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Syntheses and properties of cyanamide and cyanoguanidine complexes of platinum(II). X-Ray structure of *trans*-[Pt(CF_3)($NCNEt_2$)(PPh_3)$_2$][BF_4]

M. Fátima C. Guedes da Silva [a], Elsa M.P.R.P. Branco [a], Yu Wang [a], João J.R. Fraústo da Silva [a], Armando J.L. Pombeiro [a,*], Roberta Bertani [b], Rino A. Michelin [b,*], Mirto Mozzon [b], Franco Benetollo [c], Gabriella Bombieri [d]

[a] *Centro de Química Estrutural, Complexo I, Instituto Superior Técnico, Av. Rovisco Pais, 1096 Lisboa codex, Portugal*
[b] *Istituto di Chimica Industriale and Centro di Chimica e Tecnologia dei Composti Metallorganici degli Elementi di Transizione del C.N.R., Facoltà di Ingegneria, via Marzolo 9, Università di Padova, 35131 Padova, Italy*
[c] *Istituto di Chimica e Tecnologia dei Radioelementi del C.N.R., Corso Stati Uniti 4, 35020 Padova, 35131 Padova, Italy*
[d] *Istituto di Chimica Farmaceutica, Università di Milano, viale Abruzzi 42, 20131 Milan, Italy*

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Abstract

Complexes *trans*-[PtX(L)(PPh_3)$_2$]A [**1**: X = CF_3; A = BF_4; L = $NCNH_2$, $NCNMe_2$, $NCNEt_2$, or $NCNC(NH_2)_2$. **2**: X = Cl; A = BPh_4; L = $NCNMe_2$ or $NCNEt_2$] and *cis*-[PtCl(L)(PPh_3)$_2$][BPh_4] [**3**: L = $NCNH_2$ or $NCNC(NH_2)_2$], which appear to be the first cyanamide or cyanoguanidine complexes of platinum to be reported, have been prepared by treatment of *trans*-[PtBr(CF_3)(PPh_3)$_2$] (in CH_2Cl_2/acetone and in the presence of Ag[BF_4]) or of *cis*-[PtCl_2(PPh_3)$_2$] (in THF and in the presence of Na[BPh_4]), respectively, with the appropriate substrate. In KBr pellets or in solution **1** (L = $NCNMe_2$ or $NCNEt_2$) undergoes ready replacement of the organocyanamide (under the *trans* influence of CF_3) by bromide to regenerate *trans*-[PtBr(CF_3)(PPh_3)$_2$]. The X-ray structure of **1** (X = CF_3, A = BF_4, L = $NCNEt_2$) is also reported, and shows the presence of two apical intramolecular contacts of the metal with two *ortho*-hydrogen atoms of the phosphines, whereas the amine N atom of the diethylcyanamide is trigonal planar in the linear NCN framework with a delocalized π system.

Keywords: Platinum; Cyanamide complex; Cyanoguanidine complex; X-ray diffraction

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1. Introduction

The coordination chemistry of cyanamide ($N{\equiv}CNH_2$) is still an unexplored field of research in spite of the versatile organic chemistry which has been revealed for this species [1], as a starting material in synthesis and of its biological significance, as a recently recognized [2] substrate of nitrogenase, and as a conceivable amino acid precursor and a prebiotic molecule [3]. Moreover, its dimeric form, cyanoguanidine [or dicyandiamide, with tautomeric forms $N{\equiv}C{-}N{=}C(NH_2)_2$ and $N{\equiv}C{-}NHC({=}NH)NH_2$] is also a precursor for the syntheses of organonitrogen compounds, such as biguanides, guanylureas, etc. [4].

In our work on the activation of small unsaturated molecules of biological and synthetic interest [5], we have shown previously that cyanamide undergoes dehydrogenation at the electron-rich metal sites {M(dppe)$_2$} (M = Mo or W, dppe = $Ph_2PCH_2CH_2PPh_2$) to give the bis(cyanoimido) species *trans*-[M(NCN)$_2$(dppe)$_2$] upon its reaction with *trans*-[M(N_2)$_2$(dppe)$_2$] [6]. It simply adds to {Re(CNR)(dppe)$_2$}$^+$ (R = Me or ^{t}Bu) forming *trans*-[Re(CNR)($NCNH_2$)(dppe)$_2$][BF_4] upon its reaction with *trans*-[ReCl(CNR)(dppe)$_2$] in the presence of Tl[BF_4] [7]. The analogous Re complexes with cyanoguanidine, *trans*-[Re(CNMe){$NCNC(NH_2)_2$}(dppe)$_2$]A (A = BF_4 or Cl) have been obtained [8] by parallel procedures.

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[*] Corresponding authors.

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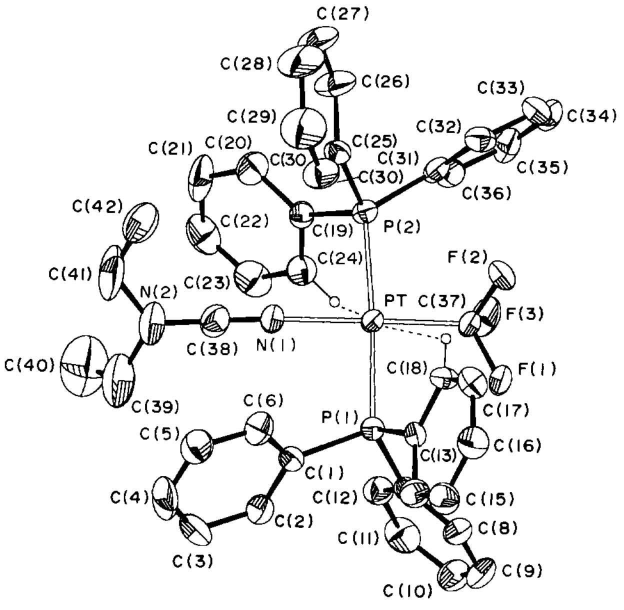


Fig. 1. Molecular structure of *trans*-$[Pt(CF_3)(NCNEt_2)(PPh_3)_2][BF_4]$.

We now report the extension of those studies to platinum(II) as well as to dialkylcyanamides. To our knowledge, the complexes obtained constitute the first examples of platinum complexes with such ligands.

2. Results and discussion

Treatment of a CH_2Cl_2 solution of *trans*-$[PtBr(CF_3)(PPh_3)_2]$ with the appropriate cyanamide or cyanoguanidine (L) (in ca. a threefold molar ratio) followed by addition of $AgBF_4$ (in acetone) in the dark leads to *trans*-$[Pt(CF_3)(L)(PPh_3)_2][BF_4]$ (**1**) [L = $NCNH_2$, $NCNMe_2$, $NCNEt_2$ or $NCNC(NH_2)_2$] (Eq. 1) which have been isolated as white solids.

$$\textit{trans-}[PtBr(CF_3)(PPh_3)_2] + L + AgBF_4$$
$$\rightarrow \textit{trans-}[Pt(CF_3)(L)(PPh_3)_2][BF_4] + AgBr \qquad (1)$$

1

This preparative method involves replacement of the bromide by the substrate (L) assisted by the silver salt, and is analogous to that followed [9] for the synthesis of the related nitrile complexes *trans*-$[PtX(NCR)(PPh_3)_2][BF_4]$ from *trans*-$[PtCl(X)(PPh_3)_2]$ (X = H, CH_3 or CF_3; R = alkyl or aryl).

Table 1
Selected bond lengths (Å) and angles (°) with e.s.d.s in parentheses for complex *trans*-$[Pt(CF_3)(NCNEt_2)(PPh_3)_2]^+$

Pt–P(1)	2.315(2)	Pt–P(2)	2.341(2)
Pt–C(37)	2.005(7)	Pt–N(1)	2.048(6)
P(1)–C(1)	1.821(7)	P(1)–C(7)	1.822(6)
P(1)–C(13)	1.814(6)	P(2)–C(19)	1.822(7)
P(2)–C(25)	1.814(7)	P(2)–C(31)	1.820(7)
C(37)–F(1)	1.343(8)	C(37)–F(2)	1.366(8)
C(37)–F(3)	1.361(8)	N(1)–C(38)	1.14(1)
N(2)–C(38)	1.29(1)	N(2)–C(39)	1.48(2)
N(2)–C(41)	1.47(2)	C(39)–C(40)	1.39(2)
C(41)–C(42)	1.40(2)	B–F(4)	1.36(2)
B–F(5)	1.33(2)	B–F(6)	1.30(2)
B–F(7)	1.33(2)		
C(37)–Pt–N(1)	175.7(3)	P(2)–Pt–N(1)	86.4(2)
P(2)–Pt–C(37)	92.8(2)	P(1)–Pt–N(1)	89.8(2)
P(1)–Pt–C(37)	91.0(2)	P(1)–Pt–P(2)	176.1(1)
Pt–C(37)–F(3)	112.2(4)	Pt–C(37)–F(2)	113.4(4)
Pt–C(37)–F(1)	118.0(4)	F(2)–C(37)–F(3)	104.6(5)
F(1)–C(37)–F(3)	104.1(5)	F(1)–C(37)–F(2)	103.2(5)
Pt–N(1)–C(38)	170.3(6)	C(39)–N(2)–C(41)	119(1)
C(38)–N(2)–C(41)	119.4(9)	C(38)–N(2)–C(39)	121.4(9)
N(1)–C(38)–N(2)	178.3(9)	N(2)–C(39)–C(40)	116(1)
N(2)–C(41)–C(42)	119(1)		

The similar complexes *trans*-$[PtCl(L)(PPh_3)_2][BPh_4]$ (**2**) (L = $NCNMe_2$ or $NCNEt_2$) have been obtained as white solids by a related route, through reaction of *cis*-$[PtCl_2(PPh_3)_2]$ in THF with the organocyanamide (L) in the presence of an excess of $Na[BPh_4]$ (Eq. 2). However, when using cyanamide or cyanoguanidine, the *cis* complexes *cis*-$[PtCl(L)(PPh_3)_2][BPh_4]$ (**3**) [L = $NCNH_2$ or $NCNC(NH_2)_2$] were the isolated products (Eq. 3).

Complexes **1**, **2** and **3** have been characterized by IR and multinuclear (^1H, ^{31}P, ^{19}F and ^{13}C) NMR spectroscopic studies, by elemental analysis and, for **1** (L = $NCNEt_2$), by an X-ray structural analysis.

2.1. Molecular structure of trans-$[Pt(CF_3)(NCNEt_2)(PPh_3)_2][BF_4]$

The crystal structure of *trans*-$[Pt(CF_3)(NCNEt_2)(PPh_3)_2]$ $[BF_4]$ (**1**) (L = $NCNEt_2$) contains discrete cations and anions units separated by normal Van der Waals distances. An ORTEP view of the complex is shown in Fig. 1 and selected bond distances and angles are listed in Table 1, and atomic coordinates and

$$\textit{cis-}[PtCl_2(PPh_3)_2] + Na[BPh_4] \xrightarrow{L(NCNMe_2 \text{ or } NCNEt_2)} \textit{trans-}[PtCl(L)(PPh_3)_2][BPh_4] \qquad (2)$$

(2)

$$\textit{cis-}[PtCl_2(PPh_3)_2] + Na[BPh_4] \xrightarrow{L[NCNH_2 \text{ or } NCNC(NH_2)_2]} \textit{cis-}[PtCl(L)(PPh_3)_2][BPh_4] \qquad (3)$$

(3)

equivalent isotropic displacement parameters are given in Table 2. In the complex cation, the Pt atom has an approximately square-planar (which tends to an octahedral-type, see below) environment with the CF_3 group *trans* to diethylcyanamide and consequently the two PPh_3 are *trans* to each other.

The weighted least-squares best mean plane through P(1), P(2), N(1), C(37) shows pronounced deviations of the atoms involved from planarity [P(1) −0.006(2), P(2) −0.006(2), N(1) 0.084(6), C(37) 0.096(7) Å] in tetrahedral sense, the Pt atom deviating by 0.0147(3) Å from the plane. The Pt–P distances are rather unexpectedly slightly different [Pt–P(1) 2.315(2) and Pt–P(2) 2.341(2) Å] as well as the angles P(1)–Pt–C(37) of 91.0(2)° and P(2)–Pt–C37 of 92.8(2)° involving the CF_3 moiety, while an asymmetric contraction of the angles P(1)–Pt–N(1) [89.8(2)°] and P(2)–Pt–N(2) [86.4(2)°] is present.

Steric factors due to the differing bulks of the CF_3 and diethylcyanamide ligands play an important role. In fact, in the complex *trans*-$[Pt(H)(CF_3)(PPh_3)_2]$ [10], the P–Pt–C angles are 94.1(2)° and 95.2(2)° with contraction of the P–Pt–H angles to about 85(3)°, indicating that in the present structure the steric balance between the CF_3 and $NCN(C_2H_5)_2$ moieties determines the bond angles and probably the difference in the Pt–P bond lengths. Moreover, for both phosphines, the Pt bond length, are larger than those in *trans*-$[Pt(H)(CF_3)(PPh_3)_2]$ (Pt–P 2.274(2) Å averaged value).

Asymmetry in the Pt–P bond distances is also present in the congested coordination sphere of *cis*, *trans*-$[(OC)(C_6F_5)_2Pt(\mu\text{-}C{\equiv}CPh)Pt(C{\equiv}CPh)(PPh_3)_2]$ with Pt(2)–P(1) of 2.324(3) and Pt(2)–P(2) of 2.350(3) Å [11a]. However, the Pt–C distance of 2.005(7) Å is comparable to that of *trans*-$[Pt(H)(CF_3)(PPh_3)_2]$ (2.009 Å) as well as that found [11b] in *trans*-$[PtCl(C_2F_5)(PMePh_2)_2]$ (2.002(9) Å). The Pt–N distance of 2.049(6) Å is somewhat longer than the value of 1.980(2) Å reported as average for Pt^{II} four coordinate derivatives [12].

The best mean plane through the N(1), C(38), N(2), C(39) and C(41) atoms of the planar part of the cyanamide forms a dihedral angle of 53.7(5)° with the coordination plane.

The skeleton of the $NCN(C_2H_5)_2$ is characterized by the N(1)–C(38) bond distance 1.14(1) Å, N(2)–C(38) 1.29(1) Å and N(2)–C(41) 1.47(2), in the usual range [12] for a triple, a double and a single bond, respectively.

The amine-N atom of the cyanamide is trigonal planar rather than pyramidal as in the uncoordinated and related dimethylcyanamide ($NCNMe_2$) [13] and in cyanamide itself ($NCNH_2$) [14]. Moreover, it is linear and the Et_2N–CN distance, 1.29(1) Å, is much shorter than the corresponding ones in related free cyanamides (1.351 Å [13] or 1.346 Å [14], respectively). Therefore, the resonance form (a) appears to predominate in the

Table 2
Atomic coordinates (×10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) with e.s.d.s in parentheses for *trans*-$[Pt(CF_3)(NCNEt_2)(PPh_3)_2][BF_4]$

Atom	x	y	z	U_{eq} [a]
Pt	3583.2(1)	1918.8(1)	1417.3(2)	34.4(1)
P(1)	4160(1)	1113.3(7)	965(2)	35.6(5)
P(2)	2935(1)	2703.8(7)	1969(2)	36.7(5)
C(37)	4549(4)	2284(3)	605(7)	43(2)
N(1)	2551(3)	1557(2)	2111(6)	51(2)
F(1)	5162(2)	1990(2)	124(5)	61(2)
F(2)	4932(3)	2613(2)	1493(5)	63(2)
F(3)	4336(3)	2591(2)	−469(5)	69(2)
N(2)	1245(4)	1140(4)	2539(10)	92(4)
C(1)	3518(4)	566(2)	1458(7)	40(2)
C(2)	3161(5)	234(3)	552(8)	53(3)
C(3)	2676(6)	−180(3)	1015(10)	72(4)
C(4)	2547(6)	−239(4)	2380(11)	78(4)
C(5)	2892(5)	94(4)	3299(9)	68(3)
C(6)	3379(5)	488(3)	2850(7)	56(3)
C(7)	4369(4)	1029(3)	−845(6)	38(2)
C(8)	5137(4)	902(3)	−1347(7)	50(3)
C(9)	5251(6)	856(3)	−2740(8)	69(3)
C(10)	4615(6)	931(3)	−3612(8)	70(3)
C(11)	3857(5)	1054(4)	−3142(8)	66(3)
C(12)	3734(5)	1110(3)	−1749(7)	55(2)
C(13)	5081(4)	995(3)	1946(6)	37(2)
C(14)	5457(5)	512(3)	1906(8)	55(3)
C(15)	6125(5)	404(3)	2717(8)	57(3)
C(16)	6410(5)	780(3)	3599(8)	56(2)
C(17)	6034(4)	1248(3)	3669(7)	53(3)
C(18)	5375(4)	1366(3)	2847(7)	43(2)
C(19)	1916(4)	2653(3)	1233(7)	42(2)
C(20)	1213(4)	2786(3)	1912(8)	61(3)
C(21)	452(5)	2686(4)	1300(11)	82(4)
C(22)	400(6)	2471(4)	38(12)	81(4)
C(23)	1096(6)	2337(4)	−631(10)	76(4)
C(24)	1850(5)	2426(3)	−45(8)	56(3)
C(25)	2811(4)	2793(3)	3791(6)	45(2)
C(26)	2488(6)	3258(4)	4295(8)	75(3)
C(27)	2433(8)	3322(5)	5690(10)	107(5)
C(28)	2676(9)	2942(5)	6563(10)	126(7)
C(29)	2987(8)	2483(5)	6080(9)	106(5)
C(30)	3060(5)	2407(3)	4695(7)	63(3)
C(31)	3363(4)	3325(3)	1429(7)	43(2)
C(32)	3976(4)	3551(3)	2221(8)	52(3)
C(33)	4354(5)	4003(3)	1794(10)	67(3)
C(34)	4122(5)	4229(3)	571(10)	67(3)
C(35)	3531(5)	4012(3)	−221(8)	62(3)
C(36)	3150(4)	3555(3)	206(7)	52(3)
C(38)	1935(5)	1368(3)	2316(9)	61(3)
C(39)	886(8)	772(6)	1538(17)	140(7)
C(40)	145(11)	917(8)	969(19)	216(14)
C(41)	831(9)	1221(9)	3846(16)	188(10)
C(42)	1228(10)	1515(7)	4854(15)	158(9)
B	3388(12)	5278(8)	7580(21)	224(12)
F(4)	4108(6)	5211(4)	8238(9)	171(3)
F(5)	3180(7)	4838(4)	6956(11)	206(4)
F(6)	3385(6)	5713(4)	6908(10)	196(4)
F(7)	2826(7)	5313(5)	8556(12)	217(5)

[a] U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

the electronic structure of the diethylcyanamide ligand, a resonance hybrid of forms (a) and (b) which have the trigonal planar or the pyramidal configurations, respectively, of the amine N atom. Hence, the lone pair of this atom participates in π-bonding to the cyano carbon atom, shortening the $Et_2N{-}CN$ bond and enhancing the electron-donor ability of the diethylcyanamide towards the cationic Pt^{II} centre.

$$\underset{(a)}{Et_2\overset{+}{N}{=}C{=}\overset{-}{N} \rightarrow Pt^-} \longleftrightarrow \underset{(b)}{Et_2\ddot{N}{-}C{\equiv}N \rightarrow Pt}$$

Similar behaviour of this ligand can be inferred in $[Cr(NCNEt_2)(CO)_5]$ [15], when it binds $\{Cr(CO)_5\}$ which possesses five strong π-electron acceptor carbonyls. Other planar structures have been observed for η^2-dialkylcyanamides with bending at the cyano carbon, in the dinuclear complexes $[M_2(OCH_2\,{}^tBu)_6L_n]$ ($L = NCNMe_2$; M = Mo, $n = 1$ [16a]; M = W, $n = 3$ [16b]) or $[(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_4\,L]$ [16c] for which both the Me_2N π-donation and the bending are believed to enhance the interaction of the cyanamide with the metal.

The C(37)–F distances, 1.343(8), 1.366(8) and 1.361(8) Å (average 1.357(8) Å), are short compared to the average of 1.409(9) Å found in *trans*-$[Pt(H)(CF_3)(PPh_3)_2]$, because the σ-donor ability of the cyanamide is lower than that of the hydride. The rather disordered BF_4 anion balances the cation positive charge.

A pecularity of the complex cation is the two intramolecular contacts of the metal with two *ortho*-hydrogen atoms of the PPh_3 moieties, Pt ... H(18) 2.98(1) Å and Pt ... H(24) 3.00(1) Å. The H(18)...Pt...H(24) angle is 165(1)° and the two hydrogen atoms are −2.36(1) Å and 2.61(1) Å from the coordination plane. The Pt coordination sphere may therefore be considered to be to an octahedron with the apices occupied by the two hydrogens.

2.2. IR spectra

Complexes **1** and **2** exhibit (Table 3) strong $\nu(N{\equiv}C)$ bands in the range 2310–2190 cm^{-1}, higher by ca. 95–50 cm^{-1} than those observed for the corresponding proligands. This is also observed [9] for the organonitriles in the related *trans*-$[PtX(NCR)(PPh_3)_2][BF_4]$ complexes. A high frequency shift of $\nu(N{\equiv}C)$ upon coordination was also observed for *trans*-$[Re(L)(CNMe)(dppe)_2][BF_4]$ ($L = NCNH_2$ [7] or $NCNC(NH_2)_2$ [8]) and is consistent with the η^1-coordination through the cyano group.

Table 3
Selected IR [a] and analytical data for *trans*-$[Pt(CF_3)(L)(PPh_3)_2][BF_4]$ (**1**), *trans*-$[PtCl(L)(PPh_3)_2][BPh_4]$ (**2**) and *cis*-$[PtCl(L)(PPh_3)_2][BPh_4]$ (**3**)

Complex, L	ν(NH)	ν(NC) [b]	Microanalysis (%) [c]		
			C	H	N
1, $NCNH_2$ [d]	3340sh,br 3250s,br 3140m,br 3060m,br	2400w 2310s	49.8 (50.5)	3.5 (3.7)	3.1 (3.2)
1, $NCNMe_2$ [e]	–	2295s [f]	46.0 (46.5)	4.0 (3.7)	2.5 (2.6)
1, $NCNEt_2$ [d]	–	2270s [f]	50.8 (50.2)	4.1 (4.1)	2.8 (2.8)
1, $NCNC(NH_2)_2$	3460m,br 3350m,br	2240s 2190m	48.1 (48.6)	3.5 (3.6)	5.3 (5.8)
2, $NCNMe_2$	–	2260s	67.2 (66.1)	4.7 (4.9)	2.3 (2.5)
2, $NCNEt_2$ [g]	–	2250s	69.5 (68.4)	5.2 (6.5)	1.7 (2.1)
3, $NCNH_2$ [d]	3450w,br 3340sh 3310m	2215s	63.5 (63.7)	4.1 (4.6)	1.7 (2.4)
3, $NCNC(NH_2)_2$	3480w 3360m		64.6 (64.4)	4.7 (4.7)	3.4 (3.6)

[a] In KBr pellets except when stated otherwise (values in cm^{-1}); w = weak, m = medium, s = strong, sh = shoulder, br = broad; strong bands for complexes **1**, centered at ca. 1090 and ca. 1020 cm^{-1} are assigned to CF_3 (e.g. 1100sh, 1085s, 1020s and 1010s cm^{-1} for **1**, $L = NCNMe_2$), overlaping with the broad band due to the BF_4^- counterion. [b] ν(NC) values for the free cyanamides are as follows: 2250 ($NCNH_2$) (KBr pellet), 2200 ($NCNMe_2$) (liquid film), 2195 ($NCNEt_2$) (liquid film), and 2185, 2140 cm^{-1} [$NCNC(NH_2)_2$] (KBr pellet). [c] Calculated values in parentheses. [d] With $0.5CH_2Cl_2$ of crystallization. [e] With $1.5CH_2Cl_2$ of crystallization. [f] In Nujol mull (see text). [g] With $2C_5H_{12}$ of crystallization.

However, in the case of the complexes **1**, the IR spectra in KBr pellets show one strong $\nu(N{\equiv}C)$ band at ca. 2200 cm^{-1} assigned to the free liquid proligand, whereas in Nujol mulls this additional band is not observed and only that expected for the coordinated cyanamide is detected. The liberation of the organocyanamide from the metal coordination sphere in the KBr pellet, was monitored by IR spectroscopy. The spectrum run immediately after a rapid preparation of the pellet still clearly shows $\nu(N{\equiv}C)$ due to the coordinated organocyanamide, at a value similar to that observed in Nujol mull, as well as the lower wave number band of this free species. Spectra run later with the same pellet show a dramatic decrease of the intensity of the former band, which is progressively replaced by the latter.

These observations suggest the replacement of the organocyanamide by bromide in the KBr pellet and this interpretation was confirmed by treatment of **1** ($L = NCNEt_2$) in THF with an excess of KBr which leads to the formation of *trans*-$[PtBr(CF_3)(PPh_3)_2]$ in good yield, identified by comparison of its IR, ^1H and ^{31}P NMR spectra with those of a genuine sample, according to Eq. (4).

$$\textit{trans}\text{-}[Pt(CF_3)(NCNR_2)(PPh_3)_2][BF_4] + KBr \rightarrow \textit{trans}\text{-}[PtBr(CF_3)(PPh_3)_2] + NCNR_2 + K[BF_4] \qquad (4)$$

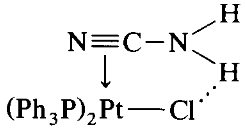
Table 4
^{1}H, ^{31}P and ^{19}F NMR data [a] for *trans*-[Pt(CF$_3$)(L)(PPh$_3$)$_2$][BF$_4$] (**1**)

L	^{1}H			^{31}P			^{19}F [b]		
	δ	Integ.	Assign.	δ	^3J(PF)	^1J(Pt–P)	δ	^3J(PF)	^2J(Pt–F)
NCNH$_2$ [c]	6.62–6.22 (m, br)	30 (30)	$\mathrm{P}Ph_3$	−117.69 (q)	20.3	2898.9	−15.19 (t)	20.3	705.2
	4.59 (s)	2 (2)	$\mathrm{N}H_2$						
NCNMe$_2$ [d]	7.72–7.56 (m)	30 (30)	$\mathrm{P}Ph_3$	−118.61 (q)	20.3	2928.3	−10.90 (t)	20.2	717.4
	1.96 (s)	~ 5 (6)	$\mathrm{C}H_3$						
NCNEt$_2$ [d]	7.73–7.24 (m)	30 (30)	$\mathrm{P}Ph_3$	−118.10 (q)	20.3	2926.6	−10.49 (t)	20.0	717.4
	2.29 (q) [e]	4 (4)	$\mathrm{C}H_2$						
	0.46 (t) [e]	6 (6)	$\mathrm{C}H_3$						
NCNC(NH$_2$)$_2$ [c]	7.8–7.5 (m)	30 (30)	$\mathrm{P}Ph_3$	−118.20 (q)	19.2	2939.2	−14.67 (t)	19.2	702.7
	5.68 (s, br)	~ 3 (4)	$\mathrm{N}H_2$						

[a] δ values in ppm relative to SiMe$_4$ (^{1}H), P(OMe)$_3$ (^{31}P) or CFCl$_3$ (^{19}F); J values in Hz; s = singlet, t = triplet, q = quartet, m = multiplet, br = broad. [b] Resonances due to the CF$_3$ ligand; a singlet at δ −151.4, with the required relative intensity, is assigned to BF$_4^-$. [c] In DMSO. [d] In CDCl$_3$. [e] ^3J(HH) = 7.2 Hz.

This displacement of the organocyanamide by bromide was observed only for the CF$_3$ complexes **1**, but not for the analogous chloro compounds **2**, indicating that CF$_3$ has a higher *trans* influence on the organocyanamide ligand than Cl.

For the *cis* complexes **3**, the IR data cannot be so clearly understood, and, in particular, no band which could be assigned to ν(N≡C) was detected for **3** [L = NCNC(NH$_2$)$_2$], whereas the cyanamide analogue **3** (L = NCNH$_2$) has ν(N≡C) at 2215 cm^{-1} (either in Nujol mull or in KBr pellet) which is 35 cm^{-1} less than that observed in the proligand. Although anomalies in the ν(NC) bands of coordinated organonitriles are known and these bands have not been detected in some cases [17], the surprising ν(N≡C) shift to ca. 100 cm^{-1} below that observed for the related *trans* complex **1** [L = NCNH$_2$)] upon coordination of NCNH$_2$ in **3** (L = NCNH$_2$) can tentatively be explained by postulating side-on coordination of the cyanamide which could be stabilized by hydrogen-bonding to the *cis* chloride (c).



(c)

Table 5
^{1}H and ^{31}P NMR data [a] for *trans*-[PtCl(L)(PPh$_3$)$_2$][BPh$_4$] (**2**) (L = NCNMe$_2$ or NCNEt$_2$) and *cis*-[PtCl(L)(PPh$_3$)$_2$][BPh$_4$] (**3**) [L = NCNH$_2$ or NCNC(NH$_2$)$_2$]

Complex, L	^{1}H			^{31}P		
	δ	Integ.	Assignment	δ	^2J(PP)	^1J(Pt–P)
2, NCNMe$_2$ [b]	7.48–7.26 (m)	38 (38)	$\mathrm{P}Ph_3 + H_{ortho}(\mathrm{BPh}_4^-)$	−119.96 (s)		3065.8
	7.03 (t) [c]	8 (8)	$H_{meta}(\mathrm{BPh}_4^-)$			
	6.85 (t) [d]	4 (4)	$H_{para}(\mathrm{BPh}_4^-)$			
	1.83 (s)	6 (6)	$\mathrm{C}H_3$			
2, NCNEt$_2$ [b]	7.51–7.29 (m)	38 (38)	$\mathrm{P}Ph_3 + H_{ortho}(\mathrm{BPh}_4^-)$	−119.32 (s)		3070.0
	7.02 (t) [e]	8 (8)	$H_{meta}(\mathrm{BPh}_4^-)$			
	6.87 (t) [d]	4 (4)	$H_{para}(\mathrm{BPh}_4^-)$			
	2.18 (q) [c]	4 (4)	$\mathrm{C}H_2$			
	0.50 (t) [c]	6 (6)	$\mathrm{C}H_3$			
3, NCNH$_2$ [f]	6.50–6.26 (m, br)	30 (30)	$\mathrm{P}Ph_3$	−131.42 (d)	18.6	3807.7
	6.16 (s, br)	8 (8)	$H_{ortho}(\mathrm{BPh}_4^-)$	−132.24 (d)		3448.2
	5.90 (t) [g]	8 (8)	$H_{meta}(\mathrm{BPh}_4^-)$			
	5.77 (t) [g]	4 (4)	$H_{para}(\mathrm{BPh}_4^-)$			
	4.71 (s, br)	2 (2)	$\mathrm{N}H_2$			
3, NCNC(NH$_2$)$_2$ [f]	6.53–6.26 (m)	30 (30)	$\mathrm{P}Ph_3$	−123.58 (d)	25.2	3211.1
	6.15 (s, br)	8 (8)	$H_{ortho}(\mathrm{BPh}_4^-)$	−128.55 (d)		3184.4
	5.90 (t) [d]	8 (8)	$H_{meta}(\mathrm{BPh}_4^-)$			
	5.76 (t) [h]	4 (4)	$H_{para}(\mathrm{BPh}_4^-)$			
	5.33 (br)					
	4.90 (br)	ca. 3 (4)	$\mathrm{N}H_2$			
	4.88 (br)					

[a] See footnote a for Table 4. [b] In CD$_2$Cl$_2$. [c] ^3J(HH) = 7.2 Hz. [d] ^3J(HH) = 7.1 Hz. [e] ^3J(HH) = 7.7 Hz. [f] In DMSO-d_6. [g] ^3J(HH) = 7.4 Hz. [h] ^3J(HH) = 6.8 Hz.

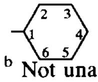
Additional broad and medium intensity bands in the range 3340–3060 cm^{-1} (L = $NCNH_2$) and 3460–3360 cm^{-1} [L = $NCNC(NH_2)_2$] are assigned to ν(NH), and other strong bands at 1585–1575 cm^{-1} (L = $NCNH_2$) or 1715–1520 cm^{-1} [L = $NCNC(NH_2)_2$] are due to δ(NH) and/or ν(N=C). Usually similar frequencies have been reported for these bands for the rhenium complexes mentioned above.

Moreover, strong bands assigned to ligating CF_3 are observed for complexes **1** at ca. 1090 and 1020 cm^{-1}, superimposed on the strong and broad band due to the BF_4^-.

Table 6
^{13}C NMR data for *trans*-[Pt(CF_3)(L)(PPh_3)$_2$][BF_4] (**1**) [a]

L	δ	^{13}C-{^{1}H}			^{13}C		Assignment
		Struct.	^{J} (Hz)		Struct.	J(CH) (Hz)	
$NCNH_2$	134.03	t	6.3	$\frac{1}{2}\vert{}^3J(CP) + {}^5J(CP)\vert$	dq′	161.3 6.3 (^2J)	$C(3) + C(5)$ (PPh_3)
	131.97	s		–	dt	161.8 6.5 (^2J)	$C(4)$ (PPh_3)
	129.22	t	5.6	$\frac{1}{2}\vert{}^2J(CP) + {}^4J(CP)\vert$	dq	162.6 5.6 (^2J)	$C(2) + C(6)$ (PPh_3)
	128.30	t	29.7	$\frac{1}{2}\vert{}^1J(CP) + {}^3J(CP)\vert$	m	–	$C(1)$ (PPh_3)
	121.45	s	~ 113	[^2J(PtC)]	s,br	–	$NCNH_2$
	109.40	q	326.3	[^1J(CF)]	–	–	CF_3
$NCNMe_2$	134.26	t	6.5	$\frac{1}{2}\vert{}^3J(CP) + {}^5J(CP)\vert$	dq′	162.5 6.5 (^2J)	$C(3) + C(5)$ (PPh_3)
	131.85	s		–	dt	162.6 6.8 (^2J)	$C(4)$ (PPh_3)
	128.98	t	5.6	$\frac{1}{2}\vert{}^2J(CP) + {}^4J(CP)\vert$	dq	162.9 5.7 (^2J)	$C(2) + C(6)$ (PPh_3)
	128.46	t	29.5	$\frac{1}{2}\vert{}^1J(CP) + {}^3J(CP)\vert$	m	–	$C(1)$ (PPh_3)
	123.04	s		–	s,br	–	$NCNMe_2$
	108.18	q	325.6	[^1J(CF)]	q	–	CF_3
	38.68	s		–	qq	142.6 3.1 (^3J)	CH_3
$NCNEt_2$	134.28	t	6.2	$\frac{1}{2}\vert{}^3J(CP) + {}^5J(CP)\vert$	dq′	162.5 6.7 (^2J)	$C(3) + C(5)$ (PPh_3)
	131.95	s		–	dt	162.4 7.4 (^2J)	$C(4)$ (PPh_3)
	129.04	t	4.9	$\frac{1}{2}\vert{}^2J(CP) + {}^4J(CP)\vert$	dq	163.2 5.6 (^2J)	$C(2) + C(6)$ (PPh_3)
	128.58	t	29.8	$\frac{1}{2}\vert{}^1J(CP) + {}^3J(CP)\vert$	tt	8.6 (^2J)	$C(1)$ (PPh_3)
	121.53	s		–	s,br	–	$NCNEt_2$
	108.15	q	320.6	[^1J(CF)]	q	–	CF_3
	45.01	s		–	tm	143.3	CH_2
	12.49	s		–	qt	127.8 3.1 (^2J)	CH_3
$NCNC(NH_2)_2$	160.08	q	~ 4.4	[^4J(CF)] [b]	m,br	–	$NCNC(NH_2)_2$
	134.23	t	6.2	$\frac{1}{2}\vert{}^3J(CP) + {}^5J(CP)\vert$	dq′	163.1 6.1 (^2J)	$C(3) + C(5)$ (PPh_3)
	131.69	s		–	dt	163.0 7.2 (^2J)	$C(4)$ (PPh_3)
	128.96	t	5.3	$\frac{1}{2}\vert{}^2J(CP) + {}^4J(CP)\vert$	dq	162.7 5.8 (^2J)	$C(2) + C(6)$ (PPh_3)
	128.79	t	29.1	$\frac{1}{2}\vert{}^1J(CP) + {}^3J(CP)\vert$	tt	7.5 (^2J)	$C(1)$ (PPh_3)
	120.71	s		–	s,br	–	$NCNC(NH_2)_2$
	111.07	q	326.8	[^1J(CF)]	q	–	CF_3

[a] Spectra recorded in DMSO-d_6 [L = $NCNH_2$ or $NCNC(NH_2)_2$] or $CDCl_3$ (L = $NCNMe_2$ or $NCNEt_2$); δ values in ppm relative to $SiMe_4$; s = singlet, t = triplet, q = quartet, m = multiplet, br = broad, dt = doublet of triplets, dq = doublet of quartets, dq′ = doublet of quintets, dm = doublet of multiplets, tt = triplet of triplets, tm = triplet of multiplets, qt = quartet of triplets, qq = quartet of quartets; phenyl carbons are labelled as follows:



[b] Not unambiguously established (see text).

Table 7
^{13}C NMR data [a] for *trans*-[PtCl(L)(PPh$_3$)$_2$][BPh$_4$] (**2**) (L = NCNMe$_2$ or NCNEt$_2$) and *cis*-[PtCl(L)(PPh$_3$)$_2$][BPh$_4$] (**3**) [L = NCNH$_2$ or NCNC(NH$_2$)$_2$]

Complex, L	δ	^{13}C-{^1H}		^{13}C		Assignment
		Struct.	J (Hz)	Struct.	^1J(CH)/(Hz)	
2, NCNMe$_2$	165.28	q [b]	49.0 [^1J(CB)]	q [b],br	–	C(1) (BPh$_4^-$)
	137.38	s	–	dt	135.2 6.4 (^2J)	C(3) + C(5) (BPh$_4^-$)
	135.42	t	6.2 $\frac{1}{2}\lvert ^3J(CP) + ^5J(CP)\rvert$	dq′	161.9 6.5 (^2J)	C(3) + C(5) (PPh$_3$)
	132.51	s	–	dt	162.6 6.7 (^2J)	C(4) (PPh$_3$)
	129.98	t	5.3 $\frac{1}{2}\lvert ^2J(CP) + ^4J(CP)\rvert$	dq	158.2 5.8 (^2J)	C(2) + C(6) (PPh$_3$)
	129.47	t	29.1 $\frac{1}{2}\lvert ^1J(CP) + ^3J(CP)\rvert$	m	–	C(1) (PPh$_3$)
	126.33	q [b]	2.9 [^2J(CB)]	dm	152.9	C(2) + C(6) (BPh$_4^-$)
	122.58	s	–	dt	156.3 7.8 (^2J)	C(4) (BPh$_4^-$)
	39.42	s	–	q	142.2	CH$_3$
2, NCNEt$_2$	165.66	q [b]	48.8 [^1J(CB)]	q [b],br	–	C(1) (BPh$_4^-$)
	137.38	s	–	dt	156.1 5.3 (^2J)	C(3) + C(5) (BPh$_4^-$)
	135.46	t	6.2 $\frac{1}{2}\lvert ^3J(CP) + ^5J(CP)\rvert$	dq′	153.1 6.0 (^2J)	C(3) + C(5) (PPh$_3$)
	132.56	s	–	dt	160.7 7.2 (^2J)	C(4) (PPh$_3$)
	130.01	t	5.3 $\frac{1}{2}\lvert ^2J(CP) + ^4J(CP)\rvert$	dq	162.9 6.0 (^2J)	C(2) + C(6) (PPh$_3$)
	129.60	t	29.4 $\frac{1}{2}\lvert ^1J(CP) + ^3J(CP)\rvert$	m	–	C(1) (PPh$_3$)
	126.32	q [b]	2.7 [^2J(CB)]	d,br	153.2	C(2) + C(6) (BPh$_4^-$)
	122.57	s	–	dt	157.6 7.6 (^2J)	C(4) (BPh$_4^-$)
	46.57	s	–	t	143.5	CH$_2$
	13.72	s	–	q	127.8	CH$_3$
3, NCNH$_2$	163.47	q [b]	49.4 [^1J(CB)]	q [b],br	–	C(1) (BPh$_4^-$)
	135.66	s		dt	143.8 8.1 (^2J)	C(3) + C(5) (BPh$_4^-$)
	134.25–133.80	m,br	–	dm,br	ca. 152	C(3) + C(5) (PPh$_3$)
	132.33–131.69	m,br	–	dm,br	ca. 157	C(4) (PPh$_3$)
	128.96–128.59	m,br	–	dm,br	ca. 164	C(2) + C(6) (PPh$_3$)
	125.42	q [b]	2.7 [^2J(CB)]	d,br	155.7	C(2) + C(6) (BPh$_4^-$)
	121.67	s	–	dt	156.9 7.8 (^2J)	C(4) (BPh$_4^-$)
3, NCNC(NH$_2$)$_2$	163.47	q [b]	49.6 [^1J(CB)]	q [b],br	–	C(1) (BPh$_4^-$)
	159.68,157.96 [c]	s,br	–	s,br	–	NCNC(NH$_2$)$_2$
	135.65	s	–	d,br	149.5	C(3) + C(5) (BPh$_4^-$)
	134.85	d	11.2 [^3J(CP)]	dm	163.2	C(3) + C(5) (PPh$_3$)
	134.25	d	11.2 [^3J(CP)]	dm	162.6	
	132.14	s,br	–	dm	164.4	C(4) (PPh$_3$)
	131.78	s,br	–	dm	164.3	
	129.14	d	11.2 [^2J(CP)]	ddd	167.5 7.5 (^2J)	C(2) + C(6) (PPh$_3$)
	128.63	d	11.2 [^2J(CP)]	ddd	163.8 6.9 (^2J)	
	127.31	d	60.1 [^1J(CP)]	m	–	C(1) (PPh$_3$)
	126.32	d	60.8 [^1J(CP)]	m	–	
	125.44	q [b]	2.7 [^1J(CB)]	dm	153.8	C(2) + C(6) (BPh$_4^-$)
	121.69	s	–	dt	156.3 7.6 (^2J)	C(4) (BPh$_4^-$)
	121.04	s	–	–	–	NCNC(NH$_2$)$_2$

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[a] Spectra recorded in (CD$_3$)$_2$CO (**2**) or in DMSO-d_6 (**3**); see also footnote a of Table 6; ddd = doublet of doublets of doublets. [b] 1 : 1 : 1 : 1 quartet. [c] Possibly corresponding to the tautomeric forms N≡C–N(H)–C(=NH)NH$_2$ and N≡C–N=C(NH$_2$)$_2$.

The *trans* geometry of complexes **1** and **2**, or the *cis* geometry of compounds **3** are suggested by the absence or the presence of a medium-strong band at ca. 550 cm^{-1} (i.e. 535 or 540 cm^{-1} for **3**, L = NCNH$_2$ or NCNC(NH$_2$)$_2$, respectively) which is known [18] to be diagnostic of the *cis* arrangement of the two phosphines. Moreover, such geometries are confirmed by ^{31}P NMR spectroscopy (see below).

2.3. ^{31}P and ^{19}F NMR spectra

A quartet [^3J(PF) ca. 20 Hz] or a singlet is observed in the ^{31}P NMR spectra of **1** (Table 4) or **2** (Table 5), respectively, at δ ca. 118 ppm relative to external P(OMe)$_3$, with the expected ^{195}Pt satellites (^1J(PPt) ca. 2940–2900 Hz or ca. 3070 Hz, respectively), consistent with the proposed *trans*-geometry.

The ^{19}F NMR spectra of **1** (Table 4) exhibits the expected triplet resonance and ^3J(PF) coupling constant, assigned to $-CF_3$ (δ ca. -10 to -15 ppm relative to CFCl$_3$). The ^{195}Pt satellites are also observed with ^2J(FPt) ca. 717–703 Hz.

The values of coupling constants are comparable with those exhibited by the related nitrile complexes *trans*-[Pt(CF$_3$)(NCR)(PPh$_3$)$_2$] [BF$_4$] [R = alkyl or aryl, ^3J(PF) ca. 22–20 Hz, ^1J(PPt) ca. 2890–2790 Hz, ^2J(FPt) ca. 728–721 Hz] [9] and the 2-oxazoline compounds *trans*-[Pt(CF$_3$){$\overline{\mathrm{N{=}C(R)OCH_2CH_2}}$}(PPh$_3$)$_2$] [BF$_4$] ($^3J$(PF) ca. 20–18 Hz, ^1J(PPt) ca. 2960–2900 Hz, ^2J(FPt) ca. 635–615 Hz).

Nevertheless, in view of the dependence of ^2J(FPt) on the type of ligand *trans* to CF$_3$ [19], this deserves further attention.

The dialkylcyanamide complexes **1** exhibit ^2J(FPt) values (ca. 717 Hz) which are similar to those of the analogous nitrile compounds and are considerably higher (by ca. 100 Hz) than those of the 2-oxazoline complexes. These indicate that the dialkylcyanamides are bonded through the cyano rather than the amino group, and that both cyanamides and the nitrile have a lower *trans* influence than the 2-oxazolines. Consistent with the first conclusion, ^2J(FPt) for *cis*-[Pt(CF$_3$)$_2$ L$_2$] (L = nitrile or amine), is ca. 80 Hz higher when CF$_3$ is *trans* to a nitrile (L = nitrile) than when *trans* to an amine (L = amine) [19].

However, for the cyanamide and the cyanoguanidine complexes **1**, the binding mode cannot be so clearly established by this method since the values of ^2J(FPt) (705.2 and 702.7 Hz, respectively) are somewhat lower than those of the dialkylcyanamide complexes (ca. 717.4 Hz). Nevertheless, they are well above the value of 600.6 Hz [19] reported for the cationic species [Pt(CF$_3$)(CO)(Me$_2$NCH$_2$CH$_2$NMe$_2$)]$^+$ with an amine *trans* to CF$_3$, which favours the cyano coordination for cyanamide and cyanoguanidine.

2.4. ^{13}C NMR spectra

In the ^{13}C NMR spectra of complexes **1** (Table 6) and **3** (L = cyanoguanidine) (Table 7), the resonance of the cyano group (N≡*C*–) occurs as a broad singlet at δ ca. 123–121 ppm, at only a slightly lower field (by ca. 2–4 ppm) than that of the corresponding free proligand. The ^{195}Pt satellites were only detected for the cyanamide compound **1** with ^2J(CPt) = 113 Hz, a value comparable with those (90–95 Hz) reported [9] for *trans*-[Pt(CF$_3$)(NCR)(PPh$_3$)$_2$][BF$_4$] and also found [20] in other Pt^{II} cationic complexes, consistent with the coordination of cyanamide through the cyano group. These values are considerably lower than those exhibited by the neutral compounds *cis*- and *trans*-[PtCl$_2$(NCR)$_2$] (234–218 Hz or 298–237 Hz, respectively) [21].

For complexes **2** (Table 7) the N≡*C*– resonance was not clearly established, conceivably being buried under resonances of the BPh$_4^-$.

For the cyanoguanidine complexes, the imine carbon NCN*C*(NH$_2$)$_2$ resonance is observed at δ ca. 160 ppm, ca. 3 ppm slightly upfield of that for the free substrate. Two resonances are detected for **3** (L = cyanoguanidine) (at δ 159.68 and 157.96 ppm), possibly corresponding to the two forms NCN(H)*C*(=NH)NH$_2$ and NCN=*C*(NH$_2$)$_2$.

In both the ^{13}C- ^{1}H coupled and decoupled spectra of **1** (L = cyanoguanidine), this resonance is a quartet conceivably due to coupling to CF_3. The value of the coupling constant, 4.4 Hz, would be acceptable for ^4J(CF), by comparison with the values of long-range C–F couplings in some organofluoro-compounds [22]. The cyanoguanidine may therefore bind through an amino group rather than the cyano group in distinction to the discussion above. However, for none of the N≡C coordinated nitriles [9] or cyanamides of this work was coupling between the cyano-carbon and CF_3 observed.

The CF_3 resonance in complexes **1** is hardly detected as a rather weak quartet (J(CF) ca. 326–321 Hz) at δ ca. 110 ppm without evident ^{195}Pt satellites. These data are similar to those reported [19] for the nitrile complexes *cis*-[Pt(CF$_3$)$_2$(NCR)$_2$] [δ ca. 111 ppm, J(CF) = 329.0 Hz (R = Me) or 329.8 Hz (R = Ph)].

For the *trans* bis(phosphine) complexes, the triplets, resulting from virtual coupling to the two ^{31}P nuclei, with $\frac{1}{2}|\,^1J(\mathrm{CP}) + {}^3J(\mathrm{CP})\,|$ ca. 30 Hz in the ^{13}C{^{1}H} NMR spectra at δ ca. 128 ppm (**1**) or ca. 129 ppm (**2**) are assigned to the C(1) carbons bonded to the P atoms (Tables 6 and 7, Fig. 2). In the ^{13}C-^{1}H undecoupled spectra, they split into a triplet of broad triplets (^2J(CH) ca. 8 Hz) (**1**) (see Fig. 2) or give an unresolved multiplet (**2**). The *para*-carbons, C(4), exhibit a singlet resonance at δ ca. 132 ppm which is split in the ^{13}C-^{1}H undecoupled spectra into the expected doublet (^1J(CH) ca. 162 Hz) of triplets (^2J(CH) ca. 7 Hz) (Fig. 2).

The resonances of the *ortho*-carbon atoms [C(2) + C(6)] or of the *meta*-carbons [C(3) + C(5)] consist of a triplet due to virtual coupling to the two ^{31}P nuclei at δ ca. 129–130 ppm [$\frac{1}{2}|^2J(\mathrm{CP}) + ^4J(\mathrm{CP})| \approx 5.5$ Hz] or ca. 134–135 ppm [$\frac{1}{2}|^3J(\mathrm{CP}) + ^5J(\mathrm{CP})| \approx 6.3$ Hz], respectively. The similarity of these coupling constants (both ca. 6 Hz) agrees with those observed for ^2J(CP) and ^3J(CP) (both ca. 11 ± 2 Hz) in other phosphine complexes of Pt$^{\mathrm{II}}$, Pd$^{\mathrm{II}}$ [23] or Pt^0 [24], and does not allow us to distinguish between the two types of carbon. Therefore, the assignment was based on the patterns observed in the ^{13}C-^{1}H undecoupled spectra (Fig. 2). A doublet [J(CH) ca. 160 Hz] of quartets (each of them corresponding to a doublet, ^2J(CH) ca. 6 Hz, of overlapping triplets) for C(2) + C(6), and a doublet (J(CH) ca. 162 Hz) of quintets (each of them corresponding to a triplet, ^2J(CH) ca. 6 Hz, of overlapping triplets) for C(3) + C(5).

The chemical shifts of the aromatic carbon atoms increase in the order *ortho*-, *para*- and *meta*- which is not that observed [24,25] for the Pt^0 phosphine complexes [Pt(olefin)(PPh$_3$)$_2$] in which the *ortho*-carbons resonate at the lowest field. However, the biggest shifts occur for the P-bound carbons [C(1)]. Their resonances (δ ca. 128–129 ppm) occur at a considerably higher field than that (δ ca. 135 ppm) reported [25] for [Pt(L)(PPh$_3$)$_2$] (L = diethyl fumarate or diethyl maleate) and than that observed (137.8 ppm) for free PPh$_3$. This substantial higher field complexation shift for C(1) is also observed in the related trifluoromethyl nitrile and 2-oxazoline complexes *trans*-[Pt(CF$_3$)(L)(PPh$_3$)$_2$][BF$_4$], as well as in the methyl compound *trans*-[Pt(CH$_3$)(NCMe)(PPh$_3$)$_2$][BF$_4$], and is considerably more extensive than that exhibited by the hydride complex *trans*-[Pt(H)(NCMe)(PPh$_3$)$_2$][BF$_4$] (δ = 130.17 ppm).

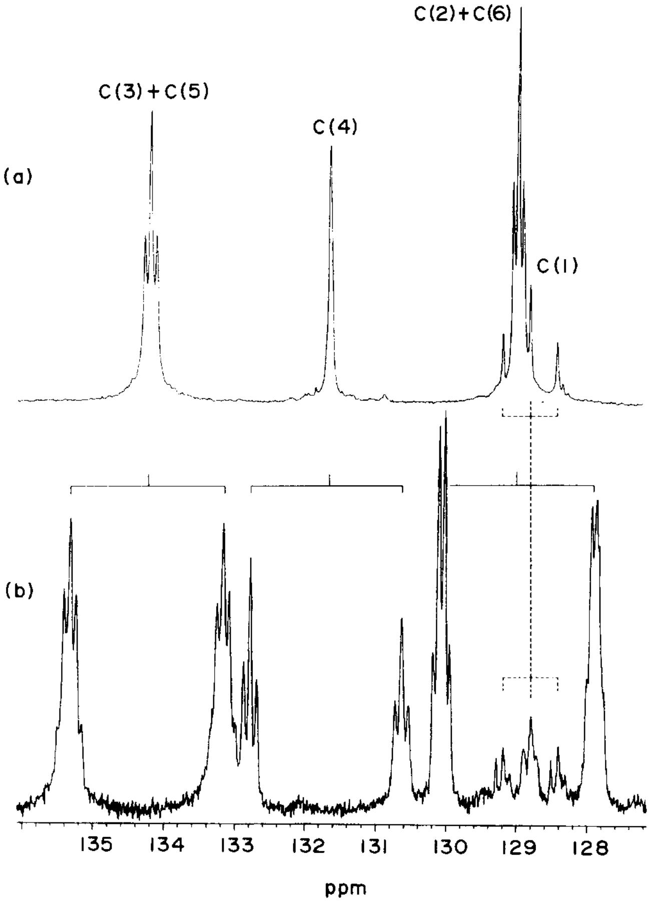

Fig. 2. (a) ^{13}C{^{1}H} NMR and (b) ^{13}C-^{1}H undecoupled NMR spectra (phenyl region) of *trans*-[Pt(CF$_3$){NCNC(NH$_2$)$_2$}(PPh$_3$)$_2$][BF$_4$] (1) (L = cyanoguanidine) (in DMSO-d_6).

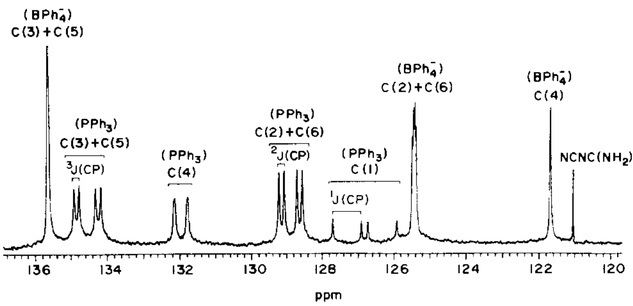

Fig. 3. ^{13}C {^{1}H} NMR spectrum (partial phenyl region) of *cis*-[PtCl{NCNC(NH$_2$)$_2$}(PPh$_3$)$_2$][BPh$_4$] (3) (L = cyanoguanidine) (in DMSO-d_6).

Therefore, the high-field phosphine complexation shift on coordination is greater for the square planar Pt$^{\mathrm{II}}$ cationic complexes than for the Pt^0 neutral compounds and is also particularly sensitive to the anionic ligand (rather than to the neutral one) which is *cis* to the phosphines.

The ^{13}C{^{1}H} NMR spectra (Table 7) of the *cis*-(bis) phosphine complexes **3** also exhibit an apparently more complex resonance pattern than the compounds **1** or **2** with the *trans* geometry, due to the non-equivalence of the two PPh$_3$ ligands. The phenyl-carbon resonances of these ligands occur as two sets of identical multiplets which are resolved for the cyanoguanidine complex *cis*-[PtCl{NCNC(NH$_2$)$_2$}(PPh$_3$)$_2$] [BPh$_4$] (**3**) (L = cyanoguanidine) and are shown in Fig. 3. The two singlets at δ ca. 132 ppm are assigned to the two non-equivalent C(4) carbons (one for each phosphine), whereas C(1), C(2) + C(6) or C(3) + C(5) present two sets (one for each phosphine) of doublets (^1J(C(1)P) ca. 60 Hz, ^2J(C(2)P) = ^3J(C(3)P) = 11.2 Hz) at δ ca. 127, 129 and 134.5 ppm, respectively. The relative positions of those resonances are identical to that found in complexes **1** and **2**.

In the ^{13}C-^{1}H undecoupled spectrum, each C(2) + C(6) doublet splits into a doublet [J(CH) ca. 165 Hz] of doublets [^2J(CP) = 11.2 Hz] of doublets [^2J(CH) ca. 7 Hz], whereas a doublet [J(CH) ca. 163 Hz] of unresolved multiplets results from each C(3) + C(5) doublet.

2.5. Final comments

Organocyanamides (N≡CNR$_2$) bind linearly and η^1 to the cationic Pt^{II} centres in this study through the cyano group with a highly delocalized π system involving electron donation from the amino nitrogen to the cyano group (possibly assisted by the electron-donor resonance ability of the organic R moieties). Hence, in an overall and qualitative way, they appear to behave similarly to a halide, as both a σ-donor and a π-electron donor to the cationic metal sites. They experience a strong *trans* influence of CF$_3$, and are readily displaced by bromide even in the solid state.

However, the binding mode of cyanamide itself or its dimer (cyanoguanidine) has not been clearly established. Although IR spectroscopic evidence supports the η^2-N≡C coordination of the former in the *cis*-chloro complex, and ^{13}C NMR spectroscopy suggests the possible binding of cyanoguanidine through an amino group in one of the complexes, no unequivocal assignment of the real structures can be given at this stage without X-ray diffraction analyses, which we have not yet succeeded in obtaining.

3. Experimental details

The complexes *trans*-[PtBr(CF$_3$)(PPh$_3$)$_2$] [26] and *cis*-[PtCl$_2$(PPh$_3$)$_2$] [27] were prepared by published methods, whereas the other reagents were purchased from Aldrich.

All reactions were carried out under dinitrogen, through standard vacuum and inert gas flow techniques. The solvents were dried by standard procedures and freshly distilled before use. IR spectra were recorded with Perkin-Elmer 683 or 457 spectrophotometers, whereas the ^{1}H, ^{31}P, ^{19}F and ^{13}C NMR spectra were recorded on a Varian Unity 300 spectrometer.

3.1. Preparation of complexes *trans*-[Pt(CF$_3$)(L)(PPh$_3$)$_2$][BF$_4$] (1) [L = NCNH$_2$, NCNC(NH$_2$)$_2$, NCNMe$_2$ or NCNEt$_2$]

A common method was used for the syntheses of these complexes, and a typical procedure is given below for compound **1** (L = NCNH$_2$). To a solution of 0.20 g (0.23 mmol) of *trans*-[PtBr(CF$_3$)(PPh$_3$)$_2$] in CH$_2$Cl$_2$ (70 cm^3) was added, in one portion, an excess of cyanamide (0.040 g, 0.90 mmol) and of AgBF$_4$ (0.44 mmol, 4 cm^3 of a recently prepared 0.10 M solution of this salt in acetone), and the reaction mixture was stirred for ca. 3 h at room temperature and in the absence of light. The grey solid formed was filtered off and the filtrate concentrated in vacuo. Dropwise addition of Et$_2$O gave a pale cream solid which was filtered-off and recrystallized from CH$_2$Cl$_2$/n-pentane to give **1** (L = NCNH$_2$) as a white solid (ca. 70% yield).

3.2. Preparation of complexes *trans*-[PtCl(L)(PPh$_3$)$_2$][BPh$_4$] (2) (L = NCNMe$_2$ or NCNEt$_2$) and *cis*-[PtCl(L)(PPh$_3$)$_2$][BPh$_4$] (3) [L = NCNH$_2$ or NCNC(NH$_2$)$_2$]

The general procedure followed in the synthesis of complexes **2** and **3** involved stirring of a suspension of *cis*-[PtCl$_2$(PPh$_3$)$_2$] (0.15 g, 0.19 mmol) in THF (70 cm^3) at room temperature with an excess of L (1:4) and of NaBPh$_4$ (1:4) until only a slight suspension remained (ca. 1 week for **3**, L = NCNC(NH$_2$)$_2$ and 1 or 2 days for the other complexes). The white precipitate of NaCl was then filtered off and the filtrate was taken to dryness. The resulting solid was dissolved in CH$_2$Cl$_2$ (ca. 20 cm^3), the solution was filtered and the solvent was again removed in vacuo. The residue was dissolved in acetone, the solution filtered and on addition of MeOH the products precipitated as white solids which were filtered off, washed with acetone/MeOH (1:3) and dried in vacuo. The products were then recrystallized from CH$_2$Cl$_2$/n-pentane to give white solids (ca. 50–70% yields).

3.3. Reaction of *trans*-[Pt(CF$_3$)(NCNEt$_2$)(PPh$_3$)$_2$][BF$_4$] (1) (L = NCNEt$_2$) with KBr

A suspension of *trans*-[Pt(CF$_3$)(NCNEt$_2$)(PPh$_3$)$_2$][BF$_4$] (38 mg, 0.031 mmol) and KBr (58 mg, 0.49 mmol) in THF (5 cm^3) was stirred for 1 day and the solvent was then removed in vacuo. Extraction with CH$_2$Cl$_2$ (ca. 5 cm^3) followed by filtration and addition of diethyl ether led to the precipitation of a white solid which was filtered-off, washed with diethyl ether and dried in vacuo (ca. 80% yield). It was identified by IR, ^{1}H and ^{31}P NMR spectroscopy (in CDCl$_3$) as trans-[PtBr(CF$_3$)(PPh$_3$)$_2$].

3.4. Crystal data

trans[Pt(CF$_3$){NCN(C$_2$H$_5$)$_2$}(PPh$_3$)$_2$][BF$_4$], M_r = 973.6, monoclinic, space group $P2\ 1/n$, $a = 16.385(3)$, $b = 25.651(4)$, $c = 9.811(3)$ Å, $\beta = 90.15(4)°$; $V = 4124(2)$ Å^3, $Z = 4$, $D_x = 1.57$ mg m^{-3}, $\lambda = (\text{Mo K}\alpha) = 0.71069$ Å, $\mu(\text{Mo K}\alpha) = 3.54$ mm^{-1}, $F(000) = 1928$, $T = 293$ K.

A prismatic white crystal of dimensions 0.28 × 0.32 × 0.42 mm was centered on a four-circle Philips PW1100 (Febo System) diffractometer with graphite-monochromated (Mo Kα) radiation ($\lambda = 0.71069$ Å). The orientation matrix and preliminary unit-cell dimensions were determined from 25 reflections found by mounting the crystal at random, varying each of the orientation angles and χ and Φ over a range of 120°, with $7 \leq \theta \leq 9°$. For the determination of precise lattice parameters, 37 strong reflections with $10 \leq \theta$ 12° were considered. Integrated intensities for *hkl* reflections ($h = \pm 20$; $k = 0 \rightarrow 30$, $\ell = 0 \rightarrow 12$ were measured in the interval $\theta = 2$–$27°$), using θ–2θ scans. Three standard reflections, 2,4,0, and −4,6,1 were collected every 200 reflections. There were no significant fluctuations of intensity other than those expected from Poisson statistics. The intensity data were corrected for Lorentz-polarization effects and for absorption as described by North et al. [28]. No correction was made for extinction.

The structure was solved by heavy atoms methods [29]. Refinement was by full-matrix least-squares minimizing the function $\Sigma w(F_o^2 - F_c^2)^2$ with weighting scheme $w = 1/[\sigma^2(F_o^2) + (0.0365P)^2 + 14.63P]$, where $P = \max(F_o^2 + 2F_c^2)/3$. All non-hydrogen atoms were refined with anisotropic thermal parameters, except for the BF_4 group refined isotropically. Hydrogen atoms were placed in calculated positions and were assigned fixed, isotropic thermal parameters (1.2 U_{equiv} of the parent carbon atom). For a total of 475 parameters, $wR' = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2} = 0.081$ (on F^2), $S = 1.258$, and conventional $R = 0.0251$ (on F). The wR' and R were calculated with the 4253 unique observed reflections having $F_o^2 \leq 3\sigma(F_o^2)$. Scattering factors were taken from [30]. Structure refinement and final geometrical calculations were carried out with SHELXL-93 [31], PARST [32] programs and drawing was produced using ORTEP II [33].

Lists of H-atom coordinates and anisotropic thermal parameters have been deposited with the Cambridge Crystallographic Data Centre.

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