Notes

Synthesis and Structure of Fe(TIM)(CNBPh$_3$)$_2$: TIM = 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene. Conversion of BPh$_4^-$ into CNBPh$_3^-$

Patrick I. Amrhein, Alan J. Lough, and
Robert H. Morris*

Department of Chemistry, University of Toronto, 80 St.
George Street, Toronto, Ontario M5S 3H6, Canada

Received February 23, 1996

Introduction

As part of our on-going investigation into the nature of the interactions between dihydrogen and transition metals, we have reported a number of complexes with the general formula [Fe(H)(H$_2$)L$_2$]$^+$ (L = chelating phosphine)[1] and [Fe(H)(H$_2$)L]$^+$ (L = tetradentate phosphine ligand).[2,3] In order to probe the influence of the ancillary ligands we are investigating the nature of complexes of the tetradentate imine donor ligand TIM (TIM = 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,4,8,10-tetraene). The bis(acetonitrile) complex *trans*-[Fe(TIM)(MeCN)$_2$](PF$_6$)$_2$ has been reported.[4] We report the novel formation of isocyanotriphenylborate from tetraphenylborate in a reaction which produces *trans*-Fe(TIM)(CNBPh$_3$)$_2$, **1**, and the crystal structure of this compound.

The isonitrile ligand, CNBPh$_3^-$, has previously been prepared by rearrangement of the nitrile analog at a metal center (Figure 1). Ginderow has reported[5] the preparation of Fe(PMe$_3$)$_2$(CO)$_2$(CH$_3$)(CNBPh$_3$).

Results and Discussion

The reaction of a solution of Fe(TIM)$^{2+}$ in the presence of glacial acetic acid, buffered with an equimolar amount of sodium acetate, with NaCN leads to a color change of the solution from opaque green to a deep blue. Adding sodium tetraphenylborate to this solution precipitates out a deep blue solid, which forms, after recrystallization from benzene, dark purple crystals. It was observed that the deep blue solid is soluble in several solvents like CD$_3$Cl, acetone, or boiling benzene to give purple colors. There is a single resonance for **1** in the ^{11}B-NMR spectrum at −9.8 ppm vs BF$_3$·Et$_2$O. The ^{1}H-NMR spectrum is complex but appears to have the expected resonances.

The X-ray crystal structure determination reveals an octahedral Fe(II) complex, *trans*-Fe(TIM)(CNBPh$_3$)$_2$ **1**, with an equatorial TIM ligand and axial CNBPh$_3$ ligands. The possibility of an NCBPh$_3$ ligand is ruled out by the magnitude of the displacement ellipsoids. The bond distances (see Table 1) between carbon and nitrogen and between nitrogen and boron in the CNBPh$_3$ ligand and between iron and carbon are similar to the distances found in the complex Fe(CH$_3$)(PMe$_3$)$_2$(CO)$_2$(CNBPh$_3$) **2** of Ginderow.[5] The complex appears to have the same structure in CDCl$_3$ solution.

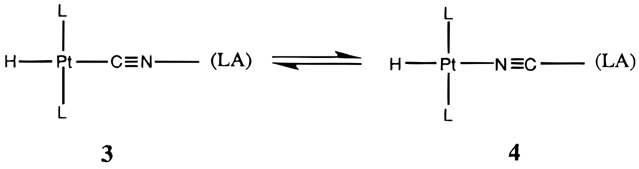

Figure 1. Equilibrium between cyano and isocyano platinum complexes according to Manzer and Anton.[6]

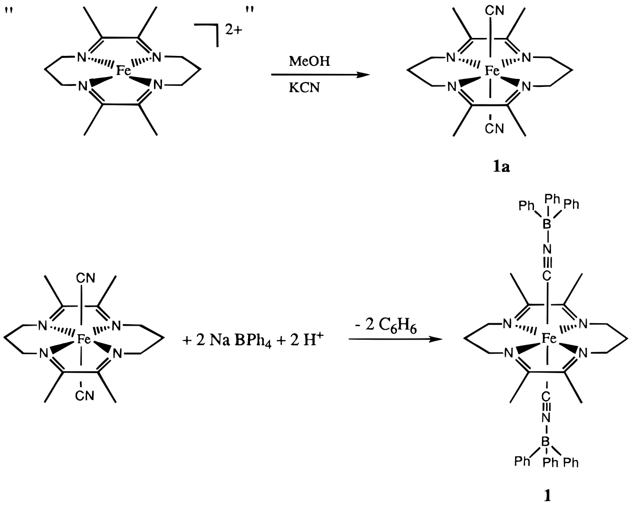

Figure 2. Proposed reaction sequence.

Table 1. Comparison of Bond Distances (Å) in the CNBPh$_3^-$ Ligand of Complex **1** and Fe(CH$_3$)(CO)$_2$(PMe$_3$)$_2$(CNBPh$_3$)[5]

	Fe(TIM)(CNBPh$_3$)$_2$ (**1**)	Fe(CH$_3$)(CO)$_2$(PMe$_3$)$_2$(CNBPh$_3$)[5]
C≡N	1.135(3)	1.146(4)
N−B	1.575(4)	1.592(4)
Fe−C	1.904(3)	1.910(3)

Table 2. Summary of Crystal Data, Details of Intensity Collection and Least-Squares Refinement Parameters

M_r	1152.9	μ(Mo Kα), cm^{-1}	2.93
space group	$C2/c$	F(000)	2448
temp, K	173	range θ collcd, deg	2.6−27.0
a, Å	28.217(5)	no. of reflcns collcd	6903
b, Å	14.434(2)	no. of indep reflcns	6767
c, Å	16.938(3)	R_{int}	0.0549
β, deg	116.008(13)	no. of obsd data [$I > 2\sigma(I)$]	3324
V, Å^3	6200(2)	R_1 [$I > 2\sigma(I)$]^a	0.0547
Z	4	wR$_2$ (all data)	0.1237
D_{calc} g cm^{-3}	1.235		

^{a} Definition of R indices: $R_1 = \Sigma(F_o - F_c)/\Sigma(F_o)$. $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$.

The unexpected abstraction of a phenyl anion from the BPh$_4^-$ anion leads to the conclusion that the reaction takes place as suggested in Figure 2. It is apparent that the biscyano complex **1a** is very electron rich and therefore functions as a strong Lewis base. A reaction between free cyanide and BPh$_4^-$ does not occur because all the cyanide is coordinated.

Manzer and Anton[6] examined the equilibrium (Figure 1) between linkage isomers of the cyanide ligand (LA = Lewis

---

(1) Bautista, M. T.; Cappellani, E. P.; Drouin, S. D.; Morris, R. H.; Schweitzer, C. T.; Sella, A.; Zubkowski, J. *J. Am. Chem. Soc.* **1991**, *113*, 4876−4887.

(2) Bautista, M. T.; Earl, K. A.; Maltby, P. A.; Morris, R. H.; Schweitzer, C. T. *Can. J. Chem.* **1994**, *72*, 547−560.

(3) Jia, G. C.; Drouin, S. D.; Jessop, P. G.; Lough, A. J.; Morris, R. H. *Organometallics* **1993**, *12*, 906−916.

(4) Reichgott, D. W.; Rose, N. J. *J. Am. Chem. Soc.* **1977**, *99*, 1813−1817.

(5) Ginderow, P. D. *Acta Crystallogr.* **1980**, *B36*, 1950−1951.

(6) Manzer, L. E.; Anton, M. F. *Inorg. Chem.* **1977**, *16*, 1229−1231.

S0020-1669(96)00201-7 CCC: $12.00

Table 3. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **4**

	x	*y*	*z*	*U*(eq)[a]
Fe(1)	2500	7500	5000	26(1)
N(1)	2305(1)	8600(2)	4297(2)	39(1)
N(2)	1874(1)	7062(2)	4025(2)	36(1)
N(3)	3221(1)	6938(2)	4178(2)	32(1)
C(1)	1885(1)	8546(2)	3553(2)	51(1)
C(2)	1632(1)	7638(3)	3417(2)	49(1)
C(3)	1684(2)	9287(3)	2899(3)	124(2)
C(4)	1123(1)	7447(3)	2624(2)	82(1)
C(5)	2612(1)	9450(2)	4544(2)	46(1)
C(6)	1668(1)	6134(2)	4020(2)	42(1)
C(7)	2094(1)	5443(2)	4480(2)	49(1)
C(8)	2936(1)	7138(2)	4457(2)	28(1)
B(1)	3667(1)	6682(2)	3893(2)	34(1)
C(11)	3454(1)	6958(2)	2875(2)	40(1)
C(12)	3664(1)	6567(3)	2351(2)	53(1)
C(13)	3507(2)	6832(3)	1497(3)	72(1)
C(14)	3142(2)	7497(4)	1131(3)	75(1)
C(15)	2928(2)	7912(3)	1618(3)	65(1)
C(16)	3077(1)	7637(2)	2475(2)	49(1)
C(21)	3790(1)	5594(2)	4096(2)	34(1)
C(22)	3446(1)	4987(2)	4213(2)	44(1)
C(23)	3557(2)	4062(2)	4386(3)	57(1)
C(24)	4017(1)	3701(2)	4444(2)	56(1)
C(25)	4370(1)	4272(2)	4333(2)	47(1)
C(26)	4255(1)	5202(2)	4164(2)	38(1)
C(31)	4171(1)	7306(2)	4506(2)	38(1)
C(32)	4513(1)	7657(2)	4200(3)	57(1)
C(33)	4945(2)	8188(3)	4726(3)	66(1)
C(34)	5049(1)	8370(3)	5568(3)	62(1)
C(35)	4726(2)	8022(3)	5889(3)	67(1)
C(36)	4295(1)	7494(3)	5369(2)	51(1)
C(1S)	3639(2)	11008(3)	4544(3)	69(1)
C(2S)	3866(2)	10210(4)	4441(4)	85(2)
C(3S)	3646(2)	9778(3)	3647(5)	88(2)
C(4S)	3213(2)	10120(3)	2983(3)	93(2)
C(5S)	2986(2)	10904(3)	3088(3)	71(1)
C(6S)	3200(2)	11351(3)	3863(3)	63(1)
C(7S)	4842(3)	5714(4)	7063(3)	132(2)
C(8S)	4691(2)	4932(5)	6631(3)	88(2)
C(9S)	4846(2)	4149(4)	7055(3)	96(2)
C(10S)	4780(5)	11552(5)	7538(7)	95(5)
C(11S)	4495(3)	10769(7)	7115(5)	76(4)
C(12S)	4754(3)	10003(5)	6994(4)	97(4)
C(13S)	5299(3)	10019(4)	7297(5)	93(3)
C(14S)	5584(3)	10802(6)	7721(5)	88(5)
C(15S)	5324(5)	11569(4)	7841(6)	84(4)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

acid). They reported that the platinum−isocyanide linkage isomer **3** is thermodynamically more stable. Similarly only the iron−isocyanide isomer is observed for complex **1** (Figure 2). Interestingly all the compounds containing a $CN\cdot BAr_3^-$ group that have been published so far were prepared via a sodium cyanotriarylboron salt.[5] Our method involves the convenient reaction of a metal cyano complex with $NaBPh_4$ in an acidic solution.

Conclusions

A new way of synthesizing an iron (II) complex with a $CNBPh_3^-$ ligand is reported. It will be interesting to see if the reaction of cyano complexes with $NaBPh_4$ in the presence of acid is general. This reaction would then omit the separate preparation of a cyanoarylboron compound. A limitation of this method is the sensitivity of many organometallic cyano compounds[7] to acidic conditions.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for **4**[a]

Fe−(1)−C(8)	1.904(3)	Fe(1)−N(1)	1.915(2)
Fe(1)−N(2)	1.920(3)	N(1)−C(1)	1.300(4)
N(1)−C(5)	1.454(4)	N(2)−C(2)	1.266(4)
N(2)−C(6)	1.459(4)	N(3)−C(8)	1.135(3)
N(3)−B(1)	1.575(4)	C(1)−C(2)	1.461(5)
C(1)−C(3)	1.463(5)	C(2)−C(4)	1.501(4)
C(5)−C(7)#1	1.497(4)	C(6)−C(7)	1.492(4)
B(1)−C(11)	1.607(5)	B(1)−C(21)	1.612(5)
B(1)−C(31)	1.618(5)		

C(8)#1−Fe(1)−C(8)	180.0	C(8)#1−Fe(1)−N(1)	90.12(11)
C(8)−Fe(1)−N(1)	89.88(11)	N(1)−Fe(1)−N(1)#1	180.0
C(8)#1−Fe(1)−N(2)	87.71(11)	C(8)−Fe(1)−N(2)	92.29(11)
N(1)−Fe(1)−N(2)	80.40(11)	N(1)#1−Fe(1)−N(2)	99.60(11)
N(2)−Fe(1)−N(2)#1	180.0	C(1)−N(1)−C(5)	120.3(3)
C(1)−N(1)−Fe(1)	116.4(2)	C(5)−N(1)−Fe(1)	123.3(2)
C(2)−N(2)−C(6)	121.8(3)	C(2)−N(2)−Fe(1)	116.6(2)
C(6)−N(2)−Fe(1)	121.5(2)	C(8)−N(3)−B(1)	173.8(3)
N(1)−C(1)−C(2)	112.4(3)	N(1)−C(1)−C(3)	125.2(3)
C(2)−C(1)−C(3)	122.4(3)	N(2)−C(2)−C(1)	114.1(3)
N(2)−C(2)−C(4)	124.8(3)	C(1)−C(2)−C(4)	121.1(3)
N(1)−C(5)−C(7)#1	112.1(3)	N(2)−C(6)−C(7)	112.5(3)
C(6)−C(7)−C(5)#1	116.0(3)	N(3)−C(8)−Fe(1)	175.9(3)
N(3)−B(1)−C(11)	107.3(3)	N(3)−B(1)−C(21)	106.8(2)
C(11)−B(1)−C(21)	114.5(3)	N(3)−B(1)−C(31)	105.6(2)
C(11)−B(1)−C(31)	111.1(3)	C(21)−B(1)−C(31)	111.0(3)
C(12)−C(11)−B(1)	121.6(3)	C(16)−C(11)−B(1)	123.1(3)
C(22)−C(21)−B(1)	123.3(3)	C(26)−C(21)−B(1)	121.5(3)
C(36)−C(31)−B(1)	122.3(3)	C(32)−C(31)−B(1)	121.9(3)

[a] Symmetry transformations used to generate equivalent atoms: #1, $-x + {}^1/_2, -y + {}^3/_2, -z + 1$; #2, $-x + 1, y, -z + {}^3/_2$.

Experimental Section

The reaction was carried out under an Ar atmosphere but the product was isolated in air. The reagents used as starting materials were obtained commercially and used without further purification. The ^1H- and ^{11}B-NMR spectra were obtained on a Varian Gemini-300 at 300 and 96.3 MHz, respectively. The boron spectrum was referenced to $BF_3\cdot Et_2O$. The ^1H spectrum was obtained in $CDCl_3$ and referenced to residual protons in the solvent.

A 0.002 molar $Fe(TIM)^{2+}$ solution was prepared according to the method of Reichgott and Rose.[4,8] Argon was bubbled through methanol (20 mL) for 15 min. Iron powder (0.15 g, 0.0027 mol) and anhydrous $FeCl_3$ (0.431g, 0.0027 mol) were added to give a brown suspension. The mixture was heated to reflux for 2 min, and after allowing the solution to cool down to 50 °C, $SnCl_2$ (0.04 g, 0.21 mmol) was added. After the addition the mixture was heated to reflux for another 2 min and then allowed to cool down to room temperature.

A second solution was prepared by bubbling Ar gas for 15 min through methanol (10 mL), followed by cooling to −5 °C. Diaminopropane (0.33 mL, 0.004 mol) and glacial acetic acid (0.85 mL, 0.015 mol) were added. 2,3-Butanedione (0.35 mL, 0.004 mol) was added dropwise to the stirring solution, leading to a color change to an orange red. The filtered Fe^{2+} solution (greenish yellow) prepared above was then added to this solution via a dropping funnel. There was a color change first to opaque blue and then to opaque green. This solution was stirred overnight. An excess of NaCN (1.5 equiv, 3 mmol, 0.15 g) in 10 mL of methanol was added to the green opaque solution, leading to an immediate color change to an opaque deep blue. This solution was stirred for 1 h before adding $NaBPh_4$ (1.03 g, 3 mmol) as a solid. The argon atmosphere was now no longer maintained, and the blue precipitate was collected via suction filtration. The precipitate was washed with small amounts of ether. The solid was recrystallized from boiling benzene to give dark red crystals (704 mg, 40% yield).

^1H-NMR (300 MHz, $CDCl_3$): 7.65−7.34 (m, 16 H, Ph-H), 7.21−7.04 (m, 14 H, Ph−H), 2.38−2.23 (m, 8H, α-CH_2), 1.55 (s, 12 H, CH_3), 1.35−1.15 ppm (m, 4 H, β-CH_2). ^{11}B-NMR (96.3 MHz, CH_2Cl_2 with C_6D_6 insert): −9.8 ppm (s). IR (Nujol): 2154 (CN), 740, 707 cm^{-1} (C═C, Ph).

---

(7) Amrhein, P. I.; Drouin, S. D.; Forde, C. E.; Lough, A. J.; Morris, R. H., *J. Chem. Soc., Chem. Commun.*, in press.

(8) Baldwin, D. A.; Pfeiffer, R. M.; Reichgott, D. W.; Rose, N. J. *J. Am. Chem. Soc.* **1973**, *95*, 5152−5158.

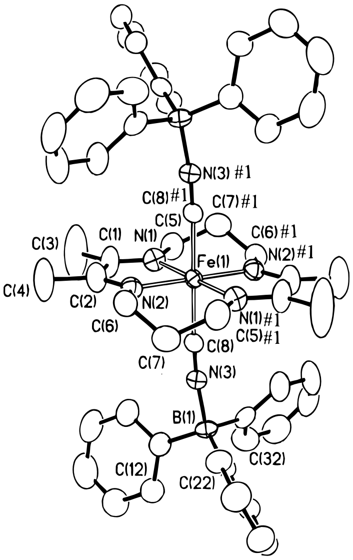

Figure 3. Crystal structure and labeling of Fe(TIM)$(CNBPh_3)_2$ **1**. Thermal ellipsoids represent the 50% probability surface.

X-ray Structure Determination of Fe(TIM)$(CNBPh_3)_2\cdot 3C_6H_6$

Data were collected on a Siemens P4 diffractometer using graphite monochromated Mo Kα radiation ($\lambda = 0.710\ 73$ Å). The intensities of three standard reflections measured every 97 reflections showed nodecay. The data were corrected for Lorentz and polarization effects and for absorption (minimum and maximum corrections were 0.3735 and 0.9298).[9] A summary of selected crystallographic data is given in Table 2.

The structure was solved and refined using the SHELXTL/PC package.[10] Refinement was by full-matrix least-squares on F^2 using all data (negative intensities included). The weighting scheme was w $= 1/[\sigma^2(F_o^2) + (0.0425P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$. Hydrogen atoms were included in calculated positions and treated as riding atoms.

With $Z = 4$ in the space group $C2/c$, the molecules must lie on special positions, and in the structure of **1**, the Fe atom lies in an inversion center. There are 4 solvent molecules of benzene associated with every molecule of **1**. Two have full occupancy and two have half-occupancy of which one lies across a 2-fold axis.

Atomic coordinates are given in Table 3, and selected bond lengths and angles are given in Table 4. Figure 3 shows the molecule with the crystallographic labeling scheme.

Acknowledgment. This work was supported by an operating grant to R.H.M. from the Natural Sciences and Engineering Research Council of Canada. We thank Nick Plavac for the assistance in using ^{11}B-NMR techniques. Finally we would like to thank the DAAD (Deutscher Akademischer Austauschdienst) for the financial support and Prof. M. Draeger (Mainz) and Prof. I. Manners (Toronto) who arranged the student exchange program.

Supporting Information Available: Tables of crystallographic parameters, atomic coordinates, thermal parameters, and bond distances and angles for **1** (5 pages). Ordering information is given on any current masthead page.

IC960201X

---

(9) Sheldrick, G. M., SHELXA-90. Program for Empirical Absorption Correction, University of Göttingen, Germany, 1990.

(10) Sheldrick, G. M. SHELXTL PC V5.0. Siemens Analytical X-ray Instruments Inc., Madison, WI, 1995.