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Synthesis and redox properties of complexes of rhenium(I) with cyanoguanidine and some derivatives. Crystal structure of *trans*-$[Re\{NCNC(NH_2)_2\}(CNMe)(Ph_2PCH_2CH_2PPh_2)_2][BF_4]$

M. Fernanda N.N. Carvalho and Armando J.L. Pombeiro

Centro de Química Estrutural, Complexo I, Instituto Superior Técnico, Av. Rovisco Pais, 1096 Lisboa codex (Portugal)

Adrian Hills, David L. Hughes and Raymond L. Richards

AFRC Institute of Plant Science Research, Nitrogen Fixation Laboratory, University of Sussex, Brighton BN1 9RQ (UK)

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Abstract

Reaction of cyanoguanidine, $NCNC(NH_2)_2$, with *trans*-$[ReCl(CNMe)(dppe)_2]$ (dppe = $Ph_2PCH_2CH_2PPh_2$) in CH_2Cl_2 in the presence or absence of $Tl[BF_4]$, forms *trans*-$[Re\{NCNC(NH_2)_2\}(CNMe)(dppe)_2]A$ [A = BF_4 (**Ia**) or Cl (**Ib**)]. The crystal structure of **Ia** has been determined by an X-ray diffraction analysis. **Ib** can also be obtained by using cyanamide, $NCNH_2$, instead of cyanoguanidine, in refluxing solvent. Treatment of **Ia** with KO^tBu affords *trans*-$[Re\{NCNC(NH)NH_2\}(CNMe)(dppe)_2]$ (**II**), *trans*-$[Re(NCNCN)(CNMe)(dppe)_2]$ (**III**) or *trans*-$[Re(NCNHCN)(CNMe)(dppe)_2][BF_4]$ (**IV**). The redox properties of these complexes have been studied by cyclic voltammetry and controlled potential electrolysis at Pt electrodes in aprotic media, and the P_L ligand parameter has been estimated for the cyanoguanidine and derived ligands. Moreover, cathodic reduction of **I** or **IV** partially generates **II** or **III**, respectively.

Key words: Rhenium; Cyanoguanidine; Cyanamide; Electrochemistry; Crystal structure

1. Introduction

Cyanoguanidine [or dicyandiamide, with tautomeric forms $N{\equiv}C{-}N{=}C(NH_2)_2$ and $N{\equiv}C{-}NHC({=}NH)NH_2$], a commercially important compound, is a versatile precursor for the syntheses of organonitrogen compounds which include biguanides, guanylureas and derivatives [1]. The coordination chemistry of these species has been the object of considerable attention [2], and X-ray structural analyses have been reported [3–7] for some cyanoguanidine complexes. Moreover, coordination of substituted guanidines is of biological relevance, in particular for the understanding of the metal binding of arginine residues. In addition, cyanoguanidine is the dimeric form of cyanamide ($N{\equiv}CNH_2$), a recently recognized [8] substrate of nitrogenases, and in pursuit of our interest in the activation by dinitrogen-binding centres of small molecules with biological significance [9], we have previously described the reactions of cyanamide with *trans*-$[M(N_2)_2(dppe)_2]$ (M = Mo or W, dppe = $Ph_2PCH_2CH_2PPh_2$) and *trans*-$[ReCl(CNR)(dppe)_2]$ (R = Me or ^tBu) to give the bis(cyanoimido) complexes *trans*-$[M(NCN)_2(dppe)_2]$ [10] and the cyanamide compounds *trans*-$[ReL(CNR)(dppe)_2]^+$ (L = $NCNH_2$ or $NCNH^-$) [11]. We now extend this type of study to cyanoguanidine and report its reactivity towards *trans*-$[ReCl(CNMe)(dppe)_2]$.

2. Results and discussion

2.1. Cyanoguanidine complexes

Treatment of a dichloromethane solution of *trans*-$[ReCl(CNMe)(dppe)_2]$ with a slight excess of cyanoguanidine, $NCNC(NH_2)_2$, and of $Tl[BF_4]$, at room tem-

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Correspondence to: Professor A.J.L. Pombeiro.

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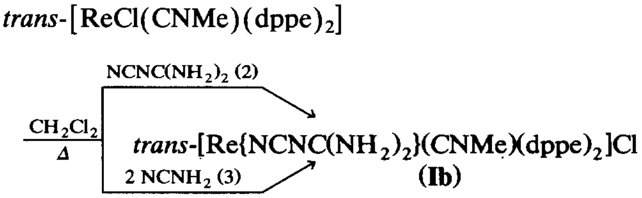
perature, for *ca.* 0.5 h, affords *trans*-[Re{NCNC$(NH_2)_2$}(CNMe)$(dppe)_2$][BF_4] (**Ia**) (eqn. (1)). A similar method has been used to synthesize the related cyanamide complexes *trans*-[Re($NCNH_2$)(CNR)$(dppe)_2$][BF_4] (R = Me or ^{t}Bu) by reaction of the corresponding isocyanide compound with $NCNH_2$ [11].

$$trans\text{-}[ReCl(CNMe)(dppe)_2] + NCNC(NH_2)_2 + Tl[BF_4] \xrightarrow{CH_2Cl_2}$$

$$trans\text{-}[Re\{NCNC(NH_2)_2\}(CNMe)(dppe)_2][BF_4] + TlCl \qquad (1)$$
$$\text{(Ia)}$$

Replacement of Cl by cyanoguanidine can also occur in the absence of Tl^+, although less effectively and under more vigorous reaction conditions. Thus *trans*-[Re{NCNC$(NH_2)_2$}(CNMe)$(dppe)_2$]Cl (**Ib**) is obtained (*ca.* 20% yield) by heating a CH_2Cl_2 solution of *trans*-[ReCl(CNMe)$(dppe)_2$] with a fivefold molar excess of cyanoguanidine under reflux for 2 days (eqn. (2)). The same product can be prepared by using cyanamide ($NCNH_2$) instead of cyanoguanidine (eqn. (3)) since the former isomerizes to the latter upon heating.

Complexes **I** have in their IR spectra (Table 1) strong ν(N≡C) bands, which are assigned to cyanoguanidine at *ca.* 2230 cm^{-1}, whereas ν(C≡N) of the ligating isocyanide occurs at *ca.* 1955 cm^{-1}. These IR features are comparable with those displayed by the cyanamide complexes *trans*-[Re($NCNH_2$)(CNR)$(dppe)_2$][BF_4] [11]. Other assignments are also given in Table 1.



$$trans\text{-}[ReCl(CNMe)(dppe)_2] \xrightarrow[\Delta]{CH_2Cl_2} \begin{cases} NCNC(NH_2)_2 \ (2) \\ 2\ NCNH_2 \ (3) \end{cases} \rightarrow trans\text{-}[Re\{NCNC(NH_2)_2\}(CNMe)(dppe)_2]Cl$$

(**Ib**)

The *trans* geometry of complexes **I** is indicated by the singlet resonance observed in their ^{31}P NMR spectra (Table 2). In the ^1H NMR spectrum (Table 2), the $CNCH_3$ resonance occurs as the expected singlet.

The molecular structure of complex **Ia** has been confirmed by a single-crystal X-ray diffraction analysis and the Re-complex cation is shown in Fig. 1; the anion is disordered over two orientations with a common **B** atom. Atomic coordinates are given in Table 3 and selected bond dimensions in Table 4.

The Re atom is coordinated in an approximately octahedral pattern by the four P atoms of two chelating diphosphine ligands (which form the equatorial plane) and a mutually *trans* disposition of isocyanide and cyanoguanidine ligands, the latter binding through the cyano group. This last arrangement shows an almost linear C–N–C–Re–N–C–N array approximately normal to the P_4 plane. The Re atom is displaced 0.057(1)

TABLE 1. Analytical and physical data for the cyanoguanidine complexes *trans*-[Re{NCNC$(NH_2)_2$}(CNMe)$(dppe)_2$]A [A = BF_4 (**Ia**) or Cl (**Ib**)] and derived *trans*-[Re{NCNC(NH)NH_2}(CNMe)$(dppe)_2$] (**II**), *trans*-[Re(NCNCN)(CNMe)$(dppe)_2$] (**III**) and *trans*-[Re(NCNHCN)(CNMe)$(dppe)_2$][BF_4] (**IV**)

Complex	Colour	Anal. found (calc.) (%)			IR [a]			Yield (%)
		C	N	H	ν(NH)	ν(N≡C)	δ(NH) ν(C=N)	
Ia	Yellow	54.9 (55.3)	5.9 (5.9)	4.9 (4.4)	3490sh 3460m 3360m	2225s 2010m 1950m	1640s 1555s	85
Ib [b]	Yellow	56.4 (56.5)	5.9 (5.8)	5.0 (4.7)	3220m	2240s 2020m 1960m	1640m 1585w	20
II	Yellow	60.7 (60.0)	6.3 (6.0)	4.9 (5.1)	3440w 3350w	2175s 1988m		70
III [c]	Yellow	60.0 (60.4)	5.2 (5.0)	4.9 (4.6)		2180m, br 1945m		70
IV [d]	Dark yellow	56.6 (56.5)	5.1 (4.6)	5.2 (4.5)	3440m	2210s, br 1900m, br	1620m 1550s	60

[a] Values in cm^{-1}, measured in KBr pellets. [b] With $3/4CH_2Cl_2$ of crystallization. [c] With $1/2$ CH_2Cl_2 of crystallization. [d] With CH_2Cl_2 of crystallization.

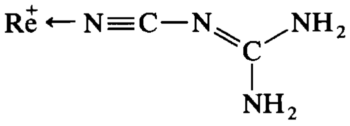
TABLE 2. ^1H and ^{31}P NMR data [a] for *trans*-$[Re\{NCNC(NH_2)_2\}(CNMe)(dppe)_2]A$ (I, A = BF_4 or Cl), *trans*-$[Re\{NCNC(NH)NH_2\}(CNMe)(dppe)_2]$ (II), *trans*-$[Re(NCNCN)(CNMe)(dppe)_2]$ (III) and *trans*-$[Re(NCNHCN)(CNMe)(dppe)_2][BF_4]$ (IV)

Complex	^1H [a]			^{31}P
	δ (ppm) [b]	Integration	Assignment	δ (ppm) [c]
I	7.3–6.8 (m)	40	C_6H_5 (dppe)	
	2.87 (s)	3	$CNCH_3$	−107.9 (s)
	2.4 (m)	4	CH_2 (dppe)	
	2.2 (m)	4		
	1.53 (s) [d]	4	$NCNC(NH_2)_2$	
II	7.5–6.9 (m)	40	C_6H_5 (dppe)	
	3.77 (s,br) [e]	3	$NCNC(NH)NH_2$	−110.5 (s)
	2.65 (s)	3	$CNCH_3$	
	2.4 (m)	8	CH_2 (dppe)	
III	7.4–6.4 (m)	40	C_6H_5 (dppe)	
	3.03 (s)	3	$CNCH_3$	−108.6 (s)
	2.7–2.5 (m)	8	CH_2 (dppe)	
IV	7.2–6.9 (m)	40	C_6H_5 (dppe)	
	2.6–2.5 (m)	8	CH_2 (dppe)	−109.4 (s)
	1.9 (s,br) [d]	1	NCNCNH	

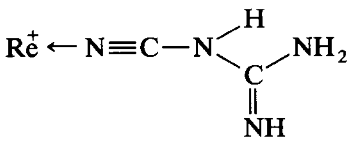
[a] In CD_2Cl_2. [b] Relative to internal $SiMe_4$. [c] Relative to $P(OMe)_3$, assigned to 4*P*(dppe). [d] Decreases in intensity on addition of D_2O. [e] Disappears upon addition of D_2O.

Å from the mean-plane of the four P atoms towards the isocyanide ligand.

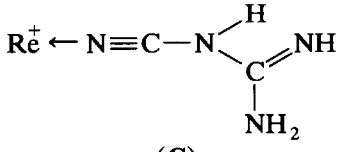
The dimensions of the N–C skeleton of the cyanoguanidine ligand do not indicate clearly the electronic condition of this ligand which has canonical forms **A**, **B** or **C**.



(A)



(B)



(C)

Some possible hydrogen atoms of the cyanoguanidine were located but they did not refine well and were not included in the final refinement cycles. We therefore estimated the positions of H-atoms in trigonal planar arrangements about the three N-atoms, N(61), N(63) and N(64), and examined their likely contacts. We found that one H atom on each of N(63) and N(64) can form a good N–H ··· F hydrogen bond; there are suitable acceptor atoms in the anion in either of its orientations (Table 3). The second H-atom on N(64) is directed towards the centre of the phenyl ring of C(21a) and, on N(63), the second H-atom makes a good contact with the side of the ring of C(11b) of a neighbouring molecule. However, a hydrogen atom

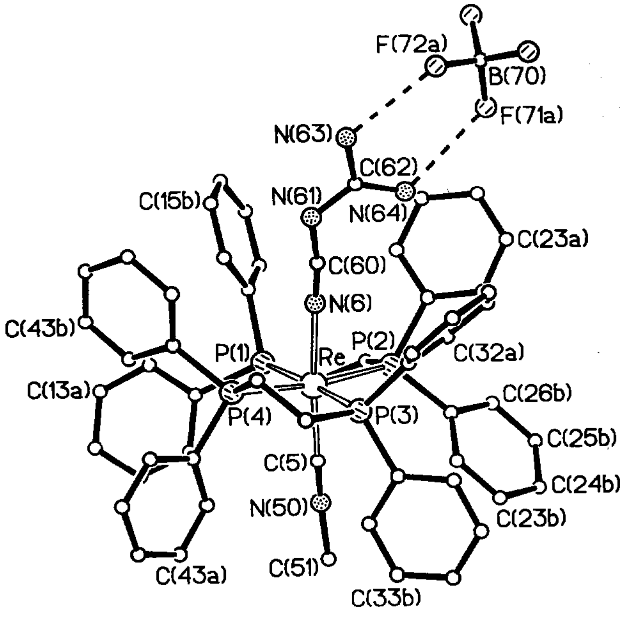


Fig. 1. Molecular structure of the Re-complex cation in *trans*-$[Re\{NCNC(NH_2)_2\}(CNMe)(dppe)_2][BF_4]$ (Ia).

TABLE 3. Final atomic coordinates (fractional ×10^4) for *trans*-[Re{NCNC(NH$_2$)$_2$}(CNMe)(dppe)$_2$]BF$_4$ (estimated standard deviations are in parentheses)

Atom	*x*	*y*	*z*
Re	297.5(2)	2194.4(2)	2642.1(2)
C(11a)	1159(5)	3347(6)	4401(5)
C(12a)	1257(6)	3302(7)	5166(6)
C(13a)	1207(7)	3981(9)	5562(7)
C(14a)	1063(7)	4711(8)	5221(8)
C(15a)	975(8)	4754(7)	4473(8)
C(16a)	1021(6)	4087(6)	4072(7)
C(11b)	1473(5)	1678(5)	4560(4)
C(12b)	2235(5)	1476(5)	4954(5)
C(13b)	2378(6)	896(6)	5504(6)
C(14b)	1765(7)	530(7)	5664(6)
C(15b)	1005(6)	717(6)	5254(6)
C(16b)	859(5)	1298(6)	4709(5)
P(1)	1226(1)	2469(1)	3838(1)
C(1)	2145(5)	2659(5)	3652(5)
C(2)	2339(5)	1990(5)	3214(5)
P(2)	1449(1)	1656(1)	2434(1)
C(21a)	1612(5)	564(5)	2494(5)
C(22a)	1622(6)	100(6)	1885(6)
C(23a)	1735(7)	−714(7)	1967(8)
C(24a)	1856(8)	−1077(8)	2636(10)
C(25a)	1845(7)	−621(7)	3255(8)
C(26a)	1710(6)	191(6)	3178(7)
C(21b)	1749(5)	1927(5)	1622(5)
C(22b)	1285(6)	2397(6)	1037(5)
C(23b)	1511(6)	2637(7)	423(6)
C(24b)	2215(7)	2384(7)	381(7)
C(25b)	2689(7)	1911(7)	946(7)
C(26b)	2464(5)	1681(6)	1553(6)
C(31a)	−893(5)	966(6)	1055(5)
C(32a)	−277(7)	497(8)	1075(7)
C(33a)	−366(9)	−249(10)	753(8)
C(34a)	−1079(9)	−552(8)	432(8)
C(35a)	−1682(9)	−108(9)	404(10)
C(36a)	−1601(8)	656(9)	708(9)
C(31b)	−706(5)	2554(6)	611(5)
C(32b)	−700(5)	3384(6)	670(6)
C(33b)	−681(6)	3848(9)	60(7)
C(34b)	−658(7)	3502(11)	−593(8)
C(35b)	−656(7)	2702(10)	−657(7)
C(36b)	−694(6)	2225(8)	−55(5)
P(3)	−700(1)	1972(1)	1445(1)
C(3)	−1649(5)	2250(6)	1534(5)
C(4)	−1658(5)	2072(5)	2330(5)
P(4)	−833(1)	2601(1)	2975(1)
C(41a)	−1236(5)	3623(6)	2843(5)
C(42a)	−898(6)	4223(6)	2572(6)
C(43a)	−1230(7)	4979(7)	2434(7)
C(44a)	−1910(7)	5113(7)	2572(7)
C(45a)	−2272(6)	4525(8)	2857(7)
C(46a)	−1930(6)	3775(6)	2986(6)
C(41b)	−903(5)	2381(5)	3901(5)
C(42b)	−623(5)	2930(6)	4483(5)
C(43b)	−605(6)	2755(7)	5218(5)
C(44b)	−893(6)	2039(7)	5360(6)
C(45b)	−1182(6)	1489(7)	4805(6)
C(46b)	−1185(6)	1660(6)	4069(6)
C(5)	611(5)	3215(6)	2313(5)
N(50)	845(5)	3801(6)	2149(5)
C(51)	1034(9)	4521(8)	1825(9)
N(6)	−20(4)	1042(4)	2939(4)
C(60)	−265(6)	456(6)	3019(5)
N(61)	−624(6)	−183(5)	3172(6)
C(62)	−525(7)	−906(7)	2909(6)
N(63)	−909(6)	−1526(5)	3084(6)
N(64)	−36(8)	−1038(6)	2534(8)
In the disordered anion [a]			
B(70)	22(5)	−3249(5)	2438(4)
F(71a)	404(5)	−2592(5)	2293(4)
F(72a)	−642(5)	−3013(5)	2589(4)
F(73a)	−175(5)	−3743(5)	1822(4)
F(74a)	500(5)	−3649(5)	3049(4)
F(71b)	409(5)	−3964(5)	2523(4)
F(72b)	−312(5)	−3166(5)	2999(4)
F(73b)	−548(5)	−3225(5)	1750(4)
F(74b)	539(5)	−2639(5)	2483(4)

[a] The anion is disordered over two sites with a common B atom; one anion, of F(71a–74a), has site occupancy refined to 0.54(2), the other, of F(71b–74b), to 0.46(2).

bound to N(61) comes very close to C(14b) of the same ring and appears unlikely. The formula **A** is therefore the most probable for this ligand.

The planarity of the whole ligand suggests extensive π-electron delocalization, as also indicated by the C(60)–N(61) and the three C(62)–N bond lengths (mean 1.336(11) Å) which lie between the expected ranges of C(sp^2)=N(sp^2) and C(sp^2)–N(sp^2) distances, *viz.* 1.28–1.33 Å and 1.34–1.36 Å, respectively, and are rather shorter than normal C(sp^2)–N(sp^3) distances (*ca.* 1.42 Å) [12].

Our cyano N(6)–C(60) bond length, 1.107(13) Å, is the shortest in any reported cyanoguanidine complex, and shorter than that found for the free molecule (1.1743 Å) in the accurate, low-temperature study of Hirshfeld and Hope [13]. Our Re–N distance, 2.138(7) Å, is correspondingly slightly longer than that in [Re{NCNC(NH$_2$)$_2$}(CO)$_5$][BF$_4$], 2.122(7) Å [2]. In comparison with other Re–N≡C complexes, our Re–N distance is long, but that distance depends strongly on the *trans* ligand, *e.g.* in *trans*-[ReCl(NCMe)(dppe)$_2$], the Re–N distance is 1.978(5) Å [14a], and in *trans*-[Re(NCtol)$_2$(dppe)$_2$]$^+$, it is 2.063(7) Å [14b]; in the last complex, we note that the N–C distance is 1.102(13) Å, as short as in our current structure.

The common mode of coordination of cyanoguanidine is "end-on" through the α-N atom of the cyano group [3–7], but additional binding, to a second metal, bridging through the γ-N atom is also known. (The proposed "side-on" binding of the terminal cyano group with a copper centre now appears unlikely [3a].) The bond lengths of the cyanoguanidine ligands in these complexes show considerable variation and no clear pattern. However, in some cases, the four primary amine H-atoms have been located, all forming hydrogen bonds [3b,4]. Other complexes, including the rhenium(I) compound [Re{NCNC(NH$_2$)$_2$}(CO)$_5$][BF$_4$] [2], a tetramethyl derivative [6], and several complexes of cimetidine [15] (a derivative of cyanoguanidine) have also been analysed, and all show the type **A** structure.

In the linear isocyanide ligand, dimensions appear in the normal ranges; the methyl hydrogen atoms were not observed or estimated.

The N–H ··· F hydrogen bonds described above link cations and anions together in discrete pairs. Other interionic contacts are at normal van der Waals' distances.

2.2. Cyanoguanidine-derived complexes

The cyanoguanidine ligand in *trans*-[Re{NCNC(NH$_2$)$_2$}(CNMe)(dppe)$_2$][BF$_4$] (**Ia**) is deprotonated by a base to yield NCNC(NH)NH$_2^-$ in *trans*-[Re{NCNC(NH)NH$_2$}(CNMe)(dppe)$_2$] (**II**) (eqn. (4)). This complex has been isolated by treatment of a THF solution of **Ia** with KO^{t}Bu (1.8 : 1 molar ratio) for 1 h.

$$\underset{\textbf{(Ia)}}{trans\text{-}[\mathrm{Re\{NCNC(NH_2)_2\}(CNMe)(dppe)_2][BF_4]}} + \mathrm{KO^tBu} \longrightarrow$$
$$\underset{\textbf{(II)}}{trans\text{-}[\mathrm{Re\{NCNC(NH)NH_2\}(CNMe)(dppe)_2]}} + \mathrm{^tBuOH} + \mathrm{K[BF_4]} \qquad (4)$$

This observed behaviour is similar to the known [11] deprotonation by KO^{t}Bu of cyanamide in *trans*-[Re(NCNH$_2$)(CNR)(dppe)$_2$][BF$_4$] (R = Me or ^{t}Bu) to give *trans*-[Re(NCNH)(CNR)(dppe)$_2$], and is consistent with the reported [7] high enhancement in acidity of other substituted guanidines and cyanamides on coordination to Co^{III} centres. Complex **I** is regenerated from **II** upon reaction with water.

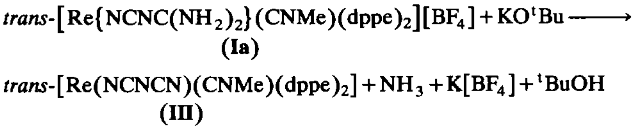
In the ^{1}H NMR spectrum of **II** in CD$_2$Cl$_2$ a broad resonance at δ *ca.* 3.8 ppm, which disappears upon addition of D$_2$O, is assigned to the N*H* and N*H*$_2$ protons which may interchange. The *trans* geometry of

TABLE 4. Selected molecular dimensions in *trans*-[Re{NCNC(NH$_2$)$_2$}(CNMe)(dppe)$_2$] BF$_4$. Bond lengths are in Ångstroms, angles in degrees (estimated standard deviations are in parentheses)

(a) About the Re atom			
Re–P(1)	2.380(2)	Re–P(4)	2.413(3)
Re–P(2)	2.408(2)	Re–C(5)	1.961(10)
Re–P(3)	2.420(2)	Re–N(6)	2.138(7)
P(1)–Re–P(2)	80.5(1)	P(3)–Re–C(5)	92.8(2)
P(1)–Re–P(3)	176.5(1)	P(4)–Re–C(5)	100.7(3)
P(2)–Re–P(3)	102.9(1)	P(1)–Re–N(6)	95.7(2)
P(1)–Re–P(4)	96.2(1)	P(2)–Re–N(6)	91.1(2)
P(2)–Re–P(4)	172.5(1)	P(3)–Re–N(6)	85.3(2)
P(3)–Re–P(4)	80.6(1)	P(4)–Re–N(6)	82.6(2)
P(1)–Re–C(5)	86.4(2)	C(5)–Re–N(6)	176.0(4)
P(2)–Re–C(5)	85.9(3)		
(b) Torsion angles in the dppe ligands			
P(1)–C(1)–C(2)–P(2)	43.1(7)		
P(3)–C(3)–C(4)–P(4)	55.7(7)		
(c) In the MeNC ligand			
C(5)–N(50)	1.149(14)	Re–C(5)–N(50)	175.4(7)
N(50)–C(51)	1.439(18)	C(5)–N(50)–C(51)	170.3(9)
(d) In the cyanoguanidine ligand			
N(6)–C(60)	1.107(13)	Re–N(6)–C(60)	171.4(6)
C(60)–N(61)	1.329(15)	N(6)–C(60)–N(61)	170.8(12)
N(61)–C(62)	1.342(15)	C(60)–N(61)–C(62)	121.2(12)
C(62)–N(63)	1.346(16)	N(61)–C(62)–N(63)	118.1(12)
C(62)–N(64)	1.306(21)	N(61)–C(62)–N(64)	122.7(11)
		N(63)–C(62)–N(64)	119.1(11)
(e) In the proposed hydrogen bonds			
N(63)...F(72a)	2.754(12)	C(62)–N(63)...F(72a)	117.4(7)
N(64)...F(71a)	2.802(13)	C(62)–N(64)...F(71a)	121.1(8)
N(63)...F(72b)	2.976(12)	C(62)–N(63)...F(72b)	118.6(7)
N(64)...F(74b)	2.891(13)	C(62)–N(64)...F(74b)	119.1(8)

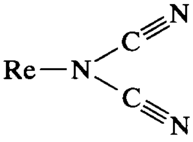
the complex is indicated by the singlet resonance in the ^{31}P NMR spectrum.

Further reaction of the cyanoguanidine ligand in **Ia** with KO^tBu has also been observed to occur in THF when using a threefold molar excess of this salt (previously well dried) and leaving the reaction to proceed for a longer period (3 h). Cyanoguanidine loses ammonia (detected spectrophotometrically [16]), to give *trans*-[Re(NCNCN)(CNMe)(dppe)$_2$] (**III**) (eqn. (5)).

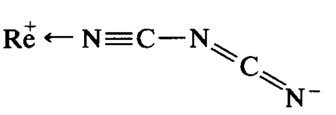


$$\underset{\textbf{(Ia)}}{\textit{trans}\text{-}[Re\{NCNC(NH_2)_2\}(CNMe)(dppe)_2][BF_4]} + KO^tBu \longrightarrow \underset{\textbf{(III)}}{\textit{trans}\text{-}[Re(NCNCN)(CNMe)(dppe)_2]} + NH_3 + K[BF_4] + {}^tBuOH \qquad (5)$$

Two distinct modes of η^1-binding for dicyanamide can be considered, through the amide (**D**) or a cyano (**E**) group.



(D)



(E)

Although we cannot unambiguously differentiate between these modes, the single medium intensity broad IR band at 2180 cm^{-1}, assigned to ν(CN) favours form **D** (more symmetrical than E), since three distinct ν(CN) bands (in the 2300–2180 cm^{-1} range) have been quoted [2] for [Re(NCNCN)(CO)$_5$], in which the **E** mode of coordination has been established by X-ray analysis. In complex **III**, the medium intensity IR band observed at 1945 cm^{-1} is assigned to ν(CN) of the isocyanide. The *trans* geometry of this compound is indicated by the singlet resonance in the ^{31}P NMR spectrum.

The dicyanamide in complex **III** appears to undergo ready protonation (even by moisture), conceivably at the amide-nitrogen atom, to give *trans*-[Re(NCNH-CN)(CNMe)(dppe)$_2$][BF$_4$] (**IV**) which has also been isolated, mixed with **III**, from the reaction of **Ia** in CH$_2$Cl$_2$, with KO^tBu. Assignments for the IR spectrum of **IV** are given in Table 1.

2.3. Electrochemical studies

The complexes of this work, in THF (or CH$_2$Cl$_2$)/0.2 M [Bu$_4$N][BF$_4$] and at a Pt electrode, exhibit, by cyclic voltammetry (Table 5), a first anodic single-electron reversible wave ($^{I}E_{1/2}^{ox}$ in the range 0.05–0.38 V *vs.* SCE), which is assigned to the Re^I → Re^{II} oxidation which is followed at higher potentials by a second irreversible ($^{II}E_p^{ox} = 0.91$–1.31 V) wave and a third ($^{III}E_{1/2}^{ox} = 1.35$–$1.52$ V) reversible wave; these have not been further investigated.

For the cationic complexes *trans*-[Re{NCNC(NH$_2$)$_2$}(CNMe)(dppe)$_2$]$^+$ (**I**) and *trans*-[Re(NCNH-CN)(CNMe)(dppe)$_2$]$^+$ (**IV**), $^{I}E_{1/2}^{ox}$ occurs, as expected, at higher values (0.38 or 0.36 V, respectively) than those observed for the neutral compounds *trans*-[Re{NCNC(NH)NH$_2$}(CNMe)(dppe)$_2$] (**II**) and *trans*-[Re(NCNCN)(CNMe)(dppe)$_2$] (**III**) (0.05 and 0.12 V, respectively). The former higher values are close to that exhibited (0.38 V) [11] by the cyanamide complex *trans*-[Re(NCNH$_2$)(CNMe)(dppe)$_2$]$^+$, whereas the latter lower values approach that reported (−0.06 V) [11] for the deprotonated cyanamide compound *trans*-[Re(NCNH)(CNMe)(dppe)$_2$]. Since for a series of closely related complexes, variations of $E_{1/2}^{ox}$ are expected to reflect changes in the energy of the HOMO which are induced by changes in the electronic properties of the ligand(s), this study should provide an opportunity for comparing cyanoguanidine, cyanamide and derived ligands. For this purpose, we have estimated the electrochemical P_L ligand parameter for these ligands (a proposed [17] measure of their net electron π-acceptor minus σ-donor character), by using (eqn. (6)) in which E_s and β are the electron-richness (1.15 V) [18] and the polarizability (0.90) [18] of the {Re(CNMe)(dppe)$_2$}$^+$ metal site {M$_s$}, and $E_{1/2}^{ox}$[M$_s$L] are $E_{1/2}^{ox}$ of our complexes.

$$E_{1/2}^{ox}[M_sL] = E_s\{M_s\} + \beta\{M_s\} \cdot P_L \qquad (6)$$

TABLE 5. Cyclic voltammetric data [a] for complexes *trans*-[Re{NCNC(NH$_2$)$_2$}(CNMe)(dppe)$_2$]$^+$ (I), *trans*-[Re{NCNC(NH)NH$_2$}(CNMe)(dppe)$_2$] (II), *trans*-[Re(NCNCN)(CNMe)(dppe)$_2$] (III) and *trans*-[Re(NCNHCN)(CNMe)(dppe)$_2$][BF$_4$] (IV), and the estimated P_L ligand parameters [b] for the cyanoguanidine and derived ligands (L)

Complex	$^{I}E_{1/2}^{ox}$	$^{II}E_p^{ox}$	$^{III}E_{1/2}^{ox}$	E_p^{red}	L	P_L [b]
I	0.38	1.24	1.46	−1.25	NCNC(NH$_2$)$_2$	−0.86
II	0.05	0.91 [c]	1.35	–	NCNC(NH)NH$_2^-$	−1.22
III [d]	0.12	1.31	1.52	–	NCNCN$^-$	−1.14
IV [d]	0.36	1.02	1.50	−1.26	NCNHCN	−0.88

[a] Values in volts ±20 mV *vs.* SCE, measured (at 200 mV s^{-1}) at a Pt electrode, in THF (unless stated otherwise)/0.2 M [Bu$_4$N][BF$_4$], using as internal standard [Fe(η^5-C$_5$H$_5$)$_2$]$^{0/+}$ ($E_{1/2}^{ox}$ = 0.545 V). [b] Values in volts. [c] Partially reversible wave. [d] In CH$_2$Cl$_2$.

The P_L values (Table 5) give a ligand order (according to their net electron π-acceptor minus δ-donor ability) as follows: $NCNH_2$ (-0.85 V [11]) $\approx$ $NCNC(NH_2)_2$ (-0.86 V) $\approx$ NCNHCN (-0.88 V) $\gg$ $NCNCN^-$ (-1.14 V) > $NCNC(NH)NH_2^-$ (-1.22 V) > $NCNH^-$ (-1.34 V) [11]).

Cyanamide, cyanoguanidine and hydrogen dicyanamide have similar net electron donor abilities which are stronger than those of *e.g.*, ammonia ($P_L = -0.77$ V) or acetonitrile ($P_L = -0.57$ V [17]), but very close to that of NCS^- ($P_L = -0.88$ V [17]). Moreover, the anionic ligands behave as much stronger net electron donors, dicyanamide ($NCNCN^-$, $P_L = -1.14$ V) being identical to NCO^- ($P_L = -1.16$ V [17]), whereas the basic form of cyanoguanidine, $NCNC(NH)NH_2^-$ ($P_L = -1.22$ V), approaches N_3^- ($P_L = -1.26$ V), both being somewhat weaker electron donors than $NCNH^-$ ($P_L = -1.34$ V [11]).

The cationic complexes *trans*-$[Re\{NCNC(NH_2)_2\}(CNMe)(dppe)_2]^+$ (**I**) and *trans*-$[Re(NCNHCN)(CNMe)(dppe)_2]^+$ (**IV**) have also shown, by cyclic voltammetry at a Pt electrode, a one-electron irreversible cathodic wave (at E_p^{red} *ca.* -1.25 V) as assessed by controlled potential electrolysis.

These cathodic cyclic voltammetric processes involve a partial dehydrogenation of the cyanoguanidine or the NCNHCN, respectively, to the corresponding basic form (eqns. (7) and (8)), as indicated by the generation of **II** or **III** which are recognized by their characteristic anodic waves.

$$\underset{\textbf{(I)}}{trans\text{-}[Re\{NCNC(NH_2)_2\}(CNMe)(dppe)_2]^+} \xrightarrow{+e(-H)} \underset{\textbf{(II)}}{trans\text{-}[Re\{NCNC(NH)NH_2\}(CNMe)(dppe)_2]} \quad (7)$$

$$\underset{\textbf{(IV)}}{trans\text{-}[Re(NCNHCN)(CNMe)(dppe)_2]^+} \xrightarrow{+e(-H)} \underset{\textbf{(III)}}{trans\text{-}[Re(NCNCN)(CNMe)(dppe)_2]} \quad (8)$$

Such processes are related to the reported [11] cathodically induced dehydrogenation of cyanamide at *trans*-$[Re(NCNH_2)(CNR)(dppe)_2]^+$ (R = Me or ^{t}Bu) to give *trans*-$[Re(NCNH)(CNR)(dppe)_2]$, and the carbyne ligands at *trans*-$[ReCl(\equiv C{-}CH_2R)(dppe)_2]^+$ to afford $[ReCl(=C=CHR)(dppe)_2]$ [19].

2.4. Final comments

At the $\{Re(CNMe)(dppe)_2\}^+$ centre, cyanoguanidine (which binds through the cyano group) undergoes ready deprotonation or deamination (by KO^{t}Bu) to give the anionic ligands $NCNC(NH)NH_2^-$ or $NCNCN^-$, respectively, the latter being easily protonated, possibly to give the NCNHCN ligand. Both cyanoguanidine and NCNHCN undergo cathodically induced dehydrogenation to give the corresponding anionic and basic forms.

In the present work, the previously reported [11] deprotonation and cathodic reduction of cyanamide has been extended to cyanoguanidine. However, cyanoguanidine is also susceptible to deamination, a reaction that was not detected for cyanamide. The ability of these compounds to behave as sources of a variety of other organonitrogen species is evident.

3. Experimental details

All manipulations and reactions were performed under dinitrogen by standard inert-gas flow and vacuum techniques. Solvents were purified by standard procedures. Cyanoguanidine and cyanamide were used as purchased from Aldrich and Merck, respectively, and *trans*-$[ReCl(CNMe)(dppe)_2]$ was prepared by a published method [20].

IR measurements were carried out on a Perkin-Elmer 683 spectrophotometer. ^1H and ^{31}P NMR spectra were recorded on a Bruker CPX 300 or a Varian 300 spectrometer. The electrochemical experiments were performed on a EG&G PARC 173 potentiostat/galvanostat and a EG&G PARC 175 universal programmer. The redox potentials of the complexes were measured by cyclic voltammetry in 0.2 mol dm^{-3} $[NBu_4][BF_4]$–tetrahydrofuran or dichloromethane at a platinum electrode. The values of the oxidation or reduction potentials are quoted relative to SCE, and were measured using as internal reference the redox couple $[Fe(\eta^5\text{-}C_5H_5)_2]^{0/+}$ ($E_{1/2}^{ox} = 0.545$ V *vs.* SCE).

3.1. Syntheses of complexes

trans-$[Re\{NCNC(NH_2)_2\}(CNMe)(dppe)_2][BF_4]$ (**Ia**). A suspension of *trans*-$[ReCl(CNMe)(dppe)_2]$ (0.25 g, 0.24 mmol), $NCNC(NH_2)_2$ (0.025 g, 0.30 mmol) and $Tl[BF_4]$ (0.10 g, 0.35 mmol) in CH_2Cl_2 (25 cm^3) was stirred for 2 h. The white solid (TlCl) was filtered off and the solution was concentrated *in vacuo* to about half of the volume. Et_2O (15 cm^3) was then added and complex **Ia** precipitated as a yellow crystalline solid which was filtered off, washed with a mixture of CH_2Cl_2/Et_2O and dried *in vacuo*. Further crops of **Ia** could be obtained from the mother liquor (total of *ca.* 0.24 g, 85% yield).

trans-$[Re\{NCNC(NH_2)_2\}(CNMe)(dppe)_2]Cl$ (**Ib**). A CH_2Cl_2 solution (40 cm^3) of *trans*-$[ReCl(CNMe)(dppe)_2]$ (0.22 g, 0.21 mmol) and $NCNC(NH_2)_2$ (0.041 g, 1.03 mmol) was heated under reflux for 2 days. Concentration *in vacuo* followed by addition of Et_2O led to the precipitation of **Ib** as a yellow solid which was filtered off and dried *in vacuo* (*ca*. 0.050 g, 20% yield).

Complex **Ib** was also prepared in lower yield using cyanamide $NCNH_2$ (41 mg, 1.0 mmol) instead of cyanoguanidine.

trans-[Re{NCNC(NH)NH$_2$}(CNMe)(dppe)$_2$] (**II**). A suspension of *trans*-[Re{NCNC(NH$_2$)$_2$}(CNMe)-(dppe)$_2$][BF$_4$] (**Ia**) (0.15 g, 0.13 mmol) and KO^{t}Bu (0.026 g, 0.23 mmol) in THF (10 cm^3) was stirred for 1 h. The solution was then filtered, concentrated *in vacuo* to *ca*. 6 cm^3 and, upon addition of pentane, complex **II** precipitated as a yellow microcrystalline solid which was filtered off, washed with Et_2O and dried *in vacuo* (*ca*. 0.10 g, 70% yield).

trans-[Re(NCNCN)(CNMe)(dppe)$_2$] (**III**). After stirring a suspension of *trans*-[Re{NCNC(NH$_2$)$_2$}(CNMe)-(dppe)$_2$][BF$_4$] (**Ia**) (0.11 g, 0.090 mmol) and KO^{t}Bu (0.030 g, 0.27 mmol) in carefully dried THF (20 cm^3) for 3 h, the solution was filtered, taken to dryness *in vacuo* and the residue washed with Et_2O. Recrystallization of the residue from CH_2Cl_2 (1 cm^3)/Et_2O (3.5 cm^3) led to the precipitation of **III** as a yellow microcrystalline solid which was filtered off, washed with Et_2O (2 cm^3) and dried *in vacuo* (*ca*. 0.069g, 70% yield).

trans-[Re(NCNHCN)(CNMe)(dppe)$_2$][BF$_4$] (**IV**). This compound was obtained in a similar way to **III**, but using CH_2Cl_2 instead of THF. The product was appreciably contaminated with **III** from which it was separated by recrystallization from CH_2Cl_2/Et_2O, the first fractions corresponding mainly to **IV** (*ca*. 60% yield).

3.2. Crystal structure analysis of trans-[Re{NCNC(NH$_2$)$_2$}(CNMe)(dppe)$_2$][BF$_4$](Ia)

Crystal data. $C_{56}H_{55}N_5P_4Re \cdot BF_4$, $M = 1195.0$. Monoclinic, space group $P2_1/n$ (equivalent to no. 14), $a = 18.060(2)$, $b = 16.769(2)$, $c = 18.678(2)$ Å, $\beta = 108.279(9)°$, $V = 5371.0$ Å^3. $Z = 4$, $D_c = 1.478$ g cm^{-3}, $F(000) = 2408$, μ(Mo-Kα) = 24.6 cm^{-1}, λ(Mo-K$\bar{\alpha}$) = 0.71069 Å.

Crystals were yellow and of irregular shape. One, *ca*. $0.33 \times 0.20 \times 0.15$ mm^3 was mounted on a glass fibre and coated with silicone grease. On our Enraf-Nonius CAD4 diffractometer (with monochromated radiation), accurate cell dimensions were calculated from the settings of 25 reflections (θ *ca*. 10.5°) each centred in four orientations, and diffraction intensities were measured to $\theta_{max} = 25°$.

The intensity data were corrected for Lorentz polarization effects, deterioration (20% over the whole data collection), absorption (by semi-empirical Ψ-scan methods), and to remove negative net intensities (by Bayesian statistical methods).

A total of 9441 unique reflections were entered into the SHELX system [21] for structure determination (by the heavy atom method) and refinement (by large-block matrix least-squares methods) which was terminated at $R = 0.074$ and $R_g = 0.062$ [21] for 7744 reflections (those with $I > \sigma_I$) weighted $w = (\sigma_F^2 + 0.000538F^2)^{-1}$.

The anion is disordered in two principal orientations and was refined as two rigid tetrahedra with a common central B atom. In the cation, all non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms of the dppe ligands were included in idealized positions with independent isotropic thermal parameters. Some of the H atoms of the C- and N-ligands were located in difference maps but did not refine well, and none were included in the final cycles of refinement.

In the final difference map, the major peaks were close to the Re atom (to *ca*. 1.35 e Å^{-3}) or in the region of the anion (to *ca*. 1.0 e Å^{-3}).

Scattering factor curves for neutral atoms were taken from reference [22]. Computer programs, in addition to SHELX, used in this analysis, have been listed in Table 4 of reference [23], and were run on the DEC MicroVAX II machine in the Nitrogen Fixation Laboratory. Full lists of atomic coordinates, anisotropic thermal parameters and molecular dimensions are available from the Cambridge Crystallographic Data Centre.

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References

1 P. Rây, *Chem. Rev., 61* (1961) 313; R.K. Rây, M.K. Bandyopadhyay and G.B. Kauffman, *Polyhedron, 8* (1989) 757.

2 W. Sacher, U. Nagel and W. Beck, *Chem. Ber., 120* (1987) 895.

3 (a) M.J. Begley, P. Hubberstey and P.H. Walton, *J. Chem. Soc., Chem. Commun.*, (1989) 502 and M.J. Begley, personal communication; (b) M.J. Begley, P. Hubberstey and C.H.M. Moore, *J. Chem. Res. (S)*, (1985) 378; (c) P. Hubberstey and C.P. Falshaw, *J. Chem. Res. (S)*, (1982) 176.

4 (a) A. Chiesi, L. Coghi, A. Mangia, M. Nardelli and G. Pelizzi, *Acta Crystallogr., Sect. B, 27* (1971) 192; (b) A. Chiesi Villa, L. Coghi, A. Mangia, M. Nardelli and G. Pelizzi, *J. Cryst. Mol. Struct., 1* (1971) 291; (c) A. Chiesi Villa, L. Coghi, A.G. Manfredotti and C. Guastini, *Cryst. Struct. Commun., 3* (1974) 739.

5 L. Coghi, A. Mangia, M. Mandelli, G. Pelizzi and L. Sozzi, *J. Chem. Soc., Chem. Commun.*, (1968) 1475.

6 H. Fisher, F. Seitz and G. Müller, *J. Organomet. Chem., 320* (1987) 185.

7 D.P. Fairlie and W.G. Jackson, *Inorg. Chem., 29* (1990) 140.

8 R.W. Miller and R.R. Eady, *Biochim. Biophys. Acta, 952* (1988) 290.

9 A.J.L. Pombeiro, *Inorg. Chim. Acta, 198–200* (1992) 179; A.J.L. Pombeiro and R.L. Richards, *Coord. Chem. Rev., 104* (1990) 13; A.J.L. Pombeiro, *Polyhedron, 8* (1989) 1595; A.J.L. Pombeiro, in U. Schubert (ed.), *Advances in Metal Carbene Chemistry*, Kluwer, Dordrecht, 1989, p. 79.

10 A.J.L. Pombeiro, M.F.C.G. Silva, D.L. Hughes and R.L. Richards, *J. Organomet. Chem., 371* (1989) C45.

11 M.F.N.N. Carvalho and A.J.L. Pombeiro, *J. Organomet. Chem., 410* (1991) 347.

12 F.H. Allen, O. Kennard, D.G. Watson, L. Brammer, A.G. Orpen and R. Taylor, *J. Chem. Soc., Perkin Trans. 2*, (1987) S1.

13 F.L. Hirshfeld and H. Hope, *Acta Crystallogr., Sect. B, 36* (1980) 406.

14 (a) A.J.L. Pombeiro, M.F.C.G. Silva, D.L. Hughes and R.L. Richards, *Polyhedron, 8* (1989) 1872; (b) M.F.C.G. Silva, A.J.L. Pombeiro, A. Hills, D.L. Hughes and R.L. Richards, *J. Organomet. Chem., 403* (1991) C1.

15 (a) L. Soto, J. Borras, A. Sancho, A. Fuertes and C. Miravitlles, *Acta Crystallogr., Sect. C, 41* (1985) 1431; (b) L. Soto, J.P. Legros and A. Sancho, *Polyhedron, 7* (1988) 307; (c) J.M. Amigó, M.M. Reventós, A. Sancho, L. Soto-Tuero and A. Cantarero, *Z. Kristallogr., 180* (1987) 123.

16 D.T. Dubin, *J. Biol. Chem., 235* (1960) 783.

17 J. Chatt, C.T. Kan, G.J. Leigh, C.J. Pickett and D.R. Stanley, *J. Chem. Soc., Dalton Trans.*, (1980) 2032.

18 M.F.N.N. Carvalho and A.J.L. Pombeiro, *J. Chem. Soc., Dalton Trans.*, (1989) 1209.

19 M.A.N.D.A. Lemos and A.J.L. Pombeiro, *J. Organomet. Chem., 356* (1988) C79.

20 A.J.L. Pombeiro, M.F.N.N. Carvalho, P.B. Hitchcock and R.L. Richards, *J. Chem. Soc., Dalton Trans.*, (1981) 1629.

21 G.M. Sheldrick, *SHELX – Program for Crystal Structure Determination*, University of Cambridge, 1976.

22 *International Tables for Crystallography*, Vol. 4, Kynoch, Birmingham, 1974, pp. 99 and 149.

23 S.N. Anderson, R.L. Richards and D.L. Hughes, *J. Chem. Soc., Dalton Trans.*, (1986) 245.