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Phosphonate−Stannylene Coupling in the Reactions of the Anion $[Mn_2\{\mu\text{-}OP(OEt)_2\}\{\mu\text{-}P(OEt)_2\}(CO)_6]^{2-}$ with SnR_2Cl_2 (R = Bu, Ph)

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Reaction of $Na_2[Mn_2\{\mu\text{-}OP(OEt)_2\}\{\mu\text{-}P(OEt)_2\}(CO)_6]$ with SnR_2Cl_2 (R = Bu, Ph) in tetrahydrofuran leads finally to the stannyl-bridged heptacarbonyl compounds $[Mn_2\{\mu\text{-}Sn{:}Sn,P\text{-}SnR_2OP(OEt)_2\}\{\mu\text{-}P(OEt)_2\}(CO)_7]$ or, in the presence of PR'_3 (R′ = Ph, *p*-tol, Cy, ^{i}Pr), to the corresponding hexacarbonyl complexes $[Mn_2\{\mu\text{-}Sn{:}Sn,P\text{-}SnR_2OP(OEt)_2\}\{\mu\text{-}P(OEt)_2\}(CO)_6(PR'_3)]$. Several intermediates are involved in these reactions, which include the expected initial stannylene product $[Mn_2(\mu\text{-}SnR_2)\{\mu\text{-}OP(OEt)_2\}\{\mu\text{-}P(OEt)_2\}(CO)_6]$, detected when R = Bu, and unstable solvent adducts. The products isolated all display a one-electron-donor stannyl bridging group derived from the O−Sn coupling between the phosphonate and stannylene ligands present in the initial intermediate, as confirmed by an X-ray study on $[Mn_2\{\mu\text{-}Sn{:}Sn,P\text{-}SnPh_2OP(OEt)_2\}(CO)_6(P^iPr_3)]$ and the spectroscopic (IR, ^{1}H and ^{31}P NMR) analysis of the new complexes.

Introduction

Heterometallic clusters that combine tin and transition metals are a subject of interest not only because of their structures and reactions[1] but also due to their use in catalysis, either as catalysts themselves in a number of processes[2] or as precursors of bimetallic nanoparticles exhibiting enhanced catalytic activity.[3] Triorganotin and related groups (SnR_3) usually bind transition-metal centers (M) through terminal M−SnR_3 bonds, while diorganotin groups (SnR_2) usually adopt bridging positions by establishing two M−Sn bonds with the metallic core.[1,2] Thus, the use of di- and polynuclear transition-metal substrates in combination with the appropriate tin reagents provides rational methods to create closed M_2Sn triangular frames.

Some time ago we reported the use of the dimanganese anion $[Mn_2\{\mu\text{-}OP(OEt)_2\}\{\mu\text{-}P(OEt)_2\}(CO)_6]^{2-}$ (**1**) as a reagent able to generate new Mn−group 11 metal and Mn−Zn heterometallic clusters having Mn_2M, Mn_2M_2, or Mn_2M_3 skeletons. Of interest to the present study was the observation that the anion **1** reacted rapidly with $[ZnCl_2(bipy)]$ to give the trinuclear cluster $[Mn_2Zn\{\mu\text{-}OP(OEt)_2\}\{\mu\text{-}P(OEt)_2\}(CO)_6(bipy)]$, which was characterized crystallographically.[4] It could thus be expected that an analogous reaction would take place between the anion **1** and diorganotindichlorides SnR_2Cl_2 to give the corresponding stannylene Mn_2Sn clusters. In this paper we report the results of such reactions of anion **1** with dibutyl- and diphenyltin dichloride. Unexpectedly, Sn−O coupling between the phosphonate and stannylene groups occurs in all these reactions to yield stannyl-bridged products. This is very unusual, as stannyl groups are almost invariably found terminally bonded to transition metals, as stated above. In fact, we are aware of only two other compounds exhibiting organostannyl groups bridging two metal atoms, these being the recently reported tin−molybdenum $[Mo_2Cp_2(\mu\text{-}SnPh_3)(\mu\text{-}PCy_2)(CO)_2]$[5] and tin−germanium [K(2,2,2,-crypt)]$[Ge_9(\mu_2\text{-}SnPh_3)]$ compounds.[6] We can also quote a few examples involving edge-bridging trichlorostannyl groups at ruthenium or iridium clusters.[7] Stannyl-bridged compounds are isolobal-related to alkyl- and silyl-bridged complexes. The latter constitute a growing family of compounds relevant in the understanding of several basic processes such as ligand exchange, ligand migrations, and oxidative addition or reaction mechanisms, including catalysis.[8]

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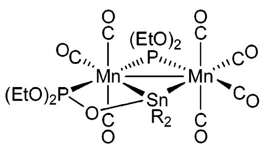
10.1021/om050250u CCC: $30.25

Chart 1



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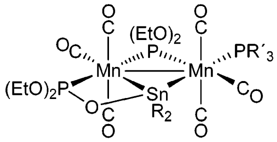

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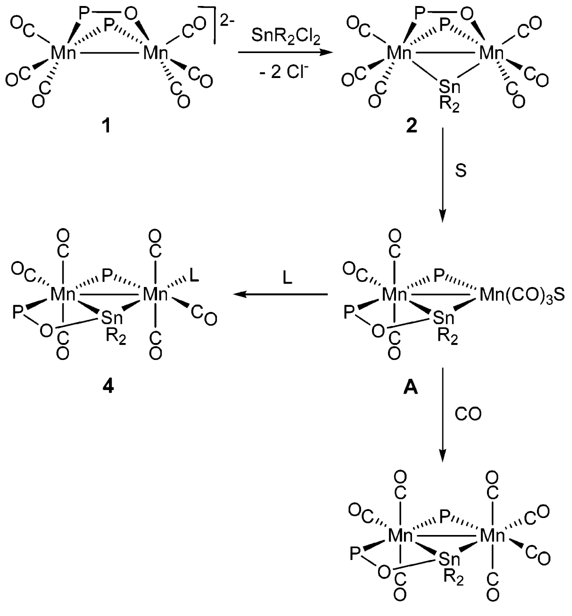
	R	R′
3a	Bu	
3b	Ph	
4a	Bu	Ph
4b	Bu	*p*-tol
4c	Ph	Ph
4d	Ph	^{i}Pr
4e	Ph	Cy

Scheme 1. Species Detected in the Reactions of Anion 1 with SnR_2Cl_2 in Tetrahydrofuran (R = Bu, Ph; P = $P(OEt)_2$; S = tetrahydrofuran; L = PR'_3, with R′ = Ph, *p*-tol, ^{i}Pr, Cy)



Results and Discussion

Anion **1** (as its Na$^+$ salt) reacts readily with SnR_2Cl_2 (R = Bu, Ph) in tetrahydrofuran at −70 °C, but the initial products formed further evolve at room temperature to finally give the corresponding heptacarbonyl complexes $[\mathrm{Mn_2}\{\mu\text{-}Sn{:}Sn,P\text{-}\mathrm{SnR_2OP(OEt)_2}\}\{\mu\text{-}\mathrm{P(OEt)_2}\}(\mathrm{CO})_7]$ (**3a**,**b**) as the major products, which can be isolated in medium yield (ca. 50%) after chromatographic separation of the reaction mixture (Chart 1). The monitoring of the above reactions by IR spectroscopy reveals that several steps are involved on the way from anion **1** to the stannyl products **3** (Scheme 1). When R = Bu, an intermediate species can be detected in the early moments of the reaction, and the C−O stretching bands of this species (Table 1) are very similar to those of the dimanganese−zinc cluster $[\mathrm{Mn_2}\{\mu\text{-}\mathrm{Zn(bipy)}\}\{\mu\text{-}\mathrm{OP(OEt)_2}\}\{\mu\text{-}\mathrm{P(OEt)_2}\}(\mathrm{CO})_6]$.[4] Therefore, this intermediate complex can be safely proposed to be the isostructural and isoelectronic manganese−tin cluster $[\mathrm{Mn_2}(\mu\text{-}\mathrm{SnBu_2})\{\mu\text{-}\mathrm{OP(OEt)_2}\}\{\mu\text{-}\mathrm{P(OEt)_2}\}(\mathrm{CO})_6]$ (**2**).

Compound **2** was found to evolve during the warming-up of the solution to give a mixture of products thought to be solvent adducts **A** of the type $[\mathrm{Mn_2}\{\mu\text{-}Sn{:}Sn,P\text{-}\mathrm{SnR_2OP(OEt)_2}\}\{\mu\text{-}\mathrm{P(OEt)_2}\}(\mathrm{CO})_6(\mathrm{S})]$ (S = tetrahydrofuran), derived from the reductive coupling of the phosphonate and stannylene groups followed by coordination of a solvent molecule. The latter can occur in three inequivalent positions, thus explaining the complexity of the IR spectra at this stage. Incidentally, we note that the solvent adducts **A** are the initial species that could be detected only in the reaction of **1** with $SnPh_2Cl_2$.

The solvent adducts **A** are unstable species at room temperature, and they progressively decompose to give the corresponding heptacarbonyls **3** in ca. 2−3 h. This decomposition is substantially accelerated by just removing the solvent and dissolving the residue in toluene, as expected for any tetrahydrofuran adduct. On the other hand, if a tertiary phosphine (PR'_3) is present (or added to) the medium, then the solvent adducts evolve to give the corresponding hexacarbonyl products $[\mathrm{Mn_2}\{\mu\text{-}Sn{:}Sn,P\text{-}\mathrm{SnR_2OP(OEt)_2}\}(\mathrm{CO})_6(\mathrm{PR'_3})]$ (**4**) rather than the heptacarbonyls **3**. In this way we have been able to prepare the stannyl-bridged complexes **4a**−**e** (R = Bu, Ph; R′ = Ph, *p*-tol, Cy, ^{i}Pr; Chart 1) in moderate yield (ca. 45%). Other minor products are formed in these reactions. In particular, we have identified the formation of the heptacarbonyl complexes $[\mathrm{Mn_2}\{\mu\text{-}\mathrm{OP(OEt)_2}\}\{\mu\text{-}\mathrm{P(OEt)_2}\}(\mathrm{CO})_7(\mathrm{PR'_3})]$ as side products of the reactions of **1** with $SnPh_2Cl_2$ in the presence of PCy_3 or P^iPr_3 (see Experimental Section). We note that the cyclohexylphosphine complex has been previously synthesized by us through the oxidation of anion **1** in the presence of P^iPr_3.[9] Thus the formation of these dimanganese side-products suggests that electron transfer (as opposed to nucleophilic substitution) between **1** and SnR_2Cl_2 occurs to some extent, at least in the reactions using $SnPh_2Cl_2$.

The structure of **4d** has been determined through an X-ray study (Tables 3 and 4), and an ORTEP view of the molecule is shown in Figure 1. The molecule can be viewed as composed of two edge-sharing octahedral manganese moieties, with diethoxyphosphide and (diethylphosphonate)diphenylstannyl groups at the bridging positions. Each manganese atom carries three carbonyl ligands arranged in a meridional fashion, thus explaining the low relative intensity of the symmetric C−O stretching bands present in the IR spectrum of **4d** (Table 1).[10] The sixth coordination position at each manganese atom is occupied by a P-donor ligand, this being the tris(isopropyl)phosphine at Mn(2) and the P-end of the phosphonate ligand in the case of Mn(1).

The most relevant feature in the structure of **4d** is the presence of a bridging stannyl ligand derived from the coupling of the phosphonate and stannylene groups, a coupling possibly driven by the great thermodynamic stability of the tin−oxygen bonds. We are aware of only one other related Sn−O coupling, this occurring in the reaction of $[\mathrm{Mo_2Cp_2}\{\mu\text{-}\mathrm{OP(OEt)_2}\}\{\mu\text{-}\mathrm{P(OEt)_2}\}(\mathrm{CO})_2]$ with $SnCl_2$ to give $[\mathrm{Mo_2Cp_2}(\mu\text{-}\mathrm{SnCl_2})\{\mu\text{-}Sn{:}P\text{-}\mathrm{SnCl_2OP(OEt)_2}\}\{\mu\text{-}\mathrm{P(OEt)_2}\}(\mathrm{CO})_2]$.[11] In this dimolybdenum complex,

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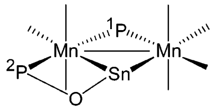
Table 1. IR Data for New Compounds[a]

compound	ν_{st}(CO)/cm^{-1}
$Na_2[Mn_2\{\mu\text{-}OP(OEt)_2\}\{\mu\text{-}P(OEt)_2\}(CO)_6]$ (**1**)[b]	1959 (s), 1901 (vs), 1857 (s), 1834 (s), 1819 (s), 1786 (w, sh)
$[Mn_2(\mu\text{-}SnBu_2)\{\mu\text{-}OP(OEt)_2\}\{\mu\text{-}P(OEt)_2\}(CO)_6]$ (**2**)[c]	2001 (w), 1970 (vs), 1922 (s), 1902 (sh, m)
$[Mn_2\{\mu\text{-}Sn{:}Sn,P\text{-}SnBu_2OP(OEt)_2\}\{\mu\text{-}P(OEt)_2\}(CO)_7]$ (**3a**)	2070 (m), 2023 (m), 1997 (vs), 1984 (s), 1967 (m), 1953 (s)
$[Mn_2\{\mu\text{-}Sn{:}Sn,P\text{-}SnPh_2OP(OEt)_2\}\{\mu\text{-}P(OEt)_2\}(CO)_7]$ (**3b**)	2074 (m), 2029 (m), 2003 (vs), 1988 (s), 1971 (m), 1961 (s)
$[Mn_2\{\mu\text{-}Sn{:}Sn,P\text{-}SnBu_2OP(OEt)_2\}\{\mu\text{-}P(OEt)_2\}(CO)_6(PPh_3)]$ (**4a**)	2037 (w), 2002 (m), 1963 (vs), 1944 (m), 1926 (w), 1912 (m)
$[Mn_2\{\mu\text{-}Sn{:}Sn,P\text{-}SnBu_2OP(OEt)_2\}\{\mu\text{-}P(OEt)_2\}(CO)_6\{P(p\text{-}tol)_3\}]$ (**4b**)	2036 (w), 2002 (m), 1962 (vs), 1943 (m), 1925 (w), 1911 (m)
$[Mn_2\{\mu\text{-}Sn{:}Sn,P\text{-}SnPh_2OP(OEt)_2\}\{\mu\text{-}P(OEt)_2\}(CO)_6(PPh_3)]$ (**4c**)	2041 (w), 2009 (m), 1968 (vs), 1947 (m), 1931 (w), 1923 (m)
$[Mn_2\{\mu\text{-}Sn{:}Sn,P\text{-}SnPh_2OP(OEt)_2\}\{\mu\text{-}P(OEt)_2\}(CO)_6(P^iPr_3)]$ (**4d**)	2038 (w), 2004 (m), 1965 (vs), 1946 (m), 1927 (w), 1915 (m)
$[Mn_2\{\mu\text{-}Sn{:}Sn,P\text{-}SnPh_2OP(OEt)_2\}\{\mu\text{-}P(OEt)_2\}(CO)_6(PCy_3)]$ (**4e**)	2037 (w), 2002 (m), 1963 (vs), 1945 (m), 1913 (m)

[a] Recorded in petroleum ether solution, unless otherwise stated. [b] Data recorded in tetrahydrofuran solution, taken from ref 8. [c] Recorded in tetrahydrofuran solution

Table 2. $^{31}P\{^1H\}$ NMR Data for New Compounds[a]



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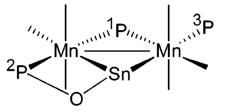

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	δ(P)/ppm			J(PP)/Hz		
compd	P1	P2	P3	J(12)	J(13)	J(2Sn)
1[b]	419.3	153.2		60		
3a	379.3	143.0		<10[c]		253
3b	375.3	144.7		<10[c]		314
4a	375.2	143.1	72.8	7	44	258
4b	375.1	143.4	69.8	7	44	272
4c	371.7	144.4	71.7	7	44	327
4d	378.9	145.9	76.8	<10[c]	44	316
4e	380.9	145.9	66.1	<10[c]	48	323

[a] Measured at 121.5 MHz, in CD_2Cl_2 solution at room temperature, unless otherwise stated; coupling constants (*J*) in Hz; labeling according to the figure; *J*(2Sn) refers to the average coupling between P2 and the ^{119}Sn and ^{117}Sn isotopes. [b] Data recorded in tetrahydrofuran solution, taken from ref 9. [c] Upper limit as estimated from the line width of the resonances involved.

Table 3. Selected Bond Lengths [Å] and Angles [deg] for Compound 4d

Mn(1)−Mn(2)	3.0698(19)	Sn−O(9)	2.245(6)
Sn−Mn(1)	2.7268(16)	Sn−Mn(2)	2.7878(15)
Sn−C(24)	2.172(5)	Sn−C(30)	2.165(5)
Mn(1)−P(1)	2.233(3)	Mn(2)−P(1)	2.247(3)
Mn(1)−P(2)	2.264(3)	Mn(2)−P(3)	2.337(3)
Mn(1)−C(1)	1.794(10)	Mn(2)−C(4)	1.806(10)
Mn(1)−C(2)	1.790(11)	Mn(2)−C(5)	1.863(11)
Mn(1)−C(3)	1.846(12)	Mn(2)−C(6)	1.810(10)
P(1)−O(7)	1.611(6)	P(1)−O(8)	1.605(7)
P(2)−O(9)	1.506(7)	P(2)−O(10)	1.605(7)
P(2)−O(11)	1.560(7)		
O(9)−Sn−Mn(2)	145.28(16)	P(1)−Mn(1)−Sn	103.95(7)
C(30)−Sn−Mn(1)	126.3(2)	P(2)−Mn(1)−Sn	70.65(7)
C(24)−Sn−Mn(1)	127.4(2)	P(1)−Mn(2)−Sn	101.69(8)
C(30)−Sn−C(24)	104.5(3)	P(3)−Mn(2)−Sn	159.23(8)
O(9)−Sn−Mn(1)	77.72(16)	P(1)−Mn(2)−P(3)	98.87(10)
Mn(1)−Sn−Mn(2)	67.64(4)	Mn(1)−P(1)−Mn(2)	86.49(9)
O(9)−P(2)−Mn(1)	111.3(3)	P(2)−O(9)−Sn	99.9(3)

Table 4. Crystallographic Data for $4d{\cdot}0.5CH_2Cl_2$

empirical formula	$C_{35.5}H_{52}ClMn_2O_{11}P_3Sn$
fw	1011.70
temperature (K)	293(2)
wavelength (Å)	0.71073
cryst syst, space group	monoclinic, *C*2/*c*
a (Å)	12.367(4)
b (Å)	20.625(5)
c (Å)	35.067(7)
α (deg)	90
β (deg)	91.24(2)
γ (deg)	90
volume (Å^3)	8942(4)
Z, calcd density (Mg m^{-3})	8, 1.503
abs coeff (mm^{-1})	1.329
F(000)	4120
cryst size (mm)	0.40 × 0.35 × 0.30
θ range for data collection (deg)	3.04 to 25.00
index ranges	$-14 \le h \le 14$, $0 \le k \le 24$, $0 \le l \le 41$
no. of reflns collected/unique	7917/7786 [*R*(int) = 0.0720]
no. of data/restraints/params	7786/0/466
goodness-of-fit on F^2	1.153
final *R* indices [$I > 2\sigma(I)$] (R_1, wR_2)[a]	0.0669, 0.1810
R indices (all data) (R_1, wR_2)[a]	0.1332, 0.2217
largest diff peak and hole (e Å^{-3})	0.784 and −0.749

[a] $GOF = [\sum[w(F_o^2 - F_c^2)^2]/(n-p)]^{1/2}$, $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$, $wR_2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = [\max(F_o^2,0) + 2F_c^2]/3$.

however, the tin atom of the (diethylphosphonate)dichlorostannyl group is bonded to a single metal center, as usually found for stannyl ligands. In contrast, the stannyl group in compound **4d** bridges the manganese atoms in a similar way to a hydride ligand. In fact, the Mn−Mn distance in **4d** (3.070(2) Å) is not much longer than that found in the isoelectronic phosphide hydride complex $[Mn_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_8]$ (ca. 2.95 Å)[12] and is comparable to those measured in the dimanganese−gold clusters $[Mn_2(\mu\text{-}AuPPh_3)(\mu\text{-}PPh_2)(CO)_8]$ (3.066(8) Å)[12b] and $[Mn_2(\mu\text{-}AuPPh_3)(\mu\text{-}Br)(CO)_6\{\mu\text{-}(EtO)_2POP(OEt)_2\}]$ (3.090(3) Å).[13] Indeed, the intermetallic Mn_2Sn interaction in **4d** can be properly described as a 3c−2e bond. In agreement with this, the Mn−Sn lengths in **4d** [Mn(1)−Sn = 2.727(2), Mn(2)−Sn = 2.788(2) Å] are significantly longer than those measured for normal (2c−2e) Mn−Sn bonds. For example, the mononuclear complexes $[Mn(SnR_3)(CO)_5]$ display Mn−Sn lengths in the range 2.65−2.69 Å,[14] and the bis(stannylene) dimanganese complex $[Mn_2(\mu\text{-}SnPh_2)_2(CO)_6\{\mu\text{-}(EtO)_2POP(OEt)_2\}]$ displays even shorter Mn−Sn distances (average value 2.61 Å, with Mn−Mn = 3.1045(5) Å).[15]

The rest of the internuclear distances in **4d** can be considered as normal for the corresponding bonds, except for the phosphonate O−Sn length. The value of the latter length, 2.245(6) Å, is significantly greater than the corresponding value in the above-mentioned dimolybdenum complex (Sn−O = 2.11(3) Å).[11] This could reflect the presence of some stress in the four-membered

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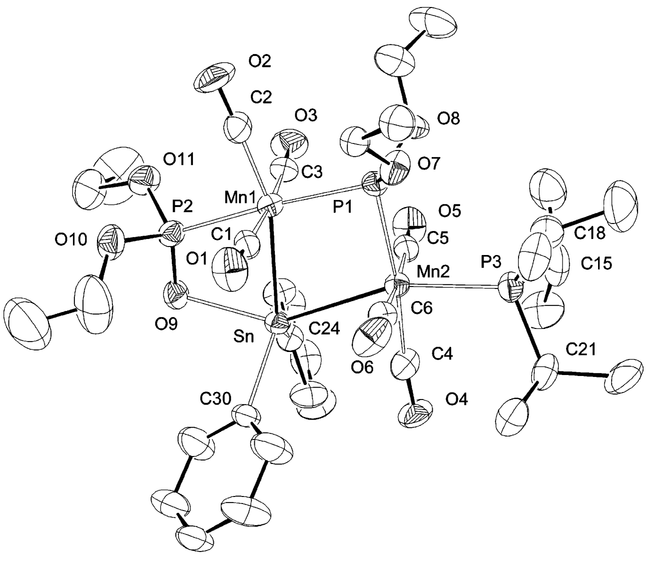

Figure 1. Molecular structure of compound **4d**. Ellipsoids represent 30% probability. For clarity the H atoms are omitted and only one image of the disordered ethyl groups is represented.

Mn−P−O−Sn ring present in compound **4d**, to be compared with the five-membered Mo−P−O−Sn−Mo ring present in the dimolybdenum compound.

The spectroscopic data in solution for **4d** are fully consistent with its solid state structure. Moreover, both the C−O stretching bands and the ^{31}P NMR resonances for all five compounds **4a**−**e** are very similar (Tables 1 and 2), thus suggesting that all these compounds have the same structure in solution. We have already mentioned that the presence of two *mer*-Mn(CO)$_3$ oscillators in these molecules is reflected in the weak to medium intensity of the two high-frequency C−O stretches in each case. In addition, the P−P couplings between the tertiary phosphine and the diethoxyphosphide ligand are almost identical in all compounds **4** (ca. 44 Hz), which is indicative of the retention of the same relative arrangement (cis) of the P atoms in these compounds. Finally, the fact that the phosphonate and phosphine ligands remain in the Mn$_2$Sn plane implies that the latter is a plane of symmetry of the molecule, thus explaining the chemical equivalence of the ethoxy groups at either the phosphonate or phosphide ligands, as deduced from the ^{1}H NMR spectra of these compounds (see Experimental Section). The low values of the P−P coupling between the phosphide and phosphonate groups in compounds **4** (J(12) in Table 1) are unexpected for two P atoms arranged trans to each other. However, it must be kept in mind that, because of the presence of significant Mn−Mn bonding interaction, the observed P−P coupling must be mainly due to both two-bond (^2J(P−Mn−P)) and three-bond (^3J(P−Mn−Mn−P)) contributions. Since ^2J and ^3J couplings are usually of comparable magnitude but opposite in sign,[16] their simultaneous operation in a molecule can lead to partial cancellation and low resulting coupling. If no Mn−Mn bonding interaction was present in compounds **4**, then the observed P−P coupling would be mainly due to the ^2J contribution and therefore should be large. In agreement with this, trans P−P couplings in the range 40−100 Hz are found between the diethoxyphosphide and phosphine ligands in the related dimanganese complexes [Mn$_2${μ-OP(OEt)$_2$}{μ-P(OEt)$_2$}(CO)$_x$(L)] (L = PR$_3$ (x = 7) or R$_2$PCH$_2$PR$_2$ (x = 6)), in which no Mn−Mn bond is present (Mn−Mn separation ca. 3.92 Å).[9]

The heptacarbonyl compounds **3a**,**b** display ^{31}P NMR resonances similar to those of compounds **4**, and are thus assumed to have the same structure, after replacing the phosphine ligand by a carbonyl. This generates a *cis*-Mn(CO)$_4$ oscillator, which is clearly denoted by the appearance in the IR spectrum of a medium-intensity C−O stretching band at higher frequency (ca. 2070 cm^{-1}), as found for the hepta- and octocarbonyl compounds [Mn$_2${μ-OP(OEt)$_2$}{μ-P(OEt)$_2$}(CO)$_7$L] (L = CO, PR$_3$).[9]

In summary, we have shown that the reaction between the anion **1** and SnR$_2$Cl$_2$ does not lead to the expected stannylene cluster **2** as a stable product. Instead, Sn−O coupling between the stannylene and phosphonate groups occurs rapidly at room temperature, this being perhaps driven by the high strength of the new Sn−O bond thus created. This reductive coupling generates a two-electron deficiency at the dimanganese center, which is initially compensated by the coordination of a molecule of solvent to give unstable solvates, which then experience progressive carbonylation to give the heptacarbonyl complexes **3** or, if a phosphine ligand is present, the hexacarbonyl derivatives **4**. Both **3** and **4** are electron-precise, stable complexes displaying a stannyl bridging group involved in a 3c−2e interaction with the dimanganese center.

Experimental Section

General Considerations. All manipulations and reactions were carried out using standard Schlenk techniques under an atmosphere of dry, oxygen-free nitrogen. Solvents were purified according to standard literature procedures[17] and distilled under nitrogen prior to use. Petroleum ether refers to that fraction distilling in the range 60−65 °C. Tetrahydrofuran solutions of Na$_2$[Mn$_2${μ-OP(OEt)$_2$}{μ-P(OEt)$_2$}(CO)$_6$] (**1**) were prepared in situ as described in ref 9 and used assuming a 100% yield. Other reagents were obtained from the usual commercial suppliers and used without further purification. Filtrations were carried out using a cannula or, more generally, through diatomaceous earth, and aluminum oxide (alumina) for column chromatography was deactivated by appropriate addition of water to the commercial material (Aldrich, neutral, activity I). Low-temperature chromatographic separations were carried out using jacketed columns refrigerated by a closed 2-propanol circuit kept at the desired temperature with a cryostat. NMR spectra were recorded at 300.13 MHz (^{1}H), 121.50 MHz (^{31}P{^{1}H}), and 75.47 MHz (^{13}C{^{1}H}), at room temperature unless otherwise stated. Chemical shifts (δ) are given in ppm, relative to internal TMS (^{1}H, ^{13}C) or external 85% H$_3$PO$_4$ aqueous solution (^{31}P), with positive values for frequencies higher than that of the reference. Coupling constants (J) are given in hertz, and J_{HSn} refers to the average coupling between ^{1}H and the ^{119}Sn and ^{117}Sn isotopes (not resolved).

Preparation of [Mn$_2${μ-*Sn*:*Sn*,*P*-SnBu$_2$OP(OEt)$_2$}{μ-P(OEt)$_2$}(CO)$_7$] (3a). A tetrahydrofuran solution (15 mL) containing ca. 0.097 mmol of compound **1** was transferred into

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[16] Jameson, C. J. In *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*; Verkade, J. G., Quin, L. D., Eds.; VCH: New York, 1987; Chapter 6.

[17] Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*; Pergamon Press: Oxford, U.K., 1988.

a Schlenk flask containing 0.030 g (0.1 mmol) of $SnBu_2Cl_2$ cooled at −80 °C. The mixture was then allowed to reach room temperature for 1 h to give a red-orange solution. The solvent was then removed under vacuum, and the residue was redissolved in toluene (10 mL) and further stirred at room temperature for 2 h. Then the solvent was again removed, the residue was extracted with petroleum ether, and the extracts were chromatographed on an alumina column (activity IV) at −45 °C. Elution with dichloromethane/petroleum ether (1/3) gave an orange fraction, which, after removal of solvents under vacuum, yielded compound **3a** (0.045 g, 58%) as an oily orange residue. All attempts to crystallize this material were unsuccessful due to its very high solubility in all common organic solvents. ^1H NMR (CD_2Cl_2): δ 4.36 (m, 4H, OCH_2), 4.15, 4.01 (2 × m, 2 × 2H, OCH_2), 1.87−1.64 (m, 8H, $SnCH_2CH_2$), 1.45 (m, 4H, CH_2), 1.44, 1.32 (2 × t, $J_{HH} = 7$, 2 × 6H, OCH_2CH_3), 0.94 (t, $J_{HH} = 7$, 6H, CH_3).

Preparation of [Mn_2{μ-*Sn*:*Sn*,*P*-$SnPh_2OP(OEt)_2${μ-$P(OEt)_2$}$(CO)_7$] (3b). The procedure is completely analogous to that described for **3a**, but using $SnPh_2Cl_2$ (0.039 g, 0.113 mmol) and starting from ca. 0.113 mmol of compound **1**. An orange fraction was eluted by using a dichloromethane/petroleum ether (1/2) mixture, which yielded compound **3b** (0.040 g, 43%) as an orange microcrystalline solid. Anal. Calcd for $C_{27}H_{30}Mn_2O_{12}P_2Sn$: C, 38.74; H, 3.61. Found: C, 38.87; H, 3.58. ^1H NMR (CD_2Cl_2): δ 7.86−7.26 (m, 10H, Ph), 4.42 (m, 4H, OCH_2), 4.22, 4.05 (2 × m, 2 × 2H, OCH_2), 1.45, 1.32 (2 × t, $J_{HH} = 7$, 2 × 6H, CH_3).

Preparation of [Mn_2{μ-*Sn*:*Sn*,*P*-$SnBu_2OP(OEt)_2${μ-$P(OEt)_2$}$(CO)_6(PPh_3)$] (4a). A tetrahydrofuran solution (15 mL) containing ca. 0.11 mmol of compound **1** was transferred into a Schlenk flask containing $SnBu_2Cl_2$ (0.034 g, 0.11 mmol) and PPh_3 (0.029 g, 0.11 mmol) cooled at −80 °C. The mixture was then allowed to react in tetrahydrofuran for 15 min and then in toluene for 2 h as described for **3a**, and the reaction products were separated analogously by chromatography on alumina (activity IV) at −45 °C. An orange fraction was collected using dichloromethane/petroleum ether (1/3), which contained a small amount of compound **3a**. Elution with dichloromethane/petroleum ether (2/1) then gave an orange fraction, which yielded compound **4a** (0.053 g, 47%) as an orange microcrystalline solid. Anal. Calcd for $C_{40}H_{53}Mn_2O_{11}P_3Sn$: C, 46.58; H, 5.18. Found: C, 46.61; H, 4.98. ^1H NMR (CD_2Cl_2): δ 7.64−7.40 (m, 15H, Ph), 4.32−3.88 (m, 8H, OCH_2), 1.95−1.72 (m, 8H, $SnCH_2CH_2$), 1.45 (m, 4H, CH_2), 1.29, 1.18 (2 × t, $J_{HH} = 7$, 2 × 6H, OCH_2CH_3), 0.95 (t, $J_{HH} = 7$, 6H, CH_3).

Preparation of [Mn_2{μ-*Sn*:*Sn*,*P*-$SnBu_2OP(OEt)_2${μ-$P(OEt)_2$}$(CO)_6${P(*p*-tol)$_3$}] (4b). The procedure is completely analogous to that described for **4a**, but using P(*p*-tol)$_3$ (0.034 g, 0.11 mmol) instead. In that way, compound **4b** (0052 g, 44%) was obtained as an orange microcrystalline solid. Anal. Calcd for $C_{43}H_{59}Mn_2O_{11}P_3Sn$: C, 48.10; H, 5.54. Found: C, 47.83; H, 5.30. ^1H NMR (CD_2Cl_2): δ 7.46 (dd, $J_{HP} = 11$, $J_{HH} = 8$, 6H, PC_6H_4), 7.20 (dd, $J_{HH} = 8$, $J_{HP} = 2$, 6H, PC_6H_4), 4.19−3.88 (m, 8H, OCH_2), 1.95−1.73 (m, 8H, $SnCH_2CH_2$), 1.44 (m, 4H, CH_2), 1.29, 1.18 (2 × t, $J_{HH} = 7$, 2 × 6H, OCH_2CH_3), 0.95 (t, $J_{HH} = 7$, 6H, CH_3).

Preparation of [Mn_2{μ-*Sn*:*Sn*,*P*-$SnPh_2OP(OEt)_2${μ-$P(OEt)_2$}$(CO)_6(PPh_3)$] (4c). The procedure is completely analogous to that described for **4a**, but using $SnPh_2Cl_2$ (0.038 g, 0.11 mmol) instead. Elution with dichloromethane/petroleum ether (1/1) gave an orange fraction containing a mixture of compounds, which was discarded. Elution with dichloromethane/petroleum ether (3/1) gave an orange fraction, which yielded compound **4c** (0.050 g, 44%) as an orange microcrystalline solid. Anal. Calcd for $C_{44}H_{45}Mn_2O_{11}P_3Sn$: C, 49.33; H, 4.23. Found: C, 50.03; H, 4.36. ^1H NMR (CD_2Cl_2): δ 7.96−7.35 (m, 25H, Ph), 4.06−3.98 (m, 8H, OCH_2), 1.26, 1.20 (2 × t, $J_{HH} = 7$, 2 × 6H, CH_3).

Preparation of [Mn_2{μ-*Sn*:*Sn*,*P*-$SnPh_2OP(OEt)_2${μ-$P(OEt)_2$}$(CO)_6(P^iPr_3)$] (4d). The procedure is analogous to that described for **4a**, but using $SnPh_2Cl_2$ (0.038 g, 0.11 mmol) and P^iPr_3 (20 μL, 0.11 mmol) instead. Elution with dichloromethane/petroleum ether (1/2) gave a minor fraction containing some [Mn_2{μ-$OP(OEt)_2$}{μ-$P(OEt)_2$}$(CO)_7(P^iPr_3)$] (see text). Elution with dichloromethane/petroleum ether (3/1) gave an orange fraction, which yielded compound **4d** (0.040 g, 38%) as an orange microcrystalline solid. The crystals used in the X-ray study were grown by slow diffusion of a layer of petroleum ether into a dichloromethane solution of the complex at −20 °C. Anal. Calcd for $C_{35}H_{51}Mn_2O_{11}P_3Sn$: C, 43.37; H, 5.31. Found: C, 42.91; H, 5.05. ^1H NMR (CD_2Cl_2): δ 7.94 (d, $J_{HH} = 7$, $J_{HSn} = 50$, 4H, SnPh), 7.38 (m, 6H, Ph), 4.52−3.93 (m, 8H, OCH_2), 2.72 (m, 3H, PCH), 1.38−1.27 (m, 30H, CH_3).

Preparation of [Mn_2{μ-*Sn*:*Sn*,*P*-$SnPh_2OP(OEt)_2${μ-$P(OEt)_2$}$(CO)_6(PCy_3)$] (4e). The procedure is analogous to that described for **4a**, but using $SnPh_2Cl_2$ (0.038 g, 0.11 mmol) and PCy_3 (0.026 g, 0.11 mmol) instead. Elution with dichloromethane/petroleum ether (1/2) gave a yellow-orange fraction, which gave 0.025 g (26%) of the known complex [Mn_2{μ-$OP(OEt)_2$}{μ-$P(OEt)_2$}$(CO)_7(PCy_3)$].[8] Elution with dichloromethane/petroleum ether (3/1) gave an orange fraction, which yielded compound **4e** (0.035 g, 37%) as an orange microcrystalline solid. Anal. Calcd for $C_{44}H_{63}Mn_2O_{11}P_3Sn$: C, 48.50; H, 5.83. Found: C, 48.13; H, 5.60. ^1H NMR (CD_2Cl_2): δ 7.92 (dd, $J_{HH} = 8, 2$, $J_{HSn} = 52$, 4H, SnPh), 7.42−7.29 (m, 6H, Ph), 4.48, 4.35, 4.16, 4.03 (4 × m, 4 × 2H, OCH_2), 2.40 (m, 3H, PCH), 1.94−1.20 (m, 30H, CH_2), 1.38, 1.30 (2 × t, $J_{HH} = 7$, 2 × 6H, CH_3).

X-ray Structure Determination for Compound 4d·0.5CH$_2$Cl$_2$. Crystals of compound **4d**·0.5CH_2Cl_2 were obtained by crystallization from dichloromethane/petroleum ether as described above, and a suitable sized crystal in a Lindemann tube was mounted on a Philips PW 1100 diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Crystallographic and experimental details are summarized in Table 4. A semiempirical method of absorption correction was applied (maximum and minimum values for the transmission coefficient were 1.000 and 0.790).[18] The structure was solved by direct methods (SIR92)[19] and refined by least-squares against F_o^2 (SHELXL-97).[20] All the non-hydrogen atoms were refined anisotropically except the C(7A), C(7B), C(8A), and C(8B) carbon atoms. These last atoms together with C(14A) and C14B) were found to be disordered in two positions and refined with an sof of 0.5. All the hydrogen atoms were introduced from geometrical calculations and refined using a riding model. The programs PARST[21] and ORTEP[22] were also used.

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Supporting Information Available: Crystallographic data for compound **4d** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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