

[*cis*-ReCl₄(py)(*N*-C₆H₃-2,6-*i*-Pr₂) · (NH₂-C₆H₃-2,6-*i*-Pr₂)]
착물의 구조(py=pyridine)

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Structure of [*cis*-ReCl₄(py)(*N*-C₆H₃-2,6-*i*-Pr₂) ·
(NH₂-C₆H₃-2,6-*i*-Pr₂)] (py=pyridine)

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요 약

Ar 기류 하에서 Re(*N*-C₆H₃-2,6-*i*-Pr₂)₂Cl₃(py) (1)과 propionaldehyde (C₂H₅CHO)가 반응하여 생성된 혼합물에서, [*cis*-ReCl₄(py)(*N*-C₆H₃-2,6-*i*-Pr₂) · (NH₂-C₆H₃-2,6-*i*-Pr₂)] (2)가 분리되었다. 이 화합물의 구조가 X-ray 회절법으로 규명되었다. 착물 2의 결정학 자료: 단사정계 공간군 *P*2₁/*n*, *a*=11.555(1) Å, *b*=27.066(3) Å, *c*=11.881(1) Å, β=117.991(8)°, *Z*=4, *R*(*wR*₂)=0.0332(0.0851).

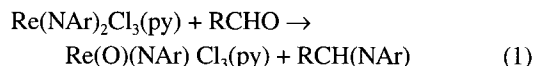
Abstract

Reaction of Re(*N*-C₆H₃-2,6-*i*-Pr₂)₂Cl₃(py) (1) with propionaldehyde (C₂H₅CHO) under argon led to a reaction mixture from which [*cis*-ReCl₄(py)(*N*-C₆H₃-2,6-*i*-Pr₂) · (NH₂-C₆H₃-2,6-*i*-Pr₂)] (2) was isolated. Compound 2 was characterized by X-ray diffraction. Crystallographic data for 2: monoclinic space group *P*2₁/*n*, *a*=11.555(1) Å, *b*=27.066(3) Å, *c*=11.881(1) Å, β=117.991(8)°, *Z*=4, *R*(*wR*₂)=0.0332(0.0851).

1. Introduction

Transition-metal imido (or nitrene, M=NR) complexes have been of continuous interest.¹⁻⁶ We have been continuously interested in Re-imido complexes (Re=NR). Recently we prepared a Re-imido complex of *mer,trans*-Re(*N*-C₆H₃-*i*-Pr₂)(PMe₃)₂Cl₃ from the reaction of Re(*N*-C₆H₃-2,6-*i*-Pr₂)₂Cl₃(py) (1) and trimethyl phosphine (PMe₃).⁷ There have been a couple of reports on reactions between organic carbonyl compounds and transition-metal imido complexes.^{8,9} These studies prompted us to investigate the reactivity of the Re-imido complex with the organic carbonyls. We therefore set out the reaction of Re(*N*-C₆H₃-2,6-*i*-Pr₂)₂Cl₃(py) (1) with propionaldehyde (C₂H₅CHO) to obtain a mono-oxo, mono-

imido Re-complex (eq 1), but the isolated compound turned out to be an unexpected product [*cis*-ReCl₄(py)(*N*-C₆H₃-2,6-*i*-Pr₂) · (NH₂-C₆H₃-2,6-*i*-Pr₂)] (2). Herein we report structure of 2.



2. Experimental Section

Unless otherwise stated, all the reactions have been performed with standard Schlenk line and canula 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, diethyl ether were distilled over sodium metal under Ar. Propionaldehyde (C_2H_5CHO) was distilled under Ar, degassed by freeze-pump-thaw cycles, and stored under Ar. $Re(N-C_6H_3-2,6-i-Pr_2)_2Cl_3(py)$ (1) was prepared by the literature method.^{10,11)}

Preparation of $[cis-ReCl_4(py)(N-C_6H_3-2,6-i-Pr_2)] \cdot (NH_2-C_6H_3-2,6-i-Pr_2)$ (2). To an opaque, dark green solution of benzene (60 ml) containing 0.32 g (0.44

mmol) of $Re(N-C_6H_3-2,6-i-Pr_2)_2Cl_3(py)$ (1) was added 0.16 ml (2.2 mmol) of propionaldehyde. The resulting solution was stirred for 18 h at room temperature and then the volatiles were removed under vacuum. The residual solids were washed with

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^3 \times 10^3$) for 2

	x	y	z	$U(eq)^a$
Re	6836(1)	1000(1)	7072(1)	32(1)
Cl(1)	8080(1)	943(1)	5936(1)	51(1)
Cl(2)	6980(1)	85(1)	7074(1)	43(1)
Cl(3)	5555(1)	840(1)	8123(1)	45(1)
Cl(4)	4893(1)	939(1)	5067(1)	41(1)
N(1)	8575(4)	936(1)	8878(4)	39(1)
N(2)	6914(4)	1627(2)	7276(4)	38(1)
N(3)	6184(4)	49(2)	3986(4)	45(1)
C(1)	8635(6)	1188(2)	9873(5)	49(1)
C(2)	9731(6)	1170(3)	11041(6)	67(2)
C(3)	10780(6)	894(2)	11212(7)	69(2)
C(4)	10718(5)	637(2)	10199(6)	62(2)
C(5)	9592(5)	662(2)	9025(5)	50(1)
C(6)	7136(5)	2119(2)	7657(5)	41(1)
C(7)	6154(5)	2376(2)	7834(5)	47(1)
C(8)	6457(6)	2852(2)	8297(6)	63(2)
C(9)	7624(7)	3075(2)	8554(7)	77(2)
C(10)	8549(7)	2819(2)	8362(8)	73(2)
C(11)	8335(5)	2340(2)	7924(5)	50(1)
C(12)	4866(5)	2152(2)	7574(6)	51(1)
C(13)	3724(6)	2485(3)	6713(8)	81(2)
C(14)	4863(9)	2055(3)	8835(7)	86(2)
C(15)	9341(6)	2065(2)	7658(7)	69(2)
C(16)	10734(7)	2128(4)	8804(11)	119(4)
C(17)	9285(10)	2230(3)	6447(10)	109(3)
C(18)	6841(5)	73(2)	3190(5)	39(1)
C(19)	7710(5)	-304(2)	3305(5)	47(1)
C(20)	8308(7)	-268(2)	2531(7)	69(2)
C(21)	8054(8)	115(3)	1712(8)	79(2)
C(22)	7172(7)	473(2)	1605(6)	64(2)
C(23)	6551(6)	466(2)	2355(5)	50(1)
C(24)	8027(6)	-727(2)	4232(6)	59(2)
C(25)	9171(9)	-596(3)	5489(7)	97(3)
C(26)	8274(8)	-1205(2)	3715(8)	85(2)
C(27)	5577(8)	867(3)	2187(7)	77(2)
C(28)	4350(9)	814(4)	921(11)	130(4)
C(29)	6209(13)	1376(3)	2360(11)	132(4)

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

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

formula	$C_{29}H_{41}N_3Cl_4Re$
fw	759.65
temperature, K	293(2)
crystal system	monoclinic
space group	$P2_1/n$
a , \AA	11.555(1)
b , \AA	27.066(3)
c , \AA	11.881(1)
β , deg	117.991(8)
V , \AA^3	3281.1(5)
Z	4
d_{cal} , $g\ cm^{-3}$	1.538
μ , mm^{-1}	4.051
T_{min}	0.4254
T_{max}	0.5711
$F(000)$	1516
Index ranges	$-1 \leq h \leq 13$ $-1 \leq k \leq 32$ $-14 \leq l \leq 12$
R (int)	0.0231
No. of reflections measured	6889
No. of reflections unique	5686
No. of reflections with $I > 2\sigma(I)$	5104
No. of parameters refined	343
2θ range ($^\circ$)	3.550.0
scan type	ω
scan speed	variable
GOF (goodness-of-fit on F^2)	1.172
Max., min. in $\Delta\rho$ ($e\ \text{\AA}^{-3}$)	1.480, -1.141
R	0.0332
wR_2^a	0.0851

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

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

Re-N2	1.710(4)	Re-N1	2.151(4)	Re-Cl3	2.381(1)
Re-Cl4	2.392(1)	Re-Cl1	2.396(1)	Re-Cl2	2.483(1)
N1-C3	1.331(6)	N1-C1	1.339(7)	N2-C6	1.391(6)
N3-C18	1.466(6)				
N2-Re-N1	88.7(2)	N2-Re-Cl3	96.3(1)		
N1-Re-Cl3	89.0(1)	N2-Re-Cl4	99.9(1)		
N1-Re-Cl4	171.4(1)	Cl3ReCl	89.21(5)		
N2-Re-Cl1	98.0(1)	N1-Re-Cl1	91.7(1)		
Cl3-Re-Cl1	165.68(5)	Cl4-Re-Cl1	88.01(5)		
N2-Re-Cl2	172.2(1)	N1-Re-Cl2	83.5(1)		
Cl3-Re-Cl2	82.90(4)	Cl4-Re-Cl2	87.86(4)		
Cl1-Re-Cl2	82.97(4)	C6-N2-Re	170.1(4)		

diethyl ether (1×30 ml) and pentane (2×30 ml) and then dried under vacuum. This product was recrystallized from dichloromethane-hexane. During recrystallization, we could obtain the crystals of [cis-ReCl₄(py)(N-C₆H₃-2,6-*i*-Pr₂)] · (NH₂-C₆H₃-2,6-*i*-Pr₂)] (2).

X-ray Structure Determination of 2. 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 39 reflections in the range $15.0^\circ < 2\theta < 25.0^\circ$. Three check reflections were measured every 100 reflections throughout data collection and showed no significant variations in intensity. Intensity data were corrected for Lorentz and polarization effects. Decay corrections were also made. The intensity data were empirically corrected with γ -scan data. All calculations were carried out with use of the SHELXTL programs.¹²⁾

A green crystal of **2**, shaped as a block, of approximate dimensions 0.70×0.60×0.60 mm³, was used for crystal and intensity data collection. The unit cell parameters and systematic absences, $h0l$ ($h+l=2n+1$) and $0k0$ ($k=2n+1$), unambiguously indicated $P2_1/n$ as a space group. The structure was solved by the direct method and refined by full-matrix least-squares calculations of F^2 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.

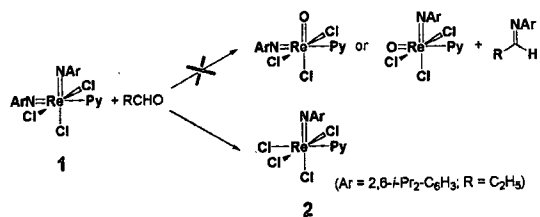
Final atomic positional parameters for non-hydrogen atoms are shown in Table 2. The selected bond distances and bond angles are shown in Table 3.

3. Results and discussion

Preparation. Compound **1** reacts with excess (5 fold) propionaldehyde (C₂H₅CHO) in benzene at room temperature for 18 h to give a reaction mixture, from which [cis-ReCl₄(py)(N-C₆H₃-2,6-*i*-Pr₂)] · (NH₂-C₆H₃-2,6-*i*-Pr₂)] (**2**) was isolated (Scheme 1). At the setout of this reaction, we tried to prepare a mono-oxo, mono-imido Re compound from **1**, but the reaction gave an uncharacterizable mixture of products whose separation has not been successful. Fortunately, compound **2** was crystalline and could be picked up by hands. Unfortunately, we could not obtain the other meaningful spectral data except X-ray diffraction due to a limited amount of **2**.

In compound **2**, the Re metal has a formal oxidation state +6 (d^1), which indicates reduction of the Re metal (from +7 in **1** to +6 in **2**). This reaction is somewhat interesting in that one of the strongly bound imido ligands (NAr) has been cleaved. Compound **2** is a formal 17-electron complex, assuming the aryl imido ligand to be a 4-electron donor. Although we cannot give a clear-cut explanation for the formation of the cocrystallized

2,6-diisopropylaniline ($\text{NH}_2\text{-C}_6\text{H}_3\text{-2,6-}i\text{-Pr}_2$), this



aniline seems to have formed from the imido ligand escaping from the Re metal during the reaction.

Structure. The molecular structures of **2**, together with the cocrystallized 2,6-diisopropylaniline linked by both intramolecular and intermolecular hydrogen bonds (see below), with the atomic numbering scheme is shown in Fig. 1. Compound **2** has four chloro ligands, one pyridine ligand, and one imido (NAr:Ar=2,6-diisopropylphenyl) ligand. The coordination sphere of Re can be described as an octahedron in which the pyridine and the NAr ligands are mutually *cis*. The equatorial plane, defined by Re, N2, Cl1, Cl2 and Cl3, is nearly planar with the average atomic displacement from the least-squares plane not exceeding 0.078 Å. The dihedral angle between the equatorial plane and the imido phenyl ring (C6-C11) is 36.4(2)°.

The Re-N2-C6 bond angle of 170.1(4)° and the Re-N2 bond distance of 1.710(4) Å are fairly typical of aryl imido ligands in high oxidation state Re complexes.³⁾ This angle and distance indicate that the imido group in **2** is linear and the Re-N bond has a triple bond character with an *sp*-hybrid nitrogen. The bond distance of Re-Cl2 (2.483(1) Å),

trans to the NAr ligand, is significantly longer than those of the other three Re-Cl bonds (2.381(1)-2.396(1) Å), presumably because of a high *trans*-influencing effect of the imido ligand (NAr).¹³⁾

There are two intramolecular hydrogen bonds, in which N3 acts as a donor to Cl2 and Cl4: N3···Cl2=3.339 Å, HN3B···Cl2=2.659 Å, N3-HN3B-Cl2=115.72° and N3···Cl4=3.386 Å, HN3A···Cl4=2.624 Å, N3-HN3A-Cl4=148.32°. There are also two intermolecular hydrogen bonds related by an inversion point (-x+1, -y, -z+1), in which N3 acts as a donor to Cl2 and Cl4: N3···Cl2=3.358 Å, HN3B···Cl2=2.875 Å, N3-HN3B-Cl2=139.35° and N3···Cl4=3.280 Å, HN3A···Cl4=2.850 Å, N3-HN3A-Cl4=112.80°.

In summary, we have isolated and structurally characterized [*cis*-ReCl₄(py)(N-C₆H₃-2,6-*i*-Pr₂)(NH₂-C₆H₃-2,6-*i*-Pr₂)] (**2**) from the reaction of Re(N-C₆H₃-2,6-*i*-Pr₂)Cl₃(py) (**1**) with propionaldehyde. In this reaction, the Re-metal has been formally reduced from +7 to +6, and compound **2** is a formal 17-electron complex.

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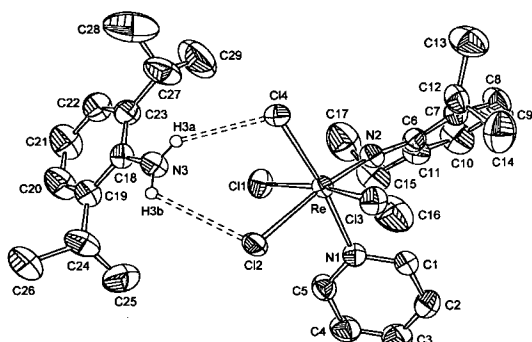


Fig. 1. ORTEP drawing¹⁴⁾ of **2**, showing the atom-labeling scheme and 50% probability thermal ellipsoids.

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