Ersch. in: Journal of Organometallic Chemistry ; 236 (1982), 2. - S. 267-272
http://dx.doi.org/10.1016/S0022-328X(00)87082-5

MOLECULAR STRUCTURE AND CHEMICAL PROPERTIES OF A BINUCLEAR CYCLOPENTADIENYLCOBALT NITROSYL CATION

FRANZ WOCHNER, EGBERT KELLER and HANS H. BRINTZINGER
Fakultät für Chemie, Universität Konstanz, Postfach 5560, 7750 Konstanz (B.R.D.)

Summary

The spectroscopic, structural and chemical properties of the binuclear cation $(C_5H_5)_2Co_2(\mu\text{-NO})_2^+$ are described.

Introduction

Cationic cyclopentadienylcobalt nitrosyl derivatives have been shown by Clamp et al. [1] to be formed in reactions of $(C_5H_5)Co(CO)_2$ with $NOPF_6$. Correspondingly, we find that reaction of $(C_5H_5)Co(CO)_2$ with nitrosyl salts in CH_2Cl_2 solution affords the binuclear mono-cation $(C_5H_5)_2Co_2(\mu\text{-NO})_2^+$, the existence of which had previously been inferred by Bernal et al. [2] from electrochemical studies on the neutral binuclear nitrosyl compound $(C_5H_5)_2Co_2(\mu\text{-NO})_2$ [3]. Since the IR spectral characteristics of this cation, a single NO-absorption at 1620 cm^{-1}, are quite different, however, from those reported for this species in ref. 1, we have established its identity by additional chemical evidence and by a determination of its crystal and molecular structure.

Results

The cation $(C_5H_5)_2Co_2(\mu\text{-NO})_2^+$ (**1**) is formed in 40—50% yield either as its PF_6 or as its BF_4 salt when $(C_5H_5)Co(CO)_2$ is treated with equimolar quantities or with a slight excess of $NOPF_6$ or $NOBF_4$ in CH_2Cl_2 at room temperature. The product crystallizes in form of dark red platelets from CH_2Cl_2/pentane. Both the BF_4 and PF_6 salts of **1** are fairly soluble (ca. 10^{-2} *M*) in CH_2Cl_2, but much less so in $CHCl_3$, CCl_4 and in less polar organic solvents. The crystalline product is quite stable in the air, but in solution, exposure to air causes decomposition within less than one hour.

The IR spectrum of the cation **1** in CH_2Cl_2 solution is dominated by a very strong ν(NO) absorption at 1620 cm^{-1} (at 1610 cm^{-1} in Nujol mull). Weaker absorptions at 3093, 1398, 1017, 992 and 810—820 cm^{-1}, assignable to the η-C_5H_5-rings, are partly hidden by the strong absorptions of the PF_6^- or the BF_4^- anion at about 845 and 1060 cm^{-1}, respectively.

Crystals suitable for X-ray structural work were obtained from CH_2Cl_2/pentane solutions of $(C_5H_5)_2Co_2(\mu\text{-}NO)_2BF_4$. X-ray diffraction intensities were determined on a Syntex-P3 four-circle diffractometer at 293 K (Mo-K_α, λ = 71.069 pm, graphite monochromator, ω-scan with $2.0 < \omega/t < 29.3°\ min^{-1}$) and $2 < 2\theta < 42°$. One standard reflection was measured for every 100 reflections during data collection as a check on crystal and instrumental stability.

The crystals are monoclinic, space group $C2/c$; a 1788(1), b 994.6(2), c 1947(1) pm, β 123.73; V 2878 $\cdot 10^6$ pm^3, d_{calc} 1.82 g/cm^{-3} for M = 394.9 and Z = 8; d_{exp} 1.76 g/cm^{-3}. The unit cell contains one BF_4^- and two crystallographically independent half-units of $(C_5H_5)_2Co_2(\mu\text{-}NO)_2^+$ per asymmetric unit; the two halves of each $(C_5H_5)_2Co_2(\mu\text{-}NO)_2^+$ unit are related to each other by a crystallographic center of symmetry.

The structure was solved by direct methods and refined (SHELXTL program [4]) using 915 reflections with $F_o > 4\sigma$ with anisotropic temperature parameters for Co, N, O and F and isotropic temperature parameters for C and B atoms. Hydrogen atoms were not determined. The refinement resulted in values of R_1 = 0.082 and R_2 = 0.084. Residual electron density was $\leqslant 1.0\ e/10^6\ pm^3$ throughout.

The results (see Table 1) indicate some disorder of the BF_4^- units: The tem-

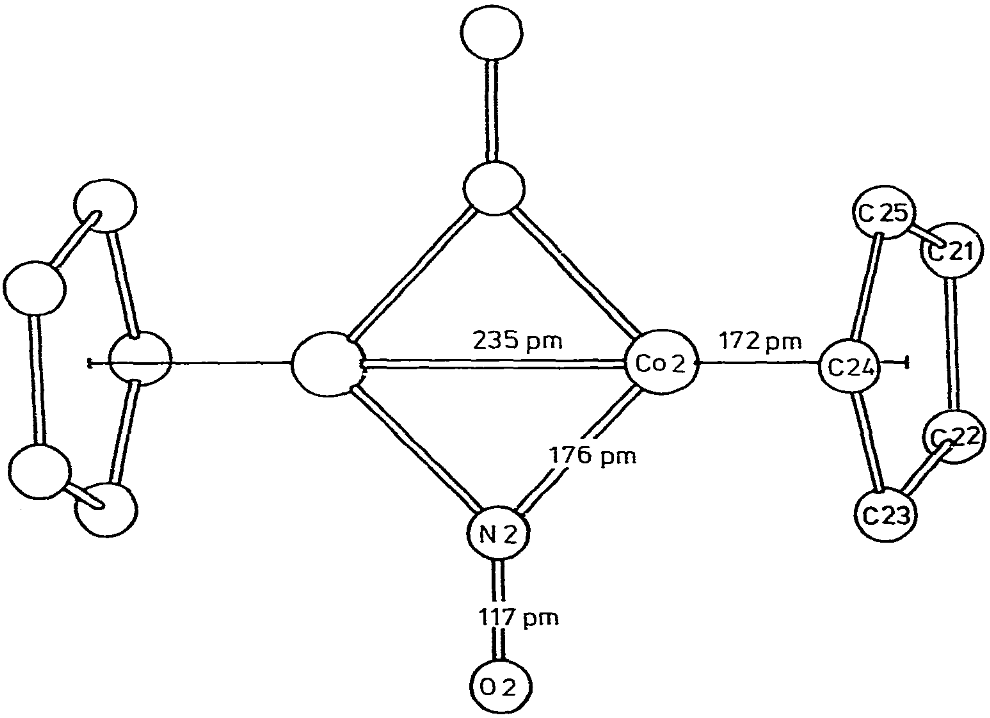


Fig. 1. Molecular structure of $(C_5H_5)_2Co_2(\mu\text{-}NO)_2^+$.

TABLE 1

STRUCTURAL PARAMETERS FOR $(C_5H_5)_2Co_2(\mu\text{-}NO)_2BF_4$

FRACTIONAL COORDINATES (with e.s.d.'s) AND THERMAL PARAMETERS

Atom	*x/a*	*y/b*	*z/c*	U_{11} or U	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Co(1)	0,4211(2)	0,0700(3)	0,2066(2)	0,074(2)	0,054(2)	0,063(2)	−0,002(2)	0,040(2)	0,003(2)
N(1)	0,504(1)	0,070(2)	0,184(1)	0,106(14)	0,101(14)	0,049(11)	0,004(11)	0,051(11)	0,012(12)
O(1)	0,510(1)	0,070(2)	0,127(1)	0,131(14)	0,152(16)	0,076(11)	−0,011(12)	0,063(11)	0,009(13)
C(11)	0,301(2)	0,018(3)	0,193(2)	0,103(8)					
C(12)	0,307(2)	−0,045(3)	0,130(2)	0,117(9)					
C(13)	0,312(2)	0,057(3)	0,084(2)	0,105(8)					
C(14)	0,310(2)	0,188(3)	0,117(1)	0,097(8)					
C(15)	0,307(2)	0,164(2)	0,184(1)	0,090(7)					
Co(2)	−0,0016(2)	0,0981(3)	0,0327(2)	0,080(2)	0,065(2)	0,075(2)	0,006(2)	0,048(2)	0,003(2)
N(2)	0,038(2)	0,067(2)	−0,030(2)	0,328(36)	0,112(18)	0,189(24)	−0,021(18)	0,216(27)	−0,076(22)
O(2)	0,070(3)	0,127(2)	−0,060(2)	0,548(55)	0,090(15)	0,357(38)	−0,030(19)	0,405(44)	−0,039(24)
C(21)	−0,085(2)	0,221(2)	0,053(1)	0,085(7)					
C(22)	−0,052(2)	0,295(3)	0,012(1)	0,100(8)					
C(23)	0,055(2)	0,293(2)	0,072(1)	0,086(7)					
C(24)	0,070(2)	0,219(3)	0,140(1)	0,097(8)					
C(25)	−0,010(2)	0,175(2)	0,129(1)	0,096(8)					
B	0,224(3)	0,941(4)	−0,150(2)	0,100(10)					
F(1)	0,289(1)	−0,027(2)	0,393(1)	0,120(13)	0,098(13)	0.315(27)	0,018(15)	0,094(16)	0,024(11)
F(2)	0,252(1)	0,162(2)	0,326(1)	0,186(17)	0,133(14)	0.134(13)	0,005(11)	0,086(13)	−0,024(13)
F(3)	0,217(2)	0,106(3)	0,407(2)	0,327(33)	0,317(33)	0,329(33)	0,059(29)	0,287(32)	0,052(29)
F(4)	0,156(2)	0,002(2)	0,295(1)	0,258(26)	0,174(20)	0,173(20)	0,066(17)	−0,045(19)	−0,103(20)

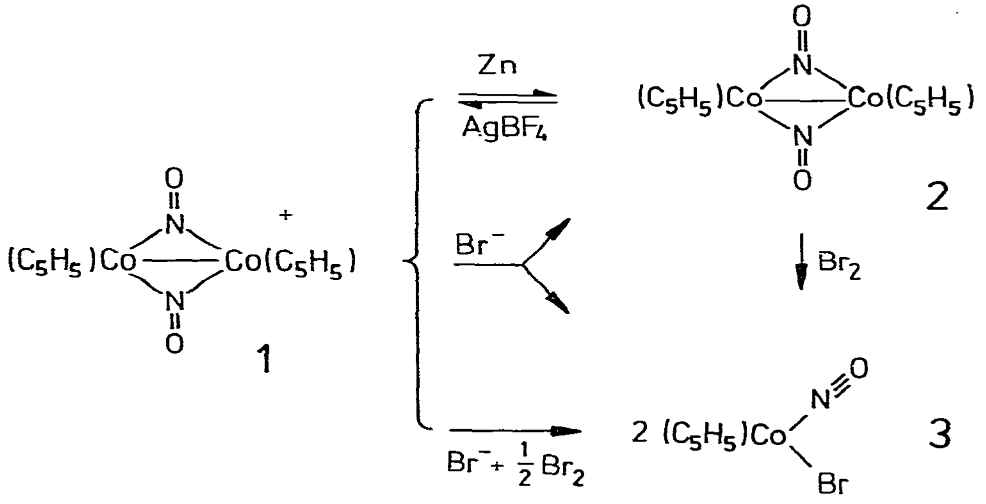
INTERATOMIC DISTANCES (in pm) AND BOND ANGLES (in degrees)

Molecule 1		Molecule 2		Molecule 1		Molecule 2	
Distances				*Angles*			
Co(1)—Co(1′)	234.77(5)	Co(2)—Co(2′)	234,8(6)	N(1)—Co(1)—N(1′)	97(1)	N(2)—Co(2)—N(2′)	96(2)
Co(1)—N(1)	177(2)	Co(2)—N(2)	175(4)	Co(1)—N(1)—Co(1′)	83(1)	Co(2)—N(2)—Co(2′)	84(1)
Co(1)—N(1′)	177(2)	Co(2)—N(2′)	176(3)	Co(1)—N(1)—O(1)	140(1)	Co(2)—N(2)—O(2)	139(2)
N(1)—O(1)	118(3)	N(2)—O(2)	117(6)	Co(1)—N(1′)—O(1′)	137(2)	Co(2)—N(2′)—O(2′)	137(3)
Co(1)—C(av)	208(3) ± 3	Co(2)—C(av)	211(3) ± 1				
C—C(av)	142(5) ± 7	C—C(av)	145(4) ± 6				
B—F(av) 128(5) ± 6				*F*—B—F(av) 109(3) ± 10			

perature parameters of the F atoms are large and a relatively high residual electron density (0.8—1 $e/10^6$ pm^3) is situated about 120—140 pm from the B atom. In one of the two independent $(C_5H_5)_2Co_2(\mu\text{-}NO)_2^+$ units, the temperature parameters of N and O are twice as large as those of the other unit; the orientations of the thermal elipsoids indicate a fairly high degree of librational freedom of both NO ligands around the Co—Co axis.

In all other respects, the two independent $(C_5H_5)_2Co_2(\mu\text{-}NO)_2^+$ units are identical within limits of standard deviations. The Co, N and O atoms of the $Co(\mu\text{-}NO)_2Co$ core are all coplanar within standard deviations. The Co—Co, Co—N and N—O bond distances (Table 1) are quite similar to, albeit marginally (2—6 pm) shorter than those reported for the isoelectronic species $(C_5R_5)_2Co_2(\mu\text{-}CO)(\mu\text{-}NO)$ [2] and $(C_5R_5)_2Co_2(\mu\text{-}CO)_2^-$ (R = H, CH_3) [5,6]. Comparison with the neutral binuclear nitrosyl **2**, $(C_5H_5)_2Co_2(\mu\text{-}NO)_2$ [2] reveals that a very slight shortening of the Co—Co bond (235 vs. 237 pm) and a somewhat more pronounced shortening of the Co—N bonds (176 ± 1 vs. 183 pm) is associated with the one-electron oxidation **2** → **1**. As with the other binuclear $(C_5H_5)_2Co_2$ compounds mentioned above, both C_5H_5 rings are parallel to each other and perpendicular to the Co—Co axis.

The close structural relationship between **1** and its neutral analogue **2** suggests a facile mutual interconversion of these two compounds by oxidation-reduction reactions. Previous cyclic voltametry studies [1,2] have indicated reversible oxidation-reduction reactions in this series. We have observed some stoichiometric reactions of the binuclear cation **1** as follows. When a solution of **1** in CH_2Cl_2 is stirred with Zn powder at room temperature, its IR spectrum changes completely to that of the neutral binuclear compound **2** (ν(NO) at 1530 and 1590 cm^{-1}) [3] during 4—5 h. Oxidation of **2** to **1** is brought about when a CH_2Cl_2 solution of **2** is stirred with solid $AgBF_4$. This reaction goes to completion, in about 5 h, using one equivalent of $AgBF_4$ per cyclopentadienylcobalt nitrosyl dimer, in accord with the mono-cationic charge of **1**.



When a solution of **1** in CH_2Cl_2 is stirred with an excess of solid KBr, its IR spectrum after about 8 h indicates conversion to a mixture of $(C_5H_5)Co(NO)Br$

(ν(NO) at 1830 cm^{-1}) [7] and $(C_5H_5)_2Co_2(\mu\text{-}NO)_2$, i.e. a disproportionation of the mixed-valence oxidation state of Co in compound **1**. If carried out with equimolar amounts of tetrabutylammonium bromide in CH_2Cl_2 solution, this disproportionation reaction is instantaneous, even at temperatures around 0°C. Since the neutral nitrosyl dimer **2** is converted in the bromo derivative **3** by treatment with Br_2, a practically quantitative conversion of the cation **1** in the nitrosyl bromo derivative **3** occurs when CH_2Cl_2 solutions of **1** are treated at 0°C with a mixture of 1 equivalent of tetraethylammonium bromide and 1/2 equivalent of bromine. This synthesis of compound **3** demonstrates that a controlled oxidation of the air-stable cation **1** represents a convenient route to mononuclear $(C_5H_5)Co(NO)$ derivatives.

Experimental

Solvents were thoroughly dried and freed from dissolved oxygen. All manipulations were performed under an atmosphere of nitrogen in Schlenk type glassware. $C_5H_5Co(CO)_2$ was prepared according to ref. 8. $NOPF_6$, $NOBF_4$ and $AgBF_4$ were purchased from Fluka AG and used without further purification.

Preparation of $(C_5H_5)_2Co_2(\mu\text{-}NO)_2PF_6$

To a slurry of 212 mg $NOPF_6$ (1.2 mmol) in 10 ml CH_2Cl_2 is added at room temperature a solution of 218 mg $C_5H_5Co(CO)_2$ (1.2 mmol) in 5 ml CH_2Cl_2. The mixture is then heated to 38°C until the IR bands at 2130 and 1900 cm^{-1} have disappeared (1.5—2 h). After removal of solvent in vacuo, the residue is washed with three 5 ml portions of toluene and then dissolved in a small volume of CH_2Cl_2; the solution is filtered, covered with a layer of pentane and kept at —50°C. $(C_5H_5)_2Co_2(\mu\text{-}NO)_2PF_6$ separates as dark red platelets.

Yield: 122 mg (45% of theory). The product was recrystallized from CH_2Cl_2/pentane.

Elemental analysis: Found: C, 26.76; H, 2.18; N, 6.06. $C_{10}H_{10}O_2N_2Co_2PF_6$ calcd.: C, 26.49; H, 2.22; N, 6.18%.

An analogous procedure using $NOBF_4$ instead of $NOPF_6$ leads to $(C_5H_5)_2Co_2(\mu\text{-}NO)_2BF_4$.

Synthesis of $(C_5H_5)Co(NO)Br$ *(3) from* $(C_5H_5)_2Co_2(\mu\text{-}NO)_2$ *(2)*

To a solution of 130 mg $(C_5H_5)_2Co_2(\mu\text{-}NO)_2$ (0.42 mmol) in 20 ml CH_2Cl_2, cooled to —78°C, a CH_2Cl_2 solution of 67.2 mg (0.42 mmol) of Br_2 is added during 1 h. The product, obtained from the dark green solution after removal of solvent at room temperature, is recrystallized twice from CH_2Cl_2/pentane. Its IR spectrum shows a strong ν(NO) absorption at 1830 cm^{-1}.

Elemental analysis: Found: C, 26.34; H, 2.10; N, 5.56. $C_5H_5NOCoBr$ calcd.: C, 25.67; H, 2.15; N, 5.99%.

Conversion of **1** *to* $(C_5H_5)Co(NO)Br$ *(3)*

To a solution of 158 mg (0.4 mmol) of $(C_5H_5)_2Co_2(\mu\text{-}NO)_2PF_6$ in 25 ml CH_2Cl_2, cooled to 0°C, is added during 2 h solution of 84 mg (0.4 mmol) of tetraethylammonium bromide and 32 mg (0.2 mmol) of Br_2 in 10 ml CH_2Cl_2. The green product solution is warmed to room temperature and evaporated to dryness. The residue is extracted with 40 ml of toluene, and the extract is covered with a layer of pentane and cooled to —40°C, whereupon $(C_5H_5)Co(NO)Br$ separates as a dark powder.

Yield: 151 mg (81% of theory).

Acknowledgements

This work was financially supported by Deutsche Forschungsgemeinschaft, by Fonds der Chemischen Industrie and by research funds of the University of Konstanz. We thank Professor Huttner for access to the diffractometer and Mr. Laszlo Zsolnai for helpful advice on the structural work.

References

1 S. Clamp, N.G. Connelly and J.D. Payne, J. Chem. Soc., Chem. Comm., (1981) 897.
2 I. Bernal, J.D. Korp, G.M. Reisner and W.A. Herrmann, J. Organometal. Chem., 139 (1977) 321.
3 H. Brunner, J. Organometal. Chem., 12 (1968) 517.
4 G.M. Sheldrick, Univ. Göttingen, 1981.
5 N.E. Schore, C.S. Ilenda and R.G. Bergman, J. Amer. Chem. Soc., 98 (1976) 256.
6 R.E. Ginsburg, L.M. Cirjak and L.F. Dahl, J. Chem. Soc., Chem. Comm., (1979) 468.
7 H. Brunner and S. Loskot, Z. Naturforsch. B, 28 (1973) 314; S. Loskot, Thesis Universität Regensburg, 1972.
8 T.S. Piper, F.A. Cotton and G. Wilkinson, J. Inorg. Nucl. Chem., 1 (1955) 165.