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 [$Mn_2(CO)_6(\mu$-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 $(CO)_3Mn$–$Mn(CO)_3$ 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 [$Mn_2(CO)_6(\mu$-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.

(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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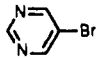
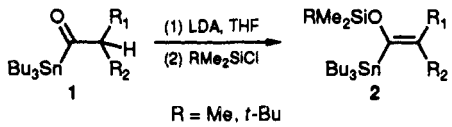
Table I. (1-((Trialkylsilyl)oxy)vinyl)tins as Equivalents of Acyl Anions in Reactions with Organic Halides

entry	organotin reagent 2	electrophile	3 (isolated yield, %)	4 (isolated yield, %)
1	**2a**	C_6H_5Br	**3a** (74)	
2	**2a**	2-MeC_6H_4Br	**3b** (63)	
3	**2a**	4-CNC_6H_4Br	**3c** (67)	
4	**2a**	4-$NO_2C_6H_4Br$	**3d** (63)	
5	**2a**	4-$CHOC_6H_4Br$	**3e** (71)	
6	**2a**		**3f** (67)	
7	**2a**	4-$MeOC_6H_4Br$		4-$MeOC_6H_4COMe$, **4g** (75)
8	**2a**	4-MeC_6H_4Br		4-MeC_6H_4COMe, **4h** (66)
9	**2a**	$C_6H_5CH{=}CHBr$		$C_6H_5CH{=}CHCOMe$, **4i** (53)
10	**2a**	$C_6H_5CH{=}CHCH_2Br$		$C_6H_5CH{=}CHCH_2COMe$, **4j** (55)
11	**2a**	4-$CNC_6H_4CH_2Br$		4-$CNC_6H_4CH_2COMe$, **4k** (72)
12	**2b**	4-MeC_6H_4Br		4-MeC_6H_4COEt, **4l** (35)
13	**2b**	4-$CH_3COC_6H_4Br$		4-$CH_3COC_6H_4COEt$, **4m** (42)
14	**2b**	4-$MeOC_6H_4Br$		4-$MeOC_6H_4COEt$, **4n** (18)
15	**2b**	4-CNC_6H_4Br		4-CNC_6H_4COEt, **4o** (47)
16	**2c**	4-MeC_6H_4Br		4-MeC_6H_4COiPr, **4p** (31)
17	**2c**	4-$CH_3COC_6H_4Br$		4-$CH_3COC_6H_4CoiPr$, **4q** (40)
18	**2c**	4-CNC_6H_4Br		4-CNC_6H_4COiPr, **4r** (43)

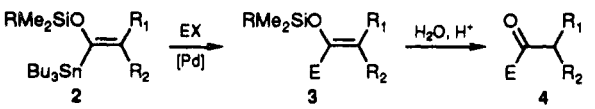
The preparation of (1-((trialkylsilyl)oxy)vinyl)tins was performed by lithiation of the corresponding acyltins[11] followed by silylation (eq 1).



(1)

As an example, the synthesis of reagent **2a** ($R_1 = R_2 = H$; R = Me) was carried out according to the following procedure. To a stirred solution of LDA (50 mmol) in THF (150 mL) at −78 °C, acetyltributyltin (50 mmol, 16.7 g) was added under a nitrogen atmosphere. The temperature was allowed to reach 0 °C for 15 min, and the solution was cooled to −78 °C. Then chlorotrimethylsilane (50 mmol) was added with a syringe pump and the reaction mixture was allowed to reach room temperature. Evaporation of the solvents and Kugelrohr distillation afforded **2a** in 65% isolated yield. The same procedure was used for the synthesis of **2b** ($R_1 = H$; $R_2 = Me$; R = Me) in 62% yield and **2c** ($R_1 = R_2 = Me$; R = Me) in 64% yield. In the case of **2d** ($R_1 = R_2 = H$; R = *t*-Bu), HMPA (20 mL) was added before quenching with water and pentane extraction of the reagent (63% yield).

Reagents **2** can be regarded as acyl anion precursors. They react smoothly with electrophilic reagents such as organic halides under palladium catalysis (eq 2) yielding silyl enolates **3**, which can be readily hydrolyzed (1 N HCl in MeOH–H_2O) to the corresponding ketones **4**.



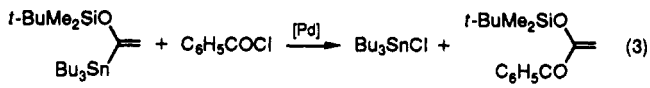
(2)

As an example the preparation of **3a** was performed as follows: A mixture of bromobenzene (5 mmol), $Pd(PPh_3)_4$ (2% molar), and **2a** (5 mmol) in 10 mL of toluene was heated at 100 °C in a sealed tube for 24 h (until precipitation of palladium black). Evaporation of the solvent and subsequent bulb to bulb distillation (bp: 110–120 °C/10 mmHg)[12] provided **3a** in 74% yield.

Table I contains examples involving aryl, benzyl, vinyl, and allyl halides that show a good tolerance for various functional groups. Entries 1–6 correspond to the obtainment of silyl enol ethers **3**, while entries 7–18 describe experiments in which the reactions mixtures were directly hydrolyzed to ketones **4**.

In the case of substituted vinyltin derivatives (**2b**, **2c**) the reactions were more tedious, and to avoid decomposition of the organotin reagent, it was slowly added to a refluxing toluene mixture of aryl bromide and palladium catalyst (2% $PdCl_2(PPh_3)_2$). However the yields show a decrease in comparison with the unsubstituted reagent **2a**.

Other electrophilic reagents are likely to be used in palladium cross-coupling with reagents **2**. For instance, in a preliminary experiment, reagent **2d** reacted in 71% yield with benzoyl chloride in refluxing toluene in the presence of 1% molar $BnPdCl(PPh_3)_2$ (eq 3).



(3)

In summary, (1-((trialkylsilyl)oxy)vinyl)tins appear to be new reagents for nucleophilic acylation reactions. They are also very promising because numerous further synthetic transformations could be performed at the silyl enol ether stage (**3**) instead of running simple hydrolysis. Also it seems possible to react **2** first as a silyl enol ether, opening routes to new functionally substituted acyltins. These further developments are presently being undertaken, and results will be published in due course.

Physical Data. All compounds were characterized by ^1H NMR spectroscopy by use of a Hitachi R 24B instrument (60 MHz). In some specified cases a Brucker WH 90 (^1H: 90 MHz) or a Brucker AC 200 (^{119}Sn: 74.63 MHz) instrument was used. Mass spectra were recorded at 70 eV on VG Micromass (16F or 7070F) spectrometers and infrared spectra on a Perkin-Elmer 683 spectrophotometer. Organotin material was removed either by treatment with KF solution or by hexane–acetonitrile partition. The reaction products were purified by distillation or column chromatography.

2a: bp 100–105 °C/0.05 mmHg; ^1H NMR (90 MHz, $CDCl_3$) δ 0.12 (s, 9 H), 0.87–1.50 (m, 27 H), 4.22 (d, J = 1 Hz, 1 H), 4.82 (d, J = 1 Hz, 1 H); ^{119}Sn NMR (C_6D_6) δ −60.63 (Me_4Sn as internal standard); IR (neat) 1580, 1415, 1250, 1000 cm^{-1}; mass m/z 349 (24.3), 323 (36), 267 (48), 209 (55), 179 (33), 177 (38), 73 (100). Anal. Calcd For $C_{17}H_{38}OSiSn$: C, 50.40; H, 9.39. Found: C, 50.36; H, 9.58.

2b: bp 105–110 °C/0.05 mmHg; (Z/E: 80/20) ^1H NMR

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($CDCl_3$) δ (*Z*) 0.13 (s, 9 H), 0.7–1.50 (m, 27 H), 1.52 (d, *J* = 6.5 Hz, 3 H), 5.56 (q, *J* = 6.5 Hz, 1 H); ^{119}Sn NMR (C_6D_6) δ –62.47 (*Z* isomer), –61.49 (*E* isomer); mass *m/z* 363 (30), 323 (75), 267 (80), 179 (18.2), 177 (18.6), 117 (20), 73 (100). Anal. Calcd for $C_{18}H_{40}OSiSn$: C, 51.58; H, 9.55. Found: C, 51.60; H, 9.63.

2c: bp 110–115 °C/0.05 mmHg; ^{1}H NMR δ 0.11 (s, 9 H), 0.70–1.50 (m, 27 H), 1.62 (bs, 6 H); ^{119}Sn NMR δ –60.87.

2d: bp 110–115 °C/0.05 mmHg; ^{1}H NMR δ 0.16 (s, 6 H), 0.96 (s, 9 H), 0.70–1.50 (m, 27 H), 4.18 (bs, 1 H), 4.81 (bs, 1 H); ^{119}Sn NMR δ –58.66.

3a: ^{1}H NMR δ 0.23 (s, 9 H), 4.40 (d, *J* = 1.2 Hz, 1 H), 4.88 (d, *J* = 1.2 Hz, 1 H), 7.30 (m, 3 H), 7.55 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 0.0, 90.95, 125.1, 128.3, 128.57, 137.46, 155.60; IR (neat) 3100, 1695, 1620, 1580, 1500, 1250 cm^{-1}; mass *m/z* 192 (55), 191 (100), 177 (79), 135 (29), 75 (43), 73 (2). Anal. Calcd for $C_{11}H_{16}OSi$: C, 68.69; H, 8.38. Found: C, 68.27; H, 8.36.

3b: ^{1}H NMR δ 0.21 (s, 9 H), 2.38 (s, 3 H), 4.40 (d, *J* = 1 Hz, 1 H), 4.52 (d, *J* = 1 Hz, 1 H), 7.29 (m, 4 H); mass *m/z* 206 (23), 205 (5.4), 191 (100), 115 (16), 75 (91), 73 (62).

3c: ^{1}H NMR δ 0.24 (s, 9 H), 4.50 (d, *J* = 1.6 Hz, 1 H), 4.96 (d, *J* = 1.6 Hz, 1 H), 7.56 (m, 4 H); mass *m/z* 217 (43), 216 (40), 202 (84), 160 (23), 75 (100), 73 (52).

3d: ^{1}H NMR δ 0.25 (s, 9 H), 4.53 (d, *J* = 2 Hz, 1 H), 5.01 (d, *J* = 2 Hz, 1 H), 7.63 (d, *J* = 9.3 Hz, 2 H), 8.10 (d, *J* = 9.3 Hz, 2 H); mass *m/z* 237 (11), 236 (7.9), 222 (44), 220 (82), 190 (44), 75 (100), 73 (78).

3e: ^{1}H NMR δ 0.24 (s, 9 H), 4.53 (d, *J* = 2 Hz, 1 H), 5.03 (d, *J* = 2 Hz, 1 H), 7.73 (s, 4 H), 9.94 (s, 1 H); mass *m/z* 220 (54), 219 (10), 205 (21), 191 (70), 102 (15), 75 (100), 73 (41).

3f: ^{1}H NMR δ 0.26 (s, 9 H), 4.44 (d, *J* = 2 Hz, 1 H), 4.86 (d, *J* = 2 Hz, 1 H), 8.77 (s, 2 H), 8.98 (s, 1 H); mass *m/z* 194 (38), 193 (53), 179 (57), 137 (27), 75 (100), 73 (78).

4g: mp 37–38 °C; ^{1}H NMR δ 2.40 (s, 3 H), 3.82 (s, 3 H), 6.90 (d, *J* = 7.6 Hz, 2 H), 7.92 (d, *J* = 7.6 Hz, 2 H).

4h: ^{1}H NMR δ 2.29 (s, 3 H), 2.39 (s, 3 H), 7.08 (d, *J* = 7 Hz, 2 H), 7.68 (d, *J* = 7 Hz).

4i: mp 41 °C; ^{1}H NMR δ 2.25 (s, 3 H), 6.57 (d, *J* = 17 Hz, 1 H), 7.34 (m, 5 H), 7.40 (d, *J* = 17 Hz, 1 H); mass *m/z* 147 (6.8), 146 (56), 145 (51), 131 (100), 103 (95), 77 (46).

4j: ^{1}H NMR δ 2.18 (s, 3 H), 3.33 (d, *J* = 5.6 Hz, 2 H), 6.24 (dd, *J* = 5.6 Hz, *J* = 16 Hz, 1 H), 6.50 (d, *J* = 16 Hz, 1 H), 7.34 (m, 5 H); mass *m/z* 160 (19), 117 (100), 115 (38), 91 (13); IR (neat) 3050, 1725, 1680, 1630, 1500, 1450, 1360, 1160 cm^{-1}.

4k: mp 76–77 °C; ^{1}H NMR δ 2.24 (s, 3 H), 3.81 (s, 2 H), 7.33 (d, *J* = 7.6 Hz, 2 H), 7.66 (d, *J* = 7.6 Hz, 2 H); mass *m/z* 159 (6), 117 (55), 116 (11), 43 (100); IR (CCl_4) 2220, 1710, 1610, 1360, 1165 cm^{-1}.

4l: ^{1}H NMR δ 1.11 (t, *J* = 6.5 Hz, 3 H), 2.31 (s, 3 H), 2.78 (q, *J* = 6.5 Hz, 2 H), 7.07 (d, *J* = 7 Hz, 2 H), 7.71 (d, *J* = 7 Hz, 2 H).

4m: ^{1}H NMR δ 1.18 (t, *J* = 6.5 Hz, 3 H), 2.55 (s, 3 H), 2.95 (q, *J* = 6.5 Hz, 2 H), 7.80 (s, 4 H); mass *m/z* 176 (9), 161 (4), 148 (9), 147 (100), 119 (11).

4n: ^{1}H NMR δ 1.12 (t, *J* = 6.5 Hz, 3 H), 2.80 (q, *J* = 6.5 Hz, 2 H), 3.72 (s, 3 H), 7.72 (d, *J* = 8 Hz, 2 H), 7.80 (d, *J* = 8 Hz, 2 H); mass *m/z* 164 (8), 136 (86), 135 (100), 107 (7), 92 (9), 77 (13).

4o: ^{1}H NMR δ 1.25 (t, *J* = 6.5 Hz, 3 H), 3.05 (q, *J* = 6.5 Hz, 2 H), 7.65 (d, *J* = 8 Hz, 2 H), 8.01 (d, *J* = 8 Hz, 2 H); mass *m/z* 159 (8), 131 (9), 130 (100), 102 (31).

4p: ^{1}H NMR δ 1.15 (d, *J* = 6 Hz, 6 H), 2.37 (s, 3 H), 3.43 (m, *J* = 6 Hz, 1 H), 7.22 (d, *J* = 7 Hz, 2 H), 7.82 (d, *J* = 7 Hz, 2 H); mass *m/z* 164 (4), 136 (4), 120 (8), 119 (100), 91 (33), 65 (10).

4q: ^{1}H NMR δ 1.20 (d, *J* = 6 Hz, 6 H), 2.55 (s, 3 H), 3.51 (m, *J* = 6 Hz, 1 H), 7.89 (s, 4 H); mass *m/z* 190 (3), 148 (9), 147 (100), 119 (8), 91 (7).

4r: ^{1}H NMR δ 1.25 (d, *J* = 6 Hz, 6 H), 3.51 (m, *J* = 6 Hz, 1 H), 6.90 (d, *J* = 8 Hz, 2 H), 7.15 (d, *J* = 8 Hz, 2 H); mass *m/z* 173 (6), 131 (9), 130 (100), 103 (8), 102 (20), 75 (4).

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