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Cationic phenyl and chloro-platinum(II) complexes with cyanamides and cyanoguanidine. X-ray structure of *trans*-[Pt(Ph)(NCNMe$_2$)(PPh$_3$)$_2$][BPh$_4$]

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Dedicated to Professor Andrew Wojcicki on the occasion of his retirement from the Ohio State University

Abstract

The phenyl-platinum(II) organocyanamide *trans*-[Pt(Ph)(NCNR$_2$)(PPh$_3$)$_2$][BPh$_4$] (R = Me **1a**, Et **1b**) or cyanoguanidine *cis*-[Pt(Ph){NCNC(NH$_2$)$_2$}(PPh$_3$)$_2$][BPh$_4$] (**2**) complexes have been prepared by treatment of *cis*-[PtCl$_2$(PPh$_3$)$_2$] in THF with NCNR$_2$ or NCNC(NH$_2$)$_2$, respectively, in the presence of Na[BPh$_4$], whereas the cyanoguanidine chloro-complex *cis*-[PtCl{NCNC(NH$_2$)$_2$}(PPh$_3$)$_2$][BF$_4$] (**3**) has been obtained by using Tl[BF$_4$] instead of Na[BPh$_4$]. Complex **3** reacts further with cyanoguanidine, in the presence of Na[BPh$_4$], to produce the di(cyanoguanidine) *cis*-[Pt{NCNC(NH$_2$)$_2$}$_2$(PPh$_3$)$_2$][BPh$_4$]$_2$ complex **5**, whereas the amine complex *cis*-[PtCl(NH$_2$R′)(PPh$_3$)$_2$][BF$_4$] (R′ = CH$_2$C$_6$H$_4$Me-4, **4**) is formed on reaction of the former with NH$_2$R′ in CH$_2$Cl$_2$. The X-ray structure of **1a** is also reported.

Keywords: Cyanoguanidine; Cyanamide; Phenylation; Platinum complexes

1. Introduction

The possible active role of the tetraphenylborate anion in coordination chemistry has been well recognized and is a matter of current interest from both the structural and synthetic points of view, with potential significance in catalysis.

The detection (by nuclear Overhauser effects) of interionic contacts in solution between BPh$_4^-$ and some organometallic complexes has been reported [1]. The anion can ligate a metal center in a variety of modes [2] and can act as a phenylation agent either to the metal [3] or to other substrates (e.g. mono- and di-enes [4], allyls [5] and acyls [6]) or even as a BPh$_3$ transfer reagent to cyanide [7] or to the cyanosilane N≡CSiMe$_3$ (or a derivative) [8] to produce the isocyanotriphenylborate CNBPh$_3^-$ ligand. The metal phenylation in some cases involves replacement of an halide ligand which normally requires solvent refluxing conditions, as in the reactions of Na[BPh$_4$] with *cis*-[PtCl$_2$(PEt$_3$)$_2$] [9], [RuCl(η^5-C$_5$H$_5$)(CO)$_2$] [10] or [NiX(L)][BPh$_4$] [X = Cl, Br; L = N(C$_2$H$_4$AsPh)$_3$] [11] to give *trans*-[Pt(Ph)$_2$(PEt$_3$)$_2$], [Ru(Ph)(η^5-C$_5$H$_5$)(CO)$_2$] or [Ni(Ph)L][BPh$_4$], respectively.

In the current study, on attempting the preparation of di(alkylcyanamide) or di(cyanoguanidine)platinum(II) complexes on reaction of a THF suspension of *cis*-[PtCl$_2$(PPh$_3$)$_2$] with the appropriate cyano-reagent in the presence of Na[BPh$_4$], we observed the occurrence of metal phenylation, smoothly and at room temperature,

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to give the corresponding phenylated mono(cyano-reagent) complexes. Their syntheses and properties, as well as of a related chloro-cyanoguanidine complex and further reactions are now described.

This work also provides a contribution to the development of the chemistry of platinum complexes with cyanamides and cyanoguanidine ligands [12–14], which is still underdeveloped in spite of the interest of these unsaturated nitrogen-compounds in synthesis [15,16] and their significance in biology [17,18]. It also falls within our interest on the extension to platinum of the investigation of the coordination chemistry of cyanamides at different transition metal centers namely of Mo [19,20], Re [21–23] and Fe [24], and, in a broader sense, on the activation of small molecules of synthetic and biological importance [25–52].

2. Results and discussion

2.1. Syntheses

Treatment of a THF solution of *cis*-$[PtCl_2(PPh_3)_2]$ with an excess of the organocyanamide $NCNR_2$ (R = Me or Et) (sixfold molar ratio) or of the cyanoguanidine $NCNC(NH_2)_2$ (fourfold molar ratio), in the presence of $Na[BPh_4]$ (added in the same molar amount as that of the cyano-reagent), resulted, at room temperature, in the formation of the corresponding complexes *trans*-$[Pt(Ph)(NCNR_2)(PPh_3)_2][BPh_4]$ (R = Me **1a**, Et **1b**) or *cis*-$[Pt(Ph)\{NCNC(NH_2)_2\}(PPh_3)_2][BPh_4]$ (**2**) (Scheme 1, reactions 1 or 2, respectively).

In these reactions, not only the expected chloride replacement by the cyano-species has occurred, but also its unusual substitution for a phenyl group originated from tetraphenylborate with the conceivable concomitant formation of the $THF{\cdot}BPh_3$ Lewis acid–base adduct. Even diphenylation was detected, in the case of the reaction with $NCNMe_2$, affording, besides **1a**, the known [53] diphenylated product *trans*-$[Pt(Ph)_2(PPh_3)_2]$.

When $Tl[BF_4]$ was used as the chloride abstractor instead of $Na[BPh_4]$, simple halide replacement was observed and *cis*-$[PtCl\{NCNC(NH_2)_2\}(PPh_3)_2][BF_4]$ (**3**) was the product from the reaction of *cis*-$[PtCl_2(PPh_3)_2]$ with cyanoguanidine (reaction 3, Scheme 1). A compound, initially formulated [12] in an analogous way but with the $[BPh_4]^-$ counter-ion, i.e. *cis*-$[PtCl\{NCNC(NH_2)_2\}(PPh_3)_2][BPh_4]$, was isolated upon addition of MeOH to an acetone solution of the product from the prolonged reaction of *cis*-$[PtCl_2(PPh_3)_2]$ with cyanoguanidine in THF, in the presence of $Na[BPh_4]$. However, it should be reformulated (on the basis of identical IR and NMR spectroscopic data and elemental analysis) as the azametallacycle *cis*-$[(PPh_3)_2$-Pt-$\{NHC(OMe)=NC(NH_2)=NH\}][BPh_4]$ [13] formed upon nucleophilic addition of the alcohol to the cyano group of a cyanoguanidine ligand at the intermediate *cis*-$[Pt\{NCNC(NH_2)_2\}_2(PPh_3)_2]^{2+}$, combined with deprotonation and chelation of the guanidine unit.

It is noteworthy to mention that in reactions (1) and (2) the metal phenylation proceeds smoothly at room temperature (for ca. 5 days) in preference to the replacement of both chloride ligands by two dialkylcyanamides, with formation of the phenylated complexes **1** and **2** instead of the expected di(alkylcyanamide) products. The use of a lower excess of $Na[BPh_4]$ and of the cyanamide, and shorter reaction times, results in the formation of the known [12] mono(alkylcyanamide) complexes *cis*-$[PtCl(NCNR_2)(PPh_3)_2][BPh_4]$.

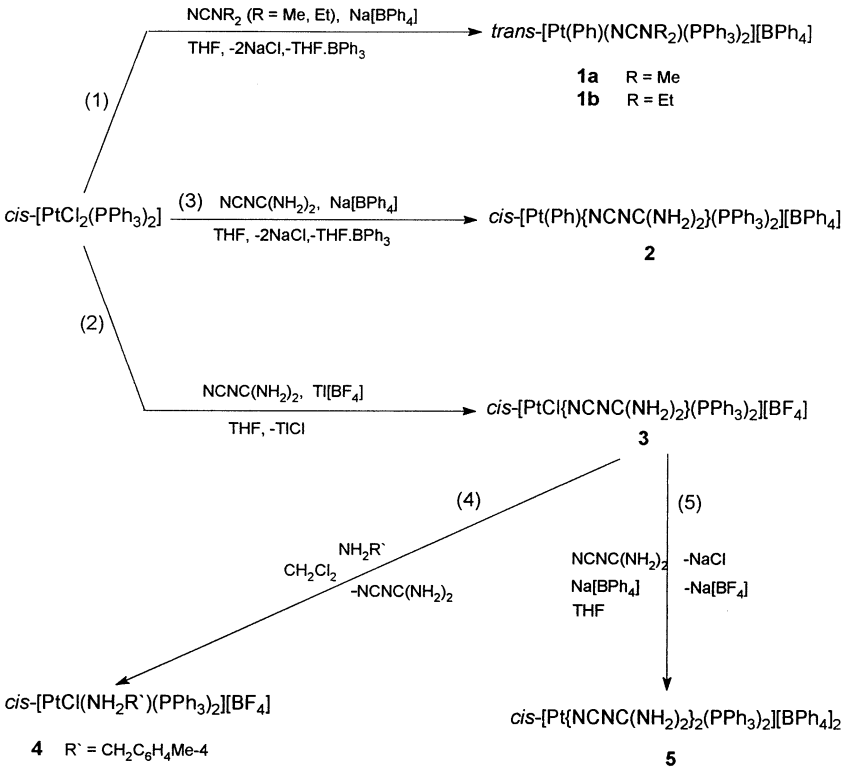
A *cis*-to-*trans* isomerization also occurs in reactions (1), as observed in the formation of *trans*-$[Pt(Ph)L(PR_3)_2]^+$ (L = MeOH, H_2O; R = Me, Et, Ph) [54] from the reaction of $[BPh_4]^-$ with *cis*-$[PtL_2(PR_3)_2]^{2+}$. However, the *cis* geometry is mainly preserved in the case of the cyanoguanidine reaction (3), although a small amount of the *trans* isomer was detected by $^{31}P\ \{^1H\}$ NMR (see below).

In *cis*-$[PtCl\{NCNC(NH_2)_2\}(PPh_3)_2][BF_4]$ (**3**), the cyanoguanidine ligand is displaced by 4-methylbenzylamine NH_2R' ($R' = CH_2C_6H_4Me$-4), in CH_2Cl_2, at room temperature, to yield (reaction 4, Scheme 1) the corresponding amine complex *cis*-$[PtCl(NH_2R')(PPh_3)_2][BF_4]$ (**4**), although no reaction was detected with *p*-toluidine under similar experimental conditions. Moreover, no nucleophilic addition by the amine or by the alcohol to the organo cyanamide or cyanoguanidine ligands was observed for any of the mono-cationic complexes **1**, **2**, or **3**, in contrast with the ready methanol addition quoted [13] for the ligated cyanoguanidine at the dicationic complex *cis*-$[Pt\{NCNC(NH_2)_2\}_2(PPh_3)_2][BPh_4]_2$ with a stronger activation towards such a type of reaction.

The remaining chloride ligand in complex **3** undergoes further replacement by cyanoguanidine upon prolonged (5 days) stirring of a THF suspension with the latter reagent (in a twofold molar ratio), in the presence of $Na[BPh_4]$, to give, although in low yield, *cis*-$[Pt\{NCNC(NH_2)_2\}(PPh_3)_2][BPh_4]_2$ (**5**) (reaction 5, Scheme 1). However, the latter complex can be obtained in a better yield and more directly from *cis*-$[PtCl_2(PPh_3)_2]$, on its reaction with cyanoguanidine in the presence of $Na[BPh_4]$ following a reported [13] procedure. Nevertheless, as shown in this study, metal phenylation then also occurs to produce **2** (reaction 2, Scheme 1).

2.2. Characterization

The complexes obtained in this study have been characterized by IR and multinuclear NMR spectroscopies, FAB MS, elemental analysis and, in the case of **1a**, also by X-ray diffraction. The data for complex **5**



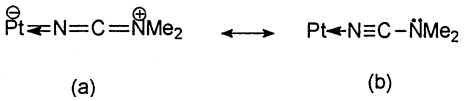
Scheme 1.

have already been reported [13] and are not discussed again.

2.2.1. Molecular structure

The molecular structure of *trans*-[Pt(Ph)($NCNMe_2$)-(PPh_3)$_2$][BPh_4] (**1a**) has been obtained by X-ray diffraction and is depicted in Fig. 1 and selected bond lengths and angles are given in Table 1. In the complex cation, the Pt atom has a square-planar environment with the phenyl ligand *trans* to the organocyanamide and the two phosphines *trans* to each other. The Pt–N(1) distance, 2.100(5) Å, is longer than the average value, 1.980(2) Å, quoted [55] for the Pt–N(nitrile) bond lengths in square-planar Pt(II) complexes, in particular that observed, 2.048(6) Å [12], for *trans*-[Pt(CF_3)($NCNEt_2$)(PPh_3)$_2$]-[BF_4]. Such an elongated Pt–N bond agrees with the strong *trans* influence of the phenyl ligand as discussed below.

Within the linear dimethyl cyanamide ligand, the amine N atom displays a distorted trigonal-planar geometry instead of the pyramidal one that is observed [56] in the uncoordinated organocyanamide. The N(2)–C(7) distance, 1.260(12) Å, is shorter than the corresponding one in the free dimethylcyanamide, 1.351 Å [56], indicating a double bond character and a significant contribution of the resonance form (a), as observed e.g. for *trans*-[Pt(CF_3)($NCNEt_2$)(PPh_3)$_2$][BF_4] [12] and [Cr($NCNEt_2$)(CO)$_5$] [57]. Hence, the dimethyl-cyanamide behaves as an effective σ and π electron-donor to the cationic Pt(II) center.



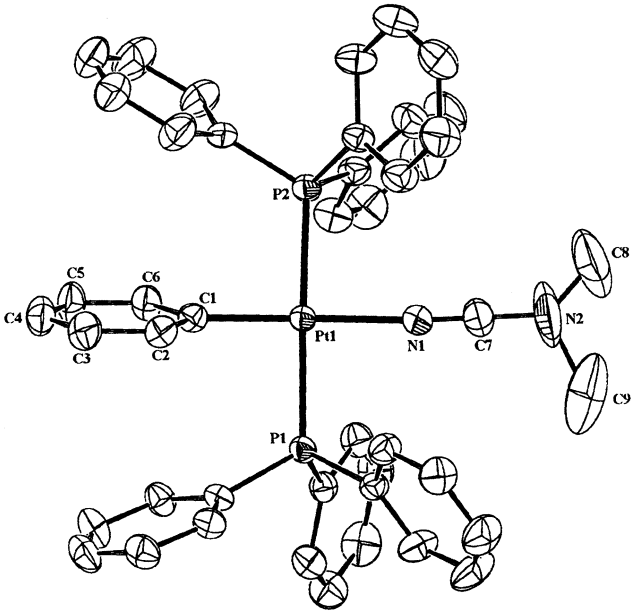


Fig. 1. Molecular structure of the complex cation *trans*-[Pt(Ph)($NCNMe_2$)(PPh_3)$_2$]$^+$ (**1a**).

Table 1
Selected bond lengths (Å) and angles (°) for *trans*-[Pt(Ph)(NCNMe$_2$)(PPh$_3$)$_2$][BPh$_4$]·Et$_2$O (**1a**) with e.s.d. in parentheses

Bond lengths			
Pt(1)–N(1)	2.100(5)		
Pt(1)–C(1)	2.016(5)	C(1)–C(2)	1.387(6)
Pt(1)–P(1)	2.3105(13)	C(2)–C(3)	1.401(7)
Pt(1)–P(2)	2.3080(13)	C(3)–C(4)	1.371(9)
N(1)–C(7)	1.107(9)	C(4)–C(5)	1.370(9)
N(2)–C(7)	1.260(12)	C(5)–C(6)	1.381(7)
N(2)–C(8)	1.241(19)	C(1)–C(6)	1.395(7)
N(2)–C(9)	1.54(2)		
Bond angles			
P(1)–Pt(1)–P(2)	173.26(4)	Pt(1)–C(1)–C(2)	120.3(3)
P(1)–Pt(1)–N(1)	89.09(13)	Pt(1)–C(1)–C(6)	121.5(3)
P(1)–Pt(1)–C(1)	90.36(14)	N(1)–C(7)–N(2)	176.2(12)
N(1)–Pt(1)–C(1)	178.20(18)	C(7)–N(2)–C(9)	112.9(13)
P(2)–Pt(1)–N(1)	88.54(13)	C(8)–N(2)–C(9)	106.9(14)
P(2)–Pt(1)–C(1)	92.19(13)	C(7)–N(2)–C(8)	137.0(12)
Pt(1)–N(1)–C(7)	173.9(6)		

The N(1)–C(7) bond length of the cyano group, 1.107(9) Å, is shorter than that known, 1.180 Å [56], for free NCNMe$_2$, being consistent with the IR ν(N≡C) coordination shift to a higher wavenumber (see below).

2.2.2. Spectroscopic data

Complexes **1**–**3** exhibit strong ν(N≡C) bands (KBr pellets) in the range 2260–2210 cm^{-1}, higher by approximately 75–25 cm^{-1} than those observed for the free cyano-compounds. They are comparable with those shown [12] by the related complexes *trans*-[Pt(CF$_3$)(L)(PPh$_3$)$_2$][BF$_4$] [L = NCNC(NH$_2$)$_2$, NCNMe$_2$ or NCNEt$_2$] and *trans*-[PtCl(NCNR$_2$)(PPh$_3$)$_2$][BPh$_4$] (R = Me or Et).

For the cyanoguanidine complexes **2** and **3**, other broad and medium or weak intensity bands in the approximately 3500–3000 cm^{-1} range, are due to ν(NH) whereas additional strong bands at 1640–1550 cm^{-1} are assigned to δ(NH) and/or ν(C=N).

The *cis* geometry for complexes **2**–**4** is suggested by the detection of a medium–strong band at approximately 540 cm^{-1} which is known [58] to be diagnostic of the *cis* arrangement of the two phosphine ligands. This geometry is confirmed by their ^{31}P {^{1}H} NMR spectra (Table 2) which exhibit two distinct resonances i.e. two doublets [$^2J_{PP}$ = 18.2 Hz for **4**] or a lower field doublet [$^2J_{PP}$ = 16–19 Hz] and an higher field unresolved resonance (for **2** and **3**), with the expected ^{195}Pt satellites.

For the non-phenylated *cis* complexes **3** and **4**, $^1J_{PPt}$ falls in the 3747–3234 Hz range, but, for the phenylated *cis* complex **2**, that corresponding to the P-nucleus *trans* to the phenyl ligand is much lower, 1564 Hz (whereas that for the other phosphorus is 4459 Hz) similarly to what has been quoted [54] for *cis*-[Pt(Ph)L(PMe$_3$)$_2$]$^+$ (L = MeOH or H$_2$O), indicating a much stronger *trans* influence (see also above) of the ligated phenyl compared with the nitrogen ligands. Complex **2**, in CDCl$_3$ solution, appears to be slightly contaminated (ca. 6%) with the *trans* isomer, as shown by the detection of the corresponding singlet at a chemical shift [δ −121.56 rel. P(OMe)$_3$] and with J_{PPt} (3098.0 Hz) that are comparable with those exhibited by the *trans* phenylated complexes **1a** or **1b** [δ −121.44 or −123.04, J_{PPt} 3061.4 or 3067.8 Hz, respectively].

The presence of the phenyl ligand in complexes **1** and **2** is clearly recognized by the detection, in the ^{1}H NMR spectrum (Table 3), at a higher field (δ ca. 6.3–6.9) than the bulky of the phenyl resonance of the PPh$_3$ ligand and the [BPh$_4$]$^-$ counter-ion, of a set of two triplets and one doublet ($^3J_{HH}$ = 6–8 Hz), the latter with the platinum satellites ($^3J_{HPt}$ = 53–59 Hz), with the expected integration, assigned to the *meta*, *para* and *ortho* protons, respectively, of the ligated Ph. The ^{13}C {^{1}H} NMR spectra (Table 3) confirm the existence of this ligand, by disclosing, for the *trans* complexes **1a** and **1b**, the expected triplet ($^2J_{CP}$ ca. 8 Hz, δ ca. 130) assigned to the *ipso*-C.

The other carbon resonances of this ligand are detected as singlets at higher fields (δ 130–123), which split into the expected doublets (J_{CH} ca. 160 Hz) in the proton-undecoupled ^{13}C NMR spectra. The cyano-carbons of the dialkylcyanamides resonate as singlets at δ ca. 123.

The resonances of the various types of aromatic carbons of the PPh$_3$ ligands have also been assigned, by comparison with those [12] of the related complexes *trans*-[Pt(CF$_3$)(L)(PPh$_3$)$_2$][BF$_4$] [L = NCNR$_2$ (R = Me, Et), NCNC(NH$_2$)$_2$], at chemical shifts which increase in the order *ipso* (δ ca. 129–130), *para* (δ ca. 132–134) and *meta* (δ ca. 134.6–136.6), with a substantial higher field complexation shift for the *ipso* carbons as observed [12] e.g. for *trans*-[Pt (CF$_3$)(L)(PPh$_3$)$_2$][BF$_4$] [L = NCNC(NH$_2$)$_2$, NCNH$_2$, NCNMe$_2$ or NCNEt$_2$].

For the complex **3**, they appear as doublets ($^1J_{CP}$ = 56.8 or 64.7 Hz, $^2J_{CP}$ = 11.6 Hz, $^4J_{CP}$ = 2.5 Hz and $^3J_{CP}$ = 10.4 or 11 Hz, respectively), whereas for **1a** and **1b** with a *trans* geometry, they consist (with the exception of the *para* carbons resonance which is a singlet) of triplets due to virtual coupling to the two *trans* ^{31}P nuclei [1/2|$^1J_{CP}$+$^3J_{CP}$| = 28.5 Hz, 1/2|$^2J_{CP}$+$^4J_{CP}$| = 5.1 or 5.9 Hz, and 1/2|$^3J_{CP}$+$^5J_{CP}$| = 6.2 Hz, for the *ipso*-, *ortho*- and *meta*- carbons, respectively].In the ^{13}C–^{1}H coupled spectra, those resonances split into the expected (or not fully resolved) patterns.

In the FAB MS spectra of all the complexes, the molecular ions M^+ are clearly detected, as well as the corresponding fragments derived from the loss of the nitrogen-ligand, [M-L]$^+$ [L = NCNR$_2$ (R = Me **1a**, Et **1b**), NCNC(NH$_2$)$_2$ (**2** or **3**) or NH$_2$CH$_2$C$_6$H$_4$Me-4 (**4**)].

Table 2
^{1}H and ^{31}P {^{1}H} NMR data for *trans*-[Pt(Ph)($NCNR_2$)(PPh_3)$_2$][BPh_4] (R = Me **1a** or Et **1b**), *cis*-[Pt(Ph){$NCNC(NH_2)_2$}(PPh_3)$_2$][BPh_4] (**2**), *cis*-[PtCl{$NCNC(NH_2)_2$}(PPh_3)$_2$][BF_4] (**3**) and *cis*-[PtCl($NH_2CH_2C_6H_4Me$-4)(PPh_3)$_2$][BF_4] (**4**)

Complex	^{1}H				^{31}P {^{1}H}		
	δ [a]	Integ.	J [b]	Assign.	δ [a]	$^{2}J_{PP}$ [b]	$^{1}J_{PPt}$ [b]
1a [c]	7.39–7.13 m	38H		P*Ph*$_3$+H$_o$ (BPh_4^-)	−121.44 s		3061.4
	7.03 t	8H	$^{3}J_{HH}$ = 7.4	H$_m$ (BPh_4^-)			
	6.88 t	4H	$^{3}J_{HH}$ = 7.4	H$_p$ (BPh_4^-)			
	6.57 d	2H	$^{3}J_{HH}$ = 8.0	H$_o$ (Ph)			
	6.47 t	1H	$^{3}J_{HH}$ = 6.3	H$_p$ (Ph)			
	6.30 t	2H	$^{3}J_{HH}$ = 7.2	H$_m$ (Ph)			
	1.51 s	6H		N(C*H*$_3$)$_2$			
1b	7.49–7.27 m	38H		P*Ph*$_3$+H$_o$ (BPh_4^-)	−123.04 s		3067.8 [d]
	7.01 t	8H	$^{3}J_{HH}$ = 7.2	H$_m$ (BPh_4^-)			
	6.86 t	4H	$^{3}J_{HH}$ = 7.1	H$_p$ (BPh_4^-)			
	6.59 d	2H	$^{3}J_{HH}$ = 7.2 ($^{3}J_{HPt}$ = 52.8)	H$_o$ (Ph)			
	6.45 t	1H	$^{3}J_{HH}$ = 7.4	H$_p$ (Ph)			
	6.27 t	2H	$^{3}J_{HH}$ = 7.5	H$_m$ (Ph)			
	2.12 q	4H	$^{3}J_{HH}$ = 7.4	N(C*H*$_2$CH$_3$)$_2$			
	0.48 t	6H	$^{3}J_{HH}$ = 7.4	N(CH$_2$C*H*$_3$)$_2$			
2	7.79–6.96 m, br	50H		P*Ph*$_3$ + (B*Ph*$_4^-$)	−124.82 d	16.0	1563.84
	6.87 d	2H	$^{3}J_{HH}$ = 7.2 ($^{3}J_{HPt}$ = 59.0)	H$_o$ (Ph)	−129.17 s, br		4458.58
	6.54 t	2H	$^{3}J_{HH}$ = 7.3	H$_m$ (Ph)			
	6.45 t	1H	$^{3}J_{HH}$ = 7.3	H$_p$ (Ph)			
	5.37 s	1H		NCNC(N*H*$_2$)$_2$			
	3.78 s, br	1H		NCNC(N*H*$_2$)$_2$			
	3.57 s, br	2H		NCNC(N*H*$_2$)$_2$			
3 [e]	7.63–7.24 m, br	30H		P*Ph*$_3$	−131.33 d	19.3	3583.1
	7.09 s, l	2H		C(N*H*$_2$)$_2$	−136.64 s, br		3731.6
	6.58 s, l	2H		C(N*H*$_2$)$_2$			
4	7.52–7.20 m	30H		P*Ph*$_3$	−127.95 d	18.2	3747
	7.12 d	2H	7.5	NH$_2$CH$_2$C$_6$*H*$_4$CH$_3$	−136.06 d	18.2	3234
	6.81 d	2H	7.5	NH$_2$CH$_2$C$_6$*H*$_4$CH$_3$			
	3.94 s, br	2H		NH$_2$C*H*$_2$C$_6$H$_4$CH$_3$			
	2.32 s, br	3H		NH$_2$CH$_2$C$_6$H$_4$C*H*$_3$			
	1.71 s,br	1H		N*H*$_2$CH$_2$C$_6$H$_4$CH$_3$			

[a] In CD_2Cl_2 unless otherwise stated; δ values in ppm relative to $SiMe_4$ (^{1}H) and $P(OMe)_3$ (^{31}P).
[b] In Hz.
[c] In $CDCl_3$.
[d] In $CDCl_3$.
[e] ^{1}H spectrum in DMSO-d_6; *o* = orto; *m* = meta; *p* = para; s = singlet; d = doublet; t = triplet; q = quartet; m = multiplet; br = broad.

3. Experimental

All reactions were carried out under dinitrogen, by using standard vacuum and inert gas flow techniques. The solvents were dried by standard procedures and freshly distilled before use. IR spectra were recorded on a Bio Rad FTS 3000 MX instrument and NMR spectra on a Varian Unity 300 spectrometer. Positive-ion FAB mass spectra were obtained on a Trio 2000 instrument by bombarding 3-nitrobenzyl alcohol (NBA) matrixes of the samples with 8 keV (ca. 1.28×10^5 J) Xe atoms. Mass calibration for data system acquisition was achieved using CsI. Elemental analyses were carried out at the Laboratório de Análises of the Instituto Superior Técnico. The complex *cis*-[$PtCl_2(PPh_3)_2$] was prepared by a published method [59], whereas the other reagents were purchased from Aldrich.

3.1. Preparation of complexes *trans*-[Pt(Ph)($NCNR_2$)(PPh_3)$_2$][BPh_4] (R = Me **1a**, Et **1b**)

A suspension of *cis*-[$PtCl_2(PPh_3)_2$] (0.15 g, 0.19 mmol) in THF (30 ml) was treated with $NCNR_2$ (91.5 μl, **1a**; 132.4 μl, **1b**; 1.14 mmol) and Na[BPh_4] (0.390 g, 1.14 mmol), and left stirred at room temperature (r.t.) for approximately 5 days. It was then filtered and the solvent removed in vacuo. Addition of CH_2Cl_2 (10 ml) to the residue followed by filtration (removal of sodium salts), concentration in vacuo and addition of Et_2O resulted in the precipitation of complex **1a** or **1b** as a white microcrystalline solid which was filtered off, washed with Et_2O and dried in vacuo (ca. 0.135 g, 60% yield). IR (KBr pellet, cm^{-1}): ν(N≡C) 2245 (s), **1a**, 2250 (s), **1b**. *Anal.* Calc. for **1a**, $C_{69}H_{61}N_2P_2BPt$: C 69.9; H 5.1; N 2.4. Found: C 69.8; H 5.1, N 2.6%. For **1b**,

Table 3
^{13}C $\{^1H\}$ and ^{13}C NMR data ^1H and ^{31}P $\{^1H\}$ NMR data for *trans*-$[Pt(Ph)(NCNR_2)(PPh_3)_2][BPh_4]$ [$R_2 = Me_2$ (**1a**) ou Et_2 (**1b**) and *cis*-$[PtCl\{NCNC(NH_2)_2\}(PPh_3)_2][BF_4]$ (**3**)

Complex	δ	^{13}C $\{^1H\}$	^{13}C	$^1J_{CH}$ (Hz)	Assign.
1a	164.83	q [a] ($^1J_{CB} = 49.4$ Hz)	q,br		C_i BPh_4^-
	136.89	s	dm	157.8	C_m BPh_4^-
	134.64	t [1/2($^3J_{CP}+^5J_{CP}$) = 6.2 Hz]	dm	157.5	C_m PPh_3
	132.78	t ($^2J_{CP} = 8.5$ Hz)	n.o		C_i Ph
	132.01	s	dm	161.2	C_p PPh_3
	129.37	t [1/2($^2J_{CP}+^4J_{CP}$) = 5.1 Hz]	dm	163.0	C_o PPh_3
	128.95	s	dm	159.3	Ph
	128.84	s	dm	159.3	Ph
	128.57	t [1/2($^1J_{CP}+^3J_{CP}$) = 28.6 Hz]	n.o		C_i PPh_3
	126.14	s	dm	155.0	C_o BPh_4^-
	123.66	s	s,br		$NCN(CH_3)_2$
	123.13	s	dm,br	159.9	Ph
	122.22	s	dt	156.3 ($^2J_{CP} = 7.9$ Hz)	C_p BPh_4^-
	39.06	s	q	142.4	$NCN(CH_3)_2$
1b	164.95	q [a] ($^1J_{CB} = 49.5$ Hz)	q,br		C_i BPh_4^-
	136.99	s	dm	158.7	C_m BPh_4^-
	134.70	t [1/2($^3J_{CP}+^5J_{CP}$) = 6.2 Hz]	dm	169.1	C_m PPh_3
	132.07	s	dm	162.9	C_p PPh_3
	129.72	t ($^2J_{CP} = 8.1$ Hz)	n.o		C_i Ph
	129.40	t [1/2($^2J_{CP}+^4J_{CP}$) = 5.9 Hz]	dm	163.3	C_o PPh_3
	128.99	s	dm	159.9	Ph
	128.84	s	dm	159.9	Ph
	128.75	t [1/2($^1J_{CP}+^3J_{CP}$) = 28.5 Hz]	t,br		C_i PPh_3
	126.07	q [a] ($^2J_{CB} = 2.7$ Hz)	dm	152.6	C_o BPh_4^-
	123.11	s	dm	159.9	Ph
	122.36	s	s,br		$NCN(CH_2CH_3)_2$
	122.18	s	dt	156.3 ($^2J_{CH} = 7.3$ Hz)	C_p BPh_4^-
	45.82	s	dt	142.5	$NCN(CH_2CH_3)_2$
	13.27	s	dq	127.8	$NCN(CH_2CH_3)_2$
3 [b]	164.72	s	s		$NCNC(NH_2)_2$
	136.58	d [$^3J_{CP} = 10.4$ Hz]	dm	159.3	C_m (PPh_3)
	135.96	d [$^3J_{CP} = 11.0$ Hz]	dm	162.3	$C_{m'}$ (PPh_3)
	133.89	d [$^4J_{CP} = 2.5$ Hz]	dm,br	160.5	C_p (PPh_3)
	133.49	d [$^4J_{CP} = 2.5$ Hz]	dm,br	162.9	$C_{p'}$ (PPh_3)
	131.19	s. f	n.o		$NCNC(NH_2)_2$
	130.66	d [$^2J_{CP} = 11.6$ Hz]	dm	163.9	C_o (PPh_3)
	130.16	d [$^2J_{CP} = 11.6$ Hz]	dm	162.1	$C_{o'}$ (PPh_3)
	129.37	d [$^1J_{CP} = 56.8$ Hz]	n.o		C_i (PPh_3)
	129.22	d [$^1J_{CP} = 64.7$ Hz]	n.o		$C_{i'}$ (PPh_3)

Spectra recorded in $CDCl_3$ unless otherwise stated; δ values in ppm relative to $SiMe_4$; *i* = *ipso*; *o* = *orto*; *m* = *meta*; *p* = *para*; s = singlet; d = doublet; t = triplet; q = quartet; dm = doublet of multiplets; dt = doublet of triplets; dq = doublet of quartets; br = broad; n.o. = not observed.
[a] Quartet with relative intensities 1:1:1:1.
[b] In CD_2Cl_2.

$C_{71}H_{65}N_2BP_2Pt$: C 69.9; H 5.3; N 2.3. Found: C 69.0; H 5.3; N 2.3%.

3.2. Preparation of *cis*-$[Pt(Ph)\{NCNC(NH_2)_2\}(PPh_3)_2][BPh_4]$ (**2**)

A suspension of *cis*-$[PtCl_2(PPh_3)_2]$ (0.15 g, 0.19 mmol) with $NCNC(NH_2)_2$ (0.063 g, 0.76 mmol) and $Na[BPh_4]$ (0.26 g, 0.76 mmol) in THF (40 ml) was stirred at r.t. for 5 days and thereafter filtered and the solvent removed in vacuo. CH_2Cl_2 (10 ml) was added to the residue, the solution filtered (removal of the sodium salts), concentrated in vacuo and Et_2O added. Complex **2** precipitated as a white solid which was filtered off, washed with Et_2O and dried in vacuo (68 mg, ca. 30% yield). IR (KBr pellet, cm^{-1}): ν(NH) 3460 (m,br), 3350 (m,br); ν(N≡C) 2210 (s); δ(NH) and/or ν(N=C) 1620 (m,br) 1550 (s,br). *Anal.* Calc. for $C_{92}H_{79}N_4B_2P_2Pt$: C 64.5; H 4.8; N 4.4. Found: C 63.8; H 4.9; N 4.6%.

3.3. Preparation of *cis*-$[PtCl\{NCNC(NH_2)_2\}(PPh_3)_2][BF_4]$ (**3**)

A suspension of *cis*-$[PtCl_2(PPh_3)_2]$ (0.20 g, 0.25 mmol) in THF (30 ml) at r.t. with a slight excess of $NCNC(NH_2)_2$ (1:1.1) and of $Tl[BF_4]$ (1:1.1) was stirred

for 5 h. The solution was then filtered and the filtrate was taken to dryness. CH_2Cl_2 (ca. 10 ml) was added to the residue, the solution filtered (removal of the thallium salts) and concentrated in vacuo. Dropwise addition of Et_2O led to the formation of an oily residue which was isolated by decantation of the supernatant solution. Addition of Et_2O followed by application of the freeze–thaw technique and vigorous stirring resulted in the formation of a white powder of compound **3** which was filtered off and dried in vacuo (150 mg, ca. 50% yield). IR (KBr pellet, cm^{-1}): ν(NH) 3460 (m,br), 3360 (m,br); ν(N≡C) 2260 (s,br), 2200 (s,br); δ(NH) 1640 (m,br) 1550 (s,br). *Anal.* Calc. for $C_{38}H_{34}N_4B_2F_4P_2Pt$: C 49.3; H 3.7; N 6.1. Found: C 49.7; H 3.8; N 5.7%.

3.4. Preparation of *cis*-[PtCl(NH$_2$R′)(PPh$_3$)$_2$][BF$_4$] (R′ = CH$_2$C$_6$H$_4$Me-4 **4**)

4-$MeC_6H_4CH_2NH_2$ (25.8 μl, 0.22 mmol) was added to a solution of *cis*-[PtCl{NCNC(NH_2)}(PPh_3)$_2$] (**3**) (0.10 g, 0.11 mmol) in CH_2Cl_2 (20 ml) which was then stirred overnight at r.t., whereafter it was filtered and concentrated in vacuo. Addition of Et_2O resulted in the precipitation of complex **5** as a white solid which was filtered off and dried in vacuo (48 mg, 45% yield). IR (KBr pellet, cm^{-1}): ν(NH) 3280 (w,br), 3220 (w,br); δ(NH) 1570 (w). *Anal.* Calc. for $C_{44}H_{41}NBP_2ClF_4Pt$: C 54.8; H 4.3; N 1.5. Found: C 54.4; H 4.9; N 1.3%.

3.5. Preparation of *cis*-[Pt{NCNC(NH$_2$)$_2$}$_2$(PPh$_3$)$_2$][BPh$_4$]$_2$ (**5**)

A THF (20 ml) solution of *cis*-[PtCl{NCNC(NH_2)$_2$}-(PPh_3)$_2$][BF_4] (**3**) (0.050 g, 0.054 mmol) was treated with NCNC(NH_2)$_2$ (0.009 g, 0.10 mmol) and Na[BPh_4] (0.037 g, 0.10 mmol) and the mixture stirred for approximately 5 days whereupon the solution was filtered and the solvent removed in vacuo. Extraction with CH_2Cl_2 (7 ml) followed by filtration and addition of Et_2O led to the separation of complex **5** as a white solid which was filtered off, washed with Et_2O and dried in vacuo (ca. 20% yield). The complex can be prepared, in a more direct way and with a better yield (40%), by starting from *cis*-[$PtCl_2(PPh_3)_2$] instead of **3**, following a previously reported [13] procedure. IR (KBr pellet, cm^{-1}): ν(NH) 3460(m,br), 3380 (m,br), 3060 (m,br), 3000 (m,br); ν(N≡C) 2250 (sh), 2200 (s,br); δ(NH) or ν(N=C) 1625 (s), 1580 (sh), 1550 (s,br), approximately 1500 (s). Other spectroscopic and analytical data as already reported [13].

Crystal data for *trans*-[Pt(Ph)($NCNMe_2$)(PPh_3)$_2$]-[BPh_4]·Et_2O (**1a**): $C_{73}H_{71}BN_2OP_2Pt$, $M = 1260.16$, monoclinic $P2_1/c$, $a = 14.954(2)$, $b = 16.228(3)$, $c = 26.884(4)$ Å, $\beta = 104.572(10)^\circ$, $V = 6314.0(17)$ Å^3, $T = 293(2)$ K, μ(Cu Kα) = 4.971 mm^{-1}, $\lambda = 1.54150$ Å, $Z = 4$, $D_{calc} = 1.326$ mg m^{-3}, $F(000) = 2576$. Cell dimension were obtained from 10 043 reflections measured, 9362 independent ($R_{int} = 0.0172$). Final $wR(F^2) = 0.0959$, $R_1 = 0.0374$. Intensity data were collected using a Enraf-Nonius CAD4 diffractometer in the range 3.05–59.97° with index ranges $-16 \le h \le 16$, $0 \le k \le 18$, $-30 \le l \le 1$. Structure was solved by direct methods using SHELXS-97 [60] program and refined with SHELXL-97 [61] with the WinGX graphical user interface [62]. The maximum and minimum peaks in the final difference electron density map were of 1.03 and −1.13 e Å^{-3} located in the immediate vicinity of the platinum atom.

4. Supplementary material

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-176397. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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