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Journal of Organometallic Chemistry 580 (1999) 66–71

Journal of Organo metallic Chemistry

Cyano-bridged Fe–CN–Pt–NC–Fe chain complexes: structural and spectroscopic characterization of four isomers of $[\{\eta^5\text{-(1-phenylborole)Fe(CO)}_2(\mu\text{-CN})\}_2\text{Pt(PEt}_3)_2]$☆

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Received 21 September 1998

Abstract

The cyanometalate $[\eta^5\text{-(1-phenylborole)Fe(CO)}_2\text{CN}]^-$ is used as a building block for the synthesis of heterometallic complexes. It reacts with platinum(II) precursors with formation of cyanide-bridged Fe/Pt complexes and various isomeric structures are observed depending upon the orientation of the CN ligand (linkage isomers Fe–(μ-CN)–Pt or Fe-(μ-NC)–Pt) and the *cis* or *trans* geometry around the platinum centre. Complex **7** with a Fe–(μ-NC)–Pt–(μ-CN)–Fe chain was obtained from the reaction of *trans*-$[\text{Pt(CN)}_2(\text{PEt}_3)_2]$ with $[\eta^5\text{-(1-phenylborole)Fe(CO)}_2(\text{OEt}_2)]$. The crystal structure of *cis*-$[\{\eta^5\text{-(1-phenylborole)Fe(CO)}_2(\mu\text{-CN})\}_2\text{Pt(PEt}_3)_2]$ (**2**) which contains a Fe–(μ-CN)–Pt–(μ-NC)–Fe chain has been determined by X-ray diffraction. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Heterometallic complexes; Iron; Platinum; Cyanide ligand; Borole ligand; Linkage isomerism

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1. Introduction

The synthesis and reactivity of oligonuclear transition metal complexes with cyanide bridges is gaining increasing interest owing to their often remarkable structural, physical and chemical properties. These have been discussed in recent review articles [1]. In contrast to its isoelectronic analogue CO, the cyanide ion displays good donor properties at both its C and N atoms. This implies that controlling the orientation of the M–CN–M′ link (with M and M′ being different metals or the same metal in different oxidation states) and the cyanide–isocyanide isomerism will represent important synthetic challenges on which many properties will depend.

We have previously used the cyanomanganate anion $[(\text{MeCp})\text{Mn(CO)}_2\text{CN}]^-$ for the synthesis of heterometallic complexes containing cyanide bridges, including a unique double-helix-type Pd_4Mn_4 cluster [2]. This led us to consider the possibility of using the isoelectronic reagent $[\eta^5\text{-(1-phenylborole)Fe(CO)}_2\text{CN}]^-$ as a building block for the synthesis of heterometallic complexes that could display interesting features.

2. Results and discussion

The reaction of *cis*-$[\text{PtCl}_2(\text{PEt}_3)_2]$ in dichloromethane with the cyanoferrate $[\eta^5\text{-(1-phenylborole)Fe(CO)}_2\text{CN}]^-$ (**1**), obtained by treating $[\eta^5\text{-(1-phenylborole)Fe(CO)}_3]$ with lithium-bis(trimethylsilyl)amid [3], afforded via halide substitution the cyano-bridged iron-platinum complex *cis*-$[\{[\text{Fe}](\mu\text{-CN})\}_2\text{Pt(PEt}_3)_2]$ (**2**) ([Fe] represents the η^5-(1-phenylborole)Fe(CO)_2 fragment).

☆ This work is based on the PhD thesis of M.N.

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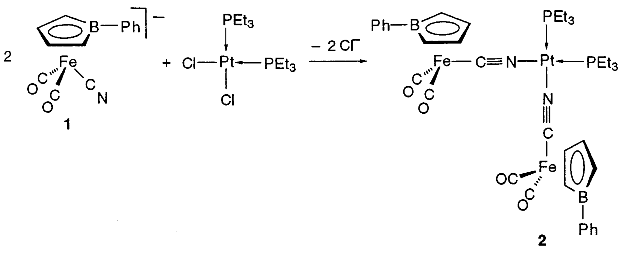
PII: S0022-328X(98)01089-4

This complex is soluble in dichloromethane but only slightly soluble in hexane Eq. (1).



(1)

Single-crystals of **2** were grown from dichloromethane/hexane as light yellow, not very air-sensitive needles. An X-ray crystal structure determination showed this compound to have C_2-symmetry with the Pt atom on the 2-fold crystallographic axis (Fig. 1). Selected interatomic distances and angles are given in Tables 1 and 2, respectively. The [Fe]CN-fragments of **2** show no unusual structural features. The 'slip-distortion' [4] of the borole ligand is of 0.048 Å and the distance between the boron atom and the best plane defined by the four carbon atoms is 0.079 Å, supporting a η^5-coordination of the borole ligand. The bridging cyano ligand is almost linearly coordinated to the iron fragment, while the coordination to the platinum atom deviates from linearity by about 12(2)°, causing the cyano group to protrude from the Pt-coordination plane. This distortion appears to result, at least in part, from steric hindrance as indicated by the opening of the P–Pt–P-angle from the ideal value of 90 to 97.2(3)°. Accordingly, the N–Pt–N-angle is reduced to 84.6(8)°. The separation between the metal centres Pt···Fe is 5.025(3) Å.

In principle, the two phosphine ligands could be either *cis* or *trans* with respect to each other and the two bridging cyano ligands could bind to platinum either through carbon or nitrogen. The resulting six possible isomers are presented in Scheme 1. Terminal cyano groups are usually bound to transition metals by the carbon atom [1,5]. Therefore the synthesis of the Fe–CN–Pt-isomers **2** and **3** has to start from cyanoferrate reagents while the Fe–NC–Pt-isomers **6** and **7** should be accessible starting from cyanoplatinum compounds (Scheme 2). However, since $[Pt(CN)_2(PEt_3)_2]$ is known only as the *trans*-isomer, the *cis*-[Fe]–NC–[Pt] isomer **6** cannot be obtained in this way. The mixed cyano/isocyano complexes **4** and **5** are not accessible by the direct syntheses presented in Scheme 2. The tricarbonyl complex [Fe]CO was irradiated in ether as solvent to give the highly reactive ether complex $[Fe](OEt_2)$. When *trans*-$[Pt(CN)_2(PEt_3)_2]$ was added subsequently, smooth formation of the trinuclear complex *trans*-$[\{[Fe]NC\}_2Pt(PEt_3)_2]$ (**7**) took place.

The ^{1}H- and ^{13}C-NMR signals of the borole ligands in the cyanoferrates differ significantly from the signals

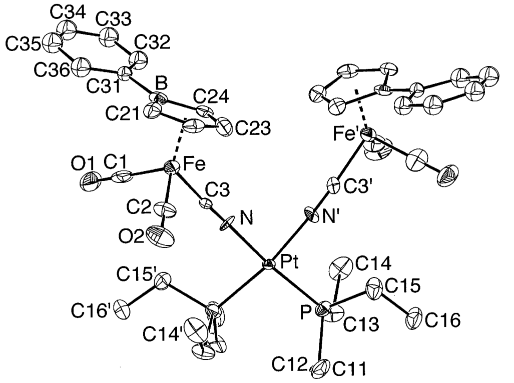
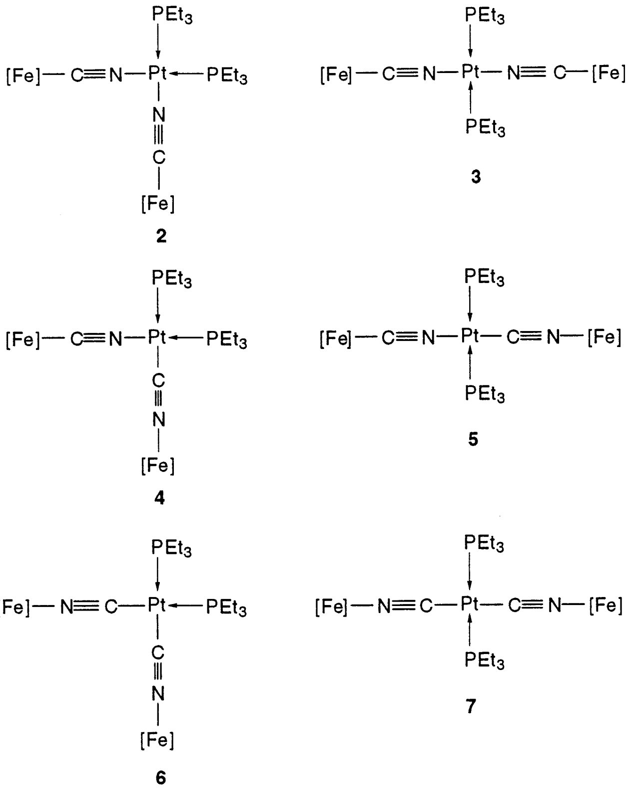


Fig. 1. PLATON-plot [16] of *cis*-$[\{[Fe](\mu\text{-}CN)\}_2Pt(PEt_3)_2]$ (**2**). Displacement ellipsoids are drawn at 30% probability.



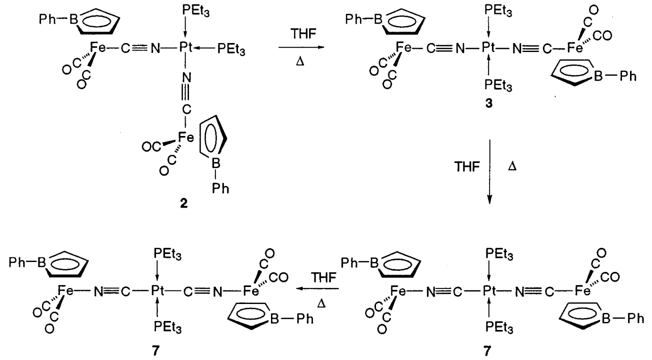
Scheme 1.

Table 1
Selected interatomic distances in *cis*-$[\{[Fe](\mu\text{-}CN)\}_2Pt(PEt_3)_2$ (**2**) (Å)

Pt–P	2.259(5)	Fe–C(22)	2.09(2)
Pt–N	2.02(1)	Fe–C(23)	2.06(2)
N–C(3)	1.12(2)	Fe–C(24)	2.12(2)
Fe–C(1)	1.77(2)	B–C(21)	1.55(2)
Fe–C(2)	1.76(2)	C(21)–C(22)	1.43(2)
Fe–C(3)	1.90(2)	C(22)–C(23)	1.43(2)
C(1)–O(1)	1.13(2)	C(23)–C(24)	1.41(3)
C(2)–O(2)	1.11(2)	C(24)–B	1.51(2)
Fe–B	2.21(2)	B–C(31)	1.58(2)
Fe–C(21)	2.12(2)		

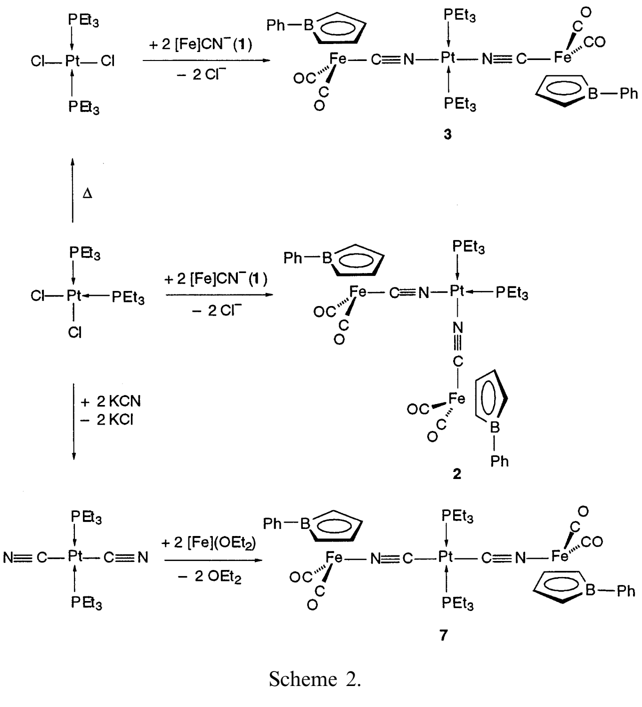
Table 2
Selected bond angles in *cis*-[{[Fe](μ-CN)}$_2$Pt(PEt$_3$)$_2$ (**2**) (°)

P–Pt–P′	97.2(3)	Fe–C(2)–O(2)	179(2)
P–Pt–N′	89.8(4)	C(1)–Fe–C(2)	96.4(9)
N–Pt–N′	84.6(8)	C(1)–Fe–C(3)	94.7(9)
Pt–P–C(11)	115.4(6)	C(2)–Fe–C(3)	91.8(7)
Pt–P–C(13)	115.8(6)	C(22)–C(21)–B	108(1)
Pt–P–C(15)	109.3(6)	C(21)–C(22)–C(23)	109(2)
Pt–N–C(3)	169(1)	C(22)–C(23)–C(24)	111(2)
N–C(3)–Fe	177(1)	C(23)–C(24)–B	108(2)
Fe–C(1)–O(1)	178(2)	C(21)–B–C(24)	104(2)



Scheme 3.

of the isocyanoferrates. The cyanoferrates show differences in the chemical shifts of the 2,5- and 3,4-borole protons and carbons of approximately 1.8 and 20 ppm, respectively, while these values are 2.3 and 27 ppm for the isocyanoferrates, respectively (see Table 3). In the IR spectra the difference between these bonding modes is even more striking since the cyanoferrates have ν_{CN} bands of high intensity while these bands are missing or only very weak in the spectra of the isocyanoferrates. The wavenumbers of the ν_{CN} bands of the cyanoferrate precursor and corresponding product are identical. The isocyanoferrates show higher wavenumbers for the ν_{CN} bands. The ^{31}P{^{1}H}-NMR spectra of all compounds show ^{195}Pt satellites which allow to distinguish between *cis* and *trans* isomers [6], although the chemical shift alone of these signals is less characteristic and therefore only used as fingerprints. The ^{195}Pt-NMR signal of compound **2** is significantly broadened by the adjacent nitrogen atom of the cyano-ligand. In the case of compound **7** with the carbon atom of the cyano groups bound to platinum, the lines are much sharper as the quadrupole relaxation is considerably less efficient. The 'hard' or 'soft' character of the ligands at the platinum atom influences the ^{195}Pt-NMR chemical shift [7]. The spectroscopic data for the starting materials, the products and of two reference compounds are presented in Tables 3 and 4.



Scheme 2.

The *cis–trans* isomerization of square-planar complexes of the type [PtX$_2$L$_2$] usually proceeds via an associative–dissociative mechanism and can therefore be catalyzed by nucleophiles [8,9]. In the case of **2**, even THF is sufficient to catalyse the isomerization. Thus, keeping a solution of this compound in THF for 3 days at 50°C afforded a mixture of three *trans* isomers with some starting material. The respective proportions were estimated by integration of the ^{31}P{^{1}H}-NMR signals to approximately 20% of *cis*-[([Fe](μ-CN)$_2$Pt(PEt$_3$)$_2$] (**2**), 5% of *trans*-[{[Fe](μ-CN)}$_2$Pt(PEt$_3$)$_2$] (**3**) and less than 1% of *trans*-[{[Fe](μ-NC)}$_2$Pt(PEt$_3$)$_2$] (**7**). The main isomer (75%) was identified as the cyano–isocyano species **5** on the basis of spectroscopic data (Scheme 3). Thus, the NMR signals of the two different borole ligands in **5** show chemical shifts typical for [Fe]–CN–Pt and [Fe]–NC–Pt units, respectively. There seems to be no influence of the *trans* ligand, which is consistent with the two [Fe]-groups being far enough from each other to constitute electronically and sterically independent units in the same molecule.

Keeping a solution of *trans*-{[Fe]CN}$_2$Pt(PEt$_3$)$_2$ (**3**) in THF at 50°C for several days also led to isomerization, although it was less advanced than the isomerization of the *cis* isomer under similar conditions. Addition of triethylphosphine did not appear to accelerate the reaction significantly. However, keeping a melt of **3** at 100°C for a few hours afforded the expected *trans* isomers as well as some decomposition products that were not further investigated. No metal formation was observed.

Attempts to isomerize *trans*-([Fe]NC)$_2$Pt(PEt$_3$)$_2$ (**7**) in THF at 50°C or as a melt at 100°C failed. Complex **7** therefore appears to be the thermodynamically more stable isomer.

Table 3
^{1}H- and ^{13}C{^{1}H}-NMR signals of the borole ligands (δ in ppm)

Compound	$H_{3,4\text{-borole}}$	$H_{2,5\text{-borole}}$	$C_{3,4\text{-borole}}$	$C_{2,5\text{-borole}}$
[Fe]CN$^-$ (**1**)[a,b]	5.04	3.15	92.2	72.3
[Fe]CN^{t}Bu[c]	5.26	3.47		
cis-([Fe]CN)$_2$Pt(PEt$_3$)$_2$ (**2**)	5.25	3.37	92.41	72.34
trans-([Fe]CN)$_2$Pt(PEt$_3$)$_2$ (**3**)	5.12	3.29	91.69	72.34
[Fe]NCMe[c]	5.40	3.20		
trans-([Fe]NC)$_2$Pt(PEt$_3$)$_2$ (**7**)	5.42	3.12	95.41	68.49
trans-([Fe]NC)([Fe]CN)Pt(PEt$_3$)$_2$ (**5**)				
[Fe]–CN–Pt	5.14	3.32	91.65	72.11
[Fe]–NC–Pt	5.43	3.12	96.55	69.61

[a] [Fe] stands for {η^5-(1-phenylborole)}Fe(CO)$_2$.
[b] Ref. [3].
[c] Ref. [15].

Table 4
ν_{CN}-absorptions (in cm^{-1}) and ^{31}P{^{1}H}- and ^{195}Pt{^{1}H}-NMR data (δ in ppm)

Compound	ν_{CN}	^{31}P{^{1}H}	^{195}Pt{^{1}H}	$^1J_{PPt}$ (Hz)
[Fe]CN$^-$ (**1**)[a,b]	2108 (m)			
[Fe]CN^{t}Bu[c]	2155 (s)			
cis-([Fe]CN)$_2$Pt(PEt$_3$)$_2$ (**2**)	2121 (s)	0.24	125	3286
trans-([Fe]CN)$_2$Pt(PEt$_3$)$_2$ (**3**)	2124 (s)	15.77		2232
[Fe]NCMe[c]	–			
trans-[Pt(CN)$_2$(PEt$_3$)$_2$]	2123[d]	13.19	−394	2163
trans-([Fe]NC)$_2$Pt(PEt$_3$)$_2$] (**7**)	2137 (vw)	15.59	−388	2065
trans-([Fe]NC)([Fe]CN)Pt(PEt$_3$)$_2$ (**5**)		17.25		2140
[Fe]–CN–Pt	2123 (s)			
[Fe]–NC–Pt	2174 (w)			
cis-PtCl$_2$(PEt$_3$)$_2$		9.0[e]	32[f]	3502[e]
trans-PtCl$_2$(PEt$_3$)$_2$		12.1[e]	584[f]	2394[e]

[a] [Fe] stands for {η^5-(1-phenylborole)}Fe(CO)$_2$.
[b] Ref. [3].
[c] Ref. [15].
[d] Ref. [12].
[e] Ref. [6].
[f] Ref. [7].

3. Experimental

Reactions were carried out under purified nitrogen, using standard Schlenk-type techniques. Solvents were distilled under nitrogen and traces of water were removed by usual methods. Infrared spectra were recorded on FT-IR Perkin-Elmer 1720 X and FT-IR Bruker IFS 66/113 spectrometers. NMR spectra were recorded on Varian VXR 500 (^{1}H, 500 MHz, relative to TMS, ^{13}C, 125.70 MHz, relative to TMS, ^{31}P, 202.33 MHz, relative to H$_3$PO$_4$) and Bruker WP 80 SY (^{195}Pt, 17.15 MHz, relative to external TMS [10] i.e. δ(PtCl$_6^{2-}$) = 4522 ppm) spectrometers. The mass spectrum was obtained with a FAB Fisons ZAB-HF spectrometer. Elemental analyses were carried out by the Analytisches Labor Pascher, Remagen (Germany). The cyanoferrate [η^5-(1-phenylborole)Fe(CO)$_2$(CN)]$^-$ (**1**) was prepared as described previously [3]. The complex [η^5-(1-phenylborole)Fe(CO)$_2$(OEt$_2$)] was obtained by UV-irradiation of [η^5-(1-phenylborole)Fe(CO)$_3$] in diethylether at −35°C for 3 h. The complex *cis*-[PtCl$_2$(NCPh)$_2$] was obtained by treating PtCl$_2$ with PhCN [11] and *cis*-[PtCl$_2$(PEt$_3$)$_2$] by substitution of PhCN with PEt$_3$. The cyano complex *trans*-[Pt(CN)$_2$(PEt$_3$)$_2$] was obtained by heating *cis*-[PtCl$_2$(PEt$_3$)$_2$] with KCN in EtOH [12].

3.1. Preparation of cis-[{[Fe](μ-CN)}$_2$Pt(PEt$_3$)$_2$] (2)

A solution of Li(THF)$_2$[{[Fe]CN}] (**1**) (340 mg, 0.8 mmol) in CH$_2$Cl$_2$ (4 ml) was added to a cooled (−70°C) solution of *cis*-[PtCl$_2$(PEt$_3$)$_2$] (200 mg, 0.4 mmol)

Table 5
Crystal data, data collection parameters, and convergence results for **2**

Empirical formula	$C_{38}H_{48}B_2Fe_2N_2O_4P_2Pt$
Crystal colour and shape	Yellow translucent rod
Crystal size (mm)	$0.10 \times 0.08 \times 0.05$
Crystal system	Monoclinic
Space group	$C2/c$
Unit cell dimensions	
a (Å)	20.26(1)
b (Å)	11.355(9)
c (Å)	18.949(9)
β(°)	105.45(5)
V (Å^3)	4203(5)
Z	4
$D_{calc.}$ (g cm^{-3})	$\rho = 1.56$
Absorption coefficient (cm^{-1})	$\mu = 41.5$
F(000)	1968
Wavelength (monochromator) (Å)	Mo–K$_\alpha$, $\lambda = 0.7107$ (graphite)
Data collection temperature (K)	253
Scan type and range	ω, $3 < \theta < 25°$
Reflections collected	4511
Independent reflections	3722
Independent reflections observed	2120 with $I > \sigma(I)$
Variables refined on F	201
Agreement factors for observed data	$R = 0.082$, $R_w = 0.062$, $w^{-1} = \sigma^2(F_o)$
Residual electron density	1.7 e Å^{-3} at 1 Å from Pt

in CH_2Cl_2 (4 ml). The reaction mixture was layered with 15 ml of hexane, thus affording *cis*-[{[Fe](μ-CN)}$_2$Pt(PEt$_3$)$_2$] (**2**) (243 mg, 0.25 mmol, 62%) as pale yellow needles. Anal. Calc. for $C_{38}H_{48}B_2Fe_2N_2O_4P_2Pt$: C, 46.24; H, 4.90; N, 2.84. Found: C, 45.83; H, 4.97; N, 2.93. IR (CH_2Cl_2): ν(CN) 2121(s), ν(CO) 1997(s), 1945(s) cm^{-1}. ^{1}H-NMR (CD_2Cl_2): δ 7.64, 7.26 (m, 10 H, phenyl), 5.25 (m, 4 H, $N = 6.1$ Hz, 3,4-borole), 3.37 (m, 4 H, $N = 6.1$ Hz, 2,5-borole), 1.87 (m, 12 H, CH_2), 1.19 (m, 18 H, CH_3). $^{13}C\{^1H\}$-NMR (CD_2Cl_2): δ 217.4 (s, 4 C, CO), 134.95 (s, 4 C, *ortho*-phenyl), 127.63 (s, 4 C, *meta*-phenyl), 124.48 (s, 2 C, *para*-phenyl), 92.41 (s, 4 C, 3,4-borole), 72.34 (s br, 4 C, 2,5-borole), 16.71 (d, 6 C, $^1J_{CP} = 40$ Hz, CH_2), 8.41 (s, 6 C, CH_3). $^{31}P\{^1H\}$-NMR (CD_2Cl_2): δ 0.24 (s with Pt satellites, 2 P, $^1J_{PPt} = 3286$ Hz). $^{195}Pt\{^1H\}$-NMR (CH_2Cl_2/CD_2Cl_2): δ 125 (t br, Pt, $^1J_{PtP} = 3300$ Hz, $\Delta\nu_{1/2} = 390$ Hz). MS (FAB$^+$, NBA): $m/z = 987$ (M$^+$/MH$^+$, 1/1.9, 1.5%), 931 (M$^+$ $-$2CO, 7%), 875 (M$^+$ $-$4CO, 17%), 679 (M$^+$ $-$ [Fe] $-$ 2CO, 2.8%).

3.2. Preparation of trans-[{[Fe](μ-CN)}$_2$Pt(PEt$_3$)$_2$] (3)

To a solution of [Fe]CO (100 mg, 0.36 mmol) in THF (5 ml) was added LiN(SiMe$_3$)$_2$ in small portions until the IR spectrum showed no bands of the starting material. Solid *trans*-[PtCl$_2$(PEt$_3$)$_2$] (90 mg, 0.18 mmol) was added to this mixture. The yellow solution was evaporated to dryness, the residue was dissolved in dichloromethane (5 ml) and the solution layered with pentane (5 ml). After 1 day at room temperature the solution was filtered and the filtrate evaporated to dryness. The solid was extracted with diethylether (10 ml). Evaporation of this extract to dryness afforded *trans*-[{[Fe]CN}$_2$Pt(PEt$_3$)$_2$] (**3**) as an oily, yellow mass (84 mg, purity ca. 75%, determined by ^{1}H-NMR). IR (CH_2Cl_2): ν(CN) 2124(s), ν(CO) 1999(s), 1947(s) cm^{-1}. ^{1}H-NMR (CD_2Cl_2): δ 7.59, 7.22 (m, 10 H, phenyl), 5.12 (m, 4 H, $N = 5.8$ Hz, 3,4-borole), 3.29 (m, 4 H, $N = 6.1$ Hz, 2,5-borole), 1.89 (m, 12 H, CH_2), 1.16 (m, 18 H, CH_3). $^{13}C\{^1H\}$-NMR (CD_2Cl_2): δ 217.4 (s, 4 C, CO), 134.84 (s, 4 C, *ortho*-phenyl), 127.69 (s, 4 C, *meta*-phenyl), 124.48 (s, 2 C, *para*-phenyl), 91.69 (s, 4 C, 3,4-borole), 72.34 (s br, 4 C, 2,5-borole), 14.98 (dd, 6 C, $^1J_{CP} = {}^3J_{CP} = 19$ Hz, CH_2), 8.03 (s, 6 C, CH_3). $^{31}P\{^1H\}$-NMR (CD_2Cl_2): δ 15.77 (s with Pt satellites, 2 P, $^1J_{PPt} = 2232$ Hz).

3.3. Preparation of trans-[{[Fe]NC}$_2$Pt(PEt$_3$)$_2$] (7)

An excess of [Fe]CO in diethylether (80 ml) was irradiated at -35°C with the UV-light from a high pressure Hg vapor lamp. The irradiation was stopped after 3 h and a slurry of *trans*-[Pt(CN)$_2$(PEt$_3$)$_2$] in diethylether was added. While the temperature was allowed to rise to ambient, a light brown precipitate formed. The $^{31}P\{^1H\}$ and $^{195}Pt\{^1H\}$-NMR spectra showed complete conversion of the Pt compound. The reaction mixture was evaporated to dryness and the residue extracted with dichloromethane/hexane (1:3). The extract was evaporated to dryness. The resulting solid, *trans*-[{[Fe]NC}$_2$Pt(PEt$_3$)$_2$] (**7**), contaminated with some [Fe]CO, was washed with hexane (yield not determined).

Spectroscopic data for *trans*-[Pt(CN)$_2$(PEt$_3$)$_2$]: IR (CH_2Cl_2): ν(CN) 2124(s) cm^{-1}; (KBr): ν(CN) 2121(s) cm^{-1}. ^{1}H-NMR (CD_2Cl_2): δ 2.16 (m, 12 H, CH_2), 1.17 (m, 18 H, CH_3). $^{31}P\{^1H\}$-NMR (CD_2Cl_2): δ 13.2 (s with Pt satellites, 2 P, $^1J_{PPt} = 2163$ Hz). ^{195}Pt-NMR (CH_2Cl_2/CD_2Cl_2): δ -394 (t, 1 Pt, $^1J_{PPt} = 2176$ Hz).

Spectroscopic data for *trans*-[{[Fe](μ-NC)}$_2$Pt(PEt$_3$)$_2$] (**7**): IR (CH_2Cl_2): ν(CN) 2135(w), ν(CO) 1999(s), 1940(s) cm^{-1}. ^{1}H-NMR (CD_2Cl_2): δ 7.56, 7.25 (m, 10 H, phenyl), 5.42 (m, 4 H, $N = 6.1$ Hz, 3,4-borole), 3.12 (m, 4 H, $N = 6.1$ Hz, 2,5-borole), 2.00 (m, 12 H, CH_2), 1.15 (m, 18 H, CH_3). $^{13}C\{^1H\}$-NMR (CD_2Cl_2): δ 218.20 (s, 4 C, CO), 167.89 (s, 2 C, CN), 134.77 (s, 4 C, *ortho*-phenyl), 128.01 (s, 2 C, *para*-phenyl), 127.53 (s, 4 C, *meta*-phenyl), 117.27 (s br, 2 C, *ipso*-phenyl), 96.51 (s, 4 C, 3,4-borole), 69.59 (s br, 4 C, 2,5-borole), 17.78 (dd, 6 C, $^1J_{CP} = {}^3J_{CP} = 17.8$ Hz, CH_2), 8.36 (s, 6 C, CH_3). $^{31}P\{^1H\}$-NMR (CD_2Cl_2): δ 15.6 (s with Pt satellites, 2 P, $^1J_{PPt} = 2065$ Hz). $^{195}Pt\{^1H\}$-NMR (CH_2Cl_2/CD_2Cl_2): δ -388 (t, Pt, $^1J_{PtP} = 2066$ Hz).

*3.4. Isomerization of (**2**)*

A solution of **2** (122 mg, 0.12 mmol) in THF (20 ml) was kept at 50°C for 3 days. The $^{31}P\{^1H\}$-NMR spectrum showed the presence of **2** (20%), **3** (5%), *trans*-[{[Fe](μ-CN)}{[Fe](μ-NC)}Pt(PEt$_3$)$_2$] (**5**) (75%) and **7** (< 1%).

Spectroscopic data for (**5**): IR (CH$_2$Cl$_2$): ν(NC) 2174(w), ν(CN) 2123(s), ν(CO) 1999(s), 1945(s) cm^{-1}. ^{1}H-NMR (CD$_2$Cl$_2$): δ 7.60, 7.24 (m, 5 H, phenyl$_{[Fe]-CN}$), 7.56, 7.26 (m, 5 H, phenyl$_{[Fe]-NC}$), 5.43 (m, 2 H, 3,4-borole$_{[Fe]-NC}$), 5.14 (m, 2 H, 3,4-borole$_{[Fe]-CN}$), 3.32 (m, 2 H, 2,5-borole$_{[Fe]-CN}$), 3.12 (m, 2 H, 2,5-borole$_{[Fe]-NC}$), 1.95 (m, 12 H, CH$_2$), 1.19 (m, 18 H, CH$_3$). $^{13}C\{^1H\}$-NMR (CD$_2$Cl$_2$): δ 218.41 (s, 2 C, CO$_{[Fe]-NC}$), 217.11 (s, 2 C, CO$_{[Fe]-CN}$), 134.93, 134.82 (s, 4 C, *ortho*-phenyl), 127.66, 127.62, 127.56, 127.46 (s, 6 C, *meta*- and *para*-phenyl), 96.55 (s, 2 C, 3,4-borole$_{[Fe]-NC}$), 91.65 (s, 2 C, 3,4-borole$_{[Fe]-CN}$), 72.11 (s (br), 2 C, 2,5-borole$_{[Fe]-CN}$), 69.61 (s br, 2 C, 2,5-borole$_{[Fe]-NC}$), 16.31 (dd, 6 C, $^1J_{CP} = {}^3J_{CP} = 17$ Hz, CH$_2$), 8.22 (s, 6 C, CH$_3$). $^{31}P\{^1H\}$-NMR (CD$_2$Cl$_2$): δ 17.25 (s with Pt satellites, 2 P, $^1J_{PPt} = 2140$ Hz).

4. Crystallography

The X-ray structure determination was performed on an ENRAF-Nonius CAD4 diffractometer. Experimental details are given in Table 5. Before averaging over symmetry-related parts of the reciprocal lattice an empirical absorption correction [13] was applied. The structure was solved by Patterson methods and refined on structure factors with the SDP [14] program system. The carbon atoms of the phenyl ring were refined with isotropic displacement parameters, other nonhydrogen atoms with anisotropic displacement parameters, hydrogen atoms were included as riding on their carbon atoms with C–H = 98 pm, $U_{iso}(H) = 1.3\ U_{eq}(C)$.

5. Supplementary material

Crystallographic data (excluding structure factors) for the structure of **2** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-102988. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

We are grateful to the DAAD for a grant to M. Neuschütz and to the Centre National de la Recherche Scientifique (Paris) for financial support.

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