Inorganica Chimica Acta, 61 (1982) 255–259 255

The Crystal and Molecular Structure of *trans*-bis(triphenylphosphine)dicarbonyl(1,3-diphenylformamidino)rhenium(I)

E. FORSELLINI, U. CASELLATO

Istituto di Chimica e Tecnologia dei Radioelementi del C.N.R., Padua, Italy

R. GRAZIANI, L. TONIOLO

Istituto di Chimica Generale e di Chimica Inorganica Industriale, Università di Padova, Padua, Italy

R. ROSSI and L. MAGON

Istituto Chimico, Università di Ferrara, Italy

Received November 11, 1981

The structure of trans-bis(triphenylphosphine)dicarbonyl(1,3-diphenylformamidino)rhenium(I) has been determined from three-dimensional X-ray diffraction data collected by counter methods. The compound crystallizes in the monoclinic space group $P2_1/n$ *with* $a = 24.13(1)$, $b = 14.47(1)$, $c = 13.25(1)$ Å *and* $\beta = 97.58(4)°$; $\rho = 1.44$ *for* $Z = 4$. *The structure was refined to the final R index of 0.056. The coordination about the rhenium atom is approximately octahedral. The formamidino ligand is coordinated to the metal atom in a bidentate mode with a N(1)–Re–N(2) angle of 60(1) and a N(1)–C(53)–N(2) angle of 112(1). The Re–N(1) and Re–N(2) bond lengths are 2.22(1) and 2.22(1) Å and the N(1)–C(49) and N(2)–C(49) distances are 1.32(1) and 1.34(1) Å, respectively. The entire rhenium–formamidino system is essentially planar, allowing a delocalization of the π electron density.*

Introduction

The chemistry of pseudo allyl ligands such as $[RN–N=NR]^-$ triazenido, and $[RN–CR=NR]^-$, amidino, is receiving growing attention because of the several modes of coordination that the ligands give rise to and, consequently, to their potentially rich chemistry [1–20].

Several X-ray diffraction studies have been published concerning triazenido [17], while benzamidino [18], acetamidino [19] and formamidino [20] complexes have been less extensively studied.

Very recently we have reported the molecular structure of $[Re(PPh_3)_2(CO)_2(dtt)]$ (dtt = 1,3-di-*p*-tolyltriazenido) in which the nitrogen ligand is coordinated to the metal atom in a bidentate mode to form a rather strained structure regarding the $\overline{Re–N\dot{-}N\dot{-}N}$ four-membered ring [17].

Following our current interest in the chemistry of rhenium complexes with these ligands, we report here the crystal and molecular structure of $[Re(PPh_3)_2(CO)_2(PhN\dot{-}CH\dot{-}NPh)]$.

Experimental

$[Re(PPh_3)_2(CO)_2(PhN\dot{-}CH\dot{-}NPh)]$ was prepared by reacting $[Re(PPh_3)_2(CO)_2Cl]$ with $Li(PhN\dot{-}CH\dot{-}NPh)$ in T.H.F., as already reported [16]; yellow crystals were obtained by recrystallization from $CH_2Cl_2/EtOH$.

A well-formed crystal with approximate dimensions 0.10 × 0.12 × 0.10 mm was mounted on the end of a glass fiber with epoxy cement. Accurate cell dimensions were determined on a Philips PW 1100 four-circle computer-controlled diffractometer using graphite-monochromatized MoKα radiation. Unit cell parameters were obtained by least-squares refinement of 30 medium-angle carefully determined reflections. Crystal data are summarized in Table I. Intensity data were collected by the $\vartheta–2\vartheta$ scan technique out to a maximum of $2\vartheta = 50°$, with a scan rate of 2° min^{-1}. Two standard reflections measured at intervals of 100 were constant within counting statistics. The 8042 independent reflections measured were reduced to 5939 considered to be significantly above background ($F_o^2 \geqslant 3\sigma(F_o^2)$). Solution of the structure was achieved by heavy-atom standard methods. Refinement of scale factor, positional and thermal parameters converged to the final agreement indices R = 5.6% and Rw = 6.8%, when the largest parameter shift in the last cycle was 0.2σ. The structure was refined with full-matrix least-squares, minimising the function $\Sigma w(/F_o/ - /F_c/)^2$, with w = 1. The agreement indices R and Rw are defined as $R = \Sigma//F_o/ - /F_c//\Sigma/F_o/$ and $Rw = (\Sigma w(/F_o/ - /F_c/)^2/\Sigma wF_o^2)^{1/2}$.

0020-1693/82/0000-0000/$02.75

TABLE I. Crystal Data for [Re(PPh$_3$)$_2$(CO)$_2$(dpf)].

$C_{51}H_{41}N_2O_2P_2Re \cdot 2H_2O$	FW 961 + 36
Crystal description	yellow prisms
System	monoclinic
Space group	P2$_1$/n
General position	±(x,y,z; 1/2 – x, 1/2 + y, 1/2 – z)
Cell dimensions	a = 24.13(2) Å
	b = 14.47(1) Å
	c = 13.25(1) Å
	β = 97.58(4)°
Volume	4586 Å^3
Density	1.44 g cm^{-3} for Z = 4
μ(MoKα)	30.80 cm^{-1}
Total reflections	8042
Observed reflections with I > 3σ(I)	5939
Final R factor	0.056

A final difference Fourier synthesis showed no significant residuals. Scattering factors for Re were from Cromer and Waber [21], those for P, O, N, C from Cromer and Mann [22]. The rhenium scattering factor was corrected for anomalous dispersion with constant average values $\Delta f' = -1.34$ and $\Delta f'' = 7.34$ for the real and imaginary components. All calculations were done using the X-ray '70 program system [23]. Final atomic positional and thermal parameters are listed in Table II. Bond distances, bond angles, and relevant contact distances are reported in Tables III–V. Least-squares planes are given in Table VI.

TABLE II. Positional Parameters (× 10^4) and Temperature Factors (× 10^3).

Atom	X	Y	Z	U
Re	5592(0)	2662(0)	3111(0)	*
P(1)	4730(1)	3550(2)	2569(2)	*
P(2)	6389(1)	1680(2)	3579(2)	*
N(1)	5230(4)	1626(6)	1980(7)	*
N(2)	5809(3)	2686(6)	1536(6)	*
O(1)	5121(4)	1998(6)	5011(7)	*
O(2)	6269(4)	4246(6)	4192(9)	*
O(3)	7755(4)	4744(6)	4727(9)	*
O(4)	7580(4)	4494(6)	6780(9)	*
C(49)	5494(4)	1948(8)	1239(9)	*
C(50)	5300(4)	2264(8)	4303(8)	*
C(51)	5992(5)	3656(8)	3784(10)	*
C(1)	4156(5)	3227(8)	3276(9)	42
C(2)	3979(6)	2315(10)	3233(10)	60
C(3)	3556(7)	2028(11)	3798(12)	74
C(4)	3322(6)	2670(12)	4392(12)	72
C(5)	3481(7)	3558(12)	4444(13)	80
C(6)	3912(6)	3879(10)	3873(12)	66
C(7)	4435(5)	3409(8)	1216(9)	40
C(8)	3922(6)	2992(9)	908(11)	58
C(9)	3733(6)	2924(10)	–172(12)	69
C(10)	4057(6)	3256(11)	–863(12)	71
C(11)	4566(6)	3687(10)	–544(11)	64
C(12)	4755(5)	3758(9)	500(10)	51
C(13)	4733(5)	4821(8)	2691(10)	47
C(14)	4355(5)	5352(8)	2049(10)	55
C(15)	4337(6)	6322(9)	2183(10)	63
C(16)	4679(6)	6726(10)	2977(11)	66
C(17)	5052(6)	5204(11)	3618(11)	76
C(18)	5071(6)	5236(9)	3479(11)	65
C(19)	7010(5)	1870(8)	2938(9)	41
C(20)	7166(5)	2765(10)	2811(10)	54
C(21)	7654(6)	2955(10)	2350(12)	66
C(22)	7969(6)	2225(10)	2038(11)	64
C(23)	7817(6)	1357(10)	2176(11)	64
C(24)	7332(5)	1163(9)	2634(10)	54
C(25)	6721(5)	1695(8)	4923(9)	46
C(26)	6512(5)	2239(10)	5638(10)	56
C(27)	6795(6)	2250(11)	6649(12)	71
C(28)	7270(6)	1723(11)	6912(12)	69
C(29)	7480(7)	1191(12)	6183(14)	80
C(30)	7202(6)	1177(10)	5174(11)	64
C(31)	6221(5)	460(8)	3345(9)	44
C(32)	6177(5)	122(8)	2340(9)	46
C(33)	5977(6)	–794(10)	2116(12)	66
C(34)	5812(7)	–1326(11)	2910(13)	74
C(35)	5858(7)	–1011(11)	3880(12)	73
C(36)	6067(6)	–117(10)	4112(11)	61
C(37)	4857(5)	880(8)	1865(9)	45
C(38)	4751(5)	402(9)	2722(10)	50
C(39)	4392(6)	–358(10)	2644(11)	61
C(40)	4114(6)	–622(11)	1703(12)	71
C(41)	4222(7)	–151(11)	818(13)	74
C(42)	4583(6)	638(9)	892(10)	56
C(43)	6182(5)	3075(8)	942(9)	42
C(44)	6293(5)	4028(9)	1049(10)	54
C(45)	6678(6)	4412(10)	445(12)	67
C(46)	6947(6)	3859(11)	–207(12)	72
C(47)	6844(6)	2933(10)	–275(11)	66
C(48)	6459(5)	2533(8)	280(9)	50

*Anisotropic thermal parameters in the form $T = \exp[-2\pi^2 \cdot (U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + U_{12}hka^*b^* + U_{13}hla^*c^* + U_{23}klb^*c^*)]$

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Re	35	35	35	–1	4	–2
P(1)	40	42	38	2	4	–1
P(2)	39	41	33	1	5	1
N(1)	42	35	42	–5	1	0
N(2)	44	50	30	–2	9	–10
O(1)	69	84	49	–14	18	3
O(2)	58	65	122	–6	–7	–40
O(3)	32	121	37	–20	–8	15
O(4)	198	60	40	–19	13	–4
C(49)	32	44	51	–1	–3	1
C(50)	49	46	38	–11	13	–2
C(51)	49	44	72	–4	1	–9

TABLE III. Bond Distances (Å).

Re–P(1)	2.47(1)	Re–P(2)	2.41(1)
Re–N(1)	2.22(1)	Re–N(2)	2.22(1)
Re–C(50)	1.90(1)	Re–C(51)	1.89(1)
C(50)–O(1)	1.15(2)	C(51–O(2)	1.17(2)
N(1)–C(49)	1.32(1)	N(2)–C(49)	1.34(1)
N(1)–C(37)	1.41(2)	N(2)–C(43)	1.39(2)
C(37)–C(38)	1.38(2)	C(43)–C(44)	1.41(2)
C(38)–C(39)	1.40(2)	C(44)–C(45)	1.42(2)
C(39)–C(40)	1.39(2)	C(45)–C(46)	1.40(2)
C(40)–C(41)	1.41(2)	C(46)–C(47)	1.36(2)
C(41)–C(42)	1.43(2)	C(47)–C(48)	1.39(2)
C(42)–C(37)	1.41(2)	C(48)–C(43)	1.41(2)
P(1)–C(1)	1.83(2)	P(2)–C(19)	1.84(2)
P(1)–C(7)	1.84(2)	P(2)–C(25)	1.86(2)
P(1)–C(13)	1.84(2)	P(2)–C(31)	1.83(2)

TABLE IV. Bond Angles (Degrees). The errors are referred to the last digit.

a) Coordination			
P(1)–Re–P(2)	175.0(1)		
P(1)–Re–N(1)	85.1(2)	P(2)–Re–N(1)	90.2(2)
P(1)–Re–N(2)	90.7(2)	P(2)–Re–N(2)	88.4(2)
P(1–Re–C(50)	90.5(3)	P(2)–Re–C(50)	88.7(3)
P(1)–Re–C(51)	95.7(4)	P(2)–Re–C(51)	89.2(4)
C(50)–Re–C(51)	94.0(1)	N(1)–Re–N(2)	60.0(1)
N(1)–Re–C(50)	101.6(4)	N(2)–Re–C(51)	105.2(5)
N(1)–Re–C(51)	164.9(5)	N(2)–Re–C(50)	161.0(4)
b) dtt ligand			
N(1)–C(49)–N(2)	112(1)		
Re–N(1)–C(49)	94(1)	Re–N(2)–C(49)	94(1)
Re–N(1)–C(37)	142(1)	Re–N(2)–C(43)	142(1)
C(49)–N(1)–C(37)	124(1)	C(49)–N(2)–C(43)	123(1)
N(1)–C(37)–C(38)	119(1)	N(2)–C(43)–C(44)	118(1)
N(1)–C(37)–C(42)	120(1)	N(2)–C(43)–C(48)	121(1)
c) CO and PPh_3			
Re–C(50)–O(1)	178(1)	Re–C(51)–O(2)	176(1)
Re–P(1)–C(1)	112(1)	Re–P(2)–C(19)	118(1)
Re–P(1)–C(7)	115(1)	Re–P(2)–C(25)	118(1)
Re–P(1)–C(13)	120(1)	Re–P(2)–C(31)	112(1)
C(1)–P(1)–C(7)	104(1)	C(19)–P(2)–C(25)	100(1)
C(1)–P(1)–C(13)	102(1)	C(19)–P(2)–C(31)	104(1)
C(7)–P(1)–C(13)	101(1)	C(25)–P(2)–C(31)	104(1)

TABLE V. Contacts.

a) Distances (Å)			
Re•••C(49)	2.67(1)		
N(1)•••N(2)	2.21(1)		
Re•••O(1)	3.05(1)	Re•••C(1)	3.59(2)
Re•••O(2)	3.06(1)	Re•••C(7)	3.66(2)
P(1)•••N(1)	3.17(1)	Re•••C(13)	3.75(2)
P(1)•••C(49)	3.57(1)	Re•••C(19)	3.64(2)
P(1)•••N(2)	3.34(1)	Re•••C(25)	3.66(2)
P(2)•••N(1)	3.28(1)	Re•••C(31)	3.52(2)
P(2)•••C(49)	3.56(1)	Re•••C(37)	3.43(2)
P(2)•••N(2)	3.23(1)	Re•••C(43)	3.42(2)
P(1)•••O(1)	3.95(1)	P(2)•••O(1)	3.83(1)
P(1)•••O(2)	>4 Å	P(2)•••O(2)	3.82(1)

b) Angles (Degrees)	
N(1)–Re•••C(53)	29.6
N(2)–Re•••C(53)	30.1
N(1)–C(53)•••Re	55.9
N(2)–C(53)•••Re	56.0
P(1)–Re•••C(53)	87.9
P(2)–Re•••C(53)	88.9
C(51)–Re•••C(53)	131.1
C(52)–Re•••C(53)	135.3

TABLE VI. Least-squares Planes and Distances (Å) of Atoms from the Planes. Equation of the plane is AX + BY + CZ = D, referred to monoclinic coordinates.

Plane I:	N(1), N(2), C(50), C(51). 18.35X – 8.63Y + 2.05Z = 8.63 Å [N(1) – 0.02, N(2) 0.02, C(50) 0.02, C(51) – 0.02, Re[a] –0.02, C(49)[a] 0.02, O(1)[a] 0.08, O(2)[a] 0.00].
Plane II:	N(1), N(2), C(49). 17.98X – 8.70Y + 2.48Z = 8.48 Å
Plane III:	C(37) to C(42). 18.90X – 8.85Y – 2.80Z = 7.87 Å [C(37) 0.01, C(38) -0.01, C(39) 0.01, C(40) –0.02, C(41) 0.01, C(42) –0.01]
Plane IV:	C(43) to C(48). 15.66X – 2.56Y + 8.58Z = 9.71 Å [C(43) 0.00, C(44) 0.01, C(45) –0.01, C(46) 0.00, C(47) 0.01, C(48) –0.01]

Angles between the planes

Planes	Angle (Deg.)	Planes	Angle (Deg.)
I–II	2.0	II–III	23.0
I–III	21.2	II–IV	36.6
I–IV	37.9	III–IV	57.6

[a] These atoms were not used in the plane calculations.

Description of the Structure

The structure is composed of loosely packed monomeric molecules of $[Re(PPh_3)_2(CO)_2(dpf)]$ (where dpf = $C_6H_5NCHNC_6H_5$). The overall molecular configuration with the numbering scheme used throughout this paper is shown in Figs. 1, 2. The Re atom is in a distorted octahedral environment with *trans* PPh_3 groups being in the axial positions and the four equatorial sites being occupied by two carbonyl groups and by the chelate ligand. Distortions from the idealized octahedral geometry arising from the geometrical constraints of the dpf group are mainly localized in the base plane where this ligand subtends at the metal atom an angle of 60°. Moreover, mean plane calculations (Table VI) show that the equatorial atoms are only approximately coplanar, being alter-

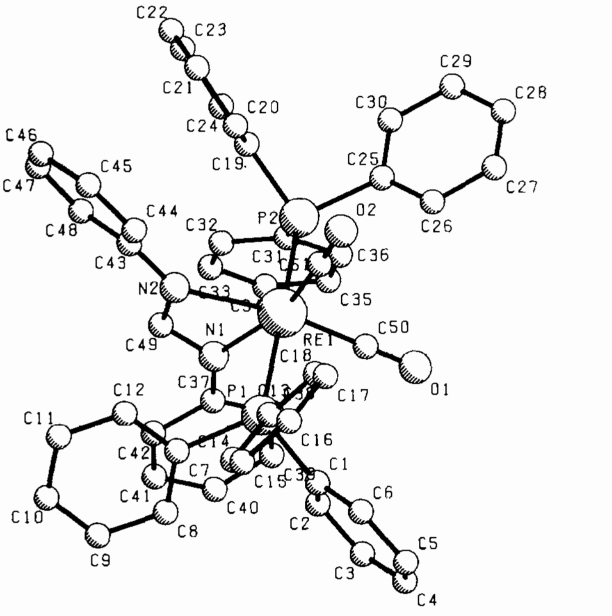

Fig. 1. Projection along the *b* axis.

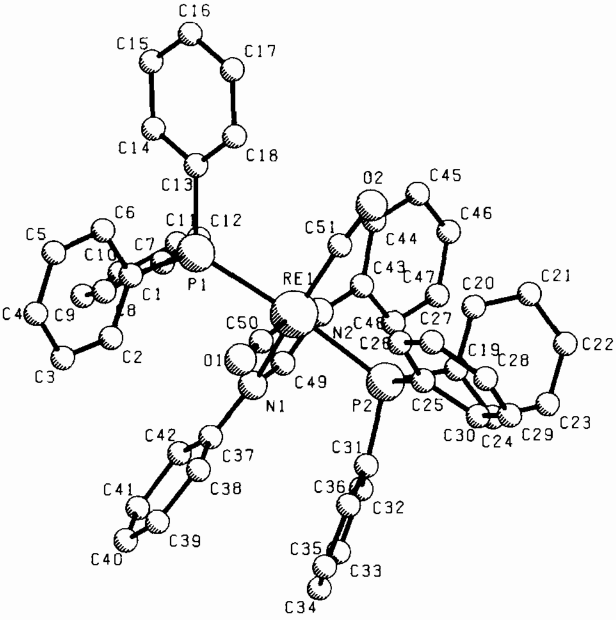

Fig. 2. Projection along the *c* axis.

nately displaced by ±0.02 Å from the base plane. A small deviation from linearity of the axial substituents is mainly due to the fact that P(1) is bent toward N(1); the angles P(1)–Re–N(1) and P(1)–Re–C(51) are 85° and 94°, respectively.

The axial PPh_3 groups have their usual configurations and the P–C distances are all similar with normal values (mean 1.84 Å). As already observed in complexes with coordinated PPh_3 groups, the Re–P–C angles (mean 116°) are larger and the C–P–C angles (mean 102.5°) are significantly smaller than the ideal value of 109° for sp^3 hybridized atoms.

The Re–P bond lengths (mean 2.44 Å) have the usual values for ***trans*** metal–phosphine complexes [17] and the Re–C bond distances (1.89 and 1.90 Å) suggest the presence of multiple bond character, which is confirmed by the relatively long CO distances (1.15 and 1.17 Å compared with 1.13 Å in free carbon monoxide).

As shown in Fig. 3 the formamidino anion is chelated to rhenium to form a four-membered ring, as does the closely related triazenido ligand. The Re–N bond lengths (both 2.22 Å) compare well with the values (mean 2.20 Å) found in the triazenido analogue [17]. The N–C(49) distances (1.32 and 1.34 Å) are shortened partial double bonds and the N–C(phenyl) distances (mean 1.40 Å) are typical for N–C bonds when C is part of an aromatic ring. These values and the near planarity of the formamidino–rhenium system suggest the possibility of an extended π-conjugation in the base plane of the molecule. This emphasizes the strained structure of the $\overline{\text{Re–N(1)–CH–N}}(2)$ four-membered ring; this feature is common to $[Re(PPh_3)_2(CO)_2(ddt)]$ and to other related compounds.

The complex also compares well with $[RuH(dtfa)(CO)(PPh_3)_2]$, in which the corresponding ligand dtfa (= N,N′-di-*p*-tolylformamidinato) is chelated to the ruthenium atom and whose crystal and molecular structure has been previously determined [20]. Apart from the metal–nitrogen distances, there are no appreciable differences in the overall structure and in the significant bond lengths and angles of the bi-

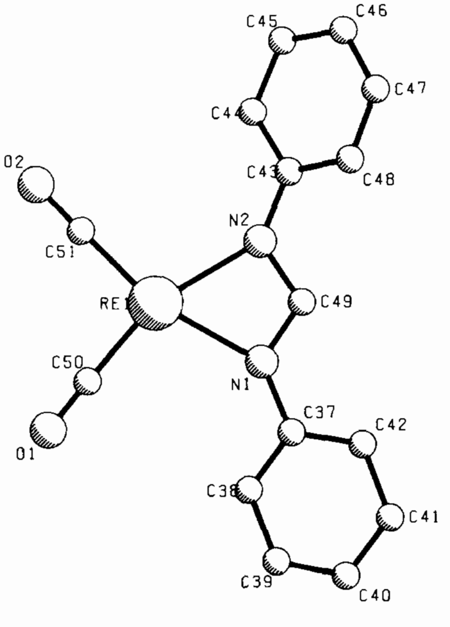

Fig. 3. Projection onto the equatorial plane. For clarity the axial substituents are omitted.

dentate ligands in the two molecules, suggesting that the C–N distances and the N–C–N angle in this type of ligand are relatively unaffected by the size and charge of the metal ion, as was already observed for the N–N distances and the N–N–N angle in several triazenido structures [17].

Acknowledgements

The authors thank Mr. M. Fratta for helpful technical assistance.

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