mL and each were fitted with a Teflon valve. NMR spectra were recorded on a Bruker AMX 400 spectrometer at the appropriate operating frequencies for the ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectra. Samples of the complexes used for ^{13}C{^{1}H} NMR spectra were enriched to ~30% ^{13}CO. The samples were prepared from more highly ^{13}CO-enriched M(CO)$_5$(X) (M = Mn, Re), which in turn was prepared by stirring the M(CO)$_5$(X) in hexane (or toluene) under ^{13}CO (99%; 2 atm) at room temperature for 24 h (13). It was found that the ^{13}CO was scrambled equally over all CO sites in the products. Analytical and spectroscopic data for the new compounds are given in Tables 1–3.

Preparation of (OC)$_4$(*t*-BuNC)OsMn(CO)$_4$(Cl) (1)

A solution of Os(CO)$_4$(CN-*t*-Bu) (30 mg, 0.078 mmol) and Mn(CO)$_5$(Cl) (17 mg, 0.074 mmol) in hexanes (15 mL) was cooled to –196°C and the solution was degassed with three cycles of freeze-pump-thaw; the vessel was covered with aluminum foil. The mixture was stirred under vacuum at room temperature for 20 h. A bright yellow precipitate resulted. The solvent was removed from the precipitate, which was washed with hexane (3 × 2 mL) and then dried on the vacuum line. The product was analytically pure; further purification was prevented by its instability in solution at room temperature. Reaction of Mn(CO)$_5$(X) (X = Br, I) under similar conditions gave the isomerized products (**1X**; see below).

Scheme 1.



Preparation of (OC)$_3$(*t*-BuNC)(I)OsMn(CO)$_5$ (1I)

To a Carius tube was added Os(CO)$_4$(CN-*t*-Bu) (39 mg, 0.10 mmol), Mn(CO)$_5$(I) (32 mg, 0.10 mmol), and hexanes (10 mL); the solution was degassed as before and the reaction tube covered with aluminum foil. The mixture was stirred under vacuum at room temperature. An IR spectrum after 2 days indicated the starting compounds were still present. The vessel was resealed and the solution degassed as before. After a further 5 days of stirring an IR spectrum indicated that only (OC)$_3$(*t*-BuNC)(I)OsMn(CO)$_5$ (**1I**) was present. The resulting yellow solution was transferred into a Schlenk tube, concentrated, and stored at –27°C to give **1I** as yellow crystals (49 mg, 73%). A second preparation under ambient light resulted in the same product plus traces of **2IA** that were separated by chromatography as described below. The chloro and bromo analogues (**1Cl** and **1Br**) were prepared in a similar manner, that is, under ambient light with a reaction period of 5 days.

Preparation of (OC)$_6$(*t*-BuNC)$_2$(I)Os$_2$Mn(CO)$_5$ (2IA and 2IB)

A solution of Os(CO)$_4$(CN-*t*-Bu) (60 mg, 0.15 mmol) and Mn(CO)$_5$(I) (24 mg, 0.075 mmol) in hexanes (10 mL) was degassed as described above and the reaction vessel sealed under vacuum. The mixture was stirred at room temperature. Compounds Os(CO)$_4$(CN-*t*-Bu) **1I** and **2I** were present after 2 days as indicated by IR spectroscopy. An IR spectrum of the reaction solution after 7 days indicated the presence of the desired product plus traces of **1I.** The resulting yellow solution was concentrated and subjected to chromatography on a silica gel column (12 × 1 cm). Elution of the column with hexanes–CH$_2$Cl$_2$ (8:1) gave two yellow bands; the first contained **1I**, the second **2IA.** The second fraction was collected, concentrated, and stored at –27°C to give **2IA** (41 mg, 53%) as yellow crystals. Further elution of the column with hexanes–CH$_2$Cl$_2$ (4:1) yielded a third yellow band from which **2IB** (5 mg, 6%) as yellow crystals was isolated in a manner similar to that for **2IA**. The chloro (**2ClA** and **2ClB**) and bromo (**2BrA** and **2BrB)** analogues were synthesized in an analogous fashion; yields are given in Table 1. It was verified on a small scale that the trinuclear complexes could be also prepared from similar reactions of Os(CO)$_4$(CN-*t*-Bu) and **1X** in a 1:1 molar ratio.

Preparation of (OC)$_9$(*t*-BuNC)$_3$(Br)Os$_3$Mn(CO)$_5$ (3Br)

A degassed solution of Os(CO)$_4$(CN-*t*-Bu) (58 mg, 0.15 mmol) and Mn(CO)$_5$(Br) (14 mg, 0.05 mmol) in hexanes (8 mL) was stirred under vacuum at room temperature for ~40 h, during which time a yellow precipitate formed. The IR spectra revealed the solution contained small amounts of **2Br**, whereas the solid was mainly **3Br**. The solution was removed from the solid, which was then recrystallized from toluene–hexanes to furnish **3Br** (28 mg,

Table 1. Analytical ^{1}H NMR data and yields for complexes **1–3X**.

Compound	Yield (%)	%C (calcd.)	%H (calcd.)	%N (calcd.)	^{1}H NMR (δ)[a]
1	65	26.31 (26.56)	1.46 (1.54)	2.14 (2.38)	1.52[b]
1Cl	67	26.62 (26.56)	1.60 (1.54)	2.33 (2.38)	1.64
1Br	41	24.85 (24.69)	1.30 (1.43)	2.11 (2.22)	1.62
1I	73	23.08 (22.99)	1.35 (1.34)	2.09 (2.06)	1.60
2ClA	71	26.97 (26.68)	2.06 (1.92)	2.89 (2.92)	1.61, 1.50
2BrA	32	25.68 (25.48)	1.94 (1.83)	2.75 (2.83)	1.59, 1.50
2IA	53	24.62 (24.33)	1.80 (1.75)	2.63 (2.70)	1.57, 1.51
2ClB	15	26.90 (26.68)	2.07 (1.92)	2.81 (2.96)	1.58
2BrB	11	25.59 (25.48)	1.93 (1.83)	2.81 (2.83)	1.57
2IB	6	24.45 (24.33)	1.74 (1.75)	2.63 (2.70)	1.55
3Cl	41	26.96 (26.74)	2.21 (2.09)	3.02 (3.23)	1.62, 1.47
3Br	41	25.91 (25.86)	1.97 (2.02)	3.02 (3.12)	1.61, 1.47
3I	26	25.07 (24.99)	2.08 (1.95)	2.98 (3.01)	1.58, 1.48
1ReCl	39	21.80 (21.71)	1.23 (1.26)	1.95 (1.95)	1.52[b]
1ReBr	27	20.91 (20.45)	1.33 (1.19)	1.87 (1.83)	1.52[b]
1ReI	44	19.39 (19.26)	1.05 (1.12)	1.66 (1.73)	1.53[b]

[a] Unless otherwise stated, NMR spectra were recorded in $CDCl_3$ at room temperature.

[b] Recorded in CD_2Cl_2 at – 40°C.

Table 2. IR spectra (in hexane) of the new complexes.

Compound	ν(CO) (cm^{-1})	ν(CN) (cm^{-1})
1[a]	2118(m), 2053(s), 2043(sh), 2013(w), 1977(s), 1924(m)	2217(m)
1Cl	2099(m), 2063(s), 2037(s), 2021(m), 2004(s), 1986(sh), 1983(s), 1970(m)	2211(m)
1Br	2098(m), 2063(s), 2036(s), 2021(w-m), 2004(s), 1984(s), 1971(m-s)	2209(w-m)
1I	2096(m-s), 2063(s), 2034(s), 2020(w), 2004(s), 1985(s), 1972(m)	2205(m)
2ClA	2088(m), 2064(s), 2034(m), 2022(s), 2002(s), 1989(s), 1983(m), 1966(m)	2207(w), 2188(m)
2ClB	2101(w), 2064(w), 2047(w), 2036(m), 2002(s), 1996(s), 1969(m), 1963(w)	2204(vw), 2178(m)
2BrA	2087(m), 2064(s), 2034(w), 2022(s), 2002(s), 1989(s), 1983(w), 1966(m)	2205(w), 2187(m)
2BrB	2102(w), 2064(w), 2040(w, sh), 2036(m), 2002(s), 1996(s), 1971(m), 1963(w)	2206(vw), 2176(m)
2IA	2086(m), 2062(s), 2034(m), 2019(s), 2002(s), 1990(s), 1984(w), 1967(m)	2202(w), 2185(m)
2IB	2101(m), 2062(w), 2040(m), 2034(s), 2002(s), 1997(s), 1972(m), 1964(w)	2206(vw), 2176(m)
3Cl	2079(vw), 2064(m), 2041(w), 2020(w), 2015(m), 1994(s), 1987(w, sh), 1961(m)	2202(w), 2183(w), 2171(w)
	2080(w), 2065(s), 2039(w), 2019(w, sh), 2013(m), 1991(vs), 1956(m)	2205(w), 2171(m)
3Br	2079(w), 2064(m-s), 2041(w), 2021(w), 2015(m), 1994(s), 1987(w, sh), 1961(m)	2201(w), 2184(w), 2171(w)
	2080(w), 2064(s), 2039(m), 2020(w, sh), 2013(m), 1991(vs), 1956(m)	2204(w), 2171(m)
3I	2079(w), 2061(m), 2040(w), 2021(w), 2013(m), 1994(s), 1987(w, sh), 1962(m)	2198(w), 2181(w), 2168(w)
	2079(w), 2062(m), 2039(w), 2019(w, sh), 2010(m), 1991(vs), 1956(m)	2201(w), 2171(m)
1ReCl[a]	2119(m), 2074(s), 2039(vs), 1978(s), 1914(s)	2217(w)
1ReBr[a]	2118(m), 2073(s), 2040(vs), 1980(s), 1915(s)	2219(w)
1ReI[a]	2118(m), 2070(s), 2040(vs), 1978(s), 1917(s)	2218(w)

[a] In CH_2Cl_2.

41%) as a yellow crystalline solid. The chloro (**3Cl**) and iodo (**3I**) congeners were synthesized similarly. It was also verified that the **2X** complexes react with excess Os(CO)$_4$(CN-*t*-Bu) under the same conditions to give the corresponding **3X** compounds.

Preparation of (OC)$_4$(*t*-BuNC)OsRe(CO)$_4$(Cl)

A degassed solution of Os(CO)$_4$(CN-*t*-Bu) (44 mg, 0.11 mmol) and [Re(μ-Cl)(CO)$_4$]$_2$ (36 mg, 0.054 mmol) in toluene (15 mL) was stirred under nitrogen at 45°C for ~20 h, during which time a yellow precipitate formed. The mother solution was removed and the precipitate washed with hexanes; the precipitate was then recrystallized from toluene–hexanes at –40°C to afford yellow crystals of (*t*-BuNC)(OC)$_4$OsRe(CO)$_4$(Cl) (30 mg, 39% yield). The bromo and iodo analogues were prepared in a similar manner.

X-ray structural determination of 1I, 2ClA, 2BrB, and 3I

The structures of **1I**, **2ClA**, and **2BrB** were determined at St. Mary's University, whereas that of **3I** was carried out at the University of Ottawa. The determinations followed the same general procedure. A single (yellow) crystal of suitable size was grown from hexane or hexane–CH_2Cl_2, and mounted on a glass fiber. Data were collected at –50°C for **1I**, **2ClA**, and **2BrB**, and at –70°C for **3I**; a Bruker (Siemens) SMART/CCD diffractometer was used in each case. Crystal data refinement parameters are summarized in Table 4, and selected interatomic distances and angles are

Table 3. ^{13}C NMR data for selected derivatives.

Compound	M–CO	Os–CO	*t*-Bu–C
1^a	221.2 (1C), 220.8 (2C), 219.2 (1C)	182.4 (2C), 177.3 (1C), 163.0 (1C)	60.8, 29.5
1I	219.8 (4C), 215.6 (1C)	177.4 (1C), 171.8 (1C), 162.4 (1C)	59.8, 30.1
2ClA^b	222.9 (4C), 218.3 (1C)	193.4 (1C),^{c} 191.9 (1C),^{c} 189.7 (1C), 183.3 (1C), 174.4 (1C), 164.1 (1C)	59.7, 58.6, 30.0
2ClB^b	223.8 (4C), 217.8 (1C)	191.9 (4C), 175.1 (1C), 166.3 (1C)	59.1, 30.2
3Cl^b	223.8 (4C), 218.9 (1C)	194.8 (2C),^{d} 194.3 (1C),^{e} 192.3 (1C),^{e} 191.1 (1C), 191.0 (1C), 185.6 (1C), 176.3 (1C), 166.0 (1C)	59.1, 58.2, 58.0, 29.8, 29.7 (2Me)
1ReCl^a	194.0 (2C), 188.8 (1C), 186.0 (1C)	180.2 (2C), 175.7 (1C), 164.2 (1C)	29.5
1ReBr^a	192.7 (2C), 188.5 (1C), 185.3 (1C)	180.3 (2C), 176.0 (1C), 163.6 (1C)	29.5
1ReI^a	190.4 (2C), 188.1 (1C), 184.2 (1C)	180.7 (2C), 176.4 (1C), 162.7 (1C)	29.5

[a] In CD_2Cl_2 at – 40°C.
[b] In $CDCl_3$ at – 40°C.
[c] *Trans*, $^2J_{C,C}$ = 31.3 Hz.
[d] Degenerate singlets.
[e] *Trans*, $^2J_{C,C}$ = 31.6 Hz.

Table 4. Details of the crystal structure determinations of **1I**, **2ClA**, **2BrB**, and **3I**.

	1I	**2ClA**	**2BrB**	**3I**
Compound	$C_{13}H_9IMnNO_8Os$	$C_{21}H_{18}ClMnN_2O_{11}Os_2$	$C_{21}H_{18}BrMnN_2O_{11}Os_2$	$C_{29}H_{27}IMnN_2O_4Os_3$
Formula weight	679.25	945.16	989.62	1393.98
Crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic
T (°C)	–50	–50	–50	–70
Space group	$P2_1/c$	$P2_1/n$	$P\bar{1}$	$P2_1/c$
a (Å)	15.0686(8)	12.2794(8)	9.0783(5)	11.503(1)
b (Å)	11.2590(6)	16.5412(11	9.8272(6)	12.394(1)
c (Å)	12.0421(7)	14.3631(10)	17.621(1)	29.959(3)
α (deg)			102.530(1)	
β (deg)	108.245(1)	91.870(1)	100.984(1)	99.894(2)
γ (deg)			95.273(1)	
Cell volume (Å^3)	1940.3(2)	2915.8(3)	1491.9(2)	4207.6(7)
Z	4	4	2	4
$D_{calcd.}$ (mg m^{-3})	2.325	2.153	2.203	2.201
Abs. coeff (mm^{-1})	8.820	9.266	10.305	10.116
Unique data ($I > 2\sigma$)	3428	5134	5198	7166
R^a	0.0313	0.0315	0.0342	0.0329
wR^b	0.0817	0.0723	0.0822	0.0478

[a] $R = \Sigma|(|F_o| - |F_c|)|/\Sigma|F_o|$.
[b] $wR = [\Sigma (w(|F_o| - |F_c|)^2)/\Sigma(wF_o{}^2)]^{1/2}$. $w = [\sigma^2(F_o)^2 + kF_o{}^2]^{-1}$.

given in Tables 5–7.[2] Unit-cell parameters were calculated from reflections obtained from 60 data frames collected at different sections of the Ewald sphere. A statistical measurement of intensity data indicated the space group, and this was borne out by successful refinement of the structure. Semiempirical absorption corrections were applied using redundant data. Full-matrix least-squares refinement on F^2 was performed after solving using Patterson methods and the solution package SHELXTL v. 5.10 (18). Anisotropic thermal parameters were applied to all non-hydrogen atoms; hydrogen atoms were generated at ideal positions and their positions were updated with each refinement cycle. The following disorders in the structures were encountered: (*i*) for **1I**: O(2), O(11), and O(13) were each disordered over two positions; all were refined satisfactorily with 0.5 occupancy factors. (*ii*) For **2ClA**: CO(15) and Cl were disordered and modeled with occupancy factors of 53:47. (*iii*) For **2BrB**: CO(22) and Br were disordered with an occupancy factor of 88:12. Rotational disorder (50%) was also observed for the methyl groups within the *t*-BuNC ligands of **2BrB**.

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[2] Supplementary material may be purchased from the Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, ON K1A 0S2, Canada. For information on obtaining material electronically go to http://www.nrc.ca/cisti/irm/unpub_e.shtml. Crystallographic information has also been deposited with the Cambridge Crystallographic Data Centre. Copies of the data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

Table 5. Selected bond lengths (Å) and angles (deg) of **1I**.

Bond lengths (Å)			
Os—Mn	2.9245(8)	Mn—C(11)	1.818(7)
Os—I	2.7734(4)	Mn—C(radial)	1.840(7)–1.857(6)
Os—C(1)	1.895(6)	O—C(Os)	1.06(3)–1.23(3)
Os—C(2)	1.940(7)	O—C(Mn)	1.09(4)–1.22(4)
Os—C(3)	1.924(6)	N—C(4)	1.160(7)
Os—C(4)	2.029(5)	N—C(5)	1.448(7)
Bond angles (deg)			
I-Os-Mn	95.38(2)	C(11)-Mn-Os	179.9(2)
C(4)-Os-Mn	89.14(15)	C(3)-Os-Mn	174.98(18)
C(2)-Os-C(4)	170.1(2)	C(4)-Os-I	85.6(2)
N-C(4)-Os	172.6(5)		
C(11)-Mn-C	92.8(3)–93.9(3)	Os-Mn-C(radial)	86.0(2)–87.30(18)
cis-C-Mn-C(radial)	87.9(3)–93.4(3)	Mn-Os-C(radial)	81.2(2)–89.1(2)
cis-C-Os-C	91.3(2)–94.2(2)		

Table 6. Selected bond lengths (Å) and angles (deg) for **2ClA** and **2BrB**.

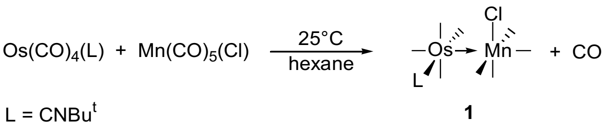
	2ClA	**2BrB**		**2ClA**	**2BrB**
Bond lengths (Å)					
Os(1)—Mn	2.900(1)	2.884(1)	Os(1)—C(9)	2.012(7)	
Os(1)—Os(2)	2.8812(4)	2.8895(4)	Os(2)—C(17)	2.033(7)	
Os(2)—X	2.58(1) (2.51(1))[a]	2.568(2) (2.44(2))[a]	Os(2)—C(23)		2.005(7)
Mn—C(1)	1.798(7)	1.808(8)	Os(2)—C(24)		2.003(7)
Mn—C(radial)	1.820(8)–1.847(9)	1.83(1)–1.85 (1)	Os —C(O)	1.921(8)–1.950(8)	1.877(7)–1.95 (1)[b]
Bond angles (deg)					
Os(2)-Os(1)-Mn	176.87(2)	177.54(3)	Os-Mn-C(radial)	83.3(3)–85.0(2)	83.1(3)–86.0(3)
Os(1)-Mn-C(1)	179.2(3)	177.9(2)	Mn-Os(1)-C	90.1(2)–92.4(2)	91.1(3)–91.9(3)
C(ax)-Os(2)-Os(1)	178.1(2)	176.8(2)	Os(1)-Os(2)-C(radial)	86.1(2)–87.6(5) (89.9(7))[a]	87.9(2)–88.6(2) (92(2))[a]
Os(1)-Os(2)-X	87.6 (3) (88.6 (3))[a]	91.15 (2) (89.1 (6))[a]			

[a] Disorder present.
[b] Os(2)—C(21).

Results and discussion

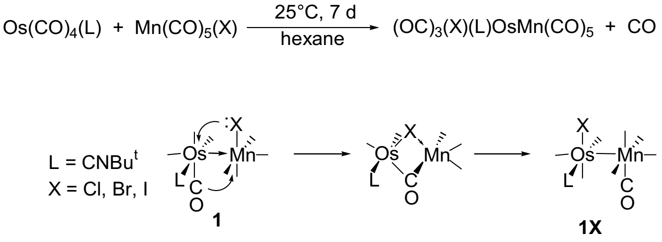
Binuclear OsMn complexes

A bright yellow precipitate resulted when $Os(CO)_4$(CN-*t*-Bu) and $Mn(CO)_5(Cl)$ in a 1:1 molar ratio in hexanes was stirred in the dark overnight. From its ^{13}C NMR spectrum at –40°C in CD_2Cl_2 and its IR spectrum it is formulated as $(OC)_4$(*t*-BuNC)$OsMn(CO)_4(Cl)$ (**1**) with a donor–acceptor OsMn bond and with both noncarbonyl ligands *cis* to the metal–metal bond (eq. [1]).

[1] 

In **1** the $18e^-$ compound $Os(CO)_4$(CN-*t*-Bu) acts as a two-electron donor ligand towards the $16e^-$ $Mn(CO)_4(Cl)$ moiety. The ^{13}C NMR spectrum of **1** has a 1:2:1 pattern in the Mn–CO region around δ 220, and a 2:1:1 pattern in the Os–CO region (δ 160–185). The latter pattern is typical of complexes such as $(OC)_4$(*t*-BuNC)$OsCr(CO)_5$ in which the $18e^-$ $Os(CO)_4$(CN-*t*-Bu) compound acts as a ligand (3). In particular, the high field resonance in the spectrum of **1** at δ 163.0 is characteristic of this type of complex and is assigned to the carbonyl *trans* to the dative metal–metal bond (1–3, 7). The chemical shift of this resonance in $(OC)_4$(*t*-BuNC)Os[Acc] (Acc = $16e^-$ acceptor fragment) complexes may be a measure of the acceptor strength of the $16e^-$ fragment (19). The shift of this resonance in **1** may be compared with δ 165.1 and 159.3, the shifts found in $(OC)_4$(*t*-BuNC)$OsCr(CO)_5$ and $(OC)_4$(*t*-BuNC)$OsOs(CO)_3(GeCl_3)(Cl)$, respectively (3, 19).

Scheme 2.



Compound **1** was insoluble in hexane at room temperature; warming **1** in hexane caused it to decompose. Although **1** was stable in CD_2Cl_2 at –40°C, it decomposed in CH_2Cl_2 at room temperature over ~90 min. Two decomposition

Table 7. Selected bond lengths (Å) and angles (deg) of **3I**.

Bond lengths (Å)			
Os(1)—Mn	2.870(1)	Mn—C(11)	1.80(1)
Os(1)—Os(2)	2.8894(5)	Mn—C(radial)	1.81(1)–1.87(1)
Os(2)—Os(3)	2.8928(5)	Os—C(CO)	1.89(1)–1.96(1)
Os(3)—I	2.7768(7)	Os—C(CNBu)	2.01(1)–2.026(9)
Bond angles (deg)			
Os(1)-Os(2)-Os(3)	177.60(2)	Os-Mn-C(radial)	82.7(3)–84.9(3)
Mn-Os(1)-Os(2)	177.04(3)	Mn-Os(1)-C	90.0(2)–93.5(3)
Os(1)-Mn-C(1)	179.5(4)	Os(1)-Os(2)-C	88.1(2)–91.5(3)
Os(2)-Os(3)-C(14)	178.5(3)	Os(2)-Os(3)-C(radial)	83.2(2)–87.8(2)
Os(2)-Os(3)-I	92.63(2)		

Fig. 1. Molecular structure of $(OC)_3(I)(t\text{-}BuNC)OsMn(CO)_5$ (**1I**).

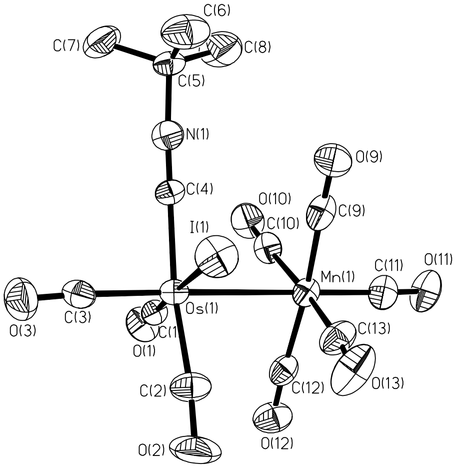
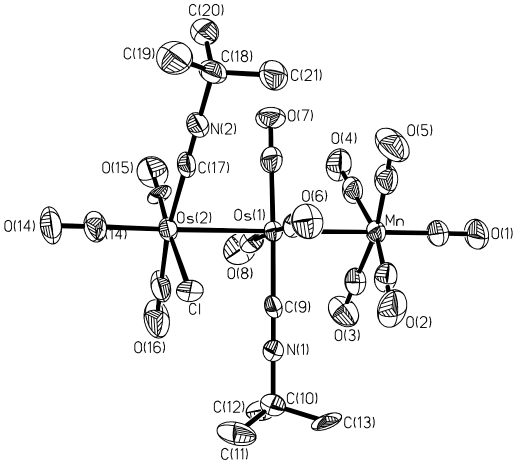


Fig. 2. Molecular structure of $(OC)_3(Cl)(CN\text{-}t\text{-}Bu)OsOs(CO)_3\text{-}(CN\text{-}t\text{-}Bu)OsMn(CO)_5$ (**2C1A**).



products were identified as $Os(CO)_4(CN\text{-}t\text{-}Bu)$ and $Mn(CO)_5(Cl)$ by IR spectroscopy. Dissociation in solution of complexes with weak dative metal–metal bonds has been observed previously (6, 11). Furthermore, in some cases these complexes react with CH_2Cl_2 (20).

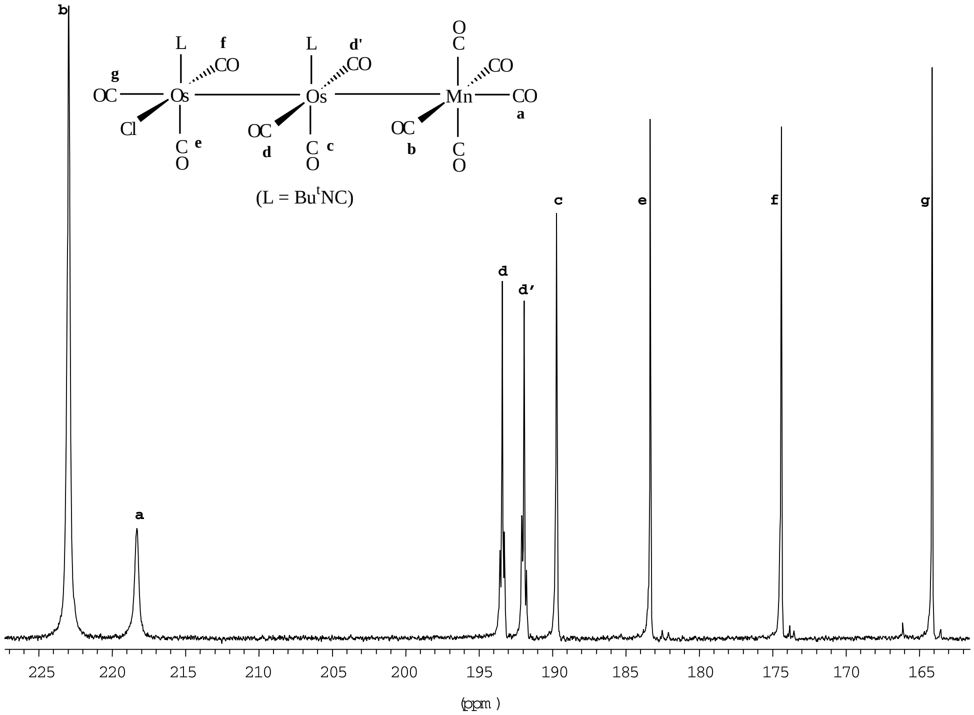
When the reaction of $Os(CO)_4(CN\text{-}t\text{-}Bu)$ and $Mn(CO)_5(Cl)$ in hexanes was carried out for 7 days in ambient light under vacuum, a second product, which was also analyzed as $MnOs(CO)_8(CN\text{-}t\text{-}Bu)(Cl)$ (**1Cl**), was obtained. The reaction with $Mn(CO)_5(X)$ (X = Br, I) and $Os(CO)_4(CN\text{-}t\text{-}Bu)$ gave the corresponding $MnOs(CO)_8(CN\text{-}t\text{-}Bu)(X)$ (**1Br**, **1I**) derivatives; there was no evidence in the latter reactions for a complex analogous to that of **1**. The crystal structure of **1I** (reported below) revealed that these compounds should be formulated as $(OC)_3(t\text{-}BuNC)(X)OsMn(CO)_5$ (X = Cl, Br, I) (Scheme 2). Since the $Mn(CO)_5$ and $Os(CO)_3(CN\text{-}t\text{-}Bu)(X)$ fragments are $17e^-$ species, the Mn–Os bonds in these molecules are considered nondative metal–metal bonds.

A view of **1I** is shown in Fig. 1; selected bond lengths and angles for the molecule are listed in Table 5. As can be seen from the figure, the Mn–Os bond is unbridged. There do not appear to be any structures of complexes with unbridged Mn–Os bonds with which to compare the Mn—Os length in **1I** of 2.9245(8) Å. In $CpMnOs_3(\mu_2\text{-}CHCHPh)(\mu\text{-}H)(\mu\text{-}CO)(CO)_{11}$ the Os—Mn length is 2.765(4) Å (21); in the $MnOs_3(\mu_4\text{-}C)(CO)_{13}$ the Os—Mn lengths range from 2.7797(9) to 2.8271(7) Å (22). From the (unbridged) metal–metal bond lengths reported for $Mn_2(CO)_{10}$ (2.9038(6) Å) (23) and $Os_3(CO)_{12}$ (average = 2.887 Å) (24) one can estimate the length of an unbridged Mn—Os bond to be ~2.895 Å. The Os–Mn distance in **1I** is, therefore, somewhat longer than expected; it is also significantly longer than the three other Os–Mn lengths reported below.

The formation of complexes of type **1X** involves an isomerization in which the halide X migrates from the Mn to the Os atom in $(OC)_4(t\text{-}BuNC)OsMn(CO)_4(X)$ with concomitant migration of a carbonyl ligand from Os to Mn as shown in Scheme 2. As mentioned in the *Introduction*, we have previously observed this type of migration in $(Me_3P)(OC)_4\text{-}OsRu(CO)_3(SiCl_3)(Br)$ (11). A similar migration is presumably also involved in the formation of $(Me_3P)(OC)_3(H)OsRe(CO)_5$ from $Re(CO)_5(H)$ and $Os(CO)_4(PMe_3)$, although the intermediate with a dative Os–Re bond is not observed (12).

Because of the donor–acceptor character of the metal–metal bond in molecules such as **1** there is expected to be a greater charge separation in these molecules compared with the isomerized derivatives (e.g., **1Cl**). Consistent with this view is that the C—O stretches in **1** (with a dative Os—Mn bond) span the range 1924–2118 cm^{-1}, whereas in **1Cl** the range is 1970–2099 cm^{-1}. It may be the relief of this charge separation that is the driving force for the isomerization. The nondative Os–Re bond in $(Me_3P)(OC)_3(Br)OsRe(CO)_5$ is slightly shorter than the dative Os–Re bond in the closely related $(Me_3P)(OC)_4OsRe(Br)(CO)_4$, an observation consistent

Fig. 3. The ^{13}C NMR spectrum (CO region) of **2C1A** (^{13}CO enriched) in CH_2Cl_2–CD_2Cl_2 (4:1) at – 40°C. The assignment of the signals is given in the inset.



with the view that nondative metal–metal bonds are somewhat stronger than similar dative metal–metal bonds (4, 12, 25).

Trinuclear OsMn complexes

Halide ligands in metal carbonyl complexes such as $M(CO)_{6-n}(X)_n$ (M = Mn (26), Re (27), n = 1; M = Fe (28), Ru, Os (29), n = 2; X = Cl, Br, I) usually activate the complex to carbonyl substitution. It was, therefore, reasoned that the **1X** complexes might undergo further carbonyl substitution by $Os(CO)_4$(CN-*t*-Bu) at the osmium atom and this possibility was found to be correct.

Reaction of **1X** with $Os(CO)_4$(CN-*t*-Bu) in a 1:1 ratio, or the reaction of $Mn(CO)_5(X)$ and $Os(CO)_4$(CN-*t*-Bu) in a 1:2 ratio, readily affords complexes of formula $MnOs_2(CO)_{12}$-(CN-*t*-Bu)$_2$(X) (**2X**) according to Scheme 3. Two isomers of this formula were isolated by column chromatography. The major isomer in each case (**2XA)** is formulated with an $MnOs_2$ backbone with an isocyanide ligand coordinated to each osmium atom. The halide ligand is placed on the terminal Os atom at a site that is both *cis* to the Os–Os bond and the *t*-BuNC ligand (Scheme 3). This is based on the crystal structure and the ^{1}H and ^{13}C NMR data of **2ClA.** The bromo and iodo analogues have similar ^{1}H NMR and IR spectra to **2ClA.**

A view of **2ClA** is shown in Fig. 2; selected bond lengths and angles are given in Table 6. The Os—Mn length in **2ClA** of 2.900(1) Å is significantly shorter than the Os—Mn length in **1I** (2.9245(8) Å). This is unexpected because in **1I** the ligands *trans* to the Os–Mn bond are π-acceptor carbonyl ligands, whereas in **2ClA** one of the *trans* ligands is $Os(CO)_3$(L)(Cl), which is probably a π-donor ligand (7). The latter property would be expected to increase the *d*π–*d*π interactions across the metal–metal bond and hence weaken the Os–Mn bond (see below). The apparent strengthening of the Os–Mn bond in **2ClA** compared with that in **1I** is tentatively assigned to more extensive delocalization and hence stabilization of the metal–metal bonding electrons in **2ClA**.

The Os—Os distance in **2ClA** of 2.8812(4) Å, may be compared with the average Os—Os length (2.887(3) Å) in $Os_3(CO)_{12}$ (24). The Os–Os distances in linear Os_3 chains are, however, somewhat longer than the distance in the triangular cluster. For example, the Os—Os lengths in $Os_3(CO)_{12}(I)_2$ (30), $Os_3(CO)_{12}(SiCl_3)_2$ (31), and $Os_3(CO)_{10}$-$[P(OMe)_3]_2(Br)_2$ (32) are 2.935(2), 2.912(1), and 2.916(2) Å, respectively. In $(OC)_3[MeC(CH_2O)_3P]_2OsOs(CO)_4W(CO)_5$ (33), $(OC)_4$(CN-*t*-Bu)$OsOs(CO)_3$(CN-*t*-Bu)$W(CO)_5$ (34), and $(Ph_3Sb)(OC)_4OsOs(CO)_4Os(CO)_3(Br)_2$ (35), the Os—Os (dative) bond lengths are 2.940(1), 2.907(2), 2.8882(5), and 2.9308 Å, respectively. The Os–Os length in **2ClA**, therefore, appears to be significantly shorter than most comparable unbridged Os–Os distances in noncluster complexes reported in the literature.

The ^{13}C NMR spectrum of **2ClA** in the CO region (Fig. 3) has the expected 1:4 pattern in the Mn–CO region due to the axial and radial carbonyls of the $Mn(CO)_5$ unit; these signals are broadened due to the quadrupole moment of 5/2 of ^{55}Mn. There are six resonances each of intensity 1 in the δ 160–195 region (the region where the resonances of Os–CO groupings normally appear (2, 3, 7, 36)). Such a spectrum is consistent with the solid-state structure when it is realized that the terminal Os atom is chiral because it has four different ligands with three unique ligands occupying a face of the octahedron. The *trans*-carbonyl ligands attached to the central Os atom (labeled d/d′ in Fig. 3) are, therefore, chemically distinct. This is similar to the AB pattern exhibited by protons of a CH_2 unit adjacent to a chiral center in organic

Scheme 3.

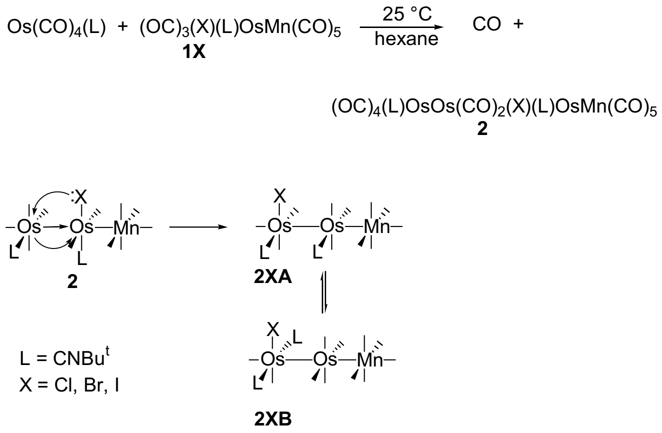
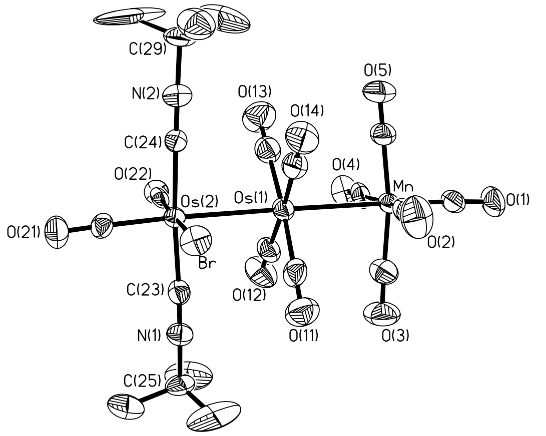


Fig. 4. Molecular structure of $(OC)_2(Br)(CN\text{-}t\text{-}Bu)OsOs(CO)_4\text{-}OsMn(CO)_5$ (**2BrB**).



molecules (37). The signals due to these carbonyls also exhibit ^{13}C–^{13}C coupling as expected for chemically different carbonyls that are mutually *trans* to each other (38) and the level of ^{13}C enrichment of the sample (~30%).

From their spectroscopic properties, the minor isomers (**2XB**) are formulated with a similar structure to **2XA**, but with both isocyanide ligands on the terminal osmium atom in a mutually *trans* orientation (Scheme 3). In each case, the ^1H NMR spectrum consists of a singlet that indicates, in the absence of chemical exchange, that both isocyanide ligands are chemically equivalent. The IR spectrum has one very weak and one strong C–N stretch consistent with the view that these ligands are in mutually *trans* sites on the same osmium atom. The ^{13}C NMR spectrum of **2ClB** in CH_2Cl_2–CD_2Cl_2 exhibits two signals in a ratio of 4:1 in the Mn–CO region and three signals in a 4:1:1 ratio in the Os–CO region, as expected.

The structure of **2BrB** was confirmed by X-ray crystallography. A view of the molecule is given in Fig. 4; selected bond lengths and angles are presented in Table 6. The Os—Mn and Os—Os lengths are 2.884(1) and 2.8895(4) Å, respectively, and may be compared with the other Os–Mn and Os–Os lengths discussed above. That the Os–Mn length in **2BrB** is somewhat shorter than that in **2ClA** may reflect fewer steric interactions between the radial ligands on the Mn and Os(1) atoms in **2BrB**.

A solution of pure **2IA** in hexane was stirred under vacuum at room temperature for 90 h. An IR spectrum of the solution at this stage indicated the presence of **2IA**, along with significant amounts of $Mn_2(CO)_{10}$ and trace amounts of **2IB**. Likewise, a solution of **2BrB** in hexane was stirred under vacuum at room temperature for 90 h and an IR spectrum then taken of the solution. The spectrum indicated the presence of **2BrA**, significant amounts of $Mn_2(CO)_{10}$, but little or no starting complex (**2BrB**). In each case there were C–O stretching bands due to unidentified products. These preliminary results indicate that the **A** and **B** forms of **2X** are present in equilibrium in hexane at room temperature. They also show that the complexes are unstable under these conditions and decompose to $Mn_2(CO)_{10}$ and other unidentified products. It may be that decomposition proceeds mainly via form **B**.

There is ample evidence that migration of carbonyl ligands across dative metal–metal is facile (2, 3, 5, 6). For example, the sample used for the spectrum shown in Fig. 3 was prepared from ^{13}CO-enriched $Mn(CO)_5(Cl)$ and unenriched $Os(CO)_4(CN\text{-}t\text{-}Bu)$. It is evident from the spectrum that the label is scrambled over all carbonyl sites in the molecule. Similar isomers to **2A** and **2B** are found for $Os_2(CO)_7\text{-}(CN\text{-}t\text{-}Bu)_2W(CO)_5$, but in this case the isomers are not in equilibrium in solution at room temperature (34). The migration of the noncarbonyl ligand to the terminal osmium atom in **2BrB** is also reminiscent of the migration observed in the formation of $(OC)_3[MeC(CH_2O)_3P]_2OsOs(CO)_4OsW(CO)_5$ from the addition of $Os(CO)_4[P(OCH_2)_3CMe]$ to $[MeC(CH_2O)_3P](OC)_4OsW(CO)_5$ at 90°C (33). The trinuclear complex in this case contains two dative metal–metal bonds in tandem and has both P ligands coordinated to the terminal Os atom, in a *trans* configuration. This type of migration results in the more bulky noncarbonyl ligand moving to a less sterically hindered site, although the radial site on the terminal Os atom is even less sterically hindered. The *trans* arrangement of the noncarbonyl ligands, which are poorer π-acceptor ligands than CO, would not be expected to be the electronically preferred structure. It is usually found that poor π-acceptor ligands prefer sites *trans* to carbonyl ligands. We have recently argued that there is an electronic preference to have a strong π-acceptor ligand (e.g., CO) *trans* to the metal–metal bond in binuclear complexes. This is because it will reduce the repulsive *d*π–*d*π interactions across the metal–metal bond (7).

Tetranuclear OsMn complexes

Reaction of $Mn(CO)_5(X)$ and $Os(CO)_4(CN\text{-}t\text{-}Bu)$ in a 1:3 ratio in solution at room temperature readily gave products that analyzed as $MnOs_3(CO)_{14}(CN\text{-}t\text{-}Bu)_3(X)$ (**3X**; eq. [2]); it was also established on a small scale that the same products could be formed from **2X** and with an excess of $Os(CO)_4(CN\text{-}t\text{-}Bu)$ under the same conditions. The X-ray crystal structure of **3I** was determined at –70°C and a view of the molecule is given in Fig. 5; structural parameters are listed in Table 7. The structure consists of an essentially linear Os_3Mn chain with an isocyanide ligand attached to each Os atom. The halide is coordinated, once again, to the terminal Os atom in a site that is *cis* to both the Os–Os bond and a *t*-BuNC ligand.

Fig. 5. Molecular stucture of $(OC)_3(I)(CN\text{-}t\text{-}Bu)OsOs(CO)_3(CN\text{-}t\text{-}Bu)Os(CO)_3(CN\text{-}t\text{-}Bu)OsMn(CO)_5$ (**31**).

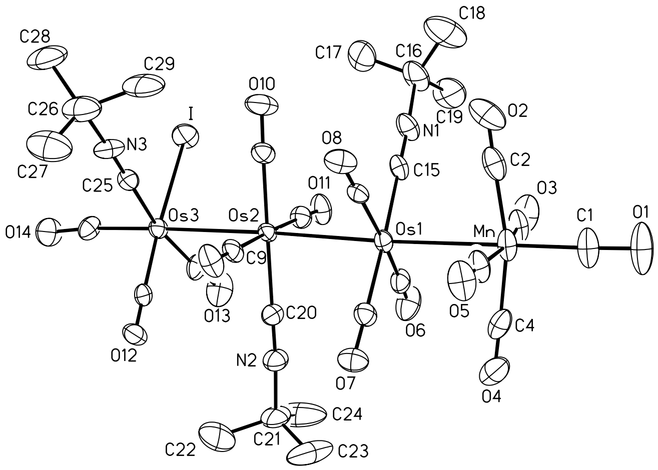
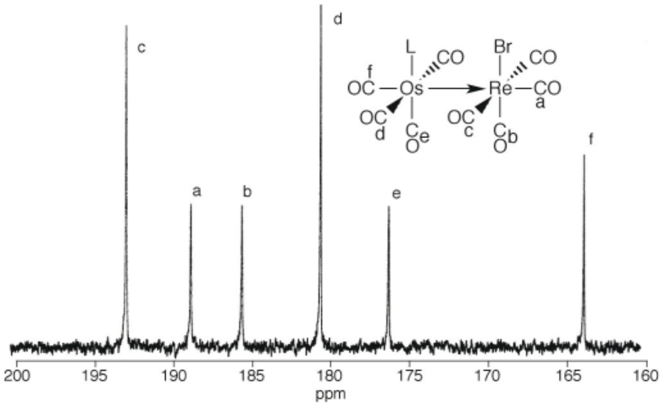
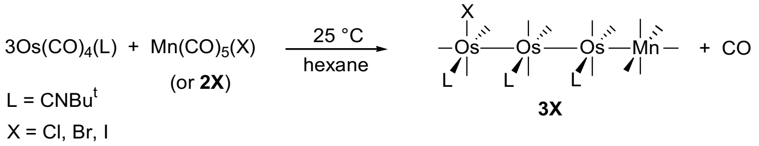


Fig. 6. The ^{13}C NMR spectrum (CO region) of $(OC)_4(t\text{-BuNC})OsRe(CO)_4$ (Br) (^{13}CO enriched) in CH_2Cl_2–CD_2Cl_2 (4:1) at −40°C. The assignment of the signals is given in the inset (L = *t*-BuNC).



[2]



$$3Os(CO)_4(L) + Mn(CO)_5(X)\ (\text{or } \mathbf{2X}) \xrightarrow[\text{hexane}]{25\ °C} \mathbf{3X} + CO$$

L = CNBu^t
X = Cl, Br, I

3X

The Os—Mn distance in **3I** at 2.870 (1) Å is the shortest of the four Os—Mn lengths determined in this study and some 0.05 Å shorter than that in **1I**. The Os—Os lengths 2.8894(5) and 2.8928(5) Å in **3I** are not significantly different from the Os—Os lengths in **2ClA** and **2BrB**, and comparable to the Os—Os lengths in $Os_3(CO)_{12}$. From a ground state point of view, therefore, the metal–metal bonds in **3I** appear strong.

The ^{13}C NMR spectrum of ^{13}CO-enriched **3Cl** (Table 3) has two signals in a 4:1 ratio to low field of δ 215 assigned to the carbonyls on manganese, and eight signals to high field of δ 195 assigned to the carbonyls attached to the osmium atoms. The latter signals are of intensity 1 except that at δ 194.8, which is of intensity 2. The spectrum is consistent with the view that **3Cl** has the same structure as found for **3I** in the solid state if two of the resonances are degenerate. As in the spectrum of **2ClA**, because the terminal osmium atom is chiral each carbonyl attached to an osmium atom is chemically different. The methyl resonances in both the ^{1}H NMR spectra of **3X** (and in ^{13}C NMR spectrum of **3Cl**) show two resonances in the ratio of 2:1. It is probable that the signals due to the methyl groups of the CN-*t*-Bu groups coordinated to the two internal osmium atoms are degenerate.

Only one isomer of **3X** was isolated and it can be assumed to be the result of addition of $Os(CO)_4(CN\text{-}t\text{-}Bu)$ to the major isomer of **2X** (i.e., **2XA**). The substitution of a carbonyl ligand of the $Os(CN\text{-}t\text{-}Bu)_2(X)(CO)_2$ unit in **2XB** would be expected to be slower than in **2XA** for both steric and electronic reasons. The presence of an additional CN-*t*-Bu ligand on the terminal Os atom would block the substitution and increase the strength of the remaining Os–CO bonds.

Attempts to prepare complexes with still longer metal chains have so far been unsuccessful. Stirring $Mn(CO)_5(X)$ in solution with a large excess of $Os(CO)_4(CN\text{-}t\text{-}Bu)$ resulted in only **3X** being formed. Carrying out the same reactions at elevated temperatures resulted in decomposition.

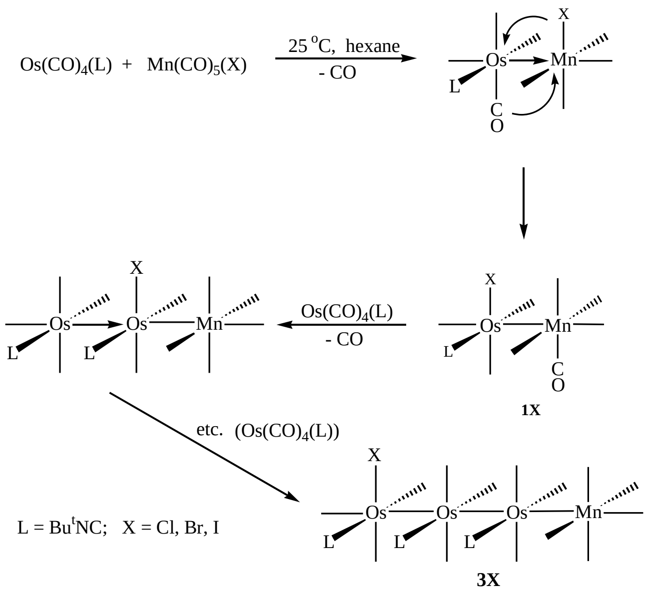
Binuclear OsRe complexes

Complexes of formula $(OC)_4(t\text{-BuNC})OsRe(CO)_4(X)$ (i.e., with dative Os–Re bonds) were synthesized according to eq. [3] as air-stable, yellow crystals. (It was found that the dimeric rhenium precursor gave purer products than the corresponding $Re(CO)_5(X)$ complexes.) The formulation of the products with a dative metal–metal bond is clearly indicated by ^{13}C NMR spectroscopy (e.g., Fig. 6). In particular, the complexes exhibit three resonances in a 2:1:1 ratio in the region δ 184–194 attributed to the carbonyls of the $Re(CO)_4(X)$ moiety (Table 2). These signals show little quadrupolar broadening presumably because of the large field gradient through the molecule arising from the polar nature of the dative Os–Re bond causing rapid quadrupolar relaxation.

$$[3]\quad 2Os(CO)_4(L) + [Re(\mu\text{-}X)(CO)_4]_2 \quad X = Cl, Br, I \quad \xrightarrow[\text{toluene}]{45°\ C} 2(OC)_4(L)OsRe(CO)_4(X)\ \ \mathbf{1ReX}$$

Attempts to isomerize the $(OC)_4(t\text{-BuNC})OsRe(CO)_4(X)$ complexes by heating them in solution at 60°C only resulted in decomposition. It has previously been found that, like nondative metal–metal bonds, dative metal–metal bonds appear strongest when both metals are third-row transition elements (2, 4, 25). The increased strength of the Os–Re bond would contribute to the barrier to the isomerization of the **1ReX** complexes compared with that of the Mn analogues. We point out here that although $(Me_3P)(OC)_4(Br)OsRe(CO)_5$ is known it was not prepared by isomerizarion of

Scheme 4.



$(Me_3P)(OC)_4OsRe(Br)(CO)_4$, but rather by reaction of $(Me_3P)(OC)_4(H)OsRe(CO)_5$ with CBr_4 (12).

Conclusions

We have previously observed the isomerization of $(Me_3P)(OC)_4OsRu(CO)_3(SiCl_3)(Br)$ with a dative Os–Ru bond to $(Me_3P)(OC)_4(Br)OsRu(CO)_3(SiCl_3)$ with a nondative Os–Ru bond (11). This type of migration has been exploited for the synthesis of $(X)[Os(CO)_3(CN\text{-}t\text{-}Bu)Os]_nMn(CO)_5$ complexes with $n = 1, 2, 3$. It is believed that there is initial replacement of CO in the $Mn(CO)_5(X)$ or $Os(CO)_3(CN\text{-}t\text{-}Bu)(X)$ unit by the $18e^-$ ligand $Os(CO)_4(CN\text{-}t\text{-}Bu)$. This is followed by rearrangement to the isomer with a nondative metal–metal bond by migration of the halogen ligand to the donor Os atom with concomitant migration in the reverse direction of a carbonyl ligand. This is summarized in Scheme 4.

There are a number of factors involved in the successful synthesis of the Os_nMn complexes. The $18e^-$ $Os(CO)_4(L)$ must be sufficiently basic to form the initial donor–acceptor complex ($Os(CO)_5$ does not undergo these reactions). The noncarbonyl ligand (L) must be sterically undemanding so that it does not block entry of an additional $Os(CO)_4(L)$ ligand. With one exception, this reaction stops at the binuclear derivative for $Os(CO)_4(PR_3)$ ligands (2, 33). Furthermore, in complexes such as $(Me_3P)(OC)_4OsW(CO)_5$ and $(Me_3P)(OC)_4OsRu(CO)_3(SiCl_3)(Br)$ the major isomer has the P ligand *trans* to the dative metal–metal bond (2, 12).

An additional requirement for the formation of the tri- and tetranuclear species is that the dative bond in the intermediates should not be too strong. For example, the $(OC)_4(t\text{-}BuNC)OsRe(CO)_4(X)$ complexes do not isomerize. In addition, the $1e^-$ ligand on the acceptor atom should readily allow the formation of the bridged intermediate. In previous work, we have shown that for $(Me_3P)(OC)_4OsRu(CO)_3(SiCl_3)(X)$ compounds isomerization occurs immediately for X = H and slowly for X = halide. On the other hand, $(Me_3P)(OC)_4OsRu(CO)_3(SiCl_3)_2$ does not undergo this rearrangement (11). Attempts to further exploit this reaction for the preparation of complexes with still longer metal chains are planned.

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