Molecular Structures and Bonding of η-Cyclopentadienyl(substituted diene)cobalt Complexes

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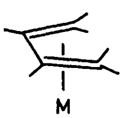
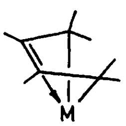
The structures of four [Co(η-C_5H_5)(diene)] complexes have been determined from *X*-ray data. The dienes of complexes (1)—(3) are 1,2,3,4-tetraphenyl-1-triethylsilylbuta-1,3-diene, 4-cyano-1-(1′,2′-methoxycarbonylethyl)-1-methoxycarbonyl-2-phenylbuta-1,3-diene, and 1,3,5,6-tetramethoxycarbonyl-2,4-diphenylcyclohexa-1,3-diene respectively. The substituents at positions 2 and 3 lie in the plane of these dienes, but those at 1 and 4 are markedly out of the plane. This deviation from planarity is explained in terms of extended-Hückel molecular-orbital theory. Finally, *X*-ray crystallographic analysis of the related but highly strained diene complex, [Co(η^5-$C_5H_4CH_2C_6H_4$){η^4-C(Ph)=C(CO_2Me)–C(Ph)=C(CO_2Me)H}] (4), is reported and compared with the above three diene complexes. Crystals of (1) are monoclinic, space group $P2_1/a$, $a = 20.364(3)$, $b = 17.603(2)$, $c = 9.141(3)$ Å, $\beta = 104.46(3)°$, $Z = 4$. Crystals of (2) are triclinic, $P\bar{1}$, $a = 9.584(1)$, $b = 17.942(4)$, $c = 7.099(2)$ Å, $\alpha = 101.52(2)$, $\beta = 90.90(2)$, $\gamma = 95.22(2)°$, $Z = 2$. Crystals of (3) are triclinic, $P\bar{1}$, $a = 14.253(2)$, $b = 19.508(3)$, $c = 10.815(2)$ Å, $\alpha = 87.70(2)$, $\beta = 95.14(3)$, $\gamma = 110.87(3)°$, $Z = 4$. Crystals of (4) are monoclinic, $C2/c$, $a = 18.639(4)$, $b = 7.372(2)$, $c = 36.708(6)$ Å, $\beta = 90.90(3)°$, and $Z = 8$.

IN recent years many conjugated diene complexes of transition metals have been investigated by *X*-ray diffractometry.[1-8] The observed geometries of the diene skeletons accord with either formulation (I) or (II),

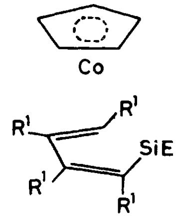


(I)

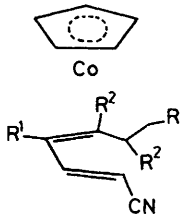


(II)

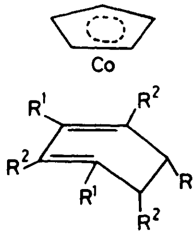
depending on the metal fragment and the substituents on the diene. Comparison of the bond lengths, C(inner)–C(inner) and C(inner)–C(outer), has often been used as a means of distinguishing between bonding modes (I) and (II), *i.e.* the extent of back donation from the metal.[1,7,8] On the other hand, surprisingly few discussions have appeared in the literature concerning the hybridization of outer (terminal) carbons, which would appear to be an essential factor for the understanding of diene–metal bonding.



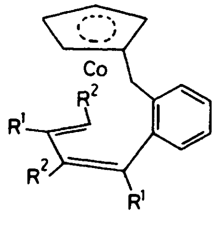
(1)



(2)



(3)



(4)

R^1 = Ph, R^2 = CO_2Me

We have undertaken *X*-ray diffraction studies on four cobalt complexes of highly substituted dienes, (1)—(4), which have enabled us to determine the precise orientations of the substituents on the outer carbons. The results were analysed by means of empirical molecular-orbital (m.o.) calculations.

EXPERIMENTAL

X-Ray Analysis.—The preparations of complexes (1)—(4) have been reported previously.[9-12] Generally speaking the crystals are stable under prolonged exposure to *X*-rays in air.

The crystal and refinement data are summarized in Table 1. *X*-Ray measurements were carried out with a Rigaku automatic four-circle diffractometer using a graphite monochromator. Intensities were measured using ω—2θ scans and 10-s stationary background counts made at the lower and upper limits of each scan. A constant scan speed of 0.06° s^{-1} was used. Lorentz and polarization corrections were applied. Corrections for absorption were made for (1) and (2), but not for (3) and (4) since the crystals of the last two complexes were cut from large plates.

The structures were solved using three-dimensional Patterson and Fourier techniques and refined by block-diagonal least squares. The Co atom in each case was located from a Patterson map. For each complex a subsequent difference–Fourier synthesis revealed the positions of all the non-hydrogen atoms. The computer programs used are listed elsewhere.[13] Anomalous-dispersion effects for Co were included in the calculation using Cromer's values of $\Delta f'$ and $\Delta f''$.[14] The atomic scattering factors were from International Tables.[15] The hydrogen atoms in (1) could be located from a difference-Fourier synthesis and included in the refinement, while the refinements of other complexes ended without location of hydrogens. Observed and calculated structure factor tables, hydrogen-atom co-

TABLE 1

Crystal data

Compound	(1)	(2)	(3)	(4)
Formula	$C_{39}H_{41}CoSi$	$C_{24}H_{24}CoNO_6\cdot0.5CH_2Cl_2$	$C_{31}H_{29}CoO_8$	$C_{32}H_{26}CoO_4$
M	596.8	523.9	588.5	533.5
Crystal size/mm	0.29 × 0.26 × 0.22	0.41 × 0.17 × 0.07	0.28 × 0.27 × 0.20	0.40 × 0.11 × 0.04
Space group (crystal system)	$P2_1/a$ (monoclinic)	$P\bar{1}$ (triclinic)	$P\bar{1}$ (triclinic)	$C2/c$ (monoclinic)
a/Å	20.364(3)	9.584(1)	14.253(2)	18.639(4)
b/Å	17.603(2)	17.942(4)	19.508(3)	7.372(2)
c/Å	9.141(3)	7.099(2)	10.815(2)	36.708(6)
α/°		101.52(2)	87.70(2)	
β/°	104.46(3)	90.90(2)	95.14(3)	90.90(3)
γ/°		95.22(2)	110.87(3)	
U/Å^3	3 173.2	1 190.5	2 798.3	5 043.3
Z	4	2	4	8
D_m(flotation)/g cm^{-3}	1.24(5)	1.44(5)	1.39(5)	1.40(5)
D_c/g cm^{-3}	1.249	1.462	1.397	1.405
F(000)	1 264	541	1 224	2 216
Radiation (λ/Å)	Cu-K_α (1.5406)	Mo-K_α (0.7107)	Mo-K_α (0.7107)	Mo-K_α (0.7107)
μ/cm^{-1}	52.6	9.0	6.9	7.5
No. of unique reflections	3 303	1 902	9 021	1 395
$[(\sin\theta)/\lambda]_{max.}$	0.63	0.59	0.70	0.59
R	0.048	0.087	0.065	0.089
R'	0.052	0.094	0.080	0.098
Residual electron density (e Å^{-3})	0.37	0.92	0.69	0.62

ordinates, and thermal parameters are deposited as Supplementary Publication No. SUP 23169 (44 pp.).†

The solvent of crystallization in (2), CH_2Cl_2, could not be resolved in the difference map; only one broad peak was observed around (0.5, 0.0, 0.5) and this was assigned to a Cl atom. No other chemically reasonable positions of other solvent atoms were indicated, despite the fact that the density and elemental and n.m.r. analysis best fitted the formula $C_{24}H_{24}CoNO_6\cdot0.5CH_2Cl_2$, leaving our model with a chemically incomplete solvent of crystallization in the large, otherwise vacant space.

Molecular-orbital Calculations.—The parameters used in the extended-Hückel calculations were taken from the work of Thorn and Hoffmann.[16] The following geometries of $[Co(C_5H_5)(C_4H_6)]$ were used (distances in Å): Co–C(C_5H_5) 2.081, Co–C(1), C(4), 2.034, Co–C(2), C(3), 1.994, C(1)–C(2) 1.458, C(2)–C(3) 1.440, C–C (cyclopentadienyl) 1.431, C–H 0.95, C(2)–C(1)–H(*anti*) 120°, C(2)–C(1)–H(*syn*) 120°, and C(3)–C(2)–C(1) 117°.

RESULTS AND DISCUSSION

Figure 1 shows perspective views and numbering schemes of complexes (1)—(4). The atomic co-ordinates are reported in Table 2 and important bond lengths and angles in Table 3.

TABLE 2

Atomic co-ordinates (× 10^4) for complexes (1)—(4) with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
(*a*) Complex (1)			
Co	2 292(1)	2 348(1)	4 391(1)
Si	3 588(1)	3 407(1)	3 497(2)
C(1)	1 997(2)	3 072(3)	2 587(5)
C(2)	2 124(2)	2 314(3)	2 146(5)
C(3)	2 775(2)	1 980(3)	2 884(5)
C(4)	3 257(2)	2 446(3)	3 957(5)
C(11)	1 339(2)	3 468(3)	2 246(5)
C(12)	1 374(3)	4 259(3)	2 420(7)
C(13)	793(3)	4 704(4)	2 163(8)

TABLE 2 (*continued*)

Atom	*x*	*y*	*z*
(*a*) Complex (1) (*continued*)			
C(14)	165(3)	4 370(4)	1 705(7)
C(15)	117(3)	3 591(4)	1 533(6)
C(16)	696(2)	3 141(3)	1 805(6)
C(21)	1 605(2)	1 850(3)	1 030(5)
C(22)	1 330(3)	1 189(3)	1 405(6)
C(23)	870(3)	785(4)	316(7)
C(24)	675(3)	1 051(4)	−1 163(7)
C(25)	942(3)	1 723(4)	−1 542(6)
C(26)	1 403(3)	2 124(3)	−445(5)
C(31)	2 901(2)	1 184(3)	2 499(5)
C(32)	2 968(3)	1 030(3)	1 063(7)
C(33)	3 110(3)	287(4)	673(8)
C(34)	3 178(4)	−297(4)	1 736(10)
C(35)	3 113(3)	−136(4)	3 141(9)
C(36)	2 976(3)	598(3)	3 534(7)
C(41)	3 844(2)	2 040(3)	5 012(5)
C(42)	4 281(2)	1 567(3)	4 491(6)
C(43)	4 862(3)	1 260(3)	5 478(7)
C(44)	5 019(3)	1 458(4)	6 997(7)
C(45)	4 606(3)	1 933(4)	7 517(6)
C(46)	4 023(3)	2 223(3)	6 545(6)
C(47)	3 357(3)	3 643(4)	1 414(6)
C(48)	3 692(5)	3 157(5)	460(8)
C(49)	4 543(2)	3 394(3)	4 057(7)
C(50)	4 858(3)	4 127(4)	3 620(9)
C(51)	3 315(3)	4 212(3)	4 571(7)
C(52)	3 693(4)	4 313(4)	6 214(7)
C(61)	1 392(3)	2 084(3)	4 990(6)
C(62)	1 878(3)	1 495(3)	5 540(6)
C(63)	2 467(3)	1 840(4)	6 529(6)
C(64)	2 324(3)	2 644(4)	6 612(6)
C(65)	1 665(3)	2 791(3)	5 659(6)
(*b*) Complex (2)			
Co	179(2)	1 866(1)	3 192(3)
C(1)	280(12)	2 902(6)	2 336(14)
C(2)	−694(11)	2 312(6)	1 170(16)
C(3)	−121(12)	1 621(7)	346(17)
C(4)	1 316(12)	1 524(7)	850(18)
C(5)	1 546(11)	3 230(6)	1 366(17)
C(6)	1 188(12)	3 935(7)	518(18)
C(11)	−192(12)	3 494(7)	3 976(18)
C(12)	−1 926(16)	4 032(9)	5 944(21)
C(21)	−2 204(12)	2 349(7)	672(17)
C(22)	−2 629(13)	3 000(7)	115(17)
C(23)	−4 025(13)	2 978(8)	−579(19)
C(24)	−4 959(14)	2 339(8)	−712(20)

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† For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

TABLE 2 (*continued*)

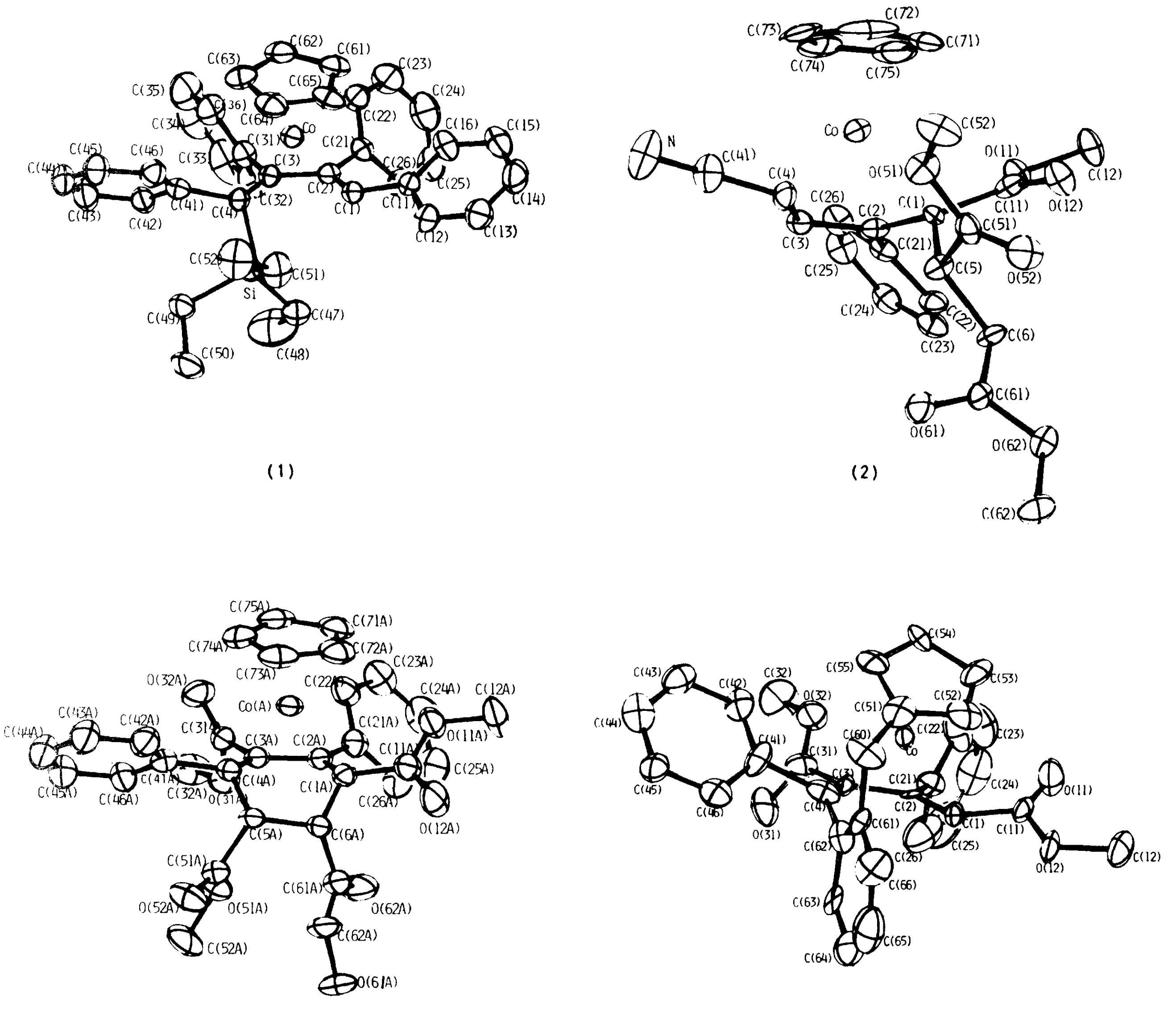
Atom	*x*	*y*	*z*
(*b*) Complex (2)	(*continued*)		
C(25)	−4 547(13)	1 712(8)	−73(21)
C(26)	−3 164(13)	1 691(8)	622(20)
C(41)	1 699(13)	769(8)	364(21)
C(51)	2 864(13)	3 466(7)	2 659(17)
C(52)	4 624(12)	3 007(9)	4 437(19)
C(61)	2 330(12)	4 104(6)	−806(17)
C(62)	3 517(18)	5 052(9)	−2 273(23)
C(71)	147(25)	2 197(9)	6 114(21)
C(72)	1 217(19)	1 719(13)	5 625(26)
C(73)	546(21)	1 019(10)	4 645(24)
C(74)	−909(18)	1 085(9)	4 552(22)
C(75)	−1 150(19)	1 808(11)	5 422(23)
N	2 073(14)	160(7)	−17(23)
O(11)	−1 546(9)	3 433(5)	4 319(12)
O(12)	627(9)	3 997(5)	4 848(13)
O(51)	3 276(8)	2 880(5)	3 372(13)
O(52)	3 546(10	4 086(5)	2 904(13)
O(61)	2 990(10)	3 642(5)	−1 733(13)
O(62)	2 464(10)	4 845(5)	−921(13)
Cl	477(1)	66(1)	449(2)
(*c*) Complex (3)			
Co(A)	7 119(1)	1 473(0)	2 706(1)
C(1A)	6 637(4)	2 064(3)	3 830(4)
C(2A)	7 731(4)	2 289(3)	3 917(4)
C(3A)	8 050(4)	1 688(3)	4 235(4)
C(4A)	7 259(4)	976(3)	4 356(4)
C(5A)	6 309(4)	888(3)	5 005(4)
C(6A)	6 042(4)	1 583(3)	4 837(4)
C(11A)	6 125(4)	2 548(3)	3 257(5)
C(12A)	6 175(6)	3 507(4)	1 861(8)
O(11A)	6 603(3)	2 976(2)	2 365(4)
O(12A)	5 349(4)	2 555(3)	3 593(5)
C(21A)	8 460(4)	3 049(3)	3 684(5)
C(22A)	9 187(4)	3 180(3)	2 837(6)
C(23A)	9 849(5)	3 902(4)	2 626(7)
C(24A)	9 787(6)	4 491(4)	3 247(7)
C(25A)	9 057(6)	4 360(4)	4 087(8)
C(26A)	8 396(5)	3 638(4)	4 322(6)
C(31A)	9 161(4)	1 801(3)	4 308(5)
C(32A)	10 714(5)	2 300(5)	5 578(6)
O(31A)	9 627(3)	2 161(2)	5 348(3)
O(32A)	9 565(3)	1 594(3)	3 568(4)
C(41A)	7 483(4)	282(3)	4 484(5)
C(42A)	6 770(5)	−367(4)	3 928(6)
C(43A)	6 908(6)	−1 038(4)	4 099(7)
C(44A)	7 759(6)	−1 055(4)	4 864(7)
C(45A)	8 455(6)	−416(4)	5 413(7)
C(46A)	8 319(5)	263(4)	5 251(6)
C(51A)	6 461(4)	670(3)	6 344(5)
C(52A)	7 490(7)	1 003(5)	8 227(6)
O(51A)	7 291(3)	1 157(2)	6 934(3)
O(52A)	5 902(4)	117(3)	6 804(4)
C(61A)	6 237(5)	2 052(4)	6 028(5)
C(62A)	5 665(8)	2 022(5)	8 017(6)
O(61A)	5 553(3)	1 657(3)	6 811(4)
O(62A)	6 861(4)	2 649(2)	6 245(4)
C(71A)	7 250(5)	1 900(4)	915(5)
C(72A)	6 212(5)	1 436(4)	1 086(5)
C(73A)	6 172(5)	717(4)	1 400(5)
C(74A)	7 200(6)	732(4)	1 460(5)
C(75A)	7 849(5)	1 461(4)	1 141(5)
Co(B)	2 546(1)	3 115(0)	1 112(1)
C(1B)	3 122(4)	2 739(3)	−235(5)
C(2B)	2 041(4)	2 563(3)	−476(5)
C(3B)	1 798(4)	3 215(3)	−473(5)
C(4B)	2 641(4)	3 902(3)	−192(5)
C(5B)	3 646(4)	4 077(3)	−769(5)
C(6B)	3 869(4)	3 366(3)	−938(5)
C(11B)	3 530(4)	2 157(3)	132(5)
C(12B)	3 276(7)	1 027(5)	1 195(10)
O(11B)	2 886(3)	1 588(3)	719(5)
O(12B)	4 379(3)	2 205(3)	−26(5)
C(21B)	1 254(4)	1 818(3)	−738(6)
C(22B)	404(5)	1 527(4)	−40(7)
C(23B)	−334(5)	825(4)	−362(8)
C(24B)	−233(6)	420(4)	−1 340(8)

TABLE 2 (*continued*)

Atom	*x*	*y*	*z*
(*c*) Complex (3)	(*continued*)		
C(25B)	621(6)	705(4)	−2 009(7)
C(26B)	1 367(5)	1 401(4)	−1 695(6)
C(31B)	702(4)	3 133(3)	−659(5)
C(32B)	−633(6)	3 063(5)	−2 209(8)
O(31B)	419(3)	3 121(3)	−1 862(4)
O(32B)	161(3)	3 104(3)	141(4)
C(41B)	2 480(4)	4 591(3)	119(5)
C(42B)	3 171(5)	5 084(4)	991(6)
C(43B)	3 029(6)	5 719(4)	1 342(7)
C(44B)	2 201(6)	5 874(4)	807(8)
C(45B)	1 532(6)	5 399(4)	−102(8)
C(46B)	1 673(5)	4 763(4)	−458(6)
C(51B)	3 663(5)	4 509(4)	−1 963(6)
C(52B)	2 791(9)	4 543(6)	−3 923(8)
O(51B)	2 847(4)	4 188(3)	−2 732(4)
O(52B)	4 337(4)	5 076(3)	−2 154(6)
C(61B)	3 805(5)	3 141(3)	−2 298(6)
C(62B)	4 665(8)	3 435(6)	−4 133(7)
O(61B)	4 628(4)	3 589(3)	−2 813(4)
O(62B)	3 160(5)	2 645(3)	−2 837(5)
C(71B)	2 179(5)	2 389(4)	2 616(6)
C(72B)	3 253(5)	2 839(4)	2 696(6)
C(73B)	3 385(5)	3 593(4)	2 736(5)
C(74B)	2 377(5)	3 624(4)	2 665(5)
C(75B)	1 647(5)	2 880(4)	2 604(6)
(*d*) Complex (4)			
Co	3 930(1)	2 443(4)	1 082(1)
C(1)	4 116(8)	−251(22)	1 000(4)
C(2)	3 373(9)	167(23)	1 045(4)
C(3)	3 205(8)	1 172(23)	1 377(4)
C(4)	3 726(9)	1 827(24)	1 627(5)
C(11)	4 358(8)	−814(24)	630(5)
C(12)	5 359(11)	−2 249(39)	348(6)
C(21)	2 770(9)	−416(26)	790(5)
C(22)	2 570(10)	476(35)	482(5)
C(23)	2 049(12)	−196(39)	239(6)
C(24)	1 742(13)	−1 740(37)	300(7)
C(25)	1 894(12)	−2 653(42)	622(7)
C(26)	2 425(11)	−2 054(32)	868(7)
C(31)	2 930(10)	1 500(26)	1 427(5)
C(32)	1 283(10)	2 535(45)	1 196(6)
C(41)	3 470(10)	3 390(27)	1 888(5)
C(42)	2 974(10)	4 659(27)	1 785(5)
C(43)	2 739(10)	5 983(29)	2 034(6)
C(44)	3 000(10)	5 869(31)	2 392(5)
C(45)	3 460(10)	4 573(27)	2 505(5)
C(46)	3 718(10)	3 278(27)	2 253(5)
C(51)	4 754(10)	4 059(28)	1 231(6)
C(52)	4 902(10)	3 218(28)	886(6)
C(53)	4 368(10)	3 681(26)	621(6)
C(54)	3 911(9)	4 981(27)	788(5)
C(55)	4 159(11)	5 210(27)	1 163(6)
C(60)	5 137(10)	3 786(30)	1 585(5)
C(61)	5 051(9)	1 835(22)	1 744(4)
C(62)	4 385(10)	981(29)	1 747(5)
C(63)	4 326(11)	−735(27)	1 914(4)
C(64)	4 967(13)	−1 648(31)	2 053(6)
C(65)	5 602(13)	−742(38)	2 033(6)
C(66)	5 650(11)	969(33)	1 884(6)
O(11)	4 085(7)	−573(20)	343(3)
O(12)	5 030(7)	−1 546(18)	686(3)
O(31)	2 101(7)	558(20)	1 667(4)
O(32)	2 079(6)	2 444(22)	1 199(3)

The unit cell of (3) contains two crystallographically distinct monomers, molecules A and B, which are almost related by a centre of symmetry but differ slightly in the conformations of the substituents.

Since complex (4) is strained by a bridge between the cyclopentadienyl ring and the diene moiety, the structures of (1)—(3) will be discussed first. The data in Table 3 indicate that the three bond lengths of the diene



(1) (2)

(3) (4)

FIGURE 1 Molecular structures of complexes (1)—(4) with the atomic numbering schemes

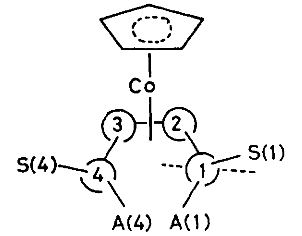
skeleton, C(1)–C(2), C(2)–C(3), and C(3)–C(4), are essentially equal within experimental error, in accord with the results for diene–iron carbonyl complexes.[5,17]

The distances of atoms from the diene plane (Table 4) show that the substituents at the 'inner' carbons of the diene skeleton lie in the plane of the diene while those at the 'outer' carbons deviate from planarity in a regular manner. The *syn* substituents are directed upward, towards the metal, and *anti* substituents downward, away from the metal. The deviations can also be evaluated in terms of the torsion angles listed in Table 3. Similar deviations from planarity have been noted by Eiss[2] for a diene–iron carbonyl complex. Developing Eiss's arguments, we explain the phenomena by assuming (*a*) twisting about the two formal 'double' bonds, (*b*) some additional sp^3 character of originally sp^2-hybridized C(1) and C(4), and (*c*) steric repulsion between *anti* substituents A(1) and A(4). As the first two effects are promoted, the overlap between metal orbitals and the diene π orbitals will increase, whilst at the same time there will be decreasing conjugation in the diene skeleton.

In order to estimate to what extent these three factors operate, calculations for a model compound, $[Co(\eta\text{-}C_5H_5)(\eta\text{-}C_4H_6)]$, were carried out using the extended-Hückel method. The molecular model employed for the calculation was taken as an average of (1)—(3), but the configuration of C(1) and C(4) was initially assumed to be sp^2 with no rotation about C(1)–C(2) and C(3)–C(4) bonds. As C(1) and C(4) are twisted inwards, stabilization occurs, as shown in Figure 2(*a*), which mainly results from increased overlap between the vacant diene b_2 orbital and the filled metal

TABLE 3

Selected bond distances (Å) and angles (°) with estimated standard deviations in parentheses



Compound	(1)	(2)	(3) Molecule A [a]	(4)
(*a*) Bond lengths				
Co–C(1)	2.052(5)	2.062(12)	2.027(6)	2.040(16)
Co–C(2)	1.996(4)	1.986(12)	1.995(5)	1.977(17)
Co–C(3)	1.991(5)	1.990(12)	1.984(5)	1.979(16)
Co–C(4)	2.107(5)	2.024(12)	2.025(5)	2.092(18)
Co–C(C_5H_5) av.	2.095(20)	2.056(11)	2.073(15)	2.084(50)
C(1)–C(2)	1.436(7)	1.456(14)	1.456(7)	1.430(22)
C(2)–C(3)	1.454(6)	1.424(16)	1.422(9)	1.464(23)
C(3)–C(4)	1.456(6)	1.451(17)	1.453(7)	1.413(23)
C–C av. (cyclopentadienyl)	1.439(7)	1.395(19)	1.435(22)	1.432(15)
(*b*) Angles				
C(2)–C(1)–A(1)		118.4(9)	120.1(5)	
C(2)–C(1)–S(1)	126.7(4)	122.5(10)	121.1(5)	118.1(13)
C(3)–C(4)–A(4)	124.6(4)		121.6(5)	128.8(17)
C(3)–C(4)–S(4)	117.1(3)	115.5(10)	121.8(5)	115.7(14)
C(1)–C(2)–C(3)	116.9(4)	115.8(10)	111.5(4)	115.2(14)
C(4)–C(3)–C(2)	117.9(4)	119.1(9)	116.4(5)	124.1(14)
(*c*) Torsion angles				
C(3)–C(2)–C(1)–A(1)		62.0(14)	46.3(7)	
180° + [C(3)–C(2)–C(1)–S(1)]	13.4(4)	27.9(11) [b]	13.3(5)	16.2(14)
– [C(2)–C(3)–C(4)–A(4)]	57.1(6)		41.8(7)	38.1(27)
180° – [C(2)–C(3)–C(4)–S(4)]	15.9(4)	14.7(11)	10.0(5)	19.7(16)

[a] Only data for molecule A are listed for simplicity. [b] The large value is due to repulsion between S(1) and A(1) (see text).

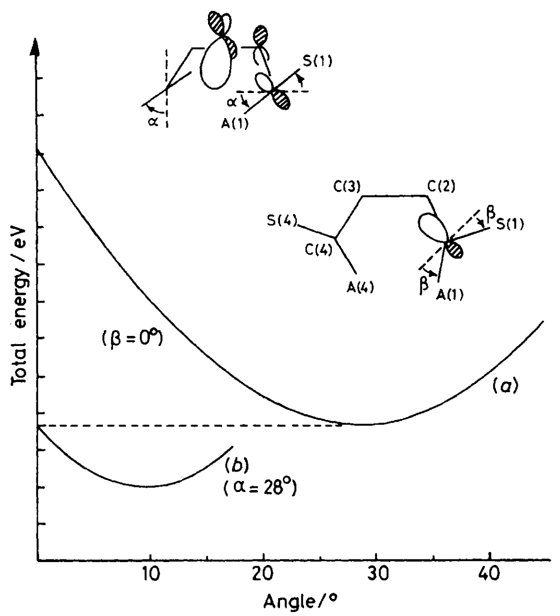


FIGURE 2 Stabilization by twisting about C(1)–C(2) and C(3)–C(4) bonds (*a*) and further stabilization by bending back of *syn* and *anti* substituents (*b*). The twisting angle, α, is expressed in terms of torsion angles, *e.g.* C(3)–C(2)–C(1)–A(1), β is also in torsion angles. The final positions of A(1) and S(1) can thus be expressed as C(3)–C(2)–C(1)–A(1) = α + β and 180° + [C(3)–C(2)–C(1)–S(1)] = α – β

d_{yz} orbital (overlap integral from 0.105 to 0.127), as well as increased interaction between the filled diene a_2 orbital and the vacant metal d_{xz} orbitals (from 0.166 to 0.177). The twisting is terminated at the optimum angle of 28° and thence the C–H bonds of the terminal carbons are bent back away from the metal, leading to further stabilization [Figure 2(*b*)]. However, this stabilization, due to addition of sp^3 character to the terminal carbons, is much smaller (0.18 eV * at 10°) than that caused by twisting of the double bonds (0.73 eV at 28°).

Thus, according to the calculated geometry at C(1) and C(4), the H(*syn*) atoms are bent towards the metal by 28 – 10° = 18° while the H(*anti*) atoms are bent away from the metal by 28 + 10° = 38°. As shown in Table 3, the deviations of S(1) and S(4) from planarity in complexes (1) and (2) fall in the range of 13—16°, in rough agreement with the calculated value of 18°. The exception is S(1) in (2), the large deviation (28°) for which is attributable to electrostatic repulsion between S(1) and A(1), the two methoxycarbonyl groups bonded to C(1) and C(5) being close to each other [C(11) · · · C(51) 3.09, O(12) · · · C(51) 2.79, O(12) · · · O(52) 3.14 Å]. On the other hand, the deviations of *anti* substituents in (1) and (2) are much larger than the estimated value of 38°, evidently as a result of steric effects between A(1) and A(4). Even in the optimized geometry of the model

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* Throughout this paper: 1 eV ≈ 1.60 × 10^{-19} J.

compound used for the m.o. calculation, the H(*anti*)–H(*anti*) distance is short (1.97 Å) and suggests the influence of van der Waals repulsion, which would be more critical in the cases of (1) and (2) with their bulky *anti* substituents.

In the case of (3), whose diene moiety is a six-membered ring, the conformation of the diene is restricted. Nevertheless, the tendency for the orientation of substituents is similar to those in (1) and (2), *i.e.* large deviations of *anti* substituents from the diene plane (42—46°) and smaller deviations of *syn* substituents (10—13°).

Unlike complexes (1)—(3) discussed above, complex (4) has a bridge between the cyclopentadienyl ring and the diene moiety. As a consequence, the dihedral angle between the cyclopentadienyl ring and the diene plane is abnormally large (32°) compared to those of (1)—(3) (7—11°) (Table 4). The *anti* substituent (Ph) at C(4) is 'pulled up' by the C_5H_5 ring and the torsion angle C(2)–C(3)–C(4)–A(4) becomes 38.1° which is markedly smaller than the corresponding angles in (1)—(3) (Table 3). Accordingly, steric repulsion between A(4) and A(1) (H) is expected to be severe and this results in a larger C(2)–C(3)–C(4) angle (124°) in (4) than in (1) and (2) (117—119°). These results indicate that (4) has a highly strained molecular structure, which is in accord with the experimental observation that (4) readily isomerizes into (5) on heating.[18]

TABLE 4

Least-squares planes * for diene and cyclopentadienyl groups with deviations (Å) from them in square brackets

(*a*) Complex (1)

Diene: C(1), C(2), C(3), C(4)

$$0.5754X + 0.3557Y - 0.8568Z = 2.2440$$

[Co −1.527(3), C(11) −0.263(9), C(21) −0.012(9), C(31) −0.061(10), C(41) −0.388(8), Si 1.354(8)]

Cyclopentadienyl: C(61), C(62), C(63), C(64), C(65)

$$0.6129X + 0.1633Y - 0.9016Z = -1.7825$$

[Co 1.699(3), C(1) 3.027(7), C(2) 3.330(7), C(3) 3.439(6), C(4) 3.290(7)]

Angle between the planes: 11.4(3)°

(*b*) Complex (2)

Diene: C(1), C(2), C(3), C(4)

$$0.2674X + 0.5018Y - 0.9000Z = 1.1805$$

[Co −1.494(8), C(5) 1.251(20), C(11) −0.624(22), C(21) −0.060(25), C(41) −0.285(23)]

Cyclopentadienyl: C(71), C(72), C(73), C(74), C(75)

$$0.0915X + 0.4792Y - 0.9495Z = -2.2095$$

[Co 1.678(9), C(1) 3.155(23), C(2) 3.348(18), C(3) 3.359(18), C(4) 3.062(22)]

Angle between the planes: 10.9(8)°

(*c*) Complex (3)

Diene: C(1A), C(2A), C(3A), C(4A)

$$-0.1326X + 0.2153Y + 0.9842Z = 3.6820$$

[Co(A) −1.529(3), C(6A) 0.989(10), C(11A) −0.303(11), C(21A) −0.080(12), C(31A) −0.072(12), C(41A) −0.205(11), C(5A) 0.825(11)]

Cyclopentadienyl: C(71A), C(72A), C(73A), C(74A), C(75A)

$$-0.0350X + 0.2478Y + 0.9686Z = 1.5151$$

[Co(A) 1.676(4), C(1A) 3.163(9), C(2A) 3.308(8), C(3A) 3.335(8), C(4A) 3.158(9)]

Angle between the planes: 7.0(3)°

(*d*) Complex (4)

Diene: C(1), C(2), C(3), C(4)

$$-0.1057X - 0.8478Y + 0.5213Z = 1.2509$$

[Co −1.481(11), C(11) −0.395(30), C(21) −0.025(36), C(31) 0.073(35), C(41) −0.440(32), C(62) 0.616(36)]

Cyclopentadienyl: C(51), C(52), C(53), C(54), C(55)

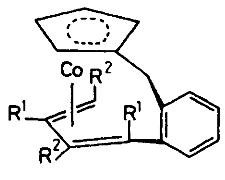
$$0.5998X + 0.7500Y - 0.2882Z = 6.2865$$

[Co 1.687(9), C(1) 2.882(26), C(2) 3.529(21), C(3) 3.512(21), C(4) 2.832(28)]

Angle between the planes: 32.4(10)°

* *x*, *y*, and *z* are co-ordinates along crystallographic axes in Å units.

Considering the hybridization of terminal carbons, we conclude that the diene complex of Co(η-C_5H_5) is better represented by bonding mode (I), although some contribution from (II) is likely. Hence, stabilization of the co-ordinated diene is largely brought about by twisting of the two formal 'double' bonds with a lesser contribution from rehybridization of the terminal carbons. The orientation of the *syn* substituents at the terminal carbons reflects these simultaneous effects, whereas that of the *anti* substituents is governed by additional steric effects. In the case of a cyclic diene, (3), or a diene linked to another ligand, (4), conformational restriction intervenes.



(5) R^1 = Ph, R^2 = CO_2Me

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