Syntheses and Properties of Aminomethyl Complexes of Manganese and Rhenium

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The interaction of a range of aminomethyltrimethyltins with carbonyl halides of manganese and rhenium has afforded the yellow volatile compounds [(η^2-R_2NCH_2)M(CO)$_4$] (M = Mn and Re). In these complexes the aminomethyl ligand functions as a formally three-electron donor, and the ligand is removed by halogen to form the corresponding methyleneammonium halide.

THE direct interaction of dimethyl(methylene)ammonium bromide and carbonyl(chloro)copper(I) produces the complex $[(Me_2N{=}CH_2)CuCl]^+Br^-$, in which it is believed the dimethylaminomethyl group acts as a π-type ligand.[1] More recently Fong and Wilkinson have demonstrated the formation of η^1 and η^2 metal complexes of the dimethylaminomethyl cation directly from various dimethyl(methylene)ammonium salts.[2]

The ready fission reactions of organotin compounds

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[1] R. Mason and G. Rucci, *Chem. Comm.*, 1971, 1132.

[2] C. W. Fong and G. Wilkinson, preceding paper.

such as amines,[3] sulphides,[4] and allyls [5] with transition-metal halides have led to a number of useful syntheses and unusual transition-metal complexes. This prompted us to examine the reaction of metal carbonyl halides with dialkylaminomethyltrialkyltins as a potential route to aminomethyl complexes of the transition metals.

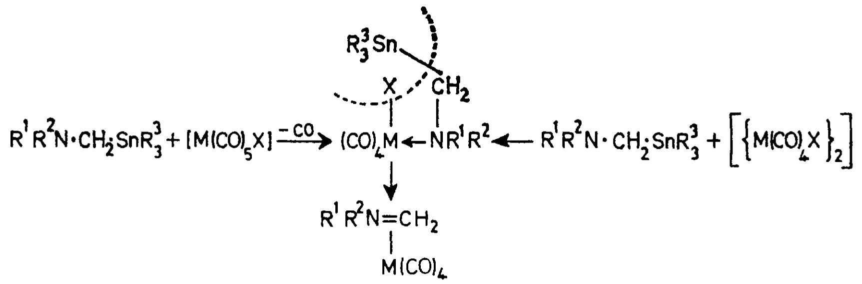
TABLE 1

Aminomethyltetracarbonyls of manganese and rhenium

Complex	Yield (%)	B.p. [m.p.] (t°/C)	^{1}H N.m.r. spectra (τ values)	ν_{CO}/cm^{-1} in n-hexane
$[(\eta^2\text{-}\mathrm{Me_2NCH_2})\mathrm{Mn(CO)_4}]$	75	[27]	7·38 (6H, s), 7·55 (2H, s)	2058w, 1966m, 1950vs, 1938s
$[(\eta^2\text{-}\mathrm{Et_2NCH_2})\mathrm{Mn(CO)_4}]$	68	*ca.* 35 at 10^{-2} mmHg	7·24 (4H, m), 7·45 (2H, s), 8·86 (6H, t, *J* 7·3 Hz)	2057w, 1965m, 1948vs, 1938s
$[(\eta^2\text{-}\mathrm{Pr^n{}_2NCH_2})\mathrm{Mn(CO)_4}]$	64	*ca.* 40 at 10^{-2} mmHg	7·30 (2H, s), 7·57 (4H, m), 8·55 (4H, m), 8·82 (6H, t, *J* 6·7 Hz)	2056w, 1965m, 1950vs, 1936s
$[(\eta^2\text{-}\mathrm{Bu^n{}_2NCH_2})\mathrm{Mn(CO)_4}]$	58	*ca.* 45 at 10^{-2} mmHg	7·32 (4H, m), 7·45 (2H, s), 8·50 (8H, m), 9·03 (6H, t, *J* 6·5 Hz)	2058w, 1968m, 1952vs, 1938s
$[\{\eta^2\text{-}\overline{\mathrm{CH_2\cdot(CH_2)_4N}}\mathrm{CH_2}\}\mathrm{Mn(CO)_4}]$	55	*ca.* 50 at 10^{-2} mmHg	7·20 (2H, m), 7·51 (2H, s), 7·73 (2H, m), 8·30 (6H, m)	2057w, 1966m, 1950vs, 1934s
$[\{\eta^2\text{-}\mathrm{Ph(Me)NCH_2}\}\mathrm{Mn(CO)_4}]$	30	*ca.* 60 at 10^{-2} mmHg	2·68 (5H, m), 7·04 (3H, s), 6·57 (1H, d, *J* 2·2 Hz), 7·26 (1H, d, *J* 2·2 Hz)	2060m, 1970s, 1957vs, 1933vs
$[\{\eta^2\text{-}\overline{\mathrm{CH_2CH_2\cdot N}}\mathrm{CH_2})\mathrm{Mn(CO)_4}]$	65	[64—66]	7·82 (2H, m), 7·84 (2H, s), 8·04 (2H, m)	2063w, 1971m, 1964vs, 1936s
$[(\eta^2\text{-}\overline{\mathrm{CHMe\cdot CH_2\cdot N}}\mathrm{CH_2})\mathrm{Mn(CO)_4}]$	10	*ca.* 35 at 10^{-2} mmHg	7·68 (3H, m), 8·10 (2H, m), 8·72 (3H, m)	2060w, 1968m, 1961vs, 1933s
$[\{\eta^2\text{-}\mathrm{C_6H_{11}(Me)NCH_2}\}\mathrm{Mn(CO)_4}]$	40	*ca.* 65 at 10^{-2} mmHg	7·41 (1H, d, *J* 1·5 Hz), 7·48 (1H, d, *J* 1·5 Hz), 7·53 (3H, s), 8·45 (10H, m)	2059w, 1967m, 1950vs, 1939s
$[\{\eta^2\text{-}\mathrm{Me(H)NCH_2}\}\mathrm{Mn(CO)_4}]$	20	*ca.* 30 at 10^{-2} mmHg	7·31 (4H, s), 7·53 (2H, s)	2058w, 1967m, 1950vs, 1939s
$[\{\eta^2\text{-}\mathrm{C_6H_{11}(H)NCH_2}\}\mathrm{Mn(CO)_4}]$	55	*ca.* 50 at 10^{-2} mmHg	7·18 (1H, m), 7·24 (1H, s), 7·53 (2H, s), 8·36 (10H, m)	2055w, 1963m, 1949vs, 1935s
$[(\eta^2\text{-}\mathrm{Me_2NCH_2})\mathrm{Re(CO)_4}]$	78	[52—54]	7·12 (6H, s), 7·73 (2H, s)	2075w, 1968m, 1961vs, 1939s
$[(\eta^2\text{-}\mathrm{Et_2NCH_2})\mathrm{Re(CO)_4}]$	68	*ca.* 50 at 10^{-2} mmHg	7·24 (4H, m), 7·72 (2H, s), 8·84 (6H, *J* 7 Hz)	2072w, 1965m, 1959vs, 1934s
$[(\eta^2\text{-}\mathrm{Pr^n{}_2NCH_2})\mathrm{Re(CO)_4}]$	39	*ca.* 55 at 10^{-2} mmHg	7·25 (4H, m), 7·63 (2H, s), 8·34 (4H, m), 9·08 (6H, t, *J* 7·5 Hz)	2071w, 1967m, 1959vs, 1933s
$[\{\eta^2\text{-}\overline{\mathrm{CH_2\cdot(CH_2)_4N}}\mathrm{CH_2}\}\mathrm{Re(CO)_4}]$	58	*ca.* 50 at 10^{-2} mmHg	6·78 (2H, m), 7·50 (2H, m), 7·63 (2H, s), 8·24 (6H, m)	2071w, 1965m, 1960vs, 1933s

The interaction of (*NN*-dimethylaminomethyl)trimethyltin and bromopentacarbonylmanganese gave a 75% yield of tetracarbonyl(η^2-dimethylaminomethyl)-manganese within 0·25 h reaction time. The product is also formed in high yield from the corresponding reaction with bromotetracarbonylmanganese dimer. A wide range of aminomethyltrialkyltins have been shown to afford analogous complexes of both manganese and rhenium (Table 1).

We have suggested previously that interaction of metal carbonyl halides with allylic derivatives of tin to produce π-allyl metal carbonyl complexes proceeds by a co-ordination–elimination sequence involving fission of the tin–carbon bond.[5] It is probable that the aminomethyl complexes are formed in a similar way by the initial displacement of carbon monoxide to form an amine complex followed by an intramolecular elimination of organotin halide. In the case of the dimeric carbonyl halides the intermediate would be formed by the initial fission of the halogen bridge without loss of CO.



In all the reactions carried out there was no indication of the formation of η^1 type of ligand complexes, which are now known to be isolable.[2] This lends support to the co-ordination–elimination mechanism which would ead directly to the η^2 type of complex. Further, we

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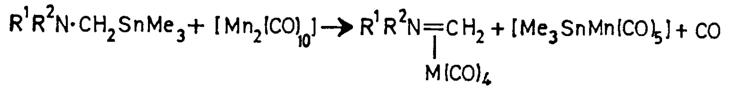
[3] T. A. George and M. F. Lappert, *Chem. Comm.*, 1966, 463.

[4] E. W. Abel, B. C. Crosse, and D. B. Brady, *J. Amer. Chem. Soc.*, 1965, **87**, 4397.

[5] E. W. Abel and S. Moorhouse, *J.C.S. Dalton*, 1974, 1706.

note that when the nitrogen of the tin–amine precursor is severely sterically hindered, as in for example $\mathrm{Pr^i{}_2NCH_2SnBu^n{}_3}$, $\mathrm{(C_6H_{11})_2NCH_2SnBu^n{}_3}$, and $\mathrm{Ph_2NCH_2SnBu^n{}_3}$, the above reactions do not take place.

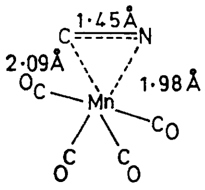


$$\mathrm{R^1R^2N{\cdot}CH_2SnMe_3 + [Mn_2(CO)_{10}] \rightarrow \underset{M(CO)_4}{R^1R^2N{=}CH_2} + [Me_3SnMn(CO)_5] + CO}$$

Although not suitable as a synthetic method, owing to difficulty in separation of the two products, the action of manganese carbonyl upon the aminomethyltrialkyltins does give modest yields of the aminomethyltetracarbonyls of manganese.

Here again amine displacement of carbon monoxide, followed by intramolecular elimination of pentacarbonyl(trimethylstannyl)manganese is possible.

The dihapto-nature of the aminomethyl ligands in these compounds has been confirmed by an *X*-ray crystal-structure determination of η^2-aziridinylmethyltetracarbonylmanganese.[6] The bonding is represented diagramatically below:



There is essentially symmetric π-bonding of the aminomethyl ligand, rather than the alternative metal–nitrogen σ-bonded arrangement. The high π-acidity of the aminomethyl ligand in these complexes is reflected in the C–N bond length, which is approaching that of a single C–N bond.

TABLE 2

Triphenylphosphine-substituted aminomethyltricarbonyls of manganese

Complex	Yield (%)	M.p. (t/°C)	Analysis (%) Found C	H	N	Required C	H	N	ν_{CO}/cm^{-1} in n-hexane
$[(\eta^2\text{-}\mathrm{Me_2NCH_2)Mn(CO)_3(PPh_3)}]$	43	127—129	61·5	4·8	2·95	62·8	5·01	3·05	1995w, 1990w, 1900s,1893s
$[(\eta^2\text{-}\mathrm{Et_2NCH_2)Mn(CO)_3(PPh_3)}]$	47	125—126	62·9	5·6	2·7	64·1	5·54	2·87	1987w, br, 1891s, 1883s
$[(\eta^2\text{-}\mathrm{Pr^n{}_2NCH_2)Mn(CO)_3(PPh_3)}]$	46	100—103	65·5	6·2	2·8	65·2	6·02	2·72	1988w, br, 1895s, 1884s
$[\{\eta^2\text{-}\overline{\mathrm{CH_2{\cdot}(CH_2)_4N}}\mathrm{CH_2}\}\mathrm{Mn(CO)_3(PPh_3)}]$	53	124—126	65·2	5·4	2·5	65·9	5·41	2·81	1990w, 1987w, sh, 1895s, 1885s, sh

The i.r. spectra of aminomethyltetracarbonylmanganese and -rhenium all show four metal-carbonyl stretching modes in the i.r. region consistent with their structure (Table 1). The proton n.m.r. chemical-shift data are listed in Table 1 and these spectra are all consistent with the proposed formulation. The asymmetry imposed upon the aminomethyl ligands by the co-ordination of the C–N system to the transition metal gives rise to some interesting multiplicities. Thus, for example, in $[(\eta^2\text{-}\mathrm{Et_2NCH_2)Mn(CO)_4}]$, whilst the two protons of the individual methyl group are equivalent, the two protons of each methylene in the ethyl group are rendered non-equivalent, resulting in an $\mathrm{ABX_3}$ spectrum. Similarly the *endo*- and *exo*-ring protons are non-equivalent in the η^2-aziridinylmethyltetracarbonylmanganese. The aziridinylmethyl compounds become particularly complicated for the ring-substituted derivative, $[(\eta^2\text{-}\mathrm{Me\overline{CH{-}CH_2{-}N}CH_2)Mn(CO)_4}]$, where four isomers are possible. The n.m.r. spectrum suggests that all four are formed, albeit in different proportions, but neither the geometrical isomers nor the diastereoisomers were separated. Under conditions of appropriate steric requirements it should be possible to use such aminomethylmetal complexes as stereospecific synthetic intermediates.

The mass spectra of the aminomethylcarbonyl–metal complexes all showed a strong parent ion, and fragment ions resulting from sequential loss of carbon monoxide. In each case, however, the most abundant ion was that of the appropriate metal-free aminomethyl ligand.

The interaction of $[(\eta^2\text{-}\mathrm{Me_2NCH_2)Mn(CO)_4}]$ and bromine causes the fission of the aminomethyl ligand from the metal carbonyl moiety. Iodine behaved in an exactly analogous manner.

$$2[(\eta^2\text{-}\mathrm{Me_2NCH_2)Mn(CO)_4}] + 2\mathrm{Br_2} \longrightarrow 2[\mathrm{Me_2N{=}CH_2}]^+\mathrm{Br}^- + [\{\mathrm{Mn(CO)_4Br}\}_2]$$

In the reaction between aminomethyltrialkyltins and the phosphine-substituted metal carbonyl halide $[\mathrm{(Ph_3P)_2Mn(CO)_3Br}]$, it would appear that the proposed initial co-ordination step takes place with loss of a molecule of triphenylphosphine rather than carbon monoxide, thus resulting in products of general formula $[(\eta^2\text{-}\mathrm{R^1R^2NCH_2)Mn(CO)_3PPh_3}]$ (Table 2). These phosphine derivatives, however, undergo disproportionation very easily upon heating (~50 °C), to the non-phosphine substituted $[(\eta^2\text{-}\mathrm{R^1R^2NCH_2)Mn(CO)_4}]$ and an insoluble and uncharacterised component. This possibly explains the complex mixtures we have obtained in our efforts to displace carbon monoxide from $[(\eta^2\text{-}\mathrm{R^1R^2NCH_2)Mn(CO)_4}]$ by pyridine, phosphines, and arsines; invariably a high proportion of the starting tetracarbonyl complex was

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[6] E. W. Abel, R. J. Rowley, R. Mason, and K. M. Thomas, *J.C.S. Chem. Comm.*, 1974, 72.

obtained, along with uncharacterised mixtures. Interestingly there was no reaction between [(bipy)Mn(CO)$_3$Br] and aminomethyltrimethyltins.

EXPERIMENTAL

All m.p.s and b.p.s are uncorrected. I.r. spectra were obtained on a Perkin-Elmer 257 grating spectrometer and n.m.r. spectra were determined using a Perkin-Elmer R10 60 MHz or a Jeol JNM-MH-100 100 MHz spectrometer, either as neat liquids or as solutions in carbon tetrachloride or deuteriochloroform. Mass spectra were obtained at an ionizing potential of 70 eV with a Hitachi–Perkin-Elmer RMU6E. All reactions and subsequent manipulations, as a matter of course, were conducted under an atmosphere of oxygen-free dry nitrogen, and solvents were redistilled from phosphorus pentaoxide or potassium–benzophenone prior to use.

The following were prepared using literature methods, [Mn$_2$(CO)$_{10}$],[7] [Mn(CO)$_5$Br],[8] [Mn$_2$(CO)$_8$Br$_2$],[8] [Re(CO)$_5$Br],[9] [(Ph$_3$P)$_2$Mn(CO)$_3$Br],[8] [(bipy)Mn(CO)$_3$Br],[8] [Me$_2$N=CH$_2$]$^+$I$^-$,[10] and *NN*-dimethylaminomethyltributyltin.[11] The syntheses of a wide variety of other aminomethyltrialkyltins used in this work will be reported at a later date.

Interaction of Bromopentacarbonylmanganese and N-*Trimethylstannylmethylaziridine*.—A mixture of the aziridine (1·2 mmol) and carbonyl halide (1·0 mmol) in tetrahydrofuran (5 ml) was heated at 67 °C for 0·25 h. After cooling, solvent was removed at 25°/15 mmHg and hexane (10 ml) was added. Trimethyltin bromide was removed by washing the hexane solution with water (5 × 10 ml). After drying (MgSO$_4$) the hexane was removed (25 °C/15 mmHg) and the orange residue sublimed (25 °C/0·001 mmHg) onto a probe at −80 °C to give η^2-aziridinylmethyltetracarbonylmanganese (0·145 g, 65%) (Found: C, 37·65; H, 2·65; N, 6·15; Mn, 24·85; O, 26·3. C$_7$H$_6$MnNO$_4$ requires C, 37·65; H, 2·71; N, 6·28; Mn, 24·62; O, 27·11%).

Alternatively, the product can be isolated in good yield by chromatography of the crude hexane solution on basic alumina and elution with hexane. Other aminomethyltetracarbonyl complexes of manganese and rhenium, synthesised and purified in an exactly analogous manner to that described above, are listed in Table 1. In addition to the data reported in Table 1, each compound has been characterised by mass spectrometry. Further, the following aminomethyl derivatives of manganese and rhenium were synthesised and characterised only by their i.r. spectra: [(η^2-Bu$^i_2$NCH$_2$)Mn(CO)$_4$], [{η^2-Me$_3$SnCH$_2$(Me)NCH$_2$}Mn(CO)$_4$], [(η^2-EtHNCH$_2$)Mn(CO)$_4$], [(η^2-Bu$^n_2$NCH$_2$)Re(CO)$_4$], and [{η^2-Ph(Me)NCH$_2$}Re(CO)$_4$].

Interaction of Decacarbonyldimanganese and Dimethylaminomethyltrimethyltin.—The carbonyl (1 mmol) and the amine (2 mmol) in diglyme (10 ml) were heated at 160 °C for 1 h. After the cooled mixture had been washed in water to remove solvent, the products were taken up in ether and dried (MgSO$_4$). Solvent was removed at 25 °C/15 mmHg and the products sublimed (50 °C/0·001 mmHg) onto a probe at −80 °C. We were unable to separate completely the two products by chromatography, but by i.r. and n.m.r. intensity comparison the sublimed yields were estimated as [(η^2-Me$_2$NCH$_2$)Mn(CO)$_4$] (20%) and [(Me$_3$Sn)Mn(CO)$_5$] (45%).

Interaction of Bromopentacarbonylrhenium and NN-*Dimethylaminomethyltrimethyltin*.—The amine (1·2 mmol) and the bromocarbonyl (1 mmol) in toluene (10 ml) were heated at 110 °C for 1 h. After removal of solvent at 20° C/0·01 mmHg, hexane was added and the products chromatographed on basic alumina to afford tetracarbonyl(η^2-dimethylaminomethyl)rhenium (0·267 g, 77%) (Found: C, 22·3; H, 2·1; N, 3·75%. C$_7$H$_8$NO$_4$Re requires C, 21·73; H, 2·25; N, 3·93%).

Interaction of Tetracarbonyl(η^2-dimethylaminomethyl)manganese with Bromine.—Bromine (0·6 mmol) in benzene (10 ml) was added dropwise to the complex (0·5 mmol) in benzene (10 ml) at 0 °C. There was rapid reaction with the formation of a white precipitate. This was filtered off and after drying (20 °C/0·001 mmHg) was characterised as [Me$_2$N=CH$_2$]$^+$Br$^-$ (55 mg, 80%), by i.r. and n.m.r. spectroscopy. The remaining solution was concentrated at reduced pressure (25 °C/0·1 mmHg) to yield [Mn$_2$(CO)$_8$Br$_2$] (80% yield).

In a similar experiment with iodine there were isolated [Me$_2$N=CH$_2$]$^+$I$^-$ (78% yield) and [Mn$_2$(CO)$_8$I$_2$] (80% yield).

Interaction of NN-*Dimethylaminomethyltrimethyltin and Bromotricarbonylbis(triphenylphosphine)manganese*.— The amine (0·3 mmol) and the carbonyl halide (0·2 mmol) in tetrahydrofuran (5 ml) were heated at 65 °C for 0·5 h. After removal of solvent (25 °C/0·1 mmHg), hexane (30 ml) was added, and the resulting solution was filtered. After concentration to 5 ml and cooling (−20 °C) the product (0·04 g, 43%) was deposited as yellow crystals and isolated by decantation. In a similar manner the other analogous products listed in Table 2 were obtained.

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[7] R. B. King, J. C. Stokes, and T. F. Korenowski, *J. Organometallic Chem.*, 1968, **11**, 641.

[8] E. W. Abel and G. Wilkinson, *J. Chem. Soc.*, 1959, 1501.

[9] R. J. Angelici and A. E. Kruse, *J. Organometallic Chem.*, 1970, **22**, 461.

[10] J. Schreiber, H. Maag, N. Hashimoto, and A. Eschenmoser, *Angew. Chem. Internat. Edn.*, 1971, **10**, 330.

[11] D. J. Peterson, *J. Organometallic Chem.*, 1970, **21**, P63.