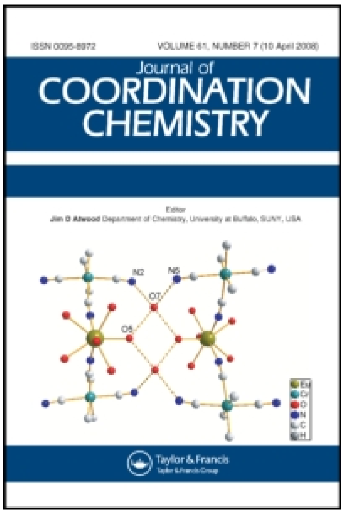

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THE REACTION BETWEEN π-CYCLOPENTADIENYLDI-CARBONYLCOBALT AND PHENYLETHYNYLSILANE, AND AN X-RAY CRYSTALLOGRAPHIC INVESTIGATION OF ONE OF THE PRODUCTS, (π-CYCLOPENTADIENYL)-[trans-DIPHENYL-DI(TRIMETHYLSILYL)-CYCLOBUTADIENE]-COBALT

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THE REACTION BETWEEN π-CYCLOPENTADIENYLDICARBONYLCOBALT AND PHENYLETHYNYLSILANE, AND AN X-RAY CRYSTALLOGRAPHIC INVESTIGATION OF ONE OF THE PRODUCTS, (π-CYCLOPENTADIENYL)-[trans-DIPHENYL-DI(TRIMETHYLSILYL)-CYCLOBUTADIENE]-COBALT

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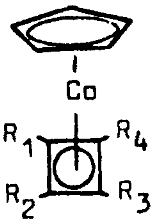
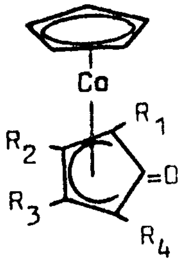
This is a report of the broad range of reactions and products that occur in refluxing xylene when π-cyclopentadienylcobalt or (π-cyclopentadienyl)-dicarbonylcobalt react with either symmetric or unsymmetrical acetylenes, specially when one of the substituents of the acetylene is an aromatic moeity. Since these reactions produce a variety of products, several of which are *cis*- and *trans*- tetrasubstituted cyclobutadiene-cobalt isomers, mnr and mass spectral methods were used to distinguish between them. In order to obtain an independent and indisputable structure assignment for the structural isomers investigated by spectral techniques, the crystal structure of the title compound was investigated by x-ray crystallographic techniques. The compound crystallizes in space group Pbca with the following cell dimensions: $a = 29.622(7)$, $b = 9.967(2)$ and $c = 17.140(3)$ Å; $V = 5060.46$ Å^3; $D(\text{exp}) = 1.23(2)$ gm-cm^{-3}, $D(\text{calc}) = 1.24$ gm-cm^{-3} for $Z = 8$ molecules/unit cell. The intensity data were collected with MoKα radiation ($\lambda = 0.71069$ Å) using a computer-controlled diffractometer equipped with a graphite monochromator. In all 6331 reflections were collected of which 3173 were independent and had $F_0{}^2 \geqslant 3\sigma\,(F_0{}^2)$. The data were corrected for absorption and the transmission coefficients ranged from 0.72 to 0.79. The (π-cyclopentadienyl) ring is planar and has normal Co–C and C–C distances which average 2.049(7) and 1.389(17) Å, respectively. The Co–(Cp ring centroid) distance is 1.67 Å and the ring librates about this axis to a small degree which is not, however, large enough to affect the C–C distances. The average value of the C–C–C angle in the π-cyclopentadienyl ring is 108° indicating that it is planar and, in fact, the largest deviation of any carbon from the least-squares plane is 0.006 Å. In the Co-cyclobutadiene moiety, the Co–C and C–C distances are 1.982(15) and 1.467(3) Å and the Co–(cyclobutadiene ring centroid) distance is 1.69 Å. The angle between the normals of the five- and four-membered rings is 1.6°. The phenyl rings and trimethylsilyl fragments have normal distances and angles and the phenyl rings are planar. The two silicon and two carbon atoms of the phenyl rings linked to the π-cyclobutadiene moeity are out of the mean plane of the ring and bend away from the Co atom.

Finally, and most important, the four-membered ring is planar (the largest deviation from planarity is 0.003 Å) and the four C–C distances are the same length; however, the internal angles are not 90.0°. Instead, the two angles at carbons bonded to phenyl rings have values of 88.1(2)° and 88.4(2)° while those at carbon atoms bonded by silicons have values of 91.6(2)° and 91.8(2)°. The final discrepancy indices for this structural analysis were $R_1 = 0.038$ and $R_2(\text{F}) = 0.044$.

INTRODUCTION

In 1967, we reported that a reaction between π-cyclopentadienyldicarbonylcobalt and diphenylacetylene proceeded readily in refluxing xylene to produce the cyclotrimerization product, hexaphenylbenzene, an organic condensation product, tetraphenylcyclopentadienone, as well as two organocobalt complexes, (π-cyclopentadienyl)-(tetraphenylcyclobutadiene)-cobalt (1) and (π-cyclopentadienyl)-(tetraphenylcyclopentadienone)-cobalt (2).[2,3] Similar studies at that time by Helling *et al.*[4] indicated that reactions between unsymmetrical acetylenes and either (π-cyclopentadienyl)-(1,5-cyclooctadiene)-cobalt or cobaltocene resulted in the formation of *cis*- and *trans*-tetrasubstituted cyclobutadiene-cobalt complexes. In an earlier communication[5] and at several meetings[6,7] we have reported that reactions between (π-cyclopentadienyl)-dicarbonylcobalt and other acetylenes, especially unsymmetrical acetylenes in





R_1, R_2, R_3, R_4 = Ph (1)
R_1, R_3 = Ph; R_2, R_4 = $SiMe_3$ (3)
R_1, R_2 = Ph; R_3, R_4 = $SiMe_3$ (4)
R_1, R_2, R_3, R_4 = Ph (2)
R_1, R_3 = Ph; R_2, R_3 = $SiMe_3$ (5)
R_1, R_3 = Ph; R_2, R_4 = $SiMe_3$ (6)
R_2, R_3 = Ph; R_1, R_4 = $SiMe_3$ (7)

which one of the substituents is aromatic, are very broad in scope, and produce a variety of isomeric cyclotrimerization products, isomeric cyclobutadiene–cobalt complexes, as well as isomeric cyclopentadienone–cobalt complexes. One of these reactions, that between (π-cyclopentadienyl)-dicarbonyl-cobalt and phenylethynyltrimethylsilane, is described in detail in this paper, together with a discussion of a method for determining structures of *cis*- and *trans*-tetrasubstituted cyclobutadiene-cobalt complexes by means of mass spectrometry, and the first x-ray crystallographic structural determination of a cyclobutadiene-cobalt complex. After our work in this area was completed, some results of a similar nature were independently described by others,[8] and these findings are in general agreement with our earlier conclusions.[5–7]

EXPERIMENTAL SECTION

All melting points were taken in sealed capillaries under nitrogen and are uncorrected. CAMAG alumina (neutral) was used for column chromatography, and CAMAG silicia for tlc was used for tlc separations. (π-Cyclopentadienyl)-dicarbonylcobalt[3] and phenylethynyltrimethylsilane[9] were prepared according to literature methods. Elemental analyses were carried out by Mr. Charles Meade and associates, Microanalytical Laboratory, Office of Research Services, University of Massachusetts. Nmr spectra were recorded on a Varian A-60 spectrometer and are referenced to tetramethylsilane as an internal standard. Mass spectra were recorded on a Perkin–Elmer Hitachi RMU-6L mass spectrometer at 70 eV.

Reaction of (π-Cyclopentadienyl)dicarbonylcobalt and Phenylethynyltrimethylsilane

Into a 200-ml, single-necked flask which had been repeatedly flushed with nitrogen, were added 100 ml of *p*-xylene, 3.48 g (0.02 mole) of phenylethynyltrimethylsilane, and 1.80 g (0.01 mole) of (π-cyclopentadienyl)dicarbonylcobalt. The flask was covered with aluminum foil and heated to reflux. After 28 h, the reaction mixture was allowed to cool to room temperature under nitrogen, filtered in air, and the black residue washed with hot benzene. The combined *p*-xylene and benzene portions were concentrated under reduced pressure to a small volume, and the concentrate was placed on a column of neutral alumina. Elution with hexane produced a broad yellow band (A), which resulted in 3.55 g (75%) of a mixture of cyclobutadiene-cobalt complexes (3) and (4).

Band A was subjected to preparative tlc using 20 x 10 cm. silica plates. Five multiple elutions using hexane separated two closely-spaced but distinct yellow bands. The product from the band of higher R_f was recrystallized from hexane to produce yellow-orange crystals of (π-cyclopentadienyl)-[*trans*-diphenyl-di(trimethylsilyl)cyclobutadiene]-cobalt (3), mp 165–167°.

Anal. Calcd. for $C_{27}H_{33}Si_2O$: C, 68.61; H, 7.04; Si, 11.88; Co, 12.47; Mol wt., 472. Found: C, 68.55; H. 6.84; Si, 11.80; Co, 12.40; Mol. wt., 472 (mass spectrometry).

Nmr ($CDCl_3$): multiplet at τ 2.6–3.0 (10H, phenyl ring protons), singlet at 5.15 (5H, cyclopentadienyl ring protons), singlet at 9.88 (18H, trimethylsilyl protons).

An nmr spectrum of the band of lower R_f indicated that the expected product, (π-cyclopentadienyl)-[*cis*-diphenyl-di(trimethylsilyl)cyclobutadiene]-cobalt (4), partially decomposed during preparative tlc, as evidenced by an additional cyclopentadienyl ring proton resonance at τ 5.28. Tlc of the material also indicated that another compound was present in addition to (4), after separation of the *trans*-isomer (3). Fortunately, this impurity remained in solution when material was recrystallized from hexane, and yellow crystals of (4), mp. 121–121.5°, were obtained.

Anal. Calcd. for $C_{27}H_{33}Si_2Co$: C, 68.61; H, 7.04; Si, 11.88; Co, 12.47; Mol. wt., 472. Found: C, 69.11;

H, 7.01; Si, 11.53; Co, 12.26; Mol. wt., 472 (mass spectrometry).

Nmr ($CDCl_3$): multiplet at τ 2.6–3.0 (10H, phenyl ring protons), singlet at 5.20 (5H, cyclopentadienyl ring protons), singlet at 9.80 (18H, trimethylsilyl protons).

Subsequent elution of the alumina column with chloroform removed an orange band (B) which contained the three isomeric cyclopentadienone–cobalt complexes (5–7). Preparative tlc of the product on silica using 10:1 dichloromethane–acetone developed two orange bands. Separation of the band of higher R_f produced 13 mg of a single cyclopentadienone–cobalt complex. Nmr ($CDCl_3$): multiplet at τ 2.6–2.9 (phenyl ring protons), singlet at 4.80 (cyclopentadienyl ring protons), singlet at 9.87 (trimethylsilyl protons); mol. wt. calcd., 500. Mol. wt. found, 500 (mass spectrometry). The lower R_f band yielded *ca.* 25 mg of a mixture of two cyclopentadienone-cobalt isomers, which could not be separated further by subsequent tlc. Nmr ($CDCl_3$): multiplet at τ 2.6–2.9 (phenyl ring protons), singlets at 4.83 and 5.20 (two cyclopentadienyl ring proton resonances), singlets at 9.72, 9.91 and 10.17 (three trimethylsilyl proton resonances); mol. wt. calcd., 500. Mol. wt. found, 500 (mass spectrometry).

Continued elution with chloroform removed two narrow dark bands, (C) and (D). Band (C) produced a dark-brown solid, while band (D) resulted in an orange solid which appeared to be pure tlc. Unfortunately, the very small amounts of these products obtained precluded a complete structural investigation, however, the mass spectra of the products and tentative assignments of their structures are presented in the Results and Discussion Section.

Crystallographic Studies

A series of precession photographs taken with $MoK\bar{\alpha}$ radiation showed the crystals to be orthorhombic and the systematic absences were consistent with the space group *Pbca*.[10a] The observed density is 1.23(2) $gm\text{-}cm^{-3}$ while the calculated density, for eight molecules in the unit cell, is 1.24 $g\text{-}cm^{-3}$. The cell constants and their standard deviations, $a = 29.622(7)$, $b = 9.967(2)$, $c = 17.140(3)$ Å, were obtained by a least-squares refinement of 30 reflections that were centered on an automated Picker diffractometer equipped with a graphite monochromator and using $MoK\alpha_1$ radiation (λ = 0.70926 Å). The rectangular crystal used in data collection had faces of the form {100} and was 0.309 x 0.817 x 0.443 mm along the [100], [010], [001] directions. Data collection was carried out with a Picker diffractometer controlled by the Brookhaven Multiple Spectrometer Control System. The scintillation counter included a pulse height analyser and a take-off angle of 1.9° was used which corresponded to 75% of the maximum intensity. Data were collected by the θ–2θ scan technique and a reflection was scanned in steps of $\Delta(2\theta) = 0.02°$, with a counting time of 2 seconds for each step. The total scan range of 1.60 $(1.0 + 1.0 \tan\theta)$ was centered about the Bragg angle which corresponds to the unweighted average wavelength of 0.7114 Å for $MoK\alpha_1$ and $MoK\alpha_2$ radiation. The intensities of 6331 unique reflections for $2\theta \leqslant 52°$ were measured. Two standard reflections were monitored every 30 reflections and both showed a 16% drop in intensity at the end of data collection. As a plot of both standards showed the decomposition to be linear, the data was scaled to standards during data processing.

The values of I and $\sigma(I)$ were corrected for Lorentz-polarization effects and absorption. The absorption coefficient, μ, for $MoK\bar{\alpha}$ radiation (λ = 0.71069 Å) is estimated to be 8.109 cm^{-1} from the mass absorption coefficients.[10b] For the crystal chosen, transmission coefficients ranged from 0.72–0.79. Of the the 6331 reflections collected, 3173 reflections had $F_0{}^2 \geqslant 3\sigma(F_0{}^2)$ where $\sigma(F_0{}^2) = 1/Lp\,[(I+B) + (0.03I)^2]^{1/2}$, where Lp is the Lorentz-polarization factor, I is the total integrated peak, and B is the time scaled background.[11]

Solution and Refinement of the Structure

The 3173 reflections for which $F_0{}^2 \geqslant 3\sigma(F_0{}^2)$ were used to solve and refine the structure. All least-squares refinements were carried out on F, the function minimized being $\Sigma w(|Fo| - |Fc|)^2$, where $|Fo|$ and $|Fc|$ are the observed and calculated structure amplitudes and $w = 4F_0{}^2/\sigma^2(F_0{}^2)$. In all calculations of Fc, the atomic scattering factors for the atoms were taken from the tabulation by Cromer.[12a] The effects of anomalous dispersion of the cobalt and silicon atoms were included in the calculation of Fc.[12b]

A Patterson function yielded approximate coordinates of the cobalt atom. Two successive difference Fourier synthesis resulted in the location of all other non-hydrogen atoms. After three cycles of least-squares refinement in which the positional and isotropic thermal parameters of the cobalt, silicon, and carbon atoms were varied, the positions of the hydrogen atoms were determined. The methyl-hydrogen atoms were located by difference Fourier sections calculated perpendicular to the Si–C vectors and then idealized to a C–H distance of 0.98 Å. The positions of the phenyl–hydrogen atoms and cyclopentadienyl hydrogen atoms were calculated using a C–H distance of 0.98 Å. The methyl–hydrogen atoms, phenyl–hydrogen atoms, and cyclopentadienyl–hydrogen atoms were assigned isotropic thermal parameters of 6.3, 4.5, and 7.0 Å^2, respectively. These parameters were used because they correspond to the average isotropic thermal parameters of the related carbon atoms. In the final stages of refinement the hydrogen atoms were added as a fixed contribution to F_c.

The positional and anisotropic thermal parameters of the cyclopentadienyl carbon atoms and the cobalt atom were varied in one cycle. In the following cycle, the positional and anisotropic thermal parameters of the cobalt atom, the silicon atoms, and the carbon atoms of the cyclobutadiene ring, the phenyl rings, and the methyl groups were allowed to refine. Such refinements converged at values of $R_1 = 0.038$ and $R_2 = 0.044$ where $R_1 = \Sigma | (|F_0| - |F_c|)/\Sigma |F_0|$ and $R_2 = \{\Sigma w(|F_0| - |F_c|)^2/\Sigma wF_0^2\}^{1/2}$. The error in an observation of unit weight was 1.90.

The final positional and thermal parameters are presented in Table II along with the associated standard deviations in these parameters as estimated from the inverse of the normal equations matrix. The root-mean-square amplitudes of vibration along the three principal axes of the thermal ellipsoid are presented in Table III and the idealized hydrogen atom positions are presented in Table IV. The final values of $10\,|F_0|$ and $10\,|F_c|$ (in electrons) are given in a table which may be obtained from the Editor's office.

The following programs were used. PROCH (initial processing of data); TOMPABS (Lorentz-polarization and absorption corrections); ECSORTH (sorting and averaging of data); JIMDAP (local version of the Zalkin Fourier summation program); CLINUS (modification of the Busing, Martin, and Levy ORFLS least-squares program)[13]; FREDFUN (local version of the ORFFE function and error program)[14]; PLANET (least-squares planes);[15] ORTEP[2] (molecular plotting).[16]

RESULTS AND DISCUSSION

The reaction between (π-cyclopentadienyl)dicarbonylcobalt and phenylethynyltrimethylsilane produces a variety of organometallic products. Isomeric cyclotrimerization products, which might be expected to be formed in such a reaction,[3,17] could not be detected. The organometallic π-complexes

TABLE I
Mass spectra of isomeric (π-Cyclopentadienyl)-] diphenyl-di(trimethylsilyl)-cyclobutadiene] -cobalt complexes

Complex (3)	*m/e*	Relative abundance[a]	Assignment
	472	62	$M^{+\cdot}$
	457	2.3	$(M-CH_3)^+$
	399	2.8	$[M-Si(CH_3)_3]^+$
	302	6.0	(8)
	298	100.0	(10)
	294	9.2	(9)
	283	8.4	$(9-CH_3)^+$
	223	6.3	$[Co(C_6H_5C{\equiv}CSi(CH_3)_3)]^+$
	159	21.0	$[C_6H_5C{\equiv}CSi(CH_3)_2]^+$
	124	34.7	$(C_5H_5Co)^+$
Complex (4)	***m/e***	**Relative abundance[a]**	**Assignment**
	472	100.0	$M^{+\cdot}$
	457	4.0	$(M-CH_3)^+$
	400	27.5	$[M-Si(CH_3)_2CH_2]^{+\cdot}$
	302	17.0	(8)
	298	100.0	(10)
	294	50.0	(9)
	283	10.0	$(9-CH_3)^+$
	159	13.0	$[C_6H_5C{\equiv}CSi(CH_3)_2]^+$
	124	50.0	$(C_5H_5Co)^{+\cdot}$

[a] Relative to base peak = 100.

TABLE II
Positional and thermal parameters

Atom	X	Y	Z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Co	0.15351(1)	0.06496(4)	0.23591(2)	0.00096(1)	0.01136(5)	0.00339(1)	0.00078(1)	−0.00017(1)	0.00148(2)
Si1	0.09681(3)	0.15617(8)	0.41104(5)	0.00143(1)	0.00864(9)	0.00331(3)	0.00002(3)	−0.00037(2)	−0.00059(4)
Si2	0.11706(3)	−0.23287(9)	0.16119(5)	0.00098(1)	0.01211(11)	0.00306(3)	0.00018(3)	0.00002(1)	−0.00090(4)
C1	0.11208(9)	0.05054(27)	0.32385(15)	0.00096(3)	0.00809(31)	0.00287(10)	−0.00044(9)	−0.00020(5)	0.00026(14)
C2	0.08835(9)	0.02774(27)	0.24598(15)	0.00092(3)	0.00872(30)	0.00273(10)	−0.00048(8)	−0.00006(4)	0.00007(14)
C3	0.11351(9)	−0.09695(29)	0.23616(15)	0.00080(3)	0.00980(33)	0.00298(10)	−0.00045(8)	0.00003(5)	0.00037(15)
C4	0.13564(9)	−0.07389(27)	0.31144(15)	0.00088(3)	0.00793(31)	0.00273(10)	−0.00051(8)	−0.00002(4)	0.00037(15)
C1,1	0.05199(9)	0.09572(29)	0.20557(15)	0.00081(3)	0.01001(37)	0.00267(10)	−0.00027(9)	−0.00004(5)	0.00057(14)
C2,1	0.02097(10)	0.02336(31)	0.16208(17)	0.00102(4)	0.01185(39)	0.00395(12)	−0.00028(10)	−0.00024(6)	−0.00025(17)
C3,1	−0.01324(11)	0.08749(37)	0.12162(20)	0.00117(4)	0.01634(52)	0.00467(15)	0.00000(12)	−0.00077(7)	−0.00040(22)
C4,1	−0.01808(11)	0.22552(38)	0.12621(20)	0.00125(5)	0.01711(52)	0.00440(14)	0.00057(13)	−0.00043(7)	0.00178(22)
C5,1	0.01165(12)	0.29779(33)	0.17040(19)	0.00149(5)	0.01137(40)	0.00496(15)	0.00037(12)	−0.00040(7)	0.00161(20)
C6,1	0.04623(11)	0.23495(31)	0.20977(18)	0.00133(4)	0.01018(39)	0.00387(12)	−0.00025(11)	−0.00033(6)	0.00060(17)
C1,2	0.16711(9)	−0.15103(28)	0.36050(15)	0.00088(3)	0.00885(34)	0.00265(10)	−0.00011(8)	0.00008(4)	0.00042(14)
C2,2	0.19959(10)	−0.08792(30)	0.40485(18)	0.00118(4)	0.00929(35)	0.00425(13)	−0.00032(10)	−0.00057(6)	0.00097(17)
C3,2	0.22855(11)	−0.15940(34)	0.45313(18)	0.00121(4)	0.01227(44)	0.00400(13)	−0.00038(11)	−0.00052(6)	0.00076(19)
C4,2	0.22553(10)	−0.29730(32)	0.45612(17)	0.00109(4)	0.01204(40)	0.00348(12)	0.00054(10)	0.00013(6)	0.00137(18)
C5,2	0.19368(12)	−0.36146(31)	0.41197(19)	0.00152(5)	0.00827(36)	0.00477(14)	0.00028(11)	0.00018(7)	0.00106(18)
C6,2	0.16419(10)	−0.28896(29)	0.36493(17)	0.00117(4)	0.00915(36)	0.00350(11)	−0.00042(9)	−0.00008(5)	0.00019(16)
C1(1)	0.1252(2)	0.3228(4)	0.4076(3)	0.0028(1)	0.0129(5)	0.0074(2)	−0.0019(2)	−0.0000(1)	−0.0027(3)
C2(1)	0.1137(2)	0.0688(4)	0.5015(2)	0.0039(1)	0.0176(6)	0.0034(1)	0.0029(2)	−0.0003(1)	0.0004(2)
C3(1)	0.0349(1)	0.1803(5)	0.4172(2)	0.0018(1)	0.0260(7)	0.0053(2)	0.0015(2)	−0.0000(1)	−0.0040(3)
C1(2)	0.0773(1)	−0.3712(3)	0.1894(2)	0.0016(1)	0.0122(4)	0.0050(2)	−0.0006(1)	0.0000(1)	−0.0017(2)
C2(2)	0.1750(1)	−0.3047(4)	0.1576(2)	0.0013(1)	0.0192(6)	0.0048(1)	0.0009(1)	0.0002(1)	−0.0020(2)
C3(2)	0.1011(1)	−0.1665(4)	0.0628(2)	0.0017(1)	0.0191(6)	0.0031(1)	0.0004(1)	−0.0001(1)	−0.0010(2)
C1,3	0.1703(2)	0.1747(6)	0.1388(2)	0.0020(1)	0.0259(1)	0.0050(2)	−0.0030(2)	−0.0002(1)	0.0055(3)
C2,3	0.1963(2)	0.0608(5)	0.1415(3)	0.0025(1)	0.0229(8)	0.0070(2)	−0.0025(2)	0.0022(1)	0.0008(4)
C3,3	0.2212(1)	0.0652(5)	0.2114(3)	0.0011(1)	0.0218(7)	0.0089(3)	−0.0006(2)	0.0008(1)	0.0052(4)
C4,3	0.2098(1)	0.1808(5)	0.2506(2)	0.0015(1)	0.0217(6)	0.0058(2)	−0.0033(2)	−0.0002(1)	0.0027(3)
C5,3	0.1776(1)	0.2497(4)	0.2055(3)	0.0021(1)	0.0123(5)	0.0089(2)	−0.0016(2)	0.0010(1)	0.0038(3)

The form of the thermal motion is $\exp-[\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl]$

TABLE III
RMS amplitudes of vibration along the three principal axes of the thermal ellipsoid (Å)

Atom	Axis 1	Axis 2	Axis 3
Co	0.189	0.207	0.268
Si1	0.199	0.220	0.262
Si2	0.203	0.211	0.254
C1	0.186	0.200	0.227
C2	0.187	0.201	0.223
C3	0.180	0.209	0.230
C4	0.177	0.200	0.219
C1,1	0.187	0.196	0.230
C2,1	0.204	0.246	0.248
C3,1	0.198	0.282	0.292
C4,1	0.207	0.265	0.307
C5,1	0.211	0.262	0.290
C6,1	0.219	0.225	0.263
C1,2	0.189	0.203	0.216
C2,2	0.205	0.210	0.277
C3,2	0.208	0.237	0.275
C4,2	0.206	0.215	0.268
C5,2	0.197	0.254	0.278
C6,2	0.205	0.225	0.240
C1(1)	0.215	0.338	0.372
C2(1)	0.220	0.269	0.437
C3(1)	0.237	0.283	0.293
C1(2)	0.223	0.265	0.293
C2(2)	0.217	0.265	0.328
C3(2)	0.211	0.276	0.315
C1,3	0.198	0.281	0.422
C2,3	0.193	0.344	0.417
C3,3	0.196	0.292	0.411
C4,3	0.181	0.282	0.387
C5,3	0.177	0.325	0.388

formed could in general be separated by a combination of column chromatography, preparative thin-layer chromatography (tlc), and recrystallization techniques.

The first band (A) to be eluted from the alumina column produced a mixture of two isomeric cyclobutadiene-cobalt complexes, (π-cyclopentadienyl)-[*trans*-diphenyl-di(trimethylsilyl)-cyclobutadiene]-cobalt (3) and the corresponding *cis*-isomer (4). The ratio of (3) to (4) obtained in a number of reactions of this type, as indicated by integration of respective proton nmr peaks and also by actual separation, was invariably nearly statistical [*ca.* 55% (3) and 45% (4)]. This result is remarkable in view of results obtained in reactions involving other unsymmetrical acetylenes under these conditions,[17] and in view of the enhanced steric requirements which might be predicted to be necessary to form the *cis*-isomer (4) in the transition state. Cobaltocycles are likely intermediates in this reaction, as will be discussed further in a subsequent paper.

TABLE IV
Idealized hydrogen atom positions

Atom	x	y	z
H2,1[a]	0.023	−0.075	0.160
H3,1	−0.033	0.036	0.089
H4,1	−0.043	0.273	0.101
H5,1	0.009	0.397	0.175
H6,1	0.067	0.288	0.241
H2,2	0.202	0.012	0.402
H3,2	0.249	−0.108	0.487
H4,2	0.246	−0.350	0.490
H5,2	0.192	−0.459	0.412
H6,2	0.141	−0.336	0.335
H1,3[b]	0.149	0.192	0.096
H2,3	0.198	−0.017	0.105
H3,3	0.244	0.004	0.230
H4,3	0.223	0.207	0.300
H5,3	0.163	0.338	0.218
H1(1,1)[c]	0.109	0.387	0.444
H1(1,2)	0.118	0.361	0.355
H1(1,3)	0.154	0.317	0.419
H2(1,1)	0.124	0.131	0.545
H2(1,2)	0.143	0.016	0.491
H2(1,3)	0.092	0.011	0.522
H3(1,1)	0.020	0.160	0.368
H3(1,2)	0.024	0.265	0.395
H3(1,3)	0.023	0.173	0.470
H1(2,1)	0.082	−0.401	0.242
H1(2,2)	0.083	−0.448	0.154
H1(2,3)	0.047	−0.341	0.183
H2(2,1)	0.186	−0.301	0.104
H2(2,2)	0.174	−0.398	0.174
H2(2,3)	0.194	−0.255	0.191
H3(2,1)	0.116	−0.221	0.023
H3(2,2)	0.112	−0.074	0.058
H3(2,3)	0.069	−0.168	0.056

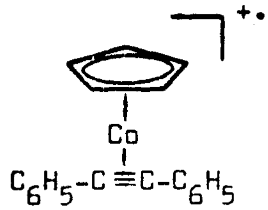
[a] H2,1 to H6,2 are attached to phenyl ring carbon atoms.

[b] H1,3 to H5,3 are attached to the cyclopentadienyl ring.

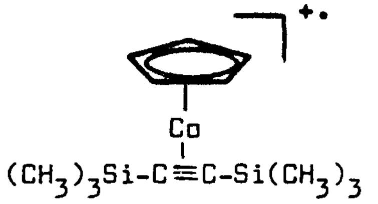
[c] H1(1,1) to H3(2,3) are methyl hydrogen atoms. H1(1,1), H1(1,2), and H1(1,3) are attached to C1(1), etc.

The isomeric cyclobutadiene–cobalt complexes (3) and (4) could only be separated by preparative tlc, using multiple elution techniques. The product of higher R_f and higher melting point was initially assigned as the *trans-isomer* (3), since the *trans-complex* might be expected to exhibit such properties as a result of higher symmetry, compared to the *cis-complex*. This assignment was subsequently supported by mass spectral studies, and unequivocally substantiated by an x-ray crystallographic investigation (*vide infra*). As might be expected, the proton nmr spectra of (3) and (4) are very similar, yet distinctive.

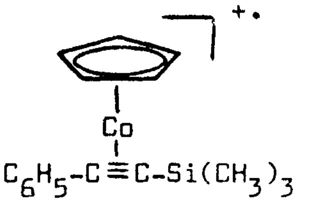
The electron impact induced fragmentation path-



(8)



(9)



(10)

ways of (3) and (4), which are typical for fragmentation pathways in this series,[6,7,17] are presented in Table I. The molecular ions are very intense, accounting for nearly 20% of the total ion current. A major fragmentation pathway for these and other π-cyclopentadienyl-tetrasubstitutedcyclobutadiene-cobalt complexes is the loss of a disubstituted acetylene to afford ions of the type (**8**–**10**). Differences in the relative abundances of these cleavage products suggest that a distinction can be made between the *trans* isomer (3) and the *cis* isomer (4). Loss of a disubstituted acetylene can occur in one of four ways. For the *trans*-isomer (3), only expulsion of an unsymmetrical acetylene to form ion (**10**) is possible in the absence of skeletal rearrangement. For the *cis*-isomer (4), however, loss of two symmtrical acetylenes and one unsymmetrical acetylene in the ratio of 1:1:2 is possible in the absence of rearrangement. Table I indicates that the product initially assigned as the *trans*-isomer (3) affords almost exclusively ion (**10**) at *m/e* 298, corresponding to loss of $C_6H_5-C{\equiv}C-Si(CH_3)_3$. The formation of very small amounts of ions (8) and (9) at *m/e* 302 and 294, respectively, may be attributed to rearrangement of the cyclobutadiene ring moiety, possibly via a valence tautomer. The product initially assigned as the *cis*-isomer (4), on the other hand, affords a ratio of ions (8:9:10) as 0.3:1.0:2.0. This result is also in reasonably good agreement with theory, considering the possible relative energy differences of the ions (8–**10**) which would be produced.

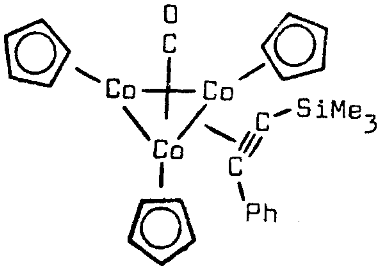
Other prominent ions in the spectra of (3) and (4) are the $(C_5H_5Co)^+$ ion (*m/e* 124), which appears in the spectra of all π-cyclopentadienyl-tetrasubstituted-cyclobutadiene–cobalt complexes, $(M{-}CH_3)^+$, $[M{-}Si(CH_3)_3]^+$, $[M{-}Si(CH_3)_2CH_2]^+$, and $[C_6H_5C{\equiv}C{-}SI(CH_3)_2]^+$ (see Table I).

The second band (B) to be eluted from the alumina column produced a mixture of isomeric cyclopentadienone–cobalt complexes (5–7). Preparative tlc was capable of separating these products into two bands. The band of higher R_f exhibited a single π-cyclopentadienyl ring proton resonance and a single trimethylsilyl proton resonance, indicating that it was either of the two possible symmetrical isomers (5) or (7). The lower R_f band could not be purified further, however, a proton nmr spectrum of the products exhibited two π-cyclopentadienyl resonances and three trimethylsilyl resonances which were similar, yet distinct, from the higher R_f isomer. This result suggests that the mixture contained one of the symmetrical isomers (5) or (7), as well as the unsymmetrical isomer (6).

The mass spectra of the products from band (B) are also consistent with their formulation as cyclopentadienone-cobalt complexes, showing intense molecular ions at *m/e* 500, loss of methyl at *m/e* 485, and characteristic fragmentations involving the trimethylsilyl group. Intense peaks at *m/e* 428 and 427 correspond to losses of $Si(CH_3)_2CH_2$ and of $Si(CH_3)_3$ from the molecular ion. The former peak is fairly intense in the spectrum of the single isomer of higher R_f. This result, together with the nmr data, suggest that the product is (7), in which case a hydrogen transfer from a trimethylsilyl group to the carbonyl oxygen would be facile.

The mass spectrum of band (D) shows an intense molecular ion and a $(M - 1)^+$ ion at *m/e* 428 and 427, respectively, as well as a fairly intense peak at *m/e* 356 corresponding to loss of $Si(CH_3)_2CH_2$. This product formally corresponds to a cyclopentadienone–cobalt complex of the type (5–7), where one of the trimethylsilyl substituents has been replaced by hydrogen. By similar reasoning as described above, it is believed that the single trimethylsilyl group is bonded to one of the carbon atoms *alpha* to the carbonyl carbon.

The mass spectrum of band (C) shows an intense molecular ion at *m/e* 574, loss of carbon monoxide (*m/e* 546) supported by the appropriate metastable peak, and an intense peak at *m/e* 189, corresponding to $[(C_5H_5)_2Co]^+$. Ions of the type $[(C_5H_5)_2M]^{+\cdot}$ have been found to be characteristic of trinuclear complex of Group VIII, Co-Triad metals. The overall spectrum suggests that band (C) is best represented by (**11**), the first example of an acetylenic trinuclear



(11)

cobalt complex. Analogous acetylenic trinuclear rhodium and irridium complexes of this type have been observed frequently in reactions of (π-cyclopentadienyl)dicarbonylrhodium and -iridium with various disubstituted acetylenes.[18,19] Further studies concerning the structure of this product are in progress.

Structural Results

The molecular configuration of (π-C_5H_5)-($C_6H_5(CH_3)_3SiC_2)_2Co$, is given in Figure 1. A stereoscopic view of the molecule is given in Figure 2 and the packing of the molecules in the unit cell is shown in Figure 3. A selection of bond distances and bond angles, together with estimated standard deviations, is given in Table V. Least squares planes through selected atoms and deviations of atoms from these planes are given in Table VI.

The π-cyclopentadienyl ring is quite normal. The C–C distances range from 1.373(6) to 1.408(6) Å to give a mean value *g* 1.389(17) Å and the C–C–C angles range from 107.2(4) to 109.4(4)° to give a mean value of 108.0°. As can be seen by examining the RMS listed on Table II and viewing Figure 2, there is considerable thermal motion associated with this ring. We have found by comparing structures such as $(C_5H_5)_2TiS_5$[20] and $[(CH_2)_3C_5H_4]TiCl_2$[21] (the latter complex has the two cyclopentadienyl rings linked by a $(-CH_2-)_3$ chain and therefore has reduced librational motion) that bond lengths are often shortened by such thermal motion. However, the motion is not as severe as in the pentasulfide and the average C–C bond length of 1.389(17) Å found in this case is comparable to the average C–C bond length of 1.399(3) Å found in $[(CH_2)_3(C_5H_4)_2]TiCl_2$[21]. The Co–C distance range from 2.042(3) to 2.057(4) Å to give a mean value of 2.049(7) Å and a distance of 1.673 Å for the Co atom from the plane of the cyclopentadienyl ring.

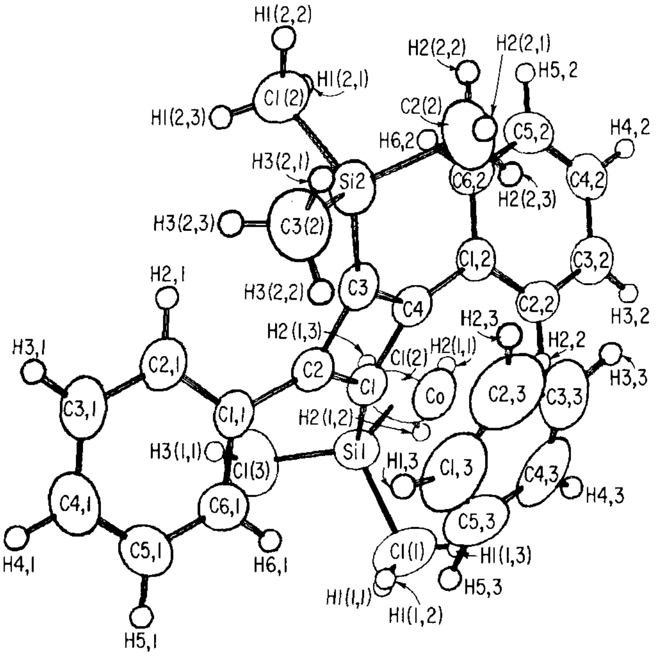


FIGURE 1 The shape of the molecule and the numbering system used in the crystallographic study. The cyclopentadienyl ring is at the upper right-hand of the figure. This view corresponds to the left image of the stereo pair shown in Figure 2.

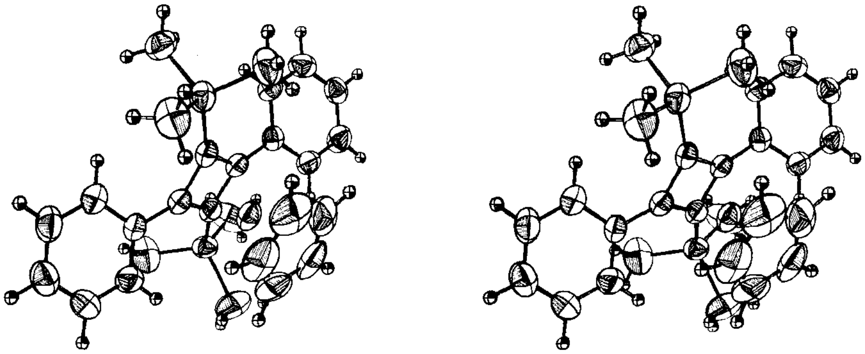


FIGURE 2 This is a stereo pair which should be examined with the aid of a hand-held stereo viewer. The hydrogen atoms were made small and isotropic for representational convenience and the anisotropic thermal parameters of the other atoms are envelopes of 50% probability.

These quantities are similar to these found in compounds such as $(\pi\text{-}C_5H_5)Co(C_6H_5{-}C_5H_5)$[22] and $(\pi\text{-}C_5H_5)Co[(CF_3)_4C_5O]$[23] in which the average Co–C distances are 2.080 and 2.075 (Å) and the Co–ring centroid distances are 1.67 and 1.68 Å, respectively.

The phenyl groups are also as one would expect. The C–C distances associated with the phenyl rings range from 1.367(5) to 1.400(4) Å to give a mean value of 1.382(9) Å. The C–C–C bond angles range from 117.6(3) to 121.7(3)° to give a mean value of 120.0°. The Si–C distances range from 1.850(4) to 1.876(4) Å to give an average value of 1.864(11) Å. The C–Si–C angles range from 106.4(2) to 112.3(2)° with a mean value of 109.5°.

The most important fragment of this substance is the cyclobutadiene ring. The C–C distances in the ring range from 1.466(4) to 1.471(4) Å and the mean value is 1.467(3) Å. The C–C–C angles range from 88.1(2) to 91.8(2)° to give a mean value of 90.0°. It is of interest to note that the internal angles associated with C1 and C3 to which the Si atoms are bonded are somewhat smaller than the angles at C2 and C4 to which the phenyl rings are attached. Bond angles associated with two cyclobutadiene carbon atoms and the first carbon atom of the phenyl ring such as C1 C2 C1,1 have a mean value of 134.0° and C–C–Si angles have a mean value of 135.1°. In $[\pi\text{-}(C_6H_5)_4C_4]Fe(CO)_3$[24] the average C–C bond length associated with the cyclobutadiene ring is 1.459 Å and in $[\pi\text{-}(CH_3)_4C_4]NiCl_2 \cdot 1/2\, C_6H_6$ the distance is 1.431 Å.[25] The latter complex, however, could not be studied as accurately as is desirable due to a disordered benzene molecule of solvation. The Co–C distances range from 1.968(3) to 2.002(3) Å with a mean value of 1.982(15) Å and a distance of 1.689 Å for the Co atom from the plane of the cyclobutadiene ring.

The normals of the cyclobutadiene and cyclopentadienyl rings make an angle of 1.6°, indicating an almost parallel arrangement of these two rings. The first carbon atoms of the phenyl rings, C1,1 and C1,2, are bent out of the plane of the cyclobutadiene ring (0.10 Å) and away from the Co atom. The C2–C1,1

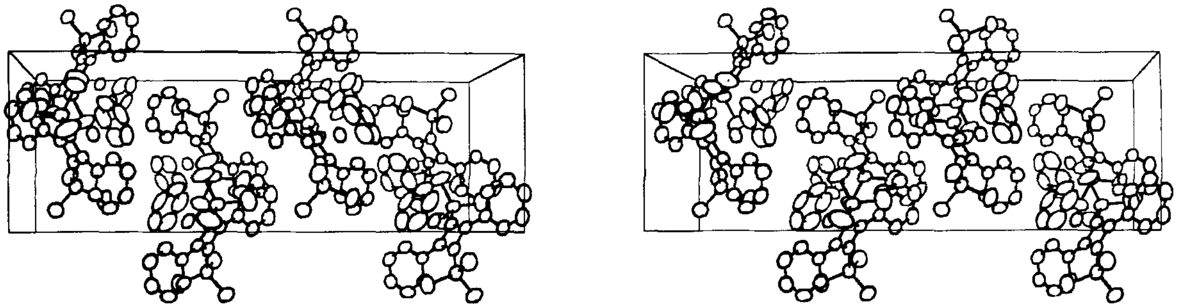


FIGURE 3 The packing of the molecules in the orthorhombic unit cell. This is also a stereo pair.

TABLE V
Interatomic distances (Å) and Angles (°)

A. Bond distances

Co–C1	1.983(3)	C1,1–C2,1	1.386(4)
Co–C2	1.976(3)	C2,1–C3,1	1.384(4)
Co–C3	2.002(3)	C3,1–C4,1	1.386(5)
Co–C4	1.968(3)	C4,1–C5,1	1.367(5)
Co–C1,3	2.053(4)	C5,1–C6,1	1.378(4)
Co–C2,3	2.057(4)	C6,1–C1,1	1.400(4)
Co–C3,3	2.049(4)		
Co–C4,3	2.042(3)	C1,2–C2,2	1.378(4)
Co–C5,3	2.042(3)	C2,2–C3,2	1.389(4)
		C3,2–C4,2	1.378(5)
C1–C2	1.471(4)	C4,2–C5,2	1.368(5)
C2–C3	1.463(4)	C5,2–C6,2	1.391(4)
C3–C4	1.466(4)	C6,2–C1,2	1.380(4)
C4–C1	1.466(4)		
		C2–C1,1	1.466(4)
C1,3–C2,3	1.373(6)	C4–C1,2	1.472(4)
C2,3–C3,3	1.408(6)		
C3,3–C4,3	1.377(6)	C1–Si1	1.871(3)
C4,3–C5,3	1.407(6)	C3–Si2	1.870(3)
C5,3–C1,3	1.382(6)		
Si1–C1(1)	1.863(4)		
Si1–C2(1)	1.847(4)		
Si1–C3(1)	1.850(4)		
Si2–C1(2)	1.876(4)		
Si2–C2(2)	1.861(4)		
Si2–C3(2)	1.871(4)		

B. Bond Angles

C4	C1	C2	88.1(2)	C1(2)	Si2	C2(2)	107.7(2)
C1	C2	C3	91.6(2)	C1(2)	Si2	C3(2)	109.8(2)
C2	C3	C4	88.4(2)	C2(2)	Si2	C3(2)	109.5(2)
C3	C4	C1	91.8(2)				
				C6,2	C1,2	C2,2	117.9(3)
C5,3	C1,3	C2,3	109.4(4)	C1,2	C2,2	C3,2	121.7(3)
C1,3	C2,3	C3,3	107.2(4)	C2,2	C3,2	C4,2	119.6(3)
C2,3	C3,3	C4,3	108.2(4)	C3,2	C4,2	C5,2	119.4(3)
C3,3	C4,3	C5,3	107.9(4)	C4,2	C5,2	C6,2	120.7(3)
C4,3	C5,3	C1,3	107.2(4)	C5,2	C6,2	C1,2	120.7(3)
C6,1	C1,1	C2,1	117.6(3)	C1	C2	C1,1	133.7(3)
C1,1	C2,1	C3,1	121.0(3)	C3	C2	C1,1	134.3(2)
C2,1	C3,1	C4,1	120.4(3)	C1	C4	C1,2	133.1(2)
C3,1	C4,1	C5,1	119.2(3)	C3	C4	C1,2	134.8(3)
C4,1	C5,1	C6,1	120.7(3)				
C5,1	C6,1	C1,1	121.1(3)	C2	C1	Si1	134.3(2)
				C4	C1	Si1	134.5(2)
C1	Si1	C1(1)	112.3(2)	C2	C3	Si2	137.6(2)
C1	Si1	C2(1)	110.3(2)	C4	C3	Si2	133.9(2)
C1	Si1	C3(1)	109.3(2)				
C1(1)	Si1	C2(1)	108.9(2)				
C1(1)	Si1	C3(1)	106.4(2)	C2	C1,1	C2,1	120.9(3)
C2(1)	Si1	C3(1)	109.4(2)	C2	C1,1	C6,1	121.5(3)
				C4	C1,2	C2,2	121.3(3)
C3	Si2	C1(2)	108.7(1)	C4	C1,2	C6,2	120.8(3)
C3	Si2	C2(2)	110.7(2)				
C3	Si2	C3(2)	110.4(2)				

TABLE VI
Planes[a]

A Plane containing C1, C2, C3, and C4.

$$0.723x + 0.559y - 0.406z = 0.124$$

C1	−0.0025	Co	1.689
C2	0.0025	Si1	−0.434
C3	−0.0026	Si2	−0.036
C4	0.0025	C1,1	−0.100
		C1,2	−0.100

B Plane containing C1,2, C2,3, C3,3, C4,3, and C5,3.

$$0.736x + 0.490y - 0.466z = 3.453$$

Co	−1.673
C1,3	0.0057
C2,3	−0.0045
C3,3	0.0004
C4,3	0.0016
C5,3	−0.0033

C Plane containing C1,1, C2,1, C3,1, C4,1, C5,1 and C6,1.

$$0.592x + 0.104y - 0.799z = -1.815$$

C1,1	0.0106	C4,1	0.0036
C2,1	−0.0132	C5,1	−0.0049
C3,1	0.0079	C6,1	−0.0029

D Plane containing C1,2, C2,2, C3,2, C4,2, C5,2 and C6,2.

$$0.651x - 0.0767y - 0.755z = -1.333$$

C1,2	0.0016	C4,2	0.0006
C2,2	0.0055	C5,2	0.0069
C3,2	−0.0070	C6,2	−0.0077

[a] The equations of the planes and distances were obtained with the Smith plane program. Weights used in the calculation equalled $1/EX \cdot EY \cdot EZ \cdot A \cdot B \cdot C)^{2/3}$ where EX, EY and EZ equal the errors in the fractional coordinates of the atom which are listed in Table I and A, B, and C are the cell constants. The equation of the plane is expressed orthogonal coordinates which are related to the fractional coordinates x, y, z by the transformation: $x = a \cdot x$; $y = b \cdot y$; $z = c \cdot z$.

and C4–C1,2 vectors make angles of 4.0° with the normal to the plane. The Si atoms are 0.43 and 0.04 Å out of the plane of the butadiene ring and away from the Co atom. The C1–Si1 vector makes an angle of 13.3° with the normal to the plane and the C3–Si2 vector makes an angle of 1.0°. In $[\pi\text{-}(C_6H_5)_4C_4]Fe(CO_3)_3$ the phenyl groups are displaced away from the Fe atom by 6.9–16.7°[24] and in $[\pi(CH_3)_4C_4]NiCl_2 \cdot 1/2\, C_6H_6$ the methyl groups are displaced away from the Ni atom by 4.6–7.2°.[25]

There are no unusual intra- or intermolecular contacts in this structure.

ACKNOWLEDGEMENTS

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