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η^4-BENZOCYCLOBUTADIENE-η^5-CYCLOPENTADIENYLCOBALT, A NEW "AROMATIC" SANDWICH COMPLEX

RICHARD L. DUCLOS, Jr., K. PETER C. VOLLHARDT * and LINCOLN S. YEE

Department of Chemistry, University of California and the Materials and Molecular Research Division, Lawrence Berkeley Laboratory, Berkeley, California 94720 (U.S.A.)

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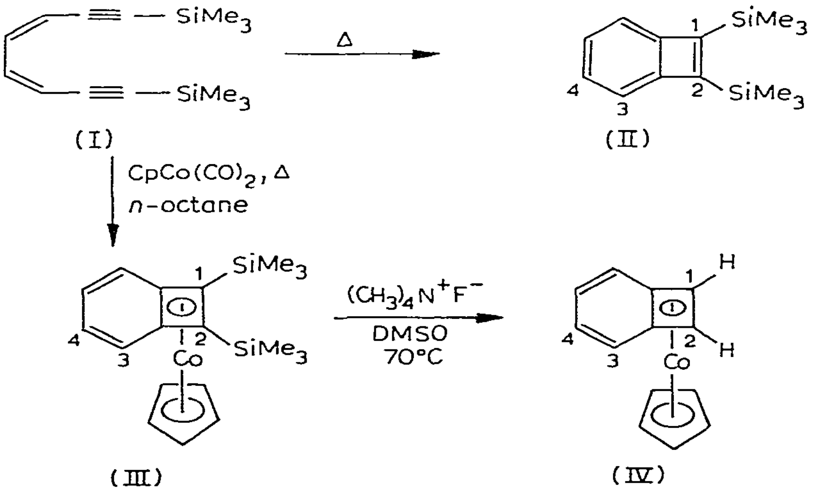
Summary

Reaction of 1,8-bis(trimethylsilyl)-*cis,cis*-3,5-octadiene-1,7-diyne with $CpCo(CO)_2$ gives η^4-1,2-bis(trimethylsilyl)benzocyclobutadiene-η^5-cyclopentadienylcobalt. Desilylation with fluoride results in the parent compound, the first known benzocyclobutadiene sandwich complex. NMR analysis provides evidence for diatropic character of the complexed as opposed to the free ligand.

We have recently reported [1] that gas phase thermolysis of dienediyne (I) results in clean rearrangement to 1,2-bis(trimethylsilyl)benzocyclobutadiene (II) in which the paratropic character [2] of the planar 8 π-electron cyclobutadienoid framework expresses itself in unusually shielded benzenic absorptions when compared with suitable model compounds (c.f. the 1,2-dihydro derivative).



Since II represents the first isolable benzocyclobutadiene containing protons directly bound to the π-periphery which can be used in the NMR experiment as a probe for the size and sign of a possible ring current we decided to investigate the effect of transition metal complexation on its physical properties.

According to the Dewar-Chatt-Duncanson model [3] interaction of II with a suitable metal should lead to an increased HOMO—LUMO gap and thus a decreased paramagnetic contribution to the ring current in the antiaromatic ligand [4]. Moreover, not only should the latter become more diatropic on complexation but the relative ordering of the chemical shifts of the benzenic protons might reverse since the system should now show naphthalenoid magnetic behavior with relatively low field α-protons rather than cyclobutadienoid character [2].

Addition of an equimolar solution of I [5] and $CpCo(CO)_2$ in n-octane to refluxing n-octane using a syringe pump (70 h) gave after chromatographic purification on alumina and crystallization brown-red air stable needles of III (48%). The structural assignment was based on the spectral and analytical data, and conversion to the parent compound (IV). The ^1H NMR spectrum depicted a characteristic AA'BB' pattern for the benzenic protons ($\tau(C_6D_6)$ 3.00, 3.38), a sharp Cp-signal (τ 5.51), and the trimethylsilyl peak (τ 9.72). ^{13}C NMR absorptions (C_6D_6) at δ 0.72, 60.5, 79.2, 94.3, 124.8, and 128.4 are consistent with the assigned structure. The two quaternary carbons (δ 60.5, 94.3) were readily identified by their relatively low intensity and the higher field signal assigned to the silylated position by comparison with the corresponding absorption (δ 51.3, vide infra) for the desilylated system (IV). The down-field shift observed on silylation of an sp^2-hybridized carbon (e.g. comparing IV with III) is of the same order of magnitude as in other molecules [8]. The comparatively low field position of the other quaternary carbon is typical of cyclobutadienoid carbons at the fusion to a benzene ring [9]. The mass spectrum had a parent ion at m/e 370 with major fragmentation peaks at 355 ($M^+ - CH_3$) and 73 ($-Si(CH_3)_3$). Unlike cyclobutadiene cyclopentadienylcobalt sandwich complexes [6] *retro*-(2 + 2) cycloadditions of the four ring in III to provide $CpCo(alkyne)^+$ fragments appear to be relatively disfavored on electron impact as evidenced by a small m/e 200 ($CpCoC_6H_4$) peak. The free ligand is not observed. For the mass spectra of benzocyclobutadieneiron carbonyl derivatives, see ref. 7.

Complexes of η^5-cyclopentadienylcobalt with dimeric and oligomeric derivatives of I constituted the major byproducts of the reaction of I with $CpCo(CO)_2$ as evidenced by preliminary spectral analysis (NMR, m/e). When purification of III on silica gel was attempted, in addition to decomposition slow desilylation took place leading to a mixture of III, IV, and monosilylated material. The ^1H NMR spectrum of this mixture revealed the expected two Cp singlets ($\tau(CCl_4)$ 5.55, 5.57), two cyclobutadiene peaks (τ 6.03, 6.13) and two trimethylsilyl absorptions (τ 9.77, 9.82). The mass spectrum displayed the appropriate molecular ions. Attempted protodesilylation of III with trifluoroacetic acid led to decomposition. For the protodesilylation of trimethylsilylcyclobutadienecyclopentadienylcobalt complexes, see ref. 10.

The parent system IV was synthesized by heating complex III in DMSO with tetramethylammonium fluoride trihydrate to 70°C for 24 h and following the progress of the reaction by TLC. Chromatography on neutral alumina gave 66%

of the brown-red complex IV in the form of needles. The ^{1}H NMR spectrum revealed an $AA'BB'$ pattern ($\tau(C_6D_6)$ 2.96, 3.37) for the benzenic portion of the molecule, a Cp singlet (τ 5.40), and a cyclobutadiene absorption (6.04). The latter appears as a broadened singlet indicating a small coupling to the H(3) protons on the six ring. This broadening is also observed in the low-field portion of the $AA'BB'$ pattern which allows the assignment of this absorption to H(3). Only four (of the five possible) lines were detected in the ^{13}C NMR spectrum for all but the quaternary carbons ($\delta(C_6D_6)$ 51.3, 79.0, 124.2, 128.7). The mass spectrum showed the anticipated parent ion (*m/e* 226) and fragmentation peaks indicating loss of acetylene and free ligand [7]. Complexes III and IV constitute the first sanwich complexes involving benzocyclobutadienes as ligands. CpFe(CO)$_2$—benzocyclobutadiene complexes in which the benzocyclobutadiene ligand is bound only in mono- and di-*hapto*-fashion are described in ref. 11.

The ^{1}H chemical shifts for II, III, and IV in various solvents are compared in Table 1. Inspection of the data results in the following conclusions: (a) solvent effects on the proton chemical shifts in the substances investigated appear negligible; (b) there is practically no substituent effect of the trimethylsilyl groups on the chemical shift of the remaining protons; (c) the proton absorptions at the benzenic locations suffer a dramatic down-field shift when going from II to III/IV, an effect that is particularly striking at the α-position (H(3)). These observations are most readily explained by postulating a pronounced reduction of the paramagnetic ring current contribution to the chemical shifts of II on complexation as might be expected on theoretical considerations [3,4]. The relatively high-field shifted H(3) protons in II ow their shielding to the close proximity to the cyclobutadienoid four-ring [2]. When the latter is complexed to cobalt the cyclobutadienoid character is removed and an "aromatic" system with relatively low lying HOMO's and high lying LUMO's is produced. The H(3) protons now lie closer to what has become a diatropic ring experiencing a relatively large down-field shift when compared with H(4). This effect is analogous to that observed in the NMR spectra of polycyclic benzenoid hydrocarbons (e.g. naphthalene) where atoms in the vicinity of other benzene rings experience increased deshielding. Finally, an alternative explanation for the observed NMR behavior based on anisotropy effects around the metal appears unlikely since, if anything, one might expect those to cause shielding rather than deshielding of the atoms located in the region of space occupied by the H(3) protons. For example, both *exo* and *endo* protons in

TABLE 1

CHEMICAL SHIFTS OF BENZOCYCLOBUTADIENE SYSTEMS (τ)

Compound	H(1)	H(3)	H(4)	Me$_3$Si	Cp	Solvent
II [1]	—	4.37	3.80	9.82	—	CCl$_4$
	—	4.25	3.70	9.81	—	CD$_3$CN
	—	4.25	3.63	9.85	—	Toluene-d_8
III	—	3.10	3.43	9.86	5.57	CCl$_4$
	—	3.00	3.38	9.72	5.51	C_6D_6
IV	6.04	2.96	3.37	—	5.40	C_6D_6

η^4-cyclopentadiene- and η^4-cyclohexadiene-cyclopentadienylcobalt complexes are shifted to higher field when compared with the uncomplexed ligand [12]. According to models the region in space occupied by H(3) in III/IV is located approximately inbetween the area occupied by the respective *exo/endo* protons of the cyclohexadiene complexes, although H(3) is further removed from the metal. Thus, it appears that without the anisotropy of the cobalt, H(3) might be found at even lower fields. Inspection of the literature reveals that the mononuclear CpCo unit has a generally shielding effect on protons in its vicinity, at least in coordinatively saturated complexes. This applies also to directly bound alkyl groups [13]. This situation is more complex with other transition metals where shielding and deshielding areas of space are to be found around the metal nucleus.

Experimental

General

Melting points were determined on a Thomas-Hoover Unimelt apparatus and are uncorrected. ^{1}H NMR spectra were recorded on a Varian-T-60 NMR spectrometer, ^{13}C NMR spectra were recorded on a Nicolet Technology Corporation Fourier transform instrument. Chemical shifts are reported relative to tetramethylsilane as an internal standard. IR spectra were obtained with a Perkin—Elmer Model 337 spectrometer and are reported as $\nu_{\max}$ values (cm^{-1}). Mass spectra and elemental analyses were provided by the Mass Spectral Service and the Microanalytical Laboratory, respectively, of the University of California, Berkeley, California.

Solvents used were thoroughly purged with dry, oxygen-free nitrogen. All reactions and transfers of cobalt complexes were carried out under an atmosphere of nitrogen. Column chromatography was carried out with Woelm neutral alumina (activity grade III) in the absence of air. Vacuum line operations were carried out on a high vacuum, multiple line apparatus.

η^4-1,2-Bis(trimethylsilyl)benzocyclobutadiene-η^5-cyclopentadienylcobalt, III

An n-octane solution (16.5 ml) of 1,8-bis(trimethylsilyl)-*cis,cis*-3,5-octadiene-1,7-diyne (I) (0.50 g, 2.04 mmol, 1.0 equivalent) and η^5-cyclopentadienyldicarbonylcobalt (0.40 g, 2.24 mmol, 1.1 equivalent) was added to refluxing n-octane (30 ml) under an atmosphere of nitrogen. The addition time (syringe pump) was 70 h. Vacuum transfer of the solvent left the crude product as a brown oil which was chromatographed on neutral alumina (75 g, hexane). The product was then vacuum microdistilled to yield a bright, brownish-red oil, b.p. 40°C/0.01 torr. Pure III was crystallized from methanol/water to yield brownish-red needles (0.36 g, 0.97 mmol, 47.7%): m.p. 58.5°C; ^{1}H NMR (benzene-d_6): τ 3.00 (AA', m, 2 H), 3.38 (BB', m, 2 H). 5.51 (s, 5 H), 9.72 (s, 18 H); ^{13}C NMR (benzene-d_6): δ 0.72, 60.5, 79.2, 94.3, 124.8, 128.4; IR (KBr): 3030, 2950, 1240, 845, 720 cm^{-1}; m/e (% rel. intensity): 370 (M^+, 100), 355 (24), 341 (2), 297 (8), 231 (9), 200 (7), 155 (28), 124 (10), 73 (73). High resolution m/e: Found: 370.0981; calcd. for $C_{19}H_{27}CoSi_2$: 370.0983. Anal. Found: C, 61.64; H, 7.39; Co, 16.2. calcd. for $C_{19}H_{27}CoSi_2$: C, 61.59; H, 7.34; Co, 15.90%.

η^4-Benzocyclobutadiene-η^5-cyclopentadienylcobalt, IV

A solution of III (0.075 g, 0.203 mmol, 1.0 equivalent) and tetramethylammonium fluoride trihydrate (0.077 g, 0.52 mmol, 2.5 equivalents) in DMSO (2.5 ml) was stirred magnetically and warmed to 70°C under an atmosphere of nitrogen. The reaction was followed by analytical thin-layer chromatography (Merck Al_2O_3 GF-254 type 60/E, hexane), and reached completion after 24 h. The product was extracted with hexane, and the hexane washed repeatedly with water to remove any traces of DMSO. The hexane solution was dried ($MgSO_4$) and the solvent removed by vacuum transfer. The brown oil which resulted was chromatographed on neutral alumina (3.0 g, petroleum ether 30—60°C). The product was then vacuum microdistilled to yield a bright, brownish-red oil, b.p. 25°C/0.01 torr. The complex IV was then crystallized from petroleum ether at —65°C to yield brownish-red needles (30.3 mg, 0.134 mmol, 66.0%); m.p. 56.5°C; ^1H NMR (benzene-d_6); τ 2.96 (AA', m, 2 H), 3.37 (BB', m, 2 H), 5.40 (s, 5 H), 6.04 (s, 2 H); ^{13}C NMR (benzene-d_6): δ 51.3, 79.0, 124.2, 128.7; IR (KBr): 3040, 1370, 1335, 1290, 1240, 1190, 1125, 1005, 975, 820, 810, 715 cm^{-1}; m/e (% rel. intensity): 226 (M^+, 100), 200 (14), 187 (10), 174 (7), 165 (69), 141 (42), 124 (27), 102 (7), 59 (48). High resolution m/e: Found: 226.0190; calcd. for $C_{13}H_{11}Co$: 226.0192. Anal. Found: C, 69.32; H, 5.05. Calcd. for $C_{13}H_{11}Co$: C, 69.04; H, 4.90%.

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References

1 K.P.C. Vollhardt and L.S. Yee, J. Amer. Chem. Soc., 99 (1977) 2010.

2 K.P.C. Vollhardt, Top. Curr. Chem., 59 (1975) 113; P. Garratt and P. Vollhardt, Aromatizität, Georg Thieme Verlag, Stuttgart, 1973.

3 M.J.S. Dewar, Bull. Soc. Chim. Fr., 18 (1951) C71; J. Chatt and L.A. Duncanson, J. Chem. Soc., (1953) 2939.

4 J.A. Pople and K.G. Untch, J. Amer. Chem. Soc., 88 (1966) 4811; T. Nakajima and S. Kohda, Bull. Chem. Soc. Jap., 39 (1966) 804; F. Baer, H. Kuhn and W. Regel, Z. Naturforsch. A, 22 (1967) 103; H.C. Longuet-Higgins, The Chemical Society, London, Special Publication No. 21, 1967, p. 109; R.C. Haddon, V.R. Haddon and L.M. Jackman, Top. Curr. Chem., 16 (1971) 103.

5 G.H. Mitchell and F. Sondheimer, J. Amer. Chem. Soc., 91 (1969) 7520.

6 J.R. Fritch and K.P.C. Vollhardt, J. Amer. Chem. Soc., 100 (1978) 3643; M.D. Rausch, I. Bernal, B.R. Davies, A. Siegel, F.A. Higbie and G.F. Westover, J. Coord. Chem., 3 (1973) 149.

7 A. Efraty, M.H.A. Huang, and C.A. Weston, J. Organometal. Chem., 91 (1975) 327.

8 J.B. Stothers, Carbon-13 NMR spectrocopy, Academic Press, New York, 1972.

9 A.J. Jones, P.J. Garratt and K.P.C. Vollhardt, Angew. Chem., 85 (1973) 260; Angew. Chem. Intern. Ed., 12 (1973) 241.

10 J.F. Helling, S.C. Rennison and A. Merijan, J. Amer. Chem. Soc., 89 (1967) 7140.

11 R.B. King, A. Efraty and W.C. Zipperer, J. Organometal. Chem., 38 (1972) 121; A. Sanders, C.V. Magatti and W.P. Giering, J. Amer. Chem. Soc., 96 (1974) 1610; A. Sanders and W.P. Giering, ibid., 96 (1974) 5247; T. Bauch, A. Sanders, C.V. Magatti, P. Waterman, D. Judelson and W.P. Giering,

J. Organometal. Chem., 99 (1975) 269; A. Sanders, T. Bauch, C.V. Magatti, C. Lorenc and W.P. Giering, ibid., 107 (1967) 359.

12 M.M. Maricq, J.S. Waugh, J.L. Fletcher and M.J. McGlinchey, J. Amer. Chem. Soc., 100 (1978) 1978; R.B. King, P.M. Treichel and F.G.A. Stone, ibid., 83 (1961) 3593; G.E. Herberich and J. Schwarzer, Angew. Chem., 81 (1969) 153; Angew. Chem. Intern. Ed., 8 (1969) 143; G.E. Herberich and J. Schwarzer, Chem. Ber., 103 (1970) 2016; G.E. Herberich and R. Michelbrink, ibid., 103 (1970) 3615; Y. Wakatsuki and H. Yamazaki, J. Organometal. Chem., 139 (1977) 169; see also: Gmelins Handbuch der anorganischen Chemie, Supplement to the 8th edition, Vol. 5, part I, 1973, p. 329.

13 N.E. Schore, C. Ilenda and R.G. Bergman, J. Amer. Chem. Soc., 98 (1976) 7436.