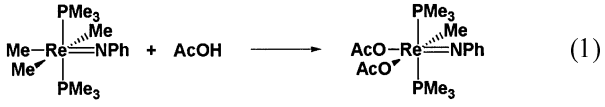
Preparation and Structure of *trans,cis*-[$ReCl_2$(N-C_6H_3-2,6-*i*-Pr_2)$_2$($C_6H_5CO_2$-*O*,*O*')]

Nam-Sun Choi and Soon W. Lee*

Department of Chemistry, Sungkyunkwan University, Natural Science Campus, Suwon 440-746, Korea
Received February 8, 2000

Transition-metal imido (or nitrene, M=NR) complexes have attracted continuous interest.[1-8] We have been continuously interested in Re-imido complexes (Re=NR). For example, we recently prepared several Re-imido complexes of the type Re(NAr)(PR_3)$_2$$Cl_3$ (PR_3=PMe_3, PEt_3, $P(OMe)_3$; Ar=C_6H_5, 2,6-*i*-Pr_2-C_6H_3) from the reactions of Re(N-C_6H_3-2,6-*i*-Pr_2)$_2$-Cl_3(py) (**1**) with small phosphines or phosphites.[9] The products were remarkably inert to carbon nucleophiles (ZnR_2: R =Me, Et; AlR_3: R=Me, Et; RMgBr: R=Me, Et; M'Cp: M' =Li, Na, Tl; NaCp*) and hydrides ($LiBEt_3H$, $LiBEt_3D$).

Reactions of transition-metal oxo or imido complexes with hydrogen halides are known to proceed by protonation of the named ligand and substitution by halide ions, generally without change in the oxidation state of the metal.[1,5] There have been only a very few reports on the reaction of the imido complex with an organic acid.[5] For instance, the Re(V)-imido complex, *mer,trans*-$ReMe_3(PMe_3)_2$(NPh), reacts with acetic acid (CH_3COOH, AcOH) to give *cis,trans*-$Re(AcO)_2$-$(PMe_3)_2$Me(NPh) (eq 1).[10] We set out the reaction of Re(N-C_6H_3-2,6-*i*-Pr_2)$_2$$Cl_3$(py) (**1**) with benzoic acid (PhCOOH) to check the reactivity of the Re-imido complex toward an aromatic carboxylic acid. Herein we report the preparation and structure of [$ReCl_2$(N-C_6H_3-2,6-*i*-Pr_2)$_2$($C_6H_5CO_2$-*O*,*O*')] (**2**).



(1)

Experimental Section

Unless otherwise stated, all the reactions have been performed with standard Schlenk line and cannula techniques under an argon atmosphere. Air-sensitive solids were manipulated in a glove box filled with argon. Glassware was soaked in KOH-saturated 2-propanol for *ca.* 24 h and washed with distilled water and acetone before use. Glassware was either flame-dried or oven-dried. Hydrocarbon solvents were stirred over concentrated H_2SO_4 for *ca.* 48 h, neutralized with K_2CO_3, stirred over sodium metal, and distilled by vacuum transfer. Benzene was distilled over sodium metal under Ar. Benzoic acid (PhCOOH) was distilled under Ar, degassed by freeze-pump-thaw cycles, and stored under Ar. Re(N-C_6H_3-2,6-*i*-Pr_2)$_2$$Cl_3$(py) (**1**) was prepared by the literature method.[11,12]

^{1}H- and ^{13}C{^{1}H}-NMR spectra were recorded with a Bruker AMX 500 MHz spectrometer with reference to internal solvent resonances and reported relative to tetramethylsilane. IR spectra were recorded with a Nicolet 205 FTIR spectrophotometer. Melting points were measured with a Thomas Hoover capillary melting point apparatus without calibration. Elemental analyses were performed by the Korea Basic Science Center.

Preparation of [$ReCl_2$(N-C_6H_3-2,6-*i*-Pr_2)$_2$($C_6H_5CO_2$-*O*,*O*')] (2). A deep green solution of **1** (0.35 g, 0.485 mmol) and benzoic acid (0.06 g, 0.485 mmol) in benzene (30 mL) was refluxed for 12 h to give a deep brown solution. The resulting solution was filtered, and the solvent was removed under vacuum to give a black brown oil. The oil was washed with hexane (20 mL × 3) and dried under vacuum to obtain 0.17 g (48% 1st crop yield) of [$ReCl_2$(N-C_6H_3-2,6-*i*-Pr_2)$_2$-($C_6H_5CO_2$-*O*,*O*')] (**2**). The hexane washings were concentrated under vacuum and then stored at -25 ºC to give brown-black crystals. These crystals were washed with cold hexane (10 mL × 2) and dried under vacuum to obtain additional 0.08 g (23% 2nd crop yield, total yield 71%) of **2**. The product was recrystallized from hexane.

^{1}H NMR ($CDCl_3$): δ 8.209 (1H, d, *ortho-H* in benzoate), 8.101 (1H, d, *ortho-H* in benzoate), 7.626 (1H, m, *para-H* in benzoate), 7.485 (2H, m, *meta-H* in benzoate), 7.365-7.113 (6H, m, imido phenyl), 3.922 (2H, sept, diastereotopic C*H*Me_2), 3.461 (2H, br, diastereotopic C*H*Me_2), 1.281 (12H, d, diastereotopic CH*Me*$_2$), 1.242 (12H, d, diastereotopic CH*Me*$_2$). ^{13}C{^{1}H}-NMR ($CDCl_3$): δ 183.503 (*C*O_2), 152.369-123.371 (phenyl), 29.349 (*C*HMe_2), 29.109 (*C*HMe_2), 26.011 (CH*Me*$_2$), 24.575 (CH*Me*$_2$). Anal. Calcd for $C_{31}H_{39}N_2O_2Cl_2Re$: C, 51.09; H, 5.39; N, 3.85; O, 4.40. Found: C, 51.44; H, 5.45; N, 4.16; O, 4.96. mp: 160-162 ºC. IR (KBr): 3058, 2965, 2929, 2870, 1589, 1506, 1451 (C=O), 1386, 1341, 919, 881, 800, 756, 715, 696 cm^{-1}.

X-ray Structure Determination. All X-ray data were collected with use of a Siemens P4 diffractometer equipped with a Mo X-ray tube and a graphite crystal monochromator. Details on crystal data and intensity data are given in Table 1. The orientation matrix and unit cell parameters were determined by least-squares analyses of the setting angles of 49 reflections in the range $15.0^o < 2\theta < 25.0^o$. Three check reflections were measured every 100 reflections throughout data collection and showed no significant variations in intensity. Intensity data were corrected for Lorenz and polarization effects. Decay corrections were also made. The intensity data were empirically corrected with psi-scan data. All calculations were carried out with use of the Siemens SHELXTL programs.[13]

A yellow crystal of **2**, shaped as a block, of approximate dimensions 0.08 × 0.12 × 0.20 mm^3, was used for crystal

*Corresponding Author: Tel: +82-331-290-7066, Fax: +82-331-290-7075, e-mail: swlee@chem.skku.ac.kr

Table 1. X-ray data collection and structure refinement for **2**

formula	$C_{31}H_{39}N_2O_2Cl_2Re$
fw	728.74
temperature, K	293(2)
crystal system	triclinic
space group	$P\bar{1}$
a, Å	9.906(2)
b, Å	10.051(3)
c, Å	18.393(4)
α, deg	104.34(1)
β, deg	92.91(1)
γ, deg	114.87(2)
V, Å^3	1584.4(7)
Z	2
d_{cal}, g cm^{-3}	1.528
μ, mm^{-1}	4.032
T_{min}	0.5046
T_{max}	0.6199
$F(000)$	728
No. of reflections measured	6637
No. of reflections unique	5347
No. of reflections with $I > 2\sigma(I)$	2933
No. of parameters refined	344
2θ range (°)	3.5-50.0
scan type	ω
scan speed	variable
GOF (goodness-of-fit on F^2)	0.999
Max., min. in $\Delta\rho$ (e Å^{-3})	0.840, -0.870
R	0.0657
wR_2[a]	0.1124

[a] $wR_2=\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]^{1/2}$

and intensity data collection. The unit cell parameters indicated the triclinic unit cell with the two possible space groups: $P\bar{1}$ and $P1$. A statistical analysis of reflection intensities suggested a centrosymmetric space group, and the structure analysis converged only in $P\bar{1}$. The structure was solved by the direct method and refined by full-matrix least-squares calculations of F^2's, initially with isotropic and finally anisotropic temperature factors for all non-hydrogen atoms. All hydrogen atoms were generated in idealized positions and refined in a riding model.

Final atomic positional parameters are shown in Table 2. The selected bond distances and bond angles are shown in Table 3.

Results and Discussion

Preparation. Compound **1**, a bis(imido) Re(VII) complex, reacts with benzoic acid (PhCOOH) in refluxing benzene to give a Re-imido benzoato compound, [$ReCl_2$(N-C_6H_3-2,6-*i*-Pr_2)$_2$($C_6H_5CO_2$-*O*,*O*')] (**2**), in 70% yield (eq 2). One chloro and one pyridine (py) ligands have been displaced by the chelating benzoato ligand during the reaction. The two imido (NAr) ligands have remained intact, and there has been no change in the formal oxidation state of the Re metal. Com-

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å$^3 \times 10^3$) for **2**

	x	*y*	*z*	*U* (eq)[a]
Re(1)	7485(1)	8057(1)	7336(1)	59(1)
Cl(1)	5881(4)	7737(5)	6259(2)	80(1)
Cl(2)	9622(4)	8701(5)	8227(2)	87(1)
O(1)	9087(10)	8253(12)	6566(5)	68(3)
O(2)	8872(10)	10245(10)	7163(4)	70(3)
N(1)	6573(11)	8767(12)	7968(5)	55(3)
N(2)	6830(13)	6105(13)	7232(5)	62(3)
C(1)	5914(13)	9535(14)	8460(6)	40(3)
C(2)	6861(14)	10992(14)	8992(6)	45(3)
C(3)	6171(15)	11665(14)	9480(7)	51(3)
C(4)	4633(16)	11011(15)	9419(7)	59(4)
C(5)	3718(14)	9646(15)	8884(6)	52(3)
C(6)	4315(14)	8861(14)	8393(6)	46(3)
C(7)	8554(15)	11728(16)	9051(8)	65(4)
C(8)	9381(17)	11750(2)	9783(8)	118(6)
C(9)	9085(19)	13280(2)	8920(12)	147(8)
C(10)	3278(15)	7378(17)	7788(7)	67(4)
C(11)	2593(17)	7740(17)	7125(8)	91(5)
C(12)	2048(17)	6315(16)	8115(8)	92(5)
C(13)	6459(15)	4645(19)	7181(6)	65(4)
C(14)	6963(16)	3776(18)	6605(7)	70(4)
C(15)	6590(2)	2250(2)	6571(8)	98(6)
C(16)	5780(2)	1610(18)	7072(9)	111(6)
C(17)	5280(2)	2440(2)	7620(8)	109(6)
C(18)	5594(17)	3916(19)	7682(7)	72(4)
C(19)	7931(19)	4540(18)	6072(8)	90(5)
C(20)	6980(2)	4440(3)	5420(11)	216(15)
C(21)	9090(2)	4010(2)	5842(13)	165(9)
C(22)	5123(19)	4853(19)	8312(8)	87(5)
C(23)	3720(2)	3860(2)	8588(9)	122(7)
C(24)	6510(2)	5730(2)	8988(8)	122(7)
C(25)	9486(16)	9610(2)	6688(7)	69(4)
C(26)	10689(17)	10570(2)	6328(7)	73(4)
C(27)	11193(18)	12160(2)	6532(8)	89(5)
C(28)	12304(19)	13080(2)	6187(8)	102(6)
C(29)	12888(19)	12360(3)	5639(9)	107(6)
C(30)	12370(2)	10810(3)	5432(10)	119(7)
C(31)	11277(17)	9927(19)	5780(8)	86(5)

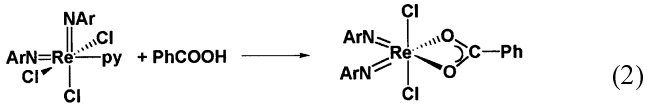
Equivalent isotropic *U* defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3. Selected bond distances (Å) and bond angles (°) in **2**

Re1-N1	1.707(8)	Re1-N2	1.742(12)	Re1-O1	2.160(8)
Re1-O2	2.162(9)	Re1-Cl1	2.341(3)	Re1-Cl2	2.358(4)
Re1-C25	2.520(16)	O1-C25	1.208(16)	O2-C25	1.281(14)
N1-C1	1.407(12)	N2-C13	1.332(16)		
N1-Re1-N2	108.8(5)	N1-Re1-O1	153.7(4)	N2-Re1-O1	97.5(4)
N1-Re1-O2	94.5(4)	N2-Re1-O2	156.6(4)	O1-Re1-O2	59.2(3)
N1-Re1-Cl1	94.3(3)	N2-Re1-Cl1	95.8(3)	O1-Re1-Cl1	83.2(2)
O2-Re1-Cl1	83.6(3)	N1-Re1-Cl2	96.6(3)	N2-Re1-Cl2	91.8(3)
O1-Re1-Cl2	81.8(3)	O2-Re1-Cl2	83.7(3)	C1-Re1-Cl2	163.96(13)
C1-N1-Re1	172.3(9)	C13-N2-Re1	174.6(9)	O1-C25-O2	118.0(14)
O1-C25-C26	122.3(13)	O2-C25-C26	119.6(15)		

pound **2** is air- and moisture-stable both in solution and in the solid state.

In ^{1}H NMR spectra of **2**, methynyl protons (C*H*Me$_2$) in the isopropyl substituents show two septets at δ 3.922 and 3.461 ppm, due to their diastereotopic relationship. The methyl protons (CH*Me*$_2$) in the isopropyl substituents also exhibit diastereotopic relationship and appear as two doublets at δ 1.281 and 1.242 ppm. The diastereotopic relationship also appears in ^{13}C{^{1}H}-NMR spectra of **2**. The IR band at 1451 cm^{-1} can be assigned to the C=O bond in the benzoato ligand.



1 **2** (Ar = 2,6-*i*-Pr$_2$-C$_6$H$_3$) (2)

Structure. The molecular structures of **2** with the atomic numbering scheme appears in Figure 1. Compound **2** has two chloro ligands, one η^2-benzoato (C$_6$H$_5$CO$_2$-O,O'), and two imido NAr (Ar=2,6-diisopropylphenyl) ligands. The coordination sphere of Re can be described as a distorted octahedron in which the two NAr ligands are mutually *cis*. The two Cl liagnds are *trans* to each other, and each NAr ligand is *trans* to the oxygen atom (O1 or O2) in the bezoato ligand. The equatorial planed, defined by N1, N2, O1, O2, and Re1, is nearly planar with the average atomic displacement of 0.0112 Å. With respect to the equatorial plane, the two imido aryl planes in the NAr ligands have dihedral angles 45.5(5)° and 12.5(7)°. The bezoate phenyl ring (C26-C30) is nearly parallel to the equatorial plane with a dihedral angle of 5.9(7)°.

The Re1-N1-C1 and Re1-N2-C13 bond angles (172.3(9)°, 174.6(9)°) and the Re-N1 and Re1-N2 bond distances (1.707(8) Å, 1.742(12) Å) are fairly typical of aryl imido ligands in high oxidation state Re complexes.[5] These angles and distances indicate that the Reimido groups (Re-N-R) in **2** are linear and the Re-N bonds have a triple bond character with an *sp*-hybrid nitrogen.

Carboxylic acids usually behave as monoanionic oxygen-donor ligands. Although the division may not be sharply distinct, three coordination modes of the carboxylic acids have been identified: monodentate, chelating, and briging.[14] Symmetrically chelating coordination is less common than monodentate coordination. The two Re-O bond distances (Re1-O1: 2.160(8) Å; Re1-O2: 2.162(9) Å) are essentially the same, suggesting the symmetrically chelating coordination of the benzoato ligand.

In summary, we have prepared a Re(VII)-imido benzoato compound, [ReCl$_2$(N-C$_6$H$_3$-2,6-*i*-Pr$_2$)$_2$(C$_6$H$_5$CO$_2$-*O*,*O*')] (**2**), by treating Re(N-C$_6$H$_3$-2,6-*i*-Pr$_2$)$_2$Cl$_3$(py) (**1**) with benzoic acid in a stoichiometic manner. In this reaction, the benzoato ligand has displaced one chloro and one pyridine (py) ligands. Compound **2** has been characterized by NMR and IR spectroscopy, and its molecular structure has been determined by X-ray diffraction.

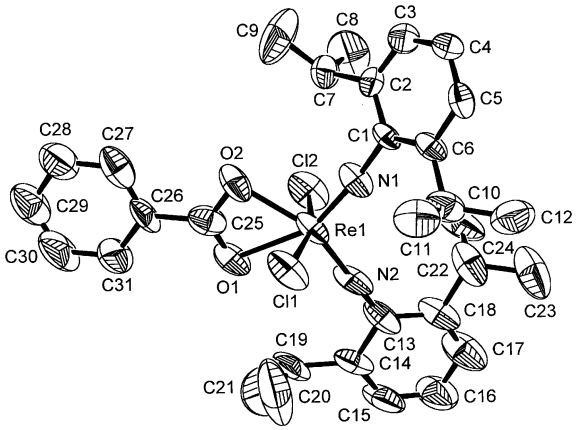


Figure 1. *ORTEP* drawing of **2** showing the atom-labeling scheme and 50% probability thermal ellipsoids.

Acknowledgment. This work is based on research sponsored by the Brain Korea 21 Project.

Supplementary Material Available. Tables of full bond distances and bond angles, anisotropic thermal parameters, positional parameters for hydrogen atoms, torsion angles (5 pages); listings of observed and calculated structure factors (13 pages). Supplementary materials are available from one of the authors (Soon W. Lee) upon request.

References

1. Ronao, C. C.; Kuhn, F. E.; Hermann, W. A. *Chem. Rev.* **1997**, *97*, 3179.
2. Che, C.-M. *Pure & Appl. Chem.* **1995**, *67*, 225.
3. Wigley, D. E. *Prog. Inorg. Chem.* **1994**, *42*, 239.
4. Lin, Z.; Hall, M. B. *Coord. Chem. Rev.* **1993**, *123*, 149.
5. Nugent, W. A. *MetalLigand Multiple Bonds*; John Wilely and Sons: New York, 1988.
6. Chisholm, M. H.; Rothwell, I. P. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon Oxford: England, 1987; Vol. 2, p 161.
7. Nugent, W. A.; Haymore, B. L. *Coord. Chem. Rev.* **1980**, *31*, 123.
8. Cenini, S.; La Monica, G. *Inorg. Chim. Acta* **1976**, *18*, 279.
9. Park, B.-G.; Choi, N.-S.; Lee, S. W. *Bull. Korean Chem. Soc.* **1999**, *20*, 314.
10. Chiu, K. W.; Wong, W.-K.; Wilkinson, G.; Galas, A. M. R.; Hursthouse, M. B. *Polyhedron* **1982**, *1*, 31.
11. Horton, A. D.; Schrock, R. R. *Polyhedron* **1988**, *7*, 1841.
12. Toreki, R.; Schrock, R. R.; Davis, W. M. *J. Am. Chem. Soc.* **1992**, *114*, 3367.
13. *Bruker, SHELXTL, Structure Determination Software Programs*; Bruker Analytical X-ray Instruments Inc.; Madison, Wisconsin, USA, 1997.
14. Oldham, C. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon Oxford: England, 1987; Vol. 2, pp 436-438.