steroid—CH=CH—I protons could be detected in the proton NMR spectrum, and the patterns of iodobenzene clearly appear in the aromatic region overlapping partially with the tin-phenyl protons. Therefore, compound **2** is identified as (*Z*)-17-[2-(diphenyliodostannyl)vinyl]-4-estren-17-ol.

After the addition of a second equivalent of iodine, the steroidal vinyl resonance is again nearly unchanged (5.40 ppm), while the two other resonances, again changed to 6.40 and 6.01 ppm, appear as doublets (${}^3J({}^1H{-}C{=}C{-}{}^1H)$ = 11 Hz) further coupled to tin with ${}^2J({}^1H{-}C{-}{}^{117/119}Sn)$ = 195/204 Hz and ${}^3J({}^1H{-}C{=}C{-}{}^{117/119}Sn)$ = 306/317 Hz. Again, no vinylic steroid—CH=CH—I signals are visible. The observation of vinylic tin-proton couplings unambiguously shows that the second group cleaved by iodine is again a phenyl one, allowing compound **3** obtained after the addition of 2 equiv of iodine to be identified as (*Z*)-17-[2-(phenyldiiodostannyl)vinyl]-4-estren-17-ol.

The coupling constant ${}^3J({}^1H{-}C{=}C{-}{}^1H)$ = 13 Hz observed for compound **1** is rather large since cis coupling constants in five-membered rings usually amount to 8 Hz or even less.[4] However, this ring, containing a tin atom, is characterized by rather abnormal bond angles. This coupling constant decreases from compound **1** to compound **3**.

Experimental Section. Chemicals. 17-Ethynyl-4-estren-17-ol ("lynestrenol") was supplied by Organon, Oss, The Netherlands. Triphenyltin hydride was prepared according to Kuivila:[6] bp 161–165 °C/0.5 Torr (lit.[6] bp 162–168 °C/0.3 Torr); n_D^{25} = 1.6343; IR ν(Sn–H) = 1835 cm^{-1}; yield 75%.

Equipment: X-ray diffractometer, Huber automated four-circle diffractometer, data collection at room temperature (ca. 21 °C); NMR, Bruker AM 270 instrument; IR, Perkin-Elmer 298 instrument; melting point microscope, Thermopan.

Reactions. Reaction of 17-Ethynyl-4-estren-17-ol with Triphenyltin Hydride. A 1.42-g amount of 17-ethynyl-4-estren-17-ol (5 mmol) and 1.76 g of triphenyltin hydride (5 mmol) were dissolved in 30 mL of dry ether in a two-necked flask and 10 mg of dibenzoyl peroxide was added. After 20 h at room temperature, ether was evaporated and the viscous material obtained was crystallized from ethanol, yielding 2.06 g of a crystalline solid, compound **1**: mp 133–135 °C; yield 65%. A 0.25-g amount of hexaphenylditin (mp 231–232 °C), only slightly soluble in ethanol, was obtained as a side product. Compound **1** was recrystallized three times from ethanol, yielding white needles (mp 134–135 °C), one of which was used for the single-crystal X-ray diffraction study.

Reaction of (*Z*)-17-[2-(Triphenylstannyl)vinyl]-4-estren-17-ol with Iodine. A 50.8-mg amount of iodine (0.2 mmol) dissolved in 5 mL of chloroform was added to 134.8 mg of **1** (0.2 mmol) dissolved in 2 mL of $CHCl_3$. The color of iodine disappeared immediately. The solvent was evaporated, and 0.5 mL of $CDCl_3$ was added for recording a ${}^1H$ NMR spectrum.

After the NMR study, an additional 50.8 mg of iodine dissolved in 5 mL of ethanol was added to this solution. The color disappeared much more slowly. When the solution had become almost colorless, the mixture was prepared as explained above for recording a further ${}^1H$ NMR spectrum.

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Registry No. 1 (coordination compound entry), 127973-41-5; **1** (stannane entry), 127973-42-6; **2**, 127973-39-1; **3**, 127973-40-4; Ph_3SnH, 892-20-6; lynestrenol, 52-76-6.

Supplementary Material Available: Tables of positional parameters, thermal parameters, angles between normals to least-squares planes, least-squares planes and deviations therefrom, and bond angles and a stereoview of **1** (23 pages); a table of observed and calculated structure factors (15 pages). Ordering information is given on any current masthead page.

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A General, High-Yield Reaction for the Formation of (Chloromethyl)oligosilanes

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Summary: (Chloromethyl)oligosilanes are conveniently synthesized in high yield (>75%) via the reaction between chlorooligosilanes and (chloromethyl)lithium generated in situ from bromochloromethane and *n*-butyllithium at −60 °C. Bis(chloromethyl)silanes are also produced from the appropriate dichlorosilanes.

The chloromethyl group attached to silanes represents one of the most useful functional groups in organosilicon chemistry. It has been widely used as a synthon for the formation of silylmethyl Grignard or alkali-metal reagents and has also demonstrated much utility for functionalizing silanes via direct halogen displacement reactions.[1,2,3,5] There are several diverse routes available for the formation of such a group, and two popular chlorination procedures are outlined in eqs 1 and 2.[4,5]

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$$\mathrm{Me_3SiCl + Cl_2 \xrightarrow{h\nu} ClCH_2SiMe_2Cl} \tag{1}$$

$$\mathrm{Me_3SiSiMe_3 + SO_2Cl_2 \xrightarrow{(PhCOO)_2} ClCH_2SiMe_2SiMe_3} \tag{2}$$

These synthetic routes are generally inapplicable to oligosilanes due to facile rupture of the Si–Si bond under such reaction conditions.[5]

In an effort to overcome the problem associated with cleavage of Ge–C, Sn–C, and Pb–C (M–C) bonds via direct halogenation, Seyferth and co-workers developed the reaction of (iodomethyl)zinc iodide or (bromomethyl)zinc bromide in THF with R_3MX, as a useful route to iodo- or bromomethyl derivatives, which may be transformed to the corresponding chloromethyl compound via use of AgCl.[6] The same group also developed the use of (haloalkyl)mercury compounds to insert the CHX group into Si–H bonds.[7] The direct insertion reaction of diazomethane into a group 14 element–chlorine bond has also been used for such transformations.[8] These synthetic procedures involve the use of potentially dangerous (CH_2N_2) and/or toxic (Hg compounds) reagents. Furthermore, a recent attempt to prepare R_3M'–$SiMe_2$–CH_2Cl (M′ = Si, Ge) with use of the reaction between chloro(chloromethyl)dimethylsilane and $R_3M'^-Li^+$ was unsuccessful due to disubstitution reactions leading to formation of R_3M'–$SiMe_2$–$CH_2M'R_3$.[9]

Due to the lack of synthetic routes leading to formation of the $ClCH_2Si$ group in oligosilanes, apart from a single report by the Kumada group on the existence of 1-$ClCH_2Me_7Si_3$, no (chloromethyl)oligosilane compounds have been reported in the literature.[10] This paucity of information on α-(halomethyl)oligosilanes represents a significant problem in organosilicon chemistry.

We now report a simple, high-yield, one-step reaction for transforming chlorosilanes into (chloromethyl)silanes applicable for systems containing Si–Si bonds via the in situ generation of (chloromethyl)lithium (reaction 3).

$$\mathrm{BrCH_2Cl + ClSiMe_2(SiMe_2)_{\mathit{n}}SiMe_3 \xrightarrow{\mathit{n}\text{-BuLi, }-60\ ^\circ C} ClCH_2SiMe_2(SiMe_2)_{\mathit{n}}SiMe_3} \tag{3}$$

$$n = 0\text{–}2$$

This reaction is a modification of the in situ generation of CH_2ILi from PhLi and CH_2I_2 used by Kauffmann et al. for the synthesis of ICH_2EPh_3 (E = Si, Ge, Sn, Pb).[11]

The same general procedure may also be used for the formation of branched (chloromethyl)oligosilanes (eq 4) and bis(chloromethyl)silanes (eqs 5 and 6).

$$\mathrm{BrCH_2Cl + ClSiMe(SiMe_3)_2 \xrightarrow{\mathit{n}\text{-BuLi, }-60\ ^\circ C} ClCH_2SiMe(SiMe_3)_2} \tag{4}$$

$$\mathrm{2BrCH_2Cl + Cl_2SiMe_2 \xrightarrow{\mathit{n}\text{-BuLi, }-60\ ^\circ C} (ClCH_2)_2SiMe_2} \tag{5}$$

$$\mathrm{2BrCH_2Cl + ClSiMe_2SiMe_2Cl \xrightarrow{\mathit{n}\text{-BuLi, }-60\ ^\circ C} ClCH_2SiMe_2SiMe_2CH_2Cl} \tag{6}$$

Table I. Yield (%), Boiling Point [°C/mmHg], Analytical, and NMR Data for New Compounds[a]

$Me_3SiSiMe_2CH_2Cl$ [78–80/41][5]	
yield	80
^1H NMR	0.07 ($SiMe_3$), 0.11 ($SiMe_2$), 2.83 (CH_2Cl)
^{13}C NMR	−4.97 ($SiMe_2$), −1.88 ($SiMe_3$), 30.84 (CH_2Cl)
^{29}Si NMR	−19.5 ($SiMe_3$), −14.8 ($SiMe_2$)
$Me_3SiSiMe_2SiMe_2CH_2Cl$ [124–125/44]	
yield	77
anal.	calcd (found): C, 40.21 (40.32); H, 9.70 (9.49)
^1H NMR	0.07 ($SiMe_3$), 0.10 ($SiMe_2$), 0.15 ($SiMe_2$), 2.84 (CH_2)
^{13}C NMR	−6.44 ($SiSiMe_2Si$), −4.01 (Me_2SiCCl), −1.20 ($SiMe_3$), 31.61 (CH_2)
^{29}Si NMR	−48.7 (Si–*Si*–Si), −16.0 ($SiMe_3$), −11.2 ($SiMe_2CCl$)
$(Me_3Si)_2SiMeCH_2Cl$ [122–124/40]	
yield	84
anal.	calcd (found): C, 40.21 (39.97); H, 9.70 (9.75)
^1H NMR	0.13 ($SiMe_3$), 0.17 (SiMe), 2.99 (CH_2)
^{13}C NMR	−9.06 (SiMe), −0.65 ($SiMe_3$), 29.75 (CH_2)
^{29}Si NMR	−39.5 (SiMe), −15.9 ($SiMe_3$)
$Me_3SiSiMe_2SiMe_2SiMe_2CH_2Cl$ [96/0.3]	
yield	88
anal.	calcd (found): C, 40.42 (40.64); H, 9.84 (9.84)
^1H NMR	0.06 ($SiMe_3$), 0.09, 0.14, 0.16 ($SiMe_2$), 2.87 (CH_2)
^{13}C NMR	−5.59 ($SiMe_3Si\mathit{Me}_2$), −5.23 ($Me_2SiSi\mathit{Me}_2SiMe_2$), −3.84 ($ClCH_2Si\mathit{Me}_2$), −0.95 ($SiMe_3$), 32.05 ($CH_2$)
^{29}Si NMR	−44.89 (2 Si, $Me_2SiSiMe_2$), −15.08 ($SiMe_3$), −10.77 (SiCCl)
$Me_2Si(CH_2Cl)_2$ [95–96/98][13]	
yield	75
^1H NMR	0.16 (SiMe), 2.81 (CH_2)
^{13}C NMR	−5.49 (SiMe), 28.4 (CH_2)
^{29}Si NMR	3.57
$ClCH_2(Me)_2SiSi(Me)_2CH_2Cl$ [115–117/32][14]	
yield	76
^1H NMR	0.16 (SiMe), 2.86 (CH_2)
^{13}C NMR	−4.34 (SiMe), 31.08 (CH_2)
^{29}Si NMR	−14.4

[a] Analyses performed by Galbraith Laboratories, Inc., Knoxville, TN. NMR specta were recorded in $CDCl_3$; chemical shifts are in ppm relative to TMS at 0.0 ppm.

The reaction described in eq 5 is particularly noteworthy since the published route to bis(chloromethyl)dimethylsilane, i.e. direct chlorination of Me_4Si, leads to significant yields of (dichloromethyl)trimethylsilane (35%) as well as the desired product (45%).[13]

In a typical reaction sequence, 5.6 g (25 mmol) of 1-chloro-1,1,2,2,3,3,3-heptamethyltrisilane[12] and 3.25 g (25 mmol) of $BrCH_2Cl$ in 75 mL of dry THF were placed in a 500-mL three-necked flask equipped with a magnetic stirring bar, rubber septum, nitrogen inlet tube, and low-temperature thermometer. To this mixture, maintained between −70 and −60 °C, was added, via syringe over 20 min, 15.6 mL (25 mmol) of a 1.6 M solution of *n*-butyllithium in hexane. The solution was stirred for an additional 20 min at the same temperature and then warmed to room temperature during 1 h. After aqueous workup and drying, the solvent was removed and the resulting liquid distilled at 124–125 °C (44 mmHg) to yield 4.6 g (19.2 mmol, 77%) of 1-(chloromethyl)-1,1,2,2,3,3,3-heptamethyltrisilane. Analytical and spectral data are recorded in Table I. Thus far the reaction is quite general and has been used for both linear and branched silanes.

The spectral data for the new compounds are as expected. The ^{29}Si NMR data show the resonance of the silicon atom attached to the chloromethyl group to be slightly deshielded, 4–5 ppm, when compared to the res-

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onance for the parent permethylated silane. This shift is attenuated as the site of the chloromethyl group becomes further removed from the specific silicon atom. Related substituent effects are observed in the ^{13}C NMR data; i.e., the methyl groups attached to the silicon containing the chloromethyl group, the α-position, are shielded by approximately 2.5 ppm, while those in the β-position are shifted to low frequency by 0.5 ppm. Such variations, while small, are regular and very useful for complete characterization of the new compounds.

Overall, this synthetic procedure provides an excellent route to a class of functional organosilicon compounds previously unavailable. The generality of this approach to a larger range of oligosilanes and related germyl-, stannyl-, and plumbylsilanes and poly(chloromethyl)silanes is under investigation, as is the chemical reactivity of the new system.

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Registry No. $BrCH_2Cl$, 74-97-5; $ClSiMe_2SiMe_3$, 1560-28-7; $Cl(SiMe_2)_2SiMe_3$, 918-19-4; $Cl(SiMe_2)_3SiMe_3$, 51531-19-2; $ClSiMe(SiMe_3)_2$, 754-38-1; Cl_2SiMe_2, 75-78-5; $Cl(SiMe_2)_2Cl$, 4342-61-4; $ClCH_2SiMe_2SiMe_3$, 5181-46-4; $ClCH_2(SiMe_2)_2SiMe_3$, 15816-06-5; $ClCH_2SiMe(SiMe_3)_2$, 125091-02-3; $ClCH_2(SiMe_2)_3SiMe_3$, 127971-49-7; $(ClCH_2)_2SiMe_2$, 2917-46-6; $ClCH_2(SiMe_2)_2CH_2Cl$, 18139-99-6.

5-Metallo-2(3*H*)-furanones by Double Carbonylation of (σ-Allenyl)platinum and -palladium Compounds

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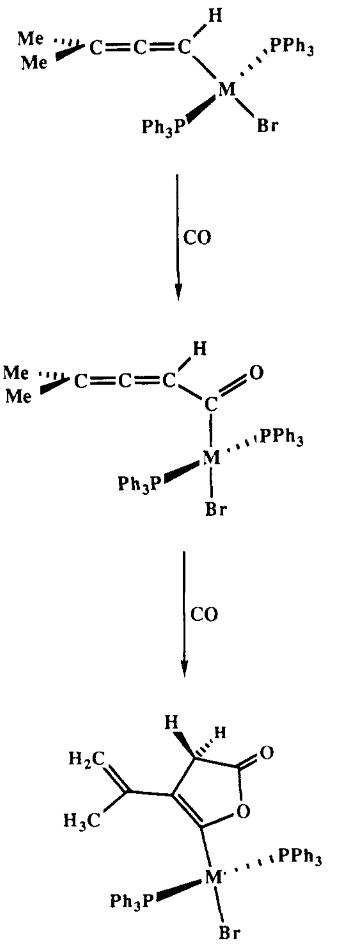
Summary: The reactions of bis(triphenylphosphine)(3-methylbuta-1,2-dien-1-yl)metal(II) bromide (M = Pd, Pt) with CO at 1.5 bar and 20 °C in benzene give the unexpected title compounds, which are formed by two successive insertions of carbon monoxide into metal–carbon bonds. An X-ray crystal structure study of the organoplatinum compound confirmed the proposed structure, featuring a square-planar bis(phosphine)organoplatinum(II) bromide in which the organic group is the unusual (nonconjugated) 2(3*H*)-furanon-5-yl moiety coordinated to platinum through an sp^2 carbon atom.

Scheme I



1a M=Pd
1b M=Pt

2a M=Pd
2b M=Pt

3a M=Pd
3b M=Pt

Studies aiming at the synthesis and isolation or observation of organometallic intermediates relevant to homogeneously catalyzed carbonylation reactions currently receive attention.[3] Apart from single migratory CO-insertion reactions quite a few double-carbonylation reactions have been reported.[4] During a study of palladium-catalyzed carbonylation reactions of allenic halides (alka-1,2-dienyl halides), we became interested in stoichiometric reactions of (σ-allenyl)palladium compounds with carbon monoxide in the absence of additional nucleophilic reagents. This interest stems from Tsuji's[5] and our[6] observation that alkoxycarbonylation of propargyl and allenyl compounds

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