Side-on Bonded Nitrosobenzene bridging Two Metal Atoms, in a Binuclear Cyclopentadienyl Cobalt Complex: Crystal Structure of $[\{Co(cp)\}_2(\mu\text{-}PhNO)_2]$†

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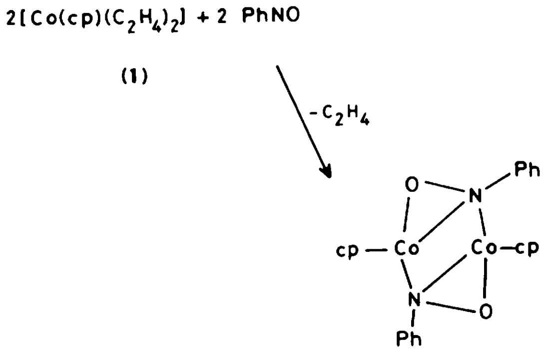
Nitrosobenzene reacts with $[Co(cp)(C_2H_4)_2]$ (cp = η^5-C_5H_5) producing in high yield (*ca.* 82%) a binuclear complex having two cobalt atoms bridged by two nitrogen atoms of nitrosobenzene side-on bonded to each cobalt, $[\{Co(cp)\}_2(\mu\text{-}PhNO)_2]$. The structure of this complex was determined by *X*-ray diffraction analysis: orthorhombic, space group *Pbca*, with $a = 12.937(9)$, $b = 19.509(6)$, $c = 7.714(6)$ Å, $Z = 4$, and $R = 0.031$.

Reaction of nitroso derivatives with metals has been mainly pursued along two lines: (*a*) the use of nitroso compounds in metal-promoted deoxygenation reaction with the generation of 'nitrenes' and 'oxo' fragments;[1] (*b*) for understanding the co-ordination mode of the RNO functionality (R = aryl),[2–4] which can be related to the reductive carbonylation of nitro compounds,[5] and to the organic compounds arising from the nitrosation of metal–olefin[6] and M–C σ-bond[7] functionalities.

In the latter context we have studied the reaction of nitrosobenzene with $[Co(cp)(C_2H_4)_2]$ (cp = η^5-C_5H_5) since this reaction and its products can be related to the nitrosation of the olefins and cobalt–carbon σ bonds studied by Bergman and co-workers[6,7] using complexes derived from the same (cp)Co fragment. The product, which is formed almost quantitatively, has some peculiar structural features.

Results and Discussion

A rather fast reaction is observed upon adding complex (**1**) to a toluene solution of nitrosobenzene [equation (1)]. Complex (**2**) crystallized out as a rather insoluble material in good yield (>80%). The ethylene ligand was displaced unchanged. The parent peak in the mass spectrum confirms the dimeric nature in the gas phase. The structure of (**2**) is shown in the Figure. The *X*-ray data are given in Table 1 and atomic co-ordinates in Table 2, while the most relevant bond distances and angles are listed in Table 3. The dimer is centrosymmetric. As a consequence the two cp planar rings are parallel, and the donor atoms N, O, N′, O′ exactly define a plane. These planes are nearly parallel, their dihedral angle being 10.7(2)°. So the structure consists of three



(1)

(**2**)

Table 1. Experimental data for the *X*-ray diffraction studies on complex (**2**)

	$C_{22}H_{20}Co_2N_2O_2$
Crystal system	Orthorhombic
Space group	*Pbca*
Cell parameters at 295 K *	
a/Å	12.937(9)
b/Å	19.509(6)
c/Å	7.714(6)
α,β,γ/°	90
U/Å^3	1 947(2)
Z	4
D_c/g cm^{-3}	1.577
M	462.3
Crystal dimensions/mm	0.20 × 0.40 × 0.59
μ/cm^{-1}	17.20
Diffractometer	Philips PW 1100
Diffraction geometry	Equatorial
Scan type	ω—2θ
Scan speed/° s^{-1}	0.075
Scan width/°	1.00
Radiation	Graphite-monochromated Mo-K_α (λ = 0.7107 Å)
2θ Range/°	6—50
Reflections measured	*h*, ±*k*, *l*
Total data	3 844
Unique total data	2 072
Observed data [$I > 3\sigma(I)$]	2 055
Unique observed data	1 108
Agreement between equivalent reflections	0.031
No. of variables	167
Overdetermination ratio	6.6
Max. shift/error on last cycle	0.6
$R = \Sigma\|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\|$	0.031

* Unit-cell parameters were obtained by least-squares analysis of the setting angles of 20 carefully centred reflections chosen from diverse regions of reciprocal space.

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† Di-μ-[*N*-phenylhydroxylaminato-*N*($Co^{1,2}$)*O*(Co^1)(2−)]-bis(η-cyclopentadienylcobalt).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.

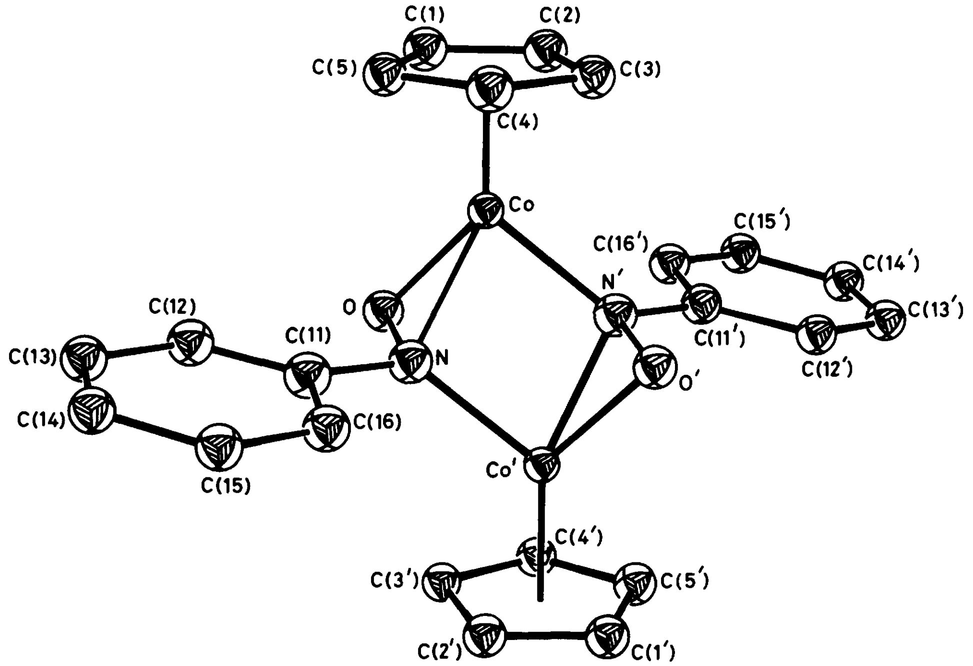

Figure. Structure of complex (**2**)

Table 2. Fractional atomic co-ordinates (× 10^4)

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Co	865.7(3)	446.8(3)	623(6)(8)
O	757(2)	301(2)	−1 808(4)
N	−216(2)	424(2)	−1 127(4)
C(1)	2 232(4)	1 002(3)	920(8)
C(2)	2 155(4)	514(3)	2 217(8)
C(3)	1 203(4)	654(3)	3 167(7)
C(4)	751(5)	1 233(3)	2 412(8)
C(5)	1 355(5)	1 441(3)	1 000(8)
C(11)	−679(3)	1 046(2)	−1 698(5)
C(12)	−228(4)	1 474(2)	−2 930(6)
C(13)	−737(4)	2 071(3)	−3 411(7)
C(14)	−1 688(5)	2 247(3)	−2 699(7)
C(15)	−2 132(4)	1 812(3)	−1 521(7)
C(16)	−1 641(4)	1 216(2)	−1 016(6)

Table 3. Selected bond distances (Å) and angles (°)

Co–O	1.902(4)	Co–Cp(1)	1.683(6)
Co–N	1.945(3)	O–N	1.385(4)
Co–N′	1.935(4)	N–C(11)	1.423(5)
N′–Co–Cp(1)	129.4(2)	Co–N–O	67.3(2)
N–Co–Cp(1)	143.7(2)	O–N–Co′	108.6(2)
N–Co–N′	78.9(1)	Co–N–Co′	101.1(1)
O–Co–Cp(1)	136.5(2)	Co–N–C(11)	119.9(3)
O–Co–N′	91.9(2)	O–N–C(11)	114.4(3)
O–Co–N	42.2(1)	Co′–N–C(11)	128.9(3)
Co–O–N	70.6(2)		

Primed atoms are located at $\bar{x},\bar{y},\bar{z}$.

almost planar entities [including the planar phenyl rings that form a dihedral angle of 9.5(2)° with the cp rings] sandwiching the two cobalt atoms. Cobalt is 1.683(6) Å from the cp ring and 1.333(1) Å from the N,O,N′,O′ mean plane. The nearly planar phenylhydroxylaminato ligand [torsion angle around C–N bond, 3.2(2)°] is η^2-N,O bonded to cobalt and bridges the other cobalt through the nitrogen atom. The Co–O bond distance [1.902(4) Å] is slightly but significantly shorter than the Co–N distances, which are very similar [Co–N 1.945(3) and Co–N′ 1.935(4) Å]. The trend in structural parameters in the cobalt–phenylhydroxylaminato moiety and the geometry of the N_2O_2 framework is quite similar to those reported for $[Co_6Fe_2(\mu\text{-}RNO)_2]$ (R = 3-Cl-2-Me-C_6H_3).[3] The N–O distance [1.385(4) Å] approaches very much a single bond[3] in agreement with the oxidative addition of the –N=O functionality to cobalt(I). Cobalt has a +3 formal oxidation state and a closed-shell configuration. In agreement with the observed deoxygenation there is no other interaction in the dimer [Co ··· Co′ 2.997(2) Å and C ··· O′ 2.715(3) Å]. The structural features of the N,O,N′,O′ unit seem to suggest that the reaction occurs on the dimer of nitrosobenzene[8] rather than on the monomer, though there is no N ··· N interaction in the final complex [N ··· N′ 2.464(5) Å].

This reaction was also applied to aliphatic nitroso derivatives, but the characterization of the polynuclear compounds, which are apparently completely different from (**2**), is far from complete.[9]

Experimental

All the operations were carried out under an atmosphere of purified nitrogen. The complex $[Co(cp)(C_2H_4)_2]$ was prepared as previously reported.[10] Nitrosobenzene was recrystallized from EtOH before use.

Reaction between $[Co(cp)(C_2H_4)_2]$ *and Nitrosobenzene*.—The complex $[Co(cp)(C_2H_4)_2]$ (5.10 g, 28.3 mmol) was added to a toluene solution (150 cm^3) of PhNO (3.03 g, 28.30 mmol). The colour of the solution changed quickly from light blue to deep violet, while C_2H_4 came out of the solution. An abundant crystalline solid formed (*ca.* 82%) (Found: C, 57.45; H, 4.40; N, 6.05. Calc. for $C_{22}H_{20}Co_2N_2O_2$: C, 57.15; H, 4.35; N, 6.05%), m/z = 462, ν(N–O) (Nujol mull) 1 047 cm^{-1}.

X-Ray Crystallography.—The crystal selected for study was mounted in a glass capillary and sealed under nitrogen. Data were collected at room temperature on a single-crystal four-circle diffractometer. Crystal data and details of the parameters associated with data collection are given in Table 1. The reduced cell quoted was obtained with use of TRACER.[11] For intensities and background the 'three-point' technique was used. The structure amplitudes were obtained after the usual Lorentz and polarization corrections[12] and the absolute scale was established by the Wilson method.[13] Data reduction, structure solution, and refinement were carried out on a Gould 32/77 computer using SHELX 76.[12] The crystal quality was tested by ψ scans showing that crystal absorption effects could be neglected. The function minimized during least-squares refinement was $\Sigma w|\Delta F|^2$. Unit weights were applied since these gave better agreement analyses and indices. Anomalous scattering corrections were included in all structure-factor calculations.[14b] Scattering factors for neutral atoms were taken from ref. 14*a* for non-hydrogen atoms and from ref. 15 for H. Among the low-angle reflections no correction for secondary extinction was deemed necessary.

The structure was solved by the heavy-atom method starting from a three-dimensional Patterson map. Refinement was carried out first isotropically, then anisotropically for non-H atoms, by blocked full-matrix least squares. Solution and refinement were based on the observed reflections. All the hydrogen atoms were located in a difference map and isotropically refined in the last stage. Refinement continued until no parameter shifted by more than 0.2 and 0.6 times its standard deviation for non-hydrogen and for hydrogen atoms respectively. The final difference map showed no unusual feature with no significant peak above the general background.

Acknowledgements

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