

to conclude that the nitrogen atoms of chxn is strong σ -donor toward chromium(III). The value of $e_{\sigma N}$ is also located within the normal range²³ for metal-ligand bonding properties of chromium(III) complexes. The complete ligand field parameters reported here may be transferable to other complexes as a basis for schematic analysis of this type of saturated hexaamine system.

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References

- (a) This is part 14 of the series *Electronic Structure and Chemical Reactivity of Transition Metal Complexes*; (b) The preceding publication in this series is Ref. 1(d); (c) Abbreviations used: chxn=*trans*-1,2-cyclohexanediamine, en=1,2-ethanediamine, tacn=1,4,7-triazacyclononane; (d) Choi, J-H.; Oh, I-G. *Bull. Basic Sci. Andong Univ.* **1993**, 4, 15.
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Preparation and Structure of $\text{Re}(\equiv\text{NC}_6\text{H}_5)(\text{CO})(\text{PPh}_3)\text{Cl}_3$

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By treating *mer, trans*- $\text{Re}(\equiv\text{NC}_6\text{H}_5)(\text{PPh}_3)_2\text{Cl}_3$, I, with 5 atm of CO at room temperature for 52 h, *fac*- $\text{Re}(\equiv\text{NC}_6\text{H}_5)(\text{CO})(\text{PPh}_3)\text{Cl}_3$, II, was obtained as dark green precipitates in 81% yield. The crystal structure of II was determined through X-ray diffraction. II crystallizes in the monoclinic system, space group $P2_1/n$ with cell parameters $a=9.740$ (2) Å, $b=16.210$ (5) Å, $c=16.192$ (6) Å, $\beta=97.50$ (2)°, and $Z=4$. Least-squares refinement of the structure led to a $R(R_w)$ factor of 0.030 (0.036) for 2878 unique reflections of $I>3\sigma(I)$ and for 241 variables. In comparison to the starting material I, the bond distance of Re-N became longer from 1.726 (6) to 1.736 (5) Å and the bond angle of Re-N-C(Ph) became smaller from 172.6 (6) to 167.0 (2)°, indicating that the Re-N bond in II is weakened and has a less triple-bond character than that in I.

Introduction

Since the first nitrene complexes, $\text{OsO}_3(\text{NR})$, were reported in 1959, transition-metal nitrene (or imido) complexes have received continuous interest¹. They are presumed to be involved in catalytic processes in such as propylene ammoxidation²,

nitride reduction³, and very recently hydrodenitrogenation catalysis⁴. Very recently, Bergman and his workers reported an insertion of CO into an $\text{Ir}\equiv\text{N}$ bond in $\text{C}_p^*\text{Ir}(\equiv\text{N}^t\text{Bu})(\text{Cp}^*=\text{C}_5(\text{CH}_3)_5)$, which is the first carbonylation of a terminal imido ligand to give an isocyanate complex⁵. The results of above studies prompted us to investigate the possibility of insertion

reactions of CO into other terminal metal nitrene centers. We set out insertion reactions of carbon monoxide into $\text{Re}\equiv\text{NR}$ bonds. When we treated *mer, trans*- $[\text{Re}(\equiv\text{NPh})(\text{PPh}_3)_2\text{Cl}_3]$, I, with CO, we got *fac*- $[\text{Re}(\equiv\text{NPh})(\text{CO})(\text{PPh}_3)_2\text{Cl}_3]$, II, which is a substitution product instead of an insertion product. We report here the preparation and structure of II.

Experimental

Unless otherwise stated, all the reactions have been performed with standard Schlenk line and cannula techniques under an argon atmosphere. Carbonylation reactions have been performed in a 60 mL of quartz pressure vessel (Kontes). 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. NMR solvents (C_6D_6 and CDCl_3) were freeze-pump-thaw degassed before use and stored over zeolite 4A under argon. Aniline was distilled from CaH_2 and stored under argon. Re metal, and triphenylphosphine (PPh_3 ; $\text{Ph}=\text{C}_6\text{H}_5$) were purchased from Aldrich Co. and used as received. CO (99.9%) was purchased from Union Gas Co. and used as received. $\text{Re}(\equiv\text{NC}_6\text{H}_5)(\text{PPh}_3)_2\text{Cl}_3$, I, was prepared by the literature method⁶.

^1H - and ^{13}C -NMR spectra were recorded with a Hitach 1100 60-MHz spectrometer and 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 $\text{Re}(\equiv\text{NC}_6\text{H}_5)(\text{CO})(\text{PPh}_3)_2\text{Cl}_3$, II. 0.10 g (0.11 mmol) of I in 40 mL of benzene was stirred for 52 h at room temperature under CO (5 atm), and then the product, $\text{Re}(\equiv\text{NC}_6\text{H}_5)(\text{CO})(\text{PPh}_3)_2\text{Cl}_3$, II, precipitated out as dark green solids. The slurry was filtered, and the solid was washed with hexanes (25×2 mL), diethyl ether (25×2 mL), benzene (25×2 mL), and then dried under vacuum to give 0.06 g (0.089 mmol, 81%) of II. The product conveniently recrystallized from CH_2Cl_2 /hexanes. ^1H -NMR (CDCl_3) δ 8.0-6.7 (m). $^{13}\text{C}\{^1\text{H}\}$ -NMR (CDCl_3) δ 126.3, 126.4, 129.2, 129.4, 130.2, 131.0, 132.5, 132.9, 134.7, 134.9. Anal. Calcd for $\text{C}_{25}\text{H}_{20}\text{NOPCl}_3\text{Re}$: C, 44.55; H, 2.97; N, 2.08. Found: C, 44.76; H, 3.07; N, 2.45. mp. (dec.) = 155°C . IR (KBr): 3058, 2055 (CO), 1481, 1434, 1093, 748, 705, 691, 523, 496 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 on crystal and intensity data are given in Table 1. The orientation matrix and unit cell parameters were determined from 25 machine-centered reflections with $3<2\theta<46^\circ$. Axial photographs were used to verify the unit cell choice. Intensities of three check reflections were monitored after every 1 h during data collection. Data were corrected for Lorentz and polarization effects. The intensity data were empirically corrected with Ψ -scan data. All calculations were carried out on a VAX computer with use of the SHELXS86, SHELX76 programs.

A brown crystal, shaped as a block, of approximate dimensions $0.3\times 0.3\times 0.5$ mm, was used for crystal and intensity

data collection. The unit cell parameters and systematic absences, OkO ($k=2n+1$) and hOl ($h+l=2n+1$), unambiguously indicated $P2_1/n$ as the space group. The structure was solved by direct methods. All non-hydrogen atoms were refined anisotropically and the phenyl rings were treated as rigid groups with fixed hydrogen atoms (0.08 \AA^2 fixed isotropic thermal parameters). All hydrogen atoms were generated in ideal positions but were not refined. Final atomic positional parameters for non-hydrogen atoms are shown in Table 2 and the selected bond distances and bond angles are shown in Table 3; anisotropic thermal parameters, hydrogen atom coordinates, and tables of observed and calculated structure factors are available as supplementary material.

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

formula	$\text{C}_{25}\text{H}_{20}\text{NOPCl}_3\text{Re}$	$F(000)$	1303.8
fw	673.98	no. of	3988
crystal system	monoclinic	unique data	
space group	$P2_1/n$	no. of reflns	2878
a , \AA	9.740(2)	used, $I>3\sigma(I)$	
b , \AA	16.210(5)	no. of params	241
c , \AA	16.192(6)	Z	4
β , deg	97.50(2)	scan range	$3<2\theta<46^\circ$
V , \AA^3	2534.7	scan type	ω -2 θ
d_{calc} , g cm^{-3}	1.90	R	0.0297
μ , cm^{-1}	54.16	R_w	0.0358
Max. in $\Delta\rho$ (e \AA^{-3})	0.89		

Table 2. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Thermal Parameters ($\text{\AA}^2 \times 10^3$)

	x	y	z	U (eq^a)
Re	10116(0)	2184(0)	978(0)	37(0)
C11	8224(2)	1494(1)	199(1)	50(1)
C12	9053(2)	1786(1)	2184(1)	55(1)
C13	8829(2)	3445(1)	949(1)	54(1)
P1	10808(2)	2662(1)	-353(1)	38(1)
O1	12049(6)	3310(4)	2175(4)	70(4)
N	11477(5)	1485(3)	1043(3)	41(3)
C1	9695(4)	3413(3)	-947(3)	45(5)
C2	10191(4)	4168(3)	-1197(3)	57(5)
C3	9296(4)	4716(3)	-1663(3)	67(7)
C4	7906(4)	4509(3)	-1878(3)	65(6)
C5	7409(4)	3755(3)	-1627(3)	66(6)
C6	8304(4)	3206(3)	-1162(3)	58(6)
C7	10917(6)	1856(2)	-1135(3)	48(5)
C8	11174(6)	2093(2)	-1928(3)	62(6)
C9	11300(6)	1497(2)	-2535(3)	77(7)
C10	11168(6)	663(2)	-2349(3)	66(6)
C11	10911(6)	425(2)	-1555(3)	57(5)
C12	10785(6)	1022(2)	-948(3)	51(5)
C13	12523(5)	3107(3)	-180(3)	46(5)
C14	13665(5)	2718(3)	-447(3)	62(6)
C15	14984(5)	3056(3)	-252(3)	84(8)

C16	15162(5)	3783(3)	213(3)	81(8)
C17	14020(5)	4171(3)	480(3)	76(7)
C18	12701(5)	3833(3)	284(3)	58(5)
C19	12740(4)	1125(3)	1104(3)	42(4)
C20	12799(4)	276(3)	974(3)	61(5)
C21	14078(4)	-121(3)	1028(3)	75(6)
C22	15298(4)	331(3)	1212(3)	82(8)
C23	15239(4)	1180(3)	1343(3)	66(6)
C24	13960(4)	1577(3)	1289(3)	57(5)
C25	11363(8)	2913(4)	1718(5)	49(5)

^aEquivalent isotropic U defined as one-third of the trace of the orthonormalized U_j tensor.

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

Bond Distances			
RE-C11	2.373(2)	RE-C12	2.414(2)
RE-C13	2.395(2)	RE-P1	2.466(2)
RE-N	1.736(5)	RE-C25	1.982(8)
P1-C1	1.819(5)	P1-C7	1.833(5)
P1-C13	1.807(5)	N-C19	1.353(7)
C25-O1	1.131(8)		
Bond Angles			
C19-N-RE	167.0(2)	O1-C25-RE	176.4(7)
C12-RE-C11	85.3(1)	C13-RE-C11	91.3(1)
C13-RE-C12	88.0(1)	P1-RE-C11	88.0(1)
P1-RE-C12	170.4(1)	P1-RE-C13	85.2(1)
N-RE-C11	105.0(2)	N-RE-C12	100.4(2)
N-RE-C13	162.1(2)	N-RE-P1	87.9(2)
C25-RE-C11	167.0(2)	C25-RE-C12	87.9(2)
C25-RE-C13	77.4(2)	C25-RE-P1	97.2(2)
C25-RE-N	87.1(3)	C1-P1-RE	117.4(2)
C7-P1-RE	115.3(1)	C13-P1-RE	110.0(2)

Results and Discussions

By treating *mer, trans*- $\text{Re}(\equiv\text{NC}_6\text{H}_5)(\text{PPh}_3)_2\text{Cl}_3$, I, with 5 atm of CO at room temperature for 52 h, *fac*- $\text{Re}(\equiv\text{NC}_6\text{H}_5)(\text{CO})(\text{PPh}_3)\text{Cl}_3$, II, was obtained as dark green precipitates which recrystallized from CH_2Cl_2 /hexanes. Compound, I, gradually changes its color from green to brown after 24 h in chlorinated solvents such as CHCl_3 and CH_2Cl_2 . This complex exhibits a strong CO absorption at 2055 cm^{-1} , corresponding to a terminal carbonyl group. In other words, II results from the substitution reaction rather than the insertion reaction. Similar reaction, in which $[\text{Re}(\equiv\text{NR}')(\text{PPh}_3)_2\text{Cl}_3]$ ($\text{R}' = \text{C}_6\text{H}_4\text{OMe-}p$) was treated with a CO pressure of 50 atm at 100°C to produce $[\text{Re}(\equiv\text{NR}')(\text{CO})(\text{PPh}_3)\text{Cl}_3]$, was reported, indicating that a $\text{Re}=\text{N}$ bond is very strong⁶. But a polymeric compound, $[\text{Re}(\equiv\text{NR}')(\text{PPh}_3)\text{Cl}_3]_n$ ($\text{R}' = \text{C}_6\text{H}_4\text{Me-}p$), which is prepared from the reaction between $[\text{Re}(\equiv\text{NR}')(\text{PPh}_3)_2\text{Cl}_3]$ and elemental sulfur, is active enough to react with CO at atmospheric pressure to give $[\text{Re}(\equiv\text{NR}')(\text{PPh}_3)(\text{CO})\text{Cl}_3]$. But the same strategy could not be applied to other analogs having $\text{R} = \text{C}_6\text{H}_5$, or $\text{C}_6\text{H}_4\text{OMe-}p$ ⁷. But in any case, there has been no report on the structure in detail, probably due to the

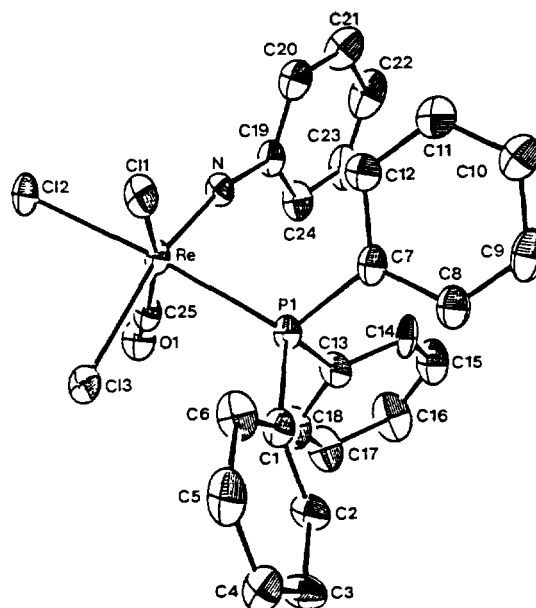
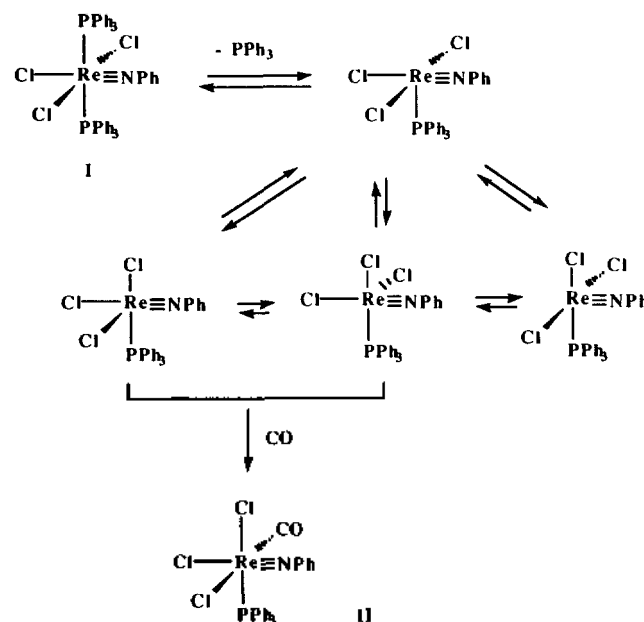


Figure 1. ORTEP drawing of II showing the atom-labeling scheme and 50% probability thermal ellipsoids.



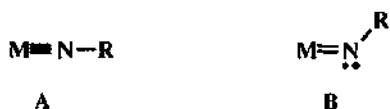
Scheme 1.

lack of X-ray crystal structures.

As shown in Figure 1 compound II has three *facial* Cl atoms, and PhN *cis* to CO. On the other hand, compound I has three *meridional* Cl atoms and two *trans* PPh₃ groups. Consequently the facial configuration indicates the rearrangement of ligands during the reaction. Compound I is an 18-electron complex and its coordination sphere is saturated. The substitution reaction is likely to proceed with the rearrangement of ligands of a 5-coordinate intermediate, which is formed by dissociation of PPh₃. Although we cannot explain clearly the reaction pathway, one of possible mechanisms is shown in Scheme 1. But this proposed mechanism cannot give a clearcut explanation for the high yield (81%)

of II.

As shown in X-ray structure, the coordination sphere of II can be described as a slightly distorted octahedron (Table 3). In comparison to the starting material I⁹, the bond distance of Re-N became longer from 1.726(6) to 1.736(5) Å and the bond angle of Re-N-C(Ph) became smaller from 172.6(6) to 167.0(2)°, indicating that the Re-N bond in II is weakened and has a less triple-bond character than that in I. For imido (or nitrene) ligands, the valence bond description suggests that the metal nitrogen bond order can be inferred from the position of the substituent. A linear M-N-R unit implies that the nitrogen is *sp* hybridized and that there is a metal-nitrogen triple bond (A structure), while substantial bending of the M-N-R linkage indicates the presence of a lone pair on the nitrogen and is usually taken as evidence for a reduced bond order (B structure)¹⁰. A triply bonded imido ligand is regarded as a dianionic 6-electron donor. Based on this description, a Re-N bond in II resembles closely the A structure and this bond can be described as a Re-N triple bond. In addition, complex II is an 18-electron complex with the Re metal in the oxidation state of +5.



The bond distance of Re-C12(2.414(2) Å), *trans* to P, is significantly longer than the other two bond distances of Re-Cl (2.373(2), 2.395(2) Å), implying that a phosphine group seems to exert a stronger *trans*-influencing effect. This phenomenon contrasts with the known fact that CO is a stronger *trans*-influencing group than triarylphosphine¹⁰. The steric effect might be important in determining the geometry for I, whereas the *trans*-influencing effect for II, in which a steric congestion is a lot relieved due to the substitution of a bulky ligand PPh₃ by CO. It should be pointed out that the extent of π -back bonding from Re to CO seems to be small, considering a high oxidation state of Re(+5), a relatively short

bond distance of C-O (1.138(8)Å), and an IR frequency of CO (2055 cm⁻¹). Therefore, Re-Cl bond distances maybe reflect the relative strengths of the σ -donating capabilities of ligands *trans* to Cl ligands. Re, Cl1, Cl3, N, and C25 atoms form a basal plane and the average displacement is 0.5785 Å from the least-squares defined by these five atoms. The nitrene phenyl ring is twisted out of the basal plane by the dihedral angle of 50.8°.

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