Inorganica Chimica Acta, *142* (1988) 23–25

Synthesis and X-ray Crystal Structure of the Mixed Organoimido, Organoamine Rhenium(V) Complex $[ReCl_3(NC_6H_4Me\text{-}p)(NH_2C_6H_4Me\text{-}p)PPh_3]$

ROBERTO ROSSI*, ANDREA MARCHI, ADRIANO DUATTI, LUCIANO MAGON*

Laboratorio di Chimica Nucleare ed Inorganica, Dipartimento di Chimica, Università di Ferrara, Ferrara, Italy

UMBERTO CASELLATO

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

and RODOLFO GRAZIANI

Dipartimento di Chimica Inorganica, Metallorganica e Analitica, Università di Padova, Padua, Italy

(Received July 27, 1987)

There is much current interest in the chemistry of transition metal complexes having an imido group NR as ligand, and many synthetic routes for obtaining such compounds are available starting from the oxo-rhenium(V) complexes $[ReOX_3L_2]$ (X = halogen, L = tertiary phosphine) [1]. Recently we have shown that pseudo allyl ligands such as triazenido and amidino can also be used as precursors of the nitrene residue [2].

In a previous paper we studied the behaviour of $[ReO(OR)Cl_2(PPh_3)_2]$ (R = Me, C_2H_5) toward hetero-allene molecules as RNCS (R = C_6H_5, p-MeC_6H_4). The reaction provides the thiouretane complexes $[ReOCl_2\{RN{=}C(OR){-}S\}PPh_3]$ as a consequence of a formal insertion of the ligand into the Re–OR bond of the starting complex [3].

As a part of a systematic study of the reactivity of these compounds it has been found that the complex $[ReOCl_2\{PhN{=}C(OC_2H_5){-}S\}PPh_3]$ reacts in non-anhydrous toluene at reflux temperature (2 h) with an excess of ToNSO (To = p-MeC_6H_4) to give the mixed imido, amine rhenium(V) complex $[Re(NTo)Cl_3(NH_2To)PPh_3]$ in poor yield as a green powder. The complex crystallized from CH_2Cl_2/acetone was characterized on the basis of elemental analysis, IR and ^1H NMR spectra.

The IR spectrum shows the phosphine band at about 1090 cm^{-1}, whereas the Re≡O stretching frequency is now absent. The organoamine ligand shows ν(NH) values at 3300 and 3200 cm^{-1}, while two near bands of medium–weak intensity at 830 and 820 cm^{-1} are related to vibrations of the phenyl rings of the two p-tolyl groups.

The NMR spectrum ($CDCl_3$) shows two very near singlets due to the non-equivalent methyl groups at δ 2.16 and 2.13, with relative intensity six. The broad resonance at *ca.* δ 1.64, with relative intensity two, confirms the presence of two amine hydrogens. The compound thus gives the opportunity to compare the geometrical parameters or To–NH_2 with those of To–N while both are bonded to the same rhenium(V) ion in a six-coordinate octahedral neutral complex.

X-ray Data

A crystal of maximum dimension 0.2 mm was selected for the measurement of intensities. Data collection was made on a Philips diffractometer with a graphite monochromator and Mo Kα radiation. Cell dimensions were determined by least-squares refinement of 25 medium-angle settings.

Crystal data: $C_{32}H_{31}Cl_3N_2Re$, $M = 735.7$, triclinic, space group $P1$, $a = 13.515(5)$, $b = 11.917(5)$, $c = 10.066(5)$ Å, $\alpha = 85.52(3)$, $\beta = 85.64(3)$, $\gamma = 104.67(3)^\circ$, $V = 1556$ Å^3, $Z = 2$, $D_c = 1.57$ g cm^{-3}, λ(Mo Kα) = 0.7107 Å, μ(Mo Kα) = 46 cm^{-1}, $F(000) = 726$.

Intensities were measured by the θ–2θ method, with a scan speed of 2° min^{-1} between 2° and 25°, yielding 5464 unique reflexions, 4713 of which were significantly above background having intensities greater than $3\sigma(I)$. The data were corrected for Lp and for absorption [4]. Two standard reflexions measured periodically were constant within counting statistics.

Solution of the structure was achieved by the heavy-atom method through Patterson and Fourier maps. Refinement of scale factor, positional and thermal parameters converged to give a final agreement index R of 0.029, when the largest parameter shift in the last cycle was 0.1. The structure was refined by full-matrix least-squares, minimizing the function $\Sigma w \Delta F^2$ with $w = 1$. Ring carbon atoms were treated as rigid bodies, together with their attached hydrogen atoms (C–C = 1.395 Å, C–H = 1.08 Å). The positions of the two H atoms attached to N(2) were determined from a Fourier difference map, and were refined separately. A fixed temperature factor = 0.06 Å^2 was assigned to all H atoms. Anisotropy was introduced for all non-hydrogen atoms. Scattering factors for Re were from ref. 5, with corrections for anomalous dispersion [6], and for H from ref. 7. Those for Cl, P, C and N were supplied internally by SHELX [8], the program system used for calculations. Final atomic parameters are listed in Table I; distances and angles are reported in Table II.

---

*Authors to whom correspondence should be addressed.

0020-1693/88/$3.50

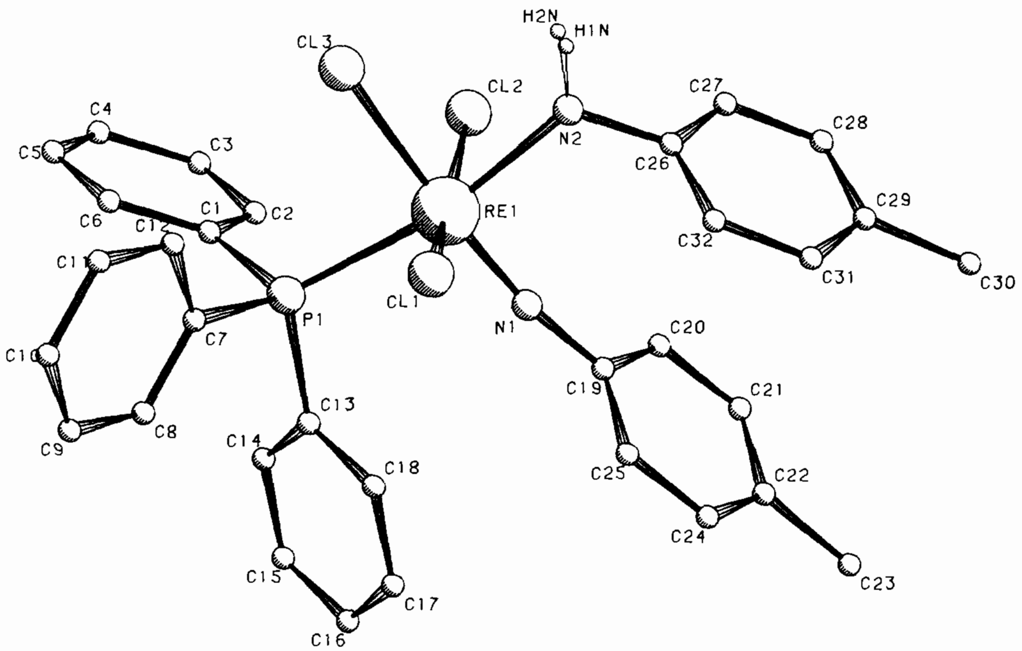

Fig. 1. Crystal structure of [$ReCl_3(NC_6H_4CH_3)(NH_2C_6H_4CH_3)PPh_3$].

TABLE I. Atomic Coordinates

Atom	*x/a*	*y/b*	*z/c*
Re1	0.59986(2)	−0.13948(2)	0.82612(2)
P1	0.7691(1)	−0.0696(1)	0.7013(1)
Cl1	0.5568(1)	0.0355(1)	0.7449(1)
Cl2	0.6276(1)	−0.3063(1)	0.9540(2)
Cl3	0.6753(1)	−0.0346(1)	1.0047(1)
N1	0.5400(3)	−0.2229(4)	0.7094(4)
N2	0.4599(4)	−0.1751(5)	0.9688(5)
C1	0.8729(3)	−0.1156(3)	0.7760(4)
C2	0.8620(3)	−0.2350(3)	0.8034(4)
C3	0.9386(3)	−0.2743(3)	0.8627(4)
C4	1.0262(3)	−0.1944(3)	0.8946(4)
C5	1.0371(3)	−0.0751(3)	0.8672(4)
C6	0.9605(3)	−0.0357(3)	0.8079(4)
C7	0.8209(3)	0.0895(3)	0.6631(3)
C8	0.8712(3)	0.1344(3)	0.5366(3)
C9	0.9151(3)	0.2540(3)	0.5087(3)
C10	0.9087(3)	0.3287(3)	0.6072(3)
C11	0.8585(3)	0.2838(3)	0.7337(3)
C12	0.8146(3)	0.1642(3)	0.7616(3)
C13	0.7693(2)	−0.1193(4)	0.5344(3)
C14	0.8442(2)	−0.1702(4)	0.4824(3)
C15	0.8407(2)	−0.2061(4)	0.3538(3)
C16	0.7624(2)	−0.1911(4)	0.2772(3)
C17	0.6875(2)	−0.1401(4)	0.3292(3)
C18	0.6910(2)	−0.1043(4)	0.4578(3)
C19	0.4804(3)	−0.2957(3)	0.6320(3)
C20	0.4563(3)	−0.4160(3)	0.6655(3)
C21	0.3926(3)	−0.4908(3)	0.5890(3)
C22	0.3531(3)	−0.4453(3)	0.4791(3)
C23	0.2860(6)	−0.5273(7)	0.3930(9)
C24	0.3772(3)	−0.3250(3)	0.4457(3)
C25	0.4408(3)	−0.2502(3)	0.5221(3)
C26	0.3704(3)	−0.2585(3)	0.9339(4)
C27	0.3466(3)	−0.3743(3)	0.9893(4)
C28	0.2643(3)	−0.4563(3)	0.9481(4)
C29	0.2060(3)	−0.4226(3)	0.8515(4)
C30	0.1175(6)	−0.5122(7)	0.8011(10)
C31	0.2299(3)	−0.3069(3)	0.7960(4)
C32	0.3121(3)	−0.2248(3)	0.8372(4)

X-ray Structure

The structure consists of discrete molecules. As shown in Fig. 1 the Re atom is a six-coordinate octahedral with meridional N(1) and Cl atoms and apical N(2) and triphenylphosphine. Atoms of the base plane Re, N(1), Cl(1), Cl(2), Cl(3) are coplanar within 0.1 Å and the imido phenylene ring is tilted by only 15° with respect to this plane. Distortion from the ideal octahedral configuration is basically determined by a movement of the ligands *cis* to the arylimido group away from the N(1) atom (see bond angles in Table II). Angles at the nitrogen atoms (171.1(4)° at N(1), 116.3(3)° at N(2)) correspond well to the different hybridization states

TABLE II. Bond Distances (A) and Angles (°)[a]

Re–Cl(1)	2.404(1)	N(1)–C(19)	1.362(6)
Re–Cl(2)	2.410(1)	N(2)–C(26)	1.444(6)
Re–Cl(3)	2.412(1)	C(22)–C(23)	1.536(8)
Re–N(1)	1.715(4)	C(29)–C(30)	1.527(8)
Re–N(2)	2.214(5)	P–C(1)	1.823(4)
Re–P	2.436(1)	P–C(7)	1.847(4)
N(2)–H(1N)	0.98(7)	P–C(13)	1.825(4)
N(2)–H(2N)	0.76(7)		
Cl(1)–Re–Cl(2)	167.5(1)	N(1)–Re–N(2)	94.4(2)
Cl(1)–Re–Cl(3)	87.5(1)	N(1)–Re–P	97.7(1)
Cl(1)–Re–N(1)	95.4(2)	N(2)–Re–P	167.7(1)
Cl(1)–Re–N(2)	86.9(1)	Re–N(1)–C(19)	171.1(4)
Cl(1)–Re–P	90.0(1)	Re–N(2)–C(26)	116.3(3)
Cl(2)–Re–Cl(3)	84.0(1)	Re–N(2)–H(1N)	109.0(4)
Cl(2)–Re–N(1)	92.5(2)	Re–N(2)–H(2N)	106.0(5)
Cl(2)–Re–N(2)	82.9(2)	H(1N)–N(2)–H(2N)	115.0(7)
Cl(2)–Re–P	98.6(1)	C(26)–N(2)–H(1N)	102.0(4)
Cl(3)–Re–N(1)	175.1(2)	C(26)–N(2)–H(2N)	108.0(5)
Cl(3)–Re–N(2)	81.8(1)	Re–P–C(1)	115.8(1)
Cl(3)–Re–P	86.6(1)	Re–P–C(7)	117.5(1)
		Re–P–C(13)	111.4(1)

[a] E.s.d.s. given in parentheses refer to the last significant digit.

of the two atoms. The formal double* Re–N(1) bond (1.715(4) Å) agrees with a mean value of 1.73 Å in [ReCl$_2$(NTo)(RN=CH–C$_6$H$_4$O)PPh$_3$] (where R = C$_6$H$_5$ or CH$_3$) [10], with 1.726(6) Å in [ReCl$_3$(NC$_6$H$_5$)(PPh$_3$)$_2$]CH$_2$Cl$_2$ [11], and with 1.71(1) Å in [ReCl$_2$(NTo)(CHOC$_6$H$_4$O)PPh$_3$] [12], whereas the Re–N(2) distance is in good agreement with previous values obtained for Re–N single bonds [13]. The C(26)–N(2) bond length is normal for aromatic C–N bonds, while the C(19)–N(1) distance (1.362(6) Å), is significantly shorter, which seems to be characteristic for arylimido compounds, being observed in the above mentioned and also in other similar complexes. The Re–P bond (2.436(1) Å) *trans* to N(2) is, as expected, shorter (by *ca.* 0.05 Å) than the corresponding distance in compounds with two phosphine ligands *trans* to one another [14, 15], confirming a structural detail already present in the molecules of ref. 10. The Re–Cl bond distances are normal. It is noteworthy that the mean (2.409 Å) of the Re–Cl bonds, which are chemically equivalent, is exactly the value found in [ReCl$_3$(NC$_6$H$_5$)(PPh$_3$)$_2$], where the three Cl atoms and the imido N atom are also meridional.

Supplementary Material

A complete list of bond angles and distances, hydrogen positional parameters, anisotropic thermal parameters and calculated and observed structure factors can be obtained from the authors.

References

1 W. A. Nugent and B. L. Haymore, *Coord. Chem. Rev., 31,* 123 (1980).
2 R. Rossi, A. Marchi, A. Duatti, L. Magon and P. Di Bernardo, *Transition Met. Chem., 10,* 151 (1985)
3 R. Rossi, A. Marchi, A. Duatti, L. Magon, U. Casellato and R. Graziani, *J. Chem. Soc., Dalton Trans.,* in press.
4 A. C. T. North, D. C. Phillips and F. S. Mathews, *Acta Crystallogr., Sect. A, 24,* 351 (1968).
5 'International Tables for X-ray Crystallography , Vol. IV, Kynoch Press, Birmingham, 1974.
6 D. T. Cromer, *Acta Crystallogr., 18,* 17 (1965).
7 R. F. Stewart, E. R. Davidson and W. T. Simpson, *J. Chem. Phys., 42,* 3175 (1965).
8 G. M. Sheldrick, 'SHELX', program for crystal structure determination, University of Cambridge, 1975.
9 J. Chatt, J. D. Garforth, N. P. Johnson and G. A. Rowe, *J. Chem. Soc.,* 1012 (1964).
10 R. Rossi, A. Marchi, A. Duatti, L Magon, U. Casellato, R. Graziani and L. Polizzotti, *Inorg. Chim. Acta, 90,* 121 (1984).
11 E. Forsellini, U. Casellato, R. Graziani, M. C. Carletti and L. Magon, *Acta Crystallogr., Sect. C, 40,* 1795 (1984).
12 A. Marchi, R. Rossi, A. Duatti, L. Magon, U. Casellato and R. Graziani, *Transition Met. Chem., 9,* 299 (1984).
13 C. J. L. Lock and G. Turner, *Acta Crystallogr., Sect. B, 11,* 1764 (1975); *34,* 923 (1978); R. S. Shandles, R. K. Murmann and E. O. Schlemper, *Inorg. Chem., 13,* 1373 (1974).
14 D. Bright and J. A. Ibers, *Inorg. Chem., 7,* 1099 (1968); *8,* 703 (1969).
15 R. J. Doedens and J. A. Ibers, *Inorg. Chem., 6,* 204 (1967).

---

*It was proposed [9] that the Re–N bond in these compounds has a considerable triple-bond character.