ON THE STRUCTURE OF [η⁴-2,5-BIS(TRIMETHYLSILYL)CYCLOPENTADIENONE](η⁵-CYCLOPENTADIENYL)COBALT

JOST H. BIERI, ANDRÉ S. DREIDING, THOMAS C.C. GARTENMANN, ERNST R.F. GESING*,
ROLAND W. KUNZ, and ROLAND PREWO

*Organisch-Chemisches Institut, Universität Zürich, Winterthurerstrasse 190, CH-8057 Zürich (Switzerland)*

Summary

X-ray diffraction study has been carried out on [η⁴-bis(trimethylsilyl)cyclopentadienone](η⁵-cyclopentadienyl)cobalt (I), the first example of a (η⁴-cyclopentadienone)(η⁵-cyclopentadienyl)cobalt complex with only two substituents on the cyclopentadienone ring. Complex I crystallizes in space group $P2_1/c$ with four molecules in the unit cell and lattice parameters a 6.5259(5), b 12.2378(9), c 21.8397(15) Å and β 90.442(7)°. Extended Hückel MO calculations are discussed for a simpler model, namely the parent cyclopentadienone complex (III).

Introduction

Stable tetrasubstituted cyclopentadienones [1,2] have played a useful role as reagents in organic synthesis, e.g. in the synthesis of tetra-*t*-butyltetrahedrane [3]. A potentially attractive synthon for other purposes is represented by the 2,5-bis(trimethylsilyl)cyclopentadienone (II), which bears only two substituents, namely the stabilizing and synthetically advantageous silyl groups [4]. The cyclopentadienone II can be obtained (76%) from the corresponding complex I by oxidative demetallation. The latter was prepared (68%) by a low-temperature photolysis from trimethylsilylacetylene and dicarbonyl(η⁵-cyclopentadienyl)cobalt in tetrahydrofuran [4,5]. Both compounds I and II have been used as precursors for functionalized cyclopentanoids [6,7], where I was a relay compound for II. We report here the results of a single crystal X-ray diffraction study of this synthetically versatile transition metal complex I.
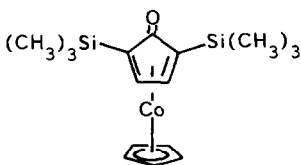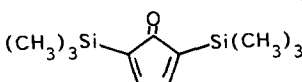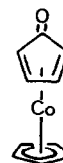
(I) (II) (III)

TABLE 1

SUMMARY OF CRYSTAL DATA, INTENSITY COLLECTION AND REFINEMENT OF [η^4-2,5-BIS(TRIMETHYLSILYL)CYCLOPENTADIENONE](η^5-CYCLOPENTADIENYL)COBALT (I)
(standard deviations for the last significant figures are given in parentheses) [a]

Asymmetric unit	$C_{16}H_{25}OSi_2Co$
Molecular weight	348.48
Unit cell data [b]	
a (Å)	6.5259(5)
b (Å)	12.2378(9)
c (Å)	21.8397(15)
β (deg.)	90.442(7)
V (Å³)	1744.1
Space group	$P2_1/c$
Z	4
Radiation	Mo-K_α (λ 0.71069 Å)
Scan method	ω
No. of symmetry independent reflections [c]	8271
$2\theta_{max}$ (degree)	72
Refinement method [d]	Blocked cascade least-squares
No. of variables	281
R	0.058
R_w [e]	0.041
w	$[\sigma^2(F)+0.0003F^2]^{-1}$

[a] For all crystallographic computations the program system SHELXTL [11] was used except for the diffractometer control and the lattice parameter refinement; the latter two calculations were performed with the standard diffractometer software [12] and with the PARAM program of the X-ray system [13], respectively. [b] The lattice constants were obtained from a restricted least-squares refinement using the 2θ-values of 72 automatically centered reflections in the range $43 < |2\theta| < 51°$. [c] The position of the cobalt atom was obtained by direct methods, those of all other atoms from difference electron density calculations. [d] All 8271 reflections weighted by w were used in the last refinement step. [e] $R_w = [\Sigma w(|F_0| - |F_c|)^2/\Sigma w|F_0|^2]^{1/2}$; ($R_w = R_G$ in SHELXTL).

Experimental

[η^4-2,5-Bis(trimethylsilyl)cyclopentadienone](η^5-cyclopentadienyl)cobalt (I), prepared as in [4,5], was crystallized as red needles from hexane/acetone (10/1) at 4°C. The X-ray data collection was performed on a Nicolet R3 diffractometer equipped with a low temperature device (LT-1) to maintain the crystal at about −140°C. Crystallographic data, including space group, lattice parameters, and the content of the asymmetric unit, are given in Table 1. The refined fractional atomic coordinates of all atoms are presented in Tables 2 and 3. A complete list of bond angles, and lists of thermal parameters and structure factors are available from the authors.

The extended Hückel MO calculations were performed on an IBM 3033 computer with a local version of an EHMO program. The diagonal elements of the Hückel matrix were iterated in self-consistent charge cycles (SCCC) for all atoms but cobalt, using the quadratic expression $H_{ii}(q) = -(Aq^2 + Bq + C)$ [8]. The H_{ii}-values of cobalt were iterated for both charge and configuration. The off-diagonal elements H_{ij} were calculated by the weighting method of Ammeter et al. [9], the

TABLE 2

FRACTIONAL ATOMIC COORDINATES FOR THE NON-HYDROGEN ATOMS IN I ($\times 10^4$) (with e.s.d.'s)

Atom	x	y	z
Co	5567(1)	4265(1)	1607(1)
C(1)	8182(2)	3095(1)	1826(1)
O(1)	10088(1)	3150(1)	1786(1)
C(2)	6721(2)	2764(1)	1339(1)
C(3)	4729(2)	2699(1)	1611(1)
C(4)	4853(2)	3128(1)	2221(1)
C(5)	6913(2)	3467(1)	2345(1)
C(6)	3104(2)	5216(1)	1344(1)
C(7)	4179(2)	5722(1)	1829(1)
C(8)	6230(3)	5915(1)	1637(1)
C(9)	6420(3)	5519(1)	1037(1)
C(10)	4499(3)	5070(1)	856(1)
Si(11)	7468(1)	2367(1)	544(1)
C(12)	8881(3)	1043(1)	564(1)
C(13)	5098(3)	2199(1)	65(1)
C(14)	9220(2)	3410(1)	208(1)
Si(15)	7974(1)	4123(1)	3053(1)
C(16)	5802(3)	4654(1)	3519(1)
C(17)	9407(3)	3067(1)	3501(1)
C(18)	9791(3)	5235(1)	2839(1)

TABLE 3

COORDINATES OF THE HYDROGEN ATOMS ($\times 10^4$) IN I (with e.s.d.'s)

Atom	x	y	z
H(3)	3573(24)	2490(14)	1415(7)
H(4)	3747(24)	3216(13)	2487(7)
H(6)	1737(29)	4953(15)	1350(8)
H(7)	3592(29)	5896(16)	2205(9)
H(8)	7215(33)	6194(19)	1855(10)
H(9)	7558(33)	5535(18)	809(10)
H(10)	4159(30)	4749(18)	491(9)
H(121)	10179(29)	1109(16)	810(9)
H(122)	9326(32)	867(17)	168(10)
H(123)	8058(32)	442(18)	745(10)
H(131)	4352(35)	2796(21)	53(11)
H(132)	4360(33)	1593(20)	183(11)
H(133)	5443(35)	2016(20)	− 344(11)
H(141)	10284(30)	3569(17)	479(9)
H(142)	8536(32)	4081(16)	98(10)
H(143)	9823(34)	3082(19)	− 176(10)
H(161)	4891(32)	4153(17)	3620(10)
H(162)	6260(33)	4941(18)	3896(10)
H(163)	5020(28)	5218(16)	3295(8)
H(171)	8555(32)	2516(18)	3632(9)
H(172)	10134(36)	3425(22)	3874(12)
H(173)	10434(37)	2802(21)	3252(12)
H(181)	10264(33)	5087(18)	2453(10)
H(182)	9244(38)	5958(21)	2826(11)
H(183)	10815(37)	5340(21)	3088(12)

double zeta STO's of [10] were taken as radial functions for carbon, oxygen and cobalt. Hydrogen was represented by a single Slater function with exponent 1.3.

Description and discussion of the crystal structure

The crystal of I contains discrete monomeric $C_{16}H_{25}OSi_2Co$ molecules as shown in Fig. 1. A stereoscopic projection of the crystal arrangement of the four molecules in the unit cell is illustrated in Fig. 2. All closest intermolecular atomic distances are greater than or equal to the sum of the Van der Waals radii. The molecule displays approximately C_s symmetry, with the mirror plane passing through the atoms O(1), C(1), Co and C(6) and bisecting the C(3)–C(4) and C(8)–C(9) bonds.

The cyclopentadienone skeleton spans essentially two planes, one defined by C(2), C(3), C(4) and C(5) (plane a) and the other by C(1), O(1), C(2) and C(5) (plane b). The dihedral angle between planes a and b is 10.2° (Fig. 3), which is somewhat less than the 21.3° found [14] for [η^4-tetrakis(trifluoromethyl)cyclopenta-dienone](η^5-cyclopentadienyl)cobalt, but slightly greater than the 9° reported [15]
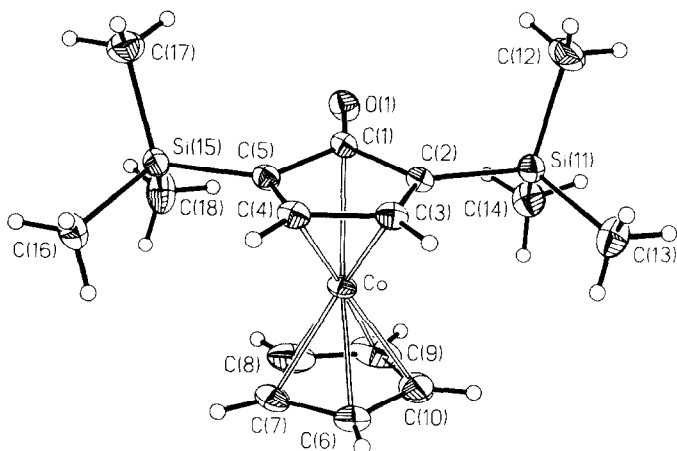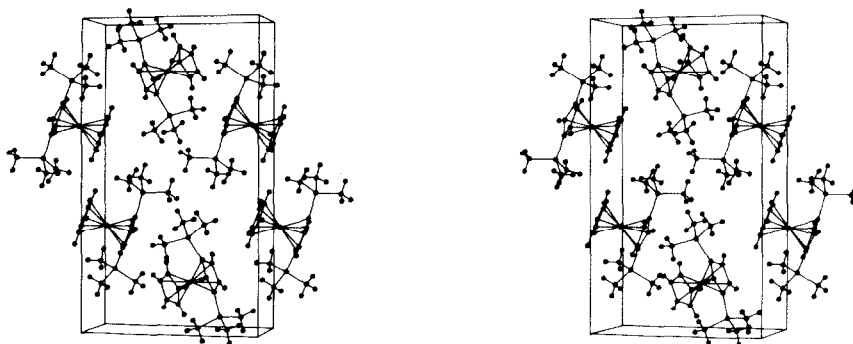

Fig. 1. Molecular structure of I.
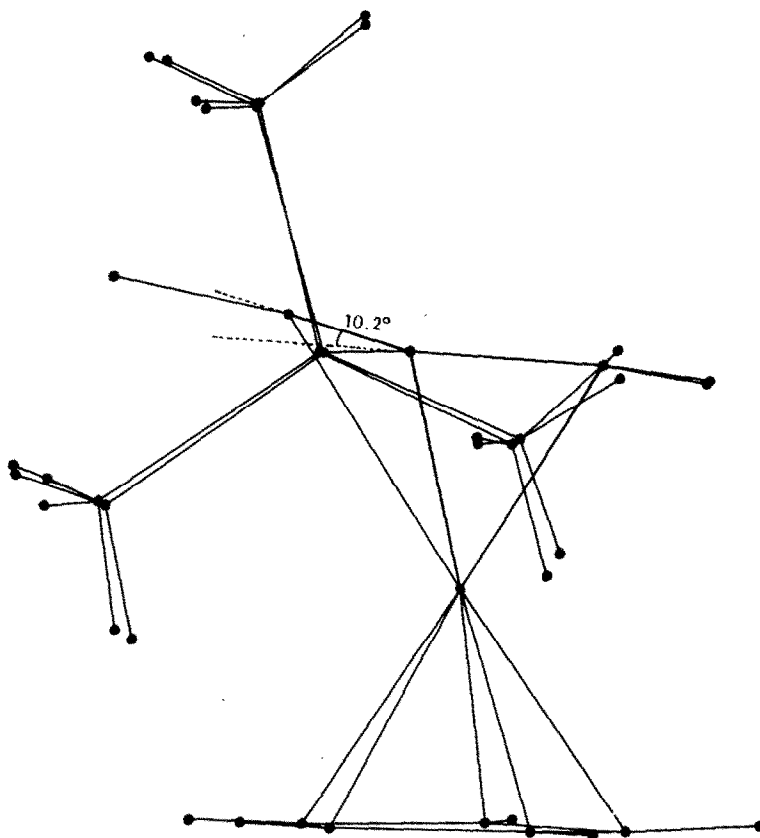

Fig. 2. Stereoscopic packing diagram in the crystal of I.

Fig. 3. Side projection of I, illustrating the two planes of the cyclopentadienone ring.

for (η^4-tetramethylcyclopentadienone)(η^5-cyclopentadienyl)cobalt. Perhaps the electron-donating CH_3 and $Si(CH_3)_3$ substituents in the α-position of the ring interact with the carbonyl group so as to cause the latter to approach the ring plane, while the electron-withdrawing CF_3 substituents disfavor such interaction and cause the carbonyl group to depart from the ring plane. However, more structural studies are needed to test this hypothesis. The cyclopentadienyl and cyclopentadienone rings are staggered with respect to one another, when the molecule is viewed along the axis passing through the middle of the two C_5-rings. The cyclopentadienyl ring and the C(2)-to-C(5)-plane of the cyclopentadienone ring are almost parallel (deviation only 3°).

The bond lengths and some selected bond angles are summarized in Table 4 and 5, respectively. The lengths of the C(2)–C(3), C(3)–C(4) and C(4)–C(5) bonds (1.431–1.435 Å) are almost equal, indicating a strong π-electron delocalization over these four atoms of the cyclopentadienone ring. These bond lengths are very similar to those in the fully delocalized cyclopentadienyl ligand (1.405–1.425 Å) *. The C(1)–O(1) bond length was found to be rather large (1.249 Å) compared to that in

---

* Owing to a relatively large vibration amplitude these values are somewhat spread.

TABLE 4

BOND LENGTHS IN I (Å) (with e.s.d.'s)

Co–C(1)	2.276(1)	Co–C(2)	2.072(1)
Co–C(3)	1.993(1)	Co–C(4)	1.991(1)
Co–C(5)	2.074(1)	Co–C(6)	2.062(1)
Co–C(7)	2.059(1)	Co–C(8)	2.066(1)
Co–C(9)	2.056(2)	Co–C(10)	2.033(2)
C(1)–O(1)	1.249(1)	C(1)–C(2)	1.479(2)
C(1)–C(5)	1.482(2)	C(2)–C(3)	1.435(2)
C(2)–Si(11)	1.871(1)	C(3)–C(4)	1.435(2)
C(4)–C(5)	1.431(2)	C(5)–Si(15)	1.871(1)
C(6)–C(7)	1.410(2)	C(6)–C(10)	1.419(2)
C(7)–C(8)	1.425(2)	C(8)–C(9)	1.405(3)
C(9)–C(10)	1.422(3)	Si(11)–C(12)	1.864(2)
Si(11)–C(13)	1.871(2)	Si(11)–C(14)	1.868(2)
Si(15)–C(16)	1.868(2)	Si(15)–C(17)	1.867(2)
Si(15)–C(18)	1.867(2)		

TABLE 5

SELECTED BOND ANGLES IN I (deg.) (with e.s.d.'s)

C(2)–C(1)–C(5)	105.9(1)	C(1)–C(2)–C(3)	107.4(1)
C(2)–C(3)–C(4)	108.6(1)	C(3)–C(4)–C(5)	109.2(1)
C(1)–C(5)–C(4)	107.2(1)	C(7)–C(6)–C(10)	107.5(1)
C(6)–C(7)–C(8)	108.4(1)	C(7)–C(8)–C(9)	107.9(2)
C(8)–C(9)–C(10)	108.0(2)	C(6)–C(10)–C(9)	108.2(1)

saturated ketones or esters (1.19–1.22 Å [16]) or that in cyclopentenones (e.g. 1.203 Å for e.g. prostaglandin A_1 [17]). The C(1)–C(2) and C(1)–C(5) bond length in I are slightly shorter (1.479–1.482 Å) than ordinary C–C single bond lengths.

Extended Hückel molecular orbital calculation

The extended Hückel molecular orbital (EHMO) or semi-empirical Wolfsberg–Helmholz model [18] has proved to be useful in the discussion of the electronic properties of transition metal complexes. In order to investigate the bonding modes of the cyclopentadienone (CpO) with the cyclopentadienylcobalt fragment (CpCo), calculations were performed on a simple model compound, namely the parent cyclopentadienone complex III, $\{(\eta^4\text{-}C_5H_4O)(\eta^5\text{-}C_5H_5)Co,$ CpOCpCo$\}$, as well as on the cyclopentadienone and cyclopentadienyl fragments. For the fragment MO (FMO) calculations the geometries and H_{ii}'s were kept constant at the values of the final cycle of the SCCC-iterations on the complex. The geometry of the model compound was created by idealizing the X-ray structure of the title compound to C_s symmetry. The corresponding coordinates are given in Table 6.

Bonding between these two fragments is accomplished by frontier molecular orbitals (FMOs) possessing an overlap in the bonding region. A partial MO-diagram containing the lower CpO π-FMOs on one hand and the CpCo d-character FMOs
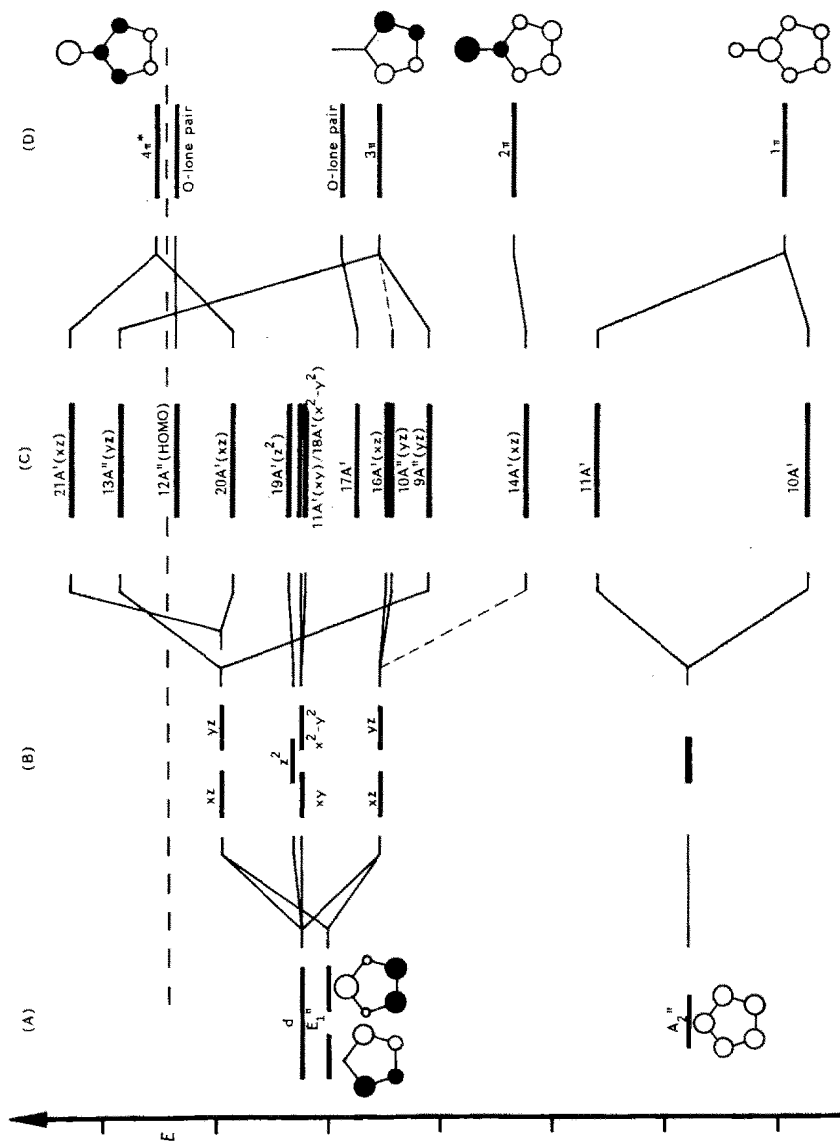
Fig. 4. Partial MO-diagram of the parent cyclopentadienonecobalt complex III. The following MOs of $[(C_5H_4O)Co(C_5H_5)]$ and its fragment are shown: (A) Occupied π-MOs of the cyclopentadienyl anion plus d-levels of the metal. (B) $Co(C_5H_5)$ occupied fragment MOs (FMOs) made up by the orbitals in (A). (C) Partial MO-diagram of $[(C_5H_4O)Co(C_5H_5)]$. MOs built up by the FMOs described in (B) and (D). (D) Occupied and first virtual π-MOs and oxygen lone pairs of the C_5H_4O fragment.
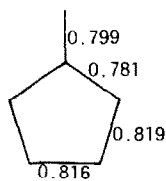
TABLE 6

AVERAGED COORDINATES FOR [η^4-CYCLOPENTADIENONE](η^5-CYCLOPENTADIENYL)-COBALT (1) [a]

Atom	x	y	z
Co	0.00000	0.00000	0.00000
O(1)	2.58205	0.00000	−2.00958
C(1)	1.34523	0.00000	−1.83625
C(2)	0.47531	1.18149	−1.63615
C(3)	−0.88048	0.71745	−1.63615
C(6)	−1.28434	0.00000	1.66279
C(7)	−0.45674	−1.12925	1.66279
C(8)	0.88110	−0.69554	1.66279
H(3)	−1.62376	1.25285	−1.57263
H(6)	−2.21520	0.00000	1.66279
H(7)	−0.77016	−1.98784	1.66279
H(8)	1.41299	−1.20417	1.66279

[a] Only symmetry-independent atoms are given in this table.
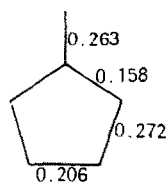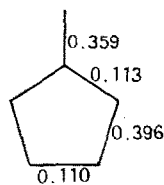
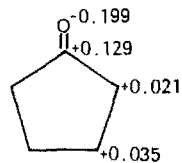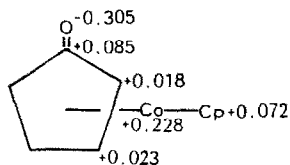Cyclopentadienone of Complex III   Cyclopentadienone Fragment
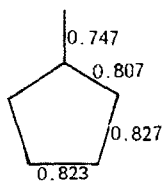
Fig. 5. σ- and π-overlap population of the complex, its fragment, as well as its charges.

on the other is shown in Fig. 4. In the CpCo fragment the "d orbitals" are split into three parts, namely the nonbonding d_{xy}, $d_{x^2-y^2}$ and d_{z^2} orbitals and the bonding as well as the antibonding combinations of d_{x^2}, d_{yz} with the E_1'' π-orbitals of Cp^-. Bonding of CpCo to CpO is mainly due to the interaction of the 3π and 4π levels of CpO with the single occupied antibonding d-E_1'' FMOs. Charge is transferred from the 3π FMO of CpO into the CpCo fragment, thereby reducing the π-overlap population (π-OP) at C(2)–C(3) and C(4)–C(5) and also lowering the antibonding interactions of C(3)–C(4). Furthermore, electrons are back-donated from the uppermost CpCo FMOs (antibonding $d_x2 - E_1''$ combination) into the formerly unoccupied 4π-orbitals of CpO, again lowering the C(2)–C(3) and C(4)–C(5) π-bond strength while simultaneously strenghtening the C(3)–C(4) bond. The σ-overlap population in CpO is merely affected by the complexation, as can be derived from Fig. 5. The alternating π-bond strenghts in this fragments are equalized during complexation by the above-mentioned mechanism. This results in an equalized total bond strength within the CpO ring which is reflected in the equal bond lengths of the X-ray diffraction analysis.

The total CpO–Co overlap population is 0.53, suggesting a total bond strength of about half that of a C–C bond which is in reasonable agreement with chemical experience. The interactions of the 3π and 4π FMOs of the CpO with the CpCo fragment modifies these orbitals enough to stabilize the CpO against the pronounced tendency to dimerize via a Diels–Alder mechanism.

Acknowledgement

References

1 M.A. Ogliaruso, M.G. Romanelli and E.J. Becker, Chem. Rev., 65 (1965) 261.
2 G. Maier, H.W. Lage and H.P. Reisenauer, Angew. Chem., 93 (1981) 1010; Angew. Chem. Int. Ed. Engl., 20 (1980) 976.
3 G. Maier, S. Pfriem, U. Schäfer, K.-D. Malsch and R. Matusch, Chem. Ber., 114 (1981) 3965.
4 E.R.F. Gesing, J.P. Tane and K.P.C. Vollhardt, Angew. Chem., 92 (1980) 1057; Angew. Chem. Int. Ed. Engl., 19 (1980) 1023.
5 For an optimization study, see: T.C.C. Gartenmann, Diploma Thesis, University of Zurich, 1983.
6 J.P. Tane and K.P.C. Vollhardt, Angew. Chem., 94 (1982) 642; Angew. Chem. Int. Ed. Engl., 21 (1982) 617; Angew. Chem. Suppl., (1982) 1360.
7 E.R.F. Gesing, H. Kaulen, J.P. Tane and K.P.C. Vollhardt, in preparation.
8 H. Basch, A. Viste and H.B. Gray, Theoret. Chim. Acta, 3 (1978) 458.
9 J.H. Ammeter, H.B. Bürgi, J.C. Thibeault and R. Hoffmann, J. Am. Chem. Soc., 100 (1978) 3686.
10 E. Clementi and C. Roetti, Atomic Data and Nuclear Data Tables, 14 (1974) 177.
11 G.M. Sheldrick, SHELXTL, Revision 3.0, University of Göttingen, 1981.
12 Data Collection Operating Manual, Nicolet XRD Corporation, Cupertino, California, 1980.
13 J.M. Stewart, G.T. Kruger, H.L. Ammon, C.W. Dickinson and S.R. Hall, The X-Ray System, Version of 1972, Technical Report No. TR-192, Computer Science Center, University of Maryland.
14 N.A. Bailey, M. Gerloch and R. Mason, Nature, 201 (1964) 72.
15 L.F. Dahl and D.L. Smith, J. Am. Chem. Soc., 83 (1961) 752.
16 J.D. Dunitz, X-ray Analysis and the Structure of Organic Molecules, Cornell University Press, Ithaca and London, 1979.
17 J.W. Edmonds and W.L. Duax, J. Am. Chem. Soc., 97 (1975) 413.
18 M. Wolfsberg and L. Helmholtz, J. Chem. Phys., 20 (1952) 837.