

fac-Trichloro(quinolin-8-ylimido-*N,N'*)-(triphenylphosphine-*P*)rhenium(V)

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Received 13 November 2000

Accepted 21 February 2001

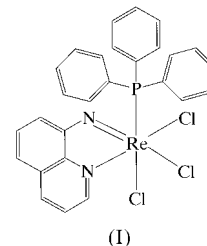
The Re atom in $[\text{Re}(\text{C}_9\text{H}_6\text{N}_2)\text{Cl}_3(\text{C}_{18}\text{H}_{15}\text{P})]$ is octahedrally coordinated by three Cl atoms in facial positions, two N atoms from 8-imidoquinoline (imq) and one P atom from triphenylphosphine. The Re–N(imido) distance [1.760 (9) and 1.772 (8) Å] for imq is very short and implies double-bond character. The *trans* influence of the P atom is indicated. Intra- and intermolecular π – π interactions between the π -rings in the complex are also observed.

Comment

Since the first arylimido Re complex, $[\text{ReCl}_3(\text{NPh})(\text{PEt}_2\text{Ph})_2]$ (Ph = phenyl and Et = ethyl), was synthesized using aniline as the source of the imido-type ligand (Chatt & Rowe, 1962), many analogous complexes have been reported (Refosco *et al.*, 1998). In complexes with such monodentate arylimido ligands, the coordinated N atom is fully deprotonated and very short Re–N(imido) distances are observed. On the other hand, Re complexes with the polydentate arylimido ligand are still rare. For example, complexes with 8-imidoquinoline (imq) have not been obtained, but the complex with 8-amidoquinoline, $[\text{ReO}(\text{Himq})_2(\text{PPh}_3)]\text{BPh}_4$, was formed by the reaction of $[\text{ReOCl}_3(\text{PPh}_3)_2]$ with 8-aminoquinoline (H_2imq) (Ahmet *et al.*, 1995). In this work, we report the structure of the Re complex with imq, $[\text{Re}(\text{imq})\text{Cl}_3(\text{PPh}_3)]$, (I). In the asymmetric unit, there are two crystallographically independent complex molecules related by an approximate *c*-glide plane. A perspective drawing of one of the molecules is shown in Fig. 1, and selected bond distances and angles are listed in Table 1. The crystal structures consist of neutral molecules in which each central Re atom is octahedrally surrounded by an imq, a PPh_3 and three Cl^- ligands. The Cl^- ligands coordinate facially to the Re atom and imq acts as a bidentate ligand.

The bond distances and angles in the crystallographically independent molecules, 1 and 2, are similar (Table 1). One of the Re–N distances ($\text{Re}_m\text{—Nm}_2$; $m = 1$ or 2 for molecule 1 and 2, respectively) for imq is significantly shorter than the other. This is inconsistent with the fact that the $M\text{—N}(\text{amine})$

and $M\text{—N}(\text{quinoline ring})$ distances for H_2imq are similar [$M = \text{Zn}$ (Kerr *et al.*, 1981) or $M = \text{Sn}$ (Hazell *et al.*, 1997)], in which both $M\text{—N}$ distances exhibit single-bond behaviour. The Re–N(amido) distances for the Re complex with the partially deprotonated Himq, $[\text{ReO}(\text{Himq})_2(\text{PPh}_3)]\text{BPh}_4$, are 1.958 (6) and 2.028 (6) Å (Ahmet *et al.*, 1995). Similar distances were observed for Re complexes containing the



partially deprotonated amido N atoms of aminophenyl derivatives [1.988 (4) Å (Ahmet *et al.*, 1995) or 1.973 (7) Å (Refosco *et al.*, 1995)], and of 3- or 4-nitro-1,2-diaminobenzene [1.96 (2)–1.98 (3) Å; Bandoli *et al.*, 2000]. On the other hand, short Re–N(imido) distances were observed for the Re complexes containing the fully deprotonated imido N atoms of aminophenyl derivatives [1.757 (4) (Ahmet *et al.*, 1995) or 1.780 (7) Å (Refosco *et al.*, 1995)]. Further, the $\text{Re}_m\text{—Nm}_2\text{—Cm}_26$ angles are somewhat larger than the corresponding angles [117.4 (5) and 120.3 (5)°] of the complex with the amido-type Himq (Ahmet *et al.*, 1995). Accordingly, the Re–N(imido) bond for imq seems to have double-bond character and the Re–N(quinoline ring) bond has a normal single-bond value; this suggests that the amino group in H_2imq is fully deprotonated, indicating that the Re atom in this complex is pentavalent. In addition, the $\text{Re}_m\text{—Cl}_m1$ distance occupying the *trans* position of the P atom is longer than those occupying the other two *cis* positions. This obviously indicates the *trans* influence of the P atom in PPh_3 .

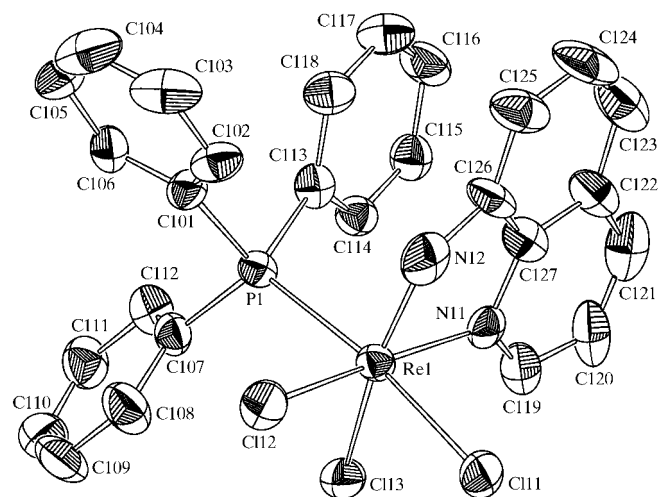


Figure 1
A view of molecule 1 with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. Molecule 2 has the corresponding numbering scheme, in which the number after each atom is '2' or '2n' instead of '1' or '1n' as shown in molecule 1.

In the bond angles concerning the Re atom and imq, the $Clm3-Rem-Nm2$ angle deviates significantly from the value of 180° (Table 1) for ideal octahedral geometry. This seems to depend on not only the acute bite angle and the Re–N(imido) double bonding of imq, but also the interaction between the aromatic rings of PPh_3 and imq. The $Nm1-Rem-Pm-Cm13$ torsion angle is $16.8(4)^\circ$ in molecule 1 and $16.4(4)^\circ$ in molecule 2, and the closest $Nm1 \cdots Cm14$ distance is $3.15(1) \text{ \AA}$ in molecule 1 and $3.11(1) \text{ \AA}$ in molecule 2. These facts suggest that the two aromatic π -rings, which are almost parallel, overlap each other, and intramolecular π - π interactions exist between their π -rings. Furthermore, imq ligands in the two molecules are almost parallel and $3.29(2) \text{ \AA}$ apart. Similar distances were observed for the tetranuclear Pd^{II} complexes with 2,2'-bipyridine, indicating π - π -stacking contacts (Yamada & Okamoto, 1999; Yamada *et al.*, 2000). Accordingly, these facts seem to indicate that intermolecular π - π interactions also exist between imq ligands for two complex molecules in the unit cell.

Experimental

To a solution containing $[ReOCl_3(PPh_3)_2]$ (2.08 g, 2.50 mmol) (Johnson *et al.*, 1967) in toluene (100 ml) was added a solution containing 8-aminoquinoline (0.518 g, 3.59 mmol) in toluene (38 ml). This mixture was stirred at 298 K for 1 d and the unreacted materials were filtered off. The dark-red solution was left standing at 298 K for two weeks and dark-red microcrystals appeared (yield 0.10 g). Found: C 47.04, H 3.30, N 4.00%; calculated for $[Re(C_9H_6N_2)Cl_3(C_{18}H_{15}P)]$: C 46.53, H 3.04, N 4.02%. Crystals suitable for X-ray analysis were obtained by recrystallization from acetonitrile at 298 K.

Crystal data

$[Re(C_9H_6N_2)Cl_3(C_{18}H_{15}P)]$	$D_x = 1.827 \text{ Mg m}^{-3}$
$M_r = 697.02$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/a$	Cell parameters from 25 reflections
$a = 17.624(5) \text{ \AA}$	$\theta = 11.1\text{--}14.4^\circ$
$b = 27.665(5) \text{ \AA}$	$\mu = 5.20 \text{ mm}^{-1}$
$c = 10.428(3) \text{ \AA}$	$T = 296.2 \text{ K}$
$\beta = 94.52(2)^\circ$	Prismatic, brown
$V = 5068(2) \text{ \AA}^3$	$0.38 \times 0.15 \times 0.15 \text{ mm}$
$Z = 8$	

Data collection

Rigaku AFC-7S diffractometer	$R_{int} = 0.035$
ω scans	$\theta_{max} = 27.5^\circ$
Absorption correction: ψ scan	$h = 0 \rightarrow 22$
(North <i>et al.</i> , 1968)	$k = 0 \rightarrow 35$
$T_{min} = 0.37, T_{max} = 0.46$	$l = -13 \rightarrow 13$
12687 measured reflections	3 standard reflections
12409 independent reflections	every 150 reflections
7306 reflections with $F^2 > 2\sigma(F^2)$	intensity decay: 2.1%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + 0.04P^2]$
$R(F) = 0.048$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.127$	$(\Delta/\sigma)_{max} = 0.001$
$S = 0.97$	$\Delta\rho_{max} = 1.81 \text{ e \AA}^{-3}$
11631 reflections	$\Delta\rho_{min} = -1.94 \text{ e \AA}^{-3}$
614 parameters	Extinction correction: Zachariassen
H-atom parameters constrained	(1967) type 2, Gaussian isotropic
	Extinction coefficient: 0.00014 (4)

Table 1

Selected geometric parameters (\AA , $^\circ$).

Re1—Cl11	2.421 (2)	Re2—Cl21	2.406 (3)
Re1—Cl12	2.347 (3)	Re2—Cl22	2.352 (3)
Re1—Cl13	2.356 (3)	Re2—Cl23	2.353 (2)
Re1—P1	2.436 (2)	Re2—P2	2.449 (2)
Re1—N11	2.204 (8)	Re2—N21	2.205 (8)
Re1—N12	1.760 (9)	Re2—N22	1.772 (8)
N12—Cl26	1.39 (1)	N22—C226	1.39 (1)
Cl11—Re1—P1	172.21 (8)	Cl21—Re2—P2	174.04 (9)
Cl12—Re1—N11	176.9 (2)	Cl22—Re2—N21	177.7 (2)
Cl13—Re1—N12	155.9 (3)	Cl23—Re2—N22	156.7 (3)
N11—Re1—N12	74.7 (4)	N21—Re2—N22	75.0 (3)
Re1—N11—Cl119	133.0 (7)	Re2—N21—C219	133.3 (7)
Re1—N11—Cl127	111.4 (7)	Re2—N21—C227	110.7 (6)
Re1—N12—Cl126	129.6 (8)	Re2—N22—C226	129.0 (7)

After checking their presence in the difference map, all H atoms were fixed geometrically and allowed to ride on their attached atoms [$C-H = N-H = 0.95 \text{ \AA}$; $U = 1.3U(C,N)$]. The major features in the final difference map are associated with the Re atoms.

Data collection: *WinAFC* (Rigaku Corporation, 1999); cell refinement: *WinAFC*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1999); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *TEXSAN*; software used to prepare material for publication: *TEXSAN*.

This work was supported by the Grant-in-Aid for Scientific Research Nos. 11640555 and 12023205 from the Ministry of Education, Science, Sports and Culture.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1586). Services for accessing these data are described at the back of the journal.

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