Reactivity of 8e S_2CPR_3 Bridges with Nucleophiles: Formation of Phosphoniodithioformate Esters as Novel 7e Bridging Ligands. X-ray Structures of $NEt_4[Mn_2(CO)_6(\mu\text{-}S_2CH)]$ and $[Mn_2(CO)_6(\mu\text{-}H)\{\mu\text{-}ClCH_2SC(S)P(c\text{-}C_6H_{11})_3\}]$

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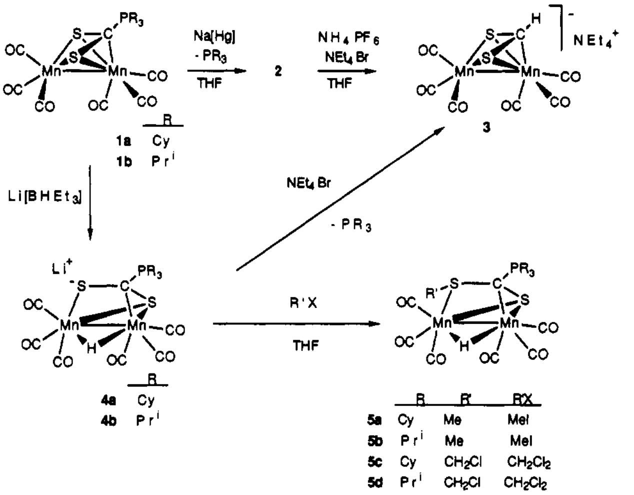
Summary: Reduction of $[Mn_2(CO)_6(\mu\text{-}S_2CPR_3)]$ (**1**) with Na[Hg] produces a highly reactive anion, which, upon protonation, gives the dithioformate complex $NEt_4[Mn_2(CO)_6(\mu\text{-}S_2CH)]$ (**3**). When treated with $Li[BHEt_3]$, compounds **1** undergo hydride addition on the Mn–Mn bond, to afford the anions $[Mn_2(CO)_6(\mu\text{-}H)(\mu\text{-}S_2CPR_3)]^-$ (**4**), which rearrange spontaneously to the dithioformate complex **3**, with loss of PR_3. Freshly prepared solutions of the anionic compounds **4** can undergo electrophilic addition of alkyl halides to one sulfur atom to give neutral $[Mn_2(CO)_6(\mu\text{-}H)(\mu\text{-}R'SC(S)PR_3)]$ (**5**), which contain the first examples of phosphoniodithioformate esters $R'SC(S)PR_3$ acting as bridging ligands.

It is well-known that chelate S_2CPR_3 ligands show electrophilic character on the central carbon, being able to undergo addition of hydride ion, leading to the formation of coordinated S_2CH^- or $S_2C(H)PR_3^-$ ligands.[1,2] As an extension of our previous work[2] on hydride additions to mononuclear manganese(I) complexes containing chelating S_2CPR_3 ligands, we have started to study the reactivity of dinuclear Mn(0) complexes containing $\eta^2(S,S'),\eta^3(S,C,S')$-$S_2CPR_3$ bridging ligands of 8e. Here we report some preliminary results that have led to the observation of a new reactivity of the coordinated S_2CPR_3 ligands and to the preparation of the first complexes containing formally cationic $R'SC(S)PR_3^+$ bridging ligands.

Reaction of compounds $[Mn_2(CO)_6(\mu\text{-}S_2CPR_3)]$ (**1a**,**b** in Scheme I)[3] with excess 1% sodium amalgam in THF at room temperature produces deep brown, highly air-sensitive solutions, whose IR spectra exhibit ν(CO) bands at very low frequencies[4] when compared to those of the parent compounds **1a**,**b**. This suggests the formation of

Scheme I



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(4) Analytical and spectroscopic data are as follows. IR spectra (cm^{-1}) were taken in THF solutions. $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2 solutions) chemical shifts are in ppm to higher frequency of external 85% H_3PO_4. ^1H (300 MHz, $CDCl_3$) and $^{13}C\{^1H\}$ NMR (75.5 MHz, CD_2Cl_2) chemical shifts are in ppm to higher frequency to internal TMS. Due to the limited solubility of compounds **5a–d**, it was not possible to observe, in their $^{13}C\{^1H\}$ NMR spectra, the signals (expected to be weak) corresponding to the carbonyl groups and to the central carbon of the R'SC(S)PR_3 ligands. Data are as follows for **2**. IR: ν(CO) 1987 m, 1946 vs, 1878 s, 1959 (sh), 1841 (sh). Data are as follows for **3**. Anal. Found: C, 37.37; H, 4.37; N, 2.95. Calcd for $C_{15}H_{21}Mn_2NO_6S_2$: C, 37.12; H, 4.36; N, 2.89. IR: ν(CO) 2004 m, 1956 vs, 1897 s, 1874 w. ^1H NMR: δ 6.07 (s, $S_2C\mathit{H}$), 3.48 (m, $NC\mathit{H}_2CH_3$), 1.62 (m, $NCH_2C\mathit{H}_3$). $^{13}C\{^1H\}$ NMR: 230.6 and 226.4 (3 + 3 *C*O), 99.8 (s, $S_2\mathit{C}H$), 55.9 (s, $N\mathit{C}H_2$), 7.7 (s, $NCH_2\mathit{C}H_3$). Data are as follows for **4a**. IR ν(CO) 1988 s, 1951 vs, 1880 vs, 1839 m. Data are as follows for **4b**. IR: ν(CO) 1989 s, 1951 vs, 1881 vs, 1841 m. Data are as follows for **5a**. Anal. Found: C, 47.83; H, 5.82. Calcd for $C_{26}H_{37}Mn_2O_6PS_2$: C, 48.00; H, 5.70. IR: ν(CO) 2022 s, 1983 vs, 1929 s, 1917 s, 1900 m, 1880 m. ^1H NMR: δ 2.20 [s, 3 H, $SC\mathit{H}_3$], 2.21–1.32 [m, 33 H, $C_6\mathit{H}_{11}$], –13.45 (s, 1 H, μ-H). $^{31}P\{^1H\}$ NMR: δ 33.2. $^{13}C\{^1H\}$ NMR: δ 35.7 (s, $S\mathit{C}H_3$), 33.1 [d, *J*(PC) = 39, C^1 of C_6H_{11}], 28.2 (s, C^3 and C^5 of C_6H_{11}), 27.1 and 26.9 [d, *J*(PC) = 11, C^2 and C^6 of C_6H_{11}], 25.7 (s, C^4 of C_6H_{11}]. Data are as follows for **5b**. Anal. Found: C, 38.27; H, 4.49. Calcd for $C_{17}H_{25}Mn_2O_6PS_2$: C, 38.50; H, 4.75. IR: ν(CO) 2022 s, 1984 vs, 1930 s, 1918 s, 1901 m, 1883 m. ^1H NMR: δ 2.55 [m, 3 H, $PC\mathit{H}(CH_3)_2$], 2.16 [s, 3 H, $SC\mathit{H}_3$], 1.57–1.44 [m, 18 H, $PCH(C\mathit{H}_3)_2$], –13.43 (s, 1 H, μ-H). $^{31}P\{^1H\}$ NMR: δ 41.1. $^{13}C\{^1H\}$ NMR: δ 35.3 (s, $S\mathit{C}H_3$), 23.4 [d, *J*(PC) = 41, $P\mathit{C}H(CH_3)_2$], 18.3 [d, *J*(PC) = 18, $PCH(\mathit{C}H_3)_2$]. Data are as follows for **5c**. Anal. Found: C, 45.30; H, 5.52. Calcd for $C_{26}H_{36}ClMn_2O_6PS_2$: C, 45.59; H, 5.30. IR: ν(CO) 2025 s, 1987 vs, 1934 s, 1924 s, 1905 m, 1984 m. ^1H NMR: δ 4.32 [s, 2 H, $SC\mathit{H}_2Cl$], 2.47–1.34 [m, 33 H, $C_6\mathit{H}_{11}$], –13.77 (s, 1 H, μ-H). $^{31}P\{^1H\}$ NMR: δ 32.9. $^{13}C\{^1H\}$ NMR: δ 61.0 (s, $S\mathit{C}H_2Cl$), 34.3 [d, *J*(PC) = 38, C^1 of C_6H_{11}], 28.5 (s, C^3 and C^5 of C_6H_{11}), 27.1 and 26.8 [d, *J*(PC) = 11, C^2 and C^6 of C_6H_{11}], 25.8 (s, C^4 of C_6H_{11}]. Data are as follows for **5d**. Anal. Found: C, 36.00; H, 4.31. Calcd for $C_{17}H_{24}ClMn_2O_6PS_2$: C, 36.15; H, 4.28. IR: ν(CO) 2026 s, 1988 vs, 1935 s, 1924 s, 1905 m, 1987 m. ^1H NMR: δ 4.31 [s, 2 H, $SC\mathit{H}_2Cl$], 2.66 [m, 3 H, $PC\mathit{H}(CH_3)_2$], 1.57–1.43 [m, 18 H, $PCH(C\mathit{H}_3)_2$], –13.75 (s, 1 H, μ-H). $^{31}P\{^1H\}$ NMR: δ 41.6. $^{13}C\{^1H\}$ NMR: δ 61.1 (s, $S\mathit{C}H_2Cl$), 23.2 [d, *J*(PC) = 40, $P\mathit{C}H(CH_3)_2$], 18.7 [d, *J*(PC) = 17, $PCH(\mathit{C}H_3)_2$].

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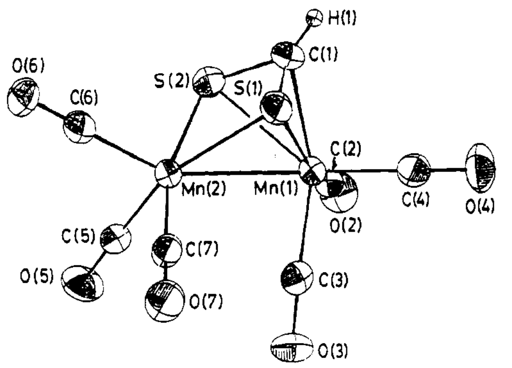

Figure 1. Perspective view of the anion $[Mn_2(CO)_6(\mu\text{-}S_2CH)]^-$ in **3**, showing the atom numbering. Selected bond distance (Å) and angles (deg): Mn(1)-Mn(2) = 2.674 (2), Mn(1)-S(1) = 2.318 (3), Mn(1)-S(2) = 2.358 (3), Mn(1)-C(1) = 2.02 (1), Mn(2)-S(1) = 2.280 (3), Mn(2)-S(2) = 2.290 (3), S(1)-C(1) = 1.72 (1), S(2)-C(1) = 1.72 (1), distances Mn-C(carbonyl) range from 1.77 (2) to 1.79 (1); S(1)-C(1)-S(2) = 107.0 (6), S(1)-Mn(1)-S(2) = 72.4 (1), S(1)-Mn(2)-S(2) = 74.4 (1), angles C(carbonyl)-Mn-C(carbonyl) range from 90.4 (4) to 96.9 (4).

an anionic species **2**. Addition of NH_4PF_6 (excess) produces a bright red solution from which red crystals of the dithioformate compound $NEt_4[Mn_2(CO)_6(\mu\text{-}S_2CH)]$ (**3**) can be obtained after cation exchange with NEt_4Br.[5] The result of an X-ray determination,[6] carried out on a crystal of **3**, can be seen in Figure 1. The anion in **3** consists of a $Mn_2(CO)_6$ unit bridged by a dithioformate ligand in a $\eta^2(S,S'),\eta^3(S,C,S')$ fashion analogous to that proposed for the complex $[CpMo(S_2CH_2)(S_2CH)MoCp]SO_3CF_3$.[7] In the structure of **3**, the distances within the Mn_2S_2C core are very close to those found in the parent compound **1a**.[3] The Mn-Mn distance [2.674 (2) Å] is slightly shorter than that in **1a** [2.737 (1) Å] and falls well into the range expected for a metal-metal bond order of 1. The formation of **3** upon protonation of the intermediate species **2** suggests that the latter would be a dianionic species $[Mn_2(CO)_6(\mu\text{-}S_2C)]^{2-}$ formed by reductive cleavage of the phosphorus-carbon bond in the parent compound **1**. This is confirmed by the $^{31}P\{^1H\}$ NMR monitoring of the reaction between **1a** and Na[Hg] (in THF; D_2O as external lock), which shows the production of free $P(C_6H_{11})_3$ (at ca. δ 10 ppm). The reductive cleavage of a phosphorus-carbon bond of a chelating S_2CPEt_3 ligand in the mononuclear complex $[(triphos)Co(S_2CPEt_3)](BPh_4)_2$ has been reported previously.[1b] Unfortunately, all the attempts to isolate **2** as NEt_4^+ or PPN^+ salts were unsuccessful, leading to extensive decomposition.

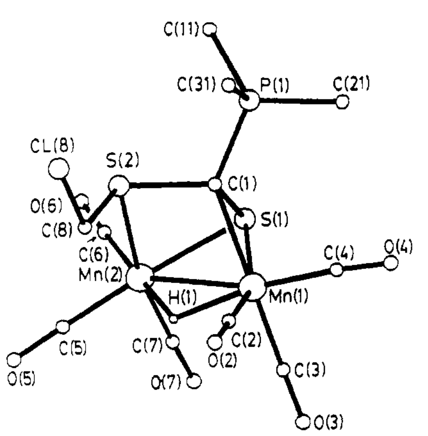

Figure 2. Perspective view of $[Mn_2(CO)_6(\mu\text{-}H)\{\mu\text{-}ClCH_2SC(S)\text{-}P(c\text{-}C_6H_{11})_3\}]$ (**5c**), showing the atom numbering. Carbon atoms C^2–C^6 of the cyclohexyl rings have been omitted for clarity. Selected bond distances (Å) and angles (deg): Mn(1)-Mn(2) = 2.866 (1), Mn(1)-S(1) = 2.235 (1), Mn(1)-C(1) = 2.136 (4), Mn(2)-S(1) = 2.304 (1), Mn(2)-S(2) = 2.352 (1), distances Mn-C(carbonyl) range from 1.781 (6) to 1.803 (5); Mn(1)-S(1)-Mn(2) = 78.30 (1), S(2)-C(1)-Mn(1) = 110.2 (2), S(1)-C(1)-S(2) = 102.9 (2), angles C(carbonyl)-Mn-C(carbonyl) range from 88.2 (2) to 95.0 (2).

On the other hand, compounds **1a,b** react with $Li[BHEt_3]$ in THF to give a red solution, whose IR spectra[4] exhibit ν(CO) bands at frequencies lower than those of the parent compounds. The infrared spectra of these solutions do not change immediately upon addition of H_2O and NEt_4Br, but on standing at room temperature, the solutions slowly transform to show ultimately the spectrum of the dithioformate complex **3**, which can be isolated in 65% yield.[8] Monitoring of the process by $^{31}P\{^1H\}$ NMR spectroscopy at room temperature shows, within 15 min after the addition of $Li[BHEt_3]$, the rapid change of the phosphorus signal from δ 31.9 ppm (for **1a**) to δ 24.1 ppm (attributable to **4a**) and then, over a period of 1 h, the slow release of free $P(C_6H_{11})_3$. Simultaneously, the ^1H NMR spectra of the mixtures (C_6D_6 as solvent) show a signal in the hydride region (δ −12.01 ppm), which slowly disappears as **4a** is transformed into the dithioformate complex **3** (S_2CH signal at δ 6.02). The initial attack of H^- to the Mn-Mn bond is in contrast with the reactivity previously observed for complexes with chelating S_2CPR_3, in which the nucleophilic attack was directed to the carbon atom of the S_2CPR_3 ligand. The transformation of **4** into **3** occurs even when the excess of $Li[BHEt_3]$ has been hydrolyzed with water. This suggests that **3** is formed by a process involving the migration of the bridging hydrido ligand in **4** to the central carbon of $S_2CP(C_6H_{11})_3$, with the concurrent loss of phosphine. A somewhat related mi-

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(5) **1a** (0.1 g, 0.158 mmol) was stirred with excess 1% Na[Hg] for 30 min in THF (20 mL), and the solution was transferred under nitrogen to another flask. NH_4PF_6 (0.05 g, excess) and NEt_4Br (0.05 g, excess) were added, and after the solution was stirred for 15 min, the solvent was evaporated in vacuo. The orange-red residue was dissolved in CH_2Cl_2/hexane (1:1), and the mixture was filtered through a short column of alumina (activity III). The filtered solution was concentrated in vacuo and cooled (−20 °C, overnight) to give red crystals of **3** (0.069 g, 90%). Same treatment of **1b** gave **3** in similar yield.

(6) Crystal data for compound **3**: $C_{15}H_{21}Mn_2NO_6S_2$, $M = 485.33$; orthorhombic, space group $P22_12_1$ (nonstandard setting of $P2_12_12$, No. 17); $a = 7.626$ (3), $b = 15.414$ (3), $c = 17.605$ (5) Å; $V = 2069$ (1) Å^3; $D_c = 1.56$ g cm^{-3}; $Z = 4$; $F(000) = 992$; λ(Mo Kα) = 0.710 69 Å; μ(Mo Kα) = 13.94 cm^{-1}; room temperature; red tabular crystal (0.2 × 0.3 × 0.4 mm); Enraf-Nonius CAD4 diffractometer, ω–2θ scan technique; 2095 reflections measured ($0 \le \theta \le 25°$), 1298 [$I \ge 3\sigma(I)$] used in the refinement; heavy atoms located from a Patterson synthesis and the remaining non H atoms by Fourier maps. All non-H atoms in the anion were refined anisotropically; those in NEt_4^+ were refined isotropically. The hydrogen atom on μ-S_2CH was located from a difference map and then refined isotropically; the remaining H atoms in the NEt_4 cation were geometrically positioned, with a fixed overall isotropic temperature factor of 0.08 Å^2. Two halves of the NEt_4 cation lie in different positions within the asymmetric unit, being related by one of the binary axes. Number of parameters = 200. $R = 0.035$ ($R_w = 0.038$). All calculations were performed with CRYSTALS.[13] Crystal data for compound **5c**: $C_{26}H_{36}ClMn_2O_6PS_2$, $M = 684.99$; triclinic, space group $P\bar{1}$; $a = 10.165$ (3), $b = 10.396$ (1), $c = 16.766$ (5) Å; $\alpha = 74.13$ (2), $\beta = 83.83$ (2), $\gamma = 63.03$ (1)°; $V = 1518$ (1) Å^3; $D_c = 1.498$ g cm^{-3}; $Z = 2$; $F(000) = 708$; λ(Mo Kα) = 0.710 73 Å; μ(Mo Kα) = 11.08 cm^{-1}; room temperature; yellow prismatic crystal (0.26 × 0.20 × 0.16 mm); 5529 reflections measured ($0 \le \theta \le 25°$), 3494 used in refinement [$I \ge 3\sigma(I)$]; heavy atoms located from a Patterson synthesis, remaining non-H atoms from Fourier maps; full-matrix least-squares refinement with SHELX76.[14] All non-H atoms were refined anisotropically. The bridging hydride was found from a difference map and refined isotropically. The remaining H atoms were geometrically positioned, with an overall isotropic temperature factor that was refined. Number of parameters = 363. Final $R = 0.038$ ($R_w = 0.040$).

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(8) **1a** was treated in THF (20 mL) with a 4-fold excess of $Li[BHEt_3]$, and the mixture was stirred for 1 h. The excess of $Li[BHEt_3]$ was hydrolyzed with water (0.2 mL). NEt_4Br was then added, and the solution was worked up as described in note 5. Yield: 70%.

gration of a hydride ion from the metal to the carbon atom of the S_2CPEt_3 ligand has been proposed to account for the formation of [Rh(triphos){$S_2C(H)PEt_3$}Cl] upon protonation of [Rh(triphos)(S_2CPEt_3)Cl].[1f]

When an alkyl halide is added to a freshly prepared solution of **4a**,**b**[9] the color changes readily from red to orange, and the IR spectra show the formation of the new compounds $[Mn_2(CO)_6(\mu\text{-}H)\{R'SC(S)PR_3\}]$ (**5a**–**d**) (see Scheme I) together with variable amounts of the dithioformate complex **3**. An X-ray determination, carried out on a crystal of **5c**,[6] reveals (Figure 2) that the chloromethyl group has been added to one of the sulfur atoms, producing the new ligand $ClCH_2SC(S)P(c\text{-}C_6H_{11})_3$, which bridges the two Mn atoms in a $\eta^2(S,S'),\eta^2(C,S')$ fashion. Additionally, one hydrido ligand acts also as a bridge between the two Mn atoms. The Mn(1)–Mn(2) distance of 2.866 (1) Å in **5c** is consistent with the presence of a Mn–Mn bond of order 1, and considering the H ligand as a 1-electron donor, the $(CO)_3Mn\text{-}Mn(CO)_3$ moiety must receive 7 electrons from the $R'SC(S)PR_3$ bridge in order to satisfy the EAN rule. Since complexes **5a**–**d** are produced by electrophilic addition of a group R^+ to the anion **4**, they can be alternatively viewed as consisting of a hydrido-bridged, dimanganese(0) moiety $[Mn_2(CO)_6(\mu\text{-}H)]^-$ attached to a positive charged $RSC(S)PR_3^+$ ligand of **6e**. In fact, S_2CPR_3 adducts can undergo electrophilic attack by alkyl halides to give unstable, cationic phosphonio dithioesters $[R'SC(S)PR_3]X$.[10] Neutral dithioesters R'SC(S)R have been used as ligands, or have been built within a bimetallic complex,[11] and two mononuclear compounds are known to contain the related ligand $CH_3SC(S)P(Ph)_2CH_2CH_2N(CH_2CH_2PPh_2)_2^+$.[12] However, to the best of our knowledge, there is no previous report of a formally cationic phosphonio dithioester acting as a bridging ligand. Some work is now in progress to explore the reactivity of the anionic complexes **3** and **4** with other electrophiles.

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Supplementary Material Available: Complete tables of atomic coordinates, anisotropic thermal parameters, and bond lengths and angles for the structures of **3** and **5c** (11 pages); tables of observed and calculated structure factor amplitudes (48 pages). Ordering information is given on any current masthead page.

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[9] **1a** and $Li[BHEt_3]$ (molar ratio 1:4) were made to react in THF for 15 min, to obtain a solution of **4a**, IMe (excess) was added, and compound **5a** was formed within 5 min. The solvent was evaporated in vacuo, and the residue was chromatographed in alumina (activity III). A small amount of **3** (lithium salt) remained strongly absorbed at the top of the column, while a yellow band of **5a** was eluted with CH_2Cl_2/hexane (1:1). Slow concentration in vacuo gave **5a** as yellow crystals. Yield: 65%. By a similar procedure were prepared **5b** (from **1b** and IMe, 5 min, 63%), **5c** (from **1a** and CH_2Cl_2, 1 h, 48%), and **5d** (from **1b** and CH_2Cl_2, 1 h, 52%).

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Nucleophilic Acylation via Palladium-Catalyzed Cross-Coupling of (1-((Trialkylsilyl)oxy)vinyl)tin Derivatives

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Summary: Silylation of acyltins provided a new class of polyfunctional compounds containing vinyltin and silyl enolate groups. The protected acyl moiety could be selectively transferred to various electrophiles via a palladium-catalyzed process.

In the course of a study on the reactivity of acyltin derivatives as potential acyl anion equivalents,[1] we were confronted with several experimental difficulties. Due to their great reactivity, acyltin derivatives are very sensitive to oxygen and temperature and, as a consequence, their reactivity in palladium-catalyzed cross-coupling with electrophiles is affected. Although they react in reasonable yield with acyl chlorides to give α-diketones, disappointing results were obtained in the case of aryl bromides, allyl halides or benzyl bromides.[2] For that reason we decided to prepare and employ masked acyltins. We describe herein the synthesis of acyltin silyl enolates and the use of these new reagents for efficient nucleophilic acylation of organic halides.

The synthesis of substituted ketones via cross-coupling of organotin derivatives with acyl chlorides has been extensively studied in the recent years, including carbonylation methods.[3-7] However, the reverse coupling of acyltins with electrophiles is poorly developed, although recent results have been obtained for nucleophilic acylation reactions using (α-ethoxyvinyl)trialkylstannane.[8-10]

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