

MOLECULAR STRUCTURE OF *trans*-BIS[1,2-BIS(DIPHENYLPHOSPHINO)-ETHANE]CHLORO(*t*-BUTYLISOCYANIDE)RHENIUM(I)-TETRAHYDROFURAN SOLVATE, *trans*-{ReCl[CN(*t*-C₄H₉)]-(Ph₂PCH₂CH₂PPh₂)₂} · C₄H₈O

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Summary

Crystals of *trans*-{ReCl[CN(*t*-C₄H₉)](Ph₂PCH₂CH₂PPh₂)₂} · C₄H₈O solvate are monoclinic, space group *P*2₁/*n*, *a* 24.098(7), *b* 16.558(5), *c* 13.402(4) Å, β 90.97(3)°, *V* 5346.82 Å³ at 25°C. *F*(000) = 2392, *Z* = 4, λ(Cu-*K*_α) 1.5418 Å, μ(Cu-*K*_α) 57.99 cm⁻¹, *D*_c 1.46 g cm⁻³. The structure was solved by Patterson and difference Fourier electron density syntheses and refined to *R*(*F*) = 0.048 and *R*_w(*F*) = 0.067 for 4763 observed reflections. The Re atom is in a distorted octahedral coordination with the chloride and the isocyanide as axial ligands and the two dppe groups as equatorial ligands. The Re–C bond length is 1.926(9) Å and the Cl–Re–C bond angle is 175.5(2)°. The CNBu^t ligand is nearly linear with a 174.0(9)° angle at the N and a C≡N bond length of 1.154(10) Å. The *t*-Bu group and the solvate molecules are disordered.

Introduction

Structural studies of isocyanide metal complexes [1] have shown different geometries for the CNR ligands ranging from linear to bent geometries at the nitrogen atom. Linear isocyanides have short C≡N bond lengths and are usually terminal ligands, while the bent isocyanides have longer C=N bond lengths and are usually bridging ligands. However, some electron-rich complexes have terminal CNR ligands which are bent.

The complexes $trans\text{-}[\text{ReCl}(\text{CNR})(\text{dppe})_2]$ ($\text{R} = \text{Me}$ or Bu^t ; $\text{dppe} = \text{Ph}_2\text{PCH}_2\text{-CH}_2\text{PPh}_2$) have been prepared and characterized by electronic absorption IR, ^1H and ^{31}P NMR spectroscopies [2]. A bent CNR ligand is proposed on the basis of the redox properties, the low infrared $\nu(\text{CN})$ frequency and the easy protonation and alkylation at the nitrogen atom [3].

This X-ray study was undertaken in order to test this prediction for a CNBu^t ligand coordinated to the electron-rich center $[\text{ReCl}(\text{dppe})_2]$. In fact, a linear CNR ligand was found.

Experimental

Crystals of $[\text{ReCl}(\text{CNBu}^t)(\text{dppe})_2] \cdot \text{C}_4\text{H}_8\text{O}$, from a tetrahydrofuran pentane solution were provided by A.J.L. Pombeiro of this Institute [2]. A crystal with dimen-

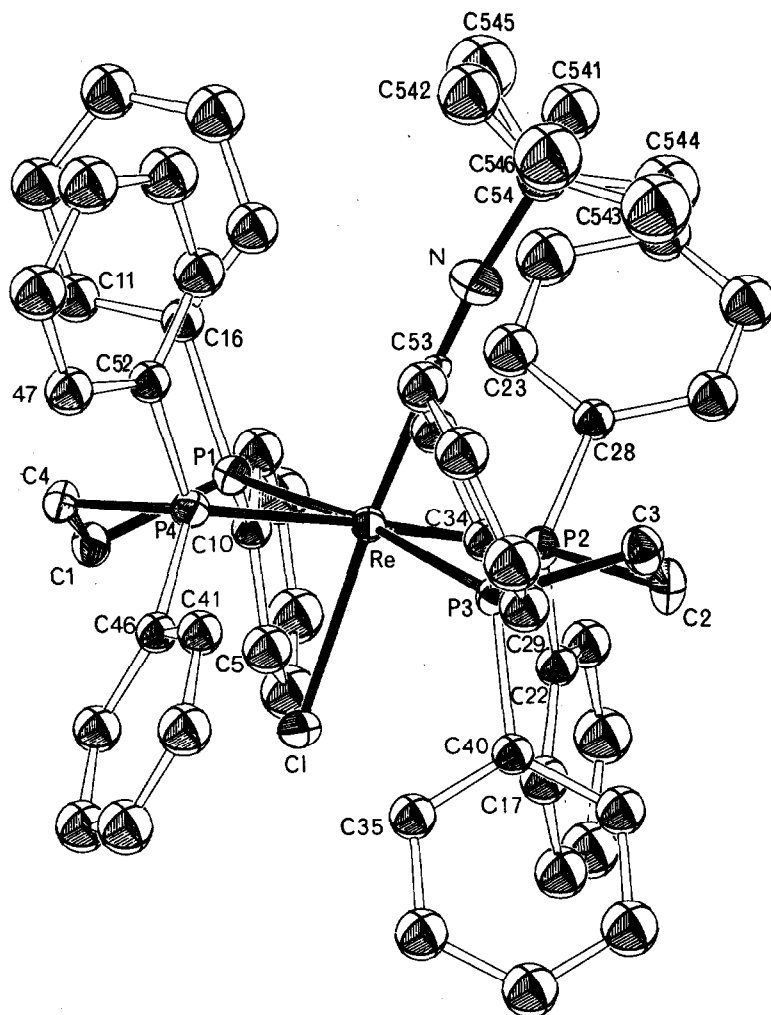


Fig. 1. Molecular structure of $trans\text{-}[\text{ReCl}(\text{CNBu}^t)(\text{dppe})_2]$. For sake of clarity only the first and last C atoms at the phenyl rings are labelled.

sions $0.21 \times 0.15 \times 0.13$ mm was mounted in a general orientation on an automatic Enraf-Nonius CAD-4 four-circle diffractometer using graphite-monochromated $\text{Cu-K}\alpha$ radiation. The unit cell dimensions and orientation matrix were determined from a least-squares refinement of $\sin^2\theta$ values of 33 reflections with $35^\circ \leq \theta \leq 46^\circ$. A total of 5619 intensities were measured at room temperature using the θ - 2θ scan technique to $\theta_{\text{max}} = 50^\circ$. No significant variation of the intensities was observed for the three standard reflections. Equivalent reflections were averaged to give 5454 unique reflections ($R_{\text{int}} = 0.0234$) of which 4763 had $F > 3\sigma(F)$. Data were corrected for Lorentz and polarization effects.

Structure analysis and refinement

The structure was solved by a combination of Patterson and difference Fourier methods and refined by least-squares using the system SHELX [4]. Blocked full-matrix isotropic refinement of the non-hydrogen atoms gave $R = 0.092$. A difference electron density map then revealed an alternative set of positions for the methyl carbon atoms of the t-butyl group which was consistent with a rotationally disordered t-butyl. The map also showed peaks which could be attributed to the presence of a tetrahydrofuran solvent molecule, the presence of which was suggested by a ^1H NMR spectrum in CD_2Cl_2 solution and confirmed by elemental analysis [2]. The data were then corrected for absorption and the refinement was continued with anisotropic non-hydrogen atoms. The carbon atoms of the phenyl rings and the disordered t-butyl group were refined as rigid groups. The atoms of the solvate

TABLE 1

ATOMIC COORDINATES ($\times 10^4$) AND EQUIVALENT ISOTROPIC TEMPERATURE FACTORS ($\times 10^3 \text{ \AA}^2$) (with e.s.d.'s in parentheses)

Atom	x	y	z	U/U_{eq}^a
Re	4087.4(2)	2406.1(2)	1666.4(3)	29.3 ^a
Cl	4385(1)	1469(1)	293(2)	59 ^a
P(1)	3178(1)	2183(1)	946(2)	41 ^a
P(2)	4336(1)	3591(1)	765(2)	34 ^a
P(3)	5025(1)	2511(1)	2242(2)	35 ^a
P(4)	3843(1)	1163(1)	2510(2)	36 ^a
N	3830(4)	3637(5)	3318(6)	60 ^a
C(53)	3915(3)	3164(5)	2707(6)	30 ^a
C(54)	3774(4)	4283(5)	4057(6)	58(3)
C(541) ^b	3376(4)	4936(5)	3656(6)	73(7)
C(542) ^b	3537(4)	3927(5)	5028(6)	83(8)
C(543) ^b	4344(4)	4654(5)	4283(6)	109(10)
C(544) ^b	4026(4)	5063(5)	3657(6)	98(12)
C(545) ^b	3155(4)	4420(5)	4277(6)	110(13)
C(546) ^b	4077(4)	4034(5)	5033(6)	104(12)
C(1)	3090(4)	1073(5)	848(7)	43 ^a
C(2)	5048(4)	3937(5)	1178(7)	48 ^a
C(3)	5196(4)	3592(5)	2196(7)	46 ^a
C(4)	3206(4)	719(5)	1906(6)	41 ^a
C(5)	3341(2)	2263(4)	-1112(5)	54(3)
C(6)	3238(2)	2533(4)	-2083(5)	69(3)

TABLE 1 (continued)

Atom	x	y	z	U/U_{eq}^a
C(7)	2793(2)	3051(4)	-2283(5)	69(3)
C(8)	2451(2)	3298(4)	-1511(5)	75(3)
C(9)	2554(2)	3028(4)	-540(5)	55(3)
C(10)	2999(2)	2510(4)	-340(5)	35(2)
C(11)	2036(3)	2069(3)	1406(4)	53(3)
C(12)	1558(3)	2271(3)	1924(4)	66(3)
C(13)	1581(3)	2861(3)	2667(4)	67(3)
C(14)	2082(3)	3249(3)	2892(4)	75(3)
C(15)	2560(3)	3047(3)	2373(4)	59(3)
C(16)	2536(3)	2457(3)	1630(4)	40(2)
C(17)	4833(2)	3055(3)	-976(4)	51(3)
C(18)	4944(2)	3051(3)	-1994(4)	60(3)
C(19)	4663(2)	3581(3)	-2635(4)	72(3)
C(20)	4271(2)	4116(3)	-2258(4)	73(3)
C(21)	4160(2)	4120(3)	-1239(4)	52(3)
C(22)	4441(2)	3589(3)	-599(4)	39(2)
C(23)	3332(3)	4402(3)	930(5)	65(3)
C(24)	2982(3)	5072(3)	969(5)	77(3)
C(25)	3206(3)	5849(3)	992(5)	64(3)
C(26)	3780(3)	5956(3)	975(5)	69(3)
C(27)	4130(3)	5286(3)	935(5)	56(3)
C(28)	3906(3)	4509(3)	912(5)	37(2)
C(29)	5768(2)	2010(4)	3783(4)	56(3)
C(30)	5901(2)	1793(4)	4764(4)	70(3)
C(31)	5494(2)	1809(4)	5491(4)	63(3)
C(32)	4953(2)	2042(4)	5236(4)	55(3)
C(33)	4820(2)	2259(4)	4255(4)	48(2)
C(34)	5228(2)	2243(4)	3529(4)	40(2)
C(35)	5573(2)	1205(3)	1395(4)	48(2)
C(36)	6004(2)	809(3)	914(4)	61(3)
C(37)	6456(2)	1248(3)	568(4)	69(3)
C(38)	6476(2)	2083(3)	702(4)	72(3)
C(39)	6045(2)	2479(3)	1182(4)	54(3)
C(40)	5594(2)	2040(3)	1529(4)	38(2)
C(41)	4767(3)	286(3)	3220(4)	44(2)
C(42)	5186(3)	-291(3)	3149(4)	63(3)
C(43)	5190(3)	-822(3)	2341(4)	68(3)
C(44)	4776(3)	-775(3)	1603(4)	61(3)
C(45)	4357(3)	-198(3)	1674(4)	50(3)
C(46)	4352(3)	333(3)	2482(4)	37(2)
C(47)	3640(3)	391(3)	4361(4)	51(3)
C(48)	3439(3)	365(3)	5330(4)	70(3)
C(49)	3200(3)	1051(3)	5748(4)	78(3)
C(50)	3162(3)	1763(3)	5196(4)	76(3)
C(51)	3363(3)	1790(3)	4227(4)	57(3)
C(52)	3602(3)	1104(3)	3809(4)	38(2)
O ^c	6563(3)	3865(4)	3793(5)	54(2)
C(56) ^c	6891(6)	4318(9)	1978(10)	99(4)
C(57) ^c	7263(12)	4781(19)	2805(21)	230(12)
C(58) ^c	7640(4)	4807(6)	3281(7)	46(2)
C(59) ^c	6966(11)	3928(18)	3148(20)	221(11)

^a $U_{\text{eq}} = \frac{1}{3}(U_{11} + U_{22} + U_{33} + 2U_{13} \cos \beta)$. ^b Disordered methyl C atoms; site occupation factors refined to 0.57 and 0.43. ^c Atoms of solvent molecule.

molecule were refined isotropically giving high thermal parameters, indicating large thermal motion or disorder. The hydrogen atoms of the phenyl and the ethane groups were included at calculated positions with C–H distances of 1.08 Å.

A final full matrix-least-squares refinement involving the same 241 parameters as the previous blocked refinement converged at $R(F) = 0.048$ and $R_w(F) = 0.067$, with $w = 3.5478/[\sigma^2(F) + 0.000408 F^2]$. There were residual peaks in the difference Fourier synthesis, in the range 1.0–0.62 eÅ⁻³. These were associated with the disordered solvent molecule. Atomic scattering factors were taken from the International Tables for X-ray Crystallography [5].

The refined anisotropic thermal parameters, hydrogen atom coordinates, a table of least-squares planes, and lists of observed and calculated structure factors are available as supplementary material.

TABLE 2
SELECTED BOND LENGTHS (Å) AND ANGLES (°)

Re–Cl	2.520(2)	P(1)–C(1)	1.854(9)
Re–P(1)	2.409(2)	P(1)–C(10)	1.850(6)
Re–P(2)	2.386(2)	P(1)–C(16)	1.866(6)
Re–P(3)	2.382(2)	P(2)–C(2)	1.882(9)
Re–P(4)	2.426(2)	P(2)–C(22)	1.849(6)
Re–C(53)	1.926(9)	P(2)–C(28)	1.853(7)
C(53)–N	1.154(10)	P(3)–C(3)	1.839(9)
N–C(54)	1.465(11)	P(3)–C(34)	1.839(6)
C(54)–C(541)	1.537(11)	P(3)–C(40)	1.855(6)
C(54)–C(542)	1.547(11)	P(4)–C(4)	1.873(9)
C(54)–C(543)	1.531(12)	P(4)–C(46)	1.844(6)
C(54)–C(544)	1.529(11)	P(4)–C(52)	1.847(6)
C(54)–C(545)	1.543(12)	C(1)–C(4)	1.554(12)
C(54)–C(546)	1.542(11)	C(2)–C(3)	1.516(12)
Cl–Re–C(53)	175.5(2)	P(1)–Re–P(2)	99.1(1)
Cl–Re–P(1)	83.2(1)	P(1)–Re–P(4)	80.2(1)
Cl–Re–P(2)	93.4(1)	P(2)–Re–P(3)	81.9(1)
Cl–Re–P(3)	90.0(1)	P(3)–Re–P(4)	98.5(1)
Cl–Re–P(4)	83.8(1)	P(1)–Re–P(3)	173.2(1)
C(53)–Re–P(1)	100.6(2)	P(2)–Re–P(4)	177.2(1)
C(53)–Re–P(2)	83.7(2)	C(53)–N–C(54)	174.0(9)
C(53)–Re–P(3)	86.2(2)	Re–C(53)–N	177.2(8)
C(53)–Re–P(4)	99.1(2)		
Re–P(1)–C(1)	106.4(3)	Re–P(3)–C(3)	105.7(3)
Re–P(1)–C(10)	121.6(2)	Re–P(3)–C(34)	121.4(2)
Re–P(1)–C(16)	121.4(2)	Re–P(3)–C(40)	120.5(2)
C(1)–P(1)–C(10)	101.6(4)	C(3)–P(3)–C(34)	102.1(4)
C(1)–P(1)–C(16)	100.5(4)	C(3)–P(3)–C(40)	103.0(4)
C(10)–P(1)–C(16)	101.8(3)	C(34)–P(3)–C(40)	101.3(3)
Re–P(2)–C(2)	109.7(3)	Re–P(4)–C(4)	109.6(3)
Re–P(2)–C(22)	122.6(2)	Re–P(4)–C(46)	117.2(2)
Re–P(2)–C(28)	118.3(2)	Re–P(4)–C(52)	124.6(2)
C(2)–P(2)–C(22)	98.8(4)	C(4)–P(4)–C(46)	103.8(3)
C(2)–P(2)–C(28)	103.2(4)	C(4)–P(4)–C(52)	96.9(4)
C(22)–P(2)–C(28)	101.1(3)	C(46)–P(4)–C(52)	101.5(3)
P(1)–C(1)–C(4)	106.9(6)	P(3)–C(3)–C(2)	110.3(6)
P(2)–C(2)–C(3)	110.5(6)	P(4)–C(4)–C(1)	112.3(6)

Discussion

The molecular structure of the title complex is shown in Fig. 1. Atomic coordinates are listed in Table 1 and bond lengths and bond angles in Table 2. The rhenium atom is octahedrally coordinated to four phosphorus atoms of two dppe ligands, to a chloride ion and to the carbon atom of the isocyanide *t*-butyl ligand. The large dppe ligands, with the ethane bridges connecting the PPh₂ groups, induce a significant distortion in the octahedral polyhedron around the metal atom, as can be seen in Table 2. This distortion has also been observed in other dppe rhenium complexes [6,7].

The rhenium and the four phosphorus atoms are approximately in a plane, with two phosphorus above and two below, and with a maximum deviation at the Re atom of 0.079 Å. The Re–P bond lengths are in the range 2.382–2.426 Å, shorter than observed in complex 7 (2.46(2) Å), but close to that observed for complex 9 (2.422(10) Å). The P–C bond lengths have a mean value of 1.862 Å, while the mean P–C(phenyl) is 1.850 Å, as in similar compounds [6,7].

The Re–Cl and Re–C bond lengths, 2.520(2) and 1.926(9) Å respectively, are comparable with the values observed in similar compounds, as shown in Table 3. The C≡N bond length is 1.154(10) Å and the C–N–Bu^t bond angle is 174.0(9)°. These values are in the range 1.12–1.18 Å and 169–176° observed in compounds 2, 3, 4 and 5 in Table 3, and in other terminal linear isocyanide ligands [14].

The common occurrence of small departures from the ideal 180° angle in R₃C–N≡C ligands can arise, in part, from the well-known geometrical sin θ factor,

TABLE 3
COMPARISON WITH SIMILAR METAL COMPLEXES

	M–Cl (Å)	M–C (Å)	C–N (Å)	C–N–R (°)	Ref.
<i>trans</i> -[ReCl(CN <i>t</i> Bu ^t)(dppe) ₂] (1)	2.520(2)	1.926(9)	1.154(10)	174.0(9)	This work
<i>mer</i> -[Re(η ¹ -S ₂ PPh ₂)(N ₂)(CNMe)(PMe ₂ Ph) ₃] (2)		1.93(1)	1.20(2)	169(1)	8
<i>mer</i> -[ReCl(N ₂)(CNMe){P(OMe) ₃ }] ₃ (3)	2.530(4)	2.07(2)	1.12(2)	169(1)	9
<i>cis</i> -[PtCl ₂ (CNPh) ₂] (4)			1.17(3)	176.2(20)	10
[Ru(CN <i>t</i> Bu ^t) ₄ PPh ₃] (5)			1.18(4) ^a	170(3)	11
[Fe(CN <i>t</i> Bu ^t) ₅] (6)			1.25(3) ^b	130(2)	11
[Fe(CN <i>t</i> Bu ^t) ₅] (6)			1.21(1)	135(1)	11
[ReCl(CNHMe)(dppe) ₂][BF ₄] (7)	2.484(6)	1.798(30)	1.347(32)	123.3(22)	2
<i>trans</i> -[Mo(CNMe) ₂ (dppe) ₂] (8)			1.10(1)	156(1)	12
ReCl(N ₂)(P(CH ₃) ₂ C ₆ H ₅) ₄ (9)	2.52(4)				13

^a Average values of two linear axial isocyanides. ^b Average values of two bent equatorial isocyanides.

combined with steric strain from the asymmetric crystal field environment. There are, however, some short intramolecular distances between N...H(15) 2.400, N...H(33), 2.602, N...H(51) 2.545 and C(546)...H(19) 2.714, C(543)...H(312) 2.835 Å, which could cause valence angle distortions in the molecules in isolation, or in solution.

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