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X-RAY CRYSTAL STRUCTURE OF THE DIMERIC η^3-CYCLOPROPENYLNICKEL(0) COMPLEX $[(C_3Ph_3)Ni(CO)Br]_2$

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Summary

The compound of empirical formula $C_{22}H_{15}BrNiO$, prepared by Gowling and Kettle in 1964, originally formulated as the dimer $[(C_3Ph_3)Ni(CO)Br]_2$, but subsequently reformulated as the monomer $[(C_3Ph_3)Ni(CO)Br]$ has now been shown by an X-ray study to be the dimer. The two nickel atoms are held together by two bridging bromine ligands, and the metal center is additionally coordinated by a carbonyl group and an η^3-cyclopropenyl ring in a tetrahedral environment. Crystal data are: *a* 11.331(6), *b* 10.790(5), *c* 8.160(4) Å, α 71.15(7), β 76.12(8), γ 78.96(7)°, triclinic, space group $P\bar{1}$, $Z = 1$. The structure was solved by the heavy atom method and refined by full-matrix least-squares techniques to R and R_w of 0.054 and 0.050, respectively, based on 1291 observed reflections.

Introduction

The cyclopropenium cation $C_3R_3^+$, which is the smallest π-aromatic ring, plays an important role in organometallic chemistry, owing to its wide versatility, and in its interaction with organometallic substrates a wide variety of modes of coordination and reactivity are possible [1].

The X-ray structure determinations of cyclopropenylmetal complexes have shown that the C_3Ph_3 ring can present a continuum of geometries, going from an η^3-coordination [2] to an oxidative addition with ring cleavage and formation of a four-membered metallocycle [3]. In particular in the $[M(C_3Ph_3)(PPh_3)_2]^+$ complexes ($M = Ni$, Pd, Pt), in which the metal achieves the 16 valence e^- configuration, the C_3Ph_3 ring is not symmetrically bound to the metal [4]. These cations display fluxional behavior and the ring-whizzing motion of the ML_2 fragment over the cyclopropenium ring has been demonstrated.

Since cyclopropenium complexes, though of general interest are still comparatively rare, and since X-ray analysis appears the only means of determining the bonding mode of the ring, we undertook the X-ray structure of the first reported

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cyclopropenium complex, prepared by Gowling and Kettle in 1964 [5]. This complex was originally formulated as the dimer, $[(C_3Ph_3)Ni(CO)Br]_2$, but subsequently reformulated as the monomer, $[(C_3Ph_3)Ni(CO)Br]$, by analogy with the corresponding tri-t-butylcyclopropenyl derivative, on the basis of solution molecular weight determinations [6].

Now we have succeeded in obtaining crystals suitable for X-ray analysis by a simple variation of the original method.

Results and discussion

The molecular structure consists of centrosymmetric dimeric complex molecules $[(C_3Ph_3)NiCOBr]_2$, shown in Fig. 1. Selected bond distances and angles are listed in Table 1.

The two metal centers are held together by two bridging bromine atoms. If the cyclopropenyl ring is considered to occupy one coordination site, the nickel atom displays a distorted tetrahedral geometry, involving coordination by two bromine atoms, one carbonyl group and one cyclopropenyl ring, with angles ranging from 96.9(1)–122.0(4)°. Since the cyclopropenyl cation donates two electrons the nickel(0) atom achieves an $18e^-$ configuration.

The triphenylcyclopropenyl ring is symmetrically bound to the metal, with Ni–C bond distances (1.95(1)–2.00(1) Å) which appear to be chemically equivalent. The distance of the nickel atom from the centroid of the ring is 1.80(1) Å. These values are comparable with the corresponding values for other η^3-cyclopropenylnickel complexes, such as $(C_3Ph_3)NiCl(Py)_2$ [2b] (Ni–C, 1.896–1.968 Å, Ni–R 1.76 Å), $(\pi\text{-}C_5H_5)Ni(\pi\text{-}C_3Ph_3)$ [2a] (Ni–C, 1.953–1.968 Å, Ni–R 1.78 Å).

Within the cyclopropenyl ring the carbon–carbon distances have an average value

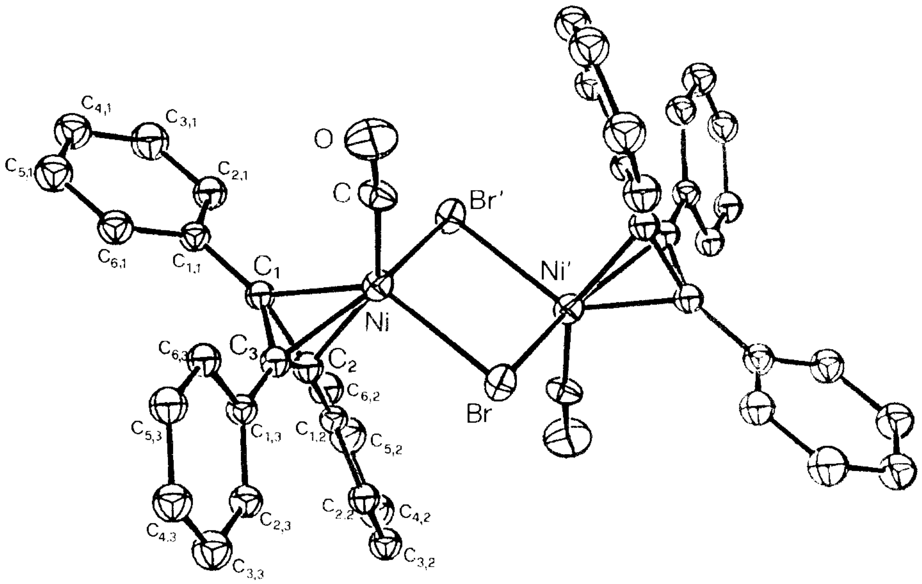

Fig. 1. Perspective view of $[(C_3Ph_3)Ni(CO)Br]_2$. ORTEP drawing with 30% probability ellipsoids.

TABLE 1

SELECTED BOND DISTANCES (Å) AND ANGLES (DEG)

Ni-Br	2.482(2)	C-O	1.105(13)
Ni-Br'	2.482(2)	C(1)-C(2)	1.422(14)
Ni-C	1.861(14)	C(1)-C(3)	1.399(14)
Ni-C(1)	1.948(11)	C(2)-C(3)	1.406(15)
Ni-C(2)	2.001(12)	C(1)-C(1,1)	1.467(13)
Ni-C(3)	1.987(12)	C(2)-C(1,2)	1.456(14)
Ni-R [a]	1.804(11)	C(3)-C(1,3)	1.467(13)
Ni $\cdots$ Ni'	3.293(3)		
Br-Ni-Br'	96.9(1)	C(2)-C(1)-C(3)	59.8(8)
Br-Ni-C	105.1(4)	C(2)-C(1)-C(1,1)	142.8(10)
Br-Ni-R	113.4(4)	C(3)-C(1)-C(1,1)	142.8(10)
Br'-Ni-C	101.0(4)	C(1)-C(2)-C(3)	59.3(8)
Br'-Ni-R	114.9(4)	C(1)-C(2)-C(1,2)	147.2(10)
C-Ni-R	122.0(4)	C(3)-C(2)-C(1,2)	148.0(11)
Ni-C-O	175.1(14)	C(1)-C(3)-C(2)	60.9(10)
C(1)-Ni-C(2)	42.2(4)	C(1)-C(3)-C(1,3)	145.2(10)
C(1)-Ni-C(3)	41.6(4)	C(2)-C(3)-C(1,3)	147.0(11)
C(2)-Ni-C(3)	41.3(4)		
Tilt angles of phenyl groups (°) [b]			
(C(1,1)-C(6,1))	23.3	(C(1,3)-C(6,3))	15.6
(C(1,2)-C(6,2))	13.8		
Twist angles of phenyl groups (°) [b]			
(C(1,1)-C(6,1))	24.6	(C(1,3)-C(6,3))	20.9
(C(1,2)-C(6,2))	1.6		

[a] R is the point at the center of the cyclopropenyl ring. [b] Tilt and twist angles are defined as in ref. 2a.

of 1.409(7) * (within $\pm 1\sigma$), which is somewhat larger than that in the free cyclopropenium ligand (1.377 Å) [7]. This lengthening was expected, and is characteristic of metal π-complexes of aromatic ligands [8]. The average value of the exocyclic C-C bond distances, 1.463(5) is only slightly shorter than that expected for a $C(sp^2)$-$C(sp^2)$ single bond, but is consistent with the values usually found in this type of compound, a contraction generally being observed as the exocyclic angles deviate from 120° [2]. In the present case the exocyclic angles range from 142.8(10) to 148.0(11)°.

The three phenyl rings are tilted out of the plane of the cyclopropenyl ring away from the nickel, the tilt angles being 23.3, 13.8, 15.6°, and are twisted around their axes by 24.6, 1.6, 20.9°, respectively, so that a propeller arrangement results. The Ni-Br bond lengths both are 2.482(2) Å, this value being comparable with those commonly found in bromine-bridged nickel complexes [9].

Experimental

Preparation. A tetrahydrofuran solution of $Ni(CO)_4$ prepared by bubbling carbon monoxide through a solution of $Ni(COD)_2$ (2 mmol) in 20 ml of THF, was

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* The estimated error on the mean was calculated according to $[\Sigma_n(d_n - d)^2/n(n-1)]^{1/2}$.

added at room temperature to a solution of C_3Ph_3Br (2 mmol) in 20 ml of methanol. A slow stream of nitrogen was passed through the resulting solution, at 40°C, and brick-red crystals rapidly formed. The product analysed as $C_{22}H_{15}BrNiO$, and the IR spectrum in the CO stretching region was identical to that reported by Gowling and Kettle.

Crystal data for $[(C_3Ph_3)NiBrCO]_2$. $C_{44}H_{30}Br_2Ni_2O_2$, mol. wt. 868.0, triclinic, space group $P\bar{1}$, a 11.331(6), b 10.790(5), c 8.160(4) Å, α 71.15(7), β 76.12(8), γ 78.96(7)°, $U = 909.5$ Å, $Z = 1$, D_c 1.584 g cm^{-3}, μ(Mo-K_α) 32.5 cm^{-1}.

Collection and reduction of X-ray data. A brick-red prism-shaped crystal of approximate dimensions 0.18 × 0.15 × 0.025 mm, coated in paraffin to prevent access of air was used for data collection. Diffraction data were collected on a Philips PW 1100 automatic diffractometer using graphite-monochromated Mo-K_α radiation. Unit cell dimensions were determined from a least-squares refinement of the angular settings of 20 carefully centered reflections. Intensity data within $2\theta \leqslant 50°$ were collected at the scan speed of 0.05°/s by using the ω-2θ scan technique, with a scan range calculated according to the expression $A + B \tan \theta$, where $A = 0.7°$ and $B = 0.3$. Stationary background measurements were taken before and after each scan for a time equal to half the scan time. Three intensity monitors were checked every 2 hours and were observed to fluctuate randomly within 2% over the entire data collection. After correction for background the

TABLE 2

POSITIONAL PARAMETERS ($\times 10^4$)

ATOM	x	y	z
Br	698(1)	604(1)	2626(2)
Ni	−818(2)	1451(2)	4888(2)
O	427(11)	3194(11)	5899(15)
C	11(13)	2509(13)	5514(17)
C(1)	−2541(10)	2168(11)	5270(15)
C(2)	−2360(11)	1292(11)	4227(15)
C(3)	−2038(11)	2580(11)	3469(15)
C(1,1)	−3406(7)	2605(6)	6686(11)
C(2,1)	−3751(7)	1684(6)	8311(11)
C(3,1)	−4602(7)	2082(6)	9648(11)
C(4,1)	−5110(7)	3401(6)	9361(11)
C(5,1)	−4765(7)	4322(6)	7737(11)
C(6,1)	−3913(7)	3924(6)	6399(11)
C(1,2)	−2737(7)	155(7)	3989(8)
C(2,2)	−2435(7)	−86(7)	2349(8)
C(3,2)	−2823(7)	−1167(7)	2139(8)
C(4,2)	−3513(7)	−2008(7)	3569(8)
C(5,2)	−3816(7)	−1767(7)	5208(8)
C(6,2)	−3428(7)	−685(7)	5418(8)
C(1,3)	−1889(7)	3716(6)	1884(11)
C(2,3)	−1981(7)	3644(6)	244(11)
C(3,3)	−1819(7)	4739(6)	−1238(11)
C(4,3)	−1564(7)	5906(6)	−1080(11)
C(5,3)	−1472(7)	5977(6)	561(11)
C(6,3)	−1634(7)	4882(6)	2043(11)

intensities were assigned standard deviations calculated as described elsewhere [10], a value of 0.03 being used for the instability factor p. Of 3214 total reflections, 1291 having $I \geqslant 3\sigma(I)$ were considered observed. Intensity data were corrected for Lorentz-polarization effects, but not for absorption.

Solution and refinement of the structure. All the calculations were carried out using the SHELX76 crystallographic system of programs [11] on a SEL 32/77 computer in this Institute. The atomic scattering factors for non-hydrogen atoms were taken from ref. 12, while those for hydrogen atoms were taken from ref. 13. Anomalous dispersion terms, both real and imaginary, were introduced into F_c for all the non-hydrogen atoms [14]. The function minimized during refinement was $\Sigma w(|F_0| - |F_c|)^2$, where $w = 1/\sigma^2(F_0)$. A three-dimensional Patterson function yielded the positions of bromine and nickel atoms. All the non-hydrogen atoms were located from successive Fourier maps. Full-matrix least-squares cycles with isotropic thermal motion on all the non-hydrogen atoms were followed by cycles where anisotropic thermal vibration was assigned to bromine, nickel, and the carbonyl groups. During the refinement the phenyl rings were treated as rigid bodies of D_{6h} symmetry. Hydrogen atoms were introduced in their calculated positions but were not refined. The refinement converged to R and R_w factors of 0.054 and 0.050, respectively. Final parameters are reported in Tables 2 and 3. Tables of thermal parameters and structure factors may be obtained from the authors.

Acknowledgements

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