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ORGANOMETALLIC COMPOUNDS

LXIX *. SYNTHESIS AND PROPERTIES OF THE FIRST CHIRAL TRIORGANOSTANNYL-MANGANESE COMPLEX

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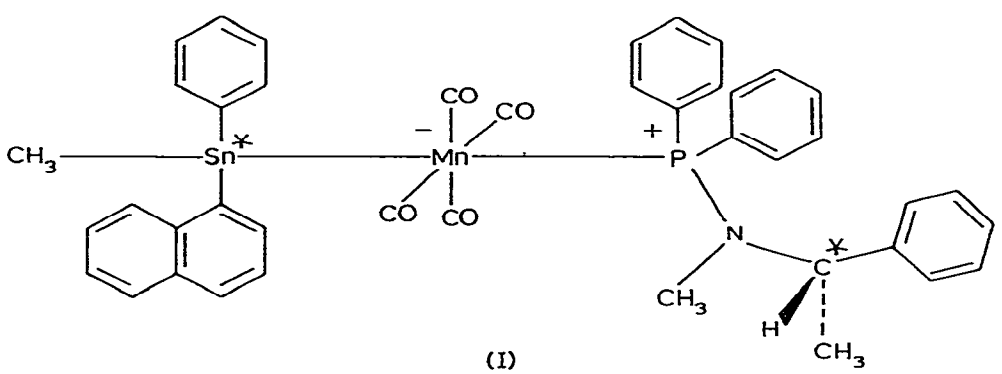
Summary

Methyl-1-naphthylphenylstannyltetracarbonyl(diphenyl-*N*-methyl-*N*-(*S*)-1-phenylethylaminophosphine)manganese (I) has been prepared by two different routes from racemic methyl-1-naphthylphenyltin chloride. Fractional recrystallizations yielded two diastereomeric fractions with $[\alpha]_{546}^{30^\circ} = +40.3^\circ$ and -71.4°, respectively, which have identical NMR and IR spectra.

Introduction

Optically active organotin compounds can be very useful in studying the stereochemistry of substitution reactions at tin [2]. Many chiral organotin compounds have been prepared [2], but only one paper has been devoted to the synthesis of chiral triorganostannyl-transition metal complexes [3].

In this paper, we describe the synthesis of another optically active triorganostannyl-transition metal compound, (I) containing, besides the asymmetric tin atom Sn*, a previously resolved (*S*) asymmetric carbon atom C* in of the aminophosphine ligand (PN*) of the manganese atom.



(I)

* For part LXVIII see ref. 1.

Results and discussion

Compound I was obtained by treating racemic methyl-1-naphthylphenyltin chloride (II) with either pentacarbonylmanganate and by replacing afterwards one carbon monoxide molecule by the chiral ligands (*S*)-(+)-$Ph_2PNMeCHMePh$-(PN*) [see ref. 4], or directly with $(PN^*)(CO)_4Mn^-$.

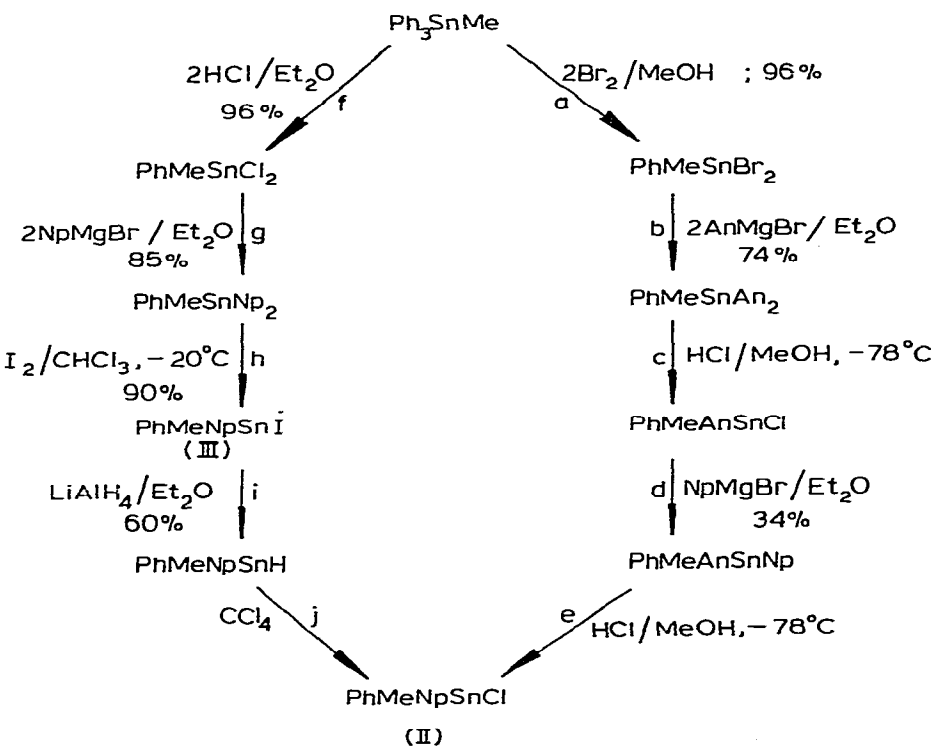
Synthesis of racemic methyl-1-naphthylphenyltin chloride (II)

Compound II had previously been prepared by Jamaï [5] (reactions a—e in Scheme 1). The rather low yield (<22%), in steps c and d led us to try another route (reactions f—j in Scheme 1), giving overal yield of 44%.

According to Lequan [6], the iododemetallation of methylbis(1-naphthyl)-phenyltin in $CHCl_3$ (reaction h) is very selective at —20°C. However, we obtained from reaction h a mixture containing 90% MeNpPhSnI (III), 5% $MePhSnI_2$, and 5% starting material. Compound III is too unstable to be distilled or chromatographed. Therefore we used a recently reported [7] purification method, involving treatment of the reaction mixture (impure III) with $LiAlH_4$ (reaction i) to convert the iodides into the corresponding hydrides. Column chromatography on SiO_2 (elution with benzene/petroleum ether, 40°) could safely be used for the separation of the different components. Methyl-1-naphthyl phenyltin hydride, which is a crystalline solid [7], can be recrystallized from n-pentane; it reacts with CCl_4 to give a quantitative yield of pure II.

SCHEME 1

PREPARATION OF RACEMIC METHYL-1-NAPHTHYLPHENYLTIN CHLORIDE (II) (Np = 1-naphthyl; An = *p*-anisyl)

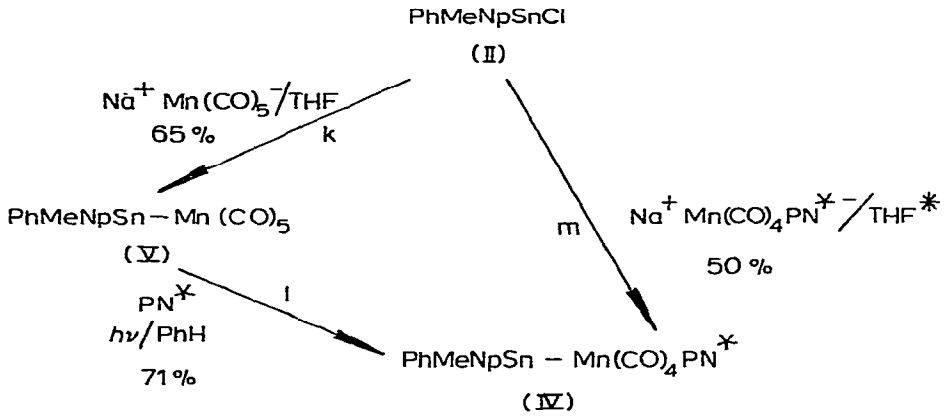


Synthesis and separation of $(R,S)_{Sn}$-PhMeNpSnMn(CO)$_4$[$(S)_C$-Ph$_2$PNMeCHMePh] IV

Compound IV was prepared in two different ways (see Scheme 2).

SCHEME 2

SYNTHESIS OF $(R,S)_{Sn}$-PhMeNpSn-Mn(CO)$_4$[$(S)_C$-Ph$_2$PNMeCHMePh] (IV)



Compound IV was purified by column chromatography on SiO_2. The diastereomers *RS* and *SS* were not separated by this method, the optical rotation of the first fraction ($[\alpha]_{546}^{30°}$ = —24.6°) and of the last fraction (—26.0°) being almost identical. Fractional recrystallization from methanol/diethyl ether gave satisfactory results: IV, with $[\alpha]_{546}^{30°}$ = —26°, a very viscous oil, was dissolved in Et_2O; methanol was added until the solution became cloudy. After one night at —30°C, a precipitate was isolated; it had $[\alpha]_{546}^{30°}$ = +12.3°. The evaporated mother liquor gave $[\alpha]_{546}^{30°}$ = —64.1. After two more similar treatments, two fractions were obtained, showing $[\alpha]_{546}^{30°}$ = +40.3° and —71.4°, respectively. Unfortunately, the 270 MHz ^{1}H NMR, 22.63 MHz ^{13}C NMR and IR spectra of these two fractions were identical, so that their compositions could not be determined.

Alternative synthesis of methyl-1-naphthylphenylstannylpentacarbonylmanganese (V)

Compound V can be made from 1-naphthylmagnesium bromide and PhMeClSnMn(CO)$_5$ but, along with the expected substitution product (28% yield), PhMeSnNp$_2$ (16%) and PhMeSn[Mn(CO)$_5$]$_2$ (20%) are also formed. The three compounds can easily be separated by column chromatography. Similar results were previously obtained for analogous reactions [4].

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* $Mn_2(CO)_{10} + 2\ PN^* \xrightarrow{h\nu/PhH} 2\ Mn(CO)_8(PN^*)_2$ (45%)

$Mn_2(CO)_8(PN^*)_2 \xrightarrow[THF]{1\%\ NaHg} 2\ Na^+Mn(CO)_4(PN^*)^-$

Experimental

Instruments

60 MHz ^{1}H NMR: Varian T60 (34°C); 270 MHz ^{1}H NMR: Bruker HDX 270 (25°C); mass spectrometry: AEI-MS 902S coupled to a NOVA computer, resolution: 900; IR: Perkin-Elmer 257 and 125; ORD: Perkin-Elmer 141.

Synthesis of compound II (route a—e, Scheme 1) [5]

Reaction a. Pure methylphenyltin dibromide [16] was prepared by adding at 0°C a methanolic bromine solution (9.9 g Br_2/100 ml MeOH) dropwise to a solution of 12 g of methyltriphenyltin in a mixture of 10 ml of benzene and 40 ml of methanol. The mixture was kept at 0°C until the yellow color disappeared. Benzene was added, and the solvents were evaporated off under reduced pressure, an azeotope of benzene/methanol coming off first, then the remaining benzene and bromobenzene. The residue of methylphenyltin dibromide was distilled (b.p. 94—98°C/0.12 Torr) [5].

Reaction b. The standard procedure (*p*-$MeOC_6H_4MgBr$ in ether, hydrolysis with ice) was used to convert methylphenyltin dibromide into methylphenyldi-*p*-anisyltin [5] (chromatography on SiO_2, elution with benzene); (m.p. 48—51°C), δ(Me): 0.623 ppm; $^2J(^{119}Sn—^1H)$ = 55.8 Hz; 70 eV monoisotopic mass spectrum [*m/e*, %Σ, fragment ion]: 426, 0.5, $An_2PhMeSn$; 411, 59.7, An_2PhSn; 396, 0.3, $AnPh_2MeSn$; 381, 7.7, $AnPh_2Sn$; 349, 2.9, An_2MeSn; 319, 5.1, AnPhMeSn; 304, 0.3; AnPhSn; 289, 1.9, Ph_2MeSn; 227, 7.0, AnSn; 212, 1.0, MePhSn; 197, 6.0, PhSn; 151, 2.0, MeOSn; 135, 0.7, MeSn; 121, 0.7, SnH; 120, 4.2, Sn (with metastable peak at *m/e* = 396 [426 → 411)] (An = *p*-MeO-C_6H_4).

Reaction c. The protiodemetallation of methylphenyldi-*p*-anisyltin was carried out with a 0.34 *N* HCl/MeOH solution at —78°C. After 2 h at —78°C, the solvents were evaporated as in the synthesis of methylphenyltin dibromide.

Reaction d. The crude methylphenyl-*p*-anisyltin chloride (70 eV monoisotopic mass spectrum: 354, 1.7, AnMePhSnCl; 339, 10.1, AnPhSnCl; 324, 0.9, $Ph_2MeSnCl$; 319, 0.4, AnPhMeSn; 309, 33.9, Ph_2SnCl; 289, 1.3, Ph_2MeSn; 277, 0.6, AnMeSnCl; 262, 0.6, AnSnCl; 247, 5.4, PhMeSnCl; 232, 1.2, PhSnCl; 227, 0.8, AnSn; 212, 0.3, PhMeSn; 197, 7.3, PhSn; 170, 1.3, MeSnCl; 155, 21.9, SnCl; 135, 8.0, MeSn; 121, 0.5, SnH; 120, 3.7, Sn; with metastable peaks at *m/e* = 325 [354 ≈ 339] and 183 [212 → 197]) which was obtained as an oil which did not crystallize, was transformed (1-naphthylmagnesium bromide in ether, hydrolysis with ice) into methyl-1-naphthyl-*p*-anisylphenyltin (m.p. 103—105°C) which was purified by chromatography on a SiO_2 column (elution with benzene) δ(Me): 0.79 ppm; $^2J(^{119}Sn—^1H)$ = 55.0 Hz; 70 eV monoisotopic mass spectrum: 446, 5.8, AnNpPhMeSn; 431, 65.4, AnNpPhSn; 369, 2.7, AnNpMeSn; 354, 0.5, AnNpSn; 339, 1.9, NpPhMeSn; 319, 2.2, AnPhMeSn; 289, 0.9, Ph_2MeSn; 247, 5.4, NpSn; 227, 3.7, AnSn; 212, 0.6, PhMeSn; 197, 4.0, PhSn; 151, 1.2, MeOSn; 145, 0.7, C_2HSn; 135, 0.5, MeSn; 121, 0.6, SnH^+; 120, 4.1, Sn; with a metastable peak at *m/e* = 416 (446 → 431). If 1-naphthyllithium is used as arylating agent, methylphenyldinaphthyltin is obtained together with the expected methyl-1-naphthyl-*p*-anisylphenyltin [5] [see also ref. 13].

Reaction e. The protiodemetallation of methyl-1-naphthyl-*p*-anisylphenyltin

was carried out as for the synthesis of methyl-*p*-anisylphenyltin chloride. Compound II was obtained as an oil which did not crystallize. 70 eV monoisotopic mass spectrum: 374, 1.2, NpMePhSnCl; 339, 0.1, MeNpPhSn; 297, 0.8, MeNpSnCl; 282, 1.0, NpSnCl; 247, 2.8, NpSn; 247, 6.6, PhMeSnCl; 232, 2.2, PhSnCl; 212, 0.1, PhMeSn; 197, 9.7, PhSn; 170, 1.7, MeSnCl; 155, 53.7, SnCl; 135, 12.8, MeSn; 120, 6.3, Sn [5].

Alternative synthesis of compound II (route f—j, cf. Scheme 1)

Reaction f. Methylphenyltin dichloride was made starting from a solution of 26 g (71 mmol) of Ph_3SnMe in 150 ml of dry Et_2O, to which 155 ml of 0.93 *N* HCl/Et_2O were added dropwise at 0°C during 2 h. The reaction was monitored by NMR spectroscopy ($\delta(CH_3)[Ph_3SnMe]$ = 0.68 ppm; $\delta(CH_3)[Ph_2SnMeCl]$ = 0.88 ppm; $\delta(CH_3)[PhMeSnCl_2]$ = 1.25 ppm for a 0.5 *M* solution in CCl_4). The reaction was complete after 48 h. After evaporation of the solvent, the residual oil (19.6 g) was crystallized in the refrigerator and purified by sublimation (30—35°C/10^{-2}—10^{-3} Torr), giving 19.2 g (96%) colorless crystals $PhMeSnCl_2$ (m.p. 46—47.5°C). (Found: C, 30.1; H, 2.99; $C_7H_8Cl_2Sn$ calcd.: C, 29.74; H, 2.86%) 70 eV monoisotopic mass spectrum [*m/e*, %Σ, fragment ion]: 309, 2.4, Ph_2SnCl; 282, 6.5, $PhMeSnCl_2$; 267, 41.6, $PhCl_2Sn$; 247, 3.9, PhMeSnCl; 232, 0.5, PhClSn; 205, 1.5, $MeSnCl_2$; 197, 1.7, PhSn; 155, 35.6, ClSn; 145, 1.4, C_2HSn; 120, 4.9, Sn.

Reaction g. The Grignard reagent made from 54 g (0.26 mol) 1-naphthyl bromide (with 7.2 g Mg in 300 ml Et_2O + 35 ml C_6H_6) was cooled at 0°C and a solution of 28.2 g (0.1 mol) of $PhMeSnCl_2$ in 150 ml Et_2O was added dropwise. After 16 h, work up gave 44 g of a light yellow oil, which solidified upon addition of methanol. It was recrystallized from 800 ml MeOH and 200 ml benzene to give 39 g (85%) of a white powder, m.p. 125.5—126.5°C (lit. [6] 126°C). (Found: C, 69.3; H, 4.9; $C_{27}H_{22}Sn$ calcd.: C, 69.72; H, 4.77%) $\delta(CH_3Sn)$: 0.95 ppm; $^2J(^{119}Sn—^1H)$: 55 Hz (0.4 *M* in CCl_4); 70 eV monoisotopic mass spectrum: 501, 0.6, Np_3Sn; 466, 7.1, $PhMeNpSn_2$; 451, 31.8, $PhNp_2Sn$; 416, 0.1, Ph_2-MeNpSn; 389, 2.7, $MeNp_2Sn$; 373, 1.0, $C_{20}H_{13}Sn$; 339, 5.5, MePhNpSn; 247, 11, NpSn; 221, 1.8; 197, 4.2, PhSn; 145, 3.5, C_2HSn; 135, 1.5, MeSn; 121, 0.9, HSn; 120, 27.3, Sn.

Reaction h. The procedure described by Lequan [6] was used for this step. The 1-naphthyl iodide formed was eliminated (after the evaporation of the solvent $CHCl_3$) using a Kugelrohrflash-distillation apparatus (100°C/5 × 10^{-3} Torr). The product mixture contained 90% of III, 5% of $PhMeSnI_2$ (δ(Me): 1.55 ppm) and 5% of starting product. The ^1H NMR spectrum of III shows a MeSn signal at 1.27 ppm $^2J(^{119}Sn—^1H)$ = 59.0 Hz (lit. [6]: δ(MeSn) = 1.27 ppm); 70 eV monoisotopic mass spectrum: 516, 0.2, Np_3MeSn; 501, 0.2, Np_3Sn; 466, 3.9 (NpPhMeSnI) + 2.6 ($Np_2PhMeSn$); 451, 6.4, (NpPhSnI) + 9.2 (Np_2PhSn); 401, 1.6, $NpPh_2Sn$; 389, 0.2, (NpMeSnI) + 1.2 (Np_2MeSn); 373, 0.3, $C_{20}H_{13}Sn$; 339, 31.9, NpPhMeSn; 323, 1.6, $C_{16}H_{11}Sn$; 289, 2.4, Ph_2MeSn; 247, 15.5, NpSn; 197; 8.8, PhSn; 169, 0.6, C_4HSn; 145, 1.5, C_2HSn; 135, 1.6, MeSn; 121, 0.8, HSn; 120, 9.5, Sn.

Reaction i. The product from reaction f was reduced with 1.2 g $LiAlH_4$ in 150 ml Et_2O, and the usual work up gave 24 g of a viscous oil containing some naphthalene, 2.5 g of which was removed by sublimation (40—50°C/12 Torr).

The solid obtained was dissolved in 40 ml pentane at 30°C and 1.5 g of $PhMeNp_2Sn$ removed by filtration. After one night at —30°C 9.5 g colorless crystals had separated. Evaporation of some solvent and recrystallization yielded a further 7.3 g of crystals (m.p. ~45°C). TLC showed the presence of some naphthalene and phenylmethyltin dihydride in this solid material, which was purified by chromatography on SiO_2 (elution with benzene/petroleum ether 40°C, 1/5) to give 13.3 g (60%) pure PhMeNpSnH; m.p. 53.5—55°C (lit. [7] 52—55°C). (Found C, 60.12; H, 4.68; $C_{17}H_{16}Sn$ calcd.: C, 60.05; H, 4.74%) IR: ν(Sn—H): 1835 cm^{-1}; ^1H NMR (0.4 M/C_6D_6): δ(MeSn): 0.50 ppm; $^2J(^{119}SnC^1H_3)$: 59.6 Hz; $^3J(^1H_3CSn^1H)$ = 2.6 Hz; δ(HSn): 6.37 ppm.

Reaction j. A solution of 10.2 g (30 mmol) of PhMeNpSnH in 50 ml of CCl_4 after 8 h in daylight gave 11.2 g (100%) of pure II and 1 equivalent of $CHCl_3$. ^1H NMR (0.6 *M* CCl_4): δ(MeSn): 1.07 ppm; $^2J(^{119}Sn—^1H)$: 60.0 Hz.

Synthesis of compound IV

Reaction k. $PhMeNpSnMn(CO)_5$ was prepared under nitrogen from II and pentacarbonylmanganate in 65% yield (white crystals, m.p. 58.5—59.5°C). (Found: C, 48.7; H, 2.9; $C_{22}H_{16}O_5SnMn$ calcd.: C, 49.49; H, 2.83%) ^1H NMR (0.2 *M*/CS_2): δ(MeSn): 0.95 ppm; $^2J(^{119}Sn—^1H)$: 45.5 Hz; 70 eV monoisotopic mass spectrum: 534, 0.3, $PhMeNpSnMn(CO)_5$; 519, 0.8, $PhNpSnMn(CO)_5$ 506, 0.1, $MePhNpSnMn(CO)_4$; 463, 1.5, $PhNpSnMn(CO)_3$; 451, 0.2, Np_2PhSn; 407, 0.2, $PhMeSnMn(CO)_5$; 394, 15.1, PhMeNpSnMn; 379, 2.6, $PhMeSnMn(CO)_4$; 339, 44.6, PhMeNpSn; 323, 0.4; $PhMeSnMn(CO)_2$; 301, 1.2, $C_{10}H_7SnMn$; 289, 0.2, Ph_2MeSn; 247, 20.9, NpSn; 221, 1.2; 197, 5.8, PhSn; 175, 0.6, SnMn; 120, 4.4, Sn; IR (10^{-2} *M*/CS_2): ν(CO): 1910(sh), 1995s, 2002m, 2024vw, 2090w cm^{-1}.

Reaction l. A solution of 2.0 g (6.3 mmol) PN* and 3.0 g (5.6 mmol) $PhMeNpSnMn(CO)_5$ in 100 ml benzene was irradiated with a 450 W high pressure Hanovia mercury lamp for 2 h, during which about 140 ml gas was evolved. After evaporation of the solvent and chromatography on SiO_2 (benzene/petroleum ether 1/5—1/2), 20 mg of naphthalene, 200 mg of starting product and 3.3 g impure of IV, contaminated with traces of an unstable red compound, were obtained. Yield: 71%; $[\alpha]_{546}^{30}$ —26.25° (*c* = 2.0; CS_2); the physical properties were identical to those of IV obtained via reaction m (see below).

Reaction m. $NaMn(CO)_4PN^*$ was prepared as described by Gorsich [14], from $[Mn(CO)_4PN^*]_2$, which had been synthesized by a procedure analogous to that used to make $[Mn(CO)_4PPh_3]_2$ [15] and recrystallized from cyclohexane [red crystals m.p. 95—98°C (dec)]; ^1H NMR (0.3 *M* in C_6D_6): $\delta(CH_3C^*)$: 1.33 ppm (doublet; ^3J(H—H) = 7 Hz); $\delta(CH_3N)$: 2.13 ppm (doublet; $^3J(^1H—^{13}P)$ = 9 Hz); $\delta(HC^*)$ = 5.17 ppm (multiplet); IR (CS_2): ν(CO): 1965s, 1985w; 1995w. (Found: C, 61.7; H, 5.04; $C_{50}H_{44}Mn_2O_8N_2P_2$ calcd.: C, 61.74; H, 4.56%.) 70 eV monoisotopic mass spectrum: 749, 0.1, $Mn(CO)_2PN^*$; 709, 0.4; 693, 0.5; $Mn(PN^*)_2$; 588, 1.5; 533, 4.7, ($Mn_2(CO)_4PN^*$) 520, 0.7; 504, 1.7; 485; 1.0, $Mn_2(CO)_2PN^*$; 458, 2.4, $Mn(CO)_3PN^*$ 451, 2.3; 430, 1.7, $Mn(CO)_2PN^*$; 390, 3.6; 374, 27.3, $MnPN^*$; 320, 41.8; 319, 36.4, PN^*; 318, 24.2; 304, 1.8, $Ph_2PNCHMePh$; 262, 78.2, (Ph_3P); 214, 47.3, Ph_2PNMe; 183, 30.9, $C_{12}H_8P$; 134, 100, MeNCHMePh.

To a solution of 3.7 g (10 mmol) of II in 20 ml of THF was added a filtered solution of $NaMn(CO)_4PN^*$. The mixture was left for 6 h at room temperature. The solvent was evaporated off and the residual IV purified by chromatography on SiO_2 (elution with benzene/petroleum ether 1/9—1/2). Four fractions which contained compound IV were collected. Their $[\alpha]_{546}^{30^\circ}$ (CS_2) values were —24.6°, —26.8°, —25.5°, and —26.0°, respectively (yield: 2.35 g, 50%). Solutions of IV decompose in the presence of air. Compound IV could not be recrystallized from hexane, pentane or hexane/benzene. ^1H NMR (0.35 M/CS_2, 60 MHz); δ(MeSn): 0.82 ppm, $^2J(^{119}Sn—^1H)$: 43 Hz; δ(MeC*): 1.33 ppm; $^3J(^1H—^1H)$: 6.8 Hz; δ(MeN): 2.15 ppm; $^3J(^1H—^1H)$: 9 Hz; π(CH); 5.03 ppm; $^3J(^{31}P—^1H)$: 11 Hz; ^1H NMR (0.05 *M*/C_6D_6, 270 MHz): 1.105 (44 Hz), 1.115 (7 Hz); 1.963 (9 Hz); 5.250 (11 Hz); ^{13}C NMR (0.3 *M*/C_6D_6; TMS; 22.63 MHz): δ(MeSn): —4.16 ppm; δ(MeC*): 17.03 ppm, $^3J(^{31}P—^{13}C)$: 1 Hz; δ(MeN): +31.28 ppm, $^2J(^{31}P—^{13}C)$: 2.8 Hz; δ(C*): 58.36 ppm $^2J(^{31}P—^{13}C)$: 13.8 Hz; δ(aromatic C(s): 125—142 ppm; δ(CO): no signal found. 70 eV monoisotopic mass spectrum: 810, 0.02, $PhNpSnMn(CO)_4PN^*$; 760, 0.05, $Ph_2SnMn(CO)_4PN^*$; 748m 0.06, $MeNPSnMn(CO)_4PN^*$; 698, 1.4, $PhNpSnMnPN^*$; 636, 0.3, $MeNpSnMnPN^*$; 586, 0.6, $MePhSnMnPN^*$; 451, 7.0, $PhNp_2Sn$; 401, 7.3; Ph_2NpSn; 389, 16.2, $MeNp_2Sn$; 374, 2.9, Np_2Sn; 339, 18.5, $PhMeNpSn^*$; 319, 6.2, PN^*; 318, 5.9; 289, 5.0, Ph_2MeSn; 277, 3.9, Me_2NpSn; 247, 10, NpSn; 197, 6.2, PhSn; 120, 8.5, Sn; IR (4×10^{-2} *M*/CS_2): ν(CO): 1950s, 1988w, 2016vw cm^{-1}.

Separation of $(R,S)_{Sn}$-PhMeNpSnMn(CO)$_4$[(S)-Ph_2PNMeCHMePh] (IV)

To a solution of 2.0 g IV in 5 ml Et_2O, methanol was added till the solution became cloudy (~3 ml). The mixture was cooled to —30°C and after 15 h, 920 mg of a white precipitate were obtained, with $[\alpha]_{546}^{30^\circ}$ +12.3 (*c* = 0.5/CS_2). This treatment of the mother liquor was repeated twice and with the precipitate to give 120 mg of (+)-IV (m.p. 150—155°C) with $[\alpha]_D^{30} = +30.0^\circ$; $[\alpha]_{546} = +40.3^\circ$; $[\alpha]_{435} = +77.0^\circ$; $[\alpha]_{407} = +93.3^\circ$ (*c* = 0.34/CS_2). The most levorotatory mother liquor solidified on addition of methanol. 135 mg of (—)-IV were obtained as a yellow powder, m.p. 70—72°C, with $[\alpha]_D^{30^\circ} = -57.4$; $[\alpha]_{546} = -71.4^\circ$; $[\alpha]_{435} = -149.2^\circ$; $[\alpha]_{407} = 197.7^\circ$. (Found (+)-IV: C, 60.70; H, 4.65; (—)-IV: C, 61.00; H, 4.60; $C_{42}H_{37}MnNO_4PSn$, calcd.: C, 61.19; H, 4.52%). The IR, ^1H NMR and ^{13}C NMR spectra of (+)-IV and of (—)-IV are identical to that of IV.

Alternative synthesis of compound V

To a solution of 8.83 g (16 mmol) of $PhMeClSnMn(CO)_5$ in ether, at 0°C was added the Grignard reagent prepared from 3.7 g (18 mmol) 1-naphthyl bromide and 0.6 g (25 mmol) of Mg in 50 ml of Et_2O. After 3 h at room temperature, hydrolysis, and usual work up, naphthalene was removed by sublimation (Kugelrohr, 50°C/10^{-2} Torr) and the product mixture was purified by chromatography on SiO_2 (benzene/petroleum ether 1/5). Three products were isolated: (a) 2.5 g of $PhMeSn[Mn(CO)_5]_2$; (b) 3.0 g of $PhMeNpSnMn(CO)_5$, (V) and (C) 1.5 g of $PhMeNp_2Sn$.

Appendix: Comparison of the ^1H NMR parameters of analogous phenyl- and *p*-anisyltin compounds

Malinovsky's additivity was applied to organotin compounds [11,12].

$$^2J(^{119}Sn—C^1H_3)(MeSnRR'R'') = \chi(R) + \chi(R') + \chi(R'')$$

From the $^2J(^{119}Sn—C^1H_3)$ coupling constant of methyl tri-*p*-anisyltin (see Table 1), the χ-value of the *p*-anisyl group were calculated

$$^2J(^{119}Sn—C^1H_3)(MeSnAn_3) = 3\chi(An) \rightarrow \chi(An) = 18.5 \text{ Hz}$$

The value obtained is very similar to that of the phenyl group ($\chi(Ph) = 18.4$ Hz). This can be confirmed by comparing the coupling constants of analogous phenyl- and *p*-anisyltin compounds (see Table 1), and suggests that the contribution of the quinonic resonance form is not very important [5].

From the values of $\chi(Me) = 18.0$ Hz and of $\chi(Np) = 17.7$ Hz [12], the $^2J(^{119}SnC^1H_3)$ coupling constants can be calculated for the tetraorganotin compounds listed in Table 1: they agree satisfactorily with the experimental values [5].

In contrast, the substitution of the *p*-hydrogen atom of the phenyl derivatives by a methoxy group changes the chemical shift of the methyl bound to tin (see Table 1) but no clear trend can be noticed [5]. The same phenomenon can be seen with t-butyltin compounds: $^3J(^{119}SnC(C^1H_3)_3)$ is 71.4 Hz for An_2PhSn—t-Bu and 71.9 Hz for the analogous Ph_3Sn—t-Bu (the chemical shifts for the t-butyl protons are 1.633 ppm and 1.380 ppm, respectively); $^3J(^{119}SnC(C^1H_3)_3)$ is equal to 94.4 Hz for AnPh-t-BuSnCl and to 94.8 Hz for Ph_2—t-BuSnCl (with δ(t-Bu) equal to 1.386 and 1.403 ppm, respectively) [5].

TABLE 1

COMPARISON OF THE NMR PARAMETERS δ(Me) AND $^2J(^{119}Sn—Me)$ OF ANALOGOUS PHENYL- AND *p*-ANISYLTIN COMPOUNDS

Organotin compound	R = *p*-MeOPh (An)		R = Ph	
	δ(Me) (ppm)	$^2J(^{119}Sn—Me)$ (Hz)	δ(Me) (ppm)	$^2J(^{119}Sn—Me)$ (Hz)
R_3SnMe	0.593	55.6	0.676	55.7
$R_2SnPhMe$	0.623	55.8	0.676	55.7
R_2SnMe_2	0.448	55.2	0.476	55.4
$RSnMe_3$	0.500	54.3	0.240	54.6
RSnAnNpMe	0.770	55.2	0.790	55.0
$R_2SnMeCl$	0.870	60.0	0.773	60.6
RSnAnMeCl	0.870	60.0	0.873	59.8
RSnNpMeCl	1.030	59.6	0.931	59.4

Methyltin tribromide [9] was made by a bromodemetallation of methyltriphenyltin [8] in boiling $CHCl_3$. Chloroform and bromobenzene were distilled off. The crude $MeSnBr_3$ was treated with AnMgBr in ether. After hydrolysis with ice, the ethereal solution was dried, and the solvent evaporated off. Chromatography on a SiO_2 column (elution with benzene) yielded methyltri-*p*-anisyltin, which was recrystallized from methanol (yield: 64%; m.p. 90—91°C).

A solution of 1 equivalent of HCl in methanol was added slowly at —70°C to a methanol/benzene (2/1) solution of methyltri-*p*-anisyltin. The mixture was kept at low temperature for 2 h. The solvents and the anisole formed were distilled off under reduced pressure, to leave methyldi-*p*-anisyltin chloride as an oil, which did not crystallyze (yield: 96%) [5].

Methyl-1-naphthyldi-*p*-anisyltin [10] was made from methyldi-*p*-anisyltin chloride and 1-naphthylmagnesium bromide by the standard procedure (hydrolysis with ice). It was purified by column chromatography on SiO_2 (elution with benzene) and recrystallized from methanol (yield: 65%; m.p. 125—126°C) [5].

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