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$Re(\equiv NC_6H_5)(DPPE)Cl_3$ 화합물의 합성 및 구조

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Preparation and Structure of $Re(\equiv NC_6H_5)(DPPE)Cl_3$, [DPPE=$Ph_2PCH_2CH_2PPh_2$]

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요 약

$Re(\equiv NC_6H_5)(PPh_3)_2Cl_3$ 화합물이 1,2-bis(diphenylphosphino)ethane (DPPE) 와 반응하여 *fac*-$Re(\equiv NC_6H_5)(DPPE)Cl_3$ 이 되었다. 이 생성물의 구조를 ^{1}H-NMR, 원소분석, 그리고 X-ray 회절법으로 규명하였다. 이 생성물은 단사정계로 (*Pc*, a = 11.083(3) Å, b = 10.930(1) Å, c = 14.081(2) Å, β = 108.37(2)° , Z = 2) 결정화되었다. 최소자승법으로 구조를 정밀화한 결과 신뢰도는 $R(wR_2)$=0.0254(0.0607)이였다.

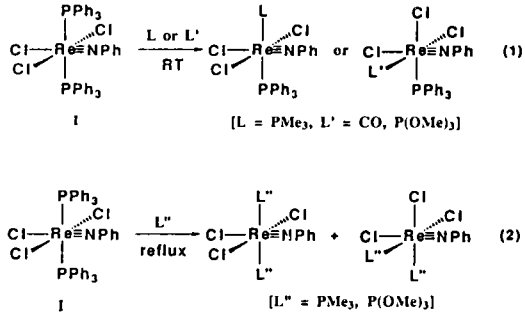
Abstract

$Re(\equiv NC_6H_5)(PPh_3)_2Cl_3$, I, reacted with, 1,2-bis(diphenylphosphino)ethane (DPPE) to give *fac*-$Re(\equiv NC_6H_5)(DPPE)Cl_3$, II. The product has been characterized by ^{1}H-NMR, elemental analysis, and X-ray crystallography. II Crystalizes in the monoclinic space group *Pc*, with cell parameters a = 11.083(3) Å, b = 10.930(1) Å, c = 14.081(2) Å, β = 108.37(2)° , and Z = 2. Least-squares refinement of the structure led to a $R(wR_2)$factor of 0.0254 (0.0607) for 2888 uniqure reflections of $I > 2\sigma(I)$ and for 352 variables.

1. Introduction

Transition-metal imido (or nitrene, MNR) complexes have been of continuous interest.[1] We have been continuously interested in Re-imido complexes (Re≡NR). Recently we have prepared several Re-imido complexes of the type $Re(\equiv NPh)Cl_3(PPh_3)L$ from the reactions of $Re(\equiv NC_6H_5)(PPh_3)_2Cl_3$, I, with small, strongly coordinating ligands (L = CO, $P(OMe)_3$, PMe_3) in benzene at room temperature (Eq. 1).[2] In addition, we have also reported preparation and structure of Re-imido complexes of the type $Re(\equiv NPh)Cl_3(PR'_3)_2$, which

have been synthesized by replacing both PPh_3 ligands in I by the ligand PR'_3 (PR'_3 = $P(OMe)_3$, PMe_3) in a refluxing benzene (Eq. 2).[3] Herein we report preparation and structure of Re(≡NPh)Cl_3(DPPE), which has a chelating ligand DPPE (DPPE = $Ph_2PCH_2CH_2PPh_2$).



2. Experimental

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 either flame-dried or oven-dried. Benzene, diethyl ether, and hydrocarbon solvents were stirred over sodium metal and distilled by vacuum transfer. NMR solvent ($CDCl_3$) was degassed by freeze-pump-thaw cycles before use and stored over molecular sieves under argon. Aniline was distilled over CaH_2 and stored under argon. Re, triphenylphosphine (PPh_3; Ph = C_6H_5), and 1,2-bis(diphenylphosphino)ethane (DPPE) were purchased from Aldrich Co. and used as received. Re(≡NC_6H_5)(PPh_3)$_2Cl_3$, I, was prepared by the literature method.[4]

^{1}H-NMR spectra were recorded with a Bruker AMX-500 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 have been performed by Korea Basic Science Center.

Preparation of Re(≡NC_6H_5)(DPPE)Cl_3, II. To 0.30 g (0.33 mmol) of I in 60 mL of benzene was added 0.13 g (0.33 mmol) of DPPE. After it was refluxed for 30 min, the solvent was removed under vacuum to give green solids. The resultant solids were washed with diethyl ether (30 mL x 2) and hexanes (30 mL x 2), and then dried under vacuum to give 0.21 g (0.27 mmol, 81%) of *fac*-Re(≡NC_6H_5)(DPPE)Cl_3, II. The compound II conveniently recrystallized from dichloromethane/hexanes. ^{1}H-NMR ($CDCl_3$) δ 7.105-7.609 (25H, m), 1.551 (4H, t, $^2J_{P-H}$=1.6 Hz, $-CH_2CH_2-$). Anal. Calcd for $C_{32}H_{29}NP_2Cl_3Re$: C, 49.14; H, 3.73; N, 1.79. Found : C, 48.74; H, 3.88; N, 2.08. Mp> 250℃. IR (KBr) : 3055, 1483, 1435, 1414, 1192, 1104, 1027, 996, 746, 694, 525, 500 cm^{-1}.

X-ray Structure Determination. All X-ray data were collected with use of an Enraf-Nonius CAD4 automated diffractometer equipped with a Mo X-ray tube and a graphite crystal monochromator. Details of crystal and intensity data are given in Table 1. The orientation matrix and unit cell parameters 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 1h 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[5] and SHELXL-93[6] programs.

A green crystal of II, shaped as a block, of approximate dimensions 0.2 x 0.3 x 0.3 mm, was

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

formula	$C_{32}H_{32}NP_2Cl_3Re$	F(000)	768
fw	782.05	no. of data	5471
temperature,K	293	collected	
crystalsystem	monoclinic	no. of reflns	2888
spacegroup	*Pc*	used, $I > 2\sigma(I)$	
a, Å	11,083(3)	no. of params	352
b, Å	10.930(1)	scan range	$3 < 2\theta < 50$
c, Å	14.081(2)	scan type	ω-2θ
β, deg	108.37(2)	Max. in $\Delta\rho$(e A^{3-})	0.64
V, Å3	1618.8(5)	GOF on F^2	1.096
Z	2	R	0.0254
d_{calc}, gcm^{-3}	1.604	wR_2[a]	0.0607
μ, cm^{-1}	4.122		

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

used for crystal and intensity data collection. The unit cell parameters and systematic absences, 00 ℓ (ℓ =2n + 1) and h0 ℓ (ℓ =2n + 1), indicated two possible space groups : *Pc* and *P2/c*. A statistical analysis of intensities suggested a noncentrosymmetric space group, and the structure converged only in the space group *Pc*. The structure was solved by the heavy atom methods. All nonhydrogen atoms were refined anisotropically. All hydrogen atoms were positioned geometrically and refined using a riding model.

Final atomic positional parameters for nonhydrogen atoms are shown in Table 2. The selected bond distances and bond angles are shown in Table 3; anisotropic thermal parameters, hydrogen atom coordinates, full bond distances and bond angles, and tables of observed and caluclated structure factors are available as supplementary material.

3. Results and Discussion

Preparation. *Fac*-Re(≡NC$_6$H$_5$)(DPPE)Cl$_3$, II was prepared by replacing the two PPh$_3$ ligands in I with DPPE. *Mer,trans*-Re(NPh)Cl$_3$(PPh$_3$)$_2$, I, reacted with DPPE in a refluxing benzene to give II which recrystallized from dichloromethane/hexanes (Eq. 3).

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic thermal parameters (Å2 x10^3) for II.

	x	y	z	U(eq)[a]
Re	-1123(1)	-1696(1)	-1159(1)	26(1)
CL1	-2613(2)	-1941(2)	-2824(1)	40(1)
CL2	530(2)	-2152(2)	-1901(1)	44(1)
CL3	-1007(2)	457(1)	-1523(1)	35(1)
P1	297(2)	-971(2)	423(1)	28(1)
P2	-2758(2)	-1060(2)	-473(1)	28(1)
N1	-1172(7)	-3125(5)	-684(5)	33(1)
C11	-1163(8)	-4294(6)	-267(5)	36(2)
C12	-1457(9)	-4453(7)	593(6)	48(2)
C13	-1326(11)	-5574(8)	1032(7)	63(3)
C14	-903(14)	-6529(9)	608(9)	71(3)
C15	-642(14)	-6385(9)	-255(9)	79(4)
C16	-732(11)	-5262(8)	-721(8)	62(3)
C1	-696(7)	-115(7)	1003(5)	34(1)
C2	-1966(6)	-729(6)	858(5)	29(1)
C21	1615(7)	49(7)	492(5)	36(2)
C22	2334(12)	-72(10)	-149(8)	55(3)
C23	3331(11)	697(12)	-76(9)	71(3)
C24	3648(12)	1601(9)	641(11)	71(3)
C26	1946(9)	976(9)	1204(7)	56(2)
C31	994(7)	-2225(7)	1265(5)	36(2)
C32	1510(8)	-3190(7)	894(7)	43(2)
C33	1966(9)	-4216(9)	1474(8)	61(3)
C34	1888(10)	-4300(10)	2427(8)	69(3)
C35	1397(12)	-3323(10)	2820(9)	71(3)
C36	955(9)	-2282(10)	2238(6)	54(2)
C41	-3695(7)	283(7)	-1025(5)	33(1)
C42	-4576(10)	166(9)	-1954(7)	47(2)
C43	-5313(10)	1171(11)	-2412(7)	58(3)
C44	-5129(10)	2266(9)	-1913(8)	60(2)
C45	-4273(10)	2384(8)	-990(7)	56(2)
C46	-3541(8)	1383(8)	-539(6)	45(2)
C51	-3954(7)	-2212(7)	-470(6)	39(2)
C52	-4255(9)	-3116(7)	-1199(7)	45(2)
C53	-5135(11)	-4013(10)	-1162(9)	69(3)
C54	-5681(15)	-4007(14)	-427(11)	101(5)
C55	-5365(16)	-3107(14)	292(12)	105(6)
C56	-4508(11)	-2216(12)	270(8)	76(3)

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

II has been characterized by ^{1}H-NMR, IR, and elemental analyses. II is air-stable both in solution and in the solid state.

Table 3. Selected Bond Distances (Å) and Bond Angles (deg).

Bond Distances			
Re-N1	1.707(5)	Re-CL1	2.420(2)
Re-CL2	2.429(2)	Re-CL3	2.420(2)
Re-P1	2.420(2)	Re-P2	2.409(2)
N1-C11	1.405(8)	P1-C1	1.823(7)
P1-C21	1.816(7)	P1-C31	1.818(7)
P2-C2	1.838(6)	P2-C41	1.824(7)
P2-C51	1.829(8)	C1-C2	1.515(10)
Bond Angles			
Re-N1-C11	177.7(6)	N1-Re-CL1	100.5(2)
N1-Re-CL2	95.9(2)	N1-Re-CL3	169.5(2)
N1-Re-P1	91.8(2)	N1-Re-P2	89.2(2)
P1-Re-P2	83.7(1)	CL1-Re-CL3	88.2(1)
C1-P1-C21	104.5(3)	C1-P1-C31	106.7(3)
C21-P1-C31	105.0(3)	C2-P2-C41	107.5(3)
C2-P2-C51	104.3(3)	C41-P2-C51	103.8(3)

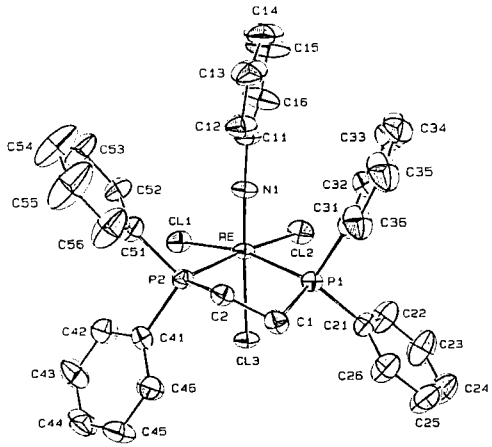
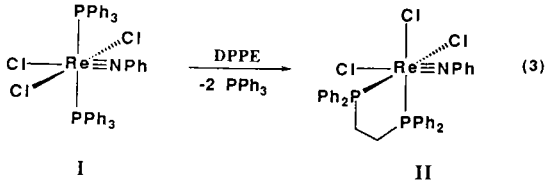


Fig 1. ORTEP drawing of II showing the atom-labeling scheme and 50% probability thermal ellipsoids.



I II (3)

Structure. The molecular structure of II with the atomic numbering scheme is shown in Figure 1. The coordination sphere of the Re metal can be described as a distorted octahedron. Compound II has a NPh group, three fac-Cl atoms and a chelating phosphine ligand DPPE. The Re-P bond distances (2.409(2) -2.420(2) Å) agree with known values (2.324 -2.470 Å).[7] The Re-Cl bond distances (2.420(2) - 2.429(2) Å) are longer than the known values (2.355 -2.387 Å)[7], probably due to the strong trans-influence effect of the DPPE and imido ligands.[1a] The Re metal lies 0.185(1) Å above the equatorial plane, defined by C11, C12, P1, and P2, on which the four atoms are coplanar with the displacement not exceeding 0.080(1) Å.

Of particular interest are the bonding parameters of the Re-N-C bond. A comparison of bond distances and bond angles is given in Table 4. The Re-N bond distances appear to be relatively insensitive to the types of phosphine and to the geometries of the coordination sphere. The Re-N-C bond angle of 177.7(6)° in 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 the metal is likely.[1a,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 distances of 1.707(6)° is also consistent with those found for aryl imido ligands coordinated to rhenium.[1a,9,10]

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Supplementary Material Available. Tables of bond distances and bond angles, anisotropic thermal parameters, positional parameters for hydrogen atom (4 pages); listings of observed and calculated

Table 4. Bonding parameters of the Re-N-C bond.

Compound	Re-N(Å)	Re-N-C(deg)	Reference
mer,trans-$Re(NPh)(PPh_3)_2Cl_3$, I	1.726(6)	172.6(6)	8
mer,trans-$Re(NPh)(Ph_3)(PMe_3)Cl_3$	1.711(6)	176.0(6)	2a
fac,cis-$Re(NPh)(PPh_3)(P(OMe)_3)Cl_3$	1.710(8)	167.9(7)	2a
mer,trans-$Re(NPh)(PMe_3)_2Cl_3$	1.708(7)	158(2)	3
fac,cis-$Re(NPh)(PMe_3)_2Cl_3$	1.724(12)	174(1)	3
fac-$Re(NPh)DPPE)_2Cl_3$, II	1.707(5)	177.7(6)	this work

structure factors (6 pages). Supplementary materials are available from one of the authors (S. W. Lee) upon request.

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