Journal of Organometallic Chemistry, 112 (1976) 325—331

REACTION OF $K[(\pi\text{-}C_5H_5)Fe(CO)(CN)_2]$ WITH BORANES AND $AlCl_3$.

PREPARATION AND INVESTIGATION OF IRON(II) COMPLEXES CONTAINING ISOCYANOBORATE LIGANDS

J. EMRI *, B. GYÖRI, A. BAKOS

Department of Inorganic and Analytical Chemistry, L. Kossuth University, H-4010 Debrecen (Hungary)

and G. CZIRA

Laboratory for Structural Research, Central Chemical Research Institute of the Hungarian Academy of Sciences, H-1088 Budapest, Puskin u. 11—13 (Hungary)

(Received December 29th, 1975)

Summary

Iron(II) complexes containing $CNBX_3^-$ or $CNBX_2NC^-$ ligands were prepared from the reaction of $K[(\pi\text{-}C_5H_5)Fe(CO)(CN)_2]$ with boranes (BX_3; X = F, Cl, Br, H, Ph). Stable, twelve-membered ring compounds containing Fe, C, N and B atoms were formed involving $CNBF_2NC^-$ and $CNBBr_2NC^-$ ligands. The reaction of $K[(\pi\text{-}C_5H_5)Fe(CO)(CN)_2]$ with $AlCl_3$ gave a four-center complex with two Fe and two Al atoms. The compounds were studied by infrared and mass spectroscopic methods.

Introduction

It is well known that the N atoms of CN ligands in the cyano complexes of transition metals can be coordinated with Lewis acids. Best known are those examples in which the N atom of the CN group is coordinated to a transition metal (cyanide bridge complexes) [1,2] or to boranes [3,8], but stable compounds are also known which contain halides of Si, Ge or Sn [9,10] or derivatives of Al and Ga [7] as Lewis acids.

Mainly neutral cyano complexes have been studied in the reaction with boranes, and simple Lewis acid addition ($CN^- \rightarrow CNBX_3^-$) took place in each case [3—8]. The same type of reaction occurred with some anionic transition metal cyanide complexes, such as $K_4[Fe(CN)_6]$ with BF_3, although in this case complexes containing isocyanoborane ($CNBX_2$) or diisocyanoborate ($CNBX_2NC^-$) ligands may also have been formed.

We have studied the reaction of some boranes and $AlCl_3$ with $K[(\pi\text{-}C_5H_5)Fe(CO)(CN)_2]$ [11] where the formation of $CNEX_2$, $CNEX_3^-$ and $CNEX_2NC^-$ (E = Al, B) ligands seems likely.

Results and discussion

Various types of reactions take place between boranes and $K[(\pi\text{-}C_5H_5)Fe(CO)(CN)_2]$ (I) depending on the borane and the composition of the solvent used. With $Et_2O \cdot BF_3$ and BBr_3 in the absence of solvent, and with Ph_2BCl (Ph = phenyl) in CH_2Cl_2, the reactions 1—3 take place. I also reacts with $Et_2O \cdot BF_3$ in

$$\text{I} + 2\,Et_2O \cdot BF_3 \xrightarrow{Et_2O \cdot BF_3} \underset{\text{(II)}}{(\pi\text{-}C_5H_5)Fe(CO)(CN)_2(BF_2)} + KBF_4 + 2\,Et_2O \qquad (1)$$

$$\text{I} + BBr_3 \xrightarrow{BBr_3} \underset{\text{(III)}}{(\pi\text{-}C_5H_5)Fe(CO)(CN)_2(BBr_2)} + KBr \qquad (2)$$

$$\text{I} + Ph_2BCl \xrightarrow{CH_2Cl_2} \underset{\text{(IV)}}{(\pi\text{-}C_5H_5)Fe(CO)(CN)_2(BPh_2)} + KCl \qquad (3)$$

ether at a 1 : 2 molar ratio by elimination of KBF_4, but the compound V obtained is markedly different from II in its chemical and physical properties. Compound V could not be separated from KBF_4. A different reaction takes place in methanol at a 1 : 1.5 = I : $Et_2O \cdot BF_3$ molar ratio (eq. 4).

$$2\,\text{I} + 3\,Et_2O \cdot BF_3 + 2\,MeOH \rightarrow 2\,H[(\pi\text{-}C_5H_5)Fe(CO)(CN)_2] + 2\,KBF_4 + BF(OMe)_2 + 3\,Et_2O \qquad (4)$$

Compound I does not react with BCl_3 in the absence of solvent at the boiling point of BCl_3, but it does react with $MeCN \cdot BCl_3$ in methylcyanide at a 1 : 1 molar ratio. Several compounds are formed in this reaction but could not be isolated in a pure form, however, the analyses and IR spectra of the various fractions suggest that a compound similar to II—IV in composition and structure (vide infra) may have been formed in a substantial amount.

Simple addition of I to triphenylborane takes place in ether, and the crystalline acetone adduct $K[(\pi\text{-}C_5H_5)Fe(CO)(CN)_2(BPh_3)_2] \cdot 2(CH_3)_2CO$ (VI), was obtained pure. I reacts with $THF \cdot BH_3$ at a 1 : 2 molar ratio in THF, and only small amounts of KBH_4 are formed. The product VII could only be isolated as an impure resinous material. In an Et_2O—THF mixture the reaction takes place at a molar ratio greater than 1 : 2 with concomitant partial hydroboration of the C_5H_5 ring.

Compound I does not react with the moderately strong Lewis acid tripyrrolylborane or with the weak Lewis acid triphenoxyborane in ether or THF.

$AlCl_3$ reacts with I in ether according to eq. 5 but the product hydrolyses very

$$\text{I} + 2\,AlCl_3 + 1/2\,Et_2O \xrightarrow{Et_2O} (\pi\text{-}C_5H_5)Fe(CO)(CN)_2(AlCl_2) \cdot 1/2\,Et_2O + KAlCl_4 \qquad (5)$$

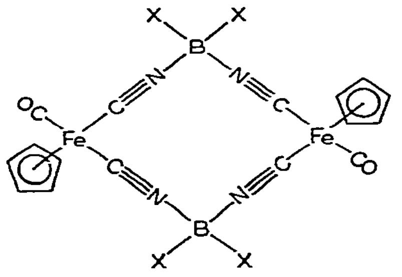
easily, in contrast to the analogous boron compounds II—IV.

Structures

Previous studies demonstrated unequivocally that coordination of the cyanide group to Lewis acids in the transition metal cyano carbonyl complexes is accompanied by a shift to higher frequency of 30—130 cm^{-1} and 20—30 cm^{-1} for $\nu(C\equiv N)$ and $\nu(C\equiv O)$ absorptions, respectively [3—7,9]. The literature data refer to cases where the charge on the complex did not change during the reaction. It is clear however, that similar changes are to be expected in the positions of the $\nu(C\equiv N)$ and $\nu(C\equiv O)$ absorptions even when the charge on the complex changes (from —1 to 0) upon coordination, since a change in the charge alone only slightly influences $\nu(C\equiv N)$ [11,12] and $\nu(C\equiv O)$ [11].

The considerable increase in the $\nu(C\equiv N)$ frequencies in compounds II—VIII (Table 1) show that the Lewis acids are coordinated to the N atom of the CN groups. The possibility of the formation of CO—Lewis acid bonds (such a bond formation is mainly to be expected in the case of VIII) must be ruled out since this would considerably decrease the frequency of vibration of the CO bond [13]. The IR spectra suggest that $-C\equiv N-BX_3$ ligands are present in VI and probably also in VII; thus, the compounds have the structure $K[(\pi\text{-}C_5H_5)Fe(CO)(CNBX_3)_2]$, where X = Ph or H.

In compounds II—IV there is only one BX_2 group for two CN ligands. The $\nu(C\equiv N)$ frequencies are only compatible with a bridged CN group and so the complexes must contain the diisocyanodifluoro-, diisocyanodibromo- and diisocyanodiphenylborate ligands, respectively, which were hitherto unknown. The possibility that these ligands are coordinated to the same Fe atom through both of their C atoms can be ruled out because the M—C—N—B chain would be linear [14,15]. Thus the experimental findings can only be explained by assuming the dimeric structure:



(II) X=F; (III) X=Br; (IV) X=Ph

The dimeric structure was confirmed by molecular weight determination in camphor (Mol. wt. = 703) in the case of IV and by mass spectrometry for II and III. Compound II gives a considerably abundant molecular ion (Table 2) corresponding to the formula $C_{16}H_{10}B_2F_4Fe_2N_4O_2$, on the basis of isotope distribution and precise mass determination (M = 499.9618 for the most intense isotope peak). There is no ion in the mass spectrum assignable to the monomer, but several interesting two-center ions of considerable intensity can be found. No molecular ion can be observed in the mass spectrum of III, but peaks corresponding to $M - CO^+$, $M - 2\,CO^+$ and $M - Br^+$ can be assigned, and the isotope distribution is in agreement with the dimeric structure.

TABLE 1

CO AND CN VIBRATIONAL FREQUENCIES IN COMPOUNDS I—VIII (cm^{-1})

Compound	$\nu(C{\equiv}N)$	$\nu(C{\equiv}O)$
$K[(\pi\text{-}C_5H_5)Fe(CO)(CN)_2]$ (I) (KBr, Nujol)	2080, 2095	1950, 1970
(acetone)	2095	1955
$(\pi\text{-}C_5H_5)Fe(CO)(CN)_2(BF_2)$ (II) (KBr)	2175	2010, 2035
$(\pi\text{-}C_5H_5)Fe(CO)(CN)_2(BBr_2)$ (III) (KBr)	2165	2020
$(\pi\text{-}C_5H_5)Fe(CO)(CN)_2(BPh_2)$ (IV) (KBr)	2175	2000
? (V) (KBr)	2140(vbr)	1995(br)
$K[(\pi\text{-}C_5H_5)Fe(CO)(CN)_2(BPh_3)_2] \cdot 2A$ (VI) [a] (KBr)	2160, 2180	1970
$K[(\pi\text{-}C_5H_5)Fe(CO)(CN)_2(BH_3)_2]$(?) (VII) (Nujol)	2165	1980
$(\pi\text{-}C_5H_5)Fe(CO)(CN)_2(AlCl_2) \cdot 1/2B$ (VIII) [b] (acetone)	2145, 2160	1990

[a] A = $(CH_3)_2CO$. [b] B = $(C_2H_5)_2O$.

It is noteworthy that the increase in $\nu(C{\equiv}O)$ frequencies for II and III is considerably greater, with respect to I, than that accompanying the formation of $CNBX_3^-$ or CNR (alkyl- and aryl-isonitrile) ligands [3—8,11]. This probably indicates that the diisonitrileborates in II and III are better π-acceptors than the $CNBX_3^-$ and CNR ligands. The remarkable resistance of II and III towards oxidising agents (O_2, H_2O_2, $KMnO_4$, etc.), as well as mineral acids and bases, can probably be attributed to this effect and to the ring structure. This resistance greatly surpasses that of I and of compounds V—VII. Such a great stability is exceptional even among compounds containing B—N bonds. II is more stable than III in every case.

In the case of V, the broad IR bands probably indicate the formation of a low molecular weight polymer that may contain CN groups not coordinated to B atoms, as is indicated from the position of IR bands. This is supported by the

TABLE 2

MONOISOTOPIC MASS SPECTRUM OF COMPOUND II

Ion	m/e	Relative intensity (70 eV)
M^+	500	9.3
$M - CO^+$	472	3.9
$M - (CO + BF_3)^+$	404	21
$M - (CO + CNBF_2)^+$	397	14
$M - (2\,CO + CNBF_2)^+$	369	11
$M - (CO + 2\,CNBF_2)^+$	322	22
$M - FeCO(CN)_2C_5H_5^+$	299	60
$M - (2\,CO + 2\,CNBF_2)^+$	294	22
$M - (2\,CO + Fe(CN)_2C_5H_5)^+$	271	42
$M - (2\,CO + CNBF_2 + FeC_5H_5F)^+$	229	12
$[Fe_2(C_5H_5)CN]^+$	203	15
$[Fe(C_5H_5)CNBF_2]^+$	196	41
$[Fe(C_5H_5)_2]^+$	186	51
$[Fe(C_5H_5)CN]^+$	147	15
$[Fe(C_5H_5)]^+$	121	100
$(C_5H_5)^+$	65	7.9
$(C_5H_4)^+$	64	10
Fe^+	56	45
$(BF_2)^+$	49	17

mass spectrum of V. The highest ionic species was detected at $m/e = 636$ (mass number corresponing to the most intense isotope peak). This ionic species contains 3 B and 3 Fe atoms based on the isotope distribution. Ions containing 2 Fe and 1 B ($m/e = 400$), 1 B and 1 Fe ($m/e = 134$) atoms and the $(C_5H_5)_2Fe^+$ and $C_5H_5Fe^+$ ions can be detected as well. The stability of the CN—B bonds is much smaller in this compound than in II or III. Compound V is rapidly hydrolyzed by water or ethanol and the anion $[(\pi\text{-}C_5H_5)Fe(CO)(CN)_2]^-$ can be trapped quantitatively as its silver or mercury(II) salt.

The structure and composition of VIII must be analogous to the dimers II—IV as is indicated from the IR spectra. Thus, this compound is a four-center cyanide-bridged complex containing 2 Fe and 2 Al atoms. This structure could not be confirmed by molecular weight determination owing to the instability of the compound.

Experimental

All experiments were performed under purified N_2 using water- and oxygen-free solvents. The $K[(\pi\text{-}C_5H_5)Fe(CO)(CN)_2]$ [11], triphenylborane [16], diphenylchloroborane [17,18], diborane [19] and tripyrrolylborane [20] were prepared by published procedures. IR spectra were recorded on a Unicam model SP200G spectrophotometer. Mass spectra were determined by use of a double-focusing AEI MS-902 mass spectrometer (ionising energy 70 eV, temperature of the ionising chamber 280°C). The exact mass determinations are referenced to perfluorotributyl amine with an accuracy of 3 ppm.

Preparation of $[(\pi\text{-}C_5H_5)Fe(CO)(CN)_2(BF_2)]_2$

$K[(\pi\text{-}C_5H_5)Fe(CO)(CN)_2]$ (2.04 g, 8.5 mmol) was suspended in freshly distilled $Et_2O \cdot BF_3$ (15.0 ml). The temperature of the stirred suspension was raised on an oil bath to 100°C over 20 min, and kept at this temperature for another 20 min. At 30—40°C the suspension was transformed to a clear solution and a pale yellow substance was precipitated at 80—90°C. After cooling to room temperature, ether (10 ml) was added, and the solid filtered off, washed with ether and dried. It was subsequently washed with 0.01 N NaOH at 80°C, then several times with water, and finally with acetone. After drying, 1.57 g (74%) of a pale yellow microcrystalline substance was obtained. (Found: B, 4.26; Fe, 21.90. $C_{16}H_{10}B_2F_4Fe_2N_4O_2$ calcd.: B, 4.33; Fe, 22.36%.)

Preparation of $[(\pi\text{-}C_5H_5)Fe(CO)(CN)_2(BBr_2)]_2$

The suspension of $K[(\pi\text{-}C_5H_5)Fe(CO)(CN)_2]$ (3.50 g, 14.6 mmol) in BBr_3 (25.0 ml, freshly distilled from Hg) was refluxed for 3 h, with stirring. The product was filtered, dried and extracted several times with CH_2Cl_2. The solid residue was washed with 0.01 M NaOH then with water at 60°C, and finally with acetone, before being dried. Yield: 2.84 g (52%). (Found: B, 2.97; Br, 42.51; Fe, 15.26. $C_{16}H_{10}B_2Br_4Fe_2N_4O_2$ calcd.: B, 2.91; Br, 43.00; Fe, 15.03%.)

Preparation of $[(\pi\text{-}C_5H_5)Fe(CO)(CN)_2(BPh_2)]_2$

To a suspension of $K[(\pi\text{-}C_5H_5)Fe(CO)(CN)_2]$ (3.70 g, 15.4 mmol) in CH_2Cl_2 (25 ml) was added a solution of Ph_2BCl (3.2 g, 16.0 mmol) in CH_2Cl_2 (25 ml), with stirring. Stirring was continued for 1.5 h, and, after filtration, the product was separated from KCl by washing with the filtrate. The extract deposited a yellow crystalline substance which was filtered, washed with ether and dried. Yield: 3.40 g (60%). (Found: C, 63.34; H, 4.08; B, 2.92; Fe, 14.92; N, 7.85. $C_{40}H_{30}B_2Fe_2N_4O_2$ calcd.: C, 65.63; H, 4.13; B, 2.95; Fe, 15.26; N, 7.65%.)

Preparation of $K[(\pi\text{-}C_5H_5)Fe(CO)(CNBPh_3)_2] \cdot 2(CH_3)_2CO$

BPh_3 (4.10 g, 8.5 mmol) dissolved in ether (50 ml) was added to a suspension of $K[(\pi\text{-}C_5H_5)Fe(CO)(CN)_2]$ (1.94 g, 8.1 mmol) in ether (20 ml). The mixture was refluxed for 2 h and filtered. The solid was washed a few times with the filtrate before being dried. It was dissolved in acetone (15 ml) and then ether (60 ml) was added. The mixture was filtered and the filtrate evaporated to 15 ml. Ether (60 ml) was added; crystallization began after a few minutes and was complete in 1—2 h. The yellow crystals were filtered, washed with ether and dried. Yield: 5.6 g (85%). (Found: B, 2.57; Fe, 6.62; K, 4.68. $C_{50}H_{47}B_2FeKN_2O_3$ calcd.: B, 2.57; Fe, 6.64; K, 4.65%.)

Preparation of $[(\pi\text{-}C_5H_5)Fe(CO)(CN)_2(AlCl_2)]_2 \cdot Et_2O$

$AlCl_3$ (5.79 g, 43.4 mmol) in ether (40 ml) was added to a suspension of $K[(\pi\text{-}C_5H_5)Fe(CO)(CN)_2]$ (2.37 g, 9.9 mmol) in ether (20 ml). The suspension was refluxed for 1.5 h, filtered, washed with ether and dried. The product was dissolved in acetone (25 ml) at room temperature, the solution filtered and the residue washed with acetone. The combined acetone solutions were added drop by drop to ether (250 ml) with vigorous stirring. The pale yellow precipitate was filtered, washed with ether and dried. Yield: 2.7 g (82%). (Found: Al, 8.12; Cl, 10.63; Fe, 16.50. $C_{20}H_{20}Al_2Cl_4Fe_2N_4O_3$ calcd.: Al, 8.03; Cl, 10.55; Fe, 16.63%.)

Acknowledgments

Our thanks are due to Dr. András Lipták and Dr. Zoltán Dinya for recording and discussing the IR spectra. We also thank József Posta for his aid in the elemental analyses, and Zsombor Nagy for his valuable assistance in the experimental work.

References

1 D.A. Dows, A. Haim and W.K. Wilmarth, J. Inorg. Nucl. Chem., 21 (1961) 33.
2 M.B. Robin, Inorg. Chem., 1 (1962) 337.
3 D.F. Shriver, J. Amer. Chem. Soc., 85 (1963) 1405.
4 D.F. Shriver and J. Posner, J. Amer. Chem. Soc., 88 (1966) 1672.
5 D. Hall and J.H. Slater. J. Chem. Soc., A, (1971) 800.
6 P.J.C. Walker and R.J. Mawby, J. Chem. Soc., A, (1971) 3006.
7 J.S. Kristoff and D.F. Shriver, Inorg. Chem., 12 (1973) 1788.
8 R.J. Haines and A.L. Du Preez, J. Organometal. Chem., 84 (1975) 357.
9 J.J. Rupp and D.F. Shriver, Inorg. Chem., 6 (1967) 755.
10 R.B. King, Inorg. Chem., 6 (1967) 25.
11 C.E. Coffey, J. Inorg. Nucl. Chem., 25 (1963) 179.
12 R.A. Penneman and L.H. Jones, J. Inorg. Nucl. Chem., 20 (1961) 19.
13 D.F. Shriver and Sr.A. Alich, Coord. Chem. Rev., 8 (1972) 15.
14 L. Malatesta and F. Bonati, Isocyanide Complexes of Metals, Wiley, New York, 1969.
15 M. Laing, G. Kruger and A.L. Du Preez, J. Organometal. Chem., 82 (1974) C40.

16 R. Köster and G. Bruno, Ann. Chem., 629 (1960) 89.
17 E.L. Muetterties, J. Amer. Chem. Soc., 82 (1960) 4163.
18 K. Niedenzu, H. Beyer and J.W. Dawson, Inorg. Chem., 1 (1962) 738.
19 H.C. Brown and P.A. Tierney, J. Amer. Chem. Soc., 80 (1958) 1552.
20 B. Győri, J. Emri and P. Szarvas, Acta. Chim. Acad. Sci. Hung., 86 (1975) 243.