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Synthesis of the pseudohalide-dinitrogen complexes *trans*-[ReX(N$_2$)(Ph$_2$PCH$_2$CH$_2$PPh$_2$)$_2$] (X = NCS, NCO or N$_3$) and crystal structures of the isothiocyanate and azide complexes

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Abstract

The isothiocyanate-, isocyanate- and azide-dinitrogen complexes *trans*-[ReX(N$_2$)(dppe)$_2$] (**1a**, X = NCS; **1b**, X = NCO; **1c**, X = N$_3$; dppe = Ph$_2$PCH$_2$CH$_2$PPh$_2$) have been prepared by reactions of NaX with *trans*-[ReCl(N$_2$)(dppe)$_2$]. The crystal structures for **1a** and **1c** are reported; **1a** is the first dinitrogen-isothiocyanate complex to be structurally characterized.

1. Introduction

In spite of the large number of dinitrogen complexes known with an anionic stabilizing co-ligand in the *trans* position (mainly hydride or chloride, and, to a lesser extent, including bromide, alkyldithiocarbamate or alkoxide) [1], there are very few examples of dinitrogen complexes with a pseudo-halide co-ligand, such as azide [2], cyanide [3] or thiocyanate [3], in particular [Ru(N$_3$)(N$_2$)(NH$_2$CH$_2$CH$_2$NH$_2$)$_2$][PF$_6$] [2] and [NBu$_4$][MoY(N$_2$)(dppe)$_2$] (Y = N$_3$, CN or SCN; the binding modes have not been ascertained) [3]. However, such types of N$_2$ complex would be of particular interest in the field of nitrogen fixation, because, for example, of the significance in this field of such pseudo-halides. In fact, azide and cyanide are recognized substrates of nitrogenase [4], and thiocyanate is known [5] to interact with isolated FeMoco. Moreover, the investigation of the mode of binding of the latter ligand (through the N or the S atom) [6] to a N$_2$-binding metal site might also provide an insight into the

relative affinity of the site for such atoms. Furthermore, possible effects on the stabilization of the metal-N$_2$ bond might also be recognized.

2. Results and discussion

In extension of our studies [7] of the activation of nitrogenase substrates or other interacting species, we have now synthesized dinitrogen complexes with an isothiocyanate, isocyanate or azide co-ligand *trans*-[ReX(N$_2$)(dppe)$_2$] (**1a**, X = NCS; **1b**, X = NCO; **1c**, X = N$_3$). To our knowledge **1a** is the first and **1c** the second example of a dinitrogen complex with such co-ligands to be structurally characterized by X-ray studies.

Complexes **1** were prepared by reacting *trans*-[ReCl(N$_2$)(dppe)$_2$] with the appropriate NaX salt (X = SCN, NCO or N$_3$, respectively), used in a *ca.* tenfold molar excess, in refluxing THF/MeOH (eqn. 1) for 3 (**1a** or **1c**) or 6 (**1b**) days. They were isolated (*ca.* 85% yields) as pink (**1a**) and yellow (**1b** and **1c**) crystalline solids, respectively (Table 1). Their *trans* geometry is consistent with the singlet resonances observed in the ^{31}P NMR spectra [δ − 106.13 (**1a**), − 107.49 (**1b**) or

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TABLE 1. Analytical[a] and physical data for complexes *trans*-[ReX(N₂)(dppe)₂] [X = NCS (**1a**), NCO (**1b**) or N₃ (**1c**)]

Complex	X	Colour	Analyses (Found (calc.) (%))			IR [b]	
			C	N	H	$\nu(N_2)$	$\nu(X)$
1a	NCS	Pink	59.69 (59.59)	4.21 (3.93)	4.68 (4.53)	1985	2090
1b [c]	NCO	Yellow	59.18 (58.63)	3.41 (3.72)	5.08 (5.18)	1952	2235
1c	N₃	Yellow	59.74 (59.34)	6.36 (6.65)	4.99 (4.60)	1965	2060

[a] Calculated values in parentheses; [b] strong bands (cm⁻¹) in KBr discs; [c] for the cyanate isomer, $\nu(N_2) = 1972$ and $\nu(X) = 2225$ cm⁻¹.

−104.04 (**1c**) ppm relative to P(OMe)₃, in CD₂Cl₂ (Table 2)].

$$trans\text{-}[ReCl(N_2)(dppe)_2] + NaX \longrightarrow$$
$$trans\text{-}[ReX(N_2)(dppe)_2] + NaCl \quad (1)$$
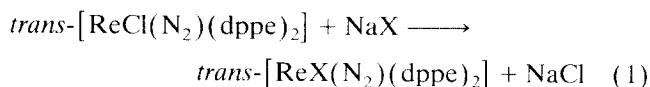
In their IR spectra (Table 1), $\nu(N_2)$ band is observed at 1985, 1952 and 1965 cm⁻¹, respectively; other strong (and sharp) bands at 2090, 2235 and 2060 cm⁻¹ are assigned to $\nu(NCS)$, $\nu(NCO)$ and $\nu(N_3)$, respectively. The band at 2090 cm⁻¹ observed for **1a** would fit the empirical criterion for either a N-bonded or a S-bonded NCS ligand since the relevant $\nu(CN)$ ranges have been reported [8] as 2100–2050 or 2130–2085 cm⁻¹, respectively. The distinction between these types of binding modes could also not be based on the expected [8] different ranges for $\nu(CS)$ (870–820 or 760–700 cm⁻¹ for a N- or a S-bonded ligand, respectively) or $\delta(NCS)$ (485–475 or 470–430 cm⁻¹ for the N- or S-coordination, respectively), because of interference by dppe bands in these frequency ranges.

However (see below), the X-ray diffraction study of **1a** revealed that the NCS ligand binds through the N-atom (*i.e.* the "hard" rather than the "soft" end) and, therefore, it must be regarded as a metal isothio-

TABLE 2. ¹H and ³¹P {¹H} NMR data[a] for complexes *trans*-[ReX(N₂)(dppe)₂] [X = NCS (**1a**), NCO (**1b**) or N₃ (**1c**)]

Complex	X	¹H			³¹P
		δ (ppm) [b]	Integration	Assignment	δ (ppm) [c]
1a	NCS	7.1–6.8 m	40	C₆H₅	−106.13 s
		2.4–2.3 m	8	CH₂	
1b	NCO	7.3–6.9 m	40	C₆H₅	−107.49 s [d]
		2.5–2.3 m	8	CH₂	
1c	N₃	7.1–6.6 m	40	C₆H₅	−104.04 s
		2.5–2.2 m	8	CH₂	

[a] In CDCl₃; s-singlet; m-complex multiplet; [b] relative to internal SiMe₄, assigned to dppe; [c] relative to P(OMe)₃, assigned to 4P(dppe); [d] −105.36 ppm (s) for the cyanate isomer.
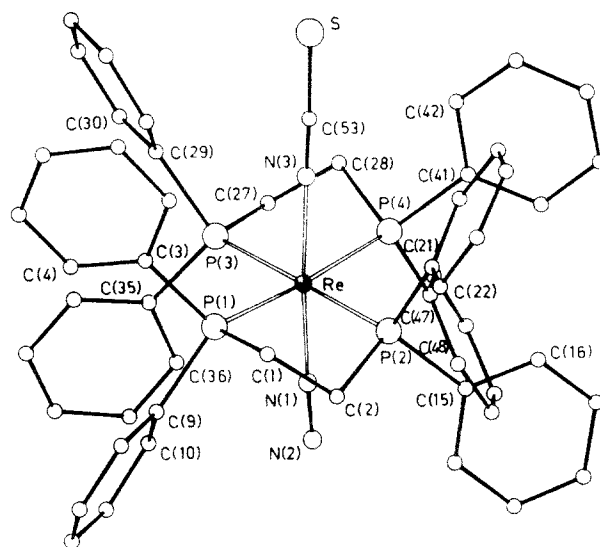
Fig. 1. View of the structure of the complex *trans*-[Re(NCS)-(N₂)(dppe)₂] (**1a**) with the atomic labelling scheme.

cyanate (M–NCS) rather than a thiocyanate species (M–SCN).

In complex **1b**, the NCO ligand is also believed to bind the metal through the N atom in view of the observed IR band (Table 1), with medium intensity, at 1330 cm⁻¹, which lies within the expected range (1370–1300 cm⁻¹) [9] for the $\nu_s(NCO)$ vibration of an isocyanate ligand.
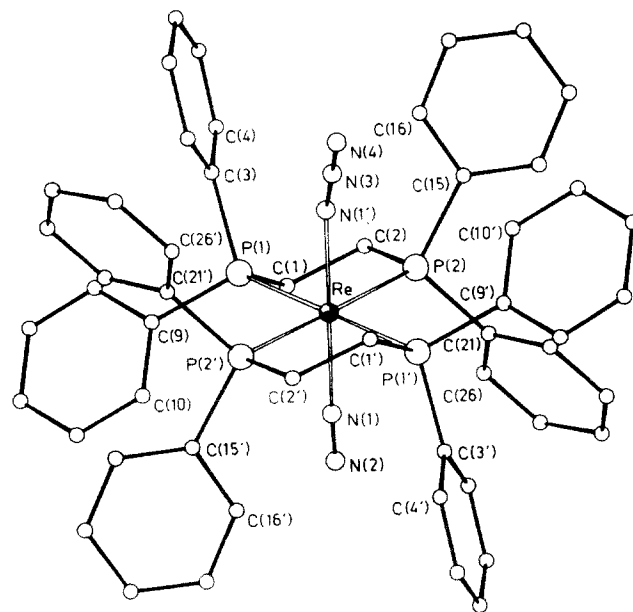
Fig. 2. View of the structure of the complex *trans*-[Re(N₃)(N₂)(dppe)₂] (**1c**) with the atomic labelling scheme. The two N₃ and N₂ ligands are disordered between the two apical positions; one of the two forms is represented in the Figure.

However, the analogous cyanate complex (with the O-bonded NCO ligand) also appears to be formed in reaction 1, (X = NCO); it was isolated when shorter refluxing periods were used (such as 3 days), but was always contaminated by the isocyanate. A weak IR band at 1265 cm^{-1} is assigned [9] to ν_s(NCO) of the O-bonded ligand, whereas ν_{as}(NCO) is observed as a strong band at 2225 cm^{-1}. ν(N$_2$) is detected as a strong band at a wavenumber (1972 cm^{-1}) slightly above that observed (1952 cm^{-1}) for the isocyanate complex 1b, suggesting that cyanate behaves as a somewhat weaker electron donor than isocyanate ligand. In the ^{31}P NMR spectrum of the cyanate complex, the expected singlet resonance is observed at δ − 105.36 ppm (Table 2).

The structures of the complexes 1a and 1c, determined by X-ray diffraction study methods, are shown in Figs. 1 and 2, respectively. The relevant bond distances and angles are given in Tables 3 and 4, respectively. In each complex, the Re atom displays an octahedral coordination, involving four P atoms from the

two chelating dppe ligands in the equatorial positions, and two N atoms (one from N$_2$ and the other from the pseudo-halide ligand) in the apical positions. The complex 1c has a crystallographic imposed C_i symmetry, so that the two apical ligands are disordered between two positions with equal occupancy factor. Because of this feature the N(1) and N(1′) atoms are not well resolved and the structural parameters involving these atoms must be regarded as not very precise.

The isothiocyanate ligand in 1a is linearly coordinated through the N atom [Re−N−C bond angle of 178.8(6)°], but in 1c the Re−N−N bond angle is 150.3(5)°. In 1a the Re−N$_2$ bond length is rather short [1.951(6) Å], indicative of considerable degree of double bond character; it is even slightly shorter than that reported for the related complex trans-[ReCl(N$_2$)(PMe$_2$Ph)$_4$], 1.97(2) Å [10].

The N−C bond length in the isothiocyanate ligand, 1.136(10) Å, is very close to that found for the N ≡ C bond of the acetonitrile ligand in trans-[ReCl(NCMe)-

TABLE 3. Selected bond distances (Å) and angles (°) with esd's in parentheses for complex [Re(NCS)(N$_2$)(dppe)$_2$] · CH$_2$Cl$_2$ (1a)

Re−N(1)	1.951(6)	P(1)−C(3)	1.845(8)
Re−N(3)	2.104(6)	P(1)−C(9)	1.851(7)
Re−P(1)	2.414(2)	P(2)−C(2)	1.845(7)
Re−P(2)	2.411(2)	P(2)−C(15)	1.820(7)
Re−P(3)	2.411(2)	P(2)−C(21)	1.835(7)
Re−P(4)	2.408(2)	P(3)−C(27)	1.849(7)
N(1)−N(2)	1.119(10)	P(3)−C(29)	1.848(7)
N(3)−C(53)	1.136(10)	P(3)−C(35)	1.833(7)
S−C(53)	1.642(9)	P(4)−C(28)	1.831(7)
C(1)−C(2)	1.514(12)	P(4)−C(41)	1.830(6)
C(27)−C(28)	1.537(10)	P(4)−C(47)	1.840(7)
P(1)−C(1)	1.857(8)		

N(1)−Re−N(3)	176.2(3)	Re−P(1)−C(3)	120.6(2)
N(1)−Re−P(1)	92.1(2)	Re−P(1)−C(9)	121.8(3)
N(1)−Re−P(2)	87.8(2)	C(1)−P(1)−C(3)	100.8(3)
N(1)−Re−P(3)	92.4(2)	C(1)−P(1)−C(9)	101.0(4)
N(1)−Re−P(4)	91.9(2)	C(3)−P(1)−C(9)	101.3(3)
N(3)−Re−P(1)	90.2(2)	Re−P(2)−C(2)	106.4(3)
N(3)−Re−P(2)	89.6(2)	Re−P(2)−C(15)	118.8(2)
N(3)−Re−P(3)	90.3(2)	Re−P(2)−C(21)	121.4(3)
N(3)−Re−P(4)	85.9(2)	C(2)−P(2)−C(15)	102.6(3)
P(1)−Re−P(2)	81.2(1)	C(2)−P(2)−C(21)	102.8(3)
P(1)−Re−P(3)	98.0(1)	C(15)−P(2)−C(21)	102.4(3)
P(1)−Re−P(4)	176.0(1)	Re−P(3)−C(27)	108.3(3)
P(2)−Re−P(3)	179.2(1)	Re−P(3)−C(29)	122.9(2)
P(2)−Re−P(4)	99.5(1)	Re−P(3)−C(35)	118.8(3)
P(3)−Re−P(4)	81.3(1)	C(27)−P(3)−C(29)	99.3(3)
Re−N(1)−N(2)	177.7(6)	C(27)−P(3)−C(35)	101.4(3)
Re−N(3)−C(53)	178.8(6)	C(29)−P(3)−C(35)	102.5(3)
S−C(53)−N(3)	177.4(7)	Re−P(4)−C(28)	107.0(3)
P(1)−C(1)−C(2)	107.6(5)	Re−P(4)−C(41)	121.9(2)
P(2)−C(2)−C(1)	106.7(5)	Re−P(4)−C(47)	118.7(2)
P(3)−C(27)−C(28)	108.2(5)	C(28)−P(4)−C(41)	101.2(3)
P(4)−C(28)−C(27)	106.9(5)	C(28)−P(4)−C(47)	102.8(3)
Re−P(1)−C(1)	107.9(3)	C(41)−P(4)−C(47)	102.3(3)

TABLE 4. Selected bond distances (Å) and angles (°) with esd's in parentheses for complex [Re(N₃)(N₂)(dppe)₂] (1c)

Re–N(1)	2.058(3)	P(1)–C(1)	1.843(3)
Re–P(1)	2.397(1)	P(1)–C(3)	1.835(2)
Re–P(2)	2.410(1)	P(1)–C(9)	1.839(3)
N(1)–N(2)	0.969(11)	P(2)–C(2)	1.865(3)
N(1')–N(3)	1.199(10)	P(2)–C(15)	1.845(3)
N(3)–N(4)	1.200(13)	P(2)–C(21)	1.842(2)
C(1)–C(2)	1.521(4)		
N(1)–Re–P(1)	86.2(1)	Re–P(1)–C(9)	124.4(1)
N(1)–Re–P(2)	86.4(1)	C(1)–P(1)–C(3)	103.3(2)
P(1)–Re–P(2)	80.6(1)	C(1)–P(1)–C(9)	98.8(2)
Re–N(1)–N(2)	176.8(7)	C(3)–P(1)–C(9)	103.0(1)
Re–N(1')–N(3)	150.3(5)	Re–P(2)–C(2)	110.0(1)
N(1')–N(3)–N(4)	175.1(10)	Re–P(2)–C(15)	121.3(1)
P(1)–C(1)–C(2)	109.1(2)	Re–P(2)–C(21)	117.3(1)
P(2)–C(2)–C(1)	111.4(2)	C(2)–P(2)–C(15)	98.1(2)
Re–P(1)–C(1)	106.2(1)	C(2)–P(2)–C(21)	103.2(2)
Re–P(1)–C(3)	117.6(1)	C(15)–P(2)–C(21)	104.0(1)

The primed atom is related to the unprimed one by the transformation $-x, -y, -z$.

(dppe)₂], 1.141(9) Å [11], and comparable with that found in [Mo(NCS)Cl(dppe)₂], 1.172(10) Å [12]. The azide group is symmetrical, i.e. it has identical N(1')–N(3) and N(3)–N(4) distances, 1.199(10) and 1.200(13) Å, as observed for [Ru(N₃)(N₂)(NH₂CH₂CH₂NH₂)₂]-[PF₆] [average 1.162(23) Å] [2] or in the ionic azide, 1.154(15) Å [13]; however, in our complex 1c, the Re–N–N bond angle, 150.3(5)°, is much larger than that in the Ru complex, 116.7(7)°, [2], suggesting a stronger involvement of the azide ligand in π-bonding to the rhenium than in that to the ruthenium centre, in these species.

This study also clearly shows that NCS⁻, NCO⁻ and N₃⁻ can act as good Re–N₂ bond-stabilizing ligands and the corresponding dinitrogen compounds can readily be prepared by simple displacement of Cl⁻ from a chloro/dinitrogen complex. The potential significance of these findings for the extension of the available range of N₂ complexes and for the study of the activation of such substrates by N₂-binding centres is being explored.

3. Experimental section

The reactions were carried out under dinitrogen by use of standard gas-flow or high-vacuum techniques. The complex trans-[ReCl(N₂)(dppe)₂] was prepared by a published method [14] and the pseudo-halide salts were used as purchased (Aldrich). The solvents were dried by standard methods and distilled under dinitrogen prior to use. Infrared spectra were recorded with a Perkin-Elmer 683 spectrophotometer and the NMR

3.1. Preparation of complexes trans-[ReX(N₂)(dppe)₂] (1a, X = NCS, 1b, X = NCO, 1c, X = N₃)

After addition of NaX [1.9 mmol, i.e., 155 mg (X = NCS) or 124 mg (X = NCO or N₃)] to a suspension of trans-[ReCl(N₂)(dppe)₂] (0.19 mmol, 200 mg) in THF/MeOH (70 cm³ of a 1:1.5 volume mixture) the mixture was refluxed under dinitrogen for 3 days (X = NCS or N₃) or 6 days (X = NCO). The solution was then filtered and concentrated under reduced pressure to ca. 5 cm³. Addition of MeOH led to precipitation of complexes 1 as a pink (1a) or a yellow (1b or 1c) solid, which was filtered off, washed with MeOH, and dried in vacuo. Crystalline products were obtained by crystallization from CH₂Cl₂/Et₂O (ca. 80% yield).

In the case of X = NCO, shorter periods of reflux led to the isolation of mixtures of 1b with the corresponding cyanate isomer.

3.2. Determination of the crystal structures of trans-[ReX(N₂)(dppe)₂] (1a, X = NCS; 1c, X = N₃)

Crystal data for 1a · CH₂Cl₂. C₅₃H₄₈N₃P₄ReS · CH₂Cl₂, M = 1154.07, triclinic, space group P1̄, a = 12.383(6), b = 13.073(3), c = 15.659(9) Å, α = 82.36(2), β = 86.41(2), γ = 82.43(2)°, V = 2488(2) Å³, Z = 2, D꜀ = 1.541 g cm⁻³, F(000) = 1160, μ(Mo Kₐ) = 27.89 cm⁻¹.

Crystal data for 1c. C₅₂H₄₈N₅P₄Re, M = 1053.08, triclinic, space group P1̄, a = 10.317(3), b = 10.531(3), c = 12.605(4) Å, α = 71.20(2), β = 87.29(2), γ = 62.37(2)°, V = 1140.1(7) Å³, Z = 1 D꜀ = 1.534 g cm⁻³, F(000) = 530, μ(Mo Kα) = 28.79 cm⁻¹.

The intensity data were collected at room temperature (22°C) on Siemens AED (1a) and Philips PW 1100 (1c) diffractometers, using niobium-filtered (1a) and graphite-monochromated (1c) Mo Kα radiation ($\bar{\lambda}$ = 0.71073 Å) and the θ–2θ scan technique. 12087 (1a) and 4996 (1c) unique reflections were measured, with θ in the range 3–28° (1a) and 3–27° (1c), 8108 (1a) and 4954 (1c), reflections with $I \geq 2\sigma(I)$ were used in the refinement. One standard reflection was monitored every 50 measurements; no significant decay was noticed over the time of data collection. The individual profiles were analyzed following Lehmann and Larsen [15]. Intensities were corrected for Lorentz and polarization effects, a correction for absorption effects [16] was applied to the data of 1a (maximum and minimum values for the transmission factors were 1.312 and 0.852 respectively).

The structures were solved by Patterson and Fourier methods and refined by blocked full-matrix (1a) and full-matrix (1c) least-squares, with anisotropic thermal

TABLE 5. Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($\mathring{A}^2 \times 10^4$) with esd's in parentheses for the non-hydrogen atoms of complex $[Re(NCS)(N_2)(dppe)_2] \cdot CH_2Cl_2$ (1a)

Atom	x	y	z	U [a]
Re	1864(1)	2660(1)	2580(1)	282(1)
S	2380(3)	295(2)	384(2)	878(11)
P(1)	510(1)	3795(1)	1744(1)	360(5)
P(2)	3048(1)	3779(1)	1745(1)	346(5)
P(3)	660(1)	1553(1)	3403(1)	360(5)
P(4)	3210(1)	1442(1)	3345(1)	326(5)
N(1)	1762(4)	3589(4)	3467(4)	394(18)
N(2)	1739(6)	4125(6)	3971(4)	617(26)
N(3)	2087(4)	1662(4)	1618(3)	373(17)
C(1)	1236(6)	4640(6)	914(5)	486(25)
C(2)	2174(7)	4977(6)	1340(5)	488(26)
C(3)	-388(6)	3259(5)	1066(4)	405(21)
C(4)	-1483(7)	3272(6)	1259(5)	529(27)
C(5)	-2135(8)	2819(7)	768(7)	683(34)
C(6)	-1697(9)	2332(7)	93(6)	711(38)
C(7)	-598(9)	2292(7)	-107(5)	629(33)
C(8)	67(7)	2773(6)	373(5)	498(25)
C(9)	-466(6)	4777(5)	2232(5)	449(23)
C(10)	-646(6)	4738(7)	3109(5)	568(29)
C(11)	-1368(8)	5512(8)	3454(7)	751(39)
C(12)	-1916(7)	6286(7)	2923(9)	775(45)
C(13)	-1749(8)	6316(7)	2047(8)	768(40)
C(14)	-1047(7)	5580(6)	1704(6)	595(30)
C(15)	4085(5)	4276(4)	2293(4)	370(20)
C(16)	5171(6)	3843(6)	2268(5)	482(25)
C(17)	5934(7)	4165(8)	2745(6)	626(33)
C(18)	5626(7)	4950(7)	3259(6)	652(34)
C(19)	4582(7)	5378(7)	3296(6)	637(33)
C(20)	3807(7)	5055(6)	2809(5)	515(26)
C(21)	3797(5)	3402(5)	764(4)	415(22)
C(22)	3889(9)	4100(7)	15(6)	760(37)
C(23)	4505(13)	3780(9)	-690(6)	1093(58)
C(24)	5029(10)	2799(9)	-674(6)	824(45)
C(25)	4948(8)	2094(8)	49(6)	652(33)
C(26)	4314(7)	2408(6)	753(4)	506(26)
C(27)	1477(6)	615(6)	4174(4)	440(23)
C(28)	2572(6)	265(5)	3717(4)	396(21)
C(29)	-57(5)	637(5)	2915(4)	391(20)
C(30)	-539(7)	-147(7)	3432(5)	625(31)
C(31)	-1032(7)	-860(7)	3076(7)	722(35)
C(32)	-1081(6)	-801(6)	2196(6)	568(29)
C(33)	-631(6)	-16(6)	1682(5)	521(26)
C(34)	-143(6)	709(5)	2035(4)	411(22)
C(35)	-404(6)	2131(6)	4124(4)	479(24)
C(36)	-107(8)	2602(7)	4807(5)	654(33)
C(37)	-885(11)	3118(10)	5312(6)	932(48)
C(38)	-1960(11)	3162(12)	5156(8)	1077(58)
C(39)	-2271(10)	2715(11)	4494(8)	1062(54)
C(40)	-1503(7)	2208(8)	3969(6)	678(34)
C(41)	4467(5)	896(5)	2806(4)	367(19)
C(42)	4421(6)	171(6)	2237(4)	470(24)
C(43)	5345(7)	-170(7)	1762(5)	601(31)
C(44)	6313(7)	206(8)	1830(6)	658(33)
C(45)	6382(7)	881(7)	2405(6)	625(32)
C(46)	5464(6)	1244(6)	2887(5)	459(24)
C(47)	3707(5)	1771(5)	4345(4)	357(19)
C(48)	4006(6)	2762(6)	4354(4)	462(24)
C(49)	4404(7)	3027(7)	5092(5)	571(29)
C(50)	4469(7)	2342(7)	5826(5)	632(32)

TABLE 5. (continued)

Atom	x	y	z	U [a]
C(51)	4175(8)	1366(7)	5835(5)	656(33)
C(52)	3795(7)	1074(6)	5097(5)	527(26)
C(53)	2225(6)	1114(6)	1105(5)	502(25)
Cl(1)	951(3)	7119(3)	2394(2)	1118(15)
Cl(2)	2999(3)	7836(3)	2610(3)	1404(20)
C(54)	1696(13)	8179(9)	2396(12)	1176(73)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

parameters in the last cycles of refinement for all the non-hydrogen atoms. In 1c the two N_2 and N_3 ligands were found to be disordered, and distributed between the two apical positions with equal occupancy factor in order to justify the crystallographically imposed C_i symmetry of the complex. Because of the overlapping of the two peaks, the N(1) and N(1') atoms are not well

TABLE 6. Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($\mathring{A}^2 \times 10^4$) with esd's in parentheses for the non-hydrogen atoms of complex $[Re(N_3)(N_2)(dppe)_2]$ (1c)

Atom	x	y	z	U [a]
Re	0	0	0	250(1)
P(1)	344(1)	1869(1)	-1496(1)	275(2)
P(2)	751(1)	1089(1)	1104(1)	295(2)
N(1)	2211(3)	-1424(3)	47(2)	414(11)
N(2)	3263(13)	-2071(11)	98(8)	543(41)
N(3)	-3432(9)	1607(9)	102(7)	449(31)
N(4)	-4626(7)	1694(9)	232(8)	953(43)
C(1)	1801(3)	2096(3)	-918(2)	324(10)
C(2)	1399(3)	2409(3)	181(2)	346(11)
C(3)	-1198(3)	3815(3)	-2001(2)	307(9)
C(4)	-1054(3)	5092(3)	-2073(2)	346(10)
C(5)	-2264(3)	6526(3)	-2400(2)	414(11)
C(6)	-3635(3)	6721(3)	-2672(3)	558(14)
C(7)	-3783(4)	5474(4)	-2633(4)	628(16)
C(8)	-2591(3)	4033(3)	-2290(3)	467(13)
C(9)	1091(3)	1589(3)	-2804(2)	319(10)
C(10)	1893(3)	127(3)	-2836(2)	373(11)
C(11)	2534(3)	-122(4)	-3796(3)	460(13)
C(12)	2407(4)	1088(4)	-4716(2)	509(14)
C(13)	1632(4)	2541(4)	-4691(2)	564(15)
C(14)	969(3)	2809(3)	-3743(2)	456(12)
C(15)	-596(3)	2407(3)	1767(2)	372(11)
C(16)	-1848(3)	3630(3)	1070(3)	486(13)
C(17)	-2880(4)	4739(4)	1461(4)	637(18)
C(18)	-2675(5)	4633(5)	2566(4)	709(23)
C(19)	-1448(4)	3422(5)	3269(3)	636(22)
C(20)	-412(4)	2307(4)	2884(3)	473(15)
C(21)	2310(3)	-230(3)	2227(2)	354(10)
C(22)	2108(3)	-1134(3)	3234(2)	447(13)
C(23)	3271(4)	-2137(4)	4083(3)	540(15)
C(24)	4652(4)	-2275(4)	3941(3)	560(15)
C(25)	4881(4)	-1423(4)	2943(3)	577(15)
C(26)	3725(3)	-414(4)	2085(3)	463(13)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

resolved. A refinement of the structure in the non-centrosymmetric space group $P1$ with each of two ligands occupying an apical position gave worse results. The hydrogen atoms were clearly localized in the final ΔF map and refined isotropically. A weighting scheme $w = K[\sigma^2(F_o) + gF_o^2]^{-1}$ was used in the last cycles of refinement with $K = 0.400$ and $g = 0.0029$ (**1a**) and $K = 1.0$ and $g = 0.0008$ (**1c**). The final R and R_w values were 0.0437 and 0.0530 (**1a**) and 0.0220 and 0.0276 (**1c**). The SHELX-76 and SHELXS-86 computer programs were used [17]. Atomic scattering factors, corrected for anomalous dispersion, were taken from ref. 18. Final atomic coordinates for the non-hydrogen atoms of **1a** and **1c** are given in Tables 5 and 6 respectively. All calculations were carried out with the Gould Powernode 6040 and Encore 91 computers of the Centro di Studio per la Strutturistica Diffrattometrica del C.N.R., Parma. Additional data are available from the authors.

Acknowledgements

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