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Inorganica Chimica Acta 280 (1998) 308–315

Inorganica Chimica Acta

Syntheses and properties of organocyanamide, cyanoguanidine and dinitrogen complexes of rhenium. Crystal structure of *mer*-[$ReCl_2(NCNEt_2)(PMePh_2)_3$]

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Received 5 November 1997; accepted 5 February 1998

Abstract

Treatment of a THF solution of *trans*-[$ReCl(N_2)L_4$] (L = $PMePh_2$) with a cyanamide, $NCNR_2$ (R = Me, Et or H) or with cyanoguanidine, $NCNC(NH_2)_2$, yields *mer*-[$ReCl(N_2)(NCNR_2)L_3$] (**1**) or *mer*-[$Re(N_2)\{NCNC(NH_2)_2\}_2L_3$]Cl (**2**), respectively, which, to our knowledge, are the first mixed dinitrogen–cyanamide-type complexes to be reported. The former products (**1**, R = Me or Et) can also be obtained from reaction of the benzoyldiazenido complex [$ReCl_2(NNCOPh)L_3$] with $NCNR_2$ in refluxing methanol; the Re(II) complex *mer*-[$ReCl_2(NCNEt_2)L_3$] (**3**) is also formed (conceivably via an unusual homolysis of the C–N bond of the benzoyldiazenido ligand) and its crystal structure is reported. It shows an unusual pyramidal conformation at the amine N atom of the diethylcyanamide ligand which also exhibits a significant structural *trans* influence on the phosphine, behaving as a stronger net electron donor than the latter ligand.

Keywords: Crystal structures; Rhenium complexes; Dinitrogen complexes; Cyanamide complexes; Cyanoguanidine complexes

1. Introduction

Dinitrogen complexes can be used as useful starting materials in the syntheses of coordination compounds with electron-rich metal centres, obtained upon simple replacement of the commonly labile N_2 ligand by another species, in particular a distinct nitrogenase substrate [1]. However, some Re(I)–chloro–dinitrogen complexes present a remarkably stable Re–N_2 bond, allowing the displacement of a labile co-ligand to occur in preference to that of dinitrogen [2,3]. We now extend this type of reaction to cyanamide-type species in view of their biological significance and synthetic interest, as well as of their still relatively unknown coordination chemistry. In fact, cyanamide itself ($NCNH_2$) has been recognized [4] as a substrate of nitrogenase, is a prebiotic molecule and a conceivable aminoacid precursor [5], whereas its dimeric form, cyanoguanidine, with tautomeric forms $N{\equiv}CN{=}C(NH_2)_2$ and $N{\equiv}CNHC(=NH)NH_2$, is also a precursor for the syntheses of organonitrogen compounds, e.g. biguanides and guanylureas [6]. We have previously obtained some cyanamide or cyanoguanidine and derived complexes, such as *trans*-[$ReL(CNR)(dppe)_2$][BF_4] [L = $NCNH_2$ or $NCNC(NH_2)_2$; R = Me or Bu^t; dppe = $Ph_2PCH_2CH_2PPh_2$) from the reaction of the isocyanide complex *trans*-[$ReCl(CNR)(dppe)_2$] with the appropriate cyanamide (L) in the presence of Tl[BF_4] [7], *trans*-[$M(NCN)_2(dppe)_2$] (M = Mo or W) in which the cyanoimido ligands were formed by dehydrogenation of CNH_2 by *trans*-[$M(N_2)_2(dppe)_2$] [8], *trans*-[$PtX(L)(PPh_3)_2$]A [X = CF_3; A = BF_4; L = $NCNH_2$, $NCNMe_2$, $NCNEt_2$ or $NCNC(NH_2)_2$. X = Cl, A = BPh_4, L = $NCNMe_2$ or $NCNEt_2$] obtained from *trans*-[$PtBr(CF_3)(PPh_3)_2$] or *cis*-[$PtCl_2(PPh_3)_2$] [9], and *cis*-[$(PPh_3)_2$ [Pt{NHC(OMe)=NC(NH$_2$)=NH}][BPh_4] presenting a novel azametallacycle which was derived from metal-promoted nucleophilic addition of methanol to the cyano group of a cyanoguanidine ligand combined with

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0020-1693/98/$ - see front matter
PII S0020-1693(98)00212-6

deprotonation of the guanidine unit which then chelates the metal [10].

We now report the reactions of the dinitrogen complex *trans*-[ReCl(N$_2$)L$_4$] (L = PMePh$_2$), which presents a rather strong Re–N$_2$ bond, with NCNR$_2$ (R = Me, Et or H) or NCNC(NH$_2$)$_2$; they follow the strategy described above, yielding the first mixed dinitrogen–cyanamide complexes, *mer*-[ReCl(N$_2$)(NCNR$_2$)L$_3$] (**1**; R = Me, Et or H) or *mer*-[Re(N$_2$){NCNC(NH$_2$)$_2$}$_2$L$_3$] Cl (**2**). In addition, the reactions of NCNR$_2$ (R = Me or Et) with the benzoyldiazenide complex [ReCl$_2$(NNCOPh)L$_3$], which is a precursor [11] for *trans*-[ReCl(N$_2$)L$_4$], are also described and shown to form the above mixed dinitrogen–cyanamide complexes (**1**, R = Me or Et); moreover, the dichloro Re(II) complex *mer*-[ReCl$_2$(NCNEt$_2$)L$_3$] (**3**) is also a product of the reaction (for R = Et), formally derived upon homolysis of the C–N bond of the benzoyldiazenido ligand, and its molecular structure has been established by single-crystal X-ray diffraction analysis. Hence, the study also provides an insight into the investigation of the coordination chemistry of organodiazenides, a matter of current interest [12], namely in the field of nitrogen fixation.

2. Results and discussion

2.1. Syntheses and spectroscopic characterization

Treatment of a tetrahydrofuran (THF) solution of *trans*-[ReCl(N$_2$)L$_4$] (L = PMePh$_2$) with dimethyl- or diethylcyanamide, NCNR$_2$ (R = Me or Et, respectively), in a stoichiometric amount, at ambient temperature, leads to the formation (reaction (1) in Scheme 1) of the corresponding mixed dinitrogen–cyanamide complexes *mer*-[ReCl(N$_2$)(NCNR$_2$)L$_3$] (**1**, R = Me or Et), which were isolated after 48 h (yields ca. 60–55%) as yellow or greenish yellow solids, respectively. Reaction (1) also appears to occur for cyanamide itself, CNH$_2$, but the product was isolated as a green oily solid in a non analytically pure form.

The formation of complexes **1** occurs via the simple replacement of a phosphine ligand by the organocyanamide with retention of the ligating dinitrogen, thus following a similar route to that involved in the syntheses of some mixed dinitrogen–isocyanide complexes, particularly *mer*-[ReX(N$_2$)(CNMe)(PMe$_2$Ph)$_3$] (X = Cl or S$_2$PPh$_2$) and [Re(S$_2$PPh$_2$)(N$_2$)(CNMe)$_2$(PMe$_2$Ph)$_2$] which we have obtained [2a] upon treatment of *trans*-[ReCl(N$_2$)(PMe$_2$Ph)$_4$] or *mer*-[Re(η^2-S$_2$PPh$_2$)(N$_2$)(PMe$_2$Ph)$_3$], respectively, with CNMe.

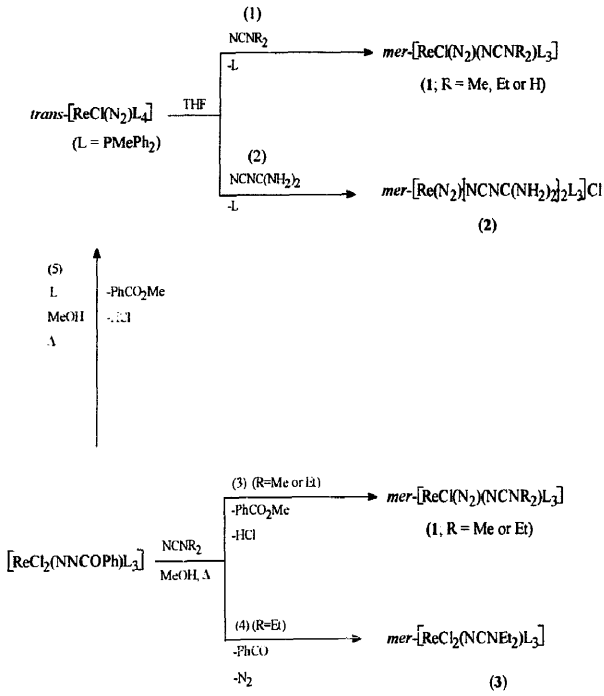
The retention of the N$_2$ ligand (a π-electron acceptor) in reaction (1) is assisted by the strong π-electron release from the chloro ligand in the *trans* position. This contrasts with the behaviour normally observed in dinitrogen complexes in which N$_2$ is a rather labile ligand [1], namely in [M(N$_2$)$_2$L$_4$] (M = Mo or W; L = PMe$_2$Ph, PMePh$_2$ or 0.5dppe) where the ligand *trans* to N$_2$ is also a π-acceptor (another N$_2$ ligand or a phosphine) [8,13].

Nevertheless, the reaction of *trans*-[ReCl(N$_2$)L$_4$] with cyanoguanidine, under similar experimental conditions to those used for the synthesis of **1**, proceeds further to give the di(cyanoguanidine) product *mer*-[Re(N$_2$){NCNC(NH$_2$)$_2$}$_2$L$_3$]Cl (**2**) upon displacement of one phosphine and the chloro ligands (reaction (2), Scheme 1). The N$_2$ ligand in **2** is still retained in spite of the loss of this stabilizing *trans* chloro π-electron donor, thus suggesting that N$_2$ can be *trans* to a cyanoguanidine ligand which could behave as a stronger net σ-electron donor/π-electron acceptor than the phosphine; this interpretation is in agreement with the observed behaviour of diethylcyanamide (see below).

Complexes **1** (R = Me or Et) are also obtained, although in a lower yield (ca. 50%) and by using more vigorous experimental conditions than those for reaction (1), by reacting the benzoyldiazenido complex [ReCl$_2$(NNCOPh)L$_3$], in refluxing methanol, with the appropriate organocyanamide (added in a threefold molar ratio relative to the complex) (reaction (3), Scheme 1). This route involves the nucleophilic displacement of the benzoyl group upon attack by methanol to form methylbenzoate, PhCO$_2$Me, thus generating in situ the N$_2$ ligand. In addition, the organocyanamide displaces one of the chloride ligands which is liberated as HCl. Hence, reaction (3) follows a pathway which relates to those involved in the known [2b,11] syntheses of dinitrogen complexes of the type *trans*-[ReCl(N$_2$)L'$_4$] (L' = phosphine and/or phosphite and/or phosphonite and/or 1/2 bidentate diphosphine) upon refluxing a methanol solution of a benzoyldiazenide complex of the general type of that used in our study in the presence of L'; in particular, *trans*-[ReCl(N$_2$)L$_4$] can be prepared [11] in this way from [ReCl$_2$(NNCOPh)(PMePh$_2$)] in the presence of PMePh$_2$ (reaction (5), Scheme 1).

However, interestingly, an unusual and different type of reaction of this benzoyldiazenide complex was recognized in addition to that mentioned above. In fact, the solid isolated from refluxing its methanol solution with NCNEt$_2$ contains not only the mixed dinitrogen–cyanamide complex (**1**, R = Et) but also the paramagnetic Re(II)–dichloro compound *mer*-[ReCl$_2$(NCNEt$_2$)L$_3$] (**3**) (reaction (4), Scheme 1) which was unambiguously identified by X-ray diffraction analysis.

The formation of **3** involves the formal homolysis of the C–N bond of the organodiazenide ligand (loss of the benzoyl group) with liberation of the generated ligating N$_2$ in view of its expectedly labile bond to the resulting Re(II) centre with a much lower π-electron releasing ability than the Re(I) sites in the above dinitrogen complexes. Such a radical mechanism contrasts with the common heterolytic N–C bond cleavage by nucleophilic displacement (which we have indicated above to yield dinitrogen complexes) and has been reported [12g] to be followed by the aryldiazenide ligand in complexes [Re(η^5-ZC$_5$H$_4$) LL'(NNC$_6$H$_4$OMe-4)] (Z = H



Scheme 1.

or Me; L and/or L' = CO, PMe_3 or $P(OMe)_3$] formed by reduction of the parent cationic precursors.

Complexes **1–3** were characterized by IR, ^1H and ^{31}P NMR (except **3** because of its paramagnetism) spectroscopies, FAB mass spectrometry, and elemental analyses (see Section 3), as well as, in the case of **3**, by X-ray diffraction.

The meridional arrangement of the phosphine ligands is clearly indicated for **1** (R = Me or Et) by the diagnostic A_2B pattern consisting of a doublet and a triplet (with 2:1 relative intensities and $^2J(P_A P_B) \approx 10$ Hz) assigned to the two *trans* (P_B) and to the unique (P_A) phosphines, respectively. This is also corroborated by the ^1H NMR triplet and doublet resonances (integrating for 6 and 3 protons, respectively) associated with the methyl groups of the phosphines, arising from virtual coupling to the two *trans*-P_B nuclei $[(1/2)|^2J(P_BH) + {}^4J(P_AH)| = 3.0$ Hz] and from coupling to the unique P_A nucleus ($^2J(P_AH) = 7.2$ Hz), respectively. These structures are not resolved for **2**.

In the IR spectra (KBr discs), $\nu(N{\equiv}N)$ of the dinitrogen ligand occurs as a strong band at about 1910–1950 cm^{-1} (complex **1**) or 1970 cm^{-1} (**2**), whereas $\nu(N{\equiv}C)$ of the cyanamide (**1** and **3**) or cyanoguanidine (**2**) ligands is observed at about 2260–2200 cm^{-1}. The $\nu(N{\equiv}N)$ frequency for **1** is comparable with those of related neutral Re(I)–N_2 complexes, e.g. 1920 cm^{-1} in the parent *trans*-$[ReCl(N_2)(PMePh_2)_4]$ complex, whereas the higher value for **2** agrees with the positive charge of the complex and the loss of the strong electron donor chloro ligand. Nevertheless, $\nu(N{\equiv}N)$ for **2** is still a relatively low value in comparison with those exhibited by related cationic complexes such as *trans*-$[Re(N_2)(PMe_3)_5]Cl$ (2030 cm^{-1}) [14] and $[Re(N_2)(NCPh)(dppe)_2][BF_4]$ (2028 cm^{-1}) [15]. This behaviour, together with the observed frequency shifts of $\nu(N{\equiv}C)$ to higher wavenumbers (by about +25 to +60 cm^{-1}) of the cyanamide or cyanoguanidine species upon coordination, indicate that N_2 is behaving as a strong π-electron acceptor in **1** and **2** and the latter co-ligands are exhibiting a strong net electron donor character in **1**, **2** and **3** (in accord with the X-ray data of **3** discussed below).

In the FAB-MS spectra, the molecular ions $[M]^+$ are clearly observed (with the expected isotopic pattern) at *m/z* 949, 983 and 955 for (**1**, R = Et), **2** and **3**, respectively, as well as some significant derived fragments such as $[M-N_2]^+$ (for the dinitrogen complexes **1** and **2**), $[M-NCNEt_2]^+$ and $[M-NCNEt_2-N_2]^+$ (for **1**, R = Et), $[M-NCNC(NH_2)_2]^+$ and $[M-NCNC(NH_2)_2-N_2]^+$ (for **2**), or $[M-Cl]^+$ and $[M-NCNEt_2]^+$ (for **3**). This technique proved to be of particular significance for the identification of both (**2**, R = Et) and **3** in their mixtures, since in view of the paramagnetism of the latter complex, its presence

in sample mixtures is not detected by ^1H or ^{31}P NMR; IR spectroscopy is also of no diagnostic value for this purpose, since $\nu(N{\equiv}C)$ in **3** and in (**1**, R = Et) appears at identical wavenumbers (2220 cm^{-1}).

2.2. Molecular structure of *mer*-[$ReCl_2(NCNEt_2)(PMePh_2)_3$] (3)

The molecular structure of *mer*-[$ReCl_2(NCNEt_2)(PMePh_2)_3$] (**3**) is shown in Fig. 1. Final atomic coordinates and equivalent U are given in Table 1, while selected bond lengths and angles are presented in Table 2. The rhenium atom has an approximately octahedral environment with two *trans* phosphines, two *trans* chloro ligands and the cyanamide *trans* to the third phosphine ligand.

The Re–N(1) distance, 2.109(5) Å, is comparable with the average of 2.098(28) Å observed [16] for hexacoordinate nitrile complexes of Re(II) or Re(I) and to the distances found in the related [$Re\{NCNC(NH_2)_2\}(CO)_5$][BF_4], 2.122(7) Å [17], and [$Re\{NCNC(NH_2)_2\}(CNMe)(dppe)_2$][$BF_4$], 2.138(7) Å [7b], complexes. The skeleton of the $NCNEt_2$ ligand exhibits N(1)–C(40), C(40)–N(2) and average N(2)–C(ethyl) bond distances with values, 1.131(9), 1.34(1) and 1.49 Å, in the usual ranges [16] for a triple, a partially double and a single bond, respectively.

The amine-N atom of $NCNEt_2$ does not exhibit the usual trigonal planar geometry found for this ligand, e.g. in [$Pt(CF_3)(NCNEt_2)(PPh_3)_2$][$BF_4$] [9] or [$Cr(NCNEt_2)(CO)_5$] [18,19]. The observed out-of-plane angle θ (angle between a least-squares plane through the atoms N(2), C(41), C(43) and a line through the atoms N(2) and C(40)) in both the alternative positions (see Section 3) of C(41) and C(43) is 31(1)°, with N(2) −0.278(8) Å out of the C(40)C(41)C(43) plane or, in the alternative position, +0.284(8) Å out of the C(40)C(41A)C(43A) plane.

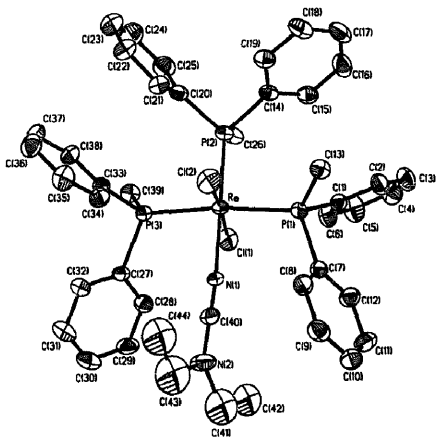


Fig. 1. Molecular structure and atom numbering scheme of *mer*-[$ReCl_2(NCNEt_2)(PMePh_2)_3$] (**3**).

These deviations from planarity are in the range observed [20] for the related free cyanamides $NCNMe_2$ and $NCNH_2$ and can be accounted for, in terms of ab initio calculations [21], by considering an sp^3 hybridization for N(2), thus indicating a higher weight of form *a* in the VB representation of the cyanamide ligand:

$$Re \leftarrow \underset{a}{N{\equiv}C{-}\ddot{N}Et_2} \leftrightarrow \bar{R}e \rightleftarrows \underset{b}{N{=}C{=}\overset{+}{N}Et_2}$$

The two alternative positions of the ethyl substituents (see Section 3) agree with the pyramidal conformation (the sum of the angles around N(2) being 349.3(5)° and 348.3(5)° for the two positions), as well as the value of the NC–NEt_2 distance, 1.34(1) Å, which is comparable with those in the related free cyanamides with pyramidal amine-N atom (1.351 [22] and 1.346 Å [23] for $NCNMe_2$ and $NCNH_2$, respectively).

Moreover, the Re–P(2) bond distance of 2.360(2) Å for the phosphine *trans* to cyanamide is significantly shorter than the values of 2.450(2) and 2.435(2) Å found respectively for Re–P(1) and Re–P(3) bond distances of the mutually *trans* phosphines. The latter values are comparable with those reported for *trans* PPh_3 ligands in [$ReCl_2(PPh_3)_2(Me_2NCHO)(NNCOOCH_3)$] (Re–P(1) 2.469(3), Re–P(2) 2.446(3) [24]). Hence, the diethyl cyanamide ligand in our complex exerts a significant structural *trans* influence on the phosphine, the shortening of the corresponding Re–P bond length being indicative of a stronger net electron donor/acceptor character of the $NCNEt_2$ ligand relative to ligating PPh_3. A related *trans* influence of the cyanamide relative to the carbonyl ligand has been reported [19] for [$Cr(NCNEt_2)(CO)_5$].

The Re–Cl bond lengths (Re–Cl(1) 2.484(4); Re–Cl(2) 2.459(4) Å) are somewhat longer than those reported in *trans*-[$ReCl_2(dppe)_2$] [25] of 2.435(2) for the THF solvate and 2.419(1) for the CD_2Cl_2 solvate. There are also significant bendings of the Cl(1)–Re–Cl(2) (173.8(1)°) and of the P(1)–Re–P(3) angles (173.44(6)°) both in the direction of the less hindering ligand $NCNEt_2$ (in the dppe [25] derivative the Cl–Re–Cl angle was 180° lying Re in a crystallographic inversion center) indicating the influence of the different steric hindrance of the phosphine ligands in the considered compounds.

2.3. Final comments

Organocyanamides and cyanoguanidine present electron donor/acceptor properties quite different from those exhibited by dinitrogen, in particular behaving as effective net electron releasers through the cyano group. In this sense, they behave in a complementary way relative to N_2 and can assist, as co-ligands, the stabilization of the coordination of the latter species. Hence, stable mixed cyanamide–dinitrogen complexes can be obtained from an N_2 parent compound by simple replacement (by the cyanamide) of a ligand such as a phosphine, with retention of the metal ligating N_2. They can

Table 1
Fractional atomic coordinates and equivalent thermal parameters ($Å^2 \times 10^3$) for *mer*-[$ReCl_2(NCNEt_2)(PMePh_2)_3$]

Atom	x	y	z	U_{eq}	pp [a]
Re	0.24637(2)	0.49463(2)	0.23370(1)	38.8(1)	
P(1)	0.3562(1)	0.7018(1)	0.3396(1)	45.5(6)	
P(2)	0.0526(1)	0.4845(1)	0.2186(1)	48.5(6)	
P(3)	0.1595(1)	0.2890(1)	0.1312(1)	42.1(6)	
Cl(1)	0.2761(2)	0.5464(2)	0.0880(2)	104(1)	
Cl(2)	0.2362(2)	0.4400(3)	0.3768(3)	128(2)	
C(1)	0.3560(5)	0.8258(5)	0.3072(5)	53(3)	
C(2)	0.3679(7)	0.9269(6)	0.3730(6)	73(3)	
C(3)	0.3659(8)	1.0175(7)	0.3458(7)	91(4)	
C(4)	0.3532(8)	1.0097(7)	0.2533(8)	99(5)	
C(5)	0.341(1)	0.9099(8)	0.1880(7)	104(5)	
C(6)	0.3440(8)	0.8199(7)	0.2150(6)	79(4)	
C(7)	0.5240(5)	0.7639(5)	0.3790(5)	50(3)	
C(8)	0.5631(6)	0.7104(6)	0.4313(5)	58(3)	
C(9)	0.6884(6)	0.7553(7)	0.4641(5)	71(3)	
C(10)	0.7751(6)	0.8552(7)	0.4470(6)	76(3)	
C(11)	0.7394(6)	0.9091(7)	0.3968(7)	84(4)	
C(12)	0.6134(6)	0.8643(6)	0.3620(6)	73(3)	
C(13)	0.3174(6)	0.7239(6)	0.4538(5)	60(3)	
C(14)	0.0276(5)	0.5866(4)	0.3126(4)	51(3)	
C(15)	0.0584(6)	0.7014(5)	0.3119(5)	67(3)	
C(16)	0.0472(7)	0.7804(7)	0.3858(7)	82(4)	
C(17)	0.0039(7)	0.7455(8)	0.4597(6)	86(4)	
C(18)	−0.0289(7)	0.6319(8)	0.4598(6)	81(4)	
C(19)	−0.0168(6)	0.5535(6)	0.3878(5)	64(3)	
C(20)	−0.0881(5)	0.3404(6)	0.2077(5)	56(3)	
C(21)	−0.0849(6)	0.2807(6)	0.2686(6)	70(3)	
C(22)	−0.1904(8)	0.1791(7)	0.2700(8)	100(5)	
C(23)	−0.2994(8)	0.1329(9)	0.209(1)	113(6)	
C(24)	−0.3031(7)	0.1875(9)	0.1445(9)	107(5)	
C(25)	−0.1990(6)	0.2933(8)	0.1437(6)	83(4)	
C(26)	0.0122(7)	0.5197(8)	0.1178(5)	81(4)	
C(27)	0.2700(5)	0.2495(5)	0.0785(4)	47(2)	
C(28)	0.3519(6)	0.3247(6)	0.0373(5)	67(3)	
C(29)	0.4308(7)	0.2960(8)	−0.0077(6)	81(4)	
C(30)	0.4307(7)	0.1925(8)	−0.0120(6)	90(5)	
C(31)	0.3508(8)	0.1165(8)	0.0285(6)	90(4)	
C(32)	0.2700(6)	0.1439(6)	0.0734(5)	63(3)	
C(33)	0.0814(5)	0.1655(5)	0.1773(4)	47(2)	
C(34)	0.1452(6)	0.1662(6)	0.2560(5)	56(3)	
C(35)	0.0928(7)	0.0719(7)	0.2911(6)	73(4)	
C(36)	−0.0251(7)	−0.0235(6)	0.2485(6)	76(3)	
C(37)	−0.0905(7)	−0.0248(6)	0.1720(6)	71(3)	
C(38)	−0.0374(5)	0.0688(5)	0.1363(5)	58(3)	
C(39)	0.0492(6)	0.2461(6)	0.0238(5)	60(3)	
C(40)	0.5067(5)	0.4975(6)	0.2493(5)	57(3)	
N(1)	0.4187(4)	0.5019(4)	0.2425(4)	44(2)	
N(2)	0.6097(5)	0.4903(6)	0.2578(6)	95(4)	
C(41)	0.700(2)	0.531(2)	0.197(1)	86(5)	0.5
C(42)	0.714(2)	0.648(2)	0.191(1)	81(5)	0.5
C(43)	0.600(2)	0.381(2)	0.276(1)	84(5)	0.5
C(44)	0.548(2)	0.379(2)	0.364(2)	99(7)	0.5
C(41A)	0.729(1)	0.587(1)	0.253(1)	78(4)	0.5
C(42A)	0.722(2)	0.607(2)	0.163(1)	118(6)	0.5
C(43A)	0.640(2)	0.443(2)	0.330(1)	95(6)	0.5
C(44A)	0.533(2)	0.328(2)	0.324(2)	121(6)	0.5

[a] pp. Parameters population.

Table 2
Selected bond lengths (Å) and angles (°) for *mer*-[$ReCl_2$-$(NCNEt_2)(PMePh_2)_3$]

Re–P(1)	2.450(2)	Re–P(2)	2.360(2)
Re–P(3)	2.435(2)	Re–Cl(1)	2.484(4)
Re–Cl(2)	2.459(4)	Re–N(1)	2.109(5)
P(1)–C(1)	1.842(8)	P(1)–C(7)	1.852(6)
P(1)–C(13)	1.819(8)	P(2)–C(14)	1.855(7)
P(2)–C(20)	1.858(6)	P(2)–C(26)	1.83(1)
P(3)–C(27)	1.850(7)	P(3)–C(33)	1.823(7)
P(3)–C(39)	1.853(7)	C(40)–N(1)	1.131(9)
C(40)–N(2)	1.34(1)	N(2)–C(ethyl)av.	1.49(2)
C–C(ethyl)av.	1.50(2)		
Cl(2)–Re–N(1)	85.6(2)	Cl(1)–Re–N(1)	88.3(2)
Cl(1)–Re–Cl(2)	173.8(1)	P(3)–Re–N(1)	86.3(1)
P(3)–Re–Cl(2)	94.13(9)	P(3)–Re–Cl(1)	84.31(8)
P(2)–Re–N(1)	178.1(2)	P(2)–Re–Cl(2)	95.94(9)
P(2)–Re–Cl(1)	90.13(9)	P(2)–Re–P(3)	92.55(6)
P(3)–Re–N(1)	87.1(1)	P(1)–Re–Cl(2)	84.73(9)
P(1)–Re–Cl(1)	96.14(8)	P(1)–Re–P(3)	173.44(6)
P(1)–Re–P(2)	93.99(6)	N(1)–C(40)–N(2)	178.8(8)
Re–N(1)–C(40)	174.3(6)		

also be prepared in a single-pot synthesis starting from a rhenium complex with benzoyldiazenide as a ligand which can generate in situ the N_2 ligand (via a nucleophilic addition to the benzoyl group) in the presence of a cyanamide which also binds the metal centre.

In addition, with the neutral benzoyldiazenide complex of this study, which presents the metal in a not too high oxidation state, a distinct reaction, i.e. the homolysis of the ReNN–COPh bond (a radical process leading to a paramagnetic metal site, $Re^{\cdot} + N_2 + PhCO^{\cdot}$) can compete with the usual heterolytic cleavage of this bond upon addition of a nucleophile (X^-, e.g. MeO^- or Cl^-) to the benzoyl carbon (to give $ReNN^- + PhCOX$). The synthetic potentialities of this process towards novel paramagnetic rhenium complexes deserve further investigation.

3. Experimental

The solvents were dried and degassed by using standard techniques. All reactions were performed under an inert atmosphere (N_2). The cyanamides and cyanoguanidine were commercially available (Aldrich). The benzoyldiazenide and the dinitrogen complexes [$ReCl_2(NNCOPh)L_3$] (L = $PMePh_2$) [26] and *trans*-[$ReCl(N_2)L_4$] [11], respectively, were prepared according to published methods.

IR spectra were run with a Perkin-Elmer 683 spectrophotometer and NMR spectra on a Varian Unity 300 spectrometer. δ values are in ppm relative to $SiMe_4$ (^1H NMR) or to H_3PO_4 (^{31}P NMR). FAB MS spectrometric measurements were performed on a Trio 2000 spectrometer. Positive-ion FAB mass spectra were obtained by bombarding 3-nitrobenzyl alcohol matrices of the samples with 8 keV (ca. 1.28×10^{-15} J) Xe atoms.

3.1. Syntheses

Complexes *mer*-[$ReCl(N_2)(NCNR_2)L_3$] (**1**; R = Me, Et or H; L = $PMePh_2$) and *mer*-[$Re(N_2)\{NCNC(NH_2)_2\}_2L_3$]Cl (**2**) can be prepared by similar procedures involving the reaction of *trans*-[$ReCl_2(N_2)L_4$] with the appropriate substrate at ambient temperature. Alternatively, (**1**, R = Me or Et) can be obtained from [$ReCl(NNCOPh)L_3$] and the appropriate organocyanamide, in refluxing methanol, a process that also leads to the formation of *mer*-[$ReCl_2$-$(NCNEt_2)L_3$] (**3**).

3.1.1. *mer*-[$ReCl(N_2)(NCNR_2)L_3$] (1; R = Me, Et or H; L = $PMePh_2$) and *mer*-[$Re(N_2)\{NCNC(NH_2)_2\}_2L_3$]Cl (2)

3.1.1.1. Syntheses from *trans*-[$ReCl(N_2)L_4$]

A solution of *trans*-[$ReCl(N_2)L_4$] (0.20 g, 0.20 mmol) in THF (40 ml) was treated with $NCNR_2$ [0.20 mmol (16 μl, R = Me; 23 μl, R = Et) or 0.60 mmol (25 mg, R = H)] and stirred for 48 h. Concentration in vacuo to about 10 ml followed by addition of pentane led to the precipitation of **1** as a brownish yellow (**1**, R = Me), greenish yellow (**1**, R = Et) or green (**1**, R = H) solid, which was filtered off, washed with n-pentane, dried in vacuo, recrystallized from CH_2Cl_2/diethyl ether, washed with diethyl ether and dried in vacuo. Further crops could be obtained from the mother liquor, in a similar way [yields ca. 60% (**1**, R = Me), 55% (**1**, R = Et) or 5% (**1**, R = H, as an oily solid)].

The complex *mer*-[$Re(N_2)\{NCNC(NH_2)_2\}_2L_3$]Cl (**2**) was obtained as a yellow solid (yield ca. 35%) by an identical procedure, using cyanoguanidine, $NCNC(NH_2)_2$ (0.20 mmol, 17 mg), instead of the cyanamide.

3.1.1.2. Syntheses from [$ReCl_2(NNCOPh)L_3$]

A suspension of [$ReCl_2(NNCOPh)L_3$] (0.20 g, 0.20 mmol) in MeOH (10 ml) was treated with $NCNR_2$ [0.60 mmol (49 μl, R = Me; 72 μl, R = Et)] and then refluxed for 4 h. Concentration of the solution in vacuo followed by addition of diethyl ether led to the precipitation of (**1**, R = Me or Et) with *mer*-[$ReCl_2(NCNEt_2)L_3$] (**3**) (for R = Et), as a yellow solid which was recrystallized from CH_2Cl_2/diethyl ether, washed with diethyl ether and dried in vacuo. Further crops could be obtained from the mother liquor in a similar way (yield ca. 50%).

3.1.1.2.1. Complex (1, R = Me)

IR (KBr pellet, cm^{-1}): ν(N≡N) 1950 (s), ν(N≡C) 2260 (w). ^1H NMR (C_6D_6): δ 8.27–7.09 (m, 30H, $P(CH_3)(C_6H_5)_2$), 2.44 (d, ^2J(PH) 7.2 Hz, 3H, $P_A(CH_3)(C_6H_5)_2$), 2.28 (t, (1/2)|^2J(PH) + ^4J(PH)|3.0 Hz, 6H, $2P_B(CH_3)(C_6H_5)_2$), 1.64 (s, 6H, $NCN(CH_3)_2$). $^{31}P\{^1H\}$ NMR (C_6D_6): δ −12.37 (d, $^2J(P_AP_B)$ 10.7 Hz, $2P_BMePh_2$), −14.71 (t, $^2J(P_AP_B)$ 10.7 Hz, P_AMePh_2). *Anal.* Calc. for $C_{42}H_{45}N_4ClP_3Re$: C, 54.8; H, 4.9; N, 6.1. Found: C, 54.6; H, 4.8; N, 5.9%.

3.1.1.2.2. Complex (1, R=Et)

IR (KBr pellet, cm^{-1}): ν(N≡N) 1925 (s), 1910(s); ν(N≡C) 2220 (m). ^1H NMR (CD_2Cl_2): δ 7.62–6.84 (m, 30H, $P(CH_3)(C_6H_5)_2$), 2.18 (q, ^3J(HH) 7.2 Hz, $NCN(CH_2CH_3)_2$), 1.91 (d, ^2J(PH) 7.2 Hz, 3H, $P_A(CH_3)(C_6H_5)_2$), 1.73 (t, $(1/2)|^2J(PH)+{}^4J(PH)|$ 3.0 Hz, 6H, 2 $P_B(CH_3)(C_6H_5)_2$), 0.70 (t, ^3J(HH) 7.2 Hz, 6H, $NCN(CH_2CH_3)_2$). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): d −13.33 (d, $^2J(P_AP_B)$ 8.5 Hz, 2 P_BMePh_2), −15.33 (t, $^2J(P_AP_B)$ 8.5 Hz, P_AMePh_2). *Anal.* Calc. for $C_{44}H_{49}N_4ClP_3Re$. 1/4 CH_2Cl_2: C, 54.8; H, 5.1; N, 5.8. Found: C, 54.9; H, 5.0; N, 5.7%. FAB mass spectrum (*m/e*): 949, $[M]^+$; 921, $[M-N_2]^+$; 851, $[M-NCNEt_2]^+$; 822, $[M-NCNEt_2-N_2]^+$; 720, $[M-N_2-PMePh_2]^+$; 651, $[M-NCNEt_2-PMePh_2]^+$.

3.1.1.2.3. Complex 1 (R=H) (not obtained in an analytically pure form)

IR (KBr pellet, cm^{-1}): ν(N≡N) 1960 (s); ν(N≡C) 2220 (m), 2180 (m).

3.1.1.2.4. Complex 2

IR (KBr pellet, cm^{-1}): ν(N≡N) 1970 (s); ν(N≡C) 2230 (m), 2180 (sh); ν(NH) 3460 (w), 3340 (w), 3160 (w), 3060 (w). ^1H NMR (C_6D_6): δ 7.74–7.19 (m, 30H, $P(CH_3)(C_6H_5)_2$), 1.79 (s, br, 3H, $P_A(CH_3)(C_6H_5)_2$), 1.40 (s, br, 6H, $2P_B(CH_3)(C_6H_5)_2$). $^{13}P\{^1H\}$ NMR (C_6D_6): δ −10.45 (s, br, P_AMePh_2), −11.08 (s, br, $2P_BMePh_2$). *Anal.* Calc. for $C_{43}H_{47}N_8ClP_3Re\cdot(1/2)CH_2Cl_2$: C, 49.2; H, 4.6; N, 13.2. Found: C, 49.8; H, 4.6; N, 13.0%. FAB mass spectrum (*m/e*): 983, $[M]^+$; 899, $[M-NCNC(NH_2)_2]^+$; 871, $[M-NCNC(NH_2)_2-N_2]^+$; 755, $[M-N_2-PMePh_2]^+$.

3.1.2. mer-[$ReCl_2(NCNEt_2)L_3$] (3, L=$PMePh_2$)

Crystals of this complex were obtained as indicated above for the preparation of **1** (R=Et) from the reaction of [$ReCl_2$(NNCOPh)L_3] with $NCNEt_2$. Recrystallization of the solid from CH_2Cl_2–diethyl ether did not allow the separation of the two complexes, **1** (R=Et) and **3**. X-ray diffraction analyses were performed on a few of the crystals obtained, showing them to consist of complex **3**. IR (KBr pellet, cm^{-1}): ν(N≡C) 2220 (s). FAB mass spectrum (*m/e*): 955, $[M]^+$; 921, $[M-Cl]^+$; 857, $[M-NCNEt_2]^+$; 755, $[M-PMePh_2]^+$.

3.2. X-ray structure determination of mer-[$ReCl_2(NCNEt_2)(PMePh_2)_3$] (3)

$C_{44}H_{49}P_3N_2Cl_2Re$, Mr=955.91, pale yellow prism (0.32 0.44 0.42 mm), triclinic, space group $P\bar{1}$, a=12.520(3), b=13.317(3), c=15.216(4) Å; V=2119(1) $Å^3$, α=104.96(3), β=93.23(3), γ=117.92(3)°, Z=2, D_x=1.498 g cm^{-3}, λ(Mo Kα)=0.71069 Å, μ(Mo Kα)=3.14 mm^{-1}, $F(000)$=962, T=293 K.

X-ray diffraction data were recorded on a four-circle Philips PW1100 (Febo System) [27] diffractometer operating in $\theta/2\theta$ scan mode with graphite-monochromated Mo Kα radiation, following standard procedures. 7127 reflections were measured ($2\theta_{max}=52°$). There were no significant fluctuations of intensities other than those expected from Poisson statistics. The intensity data were corrected for Lorentz-polarization effects and for absorption (ψ scan) [28]. The structure was solved by heavy atom methods [29] and refined by full-matrix least squares using anisotropic temperature factors for all non-hydrogen atoms, except for the carbon atoms C(41), C(42), C(43) and C(44) of the $NCNEt_2$ ligand which showed two main alternative positions (occupancy factors 0.5), refined isotropically. The hydrogen atoms, except for the ethyl groups, were introduced at calculated positions in their described geometries and during refinement were allowed to ride on the attached carbon atoms with fixed isotropic thermal parameters ($1.2U_{eq}$ of the parent carbon atom). The function minimized was $\Sigma w(F_o^2-F_c^2)^2$, with weighting scheme $w=1/[s^2(F_o^2)+(0.0714P)^2+5.93P]$, where $P=\max(F_o^2+2F_c^2)/3$. Conventional R=0.044, based on F values of 6752 reflections having $F_o^2\geq 3\sigma(F_o)^2$ and S=1.065, (wR on F^2=0.112).

The largest peaks in the final difference map (1 e $Å^{-3}$) were located near the rhenium atom position. Structure refinement was carried out with SHELXL-93 [30] using the scattering factors enclosed therein; the drawing was produced by ORTEP II [31]. Final atomic coordinates and equivalent U are given in Table 1, and selected bond lengths and angles are presented in Table 2.

Acknowledgements

This work has been partially supported by JNICT, the PRAXIS XXI programme (Portugal) and the JNICT/CNR (Italy) cooperative research programme.

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