Journal of Organometallic Chemistry, 217 (1981) 105—118
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

THE VARIETY OF COMPOUNDS FROM THE INTERACTION OF 1,5-DIYNES WITH η^5-CYCLOPENTADIENYLCOBALT: 1,6-BIS(TRIMETHYLSILYL)-1,5-HEXADIYNE, A COMPLETE PRODUCT ANALYSIS

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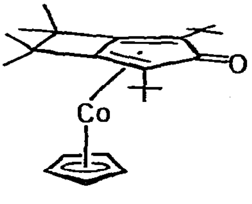
(Received February 6th, 1981)

Summary

A complete product analysis of the reaction of η^5-CpCo(CO)$_2$ with 1,6-bis(trimethylsilyl)-1,5-hexadiyne is given. This process yields eighteen characterizable complexes formed by oligomerization of the diyne to mixed cyclobutadienes, cyclopentadienones, and biscarbyne clusters.

Among the reactions of organic substrates with transition metals those involving α,ω-diynes have occupied the particular attention of organometallic chemists. This is because several carbon—carbon bonds are formed in one step with the simultaneous construction of relatively complex free or liganded organic molecules [1]. Especially interesting are the reactions of 1,5-hexadiynes since they might lead to small ring compounds. Indeed, such syntheses have been achieved en route to strained organic molecules [1a]. Considerably less is known about the potential of 1,5-hexadiynes to generate strained ligands.

Macomber [2] obtained the first cyclobutacyclopentadienone derivative as a ligand to η^5-CpCo (1) from the reaction of 2,2,5,5,6,6,9,9-octamethyldeca-3,7-diyne[1,6-bis(t-butyl)-3,3,4,4-tetramethyl-1,5-hexadiyne] with η^5-CpCo(CO)$_2$ in low absolute yield (~6%, although 85% of the starting diyne was recovered).



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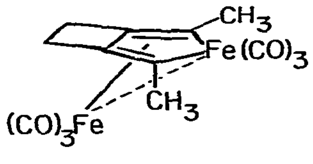

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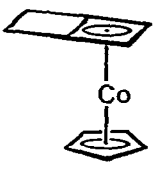


3

Interestingly, in a related system intramolecular cobaltacyclopentadiene formation has been observed from 1,6-hepta- and 1,7-octadiynes with η^5-CpCo[P$(C_6H_5)_3]_2$ [1b], but the corresponding 1,5-diyne does not furnish a cyclobutametallacycle. In contrast to the synthesis of 1, reaction of 2,6-octadiyne with η^5-CpCo$(CO)_2$ gives only intermolecular products. However, when this diyne is heated in the presence of $Fe(CO)_5$ a 1% yield of complex 2 is generated, demonstrating at least the basic feasibility of such a process [1c]. The last two transformations are associated with poor product recovery and mass balance.

We had noted earlier that 1-trimethylsilylated terminal alkynes show, under certain reaction conditions, a propensity to dimerize in the coordination sphere of η^5-CpCo to give the corresponding cyclobutadiene complexes. Moreover, we found that product desilylation could be effected under mild conditions using fluoride reagents [3]. It appeared to us that this sequence might be successfully applied to the synthesis of the theoretically interesting highly strained bicyclo[2.2.0]-1,3-diene ligand present in 3 [4]. For this purpose we have now subjected 1,6-bis(trimethylsilyl)-1,5-hexadiyne to η^5-CpCo$(CO)_2$ and undertaken a complete product analysis of the resulting mixture. None of the desired cyclobutadiene complex was formed but instead a fascinating array of other cobalt compounds bearing novel ligands.

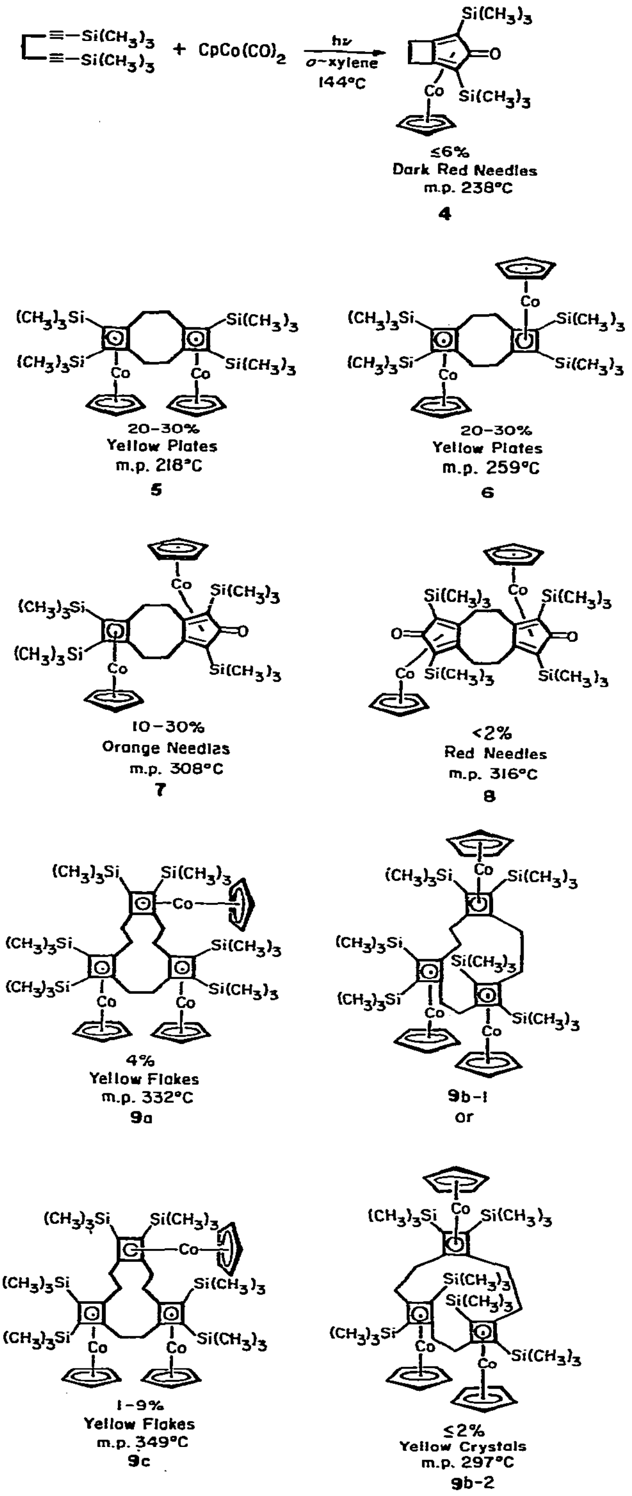
Syringe pump addition of a mixture of 1,6-bis(trimethylsilyl)-1,5-hexadiyne and CpCo$(CO)_2$ (ratio ~1 : 1) to refluxing *o*-xylene (b.p. 144°C) and simultaneous irradiation with visible light gave the mixture of cobalt complexes shown in Scheme 1. The relative amounts of the various compounds formed changed somewhat depending on the exact reaction conditions (length of addition and irradiation time), hence in Scheme 1 a yield range is given for each product. Specifically, a reaction time of five hours gave the following yield distribution: 4 (6%), 5 (21%), 6 (25.5%), 7 (26%), 8 (1.9%), 9a (4%), 9b (2%), 9c (1.5%), 10 (0.25%), 11a (1%), 12 (0.8%), 13 (0.9%), 14—16 (traces). The total mass balance was generally excellent and ranged from 85—95%. Separation of the products was achieved by careful alumina gravity column chromatography using initially n-pentane, then ether and ethanol as eluents, followed if necessary by additional fractionation through high performance liquid chromatography on Altex Ultrasphere-ODS reverse phase columns (dichloromethane/acetonitrile) [5].

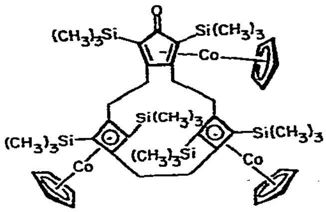
The products in Scheme 1 have been tabulated in order of increasing complexity and by compound class, not in order of elution by chromatography (see experimental section). The simplest complex isolated is the cyclobuta[c]cyclopentadienone 4, from which the free monomeric ligand may be obtained by oxidative demetallation, whereas the complexed parent ligand arises by protodesilylation with fluoride [6]. This chemical behavior in conjunction with spectral data clearly establishes its structure.

The biscyclobutadiene complexes 5 and 6 contain novel ligands which might show interesting chemical behavior on decomplexation. This is the subject of continuing investigation. The structures of 5 and 6 are in accord with spectral measurements. Their relative configuration was tentatively assigned *syn* for 5 and *anti* for 6 based on the appearance of the ^{1}H NMR spectrum. The diastereotopic bridging methylene groups in the *syn*-isomer 5 display the expected complex but symmetrical (AA'BB') ^{1}H NMR pattern. On the other hand, the analogous protons in 6 appear accidentally isochronous, possibly a reflection of the

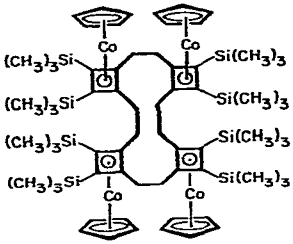
(Continued on p. 109)

SCHEME 1

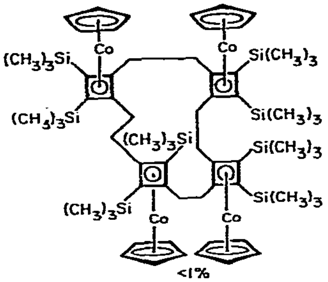

≡—Si(CH3)3
≡—Si(CH3)3
+ CpCo(CO)2
hν
o-xylene
144°C
Si(CH3)3
O
Co
Si(CH3)3
≤6%
Dark Red Needles
m.p. 238°C
4
20–30%
Yellow Plates
m.p. 218°C
5
20–30%
Yellow Plates
m.p. 259°C
6
10–30%
Orange Needles
m.p. 308°C
7
<2%
Red Needles
m.p. 316°C
8
4%
Yellow Flakes
m.p. 332°C
9a
9b-1
or
1–9%
Yellow Flakes
m.p. 349°C
9c
≤2%
Yellow Crystals
m.p. 297°C
9b-2



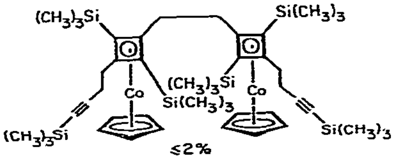
<0.3%
Yellow-Orange Plates
m.p. 329°C
10



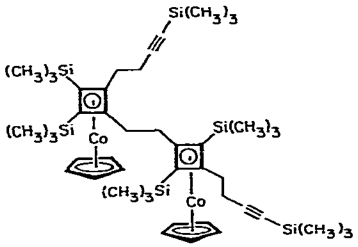
<1%
Yellow Oil
11a



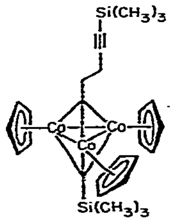
<1%
Yellow Crystals
m.p. 53°C
11b



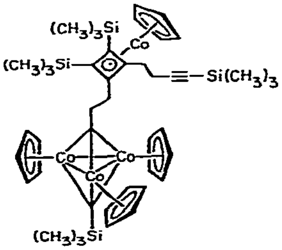
≤2%
Yellow Needles
m.p. 137°C
12



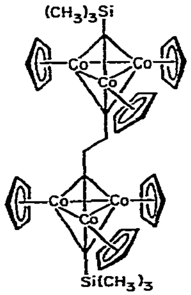
<1%
Yellow Oil
13



27%
Purple Needles
m.p. 91°C
14



<<1%
Purple-Red Needles
m.p. 189°C
15



8%
Purple Needles
m.p. 163°C
16

fact that the anisotropy of the cobalt is felt equally on both sides of the ligand plane. Of course, in the absence of any knowledge about the ground state conformations of these structures the above assignment is speculative.

Two additional compounds **7** and **8** derived from dimerization of starting diyne are formed in only one respective isomeric form. Their gross structure and symmetry is readily ascertained by their spectral properties, but the relative arrangement of the cobalt atoms is left unassigned. It is perhaps interesting to note that the spectral, particularly infrared, data of **8**, a "strainless dimer" of **4**, are very similar to those of the latter. Evidently, the strain introduced by the four-membered ring in **4** is not substantial.

The next set of ten compounds **9**—**13** was contained in one fraction inseparable by gravity column chromatography. These complexes were cleanly separated using HPLC, another manifestation of the power of this method [5]. Structural assignments rest on mass spectra which reveal the basic composition, ^{1}H NMR data which indicate the symmetry of the structures, particularly by the number of cyclopentadienyl and trimethylsilyl peaks, and infrared absorptions.

Structure **9a** has the required symmetry to produce the simple ^{1}H NMR spectrum observed: one singlet each for the respective Cp and trimethylsilyl protons. However, we cannot rule out an alternative structure in which all trimethylsilyl groups occupy nonadjacent positions on all four rings. We prefer **9**, because we believe that the precursor metallacycles to the cyclobutadiene products have a strong preference to place the trimethylsilyl group α to the metal for steric and possibly electronic reasons [1a,3,6,7].

There are three possible structural arrangements for the next two compounds designated **9b-1**, **9b-2** (one isomer), and **9c** (second isomer). We tentatively assign the first two possibilities to the minor isomer (m.p. 297°C) since they incorporate what we regard to be the less likely substitution pattern. This leaves **9c** for the major isomer (m.p. 349°C). All three structures are consistent with the fact that two different Cp-signals (2 : 1) are observed as well as three distinct pairs of trimethylsilyl groups. Models indicate that the 1,3-disubstituted cyclobutadiene rings in **9b**, particularly **9b-2**, are rotationally locked, producing in the latter nonequivalent silylsubstituents on each of the two 1,3-silylated four rings.

Another trimer derived from starting diyne has incorporated an additional carbonyl group in one cyclopentadienone ring. This compound is assigned structure **10** based on spectral data. The substitution pattern on the five ring might in principle be reverse from that shown, i.e. it could adopt a 2,5-bisalkyl-3,4-bis(trimethylsilyl) configuration with the carbonyl group located on the inside of the ligand. Based on other precedence this is deemed less likely [6].

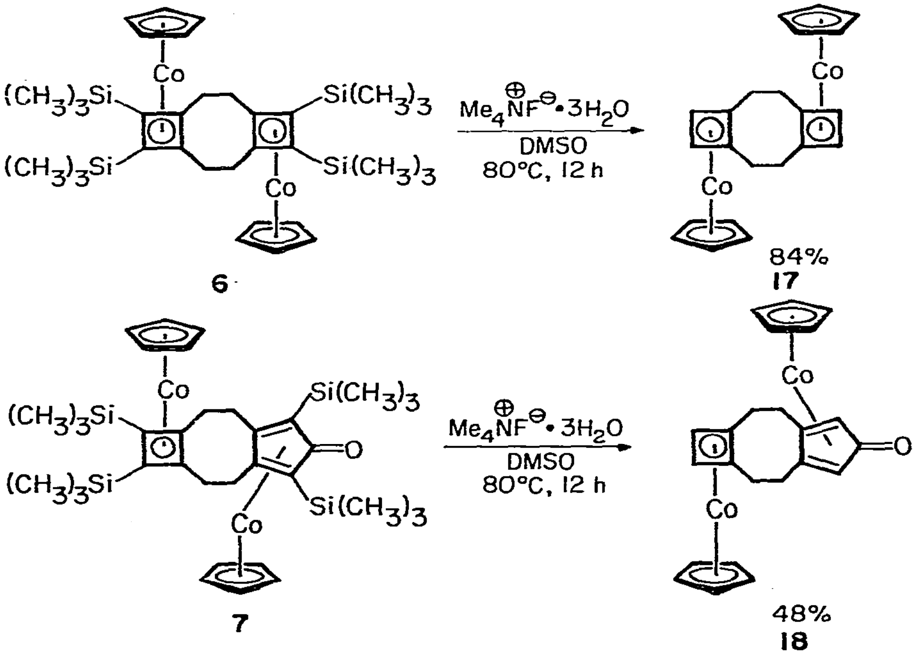
The series of tetramers **11** is very interesting. Apart from the novelty of the tetrakiscyclobutadiene ligand there are potentially many interesting conformational problems associated with the ligand framework. There are also many isomers possible depending on the substitution patterns and the location of the various CpCo groups relative to each other and the ligand. A total of four bands was separated by HPLC, labeled **11a**—**11d**. These compounds appeared pure by HPLC and elemental analysis, and three of the bands (**11b**—**11d**) gave crystalline compounds with sharp melting points. However, unambiguous structural assignments were not always possible based on the available data. Compound

11a, an oil, exhibits only one Cp-singlet but two trimethylsilyl peaks (1 : 1 ratio). A ^{13}C NMR spectrum revealed even less resolution with only one peak for these respective two sets of groups. This is inconsistent with any one structure unless accidental isochronism of the Cp-ligands is invoked. For example, this fraction could be a 1 : 1 mixture of two isomers of the type **11a** with pairs of CpCo-units (isochronous for both isomers) on opposite sides of the ligand plane. Alternatively, a structure in which two of the four rings bear the 1,3-bis-trimethylsilyl arrangement and isochronous Cp-signals is possible. The isolation of the lower "homologs" **5**, **6**, **9a**, and **9c** makes the former structural choice more likely. Crystalline isomer **11b** exhibits three Cp-resonances (ratio 1 : 2 : 1) and four trimethylsilyl peaks of equal intensity. The structure shown is consistent with this finding, assuming that the molecule is flexible enough to allow rotation of the 1,3-bissilylated cyclobutadiene ring through the ligand plane, furnishing the fourth pair of equivalent trimethylsilyl groups. The ^{1}H NMR spectra of **11c** and **11d** are relatively much more complex than those of **11a** and **11b**, with multiple absorptions both in the Cp- and trimethylsilyl-proton range. Evidently these fractions constitute HPLC-inseparable, cocrystallizing isomeric mixtures. Unfortunately, due to lack of material these fractions could not be investigated further.

Compounds **12** and **13** are open-chained trimers of the starting diyne, possible intermediates en route to some of the higher oligomers described above. Their structures are based on their highly indicative spectral characteristics.

The interesting clusters **14**—**16** are formed by alkyne cleavage, a reaction which appears to be general [8]. These compounds are generated only in trace quantities (TLC) under conditions which furnish complexes **4**—**13** in isolable amounts (boiling *o*-xylene). However, if the cyclization reaction is carried out

SCHEME 2



6

84%
17

7

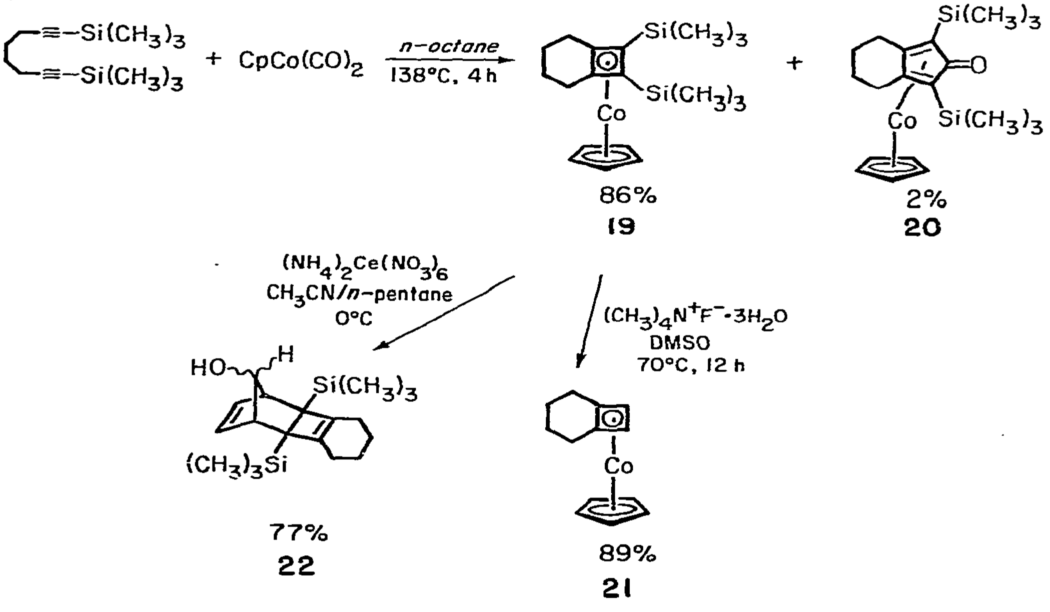
48%
18

at higher temperatures (boiling n-decane) employing excess $CpCo(CO)_2$, the yields shown are realized. In this medium only **6** (4%) is an additional contaminant of the product mixture and none of the other complexes are detected. Compound **15**, formed in minute quantities, could not be fully characterized, and its structural assignment rests on its characteristic mass spectrum and color.

We were interested in obtaining the parent compounds of some of the complexes described in order to also investigate the chemistry of the free ligands. Desilylation of **6** and **7** can indeed be achieved readily by treatment with tetramethylammonium fluoride trihydrate in DMSO at 70°C for 12 hours (Scheme 2). Attempts to use *p*-toluenesulfonic acid in methanol gave lower yields, and no reaction was observed in the presence of Amberlyst A-26 ($P\text{-}NR_3^+F^-$) [9] in methanol, only starting material was recovered. The relatively lower yield of **18** is the result of its slight solubility in water on work-up. Future work is aimed at oxidatively liberating the ligands present in **17** and **18**.

Finally, a model study was undertaken in order to ascertain that the failure to observe a derivative of the type **3** in the reaction of 1,6-bis(trimethylsilyl)-1,5-hexadiyne with $CpCo(CO)_2$ did not have causes other than strain-related factors. For this purpose 1,8-bis(trimethylsilyl)-1,7-octadiyne was exposed to similar reaction conditions (Scheme 3) to very cleanly give the cyclobutadiene complex **19** (86%) and a small amount of the cyclopentadienone **20** (2%) [6].

SCHEME 3



Intramolecular cyclization is obviously a facile process in the absence of strain. Desilylation of **19** results in **21**, which exhibits a very unusual, and to our knowledge hitherto unobserved, feature: it has a strong and long lasting odor very reminiscent of camphor. Neither **19** nor the benzocyclobutadiene analog of **21** (lacking only four hydrogens) [3c] have this property.

One might hope that oxidative demetallation of **19** should result in a stable cyclobutadiene. Interestingly, treatment of **19** with $(NH_4)_2Ce(NO_3)_6$ in acetonitrile gave 22 (77%), a compound formally derived from Diels-Alder trapping of the free cyclobutadiene with some oxidized form of the Cp-ligand. This appears to be general and experiments are underway attempting to elucidate some of the mechanistic features of this process [10].

In summary, in order to elucidate the various synthetic pathways open to 1,5-diynes in the presence of transition metals we have investigated the reaction of 1,6-bis(trimethylsilyl)-1,5-hexadiyne with $CpCo(CO)_2$. The system provides good product recovery and furnishes an array of complexes bearing theoretically and synthetically interesting ligands. The variety of products contrasts with the selectivity observed in a relatively strainless model 1,8-diyne where intramolecular cyclobutadiene formation is predominant.

Experimental

General

Melting and boiling points are uncorrected. Melting points were measured on a Thomas-Hoover Unimelt apparatus. Proton NMR spectra were recorded at 90 MHz on a Varian Associates EM-390 NMR instrument in 5 mm tubes using an internal proton lock system, unless mentioned otherwise. Most measurements for cobalt species required the use of C_6D_6 as solvent rather than CCl_4 or $CDCl_3$ owing to decomposition in chlorinated solvents. Data are reported as chemical shifts (δ) in ppm (multiplicity, integration) (s = singlet, d = doublet, t = triplet, q = quartet, qn = quintet, m = multiplet, b = broad). Infrared spectra were obtained on a Perkin-Elmer 137 and 337 and on a Beckman Microlab^{TM}620 MX computing spectrometer as neat liquid films of arbitrary thickness between sodium chloride plates, as solutions using 0.1 mm path length cells (NaCl), or as potassium bromide pellets. Data are reported as $\tilde{\nu}$ values (cm^{-1}); only selected lines are given. Electronic spectra were recorded on a Cary 118 and 219 UV spectrometer in cyclohexane. The reported UV figures are λ_{max} values (nm), log ϵ in parentheses. The abbreviation UV conveniently stands for electronic spectrum. Low and high resolution mass spectra (obtained at 70 eV) were recorded on AEI-MS 12 and DuPont CEC 21-110B instruments, respectively, on a service basis at the University of California, Berkeley. Only the strongest and/or structurally most important fragmentation peaks are reported in the mass spectra of new compounds. Peaks due to higher silicon isotopes are omitted. TMS stands for trimethylsilyl. Elemental analyses were performed by the Microanalytical Laboratory of the University of California, Berkeley. Vacuum line operations were carried out on a high vacuum (mercury diffusion) multiple line apparatus. All chromatographic separations were carrried out either on E. Merck Reagents silica gel 60 (70-230 mesh ASTM) or alumina (Alfa Products, activated neutral, CAMAG 95+% Al_2O_3, -60 mesh) deactivated with water (4.5% w/w). An Altex HPLC system equipped with an ultraviolet detector (254 and 280 nm) using reversed phase columns (Ultrasphere) ODS, 250 × 10 or 250 × 4.6 mm), generally operating isocratically, was used for some separations. Thin layer chromatography was accomplished on a pre-coated TLC plastic or aluminum sheet (E. Merck Reagents); a) Aluminum oxide 60 F_{254}, neutral (Type E), layer thickness 0.2 mm; b) precoated plastic TLC sheets, Polygram® Sil G/UV_{254}, layer thickness 0.25 mm (Machery-Nagel & Co.); c) precoated TLC glass sheets (Uniplate®)

SilicaGel GHLF, layer thickness 0.25 mm (Analtech, Inc.). Visualization was by UV absorption and I_2 vapor.

All reactions were carried out under oxygen-free atmospheres with magnetic stirring in deoxygenated solvent. The glassware used in reactions involving cobalt was silylated by treatment with hexamethyldisilazane for a few minutes followed by a pentane rinse. Solvents (Mallinckrodt, Analytical Reagent Grade) were generally used as supplied excepting THF which was distilled from sodium-benzophenone. Pentane was distilled away from higher boiling residues. $CpCo(CO)_2$ was used as supplied (Strem).

Reaction of 1,6-bis(trimethylsilyl)-1,5-hexadiyne with $CpCo(CO)_2$

1,6-Bis(trimethylsilyl)-1,5-hexadiyne (1.032 g, 4.65 mmol) in *o*-xylene (18 ml) containing $CpCo(CO)_2$ (926 mg, 5.14 mmol) (degassed three times by freeze-pump-thaw technique) was added via syringe to refluxing degassed *o*-xylene (30 ml) containing $CpCo(CO)_2$ (20 μl) over a period of 6 h. During the addition time the solution was irradiated with a multi-mirror projection lamp (General Electric, 120 V, 250 W). After the addition was complete, the solution was refluxed for another 4 h, cooled under nitrogen to room temperature and connected to a vacuum line. All volatiles were vacuum-transfereed off to give a dark red-brown oil which was chromatographed on alumina (#2.5) first with pentane, then ether, and finally with ethanol as solvent (150 ml fractions).

a) Pentane as solvent

Fraction 1: Complex 5. 320—480 mg (0.46—0.70 mmol, 20—30%); m.p. 259°C, yellow plates (from n-pentane); ^{1}H NMR (C_6D_6): δ = 4.76 (s, 10 H), 2.21 (bs, 8 H), 0.31 (s, 36 H); ($CDCl_3$): δ = 4.77 (s, 10 H), 2.30 (bs, 8 H), 0.43 (s, 36 H); IR ($CHCl_3$): 3017m, 2955m, 1246s, 728s cm^{-1}; *m/e*: 692 (100%, M^+), 677 (2%, $M^+ - CH_3$), 619 (10%, M^+ — TMS). High resolution *m/e*: Found: 692.1979. Calcd. for $C_{34}H_{54}Si_4Co_2$: 692.1966. Anal. Found: C, 59.20; H, 7.93. Calcd. for $C_{34}H_{54}Si_4Co_2$: C, 58.93; H, 7.85%.

Fraction 2: Complex 6. 315—484 mg (0.45—0.71 mmol, 20—30%); m.p. 218°C, orange yellow plates (from benzene); ^{1}H NMR (C_6D_6): δ = 4.82 (s, 10 H), 2.33 (m, 8 H), 0.27 (s, 36 H); IR ($CHCl_3$): 3021s, 2956m, 2400m, 1517m, 1422m, 1320m, 1245s, 1211s cm^{-1}; *m/e*: 692 (100%, M^+), 677 (2%, $M^+ - CH_3$), 619 (12%, M^+ — TMS). High resolution *m/e*: Found: 692.1998. Calcd. for $C_{34}H_{54}Si_4Co_2$: 692.1966. Anal. Found: C, 58.66; H, 7.82. Calcd. for $C_{34}H_{54}Si_4Co_2$: C, 58.93; H, 7.85%.

b) Ether as solvent

Fraction 3. Mixture of compounds (separated by HPLC, vide infra).

Fraction 4. Complex 10. Ca. 5 mg (0.05 mmol, <0.3%); m.p. 329°C, orange needles (from ether/acetone); ^{1}H NMR (C_6D_6): δ = 4.85 (s, 10 H), 4.49 (s, 5 H). 2.61—1.90 (m, 12 H), 0.44 (s, 18 H), 0.19 (s, 36 H); IR ($CHCl_3$): 2960m, 1579m, 1247s, 851s cm^{-1}; *m/e*: 1066 (100%, M^+), 1051 (3%, $M^+ - CH_3$), 993 (30%, M^+ — TMS). Anal. Found: C, 58.38, H, 7.60. Calcd. for $C_{52}H_{81}OSi_6Co_3$: C, 58.51; H, 7.65%.

Fraction 5: Complex 7. 165—504 mg (0.23—0.70 mmol, 10—30%); m.p. 308°C, orange needles (from acetone); ^{1}H NMR (C_6D_6): δ = 4.96 (s, 5 H), 4.62

(s, 5 H), 3.26—1.80 (m, 8 H), 0.41 (s, 18 H), 0.20 (s, 18 H); IR ($CHCl_3$): 2960s, 1570s, 1247s, 819s cm^{-1}; *m/e*: 720 (100%, M^+), 705 (4%, $M^+ - CH_3$), 647 (22%, M^+ — TMS). High resolution *m/e*: Found: 720.1903. Calcd. for $C_{35}H_{54}OSi_4Co_2$: 720.1915. Anal. Found: C, 58.20; H, 7.73. Calcd. for $C_{35}H_{54}OSi_4Co_2$: C, 58.30; H, 7.55%.

Fraction 6. η^5-Cyclopentadienyl-η^4-2,5-bis(trimethylsilyl)cyclobuta[c]cyclopentadienonecobalt, 4. 2—108 mg ($<10^{-3}$—0.29 mmol, <0.1—6.2%); m.p. 238°C, dark red needles (from acetone/ether); ^1H NMR see ref. 6; IR ($CHCl_3$): 2960s, 1559s, 1536s, 1257s cm^{-1}; *m/e*: 374 (27%, M^+), 359 (5%, $M^+ - CH_3$), 346 (100%, M^+ — CO), 301 (1%, M^+ — TMS). High resolution *m/e*: Found: 374.0926. Calcd. for $C_{18}H_{27}OSi_2Co$: 374.0932.

c) Ethanol as solvent

Fraction 7: Complex 8. 2—35 mg ($<10^{-3}$—0.05 mmol, <0.1—2%); m.p. 316°C, red crystals (from acetone); ^1H NMR (C_6D_6): $\delta = 4.53$ (s, 10 H), 2.91—1.88 (m, 8 H), 0.44 (s, 36 H); IR ($CHCl_3$): 2981m, 1561s, 1542s, 1248s; *m/e*: 748 (100%, M^+), 733 (15%, $M^+ - CH_3$), 720 (2%, M^+ — CO), 675 (8%, M^+ — TMS) 189 (83%, $(C_5H_5)_2Co$), 124 (19%, C_5H_5Co), 73 (48%, TMS). Anal. Found: C, 57.99; H, 7.09. Calcd. for $C_{36}H_{54}O_2Si_4Co_2$: C, 57.73; H, 7.27%.

The compound mixture present in fraction 3 was separated on an Altex Model 330 Isocratic Liquid Chromatographic System equipped with a preparative flow cell on two Ultrasphere-ODS reverse phase columns (250 mm length with 10 mm I.D.; 5 μm particle size, column volume 12.9 ml) installed in series.

Fraction 3a: Complex 12. $R_t = 38.1$ min; 0—27 mg (0—0.03 mmol, 0—2%); m.p. 137°C, yellow crystals (from n-pentane); ^1H NMR (C_6D_6): $\delta = 4.72$ (s, 10 H), 2.38 (bs, 12 H), 0.31 (s, 36 H), 0.24 (s, 18 H); IR ($CHCl_3$): 2995s, 2221m, 1247s, 860s; *m/e*: 914 (100%, M^+), 841 (5%, M^+ — TMS), 501 (13%), 331 (16%), 281 (55%), 279 (22%), 189 (37%, $(C_5H_5)_2Co$). Anal. Found: C, 60.48; H, 8.26. Calcd. for $C_{46}H_{76}Si_6Co_2$: C, 60.35; H, 8.37%.

Fraction 3b: Complex 13. $R_t = 41.4$ min; 3—14 mg (0.003—0.02 mmol, 0.2—1%) yellow oil; ^1H NMR (C_6D_6): $\delta = 4.67$ (s, 5 H), 4.65 (s, 5 H), 2.48 (bs, 4 H), 2.45 (bs, 4 H), 2.24 (bs, 4 H), 0.34 (s, 9 H), 0.31 (s, 9 H), 0.24 (s, 9 H), 0.22 (s, 18 H), 0.17 (s, 9 H); IR ($CHCl_3$): 2995s, 2210m, 1247s, 860s; *m/e*: 914 (25%, M^+), 8.89 (3%, $M^+ - CH_3$), 457 (100%, $M^+/2$), 235 (32%), 73 (13%, TMS). Anal. Found: C, 60.12; H, 8.30. Calcd. for $C_{46}H_{76}Si_6Co_2$: C, 60.35; H, 8.37%.

Fraction 3c: Complex 9c. $R_t = 42.9$ min; 15—140 mg (0.01—0.13 mmol, 1—8.8%); m.p. 349°C, yellow plates (from acetone); ^1H NMR (C_6D_6, 250 MHz): 4.75 (s, 10 H), 4.48 (s, 5 H), 2.40—2.29 (m, 12 H), 0.31 (s, 18 H), 0.29 (s, 18 H), 0.25 (s, 18 H); IR ($CHCl_3$): 2955s, 1245s, 1210m, 849s, 808s; *m/e*: 1038 (100%, M^+), 1023 (2%, $M^+ - CH_3$), 965 (1%, M^+ — TMS), 519 (25%), 189 (32%, $(C_5H_5)_2Co$), 73 (15%, TMS). Anal. Found: C, 59.06; H, 7.85. Calcd. for $C_{51}H_{81}Si_6Co_3$: C, 58.93; H, 7.85%.

Fraction 3d: Complex 9b. $R_t = 51.9$ min; 5—31 mg (0.005—0.03 mmol, $\leqslant 2\%$); m.p. 297°C; yellow crystals (from n-pentane/acetone); ^1H NMR (C_6D_6): $\delta = 4.76$ (s, 10 H), 4.66 (s, 5 H), 2.24 (m, 12 H), 0.34 (s, 18 H), 0.32 (s, 18 H), 0.31 (s, 18 H); IR ($CHCl_3$): 2990m, 2940w, 1247s, 1122m, 860s; *m/e*: 1038 (100%, M^+), 965 (24%, M^+ — TMS), 124 (17%, C_5H_5Co), 73 (71%, TMS). Anal.

Found: C, 58.98; H, 7.86. Calcd. for $C_{51}H_{81}Si_6Co_3$: C, 58.93; H, 7.85%.

Fraction 3e: Complex 9a. R_t = 54.0 min; 17—63 mg (0.02—0.06 mmol, <0.1—4%); m.p. 332°C, yellow crystals; ^{1}H NMR (C_6D_6): δ = 4.92 (s, 15 H), 2.21 (AA'BB', 12 H), 0.31 (s, 54 H); IR ($CHCl_3$): 2990s, 1247s, 1120w, 860s, 820m; *m/e*: 1038 (100%, M^+), 519 (18%, $M^+/2$), 189 (24%, $(C_5H_5)_2Co$). Anal. Found: C, 59.02; H, 7.81. Calcd. for $C_{51}H_{81}Si_6Co_3$: C, 58.93; H, 7.85%.

Fraction 3f: Complex 11a. R_t = 59.7 min; 5 mg (<1%); yellow oil; ^{1}H NMR: δ = 4.86 (s, 20 H), 2.48 (bs, 16 H), 0.40 (s, 36 H), 0.31 (s, 36 H); IR ($CHCl_3$): 2990s, 1335w, 1247s, 1125m, 1015w, 855s, 820m; *m/e*: 1384 (100%, M^+), 1371 (1%, $M^+ - CH_3$), 1311 (3%, M^+ — TMS), 189 (29%, $(C_5H_5)_2Co$), 124 (14%, C_5H_5Co), 73 (17%, TMS). Anal. Found: C, 59.03; H, 7.89. Calcd. for $C_{68}H_{108}Si_8Co_4$: C, 58.93; H, 7.85%.

Fraction 3g: Complex 11b. R_t = 61.2 min; ca. 5 mg (<1%); m.p. 53°C, yellow crystals (from n-pentane/ether); ^{1}H NMR (C_6D_6): δ = 5.13 (s, 5 H), 4.86 (s, 10 H), 4.52 (s, 5 H), 2.68—2.04 (m, 16 H), 0.44 (s, 18 H), 0.34 (s, 18 H), 0.30 (s, 18 H), 0.27 (s, 18 H); IR ($CHCl_3$): 2995s, 1247s, 866s; *m/e*: 1384 (100%, M^+), 189 (18%, $(C_5H_5)_2Co$), 124 (14%, C_5H_5Co), 73 (28%, TMS). Anal. Found: C, 59.17; H, 7.89. Calcd. for $C_{68}H_{108}Si_8Co_4$: C, 58.93; H, 7.85%.

Fraction 3h: Complex 11c. R_t = 62.5 min; ca. 3 mg (<1%); m.p. 47°C, yellow crystals (from n-pentane/ether); ^{1}H NMR (C_6D_6): δ = 5.03—4.55 (m, 20 H), 2.68—2.14 (m, 16 H), 0.51, 0.44, 0.31, 0.27, 0.20 (s, varying intensity, 72 H); IR ($CHCl_3$): 2990s, 1249s, 860s; *m/e*: 1384 (20%, M^+), 189 (19%, $(C_5H_5)_2Co$), 73 (99%, TMS), 44 (100%). Anal. Found: C, 58.64; H, 7.98. Calcd. for $C_{68}H_{108}Si_8Co_4$: C, 58.93; H, 7.85%.

Fraction 3i: Complex 11d. R_t = 65.0 min; ca. 3 mg (<1%); m.p. 122°C, yellow crystals (from n-pentane/ether); ^{1}H NMR (C_6D_6): δ = 5.13—4.48 (m, 20 H), 2.68—2.11 (m, 16 H), 0.65—0.17 (m, 72 H); IR ($CHCl_3$): 2995s, 1250s, 865s; *m/e*: 1384 (4%, M^+), 693 (6%), 457 (13%), 189 (6%, $(C_5H_5)_2Co$), 73 (35%, TMS), 57 (100%). Anal. Found: C, 58.94; H, 7.81. Calcd. for $C_{68}H_{108}Si_8Co_4$: C, 58.93; H, 7.85%.

Desilylation of 6 to 17

Complex 6 (121 mg, 0.17 mmol) was dissolved in DMSO (5 ml), tetramethylammonium fluoride trihydrate (500 mg, 3.4 mmol) added and the solution kept at 125°C (bath temperature) for 12 h with stirring. At this point the solution was cooled down to room temperature, water (20 ml) and ether (20 ml) were added and the organic layer extracted with water (8 × 10 ml) to remove the DMSO. The ethereal solution was dried over sodium sulfate, the solvent stripped off under reduced pressure, and the yellow residue was chromatographed on alumina with pentane.

Fraction 1: starting material 6. 4 mg (3%), identified by NMR and IR comparison with an authentic sample.

Fraction 2: 17. 57 mg (0.14 mmol, 84%); m.p. 146°C, yellow flakes (from pentane); ^{1}H NMR (C_6D_6): δ = 4.82 (s, 10 H), 3.65 (s, 4 H), 2.07 (m, 8 H); IR ($CHCl_3$): 3019s, 2400m, 1519m, 1427m, 1210s, 927m, 741s, 730s, 666s; *m/e*: 404 (100%, M^+), 279 (49%), 189 (95%, $(C_5H_5)_2Co$), 124 (87%, C_5H_5Co). High resolution *m/e*: Found: 404.0387. Calcd. for $C_{22}H_{22}Co_2$: 404.0385.

Fraction 3. 5 mg; m.p. 238°C, yellow flakes (from pentane); ^{1}H NMR (C_6D_6):

δ = 4.69 (s, 10 H), 4.58 (s, 5 H), 3.74 (s, 2 H), 3.60 (s, 2 H), 3.57 (s, 2 H), 1.90 (m, 12 H); *m/e*: 606 (100%, M^+), 417 (27%), 189 (92%), 124 (49%, C_5H_5Co). High resolution *m/e*: Found: 606.0606. The structure of this compound was left undetermined, but the spectral data are consistent with completely desilylated 9b. Since 6 is completely separable from 9b, we do not feel that 9b itself is a precursor to this unknown.

Desilylation of 7 to 18

Complex 7 (70 mg, 0.1 mmol) was dissolved in DMSO (2 ml), tetramethylammonium fluoride (56 mg, 0.4 mmol) was added and the solution kept in a stoppered flask at 80°C in an oven for 12 h. Work-up was achieved by adding water/ether (20 ml) after cooling down to room temperature and extracting the ether layer with water (8 × 5 ml). After drying over sodium sulfate, the solvent was stripped off on a rotary evaporator. The oily residue was chromatographed on alumina with ether/pentane (1/1): 21 mg (0.048 mmol, 48%); m.p. 187°C, orange needles (from ether); ^1H NMR (C_6D_6): δ = 4.89 (s, 5 H), 4.74 (s, 5 H), 4.12 (s, 2 H), 3.74 (s, 2 H), 3.06—1.92 (m, 8 H); IR ($CHCl_3$): 2998s, 1578s, 866s; *m/e*: 432 (70%, M^+), 189 (100%), 124 (33%, C_5H_5Co). Anal. Found: C, 63.77; H, 5.17. Calcd. for $C_{23}H_{22}CoO$: C, 63.90; H, 5.13%.

Reaction of 1,6-bis(trimethylsilyl)-1,5-hexadiyne with 4 equivalents of CpCo-(CO)$_2$ in boiling decane: Formation of biscarbyne clusters 14—16

1,6-Bis(trimethylsilyl)-1,5-hexadiyne (100 mg, 0.45 mmol) in n-decane (5 ml, degassed three times by freeze-pump-thaw technique) was added to refluxing, degassed n-decane (b.p. 174°C) containing $CpCo(CO)_2$ (326 mg, 1.81 mmol) over a period of 4 h via syringe-pump. The reaction flask was simultaneously irradiated with a GE multi-mirror projection lamp (120 V, 250 W). After the addition was complete, the solution was heated to reflux for 2 h, cooled under nitrogen to room temperature and connected to a vacuum line. At 80°C (bath temperature) all volatiles were vacuum transferred off to give a purple-black crystalline mass which was chromatographed on alumina with pentane to give fractions 1 and 2 and then eluted with ether to yield fraction 3.

Fraction 1: Cluster 14. 72 mg (0.21 mmol, 27%); m.p. 91°C, purple feathers (from n-pentane/acetone); ^1H NMR (C_6D_6): δ = 4.49 (s, 15 H), 2.71—2.24 (m, 4 H), 0.88 (s, 9 H), 0.20 (s, 9 H); IR ($CHCl_3$): 2965s, 1247s, 865s cm^{-1}; *m/e*: 594 (48%, M^+), 189 (100%, $(C_5H_5)_2Co$). High resolution *m/e*: Found: 594.0454. Calcd. for $C_{27}H_{37}Si_2Co_3$: 594. 0432.

Fraction 2: Cluster 15. 1 mg (<<1%); m.p. 189°C, purple-red crystals (from pentane); *m/e*: 940 (62%, M^+), 483 (100%, $M^+ - (C_5H_5Co)_3C$ TMS), 457 (20%, $(C_5H_5Co)_2CTMS$), 411 (4%), 384 (4%, 457 — TMS), 397 (1%), 371 (20%), 189 (100%, $(C_5H_5)_2Co$), 73 (13%, TMS).

Fraction 3: Cluster 16. 35 mg (0.036 mmol, 8%); m.p. 163°C, purple crystals (from n-pentane/ether); ^1H NMR (C_6D_6): δ = 4.37 (s, 30 H), 2.59 (s, 4 H), 0.73 (s, 18 H); IR ($CHCl_3$): 2980s, 1247s, 861s cm^{-1}; *m/e*: 966 (M^+, 63%), 189 (100%, $(C_5H_5)_2Co$), 73 (28%, TMS). Anal. Found: C, 51.89; H, 5.23. Calcd. for $C_{42}H_{52}Si_2Co_6$: C, 52.19; H, 5.42%.

Reaction of 1,8-bis(trimethylsilyl)-1,7-octadiyne with $CpCo(CO)_2$

1,8-Bis(trimethylsilyl)-1,7-octadiyne (975 mg, 3.90 mmol) in n-octane (15 ml), containing $CpCo(CO)_2$ (701 mg, 3.89 mmol) (degassed three times by freeze-pump-thaw technique) was added via syringe to refluxing degassed n-octane (b.p. 128° C) containing $CpCo(CO)_2$ (20 μl) over a period of 12 h. After the addition was complete the solution was heated to reflux another 4 h, cooled under nitrogen to room temperature and connected to a vacuum line. All the volatiles were vacuum-transferred off to give a yellow crystalline residue, which was chromatographed on alumina (#2.5): first with pentane to give cyclobutadiene complex **19**: 1.29 g (3.4 mmol, 86%); m.p. 61° C, yellow needles (from acetone); ^{1}H NMR (C_6D_6): δ = 4.62 (s, 5 H), 2.14—1.15 (m, 8 H), 0.29 (s, 18 H); IR ($CHCl_3$): 2951s, 2935s, 2850m, 1288m, 1245s, 1210m, 1164m, 1000m, 839s; *m/e*: 374 (100%, M^+), 359 (6%, $M^+ - CH_3$), 309 (17%), 301 (21%, M^+ — TMS), 124 (11%, C_5H_5Co), 73 (17%, TMS). High resolution *m/e*: Found: 374.1286. Calcd. for $C_{19}H_{31}CoSi_2$: 374.1296. The alumina was then eluted with ether to yield complex **20**: 32 mg, (0.8 mmol, 2%), [6].

Desilylation of 19 to complex 21

Complex **19** (203 mg, 0.54 mmol) was dissolved in dry DMSO (10 ml) and $(CH_3)_4N^+F^- \cdot 3\,H_2O$ (294 mg, 2.0 mmol) added. The solution was kept at 79° C for 12 h, water (10 ml) added and extracted with ether (3 × 30 ml). The combined ether layers were washed with water (8 × 10 ml) to remove the DMSO and then dried over sodium sulfate, the solvent stripped off and the residue chromatographed on alumina with n-pentane to give **21**: 110 mg (0.48 mmol, 89%); orange-yellow oil with a strong camphor odor; ^{1}H NMR (C_6D_6): δ = 4.75 (s, 5 H), 3.74 (s, 2 H), 2.24—1.09 (m, 8 H); IR (film): 3150m, 2980s, 2900s, 1462s, 1358m, 1307m, 1285s, 1130s, 1022s, 822s, 775m, 712m; *m/e*: 230 (50%, M^+), 124 (100%, C_5H_5Co). High resolution *m/e*: Found: 230.0507. Calcd. for $C_{13}H_{15}Co$: 230.0504.

Oxidative demetallation of 19 to 22

Complex **19** (292 mg, 0.78 mmol) was dissolved in acetone (10 ml) and cooled in an ice bath. One portion of $(NH_4)_2Ce(NO_3)_6$ (583 mg, 1.06 mmol) was added with stirring, followed by a second portion (485 mg, 0.89 mmol) 20 min later. The solution was stirred for an additional 30 min, the solvent stripped off and the residue chromatographed on silica gel with n-pentane/ether (1/1) to give **22**: 199 mg (0.60 mmol, 77%); colorless oil; ^{1}H NMR (C_6D_6, 250 MHz): δ = 5.70 (AA'BB', 2 H), 3.1—1.1 (m, 12 H), 0.16 (s, 18 H); IR ($CHCl_3$): 3300(br), 2980s, 1660s, 1250s, 1127m, 839s; *m/e*: 332 (11%, M^+), 317 (4%, $M^+ - CH_3$), 314 (3%, $M^+ - H_2O$), 266 (70%), 259 (39%, M^+ — TMS), 251 (13%), 193 (7%), 73 (100%, TMS). High resolution *m/e*: Found: 332.1993. Calcd. for $C_{19}H_{32}OSi_2$: 332.1991.

Acknowledgments

We thank the National Science Foundation CHE 79-03954 and in part the National Institute of Health (CA 20713 and GM 22479) for financial support. We appreciate preliminary experiments by Mr. R. Brainard, and thank James S.

Drage for valuable help in the measurement of high-field NMR spectra. E.R.F.G acknowledges a postdoctoral fellowship from the N.A.T.O.-Deutscher Akademischer Austauschdienst (1979—1981). K.P.C.V. is a Camille and Henry Dreyfu Teacher-Scholar (1978—1983).

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