Journal of Organometallic Chemistry, 175 (1979) 95—104

CRYSTAL AND MOLECULAR STRUCTURE OF (η^5-TRIMETHYLSILYLCYCLOPENTADIENYL)-(η^4-TETRAPHENYLCYCLOBUTADIENE)COBALT

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(Received March 8th, 1979)

Summary

The structure of (η^5-trimethylsilylcyclopentadienyl)(η^4-tetraphenylcyclobutadiene)cobalt, $((CH_3)_3SiC_5H_4)Co((C_6H_5)_4C_4)$, has been determined by single crystal X-ray diffraction techniques using three-dimensional data collected on an automatic diffractometer. The crystals are monoclinic, space group $P2_1/c$, with lattice parameters a 11.551(1), b 16.352(6), c 18.324(2) Å, β 122.85(1)° with four molecules in the unit cell. The structure consists of discrete molecules in which a cobalt atom is sandwiched between the η^5-cyclopentadienyl (Cp) and the η^4-cyclobutadiene (Cb) ligands bonded to the metal in the *hapto* mode. The perpendicular distances Co···(Cp) and Co···(Cb) of 1.688 and 1.699 Å, respectively, as well as the dihedral angle of 6.9° between the two rings and the distortions of their side groups, indicate steric interactions within the molecule. The Cb ring is planar within 0.015 Å and has a rectangular shape with edges of 1.480(5) and 1.463(3) Å. The Cp ring, which is planar to within 0.005 Å, appears to be highly distorted by the trimethylsilyl group, which induces a lengthening of the C—C distances involving the substituted carbon atom (1.440(7) Å) and a narrowing of the corresponding bond angle (105.3(2)°).

Introduction

The aromatic-type reactivity of metallocenes of the type (π-cyclopentadienyl)-(tetraphenylcyclobutadiene)cobalt has been extensively studied by Rausch and Genetti who developed a useful route to the synthesis of several π-cyclopentadienyl-substituted derivatives [1]. The structural analysis of some of such compounds has been carried out [2], but few accurate structural data are yet available, particularly for derivatives containing bulky groups which would cause some distortions in the sandwich compounds. With this aim we have undertaken the X-ray determination of the structure of the trimethylsilyl derivative (η^5-trimethylsilylcyclopentadienyl)(η^4-tetraphenylcyclobutadiene)cobalt, (Me_3SiCp)-$Co(Ph_4Cb)$.

Experimental

X-ray data

Preliminary Weissenberg and precession photographs showed the red-brown crystals to be monoclinic, space group $P2_1/c$ from systematic absences ($h0l$ with l odd and $0k0$ with k odd). Cell dimensions were determined from 31 accurately centered reflections on an AED Siemens diffractometer using the Mo-K_α radiation. (λ 0.7107 Å). The results are: a 11.551(1), b 16.352(6), c 18.324(2) Å and β 122.85(1)°; V 2907.6 Å^3. Assuming $Z = 4$ the calculated density is 1.262 g cm^{-3}.

Intensity data were collected by the $\omega - 2\vartheta$ scan technique out to a value of $2\vartheta_{max} = 54°$ with Zr-filtered Mo-K_α radiation at a 3.5° take-off angle. A total of 6414 reflections were scanned in the hkl and $\bar{h}kl$ octants. Of these 4153 were found to have intensities equal to or greater than $3\sigma(I)$ and were corrected for Lorentz and polarization factors. No correction for absorption ($\mu = 6.78$ cm^{-1} for Mo-K_α radiation, $0.14 < \mu r < 0.23$) or anomalous dispersion was applied.

Structure determination and refinement

The structure was solved by conventional Patterson and Fourier methods and refined by the block-diagonal matrix least-squares technique using programs described in ref. 3. After anisotropic refinement ($R = 0.051$) a three-dimensional difference Fourier synthesis was calculated to locate the hydrogen atoms. The calculated positions of these (C—H 0.98 Å) all occurred in regions of positive electron density. Final anisotropic refinement where the contribution of the hydrogen atoms was held constant ($B = 5$ Å^2) reduced the conventional R factor to 0.030 and R_w to 0.042. The final weighting scheme was $w = 1/(A + |F_0| + B|F_0|^2)$, where $A = 6.0$ and $B = 0.0040$ were chosen so to maintain $w(|F_0| - |F_c|)^2$ essentially constant over all ranges of F_0 and ($\sin \vartheta/\lambda$). Final atomic parameters are listed in Tables 1 and 2, together with their estimated standard deviations calculated from the residuals and the diagonal elements of the inverse matrix of the last minimization cycle. A table of structure factors is available from the authors. Atomic scattering factors were calculated according to ref. 4. Bond lengths and angles are listed in Table 3 and mean planes are given in Table 4. The numbering scheme for the atoms is shown in Fig. 1.

Results and discussion

The crystal structure consists of discrete molecules (Me_3SiCp)$Co(Ph_4Cb)$, where the metal atom is "sandwiched" between the two π ligands (Fig. 2). The cyclobutadiene ring is planar within ±0.0073 Å with an average C—C distance of 1.471(10) Å, close to that found in other metal—Cb complexes (Table 5). However it is interesting to observe that a pair of opposite distances

Cont. on p. 100.

TABLE 1

FRACTIONAL COORDINATES ($\times 10^4$) WITH STANDARD DEVIATIONS IN PARENTHESES FOR NONHYDROGEN ATOMS (Hydrogen atoms are numbered according to the atom to which they are bonded)

	x	*y*	*z*
Co	2311(0)	1615(0)	1799(0)
Si	2916(1)	—579(9)	1790(0)
C(1)	2955(2)	2707(1)	2351(1)
C(2)	4074(2)	2109(1)	2732(1)
C(3)	4018(2)	2067(1)	1909(1)
C(4)	2876(2)	2653(1)	1517(1)
C(5)	2104(2)	3078(1)	668(1)
C(6)	1759(2)	3903(2)	603(1)
C(7)	1032(3)	4278(2)	—220(2)
C(8)	655(3)	3843(2)	—964(2)
C(9)	1013(3)	3032(2)	—904(1)
C(10)	1725(2)	2651(2)	—96(1)
C(11)	2354(2)	3237(1)	2710(1)
C(12)	3137(2)	3456(1)	3589(1)
C(13)	2600(2)	3974(1)	3945(1)
C(14)	1280(2)	4277(2)	3424(1)
C(15)	492(2)	4070(2)	2551(1)
C(16)	1016(2)	3551(2)	2192(1)
C(17)	5009(2)	1773(1)	3615(1)
C(18)	6421(2)	1728(2)	3975(2)
C(19)	7275(3)	1367(3)	4799(2)
C(20)	6727(4)	1066(2)	5249(2)
C(21)	5343(3)	1126(2)	4910(1)
C(22)	4474(2)	1483(2)	4102(1)
C(23)	4964(2)	1742(1)	1671(1)
C(24)	5746(2)	1043(1)	2076(1)
C(25)	6697(2)	759(2)	1891(2)
C(26)	6884(2)	1175(2)	1298(1)
C(27)	6119(2)	1865(2)	895(1)
C(28)	5159(2)	2155(2)	1078(1)
C(29)	1860(2)	352(1)	1611(1)
C(30)	1030(2)	803(1)	819(1)
C(31)	240(2)	1394(2)	935(2)
C(32)	560(2)	1326(2)	1792(2)
C(33)	1548(2)	697(1)	2211(1)
C(34)	1864(3)	—1499(2)	1685(2)
C(35)	3342(3)	—631(2)	938(2)
C(36)	4484(3)	—588(2)	2929(2)
H(6)	2030	4222	1132
H(7)	777	4862	—270
H(8)	130	4109	—1534
H(9)	749	2711	—1436
H(10)	2004	2068	—46
H(12)	4082	3237	3961
H(13)	3165	4113	4569
H(14)	894	4642	3666
H(15)	—460	4290	2179
H(16)	439	3402	1569
H(18)	6827	1945	3656
H(19)	8283	1318	5067
H(20)	7343	814	5822
H(21)	4956	911	5241
H(22)	3478	1535	3867
H(24)	5617	750	2492
H(25)	7239	261	2182
H(26)	7565	980	1172

TABLE 1 (continued)

	x	y	z
H(27)	6254	2160	478
H(28)	4620	2652	786
H(30)	1024	720	281
H(31)	—415	1793	499
H(32)	160	1659	2050
H(33)	1956	522	2815
1H(34)	2387	—2000	1776
2H(34)	1008	—1514	1101
3H(34)	1609	—1472	2118
1H(35)	2487	—632	353
2H(35)	3873	—1122	1010
3H(35)	3891	—145	982
1H(36)	4202	—575	3352
2H(36)	5070	—115	3033
3H(36)	5022	—1092	3032

TABLE 2

ANISOTROPIC TEMPERATURE FACTORS (X 10^5) WITH STANDARD DEVIATIONS IN PARENTHESES, IN THE FORM: exp — $(h^2B_{11} + k^2B_{22} + l^2B_{33} + hkB_{12} + hlB_{13} + klB_{23})$

	B_{11}	B_{12}	B_{13}	B_{22}	B_{23}	B_{33}
Co	667(2)	14(2)	472(2)	241(1)	—27(1)	252(1)
Si	1059(5)	44(6)	826(4)	288(2)	10(4)	434(2)
C(1)	803(14)	13(17)	574(12)	268(7)	—24(11)	284(5)
C(2)	748(14)	44(17)	540(12)	272(7)	—20(11)	291(5)
C(3)	783(14)	8(17)	609(12)	273(7)	—6(11)	300(5)
C(4)	784(14)	84(17)	561(12)	272(7)	19(11)	278(5)
C(5)	834(15)	103(18)	672(12)	295(7)	92(11)	342(6)
C(6)	1344(20)	263(22)	1076(16)	330(9)	134(14)	508(8)
C(7)	1728(25)	576(28)	1402(22)	407(10)	432(17)	700(10)
C(8)	1578(26)	437(32)	987(29)	591(13)	460(18)	484(9)
C(9)	1657(27)	14(32)	863(19)	554(13)	147(17)	353(8)
C(10)	1397(21)	80(25)	780(16)	386(9)	68(14)	324(6)
C(11)	866(14)	8(16)	709(12)	248(7)	—1(10)	337(6)
C(12)	1006(16)	18(19)	678(14)	295(8)	—40(12)	333(6)
C(13)	1425(19)	—33(21)	1069(15)	308(8)	—84(12)	418(6)
C(14)	1448(17)	110(20)	1426(14)	312(8)	—22(13)	579(7)
C(15)	1072(17)	323(22)	1015(15)	409(10)	55(15)	548(8)
C(16)	943(17)	161(21)	681(15)	383(9)	—15(13)	399(7)
C(17)	932(17)	66(19)	432(15)	265(7)	—52(11)	281(6)
C(18)	914(21)	163(27)	374(22)	487(12)	—57(18)	443(10)
C(19)	1281(33)	730(39)	—6(37)	744(17)	31(28)	560(15)
C(20)	2531(53)	717(51)	408(38)	668(17)	224(24)	368(11)
C(21)	2546(39)	131(37)	955(24)	457(12)	89(17)	313(8)
C(22)	1538(24)	—59(25)	778(17)	352(9)	—31(13)	312(7)
C(23)	777(14)	—32(17)	638(12)	280(7)	—79(11)	348(6)
C(24)	1144(17)	216(20)	1116(15)	328(8)	113(14)	545(7)
C(25)	1281(19)	342(23)	1245(17)	384(10)	110(16)	664(9)
C(26)	1139(17)	86(23)	1228(15)	489(11)	—94(16)	601(8)
C(27)	1241(18)	70(24)	1195(14)	504(11)	54(15)	515(7)
C(28)	1088(16)	131(21)	922(13)	391(9)	58(13)	415(6)
C(29)	985(16)	—128(19)	654(14)	266(7)	—59(12)	349(6)
C(30)	1048(21)	—88(23)	399(18)	325(8)	—108(14)	335(7)
C(31)	733(19)	—5(24)	340(22)	378(10)	—88(18)	563(11)
C(32)	970(17)	—225(22)	1099(16)	404(10)	—248(16)	678(9)
C(33)	1133(16)	—303(20)	947(14)	332(8)	—113(13)	443(7)
C(34)	1668(24)	—95(26)	1641(22)	317(10)	—56(19)	939(13)
C(35)	1587(22)	—56(22)	1417(18)	654(15)	—215(20)	631(9)
C(36)	1456(29)	173(33)	643(26)	544(13)	407(19)	517(11)

TABLE 3

INTERATOMIC DISTANCES (Å) AND ANGLES (°) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Distances				Angles			
Co—C(1)	1.987(2)	C(17)—C(18)	1.391(3)	C(2)—C(1)—C(4)	89.8(2)	C(17)—C(18)—C(19)	119.3(3)
Co—C(2)	1.986(2)	C(17)—C(22)	1.415(4)	C(2)—C(1)—C(11)	133.7(2)	C(18)—C(19)—C(20)	120.7(3)
Co—C(3)	2.011(2)	C(18)—C(19)	1.409(4)	C(4)—C(1)—C(11)	135.7(1)	C(19)—C(20)—C(21)	120.4(3)
Co—C(4)	1.985(2)	C(19)—C(20)	1.374(7)	C(1)—C(2)—C(3)	90.3(1)	C(20)—C(21)—C(22)	120.3(3)
Co—C(29)	2.112(2)	C(20)—C(21)	1.369(5)	C(1)—C(2)—C(17)	134.6(2)	C(17)—C(22)—C(21)	120.2(2)
Co—C(30)	2.072(1)	C(21)—C(22)	1.389(3)	C(3)—C(2)—C(17)	134.5(2)	C(3)—C(23)—C(24)	120.5(2)
Co—C(31)	2.062(2)	C(23)—C(24)	1.395(2)	C(2)—C(3)—C(4)	90.0(2)	C(3)—C(23)—C(28)	120.8(2)
Co—C(32)	2.070(3)	C(23)—C(28)	1.398(3)	C(2)—C(3)—C(23)	133.5(1)	C(24)—C(23)—C(28)	118.6(2)
Co—C(33)	2.079(2)	C(24)—C(25)	1.393(4)	C(4)—C(3)—C(23)	134.7(2)	C(23)—C(24)—C(25)	120.8(2)
C(1)—C(2)	1.461(3)	C(25)—C(26)	1.395(5)	C(1)—C(4)—C(3)	89.9(1)	C(24)—C(25)—C(26)	120.2(3)
C(1)—C(4)	1.483(3)	C(26)—C(27)	1.375(4)	C(1)—C(4)—C(5)	136.0(2)	C(25)—C(26)—C(27)	119.5(3)
C(1)—C(11)	1.470(3)	C(27)—C(28)	1.404(4)	C(3)—C(4)—C(5)	133.7(2)	C(26)—C(27)—C(28)	120.6(2)
C(2)—C(3)	1.476(3)	Si—C(29)	1.865(2)	C(4)—C(5)—C(6)	121.7(2)	C(23)—C(28)—C(27)	120.3(2)
C(2)—C(17)	1.480(2)	Si—C(34)	1.877(4)	C(4)—C(5)—C(10)	119.9(2)	Si—C(29)—C(30)	127.7(2)
C(3)—C(4)	1.465(3)	Si—C(35)	1.876(4)	C(6)—C(5)—C(10)	118.4(2)	Si—C(29)—C(33)	126.5(1)
C(3)—C(23)	1.478(4)	Si—C(36)	1.880(3)	C(5)—C(6)—C(7)	119.4(2)	C(30)—C(29)—C(33)	105.3(2)
C(4)—C(5)	1.481(2)	C(29)—C(30)	1.435(2)	C(6)—C(7)—C(8)	121.2(3)	C(29)—C(30)—C(31)	109.2(2)
C(5)—C(6)	1.393(4)	C(29)—C(33)	1.445(3)	C(7)—C(8)—C(9)	119.8(3)	C(30)—C(31)—C(32)	108.1(2)
C(5)—C(10)	1.405(3)	C(30)—C(31)	1.422(4)	C(8)—C(9)—C(10)	119.7(3)	C(31)—C(32)—C(33)	108.0(3)
C(6)—C(7)	1.408(4)	C(31)—C(32)	1.409(5)	C(5)—C(10)—C(9)	121.5(3)	C(29)—C(33)—C(32)	109.4(2)
C(7)—C(8)	1.382(5)	C(32)—C(33)	1.414(3)	C(1)—C(11)—C(12)	119.9(2)	C(29)—Si—C(34)	108.1(1)
C(8)—C(9)	1.376(5)			C(1)—C(11)—C(16)	121.9(2)	C(29)—Si—C(35)	109.4(1)
C(9)—C(10)	1.391(3)			C(12)—C(11)—C(16)	118.2(2)	C(29)—Si—C(36)	110.2(1)
C(11)—C(12)	1.400(2)			C(11)—C(12)—C(13)	121.1(2)	C(34)—Si—S(35)	109.0(2)
C(11)—C(16)	1.401(3)			C(12)—C(13)—C(14)	119.8(2)	C(34)—Si—C(36)	106.7(1)
C(12)—C(13)	1.402(3)			C(13)—C(14)—C(15)	119.9(3)	C(35)—Si—C(36)	113.2(2)
C(13)—C(14)	1.379(3)			C(14)—C(15)—C(16)	120.7(2)		
C(14)—C(15)	1.387(2)			C(11)—C(16)—C(15)	120.3(2)		
C(15)—C(16)	1.397(4)			C(2)—C(17)—C(18)	120.7(3)		
				C(2)—C(17)—C(22)	120.3(2)		
				C(18)—C(17)—C(22)	119.0(2)		

TABLE 4

LEAST SQUARES PLANES WITH DEVIATIONS IN Å [a]

1. Plane containing C(1), C(2), C(3), C(4)

$6.8365\,x + 12.229\,y - 1.2659\,z = 5.0257$

C(1)	0.0072	Co	−1.699
C(2)	−0.0073	C(5)	0.0922
C(3)	0.0073	C(11)	0.1991
C(4)	−0.0072	C(17)	0.1093
		C(23)	0.2867

2. Plane containing C(5), C(6), C(7), C(8), C(9), C(10)

$11.098\,x + 4.1383\,y - 7.9002\,z = 3.0868$

C(5)	−0.0057	C(4)	0.0045
C(6)	0.0042		
C(7)	0.0027		
C(8)	−0.0080		
C(9)	0.0063		
C(10)	0.0005		

3. Plane containing C(11), C(12), C(13), C(14), C(15), C(16)

C(11)	−0.0005	C(1)	0.0310
C(12)	0.0017		
C(13)	−0.0006		
C(14)	−0.0017		
C(15)	0.0030		
C(16)	−0.0018		

4. Plane containing C(17), C(18), C(19), C(20), C(21), C(22)

$-1.3558\,x + 14.642\,y + 7.7972\,z = 4.7516$

C(17)	−0.0159	C(2)	−0.0857
C(18)	0.0075		
C(19)	0.0056		
C(20)	−0.0100		
C(21)	0.0012		
C(22)	0.0117		

5. Plane containing C(23), C(24), C(25), C(26), C(27), C(28)

$4.2354\,x + 9.2002\,y + 7.7593\,z = 5.0029$

C(23)	−0.0012	C(3)	0.0818
C(24)	0.0011		
C(25)	−0.0009		
C(26)	0.0009		
C(27)	−0.0010		
C(28)	0.0012		

6. Plane containing C(29), C(30), C(31), C(32), C(33)

$7.8621\,x + 10.892\,y - 2.0895\,z = 1.5116$

C(29)	−0.0025	Co	1.688
C(30)	0.0016	Si	−0.2237
C(31)	0.0000		
C(32)	−0.0016		
C(33)	0.0026		

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[a] x, y, z are fractional coordinates.

is longer (1.480(5) Å) than in other one (1.463(3) Å) so that the Cb ring is slightly distorted towards a rectangular shape (mean C—C—C angle, 90.0(2)°). This difference, if significant, could indicate incomplete conjugation in the four-membered cycle. Unfortunately the structures of other Cb complexes

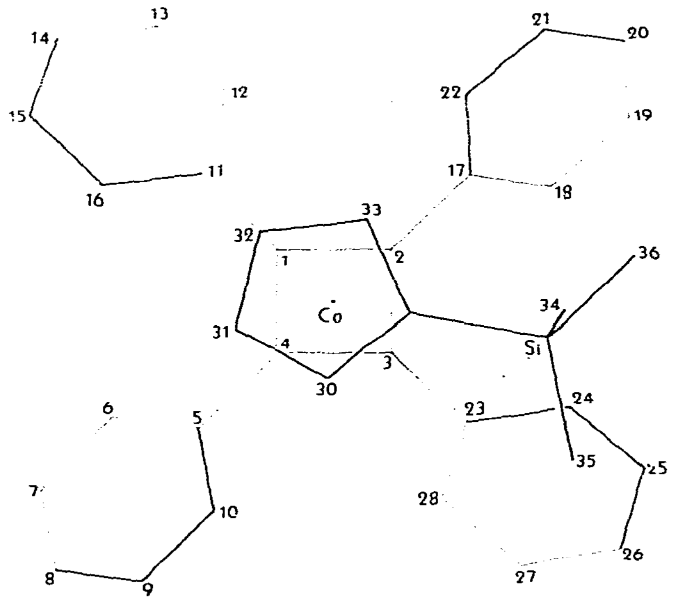

Fig. 1. A projection of the molecule along the normal to the four-membered ring with the numbering scheme for the atoms.

are not accurate enough to reveal the existence of a similar distortion. A severe distortion towards a trapezoid shape has been observed in the *cis* isomer of (bis(trimethylsilyl)(diphenylcyclobutadiene)cyclopentadienylcobalt, while a rectangular shape is clearly present in uncoordinated [4]-annulene derivatives [6,7], in agreement with photoelectron spectra which can only be explained on the basis of localized double bonds linked through essentially single bonds [8]. Thus it seems likely that the four-membered ring is actually rectangular, most of the double bond localization being removed by coordination to the cobalt atom.

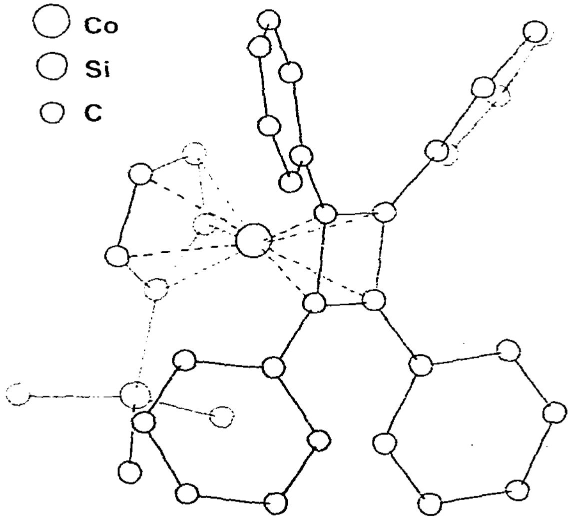

Fig. 2. A perspective view of the molecule.

TABLE 5

COMPARISON OF SOME UNSUBSTITUTED AND SUBSTITUTED (CYCLOPENTADIENYL)(CYCLOBUTADIENE)COBALT COMPLEXES [a]

Compound	C—C(Cp)	C—C(Cb)	Co···(Cp) [b]	Co···(Cb) [b]	Co—C(Cp)	Co—C(Cb)	ϕ [c]	Ref.
(Cp)Co(Cb)	1.390(6)	1.437(4)	1.660	1.681	2.036(9)	1.964(2)	0.9	15
(Cp)Co(*trans*-$Ph_2(Me_3Si)_2Cb$)	1.389(17)	1.467(3)	1.673	1.689	2.049(7)	1.982(15)	1.6	9
(Cp)Co(Ph_2ThCb)$_2$ [d]	1.400(6)	1.463(6)	1.676	1.694	2.056(4)	1.985(9)	2.7	16
(Cp)Co(*trans*-Ph_2Fc_2Cb) [e]	1.399(12)	1.462(5)	1.682	1.694	2.058(5)	1.986(5)	1.1	14
(CNCp)Co(Ph_4Cb)	1.412(6)	1.466(6)	1.671	1.689	2.057(5)	1.978(4)	1.0	2
(Me_3SiCp)Co(Ph_4Cb)	1.425(15)	1.471(10)	1.688	1.699	2.079(19)	1.982(13)	6.9	[f]

[a] The table contains the more accurate data so far available. Cp and Cb represent the cyclopentadienyl and cyclobutadiene ligands respectively. Numbers in parentheses following average values, as in the text, are standard deviations of the mean. [b] Distance of Co from the mean plane of the π ring. [c] Angle between the two normals to Cp and Cb. [d] Th represents a thiophene ring. [e] Fc represents a ferrocenyl group. [f] Present work.

The phenyl groups of the Cb ring are bent away from the metal atom (Table 4) and are twisted about their bonds to the four-membered ring at angles of 43.7, 54.9, 56.7 and 38.8° (rings at C(5), C(11), C(17) and C(23), respectively) giving a "propeller" configuration which appears to be determined by intra and inter-molecular steric interactions. As a consequence there is no significant π component in the C(Cb)—Ph bonds, whose distances range from 1.470(3) to 1.481(2) Å. The mean value of 1.477(5) Å is similar to that found in other phenyl-substituted Cb compounds (1.475(38) Å in Co(Ph_4Cb) derivatives [2], 1.469(4) Å in (Cp)Co(*trans*-$Ph_2(Me_3Si)_2Cb$) [9], and 1.469(7) Å in (Cp)Rh-(Ph_4Cb) [10]). Such values are shorter than that expected for a single $C(sp^2)$—$C(sp^2)$ bond length (1.491(2) Å) [11]. This may be explained in terms of the different hydridization states of the carbon atoms. The orbitals involved in the Cb ring must have a greater *p* character than those used in the bonding with the phenyl groups [12]. Thus the larger amount of *s* character in the exocyclic bonds causes a decrease of such distances. On the other hand an increase of *s* character in the external hybrid orbitals should increase the electronegativity of the Cb carbon atoms, which is further increased by π coordination to the metal atom. It has been shown that in mono-substituted benzene rings, Ph—X, the internal angle α at the carbon atom bearing the substituent increases with the increasing of the X-group electronegativity [11,13]. When $X = C(sp^2)$ α is found to be 117.6(1)° [11], so that the larger value found [118.6(3)°] is consistent with our suggestions for the Ph—Cb bonds. Similar values have been found in other cobalt complexes, such as (CNCp)Co(Ph_4Cb) and (I_2Cp)Co(Ph_4Cb) (118.7(3)°) [2] and (Cp)Co($Ph_2(C_5H_4FeC_5H_5)_2Cb$) (118.15(7)°) [14].

While the Cp ring is planar within ±0.0026 Å, the silicon atom is 0.224 Å out of this plane, away from the metal atom. The displacement is attributable to the steric interactions with the tetraphenylcyclobutadiene ligand, as shown by some non-bonded distances between the two ligands (C(24)···C(35) 3.462(3), C(24)···C(36) 3.764(4), C(25)···C(35) 3.984(4) Å). The C—C bond lengths in the five-membered ring range from 1.409(5) to 1.445(3) Å, the greater values corresponding to the bonds involving the carbon atom bonded to the $SiMe_3$ group, C(29). The mean value 1.425(15) Å is significantly longer than that of 1.403(12) Å found in other compounds, as shown in Table 5. Furthermore, the angle at C(29) of 105.3(2)° is narrower than the others and below the value of 108.0° expected for a regular pentagon. It seems likely that such distortions are induced by the trimethylsilyl group. Just as in the case of benzene derivatives [13], electron-releasing substituents should cause a narrowing of the angle at the substituted carbon atom and a lengthening of the relative bond distances. The Si—CH_3 and Si—C_5H_4 bond lengths of 1.878(2) and 1.865(2) Å, respectively, have the expected values for Si—$C(sp^3)$ and Si—$C(sp^2)$ bonds [13]. The C—Si—C angles range from 106.7(1) to 113.2(2)°, to give a mean value of 109.4(22)°, as found in (Cp)Co(*trans*-$Ph_2(Me_3Si)_2Cb$) [9].

The distances of the cobalt atom from the two π ligands are 1.699 and 1.688 Å, respectively, for the four- and five-membered rings, the cobalt atom being slightly displaced towards the Cp ring. Inspection of Table 5 shows that both distances increase on introducing substituents in the π rings, larger values being found in our compound with bulky groups in both ligands. Thus it seems likely that such an effect is due to steric interactions between the two ligands rather than to electronic effects induced by the substituents. In fact this trend is roughly mirrored by the deviation from parallelism of the two cycles as measured by the ϕ angle. The iodinecyclopentadienyl derivatives (ICp)Co(Ph$_4$Cb) and (I$_2$Cp)Co(Ph$_4$Cb) have not been included in Table 5 owing to the lower accuracy of their structure determination [2], however the values of 1.672(37), 1.706(4) and 1.686, 1.705 Å for the Co···(Cp) and Co···(Cb) distances in the two compounds support our hypothesis.

The lengthening of the Co—C bond distances with respect to the "parent" compound (Cp)Co(Cb) is thus a consequence of the removal of the two π fragments, the Co—C(Cp) being longer than the Co—C(Cb) distances for geometrical reasons [2].

Acknowledgements

The authors thank Professor M.D. Rausch for supplying the crystals, and C.N.R. Rome (Italy) for financial support.

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