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$Re(NC_6F_5)(PPh_3)_2Cl_3$ 화합물의 합성 및 구조

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Preparation and Structure of $Re(NC_6F_5)(PPh_3)_2Cl_3$

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요 약

$Re(O)(PPh_3)_2Cl_3$와 2,3,4,5,6-pentafluoroaniline ($C_6F_5NH_2$)의 반응으로 $Re(NC_6F_5)(PPh_3)_2Cl_3$ 생성물을 얻었다. 이 화합물의 구조를 ^{1}H-NMR, 원소분석, 그리고 X-ray 회절법으로 규명하였다. 화합물은 사방정계로 ($Pna2_1$, a = 18.763(3) Å, b = 14.737(2) Å, c = 16.707(3) Å, Z = 4) 결정화되었다. 최소자승법으로 구조를 정밀화한 결과 신뢰도는 $R(wR_2)$ = 0.0455(0.1148)였다.

Abstract

Reaction of $Re(O)(PPh_3)_2Cl_3$, Ⅰ, with 2,3,4,5,6-pentafluoroaniline, $C_6F_5NH_2$, produced $Re(NC_6F_5)(PPh_3)_2Cl_3$, Ⅱ. The product has been characterized by ^{1}H-NMR, elemental analysis, and X-ray diffraction. Ⅱ crystallizes in the orthorhombic system, space group $Pna2_1$ with cell parameters a = 18.763(3) Å, b = 14.737(2) Å, c = 16.707(3) Å, and Z = 4. Least-squares refinement of the structure led to an $R(wR_2)$factor of 0.0455(0.1148) for 3319 unique reflections of $I > 2\sigma(I)$ and for 174 variables.

Introduction

The rich chemistry of transition-metal imido (or nitrene) complexes, $L_nM{=}NR$ (R: alkyl or aryl), continues to be a subject of research, as reflected by a number of recent reviews and monographs.[1] Although imido groups are usually considered to be chemically inert, some very reactive metal-imido species have been reported to be involved, stoichiometrically or catalytically, in cycloaddition, transfer of an imido group, activation of C-H bonds, carbodiimido metathesis, and imine matathesis.[2] Two general types of imido complexes are now known. The more common complexes of metals in a high oxidation state have a linear ligand with a metal-nitrogen triple bond character.[1] In

contrast, some zero-valent metals (Cr, W) possess a bent imido ligand with the lone pair on the nitrogen.[3] Bent imido species with formal M-N double bonds are more reactive than linear ones, because nucleophilic reactivity is enhanced in the bent NR ligand.[4]

We have been continuously interested in Re-imido complexes. Recently we have reported several Re-imido complexes such as $Re(NC_6H_5)(PPh_3)Cl_3L$ (L = CO, PMe_3, $P(OMe)_3$), $Re(NC_6H_5)Cl_3L_2$ (L = PMe_3, $P(OMe)_3$), and $Re(NC_6H_5)(DPPE)Cl_3$ (DPPE = $Ph_2PCH_2CH_2PPh_2$) from the reactions of $Re(NC_6H_5)(PPh_3)_2Cl_3$ with CO and various phosphine ligands.[5] We tried to prepare a bent Re-imido complex by introducing highly electronegative substituents on the imido phenyl ring, which is expected to make the nitrogen lone pair more free. Herein we report the preparation and structure of $Re(NC_6F_5)(PPh_3)_2Cl_3$, which was synthesized by the reaction of $Re(O)(PPh_3)_2Cl_3$ with 2,3,4,5,6-pentafluoroaniline ($C_6F_5NH_2$).

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 an argon gas. Glassware was either flame-dried or oven-dried. Benzene, diethyl ether, tetrahydrofuran (THF), and hydrocarbon solvents were stirred over sodium metal and distilled under vacuum. $CDCl_3$ was freeze-pump-thaw degassed before use and stored over molecular sieves under argon. 2,3,4,5,6-Pentafluoroaniline was distilled from CaH_2 and stored under argon. Re and triphenylphosphine (PPh_3; Ph = C_6H_5) were purchased from Aldrich Co. and used as received. $Re(O)(PPh_3)_2Cl_3$, **I**, was prepared by the literature method.[6]

^{1}H-NMR spectra were recorded with a Varian 200-MHz spectrometer with reference 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 have been performed by Korea Basic Science Center.

Preparation of $Re(NC_6F_5)(PPh_3)_2Cl_3$, Ⅱ. Heating (2 h) 1.00 g (1.20 mmol) of **I** with 0.30 g (1.64 mmol) of 2,3,4,5,6-pentafluoroaniline under reflux in toluene (80 mL) gave a black green solution, and then the solution was concentrated to about 30 mL. 30 mL of hexanes was added to the resulting solution, and the mixture was stirred for 30 min, allowed to stand for 1 h, and filtered. The black green filtrate was kept at -25 ℃. After 4 d, green crystals were obtained, washed with pentane (30 mL x 3), and dried under vacuum to give 0.291 g (0.29 mmol, 24.3%) of **Ⅱ**. ^{1}H-NMR ($CDCl_3$) δ 7.200 - 7.862 (m). Anal. Calcd for $C_{42}H_{30}F_5NP_2Cl_3Re$: C, 50.04; H, 3.03; N, 1.40. Found: C, 51.70; H, 3.18; N, 1.24. mp = 134-136 ℃ IR (KBr): 3059, 3026, 1639, 1512, 1484, 1458, 1436, 1254, 1192, 1093, 1074, 1031, 1001, 743, 694, 521 cm^{-1}.

X-ray Structure Determination. All X-ray data were collected with use of an Enraf-Nonius CAD4 automated diffractometer equipped with an Mo X-ray tube and a graphite crystal monochromator. Details on crystal and intensity data are given in Table 1. The orientation matrix and unit cell parameters

Table 1. Crystallographic Data and Summary of Data Collection and Structure Refinement

formula	$C_{42}H_{30}NF_5P_2Cl_3Re$	F(000)	1960
fw	998.16	no. of	3327
crystal system	orthorhombic	unique data	
space group	$Pna2_1$	no. of reflns	3319
a, Å	18.763(3)	used, $I > 2\sigma(I)$	
b, Å	14.737(2)	no. of params	174
c, Å	16.707(3)	Z	4
V, $Å^3$	4619(1)	scan range	$3 < 2\theta < 50$
dcalc, g cm^{-3}	1.435	scan type	ω-2θ
μ, cm_{-1}	2.921	R	0.0455
Max. inΔp(eA^{3-})	0.94	wR_2[a]	0.1148
		GOF on F^2	1.040

[a] $wR_2 = \{\sum[w(Fo^2-Fc^2)^2]/\sum[w(Fo^2)^2]\}^{1/2}$

were determined from 25 machine-centered reflections with $20 < 2\theta < 30°$. Axial photographs were used to verify the unit cell choice. Intensities of three check reflections were monitored every 1 h during data collection. Data were corrected for Lorentz and polarization effects. Decay corrections were made. The intensity data were empirically corrected with ψ-scan data. All calculations were carried out on the personal computer with use of the SHELXS-86[7] and SHELXL-93[8] programs.

A green crystal of Ⅱ, shaped as a block, of approximate dimensions 0.2 x 0.3 x 0.4 mm, was used for crystal and intensity data collection. The unit cell parameters and systematic absences, $h00$ ($h = 2n + 1$), $0k0$ ($k = 2n + 1$), $00l$ ($l = 2n + 1$), and $h0l$ ($h = 2n + 1$), indicated two possible space group: $Pna2_1$ and Pnam. A statistical analysis of intensities suggested a noncentrosymmetric space group, and the structure converged only in the space group $Pna2_1$. The structure was solved by the heavy atom methods. The Re, Cl, and P atoms were refined anisotropically, and the phenyl rings were treated as rigid groups. All hydrogen atoms were positioned geometrically and refined using a riding model.

Results and Discussion

Preparation. *Mer,trans*-$Re(O)(PPh_3)_2Cl_3$, Ⅰ, reacted with $C_6F_5NH_2$ in a refluxing toluene to give *mer,trans*-$Re(NC_6F_5)(PPh_3)_2Cl_3$, Ⅱ, which recrystallized from acetone/hexanes. Compound Ⅱ has been fully characterized by ^{1}H-NMR, IR, elemental analysis, and X-ray diffraction. Ⅱ is air-stable in the solid state, but unstable in solution.

$$mer,trans\text{-}Re(O)(PPh_3)_2Cl_3 + C_6F_5NH_2 \rightarrow mer,trans\text{-}Re(NC_6F_5)(PPh_3)_2Cl_3, \text{Ⅱ} + H_2O \quad (1)$$

Structure. As shown in Figure 1, compound

Ⅱ has an NC_6F_5 group, three *mer*-Cl atoms, and *trans*-phosphine ligands. The Re, N, and three Cl atoms form a basal plane and are essentially coplanar with a mean deviation of 0.002 Å from this plane. The two PPh_3 ligands occupy axial sites and the coordination sphere of Re can be described as an octahedron (Figure 1, Table 2 and 3). The imido phenyl ring (C1 - C6) is nearly coplanar with respect to the basal plane with a dihedral angle of 0.82(9)°. The Re-N-C bond angle of 175.4(12)° in compound Ⅱ is fairly typical of phenyl imido ligands in high oxidation state complexes, in which the metal is relatively electron-deficient and some π bonding between the imido nitrogen atom and

Table 2. Atomic Coordinates (x 10^4) and Equivalent Isotropic Thermal Parameters (Å^2 x 10^3)

	x	y	z	U(eq)[a]
Re	7738(1)	9770(1)	10000	32(1)
CL1	6462(1)	9663(2)	10036(6)	45(1)
CL2	7687(4)	9756(4)	8585(5)	50(3)
CL3	7648(5)	9771(4)	11455(5)	52(2)
P1	7782(1)	8074(2)	10023(5)	38(1)
P2	7615(1)	11462(2)	10025(7)	39(1)
F2	9470(8)	9857(10)	8692(9)	82(4)
F3	10916(9)	10021(10)	8786(9)	102(4)
F4	11564(6)	10095(7)	10238(7)	88(3)
F5	10781(8)	10038(10)	11592(9)	93(4)
F6	9348(7)	9984(10)	11501(8)	79(4)
N	8640(4)	9852(5)	10109(9)	36(2)
C1	9389(7)	9897(8)	10134(11)	48(3)
C2	9789(13)	9942(16)	9437(12)	71(6)
C3	10550(12)	10031(14)	9501(12)	69(5)
C4	10840(7)	10039(10)	10185(11)	64(4)
C5	10440(9)	9998(11)	10854(10)	52(4)
C6	9740(10)	9943(13)	10823(11)	54(4)
C11	7464(7)	7437(9)	10888(7)	40(4)
C12	7756(6)	6598(9)	11076(8)	82(8)
C13	7465(7)	6080(7)	11690(9)	75(6)
C14	6882(7)	6403(8)	12116(7)	57(5)
C15	6589(6)	7243(8)	11928(7)	44(4)
C16	6880(7)	7760(7)	11314(6)	53(5)
C21	7364(7)	7475(8)	9180(7)	42(5)
C22	6797(7)	7854(8)	8762(8)	45(4)
C23	6501(6)	7396(10)	8115(8)	83(7)
C24	6773(8)	6558(9)	7886(7)	65(5)
C25	7340(7)	6178(7)	8304(8)	71(6)
C26	7635(6)	6636(8)	8951(7)	49(4)
C31	8734(3)	7792(6)	10058(10)	49(2)
C32	9148(6)	7779(9)	9369(8)	51(4)
C33	9878(5)	7629(9)	9422(7)	74(5)
C34	10194(3)	7492(8)	10165(8)	82(3)
C35	9780(7)	7505(10)	10854(7)	95(7)
C36	9050(6)	7655(9)	10801(8)	66(5)
C41	7234(7)	12066(8)	10876(7)	46(5)
C42	7477(6)	12925(9)	11085(8)	71(5)
C43	7143(7)	13405(7)	11695(8)	76(5)
C44	6566(7)	13026(8)	12095(7)	62(4)
C45	6323(6)	12167(8)	11886(7)	54(5)
C46	6657(7)	11687(7)	11277(8)	62(5)
C51	7132(6)	11998(7)	9181(7)	42(5)
C52	7282(6)	12896(7)	8987(7)	53(4)
C53	6900(6)	13327(6)	8384(7)	61(4)
C54	6368(6)	12962(7)	7976(6)	55(4)
C55	6218(6)	11965(7)	8170(7)	68(5)
C56	6600(6)	11533(6)	8773(8)	53(5)
C61	8521(4)	11899(6)	10051(12)	47(2)
C62	8816(7)	12052(12)	9300(9)	77(7)
C63	9526(7)	12306(13)	9232(8)	96(8)
C64	9942(4)	12408(8)	9915(10)	81(5)
C65	9647(6)	12255(11)	10666(8)	74(5)
C66	8936(7)	12000(11)	10734(9)	61(5)

[a]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 (deg).

Bond Distances			
Re-N	1.706(8)	Re-P1	2.501(2)
Re-CL1	2.399(3)	Re-P2	2.504(3)
Re-CL2	2.366(8)	N-C1	1.408(14)
Re-CL3	2.437(8)		
Bond Angles			
Re-N-C1	175.4(12)	N-Re-P1	92.0(3)
N-Re-CL1	172.4(6)	N-Re-P2	91.1(3)
N-Re-CL2	98.5(5)	P1-Re-P2	176.2(2)
N-Re-CL3	87.8(5)	CL1-Re-CL3	84.6(3)

the metal is likely.[1, 9] This bond angle, therefore, indicates that the imido group is linear and the Re-N bond has a triple bond character with a *sp*-hybridized nitrogen. The Re-N bond distance of 1.706(8) Å is also consistent with those found in Re complexes of aryl imido ligands.1, [9, 10] These geometric data, the bond distance of Re-N and the bond angle of Re-N-C, indicate that electronegative fluorine (F) substituents did not bring about inducing the transformation of a linear ligand to a bent one.

Of particular interest are the dihedral angles among the phenyl groups. The dihedral angles between the phenyl rings in the two *trans* PPh_3

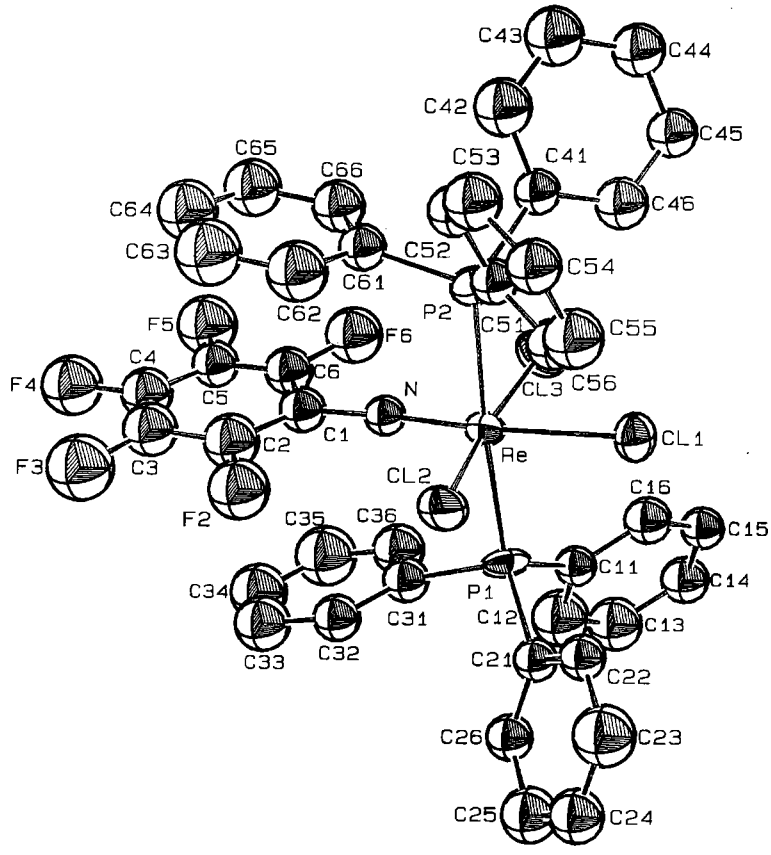

Figure 1. ORTEP drawing of Ⅱ showing the atom-labeling scheme and 50% probability thermal ellipsoids.

ligands (C31-C36, C61-C66) with respect to the imido phenyl ring (C1-C6) in compound Ⅱ are 14.1(2)°and 13.3(2)°, respectively. In an NC_6H_5 analog, *mer,trans*-$Re(NC_6H_5)(PPh_3)_2Cl_3$, our calculations show that the corresponding dihedral angles are 46. 38°and 27. 36°.[11] These values provide a possibility that a sort of π-stacking, due to the small values of the dihedral angles among the phenyl groups in the complex Ⅱ, might be able to prevent the NC_6F_5 group from transforming toward a bent form. We, however, cannot give a clear explanation for the small values of dihedral angles in complex Ⅱ at this point.

Recently, Bergman and his coworkers reported an insertion of CO into an Ir-N bond in $Cp^*Ir(N^tBu)$, ($Cp^* = C_5(CH_3)_5$), which is the first carbonylation of a terminal imido ligand to give an isocyanate complex.[12] The results of above studies prompted us to investigate the possibility of insertion of CO into an Re-nitrene bond in compound Ⅱ. No reactions with CO (up to 6 atm) have been observed.

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Supplementary Materials Available. Tables of bond distances and bond angles, anisotropic thermal parameters, positional parameters for hydrogen atom (5 pages); listings of observed and calculated structure factors (8 pages). Supplementary materials are available from one of the authors (Lee, S. W.) upon request.

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