Reactions of σ-ferrocenylplatinum complexes with carbon monoxide and isocyanide [1]

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Abstract

Reaction of the ferrocenylplatinum complexes *trans*-FcPt(PEt$_3$)$_2$X (**1**) (Fc = ferrocenyl, X = Cl, Br, NCS) with 30 kg cm^{-2} of CO at room temperature leads to the insertion of CO into the Pt–C bond of **1** to give *trans*-FcC(O)Pt(PEt$_3$)$_2$X (**2**) (X = Cl, Br, NCS) in good yield. Reactions of **1a** (X = Cl) with an equimolar amount of aryl isocyanides produce the isocyanide insertion products *trans*-FcC(=NCAr)Pt(PEt$_3$)$_2$Cl (**5**) (Ar = *p*-MeC$_6$H$_4$, *p*-MeOC$_6$H$_4$, 2,6-Me$_2$C$_6$H$_3$). In the reaction of **1a** with *p*-nitrophenyl isocyanide, a mixture of cis and trans isomers was obtained in a 4:1 ratio, while treatment with the other isocyanides gave only trans isomers. The structures of the insertion products were characterized by means of spectroscopic analyses and X-ray crystallography.
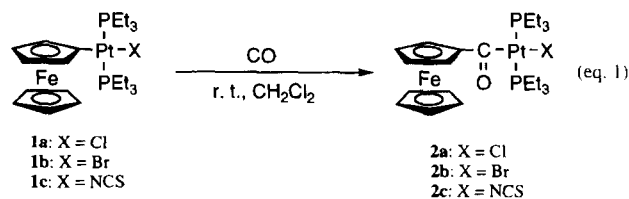
1. Introduction

Insertion of small molecules into the M–C bond of a variety of transition metal complexes has received much attention for a long time, since it is one of the fundamental reactions in organometallic chemistry [1]. In particular, insertion of carbon monoxide, which is a key step in carbonylation using a homogeneous catalyst, has been widely investigated [2]. Isocyanides having a structure which is isoelectronic with carbon monoxide are well known as undergoing a similar insertion into the M–C bond [3].

We have been studying the chemistry of σ-ferrocenyl transition metal complexes [4] and recently found that carbon monoxide inserts into the Pt–C bond of the (μ-hydroxo)-1,1′-ferrocenediyldiplatinum complex (μ-

OH){η^5-C$_5$H$_4$Pt(PPh$_3$)Cl}$_2$Fe under mild conditions (room temperature, CO at 30 kg cm^{-2}) [5]. Hence, we are interested in the high reactivity of the σ-ferrocenylplatinum complex toward carbon monoxide. In this paper we wish to describe the reactions of *trans*-FcPt(PEt$_3$)$_2$X (Fc = ferrocenyl, X = Cl, Br, NCS) with CO as well as aryl isocyanide, and X-ray crystallographic studies of the resulting insertion products.

2. Results and discussion

2.1. Reaction of trans-FcPt(PEt$_3$)$_2$X with CO

(eq. 1)

1a: X = Cl
1b: X = Br
1c: X = NCS

2a: X = Cl
2b: X = Br
2c: X = NCS

When *trans*-FcPt(PEt$_3$)$_2$Cl (**1a**), which was prepared by the ligand-exchange reaction of FcPt(cod)Cl with 2

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[1] Dedicated to Professor Max Herberhold on the occasion of his 60th birthday.

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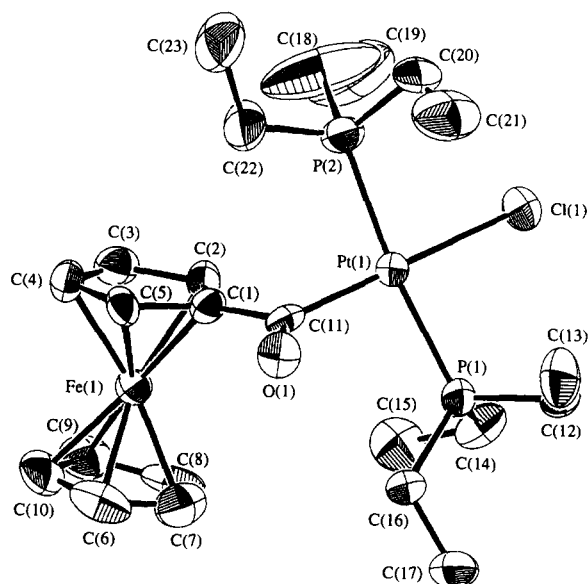
Fig. 1. Molecular structure of *trans*-FcC(O)Pt(PEt$_3$)$_2$Cl (**2a**). Hydrogen atoms have been omitted for clarity.

equiv. of triethylphosphine, was treated with 30 kg cm^{-2} of CO in CH$_2$Cl$_2$ at room temperature for 24 h, insertion into the Pt–C bond of **1a** occurred to give *trans*-FcC(O)Pt(PEt$_3$)$_2$Cl (**2a**) as red–orange crystals in almost quantitative yield [Eq. (1)]. Complex **2a** is air-

and moisture-stable at room temperature, both in the solid state and in solution. Characterization of **2a** was achieved by IR, ^{1}H, ^{13}C and ^{31}P NMR spectroscopy as well as by elemental analysis. The IR spectrum of **2a** showed a strong absorption at 1590 cm^{-1} due to the

Table 1
Crystallographic data for **2a** and *cis*-**5d** · C$_6$H$_6$

	2a	*cis*-**5d** · C$_6$H$_6$
Empirical formula	C$_{23}$H$_{39}$ClOP$_2$FePt	C$_{35}$H$_{49}$ClN$_2$O$_2$P$_2$FePt
Formula weight	679.90	878.12
Crystal color, habit	red–orange, prismatic	red, prismatic
Crystal dimensions	0.25 × 0.20 × 0.20 mm	0.35 × 0.25 × 0.10 mm
Crystal system	orthorhombic	triclinic
Lattice parameters	$a = 31.333(3)$ Å	$a = 11.773(1)$ Å
	$b = 7.609(2)$ Å	$b = 14.629(2)$ Å
	$c = 10.766(1)$ Å	$c = 11.643(1)$ Å
		$\alpha = 100.65(1)°$
		$\beta = 96.986(9)°$
		$\gamma = 105.43(1)°$
	$V = 2567(1)$ Å^3	$V = 1868.5(4)$ Å^3
Space group	$Pna2_1$ (No. 33)	$P\bar{1}$ (No. 2)
Z Value	4	2
D_{calc}	1.759 g cm^{-3}	1.561 g cm^{-3}
$F(000)$	1344	880
μ(Mo K α)	63.07 cm^{-1}	43.54 cm^{-1}
2θ range	$6° < 2\theta < 55.1°$	$6° < 2\theta < 50.1°$
No. of unique reflections	3411	6615
No. of observations	2277 ($I > 3.0\sigma(I)$)	5668 ($I > 3.0\sigma(I)$)
No. of variables	261	397
Residuals: R; R_w [a]	0.031; 0.024	0.022; 0.019
Goodness-of-fit indicator [b]	1.31	1.38
Max. peak in final diff. map	0.87 e Å^{-3}	0.29 e Å^{-3}
Min. peak in final diff. map	-1.44 e Å^{-3}	-0.47 e Å^{-3}

[a] $R = \Sigma \, \| F_o | - | F_c \| / \Sigma | F_o |$; $R_w = [\Sigma w(| F_o | - | F_c |)^2 / \Sigma w F_o^2]^{1/2}$; $w = 4F_o^2/\sigma^2(F_o)^2$.
[b] Goodness-of-fit indicator: standard deviation of an observation of unit weight $[\Sigma w(| F_o | - | F_c |)^2/(N_o - N_v)]^{1/2}$; $N_o =$ No. of observations, $N_v =$ No. of variables.

Table 2
Positional parameters and B_{eq} for complex 2a

Atom	x	y	z	B_{eq}
Pt(1)	0.15363(1)	0.02978(4)	0.0002	2.70(1)
Fe(1)	0.02056(5)	0.2592(2)	0.1165(1)	2.89(6)
Cl(1)	0.22924(8)	0.1002(4)	–0.0224(3)	4.8(2)
P(1)	0.14517(8)	0.1356(4)	–0.1984(3)	3.1(1)
P(2)	0.1692(1)	–0.1060(4)	0.1871(3)	3.8(1)
O(1)	0.0726(2)	–0.135(1)	–0.0389(6)	3.7(4)
C(1)	0.0681(3)	0.074(1)	0.1208(9)	2.8(4)
C(2)	0.0809(3)	0.229(1)	0.183(1)	3.4(5)
C(3)	0.0516(3)	0.258(2)	0.282(1)	4.1(6)
C(4)	0.0209(3)	0.128(2)	0.281(1)	4.0(6)
C(5)	0.0305(3)	0.012(1)	0.182(1)	3.4(5)
C(6)	–0.0296(3)	0.253(1)	–0.001(2)	5.3(6)
C(7)	0.0052(5)	0.328(2)	–0.059(1)	4.9(7)
C(8)	0.0165(3)	0.479(1)	0.005(2)	5.2(6)
C(9)	–0.0113(4)	0.491(2)	0.110(1)	4.8(7)
C(10)	–0.0402(4)	0.350(2)	0.102(1)	4.7(6)
C(11)	0.0914(3)	–0.021(1)	0.021(1)	2.6(4)
C(12)	0.1823(4)	0.036(2)	–0.305(1)	4.0(7)
C(13)	0.1802(4)	–0.161(2)	–0.315(1)	5.6(7)
C(14)	0.1558(4)	0.371(1)	–0.211(1)	4.7(6)
C(15)	0.1203(4)	0.479(2)	–0.143(1)	5.8(7)
C(16)	0.0934(3)	0.099(2)	–0.273(1)	3.8(5)
C(17)	0.0899(4)	0.161(2)	–0.406(1)	5.3(6)
C(18)	0.187(1)	0.034(4)	0.311(2)	15(2)
C(19)	0.2041(8)	0.179(3)	0.310(2)	12(2)
C(20)	0.2122(4)	–0.258(2)	0.169(1)	5.6(7)
C(21)	0.2054(5)	–0.393(2)	0.070(1)	7.5(9)
C(22)	0.1259(4)	–0.239(2)	0.258(1)	8(1)
C(23)	0.1372(4)	–0.355(2)	0.364(1)	8(1)

C=O stretching vibration. The ^{1}H NMR spectrum of 2a exhibited resonances at δ 4.68 and 4.27 ppm assigned to the protons of the substituted cyclopentadienyl group, and at δ 4.15 ppm attributed to the protons of non-substituted cyclopentadienyl ring. In the ^{13}C NMR spectrum of 2a, a resonance characteristic to the carbonyl carbon was observed at δ 213.7 ppm. The ^{31}P NMR spectrum showed a singlet peak at δ 19.04 ppm accompanied by ^{195}Pt satellite signals ($J_{Pt–P} = 3070$ Hz), indicating the trans configuration of two triethylphosphine ligands around a platinum atom. These data are consistent with the structure of 2a, which was confirmed by an X-ray diffraction analysis.
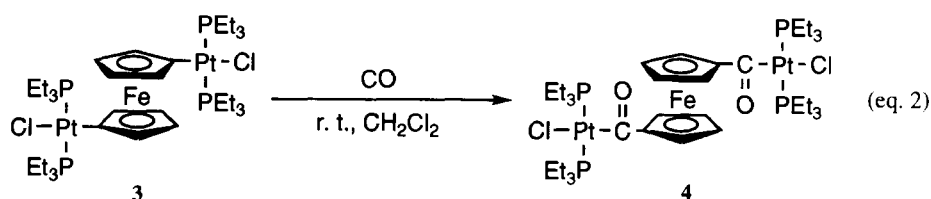
The molecular structure of 2a is shown in Fig. 1. The crystallographic data and positional parameters are listed in Tables 1 and 2, and selected bond lengths and angles are listed in Table 3, respectively. The platinum atom has a square-planar coordination geometry, in which the two triethylphosphines are in the trans positions relative to each other as expected from the ^{31}P NMR analysis. The Pt(1)–C(11) bond length of 2.001(8) Å is in agreement with an average value (1.991 Å) observed in the other acyl–platinum complexes [6]. The significantly long Pt(1)–Cl(1) bond length of 2.441(2) Å is affected by the strong trans influence of the acyl group. The dihedral angle between the Pt coordination plane and

Table 3
Selected bond lengths (Å) and angles (°) for 2a

Pt(1)–Cl(1)	2.441(2)	Pt(1)–C(11)	2.001(8)
Pt(1)–P(1)	2.300(3)	C(1)–C(11)	1.49(1)
Pt(1)–P(2)	2.315(3)	O(1)–C(11)	1.23(1)
Cl(1)–Pt(1)–P(1)	86.7(1)	P(2)–Pt(1)–C(11)	91.3(4)
Cl(1)–Pt(1)–P(2)	88.8(1)	Pt(1)–C(11)–C(1)	117.6(7)
Cl(1)–Pt(1)–C(11)	178.4(3)	Pt(1)–C(11)–O(1)	123.0(8)
P(1)–Pt(1)–P(2)	171.5(1)	O(1)–C(11)–C(1)	119.1(8)
P(1)–Pt(1)–C(11)	93.3(4)		

the plane of the carbonyl group defined by Pt(1), C(11), O(1) and C(1) is 67.3° and that between the carbonyl plane and the cyclopentadienyl ring C(1)–C(5) is 21.4°. The ferrocenyl group has an eclipsed conformation with the tilt angle of 4.8° between the two cyclopentadienyl rings.

Similar treatment of **1b** and **1c** with CO also gave insertion products, *trans*-FcC(O)Pt(PEt$_3$)$_2$Br (**2 b**) and *trans*-FcC(O)Pt(PEt$_3$)$_2$NCS (**2c**), respectively. When the 1,1′-ferrocenediyldiplatinum complex {*trans*-(η^5-C$_5$-H$_4$)Pt(PEt$_3$)$_2$Cl}$_2$Fe (**3**) was treated with CO, insertion

into both Pt–C bonds occurred to give orange crystals of {*trans*-(η^5-C$_5$H$_4$)C(O)Pt(PEt$_3$)$_2$Cl}$_2$Fe (**4**) in 84% yield [Eq. (2)]. It should be noted that the insertion was observed in the reaction of **1** under atmospheric pressure of CO at room temperature. The formation of a quantitative amount of **2a** was confirmed by ^{31}P NMR spectroscopy in the reaction of **1a** with 1 atm of CO for 69 h. Similarly, the reaction of **1b** and **1c** under atmospheric pressure of CO also afforded **2b** and **2c** respectively, in quantitative yield.

(eq. 2)

Previously it was reported that the carbonylation of *trans*-RPt(PR′$_3$)$_2$X was not achieved at room temperature under CO pressure, but at 90°C [7], which is more severe than that of our system, suggesting that the Pt–C bond of **1** is more reactive than that of the other organoplatinum complexes toward CO insertion. The mechanism of CO insertion has been investigated in depth for the complexes *trans*-RPt(PR′$_3$)$_2$X, and it has been shown that electron-donating substituents of the organic group enhance the insertion of CO into the Pt–C bond [8]. The easy carbonylation of **1** at room temperature may occur due to the high electron density of the cyclopentadienyl ring in comparison with phenyl group, as supported by the following result. In the reaction of *trans*-{(η^5-C$_5$H$_4$)Mn(CO)$_3$}Pt(PEt$_3$)$_2$Cl having a cyclopentadienyl group which was more electron poor than that of **1** [9], heating at 100°C is required for insertion of CO into the Pt–C bond [10].

2.2. Reaction of 1 with aryl isocyanide

Complex **1a** was treated with an equimolar amount of *p*-tolyl isocyanide in refluxing 1,2-dichloroethane for 6 h to give red crystals of *trans*-FcC(=NC$_6$H$_4$Me-

p)Pt(PEt$_3$)$_2$Cl (**5a**) in 48% yield [Eq. (3)]. The observation of a *ν*(C=N) absorption at 1550 cm^{-1} in the IR spectrum and a resonance assigned to the imino carbon at δ 173.8 ppm in the ^{13}C NMR spectrum indicates that **5a** was produced by the insertion of isocyanide into the Pt–C bond of **1a**. The ^{31}P NMR spectrum of **5a** showed a singlet peak at δ 14.90 ppm along with the satellite signal (J_{Pt-P} = 2904 Hz), suggesting the trans configuration around the Pt atom. The treatment of **1a** with *p*-methoxyphenyl isocyanide or 2,6-xylyl isocyanide in a similar fashion afforded the insertion products *trans*-FcC(=NC$_6$H$_4$OMe-*p*)Pt(PEt$_3$)$_2$Cl (**5b**) and *trans*-FcC(=NC$_6$H$_3$Me$_2$-2,6)Pt(PEt$_3$)$_2$Cl (**5c**) in 60% and 30% yield, respectively. The similar reaction of the diplatinum complex **3** with 2 equiv. of *p*-tolyl isocyanide red crystals gave {*trans*-(η^5-C$_5$H$_4$)C(=NC$_6$H$_4$-Me-*p*)Pt(PEt$_3$)$_2$Cl}$_2$Fe (**6**) in 38% yield [Eq. (4)]. When complex **1a** was treated with *p*-nitrophenyl isocyanide, the insertion product of FcC(=NC$_6$H$_4$NO$_2$-*p*)Pt(PEt$_3$)$_2$Cl (**5d**) was obtained as a mixture of cis and trans isomers in a 4:1 ratio, which was confirmed by ^{31}P NMR spectroscopy. Fractional recrystallization from toluene/hexane afforded the pure cis isomer of **5d** as red crystals in 70% yield. The structure of *cis*-**5d** was determined by an X-ray diffraction study.

PEt₃
[structure]—Pt—Cl   + CNAr   ──reflux──▶   [structure]—C—Pt—Cl   (eq. 3)
Fe   PEt₃   ClCH₂CH₂Cl   Fe   N   PEt₃
                                            Ar

1a

trans-**5a**: Ar = C₆H₄CH₃-*p*
trans-**5b**: Ar = C₆H₄OCH₃-*p*
trans-**5c**: Ar = C₆H₄(CH₃)₂-2,6
trans-**5d**: Ar = C₆H₄NO₂-*p*

PEt₃
[structure]—C—Pt—PEt₃
Fe   N   Cl
     Ar

cis-**5a**: Ar = C₆H₄CH₃-*p*
cis-**5b**: Ar = C₆H₄OCH₃-*p*
cis-**5c**: Ar = C₆H₄(CH₃)₂-2,6
cis-**5d**: Ar = C₆H₄NO₂-*p*

Et₃P   Fe   PEt₃   + 2 CN—[ring]—CH₃
Cl—Pt
Et₃P
3

──reflux──▶
ClCH₂CH₂Cl

[structure with CH₃, Et₃P, Cl—Pt—C, Et₃P, PEt₃, C—Pt—Cl, N PEt₃, CH₃]   (eq. 4)

6

The molecular structure of *cis*-**5d** is shown in Fig. 2. The positional parameters and selected bond lengths and angles are listed in Tables 4 and 5, respectively. The coordination around the platinum atom is essentially square-planar, with the two triethylphosphines being cis to each other as suggested by ³¹P NMR spectroscopy. The Pt(1)–C(11) bond length of 2.050(4) Å is slightly longer than those observed in other imino–platinum(II) complexes, *trans*-MeC(=NC₆H₄Cl-*p*)Pt(PEt₃)₂I [2.027(11) Å] [11] and 2,5-C₄H₂S{*trans*-C(=NC₆H₄OMe-*p*)Pt(PEt₃)₂Cl}₂ [1.99(2) and 2.01(2) Å] [12], which is probably due to the trans influence of the PEt₃ ligand. The bond length of Pt(1)–P(2) [2.354(1) Å] is longer than that of Pt(1)–P(1) [2.225(1) Å] owing to the greater trans influence of the imino group than that of the Cl ligand. The plane defined by Pt(1), C(11), C(1), N(1) and C(12) makes dihedral angles with the Pt coordination plane and the cyclopentadienyl ring C(1)–C(5) of 92.3° and 21.7°, respectively. The former is larger than the dihedral angle between the Pt coordination plane and the plane of the carbonyl group in **2a**,

while the latter is similar to the dihedral angle between the cyclopentandienyl ring and the plane of carbonyl group in **2a** (see above). The tilt angle between two cyclopentadienyl rings of ferrocene is 0.9°.

Although isomerization between *cis*- and *trans*-**5d** was not detected even at 80°C in 1,2-dichloroethane, *cis*-**5d** was converted to *trans*-**5d** by the treatment with a catalytic amount of *p*-nitrophenyl isocyanide. However, the treatment of *trans*-**5d** with *p*-nitrophenyl isocyanide did not cause isomerization to *cis*-**5d**. Thus, we carried out experiments to examine the effect of the amount of isocyanide on the ratio of the cis–trans isomers in the reaction of **1a** with isocyanide using ³¹P NMR spectroscopy. The results are summarized in Table 6 showing that treatment with a small excess of isocyanide leads to the preferential formation of the trans isomer while reaction with an insufficient amount of isocyanide gives the cis-rich isometric mixture, except for the case of 2,6-xylyl isocyanide. The results indicate that the reaction of **1** with isocyanide leads to the formation of a cis-iminoacyl complex, which is smoothly

Table 4
Positional parameters and B_{eq} for complex cis-**5d** · C_6H_6

Atom	x	y	z	B_{eq}
Pt(1)	0.42700(1)	0.20438(1)	0.17393(1)	2.738(5)
Fe(1)	0.82331(4)	0.39859(4)	0.27705(5)	3.86(2)
Cl(1)	0.56783(9)	0.11441(8)	0.1589(1)	4.69(4)
P(1)	0.31256(8)	0.30274(7)	0.2007(1)	3.74(4)
P(2)	0.3005(1)	0.06433(7)	0.21442(9)	3.72(4)
O(1)	0.1797(3)	0.1723(4)	−0.4344(3)	9.9(2)
O(2)	0.2021(4)	0.0362(4)	−0.4047(3)	10.0(2)
N(1)	0.5662(3)	0.3324(2)	0.0307(3)	3.9(1)
N(2)	0.2267(4)	0.1244(5)	−0.3781(4)	7.3(2)
C(1)	0.6444(3)	0.3799(3)	0.2349(3)	3.5(1)
C(2)	0.7125(3)	0.4773(3)	0.2390(4)	4.5(2)
C(3)	0.7810(4)	0.5179(3)	0.3555(4)	5.3(2)
C(4)	0.7579(4)	0.4478(4)	0.4226(4)	5.2(2)
C(5)	0.6732(3)	0.3616(3)	0.3491(3)	4.1(2)
C(6)	0.8646(4)	0.3058(4)	0.1486(4)	5.3(2)
C(7)	0.9317(4)	0.4023(4)	0.1548(4)	5.5(2)
C(8)	1.0006(3)	0.4408(3)	0.2701(5)	5.5(2)
C(9)	0.9757(4)	0.3677(4)	0.3349(4)	5.8(2)
C(10)	0.8919(4)	0.2841(3)	0.2594(5)	5.7(2)
C(11)	0.5556(3)	0.3128(3)	0.1334(3)	3.3(1)
C(12)	0.4844(3)	0.2768(3)	−0.0713(3)	3.8(1)
C(13)	0.4319(4)	0.3270(3)	−0.1431(4)	4.8(2)
C(14)	0.3491(4)	0.2771(4)	−0.2439(4)	5.5(2)
C(15)	0.3202(4)	0.1782(4)	−0.2739(4)	5.2(2)
C(16)	0.3737(4)	0.1259(3)	−0.2093(4)	5.0(2)
C(17)	0.4567(3)	0.1767(3)	−0.1073(3)	4.3(2)
C(18)	0.1624(3)	0.2604(3)	0.1110(4)	5.1(2)
C(19)	0.1601(4)	0.2464(4)	−0.0211(5)	7.8(3)
C(20)	0.2851(4)	0.3291(3)	0.3518(4)	5.2(2)
C(21)	0.3973(4)	0.3691(4)	0.4459(4)	7.6(2)
C(22)	0.3744(4)	0.4231(3)	0.1729(4)	5.7(2)
C(23)	0.3005(5)	0.4933(4)	0.1931(7)	11.6(4)
C(24)	0.1575(4)	0.0628(3)	0.2622(4)	5.1(2)
C(25)	0.0811(4)	−0.0327(4)	0.2786(4)	7.3(2)
C(26)	0.3777(4)	0.0204(3)	0.3286(4)	5.8(2)
C(27)	0.4394(5)	0.1003(4)	0.4380(4)	8.0(3)
C(28)	0.2614(4)	−0.0370(3)	0.0863(4)	5.5(2)
C(29)	0.1807(5)	−0.0247(4)	−0.0181(4)	7.1(2)
C(31)	0.9647(6)	0.2851(5)	0.7181(8)	8.7(3)
C(32)	0.9047(7)	0.3068(4)	0.8061(6)	8.6(3)
C(33)	0.7846(8)	0.2912(5)	0.7809(8)	9.1(4)
C(34)	0.7248(6)	0.2537(5)	0.667(1)	10.3(4)
C(35)	0.785(1)	0.2299(6)	0.5790(7)	10.4(4)
C(36)	0.9064(8)	0.2460(5)	0.6045(7)	9.8(4)

Table 5
Selected bond lengths (Å) and angles (°) for complex cis-**5d** · C_6H_6

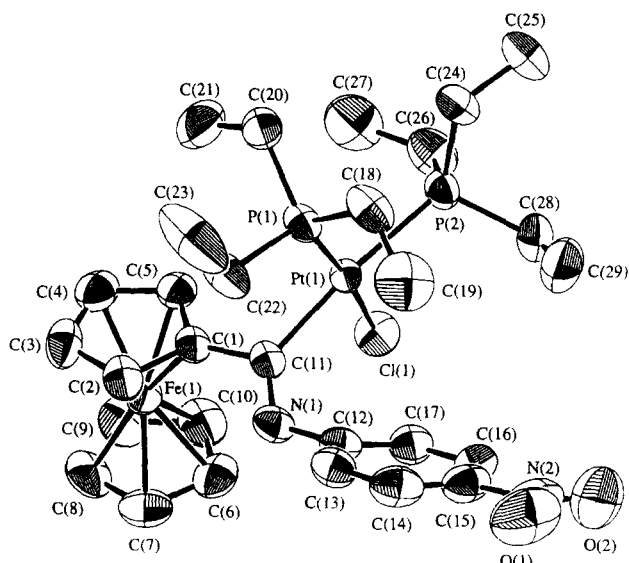|			
Pt(1)–Cl(1)	2.3786(9)	C(1)–C(11)	1.476(5)
Pt(1)–P(1)	2.225(1)	N(1)–C(11)	1.293(4)
Pt(1)–P(2)	2.354(1)	N(1)–C(12)	1.396(4)
Pt(1)–C(11)	2.050(4)		
Cl(1)–Pt(1)–P(1)	173.42(4)	P(2)–Pt(1)–C(11)	170.65(9)
Cl(1)–Pt(1)–P(2)	85.41(4)	Pt(1)–C(11)–C(1)	116.0(3)
Cl(1)–Pt(1)–C(11)	85.29(9)	Pt(1)–C(11)–N(1)	128.3(3)
P(1)–Pt(1)–P(2)	99.13(4)	N(1)–C(11)–C(1)	115.6(3)
P(1)–Pt(1)–C(11)	90.22(9)	C(11)–N(1)–C(12)	120.9(3)

Fig. 2. Molecular structure of *cis*-FcC(=NC$_6$H$_4$NO$_2$ *p*)-Pt(PEt$_3$)$_2$Cl(**5d**)·C$_6$H$_6$. The solvent molecule and hydrogen atoms have been omitted for clarity.

isomerized to a trans complex by free isocyanide through five-coordinate intermediates. Although some studies have been made on the insertion of isocyanide into the M–C bonds of *trans*-RM(PR′$_3$)$_2$X (M = Pt, Pd), only trans-iminoacyl complexes were obtained as a resulting insertion product in all reactions [13]. This is the first example of the isolation of a cis-iminoacyl complex as an intermediate in the reaction of *trans*-RPt(PR′$_3$)$_2$X giving a trans-iminoacyl complex. Since studies of the mechanism of the insertion of isocyanide into the M–C bond are sparse relative to those for CO, the result described here may provide useful information for understanding the mechanism of isocyanide insertion.

3. Experimental details

All reactions, except for those with carbon monoxide, were performed under an argon atmosphere, and the work-up was carried out in air. ^{1}H and ^{13}C NMR spectra were measured on a JEOL GX400 spectrometer using SiMe$_4$ as an internal standard and ^{31}P NMR spectra on a JEOL JMN-A400 spectrometer referred to PPh$_3$ as an external standard. IR spectra were recorded on a JASCO A-202 spectrometer. The σ-ferrocenyl-platinum complexes FcPt(cod)Cl (cod = 1,5-cyclooctadiene) and {η^5-C$_5$H$_4$Pt(cod)Cl}$_2$Fe [14], and aryl isocyanides [15] were prepared according to literature methods.

3.1. Preparation of trans-FcPt(PEt$_3$)$_2$Cl (1a)

To a solution of FcPt(cod)Cl (810 mg, 1.54 mmol) in dichloromethane (100 ml) was added PEt$_3$ (0.46 ml, 3.11 mmol). After stirring for 2 h at room temperature,

the solvent was removed under reduced pressure and the residue purified by chromatography on alumina using hexane/benzene = 1 : 2 (v/v) as an eluent. Recrystallization from hexane gave red crystals of **1a** (726 mg, yield 72%); m.p. 86–87°C. ^{1}H NMR (CDCl$_3$) δ: 4.25 (s, 2H, C$_5$H$_4$); 3.97 (s, 5H, C$_5$H$_5$); 3.76 (s, 2H, C$_5$H$_4$); 1.95–1.91 (m, 12H, CH$_2$); 1.11 (quintet, J = 8 Hz, 18H, CH$_3$) ppm. ^{13}C NMR (C$_6$D$_6$) δ: 80.7 (t, $^2J_{P-C}$ = 9 Hz, C$_5$H$_4$ *ipso*); 75.5 (s, J$_{Pt-C}$ = 66 Hz, C$_5$H$_4$); 69.0 (s, C$_5$H$_5$); 66.4 (s, J$_{Pt-C}$ = 60 Hz, C$_5$H$_4$); 13.8 (t, J = 16 Hz, CH$_2$); 8.1 (s, CH$_3$) ppm. ^{31}P NMR (CDCl$_3$) δ: 21.82 (s, $^1J_{Pt-P}$ = 2761 Hz) ppm. Anal. Found: C, 40.38; H, 6.04; Cl, 5.43; P, 9.59%. Calc. for C$_{22}$H$_{39}$ClFeP$_2$Pt: C, 40.53; H, 6.03; Cl, 5.44; P, 9.50%.
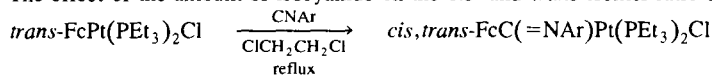
3.2. Preparation of trans-FcPt(PEt$_3$)$_2$Br (1b)

To a solution of **1a** (166 mg, 0.254 mmol) in methanol (20 ml) was added a solution of NaBr (219 mg, 2.13 mmol) in 30 ml of methanol and the mixture stirred for 3 h at room temperature. After removal of the solvent in vacuo, the residue was dissolved in 50 ml of benzene and washed with 250 ml of water three times. The organic layer was dried over Na$_2$SO$_4$ and benzene was evaporated once more under vacuum. Recrystallization from hexane gave red crystals of **1b** (136 mg, yield 77%); m.p. 97–100°C ^{1}H NMR (CDCl$_3$) δ: 4.26 (s, 2H, C$_5$H$_4$); 3.96 (s, 5H, C$_5$H$_5$); 3.75 (s, 2H, J$_{Pt-H}$ = 31 Hz, C$_5$H$_4$); 2.01–1.93 (m, 12H, CH$_2$); 1.10 (quintet, J = 7 Hz, 18H, CH$_3$) ppm. ^{13}C NMR (C$_6$D$_6$) δ: 84.3 (t, $^2J_{Pt-C}$ = 8 Hz, C$_5$H$_4$ *ipso*); 75.2 (s, J$_{Pt-C}$ = 68 Hz, C$_5$H$_4$); 69.2 (s, C$_5$H$_5$); 66.3 (s, J$_{Pt-C}$ = 63 Hz, C$_5$H$_4$); 14.4 (t, J = 17 Hz, CH$_2$); 8.2 (s, CH$_3$) ppm. ^{31}P NMR (CDCl$_3$) δ: 19.52 (s, $^1J_{Pt-P}$ = 2738 Hz) ppm. Anal. Found: C, 37.72; H, 5.56; Br, 11.36; P, 8.70%. Calc. for C$_{22}$H$_{39}$BrFeP$_2$Pt: C, 37.95; H, 5.64; Br, 11.47; P, 8.90%.

3.3. Preparation of trans-FcPt(PEt$_3$)$_2$NCS (1c)

As described in the preparation of **1b**, treatment of **1a** (365 mg, 0.560 mmol) with NaSCN (363 mg, 4.47 mmol) in 100 ml of acetone gave red crystals of **1c** (303 mg, yield 80%); m.p. 121–122°C. IR (KBr) (cm^{-1}): 2100 ν(C≡N). ^{1}H NMR (CDCl$_3$) δ: 4.26 (s, 2H, C$_5$H$_4$); 3.97 (s, 5H, C$_5$H$_5$); 3.68 (s, 2H, C$_5$H$_4$); 1.89–1.86 (m, 12H, CH$_2$); 1.13 (quintet, J = 8 Hz, 18H, CH$_3$) ppm. ^{13}C NMR (CDCl$_3$) δ: 134.2 (s, SCN); 74.6 (s, J$_{Pt-C}$ = 59 Hz, C$_5$H$_4$); 68.6 (s, C$_5$H$_5$); 66.5 (s, J$_{Pt-C}$ = 54 Hz, C$_5$H$_4$); 13.8 (t, J = 16 Hz, CH$_2$); 7.1 (s, CH$_3$) ppm; the resonance attributed to the *ipso* carbon of C$_5$H$_4$ was not detected. ^{31}P NMR (CDCl$_3$) δ: 23.43 (s, $^1J_{Pt-P}$ = 2696 Hz) ppm. Anal. Found: C, 41.16; H, 5.61; N, 2.27; P, 9.00; S, 4.66%. Calc. for C$_{23}$H$_{39}$FeNP$_2$PtS: C, 40.96; H, 5.83; N, 2.08; P, 9.18; S, 4.75%.

Table 6
The effect of the amount of isocyanide on the *cis*- and *trans*-isomer ratio of iminoacyl complexes **5**

$$\textit{trans-}FcPt(PEt_3)_2Cl \xrightarrow[\text{reflux}]{\dfrac{CNAr}{ClCH_2CH_2Cl}} \textit{cis,trans-}FcC(=NAr)Pt(PEt_3)_2Cl$$

(1a)   (5)

Fc = $(C_5H_4)Fe(C_5H_5)$

Entry	Ar	CNAr/1a	Yield (%) [a,b]	*cis/trans* [a]
1	$C_6H_4CH_3$-p	0.7	64	77:23
2	$C_6H_4CH_3$-p	1.1	90	0:100
3	$C_6H_4NO_2$-p	0.7	96	84:16
4	$C_6H_4NO_2$-p	1.1	100	19:81
5 [c]	$C_6H_3(CH_3)_2$-2,6	0.7	57	34:66
6 [c]	$C_6H_3(CH_3)_2$-2,6	1.1	61	35:65

[a] Determined by ^{31}P NMR spectroscopy. [b] Entry Nos. 1, 3 and 5: based on CNAr; Entry Nos. 2, 4 and 6: Based on **1a**. [c] ^{31}P NMR spectra were measured after Al_2O_3 column chromatography since the signals were broad.

3.4. Preparation of (trans-$\{\eta^5$-$C_5H_4\}Pt(PEt_3)_2Cl\}_2Fe$ (3)

Treatment of $\{\eta^5$-$C_5H_4Pt(cod)Cl\}_2Fe$ (307 mg, 0.356 mmol) with PEt_3 (0.22 ml, 1.49 mmol) similar to that of **1a** gave red crystals of **3** (292 mg, yield 73%); m.p. 119–120°C. ^{1}H NMR (CDCl$_3$) δ: 4.06 (s, 4H, C_5H_4); 3.46 (s, 4H, $J_{Pt-H} = 29$ Hz, C_5H_4); 1.96–1.91 (m, 24H, CH_2); 1.12 (quintet, $J = 8$ Hz, 36H, CH_3) ppm. ^{13}C NMR (CDCl$_3$) δ: 76.2 (s, C_5H_4); 66.7 (s, C_5H_4); 13.6 (t, $J = 16$ Hz, CH_2); 8.0 (s, CH_3) ppm; the resonance attributed to the *ipso* carbon of C_5H_4 was not detected. ^{31}P NMR (CDCl$_3$) δ: 20.98 (s, $^1J_{Pt-P} = 2803$ Hz) ppm. Anal. Found: C, 36.83; H, 5.93; Cl, 6.54; P, 11.00%. Calc. for $C_{34}H_{68}Cl_2FeP_4Pt_2$: C, 36.54; H, 6.13; Cl, 6.06; P, 11.08%.

3.5. Reaction of trans-FcPt(PEt$_3$)$_2$Cl (1a) with CO

A dichloromethane solution of **1a** (79 mg, 0.121 mmol) was placed in an autoclave of 100 ml volume and the reaction system charged with CO (30 kg cm^{-2}). After standing for 24 h at room temperature, the solvent was removed under vacuum. Red–orange crystals of **2a** (74 mg, yield 90%) were obtained by recrystallization from toluene/hexane; m.p. 154–155°C. IR (KBr) (cm^{-1}): 1590 ν(C=O). ^{1}H NMR (CDCl$_3$) δ: 4.69 (t, 2H, $J = 2$ Hz, C_5H_4); 4.27 (s, 2H, C_5H_4); 4.16 (s, 5H, C_5H_5); 1.90–1.74 (m, 12H, CH_2); 1.14 (quintet, $J = 8$ Hz, 18H, CH_3) ppm. ^{13}C NMR (CDCl$_3$) δ: 213.7 (s, CO); 97.2 (t, $^3J_{P-C} = 4$ Hz, C_5H_4 *ipso*); 69.2 (s, C_5H_5); 69.0 (s, C_5H_4); 68.5 (s, C_5H_4); 14.4 (t, $J = 17$ Hz, CH_2); 7.9 (s, CH_3) ppm. ^{31}P NMR (CDCl$_3$) δ: 19.04 (s, $^1J_{Pt-P} = 3070$ Hz) ppm. Anal. Found: C, 40.90; H, 5.82; Cl, 5.11; P, 9.00%. Calc. for $C_{23}H_{39}ClFeOP_2Pt$: C, 40.63; H, 5.78; Cl, 5.21; P, 9.11%.

3.6. Reactions of trans-FcPt(PEt$_3$)$_2$Br (1b), trans-FcPt(PEt$_3$)$_2$NCS (1c) or {trans-(η^5-C_5H_4)Pt(PEt$_3$)$_2$Cl}$_2$Fe (3) with CO

These reactions were carried out by a procedure similar to that of **1a**.

Compound **2b**: Red–orange crystals, yield 89%; m.p. 161–162°C. IR (KBr) (cm^{-1}): 1590 ν(C=O). ^{1}H NMR (CDCl$_3$) δ: 4.69 (s, 2H, C_5H_4); 4.27 (s, 2H, C_5H_4); 4.16 (s, 5H, C_5H_5); 2.00–1.76 (m, 12H, CH_2); 1.13 (quintet, $J = 8$ Hz, 18H, CH_3) ppm. ^{13}C NMR (CDCl$_3$) δ: 214.3 (s, CO); 96.7 (t, $^3J_{P-C} = 5$ Hz, C_5H_4 *ipso*); 69.2 (s, C_5H_5); 69.2 (s, C_5H_4); 68.6 (s, C_5H_4); 15.0 (t, $J = 17$ Hz, CH_2); 7.9 (s, CH_3) ppm. ^{31}P NMR (CDCl$_3$) δ: 18.75 (s, $^1J_{Pt-P} = 3058$ Hz) ppm. Anal. Found: C, 38.13; H, 5.25; Br, 11.04; P, 8.78%. Calc. for $C_{23}H_{39}BrFeOP_2Pt$: C, 38.14; H, 5.43; Br, 11.03; P, 8.55%.

Compound **2c**: Red crystals, yield 93%; m.p. 146–147°C. IR (KBr) (cm^{-1}): 2120 ν(C≡N); 1595 ν(C=O). ^{1}H NMR (CDCl$_3$) δ: 4.61 (t, $J = 2$ Hz, 2H, C_5H_4); 4.29 (t, $J = 2$ Hz, 2H, C_5H_4); 4.14 (s, 5H, C_5H_5); 1.82–1.65 (m, 12H, CH_2); 1.16 (quintet, $J = 8$ Hz, 18H, CH_3) ppm. ^{13}C NMR (CDCl$_3$) δ: 216.3 (s, CO); 137.6 (s, SCN); 97.0 (t, $^3J_{P-C} = 4$ Hz, C_5H_4 *ipso*); 69.2 (s, C_5H_5); 68.9 (s, C_5H_4); 68.8 (s, C_5H_4); 15.0 (t, $J = 16$ Hz, CH_2); 7.9 (s, CH_3) ppm. ^{31}P NMR (CDCl$_3$) δ: 19.81 (s, $^1J_{Pt-P} = 2993$ Hz) ppm. Anal. Found: C, 41.25; H, 5.47; N, 2.14; P, 8.80; S, 4.56%. Calc. for $C_{24}H_{39}FeONP_2PtS$: C, 41.03; H, 5.60; N, 1.99; P, 8.82; S, 4.56%.

Compound **4**: This compound was purified by chromatography on silica gel using chloroform as an eluent. Orange crystals, yield 84%; m.p. 147–148°C. IR (KBr) (cm^{-1}): 1590 ν(C=O). ^{1}H NMR (CDCl$_3$) δ: 4.63 (t, $J = 2$ Hz, 4H, C_5H_4); 4.26 (t, $J = 2$ Hz, 4H, C_5H_4); 1.90–1.72 (m, 24H, CH_2); 1.13 (quintet, $J = 8$ Hz, 36H, CH_3) ppm. ^{13}C NMR (CDCl$_3$) δ: 213.4 (s, CO);

97.8 (t, $^3J_{P-C}$ = 5 Hz, C_5H_4 ipso); 70.4 (s, C_5H_4); 69.6 (s, C_5H_4); 14.4 (t, J = 16 Hz, CH_2); 7.9 (s, CH_3) ppm. ^{31}P NMR (CDCl$_3$) δ: 19.33 (s, J_{Pt-P} = 3046 Hz) ppm. Anal. Found: C, 36.67; H, 5.81; Cl, 6.27; P, 10.77%. Calc. for $C_{36}H_{68}Cl_2FeO_2P_4Pt_2$: C, 36.84; H, 5.84; Cl, 6.04; P, 10.56%.

3.7. Reaction of trans-FcPt(PEt$_3$)$_2$Cl (1a) with an equimolar amount of p-tolyl isocyanide

To a solution of **1a** (158 mg, 0.242 mmol) in 20 ml of 1,2-dichloroethane was added p-tolyl isocyanide (32 mg, 0.273 mmol) and the mixture stirred under reflux for 6 h. After removal of the solvent, the residue was chromatographed on an alumina column with chloroform. Recrystallization from toluene/hexane gave red crystals of trans-**5a** (89 mg, yield 48%); m.p. 195–197°C. IR (KBr) (cm^{-1}): 1550 ν(C=N). ^{1}H NMR (CDCl$_3$) δ: 7.66 (d, J = 9 Hz, 2H, Ar); 7.09 (d, J = 9 Hz, 2H, Ar); 4.75 (s, 2H, C_5H_4); 4.21 (s, 5H, C_5H_5); 4.20 (s, 2H, C_5H_4); 2.30 (s, 3H, ArCH_3); 1.77–1.57 (m, 12H, CH_2); 1.02 (quintet, J = 8 Hz, 18H, PCH$_2$CH_3) ppm. ^{13}C NMR (CDCl$_3$) δ: 173.8 (s, C=N); 151.5 (s, ipso C of Ar bound to -N=C); 133.2 (s, ipso C of Ar bound to CH$_3$); 128.6 (s, Ar); 121.2 (s, Ar); 97.5 (s, ipso C of C_5H_4); 70.8 (s, C_5H_4); 69.4 (s, C_5H_5); 67.3 (s, C_5H_4); 20.9 (s, ArCH_3); 15.1 (t, J = 17 Hz, CH_2); 8.0 (s, PCH$_2$CH_3) ppm. ^{31}P NMR (CDCl$_3$) δ: 14.90 (s, $^1J_{Pt-P}$ = 2904 Hz) ppm. Anal. Found: C, 46.56; H, 6.02; Cl, 4.54; N, 1.73; P, 8.01%. Calc. for $C_{30}H_{46}ClFeNP_2Pt$: C, 46.85; H, 6.03; Cl, 4.61; N, 1.82; P, 8.06%.

3.8. Reaction of trans-FcPt(PEt$_3$)$_2$Cl (1a) with an equimolar amount of p-methoxyphenyl, 2,6-xylyl or p-nitrophenyl isocyanide

These reactions were carried out by a procedure similar to that with p-tolyl isocyanide.

trans-**5b**: Red–orange crystals, yield 60%; m.p. 167–168°C. IR (KBr) (cm^{-1}): 1550 ν(C=N). ^{1}H NMR (CDCl$_3$) δ: 7.78 (d, J = 9 Hz, 2H, Ar); 6.85 (d, J = 9 Hz, 2H, Ar); 4.73 (t, J = 2 Hz, 2H, C_5H_4); 4.21 (s, 5H, C_5H_5); 4.20 (s, 2H, C_5H_4); 3.80 (s, 3H, OCH$_3$); 1.78–1.58 (m, 12H, CH_2); 1.03 (quintet, J = 8 Hz, 18H, CH$_2$CH_3) ppm. ^{13}C NMR (CDCl$_3$) δ: 172.8 (s, C=N); 156.7 (s, ipso C of Ar bound to OCH$_3$); 147.6 (s, $^3J_{Pt-C}$ = 73 Hz, ipso C of Ar bound to -N=C); 122.4 (s, Ar); 113.5 (s, Ar); 97.5 (s, ipso C of C_5H_4); 70.8 (s, C_5H_4); 69.4 (s, C_5H_5); 67.4 (s, C_5H_4); 55.6 (s, OCH$_3$); 15.0 (t, J = 16 Hz, CH_2); 8.1 (s, CH$_2$CH_3) ppm. ^{31}P NMR (CDCl$_3$) δ: 14.87 (s, $^1J_{Pt-P}$ = 2904 Hz) ppm. Anal. Found: C, 46.10; H, 5.92; Cl, 4.59; N, 1.77; P, 8.03%. Calc. for $C_{30}H_{46}ClFeNOP_2Pt$: C, 45.90; H, 5.91; Cl, 4.52; N, 1.78; P, 7.89%.

trans-**5c**: Red–orange crystals, yield 30%; m.p. 203–205°C. IR (KBr) (cm^{-1}): 1555 ν(C=N). ^{1}H NMR (CDCl$_3$) δ: 6.98 (d, J = 8 Hz, 2H, Ar); 6.85 (t, J = 8 Hz, 1H, Ar); 4.87 (t, J = 2 Hz, 2H, C_5H_4); 4.26 (t, J = 2 Hz, C_5H_4); 4.20 (s, 5H, C_5H_5); 2.58 (s, 6H, ArCH_3); 1.67–1.62 (m, 12H, CH_2); 1.01 (quintet, J = 8 Hz, 18H, CH$_2$CH_3) ppm. ^{13}C NMR (CDCl$_3$) δ: 170.3 (s, C=N); 150.1 (s, ipso C of Ar bound to -N=C); 128.6 (s, Ar); 128.3 (s, ipso C of Ar bound to CH$_3$); 122.4 (s, Ar); 100.5 (s, ipso C of C_5H_4); 71.0 (s, C_5H_4); 69.0 (s, C_5H_5); 67.0 (s, C_5H_4); 21.9 (s, ArCH_3); 15.5 (t, J = 16 Hz, CH_2); 8.4 (s, CH$_2$CH_3) ppm. ^{31}P NMR (CDCl$_3$) δ: 13.95 (s, $^1J_{Pt-P}$ = 3004 Hz) ppm. Anal. Found: C, 47.52; H, 6.12; Cl, 4.33; N, 1.66; P, 7.86%. Calc. for $C_{31}H_{48}ClFeNP_2Pt$: C, 47.55; H, 6.18; Cl, 4.53; N, 1.79; P, 7.91%.

cis-**5d**: Red crystals, yield 70%; m.p. 192–193°C. IR (KBr) (cm^{-1}): 1550 ν(C=N). ^{1}H NMR (CDCl$_3$) δ: 8.18 (d, J = 9 Hz, 2H, Ar); 7.76 (d, J = 9 Hz, 2H, Ar); 4.97 (s, 1H, C_5H_4); 4.90 (s, 1H, C_5H_4); 4.35 (s, 1H, C_5H_4); 4.34 (s, 5H, C_5H_5); 4.28 (s, 1H, C_5H_4); 1.99–1.92 (m, 6H, CH_2); 1.61 (quintet, J = 8 Hz, 6H, CH_2); 1.15 (dt, J_{H-H} = 8 Hz, $^3J_{P-H}$ = 16 Hz, 9H, CH$_3$); 0.68 (dt, J_{H-H} = 8 Hz, $^3J_{P-H}$ = 17 Hz, 9H, CH$_2$CH_3) ppm. ^{13}C NMR (CDCl$_3$) δ: 200.4 (dd, $^2J_{P-C}$ = 106, 5 Hz, C=N); 161.7 (d, $^4J_{P-C}$ = 8 Hz, ipso C of Ar bound to -N=C); 142.4 (s, ipso C of Ar bound to NO$_2$); 124.1 (s, Ar); 122.1 (s, Ar); 93.7 (d, $^3J_{P-C}$ = 15 Hz, ipso C of C_5H_4); 72.7 (s, C_5H_4); 70.4 (s, C_5H_5 and C_5H_4); 69.0 (s, C_5H_4); 68.3 (s, C_5H_4); 17.3 (dd, $^1J_{P-C}$ = 38 Hz, $^3J_{P-C}$ = 3 Hz, CH_2); 14.1 (d, $^1J_{P-C}$ = 27 Hz, CH_2); 7.9 (s, CH$_3$); 7.4 (s, CH$_3$) ppm. ^{31}P NMR (CDCl$_3$) δ: 13.90 (d, $^1J_{Pt-P}$ = 1588 Hz, $^2J_{P-P}$ = 18 Hz); 9.54 (d, $^1J_{Pt-P}$ = 4219 Hz, $^2J_{P-P}$ = 18 Hz) ppm. Anal. Found: C, 43.64; H, 5.49; Cl, 4.45; N, 3.32; P, 7.76%. Calc. for $C_{29}H_{43}ClFeN_2O_2P_2Pt$: C, 43.54; H, 5.42; Cl, 4.43; N, 3.50; P, 7.74%.

3.9. Reaction of {trans-(η^5-C$_5$H$_4$)Pt(PEt$_3$)$_2$Cl}$_2$Fe (3) with 2 equiv. of p-tolyl isocyanide

Treatment of **3** similar to that of **1a** afforded **6** as red crystals in 38% yield; m.p. 217–218°C. IR (KBr) (cm^{-1}): 1545 ν(C=N). ^{1}H NMR (CDCl$_3$) δ: 7.69 (d, J = 9 Hz, 4H, Ar); 7.09 (d, J = 9 Hz, 4H, Ar); 4.78 (s, 4H, C_5H_4); 4.29 (s, 4H, C_5H_4); 2.30 (s, 6H, ArCH_3); 1.75–1.59 (m, 24H, CH_2); 1.03 (quintet, J = 8 Hz, 36H, PCH$_2$CH_3) ppm. ^{13}C NMR (CDCl$_3$) δ: 173.8 (s, C=N); 151.3 (s, ipso C of Ar bound to -N=C); 133.4 (s, ipso C of Ar bound to CH$_3$); 128.7 (s, Ar); 121.2 (s, Ar); 97.1 (s, ipso C of C_5H_4); 71.3 (s, C_5H_4); 71.2 (s, C_5H_4); 20.9 (s, ArCH_3); 15.1 (t, J = 16 Hz, CH_2); 8.1 (s, PCH$_2$CH_3) ppm. ^{31}P NMR (CDCl$_3$) δ: 14.94 (s, J_{Pt-P} = 2904 Hz) ppm. Anal. Found: C, 44.68; H, 5.96; Cl, 4.97; N, 1.83; P, 9.13%. Calc. for

$C_{50}H_{82}Cl_2FeN_2P_4Pt_2$: C, 44.42; H, 6.11; Cl, 5.24; N, 2.07; P, 9.16%.

3.10. Reaction of trans-FcPt(PEt$_3$)$_2$Cl (1a) with 0.7 equiv. of p-tolyl isocyanide

Complex 1a (241 mg, 0.369 mmol) was treated with p-tolyl isocyanide (34 mg, 0.290 mmol) under reflux in 20 ml of 1,2-dichloroethane for 6 h. The solvent was evaporated under reduced pressure and the residue purified by column chromatography on alumina using chloroform as an eluent. Recrystallization from toluene/hexane gave red crystals of cis-5a (86 mg, yield 39%); m.p. 167–168°C. IR (KBr) (cm^{-1}): 1550 ν(C=N). ^{1}H NMR (CDCl$_3$) δ: 7.56 (d, J = 8 Hz, 2H, Ar); 7.02 (d, J = 8 Hz, 2H, Ar); 4.93 (t, J = 1 Hz, 1H, C$_5$H$_4$); 4.85 (s, 1H, C$_5$H$_4$); 4.28 (s, 5H, C$_5$H$_5$); 4.21–4.19 (m, 1H, C$_5$H$_4$); 4.15 (s, 1H, C$_5$H$_4$); 2.26 (s, 3H, ArCH_3); 1.93–1.86 (m, 6H, CH$_2$); 1.59–1.46 (m, 6H, CH$_2$); 1.12 (dt, J_{H-H} = 8 Hz, $^3J_{P-H}$ = 16 Hz, 9H, PCH$_2$CH_3); 0.57 (dt, J_{H-H} = 8 Hz, $^3J_{P-H}$ = 17 Hz, 9H, PCH$_2$CH_3) ppm. ^{13}C NMR (CDCl$_3$) δ: 194.2 (d, $^2J_{P-C}$ = 106 Hz, C=N); 153.3 (d, $^4J_{P-C}$ = 10 Hz, ipso C of Ar bound to –N=C); 131.7 (s, ipso C of Ar bound to CH$_3$); 128.5 (s, Ar); 122.2 (s, Ar); 94.4 (d, $^3J_{P-C}$ = 17 Hz, ipso C of C$_5$H$_4$); 72.7 (s, C$_5$H$_4$); 70.3 (s, C$_5$H$_5$); 69.8 (s, C$_5$H$_4$); 68.2 (s, C$_5$H$_4$); 67.6 (s, C$_5$H$_4$); 20.9 (s, ArCH$_3$); 17.4 (dd, $^1J_{P-C}$ = 38 Hz, $^3J_{P-C}$ = 3 Hz, CH$_2$); 14.1 (d, $^1J_{P-C}$ = 25 Hz, CH$_2$); 7.9 (s, CH$_2$CH_3); 7.1 (s, CH$_2$CH_3) ppm. ^{31}P NMR (CDCl$_3$) δ: 14.53 (d, $^1J_{Pt-P}$ = 1559 Hz, $^2J_{P-P}$ = 18 Hz); 9.46 (d, $^1J_{Pt-P}$ = 4337 Hz, $^2J_{P-P}$ = 18 Hz) ppm. Anal. Found: C, 46.66; H, 6.04; Cl, 4.55; N, 1.72; P, 8.03%. Calc. for C$_{30}$H$_{46}$ClFeNP$_2$Pt: C, 46.85; H, 6.03; Cl, 4.61; N, 1.82; P, 8.06%.

3.11. Reaction of trans-FcPt(PEt$_3$)$_2$Cl (1a) with 1.1 equiv. of p-nitrophenyl isocyanide

Similar treatment of 1a (42 mg, 0.64 mmol) with p-nitrophenyl isocyanide (11 mg, 0.074 mmol) afforded trans-5d (40 mg, yield 78%); m.p. 200–201°C. IR (KBr) (cm^{-1}): 1540 ν(C=N). ^{1}H NMR (CDCl$_3$) δ: 8.19 (d, J = 9 Hz, 2H, Ar); 7.76 (d, J = 9 Hz, 2H, Ar); 4.78 (s, 2H, C$_5$H$_4$); 4.29 (s, 2H, C$_5$H$_4$); 4.21 (s, 5H, C$_5$H$_5$); 2.30 (s, 3H, ArCH_3); 1.76–1.64 (m, 12H, CH$_2$); 1.02 (quintet, J = 8 Hz, 18H, PCH$_2$CH_3) ppm. ^{13}C NMR (CDCl$_3$) δ: 183.1 (s, C=N); 159.4 (s, ipso C of Ar bound to –N=C); 143.3 (s, ipso C of Ar bound to NO$_2$); 124.2 (s, Ar); 121.0 (s, Ar); 96.7 (s, ipso C of C$_5$H$_4$); 71.0 (s, C$_5$H$_4$); 69.6 (s, C$_5$H$_5$); 68.2 (s, C$_5$H$_4$); 15.0 (t, J = 17 Hz, CH$_2$); 8.0 (s, CH$_3$) ppm. ^{31}P NMR (CDCl$_3$) δ: 15.93 (s, $^1J_{Pt-P}$ = 2821 Hz) ppm. Anal. Found: C, 43.60; H, 5.41; Cl, 4.55; N, 3.69; P, 7.71%. Calc. for C$_{29}$H$_{43}$ClFeN$_2$O$_2$P$_2$Pt: C, 43.54; H, 5.42; Cl, 4.43; N, 3.50; P, 7.74%.

3.12. Reaction of trans-FcPt(PEt$_3$)$_2$Cl (1a) with 0.7 equiv. of 2,6-xylyl isocyanide

Similar treatment of 1a (206 mg, 0.316 mmol) with 2,6-xylyl isocyanide (30 mg, 0.228 mmol) afforded a mixture of trans- and cis-5c. Although cis-5c was not isolated due to the low yield, its existence was detected by the appearance in the ^{31}P NMR spectrum of the signal at δ 12.73 (d, $^1J_{Pt-P}$ = 1508 Hz, $^2J_{P-P}$ = 17 Hz); and 17.11 (d, $^1J_{Pt-P}$ = 4356 Hz, $^2J_{P-P}$ = 17 Hz) ppm.

3.13. X-ray crystallographic studies of 2a and cis-5d

Single crystals of 2a and 5d suitable for an X-ray diffraction analysis were obtained by slow evaporation of benzene solutions, and mounted on glass fibers with epoxy resin. Diffraction measurements were made on a Rigaku AFC5R diffractometer with graphite monochromated Mo Kα radiation (λ = 0.71069 Å) using an ω–2θ scan technique with a scan rate of 8 deg min^{-1}. Unit cells were determined and refined by a least-square method using 24 reflections in the range $18° < 2\theta < 25°$ for 2a and 25 reflections in the range $34° < 2\theta < 35°$ for 5d. The data for weak reflections [$I < 10\sigma(I)$] were measured three times and averaged. Three standard reflections were monitored at every 150 measurements and no damage was observed. Intensities were corrected for Lorentz and polarization effects and an empirical absorption correction was made using the ψ-scan technique.

Complexes 2a and 5d crystallized in the orthorhombic and triclinic systems, respectively. The positions of the metal atoms were located by the Patterson method. Subsequent difference Fourier maps revealed the positions of all the non-hydrogen atoms. All non-hydrogen atoms were refined anisotropically and all hydrogen atoms were included at the calculated positions using isotropic thermal parameters. The final cycles of full-matrix least-squares refinement were converged, and the largest parameter shifts against errors were 0.27 for 2a and 0.63 for 5d, respectively. The unweighted and weighted agreement factors were $R = \Sigma \mid \mid F_o \mid - \mid F_c \mid \mid / \Sigma \mid F_o \mid = 0.031$ and $R_w = [\Sigma w(\mid F_o \mid - \mid F_c \mid)^2 / \sigma wF_o^2]^{1/2} = 0.024$ for 2a, and $R = 0.022$ and $R_w = 0.019$ for 5d, respectively. All calculations were performed on a VAX 3100 station using the TEXSAN crystallographic software package.

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