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REACTIVITY OF METAL–METAL BONDS

I. CLEAVAGE OF MOLYBDENUM–TIN AND TUNGSTEN–TIN BONDS AND SYNTHESIS OF NOVEL ORGANOMERCURY DERIVATIVES

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SUMMARY

Cleavage of $Me_3SnM(Cp)(CO)_3$ ($M = Mo, W$) by iodine in various solvents resulted in dominant Sn–M bond fission, accompanied by effervescence in more polar media due to displacement of CO by solvent. Similar cleavages occurred with mercuric salts but without CO elimination. Iodination of the triallyltin analogues proceeded by a more complex pathway, with some Sn–C bond fission which became dominant when mercuric salts were used as the electrophilic reagents. A very facile reaction occurred when the trimethyltin compounds were treated with RHgCl (R = Me, Ph and allyl) in acetone, yielding firstly $RHgM(Cp)(CO)_3$ which subsequently underwent a symmetrisation reaction in accordance with eqns. (1) and (2)

$$Me_3SnM(Cp)(CO)_3 + RHgCl \rightarrow Me_3SnCl + RHgM(Cp)(CO)_3 \quad (1)$$

$$2RHgM(Cp)(CO)_3 \rightarrow R_2Hg + Hg[M(Cp)(CO)_3]_2 \quad (2)$$

The new organomercury derivatives obtained by reaction (1) were isolated and characterised.

Infrared data indicated the absence of any marked interaction between the olefinic double bonds and M in the triallyltin derivatives.

INTRODUCTION

Although the first examples of covalent metal–metal bonds between transition metals and Group IVA elements appeared some 30 years ago[1,2], it was not until comparatively recently that this class of compound was fully characterised through the pioneer work of Gorsich[3] on complexes of the type $R_{4-n}M[Mn(CO)_5]_n$. Since then, this area of organometallic chemistry has expanded rapidly, and now encompasses a wide range of transition metals[4]. The derivatives of manganese, molybdenum and tungsten are particularly stable, both thermally and with respect to atmospheric oxidation, thus lending themselves to both structural and mechanistic investigations. Graham *et al.*[5] have synthesised a large number of these compounds, whilst Clark and Tsai[6] have studied the addition of $Me_3SnMn(CO)_5$ across perfluorinated olefinic double bonds; this molecule is also cleaved by halogens to give Me_3SnX and XMn-

$(CO)_5$, but C–Sn bond fission occurs with halogen acids[7]. Halogenation of the triphenyl analogue also results in C–Sn bond fission[7].

Little is known as yet about the reaction mechanisms of these cleavages. Nesmeyanov *et al.*[8] have investigated the protodemercuration of some mercury derivatives of ferrocene and cyclopentadienyl manganese tricarbonyl, the former acting as an electron donor and the latter as a weak electron acceptor in the protolysis reactions. More recently, McDonald and Basolo[9] have made a kinetic study of the now well established oxidative elimination of $M(CO)_4L_2$ derivatives (M = Mo, W; L_2 = 2-2'bipyridine and 1,10 phenanthroline) by mercuric salts, and have proposed the following reaction sequence.

$$M(CO)_4L_2 + 2HgX_2 \rightleftarrows M(CO)_4L_2 \cdot 2HgX_2 \qquad (1)$$

$$M(CO)_4L_2 \cdot 2HgX_2 \rightarrow M(CO)_3L_2(HgX)X + HgX_2 + CO \qquad (2)$$

Attempts to prepare the alkyl- and arylmercury derivatives of molybdenum have so far met with failure[10], indeed the only organomercury–transition metal complexes so far described are $RHgTa(CO)_6$[20], $(RHg)_2Fe(CO)_4$[21] and $C_6F_5HgFe(Cp)(CO)_2$. The transient existence of the latter has very recently been demonstrated[11];

$$feHgCl + C_6F_5Li \rightarrow feHgC_6F_5 + LiCl \qquad (3)$$

$$2feHgC_6F_5 \rightarrow fe_2Hg + (C_6F_5)_2Hg \qquad (4)$$

where:

$$fe = Fe(Cp)(CO)_2$$

The purpose of this paper is to report on the cleavage of some trimethyl- and triallyl-tin derivatives of molybdenum and tungsten by mercuric salts and iodine, and a subsequent study of cleavages by alkyl- and aryl-mercury salts, establishing the generality of eqns. (3) and (4) and synthesising some new alkyl- and arylmercury derivatives of these transition metals.

RESULTS AND DISCUSSION

The work described relates to compounds of the general formula $R_3SnMC_5H_5(CO)_3$. Four such compounds were synthesised:

$Me_3SnMoC_5H_5(CO)_3$ (I) $Me_3SnWC_5H_5(CO)_3$ (II)

$(CH_2{=}CHCH_2)_3SnMoC_5H_5(CO)_3$ (III) $(CH_2{=}CHCH_2)_3SnWC_5H_5(CO)_3$ (IV)

The investigation comprises a study of their reactivity with iodine, mercuric halides and organomercury chlorides.

Iodination reactions

The reactions of the trimethyltin compounds were accompanied by effervescence in the more polar solvents, and proceeded with dominant Sn–M bond fission (Table 1) in accordance with eqn. (5), no methyl iodide being produced.

$$Me_3SnM(Cp)(CO)_3 + I_2 \rightarrow Me_3SnI + IM(Cp)(CO)_3 \qquad (5)$$

TABLE 1

PROTON RESONANCES (δ IN PPM) OF PRODUCTS OF IODINATION OF $Me_3SnMo(Cp)(CO)_3$ (I) AND $Me_3SnW(Cp)(CO)_3$ (II) IN VARIOUS SOLVENTS

Solvent	*Compound*	*Me_3Sn–*	*Cp*	*Me_3SnI^a*	*MeI^a*
CCl_4	(I)	0.87	5.62	0.87	2.15
CCl_4	(II)	0.87	5.72		
Dioxane	(I)	0.86	5.73^b	0.86	2.14
Dioxane	(II)	0.86	5.84		
MeOH	$(I)^c$	0.80	^{d}	0.79	2.16
MeOH	$(II)^c$	0.79			
MeCN	$(I)^c$	0.88	5.72	0.87	2.20
MeCN	(II)	0.86	5.82		
DMSO	$(I)^c$	0.61	5.94	0.59	2.18
DMSO	(II)	0.60	6.07		

^{a} Calibrants. ^{b} *Cf.* value of 5.74 ppm for $IMo(Cp)(CO)_3$ in THF (Ref. 19). ^{c} Effervescence accompanied reaction. ^{d} Not measured.

The observed effervescence is probably due to the expulsion of CO from the product by the strong donor solvent molecules.

$$IM(Cp)(CO)_3 + nS \rightarrow IM(S)_n(Cp)(CO)_{3-n} + nCO \tag{6}$$

In a typical reaction using 0.1 *M* solutions in solvent DMSO, (II) and iodine yielded a solution whose NMR spectrum consisted of two sharp singlets (δ 6.06, 0.61 ppm) with relative intensities of 5/9. The upfield resonance showed tin satellites [$J(^{119}Sn\text{–}H)$ 69.0; $J(^{117}Sn\text{–}H)$ 66.2 Hz] which agreed well with values of 69.5 and 66.3 Hz for Me_3SnI (δ 0.59 ppm) in DMSO. This establishes the main features of eqn. (5), though the ultimate fate of $IM(Cp)(CO)_3$ is still uncertain. The corresponding cleavage of (IV) resulted in the production of three well defined singlets in the olefinic region superposed on a typical σ-bonded allylic spectrum ($ABCX_2$). The upfield singlet (5.83 ppm) decreased at the expense of the low field singlet (6.34 ppm), whilst the central resonance (6.04 ppm) remained virtually constant in intensity. The upfield signal finally disappeared, leaving the two remaining singlets in the ratio of 3 (6.04 ppm) to 2 (6.34 ppm). It seems likely that Sn–M bond fission is still dominant, but that other competing (Sn–C fission?) and subsequent reactions occur.

Reactions with mercuric salts

No effervescence was observed in these reactions, which, for the trimethyltin derivatives, again proceeded with dominant Sn–M bond cleavage.

$$Me_3SnM(Cp)(CO)_3 + HgX_2 \rightarrow Me_3SnX + XHgM(Cp)(CO)_3 \tag{6}$$

Presumably the product halomercurial does not lose CO in the manner described above.

A typical reaction solution using (II) and HgI_2 (0.1 *M* in solvent methanol) gave an NMR spectrum showing two singlet resonances at δ 6.03 and 0.68 ppm. The upfield signal had attendant tin satellites [$J(^{119}Sn\text{–}H)$ 67.0, $J(^{117}Sn\text{–}H)$ 64.2 Hz] which again corresponded well with values for Me_3SnI (66.3, 63.5 Hz) in this solvent, but was at variance with the chemical shift of Me_3SnI (δ 0.79 ppm). It has been established[12,13] that cleavage of tetraalkyltin compounds by mercuric salts proceeds as follows:

$$R_4Sn + HgX_2 \xrightarrow{\text{slow}} RHgX + R_3SnX \qquad (7)$$

$$R_3SnX + HgX_2 \overset{\text{rapid}}{\rightleftharpoons} R_3SnX \cdot HgX_2 \qquad (8)$$

and the trialkyltin halide formed exists as a 1/1 complex with HgX_2. The reaction solution of Me_4Sn and HgI_2 in MeOH gave an NMR spectrum comprising two singlets (0.69 ppm, $Me_3SnI \cdot HgI_2$; 0.06 ppm MeHgI). The tin–proton coupling constants of the complex were 66.6 and 63.7 Hz respectively. Reaction (6) therefore must be modified in terms of eqn. (7) and (8). The halomercurials formed by reaction (6) were isolated and characterised for both the molybdenum and tungsten derivatives (X = Cl, Br, I).

In the case of the triallyl derivatives however, Sn–C bond fission was observed;

$$(CH_2{=}CHCH_2)_3SnM(Cp)(CO)_3 + HgX_2 \rightarrow CH_2{=}CHCH_2HgX + (CH_2{=}CHCH_2)_2Sn(X)M(Cp)(CO)_3 \qquad (9)$$

and almost quantitative yields of the corresponding allylmercury halides were obtained. This was confirmed by NMR experiments. Cleavage of (IV) by HgI_2 in DMSO gave a reaction solution with an NMR spectrum showing a sharp singlet at 5.63 ppm superimposed on a typical allylmercury spectrum.

Reactions with organomercury halides

When solutions of (I) and MeHgCl in a polar solvent were mixed, a marked yellow colouration was produced. On standing, bright yellow crystals were slowly formed which were identified as $Hg[Mo(Cp)(CO)_3]_2$. The same product was obtained using allylmercury chloride and also with phenylmercury chloride, though the latter gave the above product much more slowly. This rather surprising result was investigated further by following changes in the NMR spectrum of the reaction solution. Immediately after mixing (I) and MeHgCl (0.1 M, acetone-d_6), the NMR spectrum was run at 40°. The original singlet resonances of the starting materials [(I) 5.47, 0.45 ppm; MeHgCl 1.02 ppm] were replaced by singlets at (a) 5.64, (b) 5.52, (c) 0.69, (d) 0.62, (e) 0.20 ppm. Peaks (a) and (e), initially of low intensity, increased with time at the expense of (b) and (c), (d) remaining relatively constant. After 24 h (b) and (c) had disappeared, leaving (a), (d) and (e) in the ratio of 5/9/3. (d) Possessed tin satellites [$J(^{119}Sn–H)$ 65.2, $J(^{117}Sn–H)$ 62.4 Hz] and corresponded in chemical shift to Me_3SnCl [δ 0.62 ppm, $J(^{119}Sn–H)$ 64.9, $J(^{117}Sn–H)$ 62.1 Hz]. (a) Corresponds very closely to the cyclopentadienyl resonances (5.63) in $Hg[Mo(Cp)(CO)_3]_2$. (e) Did not show tin satellites but had singlet satellites (J 104 Hz) which were not spinning side bands, and were typical of ^{119}Hg–CH coupling. This suggested that the upfield resonance was due to a methylmercury derivative. Since one of the products of this secondary reaction was $Hg[Mo(Cp)(CO)_3]_2$, it seems likely that the other product is Me_2Hg [$J(^{199}Hg–H)$ 101–104 Hz in various solvents][14]. Thus the following reaction sequence is indicated (*cf.* Ref. 11).

$$Me_3SnMo(Cp)(CO)_3 + MeHgCl \xrightarrow{\text{rapid}} MeHgMo(Cp)(CO)_3 + Me_3SnCl \quad (10)$$

$$2MeHgMo(Cp)(CO)_3 \xrightarrow{\text{slow}} Me_2Hg + Hg[Mo(Cp)(CO)_3]_2 \quad (11)$$

The above stoichiometry is in accordance with the observed proton ratios and was confirmed by the isolation of $MeHgMo(Cp)(CO)_3$ by rapidly quenching the reaction mixture in water. This product belongs to a new class of organomercury compounds. It was stable enough in acetone-d_6 for its NMR spectrum to be run and gave two singlets at 5.53 and 0.61 ppm, the latter showing ^{199}Hg–H satellites (J 132.1 Hz). The compound was much more stable in polar than nonpolar solvents such as CCl_4 in which very rapid decomposition occurred to give a dark green solution. On standing, reaction (11) occurred slowly in acetone-d_6. The latter reaction is a symmetrisation reaction[15] and is unusual in organomercury chemistry, since a strong complexing agent such as ammonia is required to drive equilibrium (12) to the right.

$$2RHgX \rightleftarrows R_2Hg + HgX_2 \quad (12)$$

Mays and Robb[10] have recently shown that K_{eq} for the equilibrium:

$$Hg[Mo(Cp)(CO)_3]_2 + HgX_2 \overset{K_{eq}}{\rightleftarrows} 2XHgMo(Cp)(CO)_3 \quad (13)$$

has a value of at least 10^3. $Hg[Mo(Cp)(CO)_3]_2$ has marked thermal stability which may act as the driving force for process (11).

The above reaction pattern was observed in solvent DMSO at 40°, though step (11) appeared slower (40% conversion at 40 min compared with 80% in acetone-d_6. PhHgCl is only slightly soluble in acetone, but soluble in DMSO, and its reaction with (I) could be followed by NMR in the latter solvent. No change in the aromatic multiplet was observed over a period of 24 h. The product obtained by rapidly quenching the reaction mixture in water showed aromatic (6.85–7.85 ppm) and cyclopentadienyl (5.63 ppm) proton resonances (relative intensities 5/5.2) which were exactly superposable on those of the original product solution. The ratio of aromatic, cyclopentadienyl, and trimethyltin protons for the latter solution was found to be 5/4.9/8.6. On this evidence, reaction (14) is very slow.

$$2PhHgMo(Cp)(CO)_3 \rightarrow Ph_2Hg + Hg[Mo(Cp)(CO)_3]_2 \quad (14)$$

Structure of allyl$_3$SnW(Cp)(CO)$_3$ (IV)

The ν(C=C) of (IV) appeared at 1620 cm^{-1} compared with 1625 cm^{-1} for tetraallyltin[16] which has an unperturbed olefinic double bond. It seems, therefore, that there is little if any olefin–tungsten interaction in the ground state of (IV).

EXPERIMENTAL

Purification of starting materials

All solvents were purified using standard procedures. Acetone-d_6 was supplied by Ryvan Chemicals Ltd., Iodine was resublimed prior to use. Mercuric salts were recrystallised from acetone/methanol mixtures.

Preparations

MeHgCl and Me_3SnCl were prepared from the reaction of Me_4Sn with $HgCl_2$ in abs. EtOH. Tetraallyltin was prepared in 62% yield by the method of Vijayaraghavan[18], and converted to triallyltin chloride in 90% yield by treatment with $SnCl_4$ (3/1 mole ratio) at room temperature[16]. $Me_3SnMo(Cp)(CO)_3$ was prepared in 52% yield by reacting NaC_5H_5 with $Mo(CO)_6$ under N_2 in dry, peroxide-free THF and treating the resultant solution with Me_3SnCl[5]. $Me_3SnW(Cp)(CO)_3$ was prepared in 61% yield in a similar fashion using dry peroxide-free diglyme[5].

(Triallylstannyl)-π-cyclopentadienyltungsten tricarbonyl (nc)

The method used was identical with that of the trimethyl analogue, using $allyl_3SnCl$ (3.7 g) in place of Me_3SnCl. The final filtrate was much darker and did not yield crystals on standing. The mixture was treated with hexane and chromatographed on alumina (Brockmann II), eluting with CH_2Cl_2. This yielded a golden brown oil which solidified at 0° to an orange-yellow waxy solid (3.5 g) m.p. 37–38°. (Found: C, 35.4; H, 3.59; O, 8.48. $C_{17}H_{20}O_3SnW$ calcd.: C, 35.6; H, 3.49; O, 8.37%.) The desired product was thus formed in 45% yield. The infrared spectrum of the product was run in CCl_4 (20 mg/10 ml) and showed strong ν(CO) peaks at 1993, 1921 and 1894 cm^{-1}, and ν(C=C) at 1620 cm^{-1}. The solution was not very stable and threw down a greenish precipitate on standing for 1 h at 20°.

The attempted preparation of the molybdenum analogue using the same general method resulted in a golden yellow oil which decomposed on distillation at 10^{-3} mm, and on standing. The elemental analysis was thus not meaningful. The NMR spectrum was very similar to that of the tungsten derivative showing a cyclopentadienyl resonance (5.37 ppm) superposed on a typical CH_2=$CHCH_2$–Sn spectrum with an olefinic to methylene proton ratio of 2.40/1 (2.33/1 being the correct value for the compound). This suggests that the freshly prepared product is reasonably pure $allyl_3SnMo(Cp)(CO)_3$ (nc). The infrared spectrum (CCl_4) showed ν(CO) at 1995, 1931, 1902 cm^{-1} with similar intensities to those of the tungsten derivative, and ν(C=C) at 1621 cm^{-1}.

Cleavage of $Me_3SnMo(Cp)(CO)_3$ by mercuric bromide

$HgBr_2$ (0.72 g; 2 mmole) was dissolved in dry MeOH (5 ml) and added to a solution of $Me_3SnMo(Cp)(CO)_3$ (0.40 g; 1 mmole) in dry MeOH (10 ml). A bright yellow precipitate appeared which was washed with cold MeOH and sucked dry (0.32 g). The product was recrystallised from hot abs. EtOH to give yellow plates m.p. 199–200°, which gave a strong positive Beilstein halogen test. (Found: C, 18.46; H, 1.05; O, 8.96. $C_8H_5O_3BrHgMo$ calcd.: C, 18.25; H, 0.95; O, 9.1%.) This identifies the product as $BrHgMo(Cp)(CO)_3$ (yield 62%). The corresponding cleavage of the tungsten derivative yielded 67% $BrHgW(Cp)(CO)_3$ m.p. 208–209° dec. (Found: C, 15.82; H, 0.85; O, 7.96. $C_8H_5O_3BrHgW$ calcd.: C, 15.7; H, 0.81; O, 7.83%.) Similar products, were obtained from cleavage by $HgCl_2$ and HgI_2.

On reacting $allyl_3SnW(Cp)(CO)_3$ with $HgBr_2$ in the same manner no precipitate was formed on mixing the solutions, but on standing at 0° overnight orange-yellow crystals appeared. These were filtered off and sucked dry (0.28 g) m.p. 122–123°. The product had an IR spectrum identical with that of an authentic specimen of allylmercuric bromide. (Yield 88%).

Synthesis of $Hg[Mo(Cp)(CO)_3]_2$ *and* $MeHgMo(Cp)(CO)_3$

MeHgCl (0.25 g, 1.0 mmole) in dry acetone (0.5 ml) was added to $Me_3SnMo(Cp)(CO)_3$ (0.41 g, 1.0 mmole) in the same solvent (0.5 ml). A deep yellow colour was produced. The mixture was kept at 0° overnight, whereupon yellow crystals appeared; these were filtered off and recrystallised from hot ethanol to give yellow plates (0.25 g) m.p. 204–205°. (Found: C, 27.79; H, 1.47; O, 14.04. $C_{16}H_{10}O_6HgMo_2$ calcd.: C, 27.80; H, 1.45; O, 13.9%.) The analysis and m.p. correspond very accurately to $Hg[Mo(Cp)(CO)_3]_2$. The NMR spectrum of the product showed one singlet only at 5.63 ppm. Yield based on eqns. (10) and (11) is 72%. $Hg[W(Cp)(CO)_3]_2$ m.p. 190 dec. was formed when $Me_3SnW(Cp)(CO)_3$ was similarly reacted. (Found: C, 21.96; H, 1.15; O, 11.13. $C_{16}H_{10}O_6HgW_2$ calcd.: C, 22.2; H, 1.15; O, 11.1%.) The same two products were formed irrespective of the organomercurial used.

In a similar experiment using $Me_3SnMo(Cp)(CO)_3$ and MeHgCl, the mixture was shaken for 1 min, then poured into ice-water (50 ml) whereupon a pale yellow precipitate formed. This was filtered off and sucked dry m.p. 91–92°, 0.34 g. In view of the symmetrisation reaction described above, no attempt was made at recrystallisation. The NMR of the product in acetone-d_6 consisted of two singlets at 5.53 and 0.61 ppm in the ratio 5/2.97. The upfield signal showed ^{199}Hg–H satellites (J 132.1 Hz) This data is fully in accord with the structure $MeHgMo(Cp)(CO)_3$ (nc). (Found*: C, 25.0; H, 1.79; O, 11.1. $C_9H_8O_3HgMo$ calcd.: C, 23.5; H, 1.74; O, 10.43%.) The yield of product was 74%.

The tungsten analogue (nc) was also prepared in 65% yield. M.p. 95–98° dec., with δ(Cp) 5.62, δ(Me) 0.53 ppm, $J(^{199}Hg\text{–}H)$ 127 Hz. (Found*: C, 21.17; H, 1.46; O, 8.71. $C_9H_8O_3HgW$ calcd.: C, 19.7; H, 1.46; O, 8.75%.)

$PhHgMo(Cp)(CO)_3$ (nc) (83%) was prepared using DMSO as the solvent. M.p. 110° dec. (Found: C, 32.1; H, 2.01; O, 9.16. $C_{14}H_{10}O_3HgMo$ calcd.: C, 32.1; H, 1.91; O, 9.18%.) Attempts to prepare the allylic derivatives gave $Hg[MCp(CO)_3]_2$ in almost quantitative yield, indicating that symmetrisation was rapid.

Spectra

NMR spectra were run on a Varian A60A spectrometer with the probe thermostatted at 40°. Tetramethylsilane (TMS) was normally used as an internal reference and chemical shifts (δ) quoted in parts per million (ppm) relative to TMS with standard deviation ±0.01 ppm. Routine infrared spectra were run on a Perkin–Elmer SP200 but solution spectra were obtained using a Hilger–Watts Infrascan instrument.

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