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SILICON-, GERMANIUM- AND TIN-SUBSTITUTED ACETYLENES AND THEIR DICOBALT HEXACARBONYL COMPLEXES

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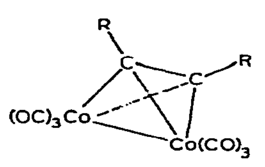
SUMMARY

A number of Group IV element-substituted acetylenes have been prepared, including the new $Me_3SiC{\equiv}CSiMe_2H$, $Me_2HSiC{\equiv}CSiMe_2H$, $Me_3SiC{\equiv}CCMe_3$ and $Me_3SnC{\equiv}CCMe_3$. The dicobalt hexacarbonyl complexes of $Me_3SnC{\equiv}CSnMe_3$, $Me_3SnC{\equiv}CH$, $Me_3GeC{\equiv}CGeMe_3$, $Me_3SnC{\equiv}CCMe_3$, $Me_3GeC{\equiv}CSiMe_3$ and $Me_3SnC{\equiv}CSiMe_3$ have been prepared by reaction of the appropriate acetylene with dicobalt octacarbonyl. Reaction of $(Me_3SnC_2H)Co_2(CO)_6$ and $(Me_3SnC_2CMe_3)Co_2(CO)_6$ with $CH_3COCl/AlCl_3$ in methylene chloride gave $(CH_3COC_2H)Co_2(CO)_6$ and $(CH_3COC_2CMe_3)Co_2(CO)_6$, respectively.

For a study of the Diels–Alder reactions of Group IV element-substituted acetylenes with α-pyrone[1,2] we required acetylenes containing silyl, germyl and stannyl substituents of type $R_3MC{\equiv}CMR_3$ and $R_3MC{\equiv}CM'R_3$. These compounds were prepared by coupling the appropriate organometallic halides with an organometallic derivative of acetylene. Of interest is the use of the commercially available $LiC{\equiv}CLi$ in the preparation of $Me_3GeC{\equiv}CGeMe_3$ and $Me_3SnC{\equiv}CSnMe_3$. Acetylenes of type $Me_3SiC{\equiv}CMR_2R'$ (M = Si, Ge, Sn; R = Me; R' = Me, H) were synthesized from $Me_3SiC{\equiv}CMgBr$ and $Me_3CC{\equiv}CMgBr$ was used in the preparation of $Me_3CC{\equiv}CMR_2R'$ compounds. The compounds prepared are shown in Table 1.

Current interest in the chemistry of organocobalt compounds of type (I) (*e.g.*, ref. 3) has led us to prepare the dicobalt hexacarbonyl complexes of some of these acetylenes. These derivatives were obtained in good (50–90%) yields and were isolated as air-stable, purple-black solids which appeared dark brown when crushed or scraped. The complexes prepared included those derived from $Me_3SnC{\equiv}CSnMe_3$, $Me_3SnC{\equiv}CH$, $Me_3GeC{\equiv}CGeMe_3$, $Me_3SnC{\equiv}CCMe_3$, $Me_3SiC{\equiv}CGeMe_3$ and Me_3-



$\equiv (RC_2R)Co_2(CO)_6$

(I)

TABLE 1

PREPARATION OF GROUP IV ELEMENT-SUBSTITUTED ACETYLENES

Acetylene	Prepared via	Yield (%)	B.p. (°C/mm) or m.p. (°C)	n_D^{25}
$Me_3GeC{\equiv}CGeMe_3$	$LiC{\equiv}CLi$	42	m.p. 38.5–39.5^a	
$Me_3SnC{\equiv}CSnMe_3$	$LiC{\equiv}CLi$	69	m.p. 58–59	
$Me_3SiC{\equiv}CGeMe_3$	$Me_3SiC{\equiv}CMgBr$	73	b.p. 81–82/70^b m.p. 30–31	1.4405^e
$Me_3SiC{\equiv}CSnMe_3$	$Me_3SiC{\equiv}CMgBr$	27	b.p. 70–72/15^c	1.4695
$Me_2HSiC{\equiv}CSiMe_2H^d$	$BrMgC{\equiv}CMgBr$	21	b.p. 120–122	1.4290
$Me_3SiC{\equiv}CSiMe_2H^d$	$Me_3SiC{\equiv}CMgBr$	47	b.p. 128–130	1.4275
$Me_3CC{\equiv}CSnMe_3{}^d$	$Me_3CC{\equiv}CMgBr$	15	b.p. 65/20	1.4589
$Me_3CC{\equiv}CSiMe_3{}^d$	$Me_3CC{\equiv}CMgBr$	65	b.p. 55–56.5/58	1.4148

[a] Ref. 4 reports m.p. 35°. [b] Ref. 5 reports b.p. 25°/1 mm, m.p. 24–25°. [c] Ref. 5 reports b.p. 150–151°/750 mm, m.p. 25°. [d] New compound. [e] At 28°. Found: C, 44.78; H, 8.46. $C_8H_{18}SiGe$ calcd.: C, 44.71; H, 8.44%.

$SiC{\equiv}CSnMe_3$. In view of the well-known lability of the C–Sn bond, substitution of the Me_3Sn groups in the stannyl-substituted complexes by other functions seemed an attractive possibility. This approach has met with limited success.

The reaction of acyl halides with arylsilicon compounds in the presence of aluminum chloride to give ketones has been known for some years[6,7] and has been developed as a synthetic route more recently[8]. A similar reaction of aryl–tin compounds occurred much more readily[8]. We have used this type of reaction to prepare acetyl-substituted acetylenedicobalt hexacarbonyl complexes:

$$(Me_3CC_2SnMe_3)Co_2(CO)_6 \xrightarrow[CH_2Cl_2]{CH_3COCl,\ AlCl_3} (Me_3CC_2COCH_3)Co_2(CO)_6 + Me_3SnCl$$

$$(HC_2SnMe_3)Co_2(CO)_6 \xrightarrow[CH_2Cl_2]{CH_3COCl,AlCl_3} (HC_2COCH_3)Co_2(CO)_6 + Me_3SnCl$$

The product yields, however, were low. Treatment of bis(trimethyltin)acetylenedicobalt hexacarbonyl with an excess of acetyl chloride/aluminum chloride reagent gave $(HC_2COCH_3)Co_2(CO)_6$ in 38% yield. Presumably the first acetyl group inhibited substitution of the remaining Me_3Sn group, which then was cleaved during hydrolytic work-up.

This general approach to introducing useful functional groups into acetylenedicobalt hexacarbonyl complexes merits further study, especially since the acetylenic ligands can be recovered in high yield from such complexes after the functional group has been introduced[3].

EXPERIMENTAL

General comments

All reactions were carried out in flame-dried glassware under an atmosphere of prepurified nitrogen or argon. All solvents were rigorously dried. Infrared spectra were recorded using Perkin–Elmer Model No. 237, 257 or 337 grating infrared spectrophotometers, NMR spectra using Varian Associates A60 or T60 spectrometers.

Chemical shifts are given in δ units (ppm) downfield from TMS. Dilithium acetylide was purchased from Alfa Inorganics, Inc., dicobalt octacarbonyl from Strem Chemicals, Inc.

Preparation of Group IV element-substituted acetylenes

(*a*). *Via dilithium acetylide.* A 100 ml, three-necked flask equipped with a reflux condenser topped with a nitrogen inlet tube and a magnetic stirring assembly was charged with 50 ml of THF, 19.9 g (0.10 mole) of trimethyltin chloride and 2.3 g (0.061 mole) of Li_2C_2. The initial reaction was mildly exothermic. The reaction mixture was heated at reflux for 36 h. Subsequently, the mixture was filtered under nitrogen through a Schlenk-type filter. The solvent was removed from the filtrate under reduced pressure (25° at 0.5 mm). The residue was taken up in a minimum amount of ether and transferred to a vacuum sublimator. Sublimation at 25° and 0.05 mm gave 12.2 g (69%) of bis(trimethyltin)acetylene.

(*b*). *Via* $Me_3SiC{\equiv}CMgBr$. A one-liter, three-necked flask equipped with a mechanical stirrer, a 250 ml pressure-equalizing addition funnel and gas inlet and outlet tubes was charged with 80 ml of THF. The THF was saturated with acetylene gas (Airco) which had been passed through a dry-ice/acetone-cooled trap and an alumina tower. The acetylene flow was continued while 0.2 mole of EtMgBr in 140 ml of THF was added dropwise. The resulting solution of $HC{\equiv}CMgBr$[9] was stirred for 1 h at room temperature and then 15.2 g (0.14 mole) of trimethylchlorosilane was added. The reaction mixture was heated at reflux for 2 h and then was trap-to-trap distilled (0.1 mm, pot temperature to 95°) into a receiver at $-78°$. The distillate was redistilled at atmospheric pressure through a Widmer column into a 500 ml, pressure-equalizing addition funnel, taking over all volatiles boiling $\leqslant 66°$. Approximately 5 ml of liquid remained.

The THF solution of $Me_3SiC{\equiv}CH$ thus obtained was added dropwise to 0.1 mole of EtMgBr in 70 ml of THF contained in a one-liter, three-necked flask equipped in the usual manner. The reaction mixture was stirred at reflux under argon for 2 h and subsequently was treated with 9.55 g (0.10 mole) of Me_2HSiCl. The resulting mixture was heated at reflux for 3 h, concentrated to 50 ml (Widmer column), diluted with 25 ml of pentane and hydrolyzed with saturated aqueous ammonium chloride. The dried organic layer was fractionally distilled to give 7.40 g (47%) of $Me_3SiC{\equiv}CSiMe_2H$, b.p. 128–130°. IR (liquid film): 2980 s, 2900 w, 2140 s, 1250 s, 892 s, 855 (sh), 840 s, 770 s, 735 s, 695 w cm^{-1}. NMR (CCl_4): δ 4.83 (septet, 1 H, J 4 Hz), 0.18 (d, 6, J 4 Hz) and 0.13 ppm (s, 9 H). (Found: C, 53.81; H, 10.35. $C_7H_{16}Si_2$ calcd.: C, 53.76; H, 10.31%.)

(*c*). *Via* $Me_3CC{\equiv}CMgBr$. tert-Butylethynylmagnesium bromide was prepared by dropwise addition of 8.21 g (0.10 mole) of tert-butylacetylene[10] to 0.11 mole of EtMgBr in 100 ml of diethyl ether in a 500 ml, three-necked flask equipped in the usual manner. The mixture was stirred at reflux for 2 h. To the $Me_3CC{\equiv}CMgBr$ slurry was added 0.25 g of CuCl and then, dropwise, 11.95 g (0.11 mole) of trimethylchlorosilane. The reaction mixture was heated at reflux for 2 h, cooled and filtered. Trap-to-trap distillation of the filtrate at 0.5 mm was followed by distillation of the distillate to give 10.0 g (65%) of $Me_3SiC{\equiv}CCMe_3$, b.p. 55–56.6°/58 mm. IR (liquid film): 2970 s, 2925 m, 2900 m, 2870 m, 2180 (sh), 2150 s, 1477 w, 1459 w, 1407 w, 1365 m, 1255 s, 1205 m, 945 s, 845 s, 765 s, and 700 s cm^{-1}. NMR (CCl_4): δ 1.20 (s, 9 H) and 0.12 ppm (s, 9 H). (Found: C, 70.10; H, 11.88. $C_9H_{18}Si$ calcd.: C, 70.04; H, 11.76%.)

Also prepared in this manner was $Me_3SnC{\equiv}CCMe_3$. IR (liquid film): 2960 s, 2920 s, 2870 m, 2360 w, 2165 m, 2130 w, 1475 m, 1455 m, 1360 s, 1250 s, 1205 m, 1190 (sh), 910 m, 780 s, 740 s, and 730 (sh) cm^{-1}. NMR (CCl_4): δ 1.20 (s, 9 H) and 0.24 ppm [s, 9 H, $J(^{117}Sn-^1H)$ 57 and $J(^{119}Sn-^1H)$ 59 Hz]. (Found: C, 44.03; H, 7.39. $C_9H_{18}Sn$ calcd.: C, 44.13; H, 7.41%.)

(*d*). *Via* $BrMgC{\equiv}CMgBr$. A solution of this reagent (prepared from 0.50 mole of EtMgBr and acetylene in diethyl ether) was treated with 0.50 mole of Me_2HSiCl. The mixture was heated at reflux for 12 h, hydrolyzed with saturated aqueous ammonium chloride, and the organic phase was distilled. Bis(dimethylsilyl)acetylene was obtained in 21% yield (7.55 g). IR (liquid film): 2960 m, 2900 m, 2800 w, 2140 s, 2085 m, 1955 w, 1911 w, 1895 w, 1475 w, 1428 w, 1250 s, 1070 w, 895 s, 877 (sh), 866 s, 840 s, 782 s, 773 s and 735 s cm^{-1}. NMR (CCl_4): δ 4.08 (septet, 2 H, J 4 Hz) and 0.23 ppm (d, 12 H, J 4 Hz). (Found: C, 50.38; H, 9.78. $C_6H_{14}Si_2$ calcd.: C, 50.62; H, 9.91%.)

Preparation of Group IV element-substituted acetylenedicobalt hexacarbonyl complexes

A 300 ml, three-necked flask equipped with a magnetic stirring assembly and an argon inlet tube was charged with dicobalt octacarbonyl, hexane (ca. 5 ml per mmole of dicobalt octacarbonyl) and an equimolar amount of the acetylene. An immediate evolution of gas was observed. The reaction mixture was stirred overnight at room temperature and then was cooled to −78°. The dark-brown, crystalline precipitate which resulted was filtered. The filtrate was concentrated at reduced pressure and a second crop of dark crystals was isolated. The combined solids were sublimed at 60°/0.03 mm, leaving a fluffy, grey-green residue. In each case the sublimed product was a purple-black, crystalline solid. The complexes were stable and could be handled in air without difficulty. Some decomposition did, however, occur upon prolonged storage at room temperature. The product yields ranged from 51–91%. The melting points were difficult to observe in melting point capillaries and therefore were determined using a hot-stage microscope. The following complexes were prepared.

$(Me_3SnC_2SnMe_3)Co_2(CO)_6$. 80% yield; dec. 115°. IR (KBr): 2990 w, 2920 w, 2060 vs, 2040 vs, 2015 vs, 2002 vs, 1965 vs, 1950 m, 1940 m, 1705 m, 1625 m, 1540 m, 1360 w, 1230 w, 1190 w, 775 m, 532 m, 523 m, 510 (sh), 495 m, 460 w, 448 w and 430 w cm^{-1}. NMR (CCl_4): δ 0.40 ppm [s, $J(^{117}Sn-^1H)$ 53, $J(^{119}Sn-^1H)$ 56 Hz]. (Found: C, 26.26; H, 2.89. $C_{14}H_{18}O_6Sn_2Co_2$ calcd.: C, 26.44; H, 2.85%.)

$(Me_3SnC_2H)Co_2(CO)_6$. 51% yield; m.p. 46–48° (open capillary tube). IR (KBr): 3100 w, 2980 w, 2915 w, 2080 vs, 2050 vs, 2040 (sh), 2020 vs, 2005 (sh), 1995 vs, 1630 w, 1475 w, 1260 w, 1193 w, 855 w, 838 w, 770 w, 720 w, 550 w, 518 w, 495 w and 455 w cm^{-1}. NMR (CCl_4): δ 6.25 (s, 1 H) and 0.42 ppm [s, 9H, $J(^{117}Sn-^1H)$ 53, $J(^{119}Sn-^1H)$ 56 Hz]. (Found: C, 28.06; H, 2.21. $C_{11}H_{10}O_6SnCo_2$ calcd.: C, 27.83; H, 2.12%.)

$(Me_3GeC_2GeMe_3)Co_2(CO)_6$. 65% yield; dec. 105°. IR (CCl_4): 2980 m, 2910 m, 2800 w, 2090 vs, 2050 vs, 2010 vs, 1965 vs, 1410 m, 1250 m, and 1240 s cm^{-1}. NMR (CCl_4): δ 0.47 ppm (s). (Found: C, 30.77; H, 3.33. $C_{14}H_{18}O_6Ge_2Co_2$ calcd.: C, 30.83; H, 3.33%.)

$(Me_3SnC_2CMe_3)Co_2(CO)_6$. 73% yield; dec. 88°. IR (CCl_4): 2970 s, 2950 (sh), 2930 m, 2905 m, 2870 m, 2085 vs, 2045 vs, 2010 vs, 1965 vs, 1470 m, 1457 m, 1445 w, 1390 m, 1360 m, 1225 m, 1195 m, 1023 w, 935 w and 915 m cm^{-1}. NMR (CCl_4):

δ 1.35 (s, 9 H) and 0.43 ppm [s, 9 H, $J(^{117}Sn-^{1}H)$ 55, $J(^{119}Sn-^{1}H)$ 58 Hz]. (Found: C, 33.94; H, 3.42. $C_{15}H_{18}O_6SnCo_2$ calcd.: C, 33.94; H, 3.42%.)

$(Me_3GeC_2SiMe_3)Co_2(CO)_6$. 91% yield; dec. 100°. IR (CCl_4): 2965 s, 2910 s, 2805 w, 2090 vs, 2050 vs, 2010 vs, 1965 vs, 1440 w, 1410 s, 1250 s, 1240 (sh), and 700 w cm^{-1}. NMR (CCl_4): singlets at δ 0.55 and 0.40 ppm. (Found: C, 33.61; H, 3.60. $C_{14}H_{18}O_6SiGeCo_2$ calcd.: C, 33.57; H, 3.62%.)

$(Me_3SnC_2SiMe_3)Co_2(CO)_6$. Dec. 110°. IR ($CCl_4$): 2900 (sh), 2960 m, 2910 w, 2090 vs, 2050 vs, 2015 vs, 1965 vs, 1410 w, 1265 (sh), 1250 s, 1195 m, 865 s and 848 s cm^{-1}. NMR (CCl_4): δ 0.42 [s, 9 H, $J(^{117}Sn-^{1}H)$ 55, $J(^{119}Sn-^{1}H)$ 58 Hz] and 0.30 ppm (s, 9 H). (Found: C, 30.75; H, 3.36. $C_{14}H_{18}O_6SiSnCo_2$ calcd.: C, 30.74; H, 3.32%.)

Reaction of $(Me_3SnC_2H)Co_2(CO)_6$ with acetyl chloride and aluminum chloride

A 100 ml, three-necked flask equipped with a magnetic stirring unit, a pressure-equalizing addition funnel and an argon inlet tube was charged with 1.32 g (3.0 mmole) of the acetylene complex and 15 ml of methylene chloride and cooled in an ice bath. To this solution was added a solution of 0.31 g (4.0 mmole) of acetyl chloride and 0.54 g (4.0 mmole) of $AlCl_3$ in 15 ml of methylene chloride. The reaction mixture was stirred at 0° for 30 min and at room temperature for 3 h and subsequently was hydrolyzed with saturated aqueous ammonium chloride. The dried organic phase was concentrated at reduced pressure and the residue was chromatographed on a 40 x 130 mm column of silicic acid (Mallickrodt 100 mesh) using CH_2Cl_2/hexane (1/1) as eluant. There were several very minor purple or purple-brown bands in addition to an insoluble green solid at the top of the column. The only major band, red in color, was collected. The solid in question was isolated and sublimed at 25°/0.02 mm onto a dry-ice/acetone-cooled probe to give 0.2 g (20%) of dark red crystals of acetylacetylenedicobalt hexacarbonyl, m.p. 37–37.5°. IR (CCl_4): 3100 w, 3005 w, 2970 w, 2935 w, 2100 vs, 2065 vs, 2040 vs, 1990 vs, 1675 s, 1420 w, 1350 m, 1165 s, 965 w and 870 w cm^{-1}. NMR (CCl_4): δ 6.18 (s, 1 H) and 2.43 ppm (s, 3 H). (Found: C, 33.98; H, 1.25. $C_{10}H_4O_7Co_2$ calcd.: C, 33.93; H, 1.14%.)

The same product was obtained when a reaction was carried out between $(Me_3SnC_2SnMe_3)Co_2(CO)_6$ (2.0 mmole) and 8.0 mmole each of acetyl chloride and aluminum chloride in CH_2Cl_2 in a similar manner and using the same work-up procedure. The yield of acetylacetylenedicobalt hexacarbonyl was 38%.

Essentially the same procedure was used in the reaction of 2.0 mmole of $(Me_3SnC_2CMe_3)Co_2(CO)_6$ with 3.0 mmole each of acetyl chloride and aluminum chloride in CH_2Cl_2, except that more vigorous conditions were required to effect the reaction: 20 h at room temperature and 8 h at reflux. At the end of this time thin layer chromatography indicated that the starting complex had been consumed. Acetyl-tert-butylacetylene, a red solid, dec. 70°, was obtained in 12% yield. IR (CCl_4): 2980 s, 2955 m, 2940 m, 2910 w, 2878 m, 2105 vs, 2070 vs, 2040 vs, 1980 vs, 1668 s, 1475 m, 1460 m, 1420 w, 1390 w, 1363 s, 1352 m, 1238 m, 1180 s, 1027 w, 990 w and 942 m cm^{-1}. NMR (CCl_4): δ 2.48 (s, 3 H) and 1.38 ppm (s, 9 H). (Found: C, 41.06; H, 3.15; $C_{14}H_{12}O_7Co_2$ calcd.: C, 41.00; H, 2.95%.)

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