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Preliminary communication

THE CRYSTAL AND MOLECULAR STRUCTURE OF THE TRIPHENYLBORON ADDUCT OF DICARBONYL-π-CYCLOPENTADIENYLIRON CYANIDE

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Summary

The complex $[(\pi\text{-}C_5H_5)Fe(CO)_2CNB(C_6H_5)_3]$ contains a Fe—C—N—B bonding arrangement.

The preparation of the title compound and of the ruthenium analogue was recently described [1]. On the basis of chemical and infrared evidence, the ruthenium compound was assigned the structure $[(\pi\text{-}C_5H_5)Ru(CO)_2NCB(C_6H_5)_3]$. The structure of the related triphenylphosphine derivative was considered to be $[(\pi\text{-}C_5H_5)Ru\{P(C_6H_5)_3\}_2CNB(C_6H_5)_3]$. On heating, the ruthenium carbonyl compound readily decomposed to yield $[(\pi\text{-}C_5H_5)Ru(CO)_2CN]$, but the iron compound did not, and it was therefore concluded that the iron was most probably N-bonded to the triphenyl boron. A study [2] of the CO and CN stretching frequencies in the infrared for compounds $[(\pi\text{-}C_5H_5)Fe(CO)_2(CNBX_3)]$, (X = H, Cl, Br, CH_3), assumed that the bonding was Fe—C—N—B, while the compound $[\{P(C_6H_5)_3\}_2Cu(NCBH_3)]_2$ has been shown [3] to have the arrangement Cu—N—C—B. Because of the uncertainty about the true structure of $[(\pi\text{-}C_5H_5)Fe(CO)_2L]$ (L = $B(C_6H_5)_3CN$), a crystal structure determination was undertaken.

Suitable crystals, $FeC_{26}H_{20}O_2NB$, obtained from dichloromethane, were triclinic, space group $P\bar{1}$, a = 11.58, b = 10.20, c = 10.25 (± 0.01) Å, α = 111.7, β = 79.9, γ = 97.4 (± 0.1)°, Volume 1105 Å^3, D_{meas} = 1.34, $D_{calcd.}$ 1.34 g cm^{-3},

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$Z = 2$. Three-dimensional intensity data were collected on a Philips four-circle diffractometer with graphite monochromated Mo-K_α radiation to θ = 25°. Of 3864 measured intensities, 3520 were judged to be above background. The position of the iron atom was readily deduced from a three-dimensional Patterson map and the remaining atoms were located in the subsequent Fourier maps. The 31-atom structure was refined anisotropically by block diagonal least squares to R = 0.059. A difference Fourier map at this stage clearly showed all hydrogen atom contributions. A projection of the molecule down the c axis is shown (Fig.1).

The structure determination shows quite conclusively that the bonding arrangement is Fe—C—N—B (relative peak heights in the final observed Fourier map are C 100, N 117 units). The pertinent bond lengths and angles are: Fe—C(3) 1.89, C(3)—N 1.14, N—B 1.59 (± 0.01) Å; Fe—C(3)—N 175°, C(3)—N—B 169 (± 1)°.

The 5 atoms of the cyclopentadienyl ring are coplanar within 0.005 Å, with the C—C bond lengths ranging from 1.39 to 1.41 Å. The Fe—C(Cp) distances range from 2.07 to 2.11 Å. The cyanide group and the two carbonyl groups are mutually perpendicular: C(1)—Fe—C(2) 95, C(1)—Fe—C(3) 91, C(2)—Fe—C(3) 92°. Other bond lengths are normal: average Fe—CO 1.78, C≡O 1.12, B—C(Ph) 1.63; (Ph)C—C(Ph) 1.39 Å. The bond lengths and angles in the Fe—C—N—B unit may be compared [4] with those in the cyano- and isocyano-bridged complexes of Co^{III}.

One may now conlcude that not only the iron carbonyl but also the ruthenium carbonyl and triphenylphosphine compounds are metal—C bonded to the triphenylboron, i.e., the general structural formula is $[(\pi\text{-}C_5H_5)M(L)_2\text{-}CNB(C_6H_5)_3]$, where M = Fe, Ru; L = CO, $P(C_6H_5)_3$. These results confirm previous comments [5] that the observed stretching frequency ν(CN) can be completely misleading and should not be used as a criterion for differentiation between cyano and isocyano links in structure determination because the difference between the frequency of the coordinated group and that of the free CN group can be either positive or negative, irrespective of the mode of coordination.

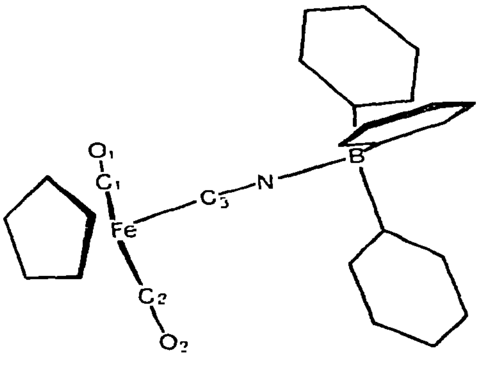

Fig.1. A projection of the molecule $[(\pi\text{-}C_5H_5)Fe(CO)_2CNB(C_6H_5)_3]$ down the z axis.

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