

THE SYNTHESIS OF SILYL-, DISILYL- AND SILYLMETHYL-SUBSTITUTED π -CYCLOPENTADIENYL METAL CARBONYLS VIA ORGANOTIN INTERMEDIATES

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SUMMARY

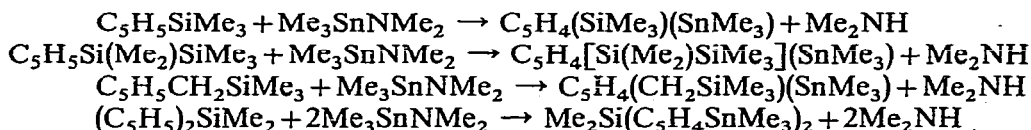
Interaction of (trimethylstannyl)(trimethylsilyl)cyclopentadiene with the appropriate metal carbonyl halides has afforded $(\text{Me}_3\text{Si}-\pi\text{-C}_5\text{H}_4)\text{Mn}(\text{CO})_3$, $(\text{Me}_3\text{Si}-\pi\text{-C}_5\text{H}_4)\text{Re}(\text{CO})_3$ and $(\text{Me}_3\text{Si}-\pi\text{-C}_5\text{H}_4)\text{Rh}(\text{CO})_2$ by elimination of the organotin halide. By similar metatheses the following silyl-substituted π -cyclopentadienyl metal carbonyls have been synthesised: $(\text{Me}_5\text{Si}_2-\pi\text{-C}_5\text{H}_4)\text{Mn}(\text{CO})_3$, $(\text{Me}_5\text{Si}_2-\pi\text{-C}_5\text{H}_4)\text{Re}(\text{CO})_3$, $(\text{Me}_3\text{SiCH}_2-\pi\text{-C}_5\text{H}_4)\text{Mn}(\text{CO})_3$, $(\text{Me}_3\text{SiCH}_2-\pi\text{-C}_5\text{H}_4)\text{Re}(\text{CO})_3$, $(\text{Me}_3\text{SiCH}_2-\pi\text{-C}_5\text{H}_4)\text{Co}(\text{CO})_2$, $\text{Me}_2\text{Si}[\pi\text{-C}_5\text{H}_4\text{Mn}(\text{CO})_3]_2$, $\text{Me}_2\text{Si}[\pi\text{-C}_5\text{H}_4\text{Re}(\text{CO})_3]_2$, $[(\text{Me}_3\text{Si})_2-\pi\text{-C}_5\text{H}_3]\text{Mn}(\text{CO})_3$ and $[(\text{Me}_3\text{Si})_2-\pi\text{-C}_5\text{H}_3]\text{Re}(\text{CO})_3$.

INTRODUCTION

In some cases the interaction of metal carbonyls and (trimethylsilyl)cyclopentadiene yield the (trimethylsilyl)- π -cyclopentadienyl metal carbonyls directly^{1,2}. The action of organotin allyls and cyclopentadienyls with metal carbonyl halides has, however, proved a very general method for the formation of π -allyl and π -cyclopentadienyl metal carbonyls. Such fissions have been extended herein to enable synthesis of a wide range of silyl-, disilyl- and silylmethyl-substituted cyclopentadienyl metal carbonyls.

RESULTS AND DISCUSSION

The synthetic intermediates (trimethylsilyl)(trimethylstannyl)cyclopentadiene, (pentamethyldisilyl)(trimethylstannyl)cyclopentadiene and bis[(trimethylstannyl)-cyclopentadienyl]dimethylsilane were prepared by the amine displacement method³, as outlined below.



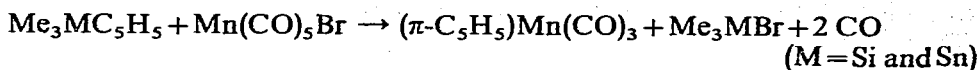
Both (trimethylsilyl)⁴- and (trimethylstannyl)⁵-cyclopentadiene are known to

TABLE I
 REACTIONS OF (TRIMETHYLSTANNYL)CYCLOPENTADIENYL COMPOUNDS WITH METAL CARBONYL HALIDES AND COBALT CARBONYL

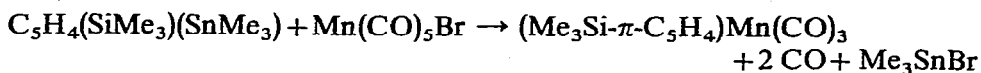
Reactants	Conditions	Product	Yield %	M.p. (°C)	Analysis		Found	
					Calcd. C	H	C	H
(Me ₃ Si)(Me ₃ Sn)C ₅ H ₄ + Mn(CO) ₅ Br	67°/2 h	(Me ₃ Si-π-C ₅ H ₄)Mn(CO) ₃	80	liq.	47.8	4.7	47.5	4.8
(Me ₃ Si)(Me ₃ Sn)C ₅ H ₄ + Re(CO) ₅ Br	67°/5 h	(Me ₃ Si-π-C ₅ H ₄)Re(CO) ₃	97	59°	32.3	3.2	32.6	3.2
(Me ₃ Si) ₂ (Me ₃ Sn)C ₅ H ₄ + Mn(CO) ₅ Br	67°/3 h	(Me ₃ Si) ₂ -π-C ₅ H ₄]Mn(CO) ₃	37	31.5°	46.7	5.7	46.8	5.9
(Me ₃ Si) ₂ (Me ₃ Sn)C ₅ H ₄ + Re(CO) ₅ Br	67°/4 h	(Me ₃ Si) ₂ -π-C ₅ H ₄]Re(CO) ₃ ^a	67	49°	33.6	4.1	33.6	4.1
(Me ₃ SiCH ₂)(Me ₃ Sn)C ₅ H ₄ + Mn(CO) ₅ Br	67°/2 h	(Me ₃ SiCH ₂ -π-C ₅ H ₄)Mn(CO) ₃ ^b	68	65-67°	49.7	5.2	49.3	5.3
(Me ₃ SiCH ₂)(Me ₃ Sn)C ₅ H ₄ + Re(CO) ₅ Br	67°/6 h	(Me ₃ SiCH ₂ -π-C ₅ H ₄)Re(CO) ₃	71	90-95°	34.2	3.6	34.5	3.9
(Me ₃ SiCH ₂)(Me ₃ Sn)C ₅ H ₄ + Co ₂ (CO) ₈	28°/1 h	(Me ₃ SiCH ₂ -π-C ₅ H ₄)Co(CO) ₂	61	liq.	49.6	5.6	50.0	5.7
(Me ₃ SnC ₅ H ₄) ₂ SiMe ₂ + Mn(CO) ₅ Br	67°/8 h	Me ₂ Si[π-C ₅ H ₄]Mn(CO) ₃ ₂	21	61-63°	46.6	3.2	46.9	3.1
(Me ₃ SnC ₅ H ₄) ₂ SiMe ₂ + Re(CO) ₅ Br	67°/12 h	Me ₂ Si[π-C ₅ H ₄]Re(CO) ₃ ₂	24	120-123°	29.7	1.9	29.3	1.8
(Me ₃ SnC ₅ H ₄) ₂ SiMe ₂ + Co ₂ (CO) ₈	35°/1 h	Me ₂ Si[π-C ₅ H ₄]Co(CO) ₂ ₂	31	liq.	46.1	3.4	45.8	3.3
(Me ₃ Si) ₂ (Me ₃ Sn)C ₅ H ₄ + Mn(CO) ₅ Br	67°/2 h	[(Me ₃ Si) ₂ -π-C ₅ H ₄]Mn(CO) ₃ ^c	42	82-84°	48.4	6.0	48.5	6.0
(Me ₃ Si) ₂ (Me ₃ Sn)C ₅ H ₄ + Re(CO) ₅ Br	67°/5 h	[(Me ₃ Si) ₂ -π-C ₅ H ₄]Re(CO) ₃	42	119°	35.2	4.4	34.6	4.4
(Me ₃ Si)(Me ₃ Sn)C ₅ H ₄ + [Rh(CO) ₂ Cl] ₂	28°/1 h	(Me ₃ Si-π-C ₅ H ₄)Rh(CO) ₂	85	liq.	40.5	4.4	41.0	4.6

^a Calcd. for Re, 40.0%; found, 40.3%. ^b Calcd. for Mn, 19.0%; found, 19.2%. ^c Calcd. for Mn, 15.8%; found, 16.1%.

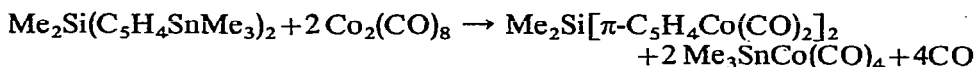
undergo reaction with manganese pentacarbonyl bromide by the following reaction.



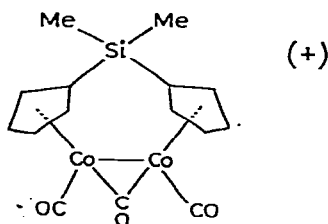
We find, however, that with both organosilicon and organotin substituents upon the cyclopentadienyl ring, exclusive cleavage of the organotin group occurs. Thus for example, (trimethylsilyl)(trimethylstannyl)cyclopentadiene and manganese pentacarbonyl bromide yield [(trimethylsilyl)- π -cyclopentadienyl]manganese tricarbonyl, with no trace of the organotin analogue.



Similar reactions with different metal carbonyl halides and various organotin cyclopentadienyls are detailed in Table 1. In the case of cobalt, the non-availability of cobalt carbonyl halides is not an obstacle for this synthetic method, as cobalt octacarbonyl itself causes the fission of the tin-cyclopentadienyl bond⁶, with the formation of the organotin-cobalt tetracarbonyl as a by product, as exemplified below:



All of the compounds reported in Table 1 exhibit a parent ion in the mass spectrum with the exception of $\text{Me}_2\text{Si}[\pi\text{-C}_5\text{H}_4\text{Co}(\text{CO})_2]_2$ which shows its highest peak in the mass spectrum at $(\text{P}-\text{CO})^+$, for which ion, the structure below is proposed.



The proton magnetic resonance spectra of these compounds have one particular feature of interest. In the (trimethylsilyl)- and even the bis(trimethylsilyl)cyclopentadienyl metal carbonyls of manganese and rhenium the ring protons are a sharp singlet and no splitting takes place upon cooling. Nevertheless, when pentamethyl-disilyl and (trimethylsilyl)methyl substituents are present on the cyclopentadienyl ring of these substituted π -cyclopentadienyl metal carbonyls the protons appear as the expected pair of triplets.

EXPERIMENTAL

Solvents used in these reactions were purified by distillation of lithium aluminium hydride immediately before use. (Dimethylamino)trimethyltin⁷, cyclopentadienyltrimethylsilane^{8,9}, (pentamethyldisilyl)cyclopentadiene¹⁰, [(trimethylsilyl)methyl]cyclopentadiene¹¹ and bis(cyclopentadienyl)dimethylsilane⁹ were prepared by published procedures.

TABLE 2

PROTON MAGNETIC RESONANCE AND CARBONYL INFRARED SPECTRA OF SILYL-SUBSTITUTED π -CYCLOPENTADIENYL METAL CARBOXYLS

Compound	τ Me ₃ Si	τ Me ₂ Si	τ CH ₂	τ^a C ₃ H ₄ or C ₅ H ₃	$\nu(\text{CO})^b$ (cm ⁻¹)
(Me ₃ Si- π -C ₅ H ₄)Mn(CO) ₃	9.82			5.34 (s)	2024[8], 1943[10]
(Me ₃ Si- π -C ₅ H ₄)Re(CO) ₃	9.85			4.78 (s)	2027[7], 1937[10]
(Me ₃ Si ₂ - π -C ₅ H ₄)Mn(CO) ₃	9.83	9.66		5.21 (t), 5.27 (t)	2022[9], 1941[10]
(Me ₃ Si ₂ - π -C ₅ H ₄)Re(CO) ₃	9.83	9.72		4.61 (t), 4.74 (t)	2029[7], 1938[10]
(Me ₃ SiCH ₂ - π -C ₅ H ₄)Mn(CO) ₃	10.03		8.45	5.59 (t), 5.80 (t)	2022[8], 1939[10]
(Me ₃ SiCH ₂ - π -C ₅ H ₄)Re(CO) ₃	9.98		8.28	5.06 (t), 5.20 (t)	2026[7], 1935[10]
(Me ₃ SiCH ₂ - π -C ₅ H ₄)Co(CO) ₂	10.00		8.40	5.20 (t), 5.30 (t)	2023[9], 1963[10]
Me ₂ Si[π -C ₅ H ₄ Mn(CO) ₃] ₂		9.49		5.18 (s)	2028[7.5], 1948[10] (br) ^f
Me ₂ Si[π -C ₅ H ₄ Re(CO) ₃] ₂		9.62		4.73 (s)	2031[7], 1944[10] (br) ^d
Me ₂ Si[π -C ₅ H ₄ Co(CO) ₂] ₂		9.62		4.88 (t), 5.20 (t)	2031[8], 2026[9], 1970[10]
[(Me ₃ Si) ₂ - π -C ₅ H ₃]Mn(CO) ₃	9.82			5.31 (s)	2023[7], 1942[10]
[(Me ₃ Si) ₂ - π -C ₅ H ₃]Re(CO) ₃	9.81			4.76 (s)	2027[7], 1936[10]
(Me ₃ Si- π -C ₅ H ₄)Rh(CO) ₂	9.84			4.55 (t), 4.78 (t)	2044[10], 1982[9]

^a (s) = sharp singlet, (t) = triplet. ^b In cyclohexane solution; relative intensities in brackets; br = broad. ^c Shoulder at 2030 cm⁻¹. ^d Shoulder at 2033 cm⁻¹.

(Trimethylsilyl)(trimethylstannyl)cyclopentadiene

To cyclopentadienyltrimethylsilane (13.8 g, 1 mol.) was added dropwise over 2 h (dimethylamino)trimethyltin (20.8 g, 1 mol.). After the vigorous evolution of dimethylamine, stirring was continued for 6 h followed by distillation to yield the product (18.1 g, 60%), b.p. 45°/0.02 mm. (Found C, 44.2; H, 7.3; Si, 9.2. C₁₁H₂₂SiSn calcd.: C, 43.8; H, 7.3; Si, 9.3%.) The proton magnetic resonance spectrum of the pure compound shows, at room temperature, a complex doublet at τ 4.0 ppm (ring protons), and a sharp singlet at 10.0 ppm (Me₃Si and Me₃Sn protons). The intensities of the C₅H₄ resonance and the Me₃Si + Me₃Sn resonance were in the expected relative intensity ratio of 2/9.

(Pentamethyldisilyl)(trimethylstannyl)cyclopentadiene

To (pentamethyldisilyl)cyclopentadiene (4.9 g, 1 mol.) was added (dimethylamino)trimethyltin (5.2 g, 1 mol.) over 2 h. After a further 2 h stirring, distillation yielded the product (5.2 g, 58%), b.p. 90°/0.1 mm. (Found C, 44.4; H, 8.0. C₁₃H₂₇Si₂Sn Calcd.: C, 43.5; H, 7.8%.)

[(Trimethylsilyl)methyl](trimethylstannyl)cyclopentadiene

To [(trimethylsilyl)methyl]cyclopentadiene (3.80 g, 1 mol.) was added (dimethylamino)trimethyltin (5.20 g, 1 mol.) over 2 h. The mixture was then maintained at 70° for a further 2 h, then distilled to yield pure product (2.0 g, 26%), b.p. 72°/0.2 mm.

Bis[(trimethylstannyl)cyclopentadienyl]dimethylsilane.

To dicyclopentadienyldimethylsilane (18.8 g, 1 mol.) was added (dimethylamino)trimethyltin (41.6 g, 2 mol.) over 3h. This product proved to be too involatile to distil without decomposition. Thus after removal of dimethylamine and other volatiles at 80°/0.1 mm. the reagent was used without further purification.

Bis(trimethylsilyl)cyclopentadiene

To lithium (trimethylsilyl)cyclopentadienide (1 mole) [prepared from *n*-butyllithium and (trimethylsilyl)cyclopentadiene] in tetrahydrofuran (750 ml) was added dropwise trimethylchlorosilane (108.5 g, 1 mole) with stirring over 6 h. Throughout the reaction the temperature was maintained at 0°, and after addition was completed, the mixture was warmed to room temperature, and stirred for 1 h. The mixture was then poured into ice-water (3 litres), and the organic layer extracted with ether (150 ml) twice. The ethereal layer was washed with water, and after drying (MgSO₄) ether and tetrahydrofuran were removed (20°/15 mm.). Distillation of the residual oil yielded the product (107 g, 51%), b.p. 44.5°/0.2 mm. (Found: C, 62.8; H, 10.7; Si, 26.4; mol. wt., 216. C₁₁H₂₂Si₂ calcd.: C, 62.9; H, 10.5; Si, 26.7%; mol. wt., 210.)

Bis(trimethylsilyl)(trimethylstannyl)cyclopentadiene

To bis(trimethylsilyl)cyclopentadiene (10.5 g, 1 mol.) was added (dimethylamino)trimethyltin (10.4 g, 1 mol.), and the mixture was heated at 70°/3 h to remove dimethylamine. The product could not be distilled without some decomposition, and was used as a reagent without further purification.

The interaction of the organosilicon and organotin substituted cyclopentadienes are recorded in Table 1. Details of the reaction methods are reported briefly below.

[(Trimethylsilyl)cyclopentadienyl]manganese and -rhenium tricarbonyls

(Trimethylsilyl)(trimethylstannyl)cyclopentadiene (1 mol.) and the pentacarbonyl halide (1 mol.) were heated under reflux in tetrahydrofuran. The trimethyltin halide by-product was removed by water-washing, and the product taken up in ether. After several washings of the ethereal layer, and subsequent drying (MgSO₄), the ether was removed in a stream of nitrogen, and the residue was sublimed onto a -80° probe to afford the product.

[(Pentamethyldisilyl)cyclopentadienyl]manganese and -rhenium tricarbonyls

These reactions were carried out in a manner analogous to those immediately above. The rhenium compound appears indefinitely stable in air, whereas the manganese compound darkens appreciably in the air after several days.

Bis(cyclopentadienyltricarbonylmanganese)dimethylsilane and bis(cyclopentadienyltricarbonylrhenium)dimethylsilane

Bis[(trimethylstannyl)cyclopentadienyl]dimethylsilane (1 mol.) and the metal pentacarbonyl halide (2 mol.) were heated under reflux in tetrahydrofuran. Monitoring of the reaction by infrared spectra showed the formation of the metal decacarbonyls and trimethyltin metal pentacarbonyls as minority products. After completion of the reaction, trimethyltin halide was removed by water-washing, and the metal decacarbonyl and trimethyltin metal pentacarbonyl were removed at 50°/0.1 mm. The remaining residue was chromatographed on silica in pentane. The eluted products were viscous oils upon removal of solvent, but were recrystallized from methylcyclohexane, followed by vacuum sublimation to yield crystals.

[(Trimethylsilylmethyl)cyclopentadienyl]manganese and -rhenium tricarbonyls

(Trimethylsilylmethyl)(trimethylstannyl)cyclopentadiene (1 mol.) and the

metal pentacarbonyl halide (1 mol.) were heated under reflux in tetrahydrofuran. Solvent was removed at 20°/10 mm, and trimethyltin halide was removed by water-washing. Subsequent recrystallization of the residue from hexane, and vacuum sublimation yielded the pure products.

Bis[(trimethylsilyl)cyclopentadienyl]manganese and -rhenium tricarbonyls

Bis(trimethylsilyl)(trimethylstannyl)cyclopentadiene (1 mol.) and the metal pentacarbonyl halide (1 mol.) were heated under reflux in tetrahydrofuran. After solvent removal and water washing to remove trimethyltin halide, the residue was chromatographed on silica in hexane to yield the pure product.

[(Trimethylsilyl)cyclopentadienyl]rhodium dicarbonyl

To a solution of rhodium dicarbonyl chloride (0.389 g, 1 mol.) in dry ether (15 ml) was added (trimethylsilyl)(trimethylstannyl)cyclopentadiene (0.602 g, 2 mol.). The mixture immediately turned blood red, and was allowed to stand 1 h. After water-washing to remove trimethyltin chloride, the ether layer was dried (MgSO₄) and solvent removed to leave the crude product, as a red oil. This was purified by distillation in a molecular still-type apparatus, to yield the somewhat air-sensitive liquid product (0.506 g, 85%).

[(Trimethylsilylmethyl)cyclopentadienyl]cobalt dicarbonyl

(Trimethylsilylmethyl)(trimethylstannyl)cyclopentadiene (1 mol.) and dicobalt octacarbonyl (1 mol.) were stirred in ether 20°/1 h. Solvent was removed in a stream of nitrogen, and subsequent chromatography on florasil in pentane afforded trimethyltin cobalt tetracarbonyl, and [(trimethylsilylmethyl)cyclopentadienyl]cobalt dicarbonyl (61%).

Bis(cyclopentadienyldicarbonylcobalt)dimethylsilane

Bis[(trimethylstannyl)cyclopentadienyl] dimethylsilane (1 mol.) and cobalt octacarbonyl (2 mol.) in ether were stirred at 35°/1 h. Solvent was then removed in a stream of nitrogen, and the residue chromatographed on florasil in pentane to yield trimethyltin cobalt tetracarbonyl and the product, which was further sublimed in a molecular still type apparatus to afford pure bis(cyclopentadienyldicarbonylcobalt)-dimethylsilane (31%), as a red oily liquid.

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