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Synthesis and Characterization of a Rhenium–Dioxygen Complex. The Crystal and Molecular Structure of $[ReCl_2(PPh_3)_2(NNCO_2Me)(O_2)]$, a Precursor in the Synthesis of Organosulfinato Complexes of Rhenium

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The rhenium–benzoylhydrazido(3–)(*N*,*O*) chelate complex $[ReCl_2(PPh_3)_2(NNCOPh)]$ has received considerable attention as a synthetic precursor, in part as a consequence of the facile displacement of the carbonyl oxygen of the benzoylhydrazido group by a variety of neutral ligands to yield benzoylazo-derivatives of the type $[ReCl_2(PPh_3)_2(NNCOPh)L]$ [1–3]. We have recently demonstrated that the analogous carboxymethylhydrazido-derivative $[ReCl_2(PPh_3)_2(NNCO_2Me)]$ (**I**) is considerably more reactive toward a variety of neutral ligands and may be most conveniently isolated as the dimethylformamide adduct $[ReCl_2(PPh_3)_2(NNCO_2Me)(DMF)]$ (**II**) [4]. In the course of our studies of the reaction chemistry of **II**, we observed that a benzene suspension of **II**, upon exposure to atmospheric oxygen, gradually solubilizes to produce a bright red solution of the dioxygen adduct $[ReCl_2(PPh_3)_2(NNCO_2Me)(O_2)]$ (**III**), whose synthesis and structural characteristics are reported herein.

Oxotrichlorobis(triphenylphosphine)rhenium [5] reacts with methylhydrazinocarboxylate in a solution of HCl, ethanol, and dimethylformamide to yield a red–purple precipitate, $[ReCl_2(PPh_3)_2(NNCO_2Me)(DMF)]$ (**II**). When dioxygen is introduced into a suspension of **II** in refluxing benzene, dissolution occurs in a period of 0.5 h to produce a bright red solution from which irregular crystals of $[ReCl_2(PPh_3)_2(NNCO_2Me)(O_2)]$ (**III**) are isolated after one week standing. *Anal.* Calc. for $ReC_{38}H_{33}N_2O_4P_2Cl_2$: C, 50.7; H, 3.69; N, 3.11; O, 7.10; Cl, 7.87. Found: C, 50.6; H, 3.66; N, 2.98; O, 6.84; Cl, 8.18%. The infrared spectrum displays bands at 1731 and 1582 cm^{-1} characteristic of $\nu(C=O)$ of the free carbonyl of the methyldiazenidocarboxylate ligand and of the diazenido $\nu(N=N)$, respectively. The medium intensity band at 905 cm^{-1} is in the range associated with O–O vibrations for 'sideways' or η^2-bound O_2 [6], an assignment confirmed by the X-ray structure. A weak band at 610 cm^{-1} may be associated with $\nu(Re-O_2)$.

Crystal data: $ReC_{38}H_{33}N_2O_4P_2Cl_2$ (III), monoclinic space group, *Pa*, with $a = 11.354(2)$, $b = 19.448(3)$, $c = 10.269(2)$ Å, $\beta = 125.73(1)°$, $V = 1840.7(9)$

TABLE I. Atom Coordinate (× 10^4) and Temperature Factors ($Å^2 \times 10^3$)

Atom	*x*	*y*	*z*	U_{iso} [a]
Re(1)	7500	7618(1)	7500	37(1)*
P(1)	6962(9)	6447(4)	6169(10)	31(4)*
P(2)	8542(10)	8662(4)	9358(10)	33(5)*
C(11)	7630(50)	5698(12)	7439(59)	43(7)
C(12)	7313(40)	5649(17)	8585(40)	53(9)
C(13)	7695(39)	5037(19)	9466(41)	58(10)
C(14)	8343(45)	4542(20)	9323(47)	72(12)
C(15)	8731(44)	4558(20)	8255(43)	66(11)
C(16)	8388(46)	5144(18)	7327(48)	66(10)
C(21)	7641(31)	6411(14)	4960(32)	31(7)
C(22)	6683(41)	6527(18)	3314(41)	59(10)
C(23)	7216(43)	6557(15)	2359(50)	48(10)
C(24)	8714(41)	6443(16)	3102(40)	49(9)
C(25)	9590(42)	6343(16)	4676(42)	54(9)
C(26)	9126(37)	6314(16)	5670(41)	48(9)
C(31)	4984(32)	6256(14)	4835(33)	32(7)
C(32)	3930(35)	6720(16)	4510(36)	43(8)
C(33)	2497(37)	6546(17)	3576(38)	50(9)
C(34)	2097(40)	5905(16)	3055(38)	48(9)
C(35)	3097(37)	5419(17)	3397(37)	46(9)
C(36)	4624(34)	5589(14)	4288(34)	34(7)
C(41)	10580(32)	8826(14)	10731(33)	32(7)
C(42)	11011(42)	9466(18)	11401(41)	57(10)
C(43)	12331(47)	9621(13)	12443(49)	40(8)
C(44)	13410(44)	9159(17)	12756(43)	63(10)
C(45)	13027(39)	8510(17)	12071(39)	53(9)
C(46)	11553(36)	8356(16)	11051(37)	44(8)
C(51)	7867(31)	9446(13)	8233(32)	26(7)
C(52)	8152(39)	9600(17)	7143(41)	53(9)
C(53)	7854(47)	10255(20)	6377(50)	78(13)
C(54)	7075(43)	10717(19)	6625(43)	63(10)
C(55)	6810(46)	10584(22)	7741(49)	77(12)
C(56)	7213(32)	9952(15)	8540(33)	33(7)
C(61)	7923(31)	8635(13)	10685(32)	28(7)
C(62)	6541(32)	8678(13)	10013(35)	31(7)
C(63)	5978(47)	8627(18)	10955(44)	62(11)
C(64)	7132(44)	8435(19)	12636(51)	65(12)
C(65)	8478(46)	8392(19)	13240(55)	56(10)
C(66)	8940(37)	8473(15)	12296(38)	44(8)
Cl(1)	9280(10)	7039(5)	9824(9)	54(5)*
Cl(2)	9374(10)	7829(4)	7110(10)	52(5)*
O(1)	6061(25)	7799(11)	5057(27)	54(6)
O(2)	6379(27)	8344(13)	5856(28)	53(8)
N(1)	6331(30)	7395(13)	8083(31)	51(7)
N(2)	5767(30)	7203(13)	8599(31)	48(7)
O(3)	3551(29)	7727(13)	6879(29)	71(7)
O(4)	3910(30)	7171(13)	8855(30)	72(7)
C(1)	4340(36)	7383(16)	8000(37)	49(8)
C(2)	2529(47)	7347(21)	8487(52)	79(12)

[a] Starred items: equivalent isotropic *U* defined as one third of the trace of the orthogonalised U_{iso} tensor.

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Å^3, $Z = 2$ to give $D_{calc} = 1.62$ g cm^{-3}. Structure solution and refinement based upon 1980 reflections with $I_o \geqslant 3\sigma(I_o)$ (Mo Kα radiation, $\lambda = 0.71073$ Å, $\mu = 37.67$ cm^{-1}) converged with a conventional discrepancy factor of 0.067.

Atom coordinates and temperature factors are given in Table I, bond lengths in Table II and bond angles in Table III.

TABLE II. Bond Lengths (Å)

Re(1)–P(1)	2.539(8)	Re(1)–P(2)	2.555(8)
Re(1)–Cl(1)	2.327(7)	Re(1)–Cl(2)	2.419(13)
Re(1)–O(1)	2.074(21)	Re(1)–O(2)	1.989(23)
Re(1)–N(1)	1.798(40)	P(1)–C(11)	1.800(35)
P(1)–C(21)	1.805(44)	P(1)–C(31)	1.862(30)
P(2)–C(41)	1.906(30)	P(2)–C(51)	1.792(27)
P(2)–C(61)	1.863(44)	C(11)–C(12)	1.421(89)
C(11)–C(16)	1.425(68)	C(12)–C(13)	1.402(50)
C(13)–C(14)	1.270(66)	C(14)–C(15)	1.401(84)
C(15)–C(16)	1.387(55)	C(21)–C(22)	1.394(41)
C(21)–C(26)	1.406(51)	C(22)–C(23)	1.422(84)
C(23)–C(24)	1.417(61)	C(24)–C(25)	1.326(47)
C(25)–C(26)	1.397(77)	C(31)–C(32)	1.375(49)
C(31)–C(36)	1.379(38)	C(32)–C(33)	1.364(47)
C(33)–C(34)	1.328(45)	C(34)–C(35)	1.357(54)
C(35)–C(36)	1.449(48)	C(41)–C(42)	1.369(43)
C(41)–C(46)	1.318(49)	C(42)–C(43)	1.268(51)
C(43)–C(44)	1.397(63)	C(44)–C(45)	1.384(46)
C(45)–C(46)	1.393(47)	C(51)–C(52)	1.368(66)
C(51)–C(56)	1.376(50)	C(52)–C(53)	1.429(53)
C(53)–C(54)	1.386(74)	C(54)–C(55)	1.369(83)
C(55)–C(56)	1.398(51)	C(61)–C(62)	1.296(46)
C(61)–C(66)	1.392(38)	C(62)–C(63)	1.442(76)
C(63)–C(64)	1.481(49)	C(64)–C(65)	1.273(69)
C(65)–C(66)	1.354(84)	O(1)–O(2)	1.257(34)
N(1)–N(2)	1.108(56)	N(2)–C(1)	1.400(50)
O(3)–C(1)	1.171(36)	O(4)–C(1)	1.298(62)
O(4)–C(2)	1.424(65)		

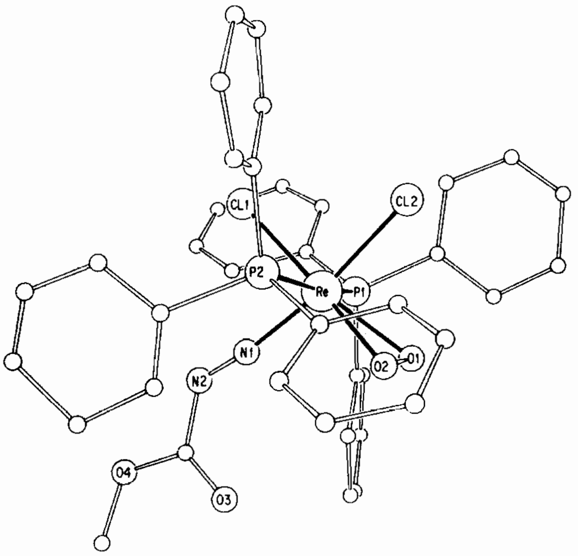

Fig. 1. ORTEP view of the structure of [ReCl$_2$(PPh$_3$)$_2$(NNCO$_2$Me)(O$_2$)] (III). Selected bond lengths (Å) and angles (°): Re–P1, 2.539(8); Re–P2, 2.555(8); Re–Cl1, 2.327(7); Re–Cl2, 2.449(7); Re–O1, 2.07(2); Re–O2, 1.99(2); Re–N1, 1.70(3); O1–O2, 1.26(3); N1–N2, 1.11(4); P1–Re–P2, 167.3(2); Cl1–Re–Cl2, 86.0(4); Cl1–Re–O1, 157.2(8); Cl1–Re–O2, 163.0(7); Cl2–Re–N1, 170.9(7); P1–Re–O1, 74.3(6); P2–Re–O2, 81.8(7); O1–Re–O2, 36.0(9); Re–N1–N2, 170.2(20).

The structure of **III** is illustrated in Fig. 1, and relevant bond lengths and angles are presented in the caption. The structure consists of discrete mononuclear rhenium centers, exhibiting distorted pentagonal bipyramidal geometry. The axial positions are defined by Cl2 and N1 of the linearly coordinated organodiazenido ligand. The distorted pentagonal plane is occupied by the phosphorus donors of the triphenylphosphine ligands, Cl1, and the η^2-coordinated

TABLE III. Bond Angles (°)

P(1)–Re(1)–P(2)	167.3(2)	P(1)–Re(1)–Cl(1)	84.8(3)
P(2)–Re(1)–Cl(1)	82.7(3)	P(1)–Re(1)–Cl(2)	91.2(3)
P(2)–Re(1)–Cl(2)	85.4(4)	Cl(1)–Re(1)–Cl(2)	86.0(4)
P(1)–Re(1)–O(1)	74.3(6)	P(2)–Re(1)–O(1)	117.5(6)
Cl(1)–Re(1)–O(1)	157.2(8)	Cl(2)–Re(1)–O(1)	85.3(9)
P(1)–Re(1)–O(2)	110.2(7)	P(2)–Re(1)–O(2)	81.8(7)
Cl(1)–Re(1)–O(2)	163.0(7)	Cl(2)–Re(1)–O(2)	85.8(11)
O(1)–Re(1)–O(2)	36.0(9)	P(1)–Re(1)–N(1)	88.4(9)
P(2)–Re(1)–N(1)	93.0(9)	Cl(1)–Re(1)–N(1)	84.8(8)
Cl(2)–Re(1)–N(1)	170.9(7)	O(1)–Re(1)–N(1)	103.3(11)
O(2)–Re(1)–N(1)	102.9(13)	Re(1)–P(1)–C(11)	117.9(15)
Re(1)–P(1)–C(21)	109.9(9)	C(11)–P(1)–C(21)	107.3(25)
Re(1)–P(1)–C(31)	112.5(11)	C(11)–P(1)–C(31)	100.9(18)
C(21)–P(1)–C(31)	107.6(15)	Re(1)–P(2)–C(41)	121.2(11)
Re(1)–P(2)–C(51)	110.9(9)	C(41)–P(2)–C(51)	102.3(13)
Re(1)–P(2)–C(61)	108.4(9)	C(41)–P(2)–C(61)	106.1(15)
C(51)–P(2)–C(61)	107.1(16)	P(1)–C(11)–C(12)	116.8(33)

(continued)

TABLE III. *(continued)*

P(1)–C(11)–C(16)	124.9(51)	C(12)–C(11)–C(16)	118.2(36)
C(11)–C(12)–C(13)	117.3(39)	C(12)–C(13)–C(14)	123.4(51)
C(13)–C(14)–C(15)	122.8(41)	C(14)–C(15)–C(16)	117.7(44)
C(11)–C(16)–C(15)	120.4(55)	P(1)–C(21)–C(22)	118.9(31)
P(1)–C(21)–C(26)	120.9(25)	C(22)–C(21)–C(26)	120.1(42)
C(21)–C(22)–C(23)	119.9(37)	C(22)–C(23)–C(24)	118.8(35)
C(23)–C(24)–C(25)	119.3(51)	C(24)–C(25)–C(26)	124.1(42)
C(21)–C(26)–C(25)	117.7(30)	P(1)–C(31)–C(32)	123.6(21)
P(1)–C(31)–C(36)	115.5(24)	C(32)–C(31)–C(36)	120.7(29)
C(31)–C(32)–C(33)	121.3(29)	C(32)–C(33)–C(34)	120.2(35)
C(33)–C(34)–C(35)	120.9(35)	C(34)–C(35)–C(36)	121.1(29)
C(31)–C(36)–C(35)	115.6(31)	P(2)–C(41)–C(42)	116.5(27)
P(2)–C(41)–C(46)	123.2(21)	C(42)–C(41)–C(46)	120.3(30)
C(41)–C(42)–C(43)	122.6(36)	C(42)–C(43)–C(44)	119.2(32)
C(43)–C(44)–C(45)	119.7(35)	C(44)–C(45)–C(46)	117.5(37)
C(41)–C(46)–C(45)	120.1(29)	P(2)–C(51)–C(52)	119.9(27)
P(2)–C(51)–C(56)	123.1(29)	C(52)–C(51)–C(56)	116.6(28)
C(51)–C(52)–C(53)	123.6(42)	C(52)–C(53)–C(54)	116.7(53)
C(53)–C(54)–C(55)	120.5(38)	C(54)–C(55)–C(56)	120.1(46)
C(51)–C(56)–C(55)	122.0(42)	P(2)–C(61)–C(62)	117.7(24)
P(2)–C(61)–C(66)	118.1(30)	C(62)–C(61)–C(66)	123.6(41)
C(61)–C(62)–C(63)	120.8(29)	C(62)–C(63)–C(64)	111.3(41)
C(63)–C(64)–C(65)	125.3(59)	C(64)–C(65)–C(66)	120.0(42)
C(61)–C(66)–C(65)	118.6(37)	Re(1)–O(1)–O(2)	68.3(14)
Re(1)–O(2)–O(1)	75.7(15)	Re(1)–N(1)–N(2)	170.2(22)
N(1)–N(2)–C(1)	123.3(29)	C(1)–O(4)–C(2)	122.4(30)
N(2)–C(1)–O(3)	126.9(45)	N(2)–C(1)–O(4)	114.8(27)
O(3)–C(1)–O(4)	118.2(41)		

O_2 ligand. The O_2-complex may be classified as a type IIa peroxo-species according to Vaska's scheme [7]. The O–O distance of 1.26(3) Å falls within the range observed for η^2-O_2 complexes, although it is shorter than that most commonly observed (1.45 Å). The Re–O distances are non-equivalent, 2.07(2) and 1.99(2) Å. The inequivalence of the Re–Cl distances is a consequence of the occupancy of axial and equatorial sites and of the *trans* influence of the organodiazenido ligand. The O–O bond vector eclipses the Re–P bond vectors and is nearly normal to the Re–Cl1 bond vector. The steric requirements of the η^2-coordinated O_2 ligand are manifest in the P1–Re–P2 angle of 167.3(2)°, rather than the idealized limit of 180° generally found in complexes of the type $[ReCl_2(PPh_3)_2(NNR)L]$ [4].

The reaction chemistry of **III** is consistent with the η^2-O_2 acting as a nucleophile. Thus, in reactions with thiolate ligands, the thiolate is oxidized to the sulfinate ^-O_2SR to give a variety of rhenium–sulfinato complexes, such as the previously characterized $[Re(O_2SCH_2CH_2NMeCH_2CH_2NMeCH_2CH_2SO_2)(NNR)(PPh_3)]$ [8]. Although the oxidation of thiolate groups to sulfinato ligands has been described in the chemistry of cobalt and copper [9], this is, to our knowledge, a unique example in the chemistry of rhenium; nor are we aware of other structurally characterized examples of rhenium–η^2 peroxo complexes.

References

1 J. Chatt, J. R. Dilworth, G. J. Leigh and V. D. Gupta, *J. Chem. Soc. A*, 2631 (1971).

2 J. Chatt, J. R. Dilworth and G. J. Leigh, *J. Chem. Soc., Dalton Trans.*, 612 (1973).

3 T. Nicholson and J. Zubieta, *J. Chem. Soc., Chem. Commun.*, 367 (1985).

4 T. Nicholson and J. Zubieta, *Polyhedron, 7* (1988), in press.

5 J. Chatt and G. A. Rowe, *J. Chem. Soc.*, 4019 (1962).

6 M. H. Gubelmann and A. F. Williams, *Struct. Bonding (Berlin), 55,* 1 (1983).

7 L. Vaska, *Acc. Chem. Res., 9,* 175 (1976).

8 T. Nicholson and J. Zubieta, *Inorg. Chem., 26,* 2094 (1987).

9 B. A. Lange, K. Libson, E. Deutsch and R. C. Elder, *Inorg. Chem., 15,* 2985 (1976); M. Lundeen, R. L. Firor and K. Seff, *Inorg. Chem., 17,* 701 (1978); L. S. Higashi, M. Lundeen, E. Hilti and K. Seff, *Inorg. Chem., 16,* 310 (1977).