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Transition Metals in Homogeneous Catalysis Part II: Dinuclear Iron Butterfly Adducts with BF_3

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ABSTRACT. The reactivity of dinuclear iron complexes with bridging thiophenyl groups and various phosphorous donor ligands towards BF_3 has been investigated.

Complexes containing BF_3 were obtained by reaction of $[\mu SC_6H_5Fe(CO)_2L]_2$ with BF_3. ET_2O or with $Cu(BF_4)_2$. IR and ^{1}HNMR provides strong evidence for a structure involving Fe_2-BF_3, a three-center donor-acceptor bond interaction.

A major concern to the chemist working on homogeneous catalysis is the development of specific organometallic compounds to be used in the efficient production of useful industrial chemicals.

Catalytic reactions are multistep processes involving many organometallic intermediates. The discovery of a new catalyst is not a trivial matter and must proceed *via* the examination of key intermediates. The finding by Ziegler and Natta that alkyl aluminium transition metal halide mixtures are active in the stereospecific polymerization of olefins has stimulated research in the field of donor-acceptor properties of transition metal complexes with Lewis acids.

We previously described the isolation of a new copper coordination complex (Arabi and Sharrock 1983). Continuing our study of new transition metal complexes, we examined the reactivity of carbonyl dinuclear species containing iron in a low oxidation state stabilized by phosphines, and phosphites.

The ability of many transition metal compounds to act as Lewis bases toward boron halides and related compounds is well established, and compounds of the types $(C_5H_5)_2WH_2.BF_3$, (Shriver 1963), $[(C_6H_5)_3P]_2Ir(CO)Cl.BF_3$ (Vaska *et al.* 1968), $[(C_6H_5)_3P]_3Pt.2BCl_3$ (Wallbridge *et al.* 1976) have been reported. Recently,

Manning *et al.* (1982) reported the isolation of $[Fe(\eta-C_5H_5)(CO)(CH_3CN)_2][BF_4]$, a cleavage product resulting from the reaction between $BF_3.OEt_2$ and the dimer $[Fe_2(\eta-C_5H_5)_2(CO)_2(CH_3CN)_2]$. During the course of the study of the basicity of $[\mu-SCH_3Fe(CO)_2L]_2$ complexes (Arabi *et al.* 1977, 1979b, 1980) we have shown that the metal-metal bond is the nucleophilic center toward mercuric chloride, a proton, and sulfur dioxide. Moreover the nucleophilicity of the metal-metal bond toward H^+ and SO_2 is strongly dependent on the basicity of ligand L but is less dependent for mercuric chloride. We now report a study of the action of BF_3 on $[\mu SC_6H_5Fe(CO)_2L]_2$ with L = $P(CH_3)_{3-n}(C_6H_5)_n$, n = 0, 1, 2, 3; $P(OCH_3)_3$. These five cases were chosen to determine whether the basicity of the ligands plays here as prominent a part as it does in protonation, and SO_2 insertion.

Experimental

All reactions were performed under nitrogen. IR spectra were recorded on a Perkin Elmer model C21 and proton NMR spectra on Bruker FT spectrometers. The ligands $P(CH_3)_3$, $P(CH_3)_2C_6H_5$, $PCH_3(C_6H_5)_2$, $P(C_6H_5)_3$, and $P(OCH_3)_3$ were purchased from Strem chemicals. $[Fe(\mu SC_6H_5)(CO)_3]_2$ was prepared by treatment of $Fe_2(CO)_9$ with C_6H_5SH in benzene at room temperature (Haines and De Beer 1970). $[Fe(\mu SC_6H_5)(CO)_2L]_2$ complexes were prepared according to published procedures (Arabi *et al.* 1979a).

Solvents were dried by distillation from calcium hydride and they were freed from oxygen by either a nitrogen purge or by outgassing under vacuum.

Preparation of $Fe_2(\mu SC_6H_5)_2(CO)_4L_2.BF_3$ Complexes

Two procedures were used to prepare BF_3 complexes:

a) An excess of $BF_3.OEt_2$ is added to a solution of $Fe_2(\mu SC_6H_5)_2(CO)_4L_2$ in CH_2Cl_2 [L = $P(CH_3)_3$, $P(CH_3)_2C_6H_5$, $PCH_3(C_6H_5)_2$, $P(OCH_3)_3$], and the solution is stirred at room temperature for 1.5 hr. The solvent is evaporated and recrystallization of the residue from CH_2Cl_2/pentane gives orange crystals (34% yield). The elemental analyses are consistent with the formulation as $Fe_2(\mu SC_6H_5)_2(CO)_4L_2.BF_3$.

b) An excess of $Cu(BF_4)_2$ is added to a solution of $Fe_2(\mu SC_6H_5)_2(CO)_4L_2$ (L = $P(CH_3)_3$, $P(CH_3)_2C_6H_5$, $PCH_3(C_6H_5)_2$, $P(OCH_3)_3$ in acetone and the solution is stirred at room temperature for 1.5 hr. Within 30 min, a brown solid begins to precipitate (probably Cu compound). The reaction mixture is filtered, and the solvent evaporated. Recrystallization from CH_2Cl_2/pentane gives orange crystals (57% yield).

The reactions do not occur when L = $P(C_6H_5)_3$. Attempts were made to obtain the mass spectra of BF_3 complexes on a VG high resolution mass spectrometer, however, only ions due to $Fe_2(\mu SC_6H_5)_2(CO)_4L_2$ were detected.

Results and Discussion

The reaction of BF_3 or BF_4^- with the butterfly iron dimers proceeds well at room temperature in dichloromethane or acetone but failes to yield the desired products in benzene. Viscous oils are usually obtained by evaporation of the reaction solvents, and attempts to purify the products by chromatography were unsuccessful, probably due to dissociation of the complexes on the polar SiO_2 surface. Pure products can be obtained by repeated careful recrystallization in selected solvent mixtures.

Rapid dissociation may also explain the absence of molecular ions for the adduct in the mass spectrum. Manning and coworkers (1982) noted the same phenomenon in analogous complexes, observing only ions due to the parent compounds.

Infrared data are gathered in Table 1. Three infrared active bands are observed in the ν(CO) stretching region when L = $P(CH_3)_3$, $P(CH_3)_2C_6H_5$ or $P(OCH_3)_3$. When L = $PCH_3(C_6H_5)_2$ only two bands are observed for the CO vibrations as shown in Fig. 1. In general, it can be said that the products obtained by reaction with BF_3 have either a higher symmetry than the starting materials or fewer isomers are present in solution due to a more rigid structure. Indeed the parent butterfly complexes, listed in Table 1 for comparison, show up to six absorption bands. This leads us to propose for the BF_3 adducts the structures shown in Fig. 2. The increase in CO stretching frequencies compared with the starting material is about 50 cm^{-1}.

Table 1. Infrared data for $[\mu SC_6H_5Fe(CO)_2L]_2$ and $[\mu SC_6H_5Fe(CO)_2L]_2.BF_3$.

Complex	L	νCOcm^{-1} [a]	νB-F
$[\mu SC_6H_5Fe(CO)_2L]_2$	$P(CH_3)_3$	1990m, 1952s, 1923m 1910w	
	$P(CH_3)_2C_6H_5$	1994vs, 1956vs, 1940m 1926s, 1912w	
	$PCH_3(C_6H_5)_2$	2000s, 1988sh, 1960s 1945m, 1935m, 1920w	
	$P(OCH_3)_3$	2000m, 1970s, 1950s, 1925m.	
$[\mu SC_6H_5Fe(CO)_2L]_2.BF_3$	$P(CH_3)_3$	2048sh, 2022s, 1999s	1045L 945m
	$P(CH_3)_2C_6H_5$	2048s, 2029m, 1995s	1050L
	$PCH_3(C_6H_5)_2$	2040s, 1980s,	1080L
	$P(OCH_3)_3$	2063sh, 2052s, 2014s	1030L

[a] Measured in CH_2Cl_2.

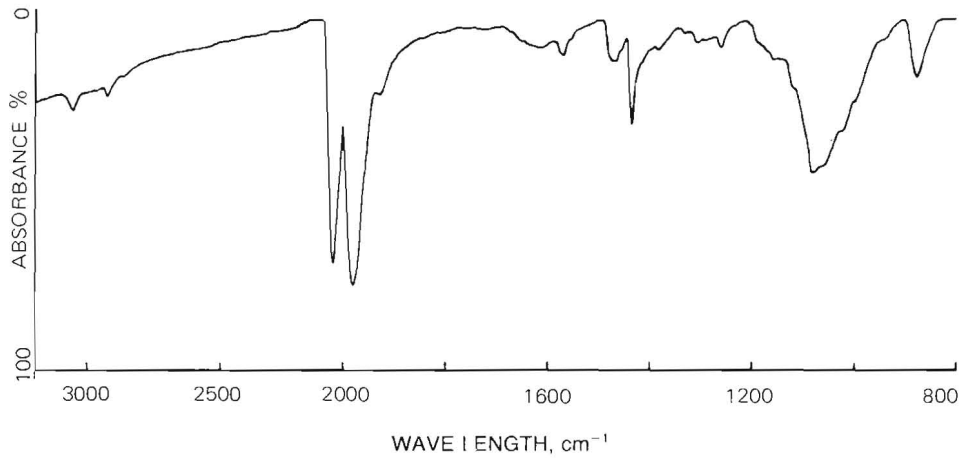

Fig. 1. Infrared absorption spectrum of $Fe_2(\mu SC_6H_5)_2(CO)_4[PCH_3(C_6H_5)_2]_2.BF_3$ in KBr.

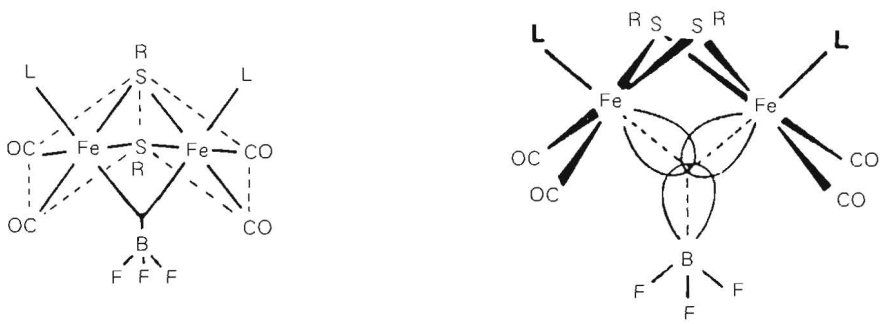

Fig 2. Two different views of the insertion of BF_3 (A), and the orbital overlap scheme (B) in the BF_3 adduct of $Fe_2(\mu SC_6H_5)_2(CO)_4L_2$.

This is consistent with the Lewis acid properties of BF_3 which is withdrawing electron density from the two iron centers. Mononuclear complexes (Vaska *et al.* 1968) of the type $IrClCO(P(C_6H_5)_3)_2$ when reacted with BF_3 show a similar effect but with shifts of about twice the magnitude. Furthermore, the IR spectra show absorptions around 1000-1100 cm^{-1} which are typical of B-F vibrations in coordinated BF_3.

Proton NMR spectra are consistent with the structure formulated in Fig. 2. At room temperature, one doublet (Fig. 3) is observed for the methyl groups of the coordinated phosphines, when L = $P(CH_3)_3$, $PCH_3(C_6H_5)_2$ and $P(OCH_3)_3$. The two doublets observed, when L = $P(CH_3)_2C_6H_5$ can be explained by the structure

shown in Fig. 4, where there is no plane of symmetry through the Fe-P bond. The two phenyl group resonances which can be resolved may be attributed to the two orientations possible for these groups, syn and anti (Arabi 1978). The various chemical shifts and values of the coupling constants are listed in Table 2.

We are examining the phenomenon of stereochemical nonrigidity in these complexes. Preliminary results show that the spectra are temperature-dependent. Further studies are under way by ^{31}P and ^{13}C NMR in addition to high-frequency ^{1}H NMR, and a detailed report will follow.

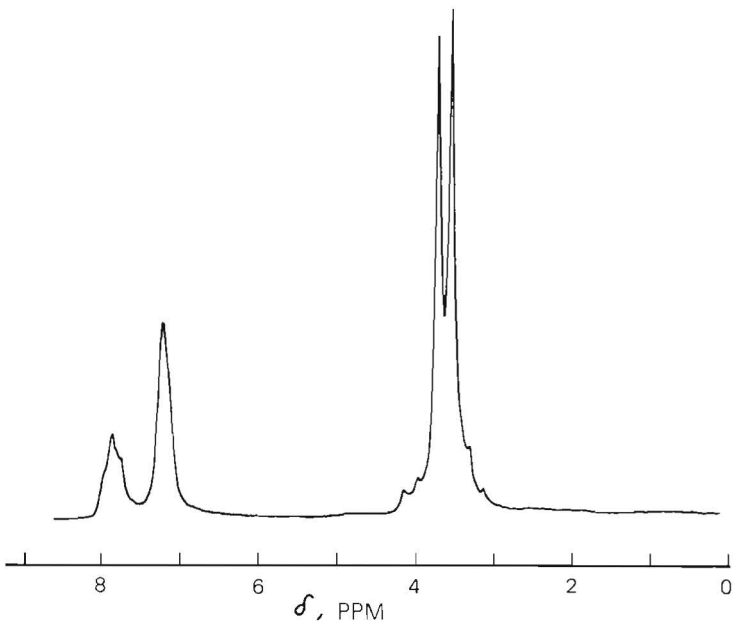

Fig 3. ^{1}H NMR spectrum of $Fe_2(\mu SC_6H_5)_2(CO)_4[P(OCH_3)_3]_2.BF_3$ at room temperature.

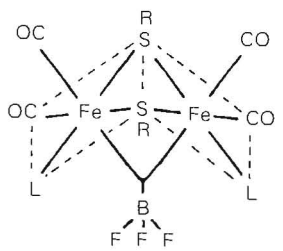

Fig. 4. Structure proposed for the unsymmetrical BF_3 adduct of $Fe_2(\mu SC_6H_5)_2(CO)_4[P(CH_3)_2C_6H_5]_2$.

Table 2. ^{1}HNMR data[a] for $[\mu SC_6H_5Fe(CO)_2L]_2.BF_3$ complexes τ.

L	τ(Ph) (ppm)	$\tau(CH_3)$ (ppm)	JPCH or JPOCH (Hz)
$P(CH_3)_3$	2.0 2.7	8.6[d]	10.8
$P(CH_3)_2C_6H_5$	2.7	8.1[d] 8.4[d]	14 11.3
$PCH_3(C_6H_5)_2$	2.7	8.1[d]	10.7
$P(OCH_3)_3$	2.1 2.7	6.2[d]	10.6

[a] Measured in CD_2Cl_2,
[d] doublet.

In conclusion, we can assert that BF_3 acts as a Lewis acid toward the metal-metal bond in these butterfly complexes. The basicity of the phosphorous ligand does not seem to be a critical factor in this reaction. However, steric interactions may be important in explaining why we could not obtain similar products in the case where L = triphenyl phosphine. The electrons in the two available orbitals shown in Fig. 2 combine with the empty boron orbital in formation of a donor-acceptor complex. The result is a rare example of insertion of BF_3 in a metal-metal bond. Such results may be significant in understanding the catalytic behaviour of dinuclear and cluster complexes of the transition metals.

References

Arabi, S. (1978) *Contribution à l'étude de la structure et de la basicité des complexes mononucléaires* $M(CO)_{6-n}L_n$ [M = Mo,W], *et dinucléaires à liaison* métal-métal $Fe_2(\mu - A)(\mu - A')(CO)_4L_2$[A = A' = SR,$PR_2$; A = SR,A' = PR_2], Thèse de Doctorat d'état, 121-123. Université Paul Sabatier, Toulouse, France

Arabi, S., Mathieu, R., and **Poilblanc, R.** (1977) A study of the basicity of metal-metal bonding in $[\mu SCH_3Fe(CO)_2L]_2$ complexes. II. Interaction with Mercuric chloride, *Inorg. Chimica Acta* **23**: L17-L18.

Arabi, S., Mathieu, R., and **Poilblanc, R.** (1979a) Protonation of the metal-metal bond in $Fe_2(\mu A)(\mu A')(CO)_4L_2$ complexes [A = A' = SC_6H_5, $P(C_6H_5)_2$, $P(CH_3)_2$; A = SC_6H_5, A' = $P(C_6H_5)_2$; L = $P(C_6H_5)_{3-n}(CH_3)_n$]. III. Experimental study of the influence of the A and A' bridges on the basicity of the metal-metal bond, *J. organometal. Chem.* **177**: 199-209.

Arabi, S., Mathieu, R. and **Poilblanc, R.** (1979b) A study of the basicity of the metal-metal bond in $[\mu SCH_3Fe(CO)_2L]_2$ complexes. IV. Interaction with sulfur dioxide and reactivity of the coordinated sulfur dioxide toward Oxygen, *Inorg. Chimica Acta.* **34**: L207-L208.

Arabi, S., Mathieu, R. and **Taylor, N.** (1980) Crystal structure of the sulfur dioxide adduct of Bis[μ(methylthio)]-bis[(trimethyl phosphine) dicarbonyl iron (I)]: A product of insertion of sulfur dioxide into the metal-metal bond, *Inorg. Chem.* **19**: 1740-1742.

Arabi, S. and **Sharrock, P.** (1983) Transition metals in homogeneous catalysis. Part I: Cupric amino acid complexes, *Arab Gulf J. scient. Res.* **1**: 105-112.

Haines, R.J. and **De Beer, J.A.** (1970) Reactions of metal carbonyl derivatives, IV. Bridged sulphido derivatives of Iron Carbonyl, *Organometal. Chem.* **24**: 757-763.

Manning, A.R., Kumar, R., Willis, S. and **Stephens, F.S.** (1982) Reactions of $[Fe_2(\eta - C_5H_5)_2(CO)_2(L)(CNMe)]$ (L = CO or CNMe) with Lewis acids resulting in adduct formation, dimer Scission or both. Structure of $[Fe(\eta - C_5H_5)(CO)(CNMe)_2][BF_4]$, *Inorg. Chimica Acta*, **61**: 141-147.

Shriver, D.F. (1963) Lewis basicity of a transition metal. A boron Trifluoride adduct of bicyclopentadienyltungsten dihydride. *J. Am. chem. Soc.* **85**: 3509-3510.

Vaska, L., Scott, R.N. and **Shriver, D.F.** (1968) Lewis acid Adducts of planar fourcoordinated d^8 complexes. $BF_3-[IrClCO[P(C_6H_5)_3]_2]$ and related systems, *J. Am. chem. Soc.* **90**: 1079-1080.

Wallbridge, M.G.H., Fishwick, M. Noth, H. and **Petz, W.** (1976) Reaction of some boron halide compounds with platinum (O) and platinum (II) Species, *Inorg. Chem.* **15**: 490-492.

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العناصر الانتقالية فى الحفز المتجانس الجزء الثانى: الحديد الفراشى ثنائى البنية المضاف مع BF_3

باتريك شاروك و سمير عرابى

قسم الكيمياء - جامعة شير بروك - شير بروك - كيبك - كندا

دُرست معقدات الحديد ثنائى البنية والمتضمنة جسراً من مجموعة الثيوفينيل وعدة زمر من الفوسفور المعطية للإلكترونات تجاه BF_3. تم الحصول على معقدات تتضمن BF_3 عن طريق التفاعل ما بين $[\mu SC_6H_5Fe(CO)_2]_2$ مع $BF_3.Et_2O$ أو $Cu(BF_4)_2$. يقدم الـ IR والـ ^1H NMR دليلا قويا على وجود بنية تتضمن Fe_2-BF_3، رابطة ناتجه عن تداخل ثلاثة مراكز معطية - آخذة.