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THE SYNTHESIS OF ORGANOTIN–TRANSITION METAL CARBONYL COMPLEXES FROM TRIS(TRIMETHYLSTANNYL)AMINE AND HEXAMETHYLDISTANNOXANE

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SUMMARY

Trimethyltin derivatives of metal carbonyls containing Sn–Mn, Sn–Mo, Sn–Fe, Sn–Co and Sn–Ni bonds have been obtained by the action of metal–metal bonded dimeric metal carbonyls with tris(trimethylstannyl)amine or hexamethyldistannoxane.

INTRODUCTION

The synthesis of organotin–metal carbonyls has been achieved by a wide variety of methods[1–3]. In addition to the well established anion method, exemplified[4] by eqn. (1) below, there have been reported various metatheses involving the evolution of gaseous by-products, as illustrated[5] by eqn. (2), the proportionation type of reaction[6], as in eqn. (3), and the oxidative addition, as typified[7] by eqn. (4).

$$\text{n-Bu}_3\text{SnCl} + \text{Co(CO)}_4^- \rightarrow \text{n-Bu}_3\text{SnCo(CO)}_4 + \text{Cl}^- \quad (1)$$

$$\text{Me}_3\text{SnNMe}_2 + (\pi\text{-C}_5\text{H}_5)\text{W(CO)}_3\text{H} \rightarrow \text{Me}_3\text{SnW(CO)}_3(\pi\text{-C}_5\text{H}_5) + \text{Me}_2\text{NH} \quad (2)$$

$$\text{Me}_3\text{SnSnMe}_3 + \text{Mn}_2\text{(CO)}_{10} \rightarrow 2\text{Me}_3\text{SnMn(CO)}_5 \quad (3)$$

$$3\text{Me}_3\text{SnH} + \text{Os}_3\text{(CO)}_{12} \rightarrow 3\text{Me}_3\text{SnOs(CO)}_4\text{H} \quad (4)$$

As part of a general investigation of the reactions of organometallic bases[8–10] with metal carbonyls we have been somewhat surprised to find tris(trimethylstannyl)amine and hexamethyldistannoxane to be excellent reagents for the transference of trimethyltin groups to form tin–metal bonds in a range of metal carbonyl complexes. Both tris(trimethylstannyl)amine and hexamethyldistannoxane are readily prepared in high yield, and are thus convenient precursors.

RESULTS AND DISCUSSION

Bis(π-cyclopentadienylmolybdenum tricarbonyl), bis(π-cyclopentadienyliron dicarbonyl), bis(π-cyclopentadienylnickel carbonyl), dimanganese decacarbonyl and dicobalt octacarbonyl all undergo reaction with both hexamethyldistannoxane and tris(trimethylstannyl)amine to form the various organotin–metal carbonyls as outlined below.

TABLE 1

REACTIONS OF HEXAMETHYLDISTANNOXANE AND TRIS(TRIMETHYLSTANNYL)AMINE

Reagents	*Solvent (ml); temp. °C reaction time*	*Purification procedure*
$[(\pi\text{-}C_5H_5)Mo(CO)_3]_2 + (Me_3Sn)_2O$ $[(\pi\text{-}C_5H_5)Mo(CO)_3]_2 + (Me_3Sn)_3N$	Xylene, (15), 140, 2 h	Sublimation (20°/0.01 mmHg Probe −78°
$[(\pi\text{-}C_5H_5)Fe(CO)_2]_2 + (Me_3Sn)_2O$ $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2 + (Me_3Sn)_3N$	Xylene (15), 140, 15 h	Molecular distillation (70°/0.005 mmHg
$[(\pi\text{-}C_5H_5)NiCO]_2 + (Me_3Sn)_2O$ $[(\pi\text{-}C_5H_5)NiCO]_2 + (Me_3Sn)_3N$	Hexane (15), 70, 48 h	Distillation (60°/0.01 mmHg)
$Mn_2(CO)_{10} + (Me_3Sn)_2O$ $Mn_2(CO)_{10} + (Me_3Sn)_3N$	Dioxane (15), 100, 12 h	Sublimation (0°/0.01 mmHg) Probe −78°
$Co_2(CO)_8 + (Me_3Sn)_2O$ $Co_2(CO)_8 + (Me_3Sn)_3N$	Diethylether, (20), 20, 15 min	Sublimation (0°/0.01 mmHg) Probe −78°

[a] Cyclohexane solutions in 0.1 mm CaF_2 cells. [b] Carbon tetrachloride solutions with benzene as intern compound for analysis without decomposition. We believe the final distilled sample, however, to be bette slowly upon storage.

$$(Me_3Sn)_2O + [(\pi\text{-}C_5H_5)Mo(CO)_3]_2 \rightarrow 2Me_3SnMo(CO)_3(\pi\text{-}C_5H_5) + (O_2\,?) \quad (5)$$

$$2(Me_3Sn)_3N + 3[(\pi\text{-}C_5H_5)Mo(CO)_3]_2 \rightarrow 6Me_3SnMo(CO)_3(\pi\text{-}C_5H_5) + (N_2\,?) \quad (6)$$

$$(Me_3Sn)_2O + [(\pi\text{-}C_5H_5)Fe(CO)_2]_2 \rightarrow 2Me_3SnFe(CO)_2(\pi\text{-}C_5H_5) + (O_2\,?) \quad (7)$$

$$2(Me_3Sn)_3N + 3[(\pi\text{-}C_5H_5)Fe(CO)_2]_2 \rightarrow 6Me_3SnFe(CO)_2(\pi\text{-}C_5H_5) + (N_2\,?) \quad (8)$$

$$(Me_3Sn)_2O + [(\pi\text{-}C_5H_5)NiCO]_2 \rightarrow 2Me_3SnNi(CO)(\pi\text{-}C_5H_5) + (O_2\,?) \quad (9)$$

$$2(Me_3Sn)_3N + 3[(\pi\text{-}C_5H_5)NiCO]_2 \rightarrow 6Me_3SnNi(CO)(\pi\text{-}C_5H_5) + (N_2\,?) \quad (10)$$

$$(Me_3Sn)_2O + Mn_2(CO)_{10} \rightarrow 2Me_3SnMn(CO)_5 + (O_2?) \quad (11)$$

$$2(Me_3Sn)_3N + 3Mn_2(CO)_{10} \rightarrow 6Me_3SnMn(CO)_5 + (N_2\,?) \quad (12)$$

$$(Me_3Sn)_2O + Co_2(CO)_8 \rightarrow 2Me_3SnCo(CO)_4 + (O_2\,?) \quad (13)$$

$$2(Me_3Sn)_3N + 3Co_2(CO)_8 \rightarrow 6Me_3SnCo(CO)_4 + (N_2?) \quad (14)$$

The organometallic products are characterized in Table 1, but we have been unable to fully ascertain the fate of the nitrogen and oxygen by-products. It was not possible to prove that any molecular nitrogen or oxygen present came from the reaction, and we failed to detect by mass spectrometry any products such as ammonia, or

WITH VARIOUS METAL CARBONYL COMPLEXES.

Product	M.p. (°C) or b.p. (°C/mmHg)	Yield %	Analysis found (calcd.) (%) C	H	CO stretching[a] frequencies (cm^{-1})	τ^b values in NMR
$(\pi\text{-}C_5H_5)(CO)_3MoSnMe_3$	98	63	32.6	3.70	1903(10)	9.57(Me)
			(32.3)	(3.50)	1926(6)	
	99	70	32.5	3.80	2000(9)	4.58(C_5H_5)
$(\pi\text{-}C_5H_5)(CO)_2FeSnMe_3$		45	35.5	4.4	1943(10)	9.55(Me)
			(35.2)	(4.1)		
		50	35.6	4.4	1992(8)	5.10(C_5H_5)
$(\pi\text{-}C_5H_5)(CO)NiSnMe_3$	60/0.01	30		[c]	1994	
	60/0.01	30		[c]		
$CO)_5MnSnMe_3$	26–28	40	26.4	2.70	1953(1)	
			(26.8)	(2.53)	1988(10) 1995(9)	9.55(Me)
	25–27	42	26.5	2.70	2086(3)	
$CO)_4CoSnMe_3$		84		[d]	1986(10)	
			(25.1)	(2.70)	2016(4.5)	9.37(Me)
	72–74	75	24.4	2.68	2080(5)	

reference. [c] $(\pi\text{-}C_5H_5)(CO)NiSnMe_3$ is a very unstable compound, and we were unable to transport the than 97% pure. [d] Although spectroscopically pure when isolated, this particular sample decomposed

organic nitrogen or oxygen compounds that may have been formed by the evolved by-products reacting with the solvent.

The conditions for these reactions were quite varied, and appeared to depend largely upon the ease of fission of the metal–metal bond of the metal carbonyl. Tris-(trimethylstannyl)amine and dicobalt octacarbonyl underwent reaction [eqn. (14)] at 20° in ether and after fifteen minutes a 75% yield of (trimethylstannyl)cobalt tetracarbonyl was obtained. During the reaction gas evolution was observed and the mixture became quite warm. We believe that the gas evolved was nitrogen, and in this case the organotin–metal carbonyl product was formed in a state of very high purity. On using hexamethyldistannoxane [eqn. (13)], the reaction proceeded just as easily, and in even slightly higher yield; but here a very slightly brown coloured product was always obtained, suggesting slight oxidation, possibly by the oxygen evolved.

Many different solvents and conditions were tried for the reactions [eqn. (5)–(14)], and those reported in Table 1 represent the optimum conditions we have found for maximum yields of the organotin metal carbonyls.

EXPERIMENTAL

All reactions were performed under an atmosphere of dry nitrogen. Solvents were dried by distillation off lithium aluminium hydride in an atmosphere of dry nitrogen. Infrared spectra were recorded in cyclohexane on a Perkin–Elmer 257 spectrophotometer; and numerals in parentheses after the frequencies in Table 1 refer to the relative intensity of the mode with reference to the strongest mode which is assigned[10]. ^1H NMR spectra were recorded on a Varian T60 spectrometer.

Tris(trimethylstannyl)amine was prepared by the literature[11] method, and hexamethyldistannoxane was prepared in very good yield by the calcium hydride dehydration of trimethyltin hydroxide in tetrahydrofuran under reflux.

The general reaction method for a few examples is given below, and specific conditions for each reaction will be found in Table 1. All reactions were performed on an approximately 0.05 molar scale with respect to each carbonyl, and reagents were used in the stoichiometries indicated by eqns. (5)–(14).

Interaction of tris(trimethylstannyl)amine and dimanganese decacarbonyl [eqn. (12)]

The carbonyl (1.80 g) and stannylamine (1.67 g) were heated under reflux in dioxane (15 ml) for 12 h. The solvent was removed at reduced pressure (25°/15 mmHg) and sublimation (0°/0.01 mmHg) afforded (trimethylstannyl)manganese pentacarbonyl (1.50 g, 42%) as white crystals. (See Table 1).

Interaction of hexamethyldistannoxane and bis(π-cyclopentadienyliron dicarbonyl) [eqn. (7)]

The carbonyl (1.77 g) and stannoxane (1.73 g) were heated in xylene (15 ml) at 140° for 15 h. Xylene was removed at 30°/0.01 mmHg. The residue was taken up in hexane (5 ml) and transferred to a small molecular still type of apparatus. The hexane was removed (20°/0.1 mmHg) and the crude product distilled at 70° under pressure 0.01 mmHg to yield the pure yellow/brown oil (1.55 g, 50%). (See Table 1).

Interaction of tris(trimethylstannyl)amine and dicobalt octacarbonyl [eqn. (14)]

The stannylamine (1.67 g) in ether (5 ml) was added dropwise to dicobalt octacarbonyl (1.70 g) in ether (20 ml) and stirred at 20° for 15 min. Slight warming was noted, and a gas, presumed to be nitrogen was evolved. After removal of solvent (20°/15 mmHg) the residue was sublimed (0°/0.01 mmHg) on a probe maintained at −78° to give a very pure white crystalline product (2.50 g, 75%). (See Table 1).

CONCLUSION

The use of hexamethyldistannoxane and tris(trimethylstannyl)amine gives an interesting new synthetic approach to organotin–metal carbonyl complexes, but the fate of the by-products oxygen and nitrogen cannot be ascertained with confidence.

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