Preparation and Structure of Re(≡NC₆H₅)(PMe₃)₂Cl₃

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Mer,trans-Re(≡NC₆H₅)(PPh₃)₂Cl₃, I, reacted with trimethylphosphine to give a mixture of two stereoisomers, *mer,trans*-Re(≡NC₆H₅)(PMe₃)₂Cl₃, II, and *fac,cis*-Re(≡NC₆H₅)(PMe₃)₂Cl₃, III. These compounds could also be prepared from the reaction of Re(≡NC₆H₅)(PMe₃)(PPh₃)Cl₃ with trimethylphosphine. In both reactions the *mer,trans*-isomer is a major product. The products have been characterized by NMR, elemental analysis, and X-ray crystallography. Crystal data for II: monoclinic space group $P2_1$, a = 10.053(1) Å, b = 10.844(1) Å, c = 10.058(2) Å, β = 113.45(2)°, Z = 2, $R(wR_2)$ = 0.0348 (0.0894). Crystal data for III: monoclinic space group $P2_1/n$, a = 7.183(2) Å, b = 16.983(4) Å, c = 15.543(4) Å, β = 90.38(2)°, Z = 4, $R(wR_2)$ = 0.0603 (0.1484).

Introduction

Transition-metal imido (or nitrene, MNR) complexes have been of continuous interest.[1] Two types of imido complexes are now known. The more common complexes of metals in a high oxidation state generally have a linear imido ligand with a metal-nitrogen triple bond character (A). In contrast, some zero-valent metals (Cr, W) possess a bent imido ligand with a lone pair on the nitrogen (B).[2] For imido 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), 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).[1a] Recently we have prepared several Re-imido complexes of the type Re(≡NPh)Cl₃(PPh₃)L from the reactions of Re(≡NC₆H₅)(PPh₃)₂Cl₃, I, with small, strongly coordinating ligands (L = CO, P(OMe)₃, PMe₃) (Eq. 1).[3] However, replacement of both PPh₃ ligands in I has not been successful. Herein, we report preparation and structures of the two Re-imido isomers of Re(≡NPh)Cl₃(PMe₃)₂, which have been synthesized by replacing both PPh₃ ligands in I by PMe₃.

$$[L = PMe_3, L' = CO, P(OMe)_3]$$
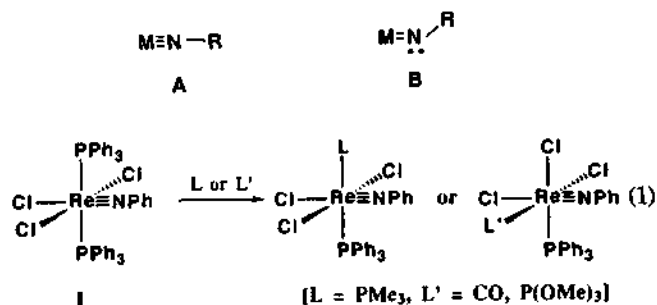
Experimental

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. Carbonylation reactions have been performed in a 60 mL of quartz pressure vessel (Kontes). 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 solvents (C₆D₆ and CDCl₃) were degassed by freeze-pump-thaw cycles before use and stored over molecular sieves under argon. Aniline was distilled over CaH₂ and stored under argon. CO (99.9%) was purchased from Union Gas Co. and used as received. Re metal, trimethylphosphine (PMe₃, 1 M in toluene), and triphenylphosphine (PPh₃) were purchased from Aldrich Co. and used as received. Re(≡NC₆H₅)(PPh₃)₂Cl₃, I[4], and Re(≡NC₆H₅)(PMe₃)(PPh₃)Cl₃[3a] were prepared by the literature methods.

¹H- and ¹³C{¹H}-NMR spectra were recorded with a Hitach 1100 60-MHz spectrometer and a Varian 200-MHz spectrometer with reference to internal solvent resonances and reported relative to tetramethylsilane. ³¹P{¹H}-NMR spectra were recorded with a Bruker AMX-500 spectrometer with reference to external 85% H₃PO₄. 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(≡NC₆H₅)(PMe₃)₂Cl₃. The compounds have been prepared by one of the following ways.

Method A. Heating (18 h) 0.60 g (0.66 mmol) of I with 6.6 mL of PMe₃ (1 M in toluene) under reflux in benzene (60 mL) gave a black green solution, and then the solvent was removed under vacuum to give green solids. The resultant solids were extracted with diethyl ether (30 mL×3), and then the diethyl ether solution was dried under vacuum to produce 0.21 g (0.39 mmol, 59%) of *mer,trans*-Re(≡NC₆H₅)(PMe₃)₂Cl₃, II. The compound II was conveniently recrystallized from benzene/hexanes. The remaining gray-green solids after the extraction by diethyl ether were dried under vacuum to give 0.046 g (0.086 mmol, 13%) of *fac,cis*-Re(≡NC₆H₅)(PMe₃)₂Cl₃, III. The compound III was also recrystallized from benzene/hexanes.

Method B. Heating (3 h) 0.36 g (0.50 mmol) of Re(≡NC₆H₅)(PMe₃)(PPh₃)Cl₃ with 5.0 mL of PMe₃ (1 M in toluene) under reflux in benzene (60 mL) gave a black green solution, and then the solvent was removed under vacuum to give green solids. The resultant solids were extracted with diethyl ether (30 mL×3), and then the diethyl ether solution was

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

	II	III
formula	$C_{12}H_{23}NP_2Cl_3Re$	$ReC_{12}H_{23}NP_2Cl_3Re$
fw	535.80	535.80
temperature, K	293	293
crystal system	monoclinic	monoclinic
space group	$P2_1$	$P2_1/n$
a, Å	10.053(1)	7.183(2)
b, Å	10.844(1)	16.983(4)
c, Å	10.058(2)	15.543(4)
β, deg	113.45(2)	90.38(2)
V, Å³	1005.9(2)	1896.0(8)
Z	2	4
d_{calc}, g cm⁻³	1.769	1.877
μ, cm⁻¹	6.586	6.988
F(000)	516	1032
no. of data collected	1829	2645
no. of reflns used, I>2 σ(I)	1641	2462
no. of params	148	172
scan range	3<2θ<50	3<2θ<50
scan type	ω-2θ	ω-2θ
Max. in Δρ (e Å³⁻)	0.94	0.87
GOF on F²	1.068	1.097
R	0.0348	0.0603
$wR_2{}^a$	0.0894	0.1484

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

dried under vacuum to produce 0.21 g (0.39 mmol, 78%) of II. The remaining gray-green solids after the extraction by diethyl ether were dried under vacuum to give 0.016 g (0.030 mmol, 6%) of III.

Compound II. ¹H NMR (CDCl₃) δ 7.297-7.769 (5H, m), 1.658 (18H, t, J_{P-H}=4.6 Hz, PMe₃). ¹³C{¹H}-NMR (CDCl₃) δ 130.09, 129.05, 120.97 (NC₆H₅), 12.82 (d, J_{P-C}=66 Hz, PMe₃). ³¹P{¹H}-NMR (CDCl₃) δ −39.34 (s). Anal. Calcd for $C_{12}H_{23}NP_2$ Cl_3Re: C, 26.90; H, 4.33; N, 2.61. Found: C, 27.19; H, 4.10; N, 2.55. Mp=215-217 ℃. IR (KBr): 2981, 2910, 1411, 1285, 1179, 1156, 1119, 948, 769, 747, 723, 696, 684, 540 cm⁻¹.

Compound III. ¹H NMR (CDCl₃) δ 7.316-7.799 (5H, m), 1.920 (18H, d, $^2J_{P-H}$=10.6 Hz, PMe₃). ¹³C{¹H}-NMR (CDCl₃) δ 130.13, 129.94, 124.22 (NC₆H₅), 19.33 (d, J_{P-C}=162 Hz, PMe₃). ³¹P{¹H}-NMR (CDCl₃) δ −33.98 (d, $^2J_{P-P}$=11.9 Hz), −37.56 (d, $^2J_{P-P}$=11.9 Hz). Anal. Calcd for $C_{12}H_{23}NP_2Cl_3Re$: C, 26.90; H, 4.33; N, 2.61. Found: C, 27.40; H, 4.31; N, 2.61. Mp=212-214 ℃. IR (KBr): 2981, 2910, 1478, 1448, 1411, 1286, 1155, 949, 770, 747, 684, 674 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 20<2θ<30°. Axial photographs were used to verify the unit cell choice. Intensities of three check reflec-

Table 2. Atomic coordinates (×10⁴) and equivalent isotropic thermal parameters (Å²×10³) for II

	x	y	z	U (eq)^a
Re	1968(1)	0	8032(1)	36(1)
CL1	−285(3)	12(13)	5916(3)	62(1)
CL2	4082(3)	22(12)	10287(3)	62(1)
CL3	530(4)	−19(13)	9486(4)	71(1)
P1	1812(10)	2235(9)	8208(9)	58(2)
P2	1768(9)	−2218(8)	8208(9)	52(2)
N1	2947(8)	194(18)	6995(8)	33(4)
C1	3778(13)	−144(15)	6161(12)	30(3)
C2	3115(24)	214(31)	4701(22)	110(4)
C3	3921(25)	194(39)	3918(25)	110(4)
C4	5200(27)	−78(43)	4384(26)	110(4)
C5	6095(28)	−151(29)	6100(26)	110(4)
C6	5292(24)	12(54)	6822(24)	110(4)
C11	2536(46)	3063(39)	7104(36)	110(12)
C12	2758(40)	2837(30)	10003(51)	99(11)
C13	−4(38)	2841(22)	7481(29)	102(13)
C21	2824(26)	−2968(24)	7324(32)	62(6)
C22	2418(35)	−2870(25)	10069(45)	78(7)
C23	−22(25)	−2877(29)	7437(49)	129(16)

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

tions were monitored after 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 y-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 0.2×0.2×0.3 mm, was used for crystal and intensity data collection. The unit cell parameters and systematic absences, 0k0 (k=2n+1), indicated two possible space groups: $P2_1$ and $P2_1/m$. A statistical analysis of intensities suggested a noncentrosymmetric space group, and the structure converged only in the space group $P2_1$. The structure was solved by the heavy atom methods. All nonhydrogen atoms were refined anisotropically. The five carbons (C2-C6) in two trimethylphosphine groups showed very high values of thermal parameters, and so they were refined with the same anisotropic displacement parameters. All hydrogen atoms were positioned geometrically and refined using a riding model.

A green crystal of III, shaped as a block, of approximate dimensions 0.2×0.3×0.3 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+l=2n+1), unambiguously indicated $P2_1/n$ as a space group. The structure was solved by the direct 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 and 3. The selected bond distances and bond angles are shown in Table 4; anisotropic thermal

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Table 3. Atomic coordinates (×10⁴) and equivalent isotropic thermal parameters ($\text{Å}^2 \times 10^3$) for III

	x	y	z	U (eq)ᵃ
Re	122(1)	1402(1)	2272(1)	34(1)
CL1	1426(5)	2450(2)	1420(3)	51(1)
CL2	2176(5)	468(3)	1553(3)	57(1)
CL3	2639(6)	1601(3)	3313(3)	58(1)
P1	−1360(5)	2477(2)	3021(2)	44(1)
P2	−1853(5)	1214(2)	1026(2)	41(1)
N1	−1105(16)	706(8)	2843(7)	46(3)
C1	−2039(19)	204(8)	3372(8)	39(3)
C2	−1003(28)	−244(10)	3932(11)	65(5)
C3	−1961(35)	−787(13)	4476(12)	81(6)
C4	−3768(36)	−856(13)	4419(12)	83(6)
C5	−4805(25)	−429(12)	3834(12)	67(5)
C6	−3913(21)	111(9)	3319(10)	53(4)
C11	212(27)	3292(11)	3241(14)	72(5)
C12	−3382(24)	2966(11)	2601(11)	64(5)
C13	−2165(25)	2158(11)	4066(10)	66(5)
C21	−2670(23)	206(10)	968(11)	58(4)
C22	−3916(22)	1796(12)	862(11)	65(5)
C23	−750(29)	1334(13)	26(11)	78(6)

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

**Table 4.** Selected Bond Distances (Å) and Bond Angles (deg)

	II	III
Bond Distances		
Re-N	1.708(7)	1.724(12)
Re-CL1	2.413(3)	2.412(4)
Re-CL2	2.414(3)	2.442(4)
Re-CL3	2.431(3)	2.442(4)
Re-P1	2.439(10)	2.416(4)
Re-P2	2.426(9)	2.413(4)
N-C1	1.45(1)	1.36(2)
Bond Angles		
RE-N-C1	158(2)	174(1)
N-RE-CL1	91.6(3)	172.1(4)
N-RE-CL2	93.8(3)	95.9(4)
N-RE-CL3	173.3(8)	97.6(4)
N-RE-P1	89.5(7)	92.4(5)
N-RE-P2	104.6(7)	91.3(4)
P1-RE-P2	165.9(1)	103.2(1)
CL1-RE-CL3	87.5(1)	88.5(2)

parameters, hydrogen atom coordinates, full bond distances and bond angles, and tables of observed and calculated structure factors are available as supplementary materials.

Results and Discussion

Preparation. *Mer,trans*-Re(≡NPh)Cl₃(PPh₃)₂, **I**, reacted with PMe₃ in a refluxing benzene to give a mixture of two stereoisomers of *mer,trans*-Re(≡NC₆H₅)(PMe₃)₂Cl₃, **II**, and *fac, cis*-Re(≡NC₆H₅)(PMe₃)₂Cl₃, **III**, both of which were recrystallized from benzene/hexanes (Eq. 2). On the basis of isolated yields, the ratio of **II** to **III** is approximately 4.5. These compounds could also be prepared from the reaction of Re(≡NC₆H₅)(PMe₃)(PPh₃)Cl₃ with PMe₃ in a refluxing benzene, in which the reaction appeared to be more stereoselective considering the ratio of the isolated products (II/III≈13) (Eq. 3). In both reactions **II** is a major product. **II** and **III** are air-stable both in solution and in the solid state.
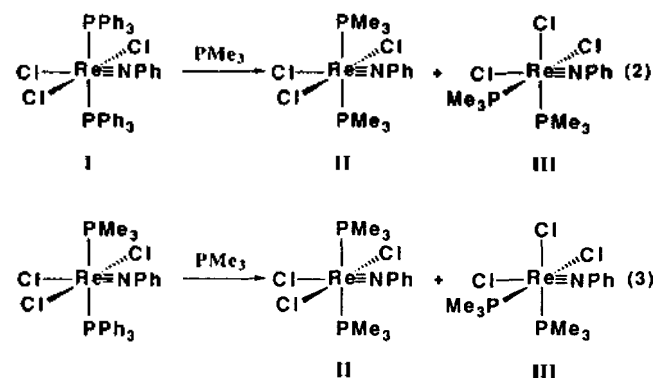
In ¹³C{H}-NMR spectra, both **II** and **III** show a doublet for P*Me₃* at 12.82 ($J_{P-C}=66$ Hz) and at 19.33 ppm ($J_{P-C}=162$ Hz), respectively, due to carbon-phosphorus couplings. In ³¹P{¹H}-NMR spectra, **II** shows a singlet for P*Me₃* at −39.34 ppm, whereas **III** exhibits two doublets at −33.98 and −37.56 ppm ($^2J_{P-P}=11.9$ Hz). The existence of two doublets for **III** in ³¹P{¹H}-NMR spectra indicates two inequivalent, *cis*-coordinated phosphorus nuclei. In the solid state structure (Figure 2), the two phosphine groups appear to be equivalent, even though the dihedral angle between a phenyl ring and an equatorial plane, defined by P1, P2, Cl2, Cl3, and Re, is 86.0(3)°. This tilt of the phenyl ring is maybe able to account for the inequvalency of the two phosphorus nuclei in solution, but we cannot give any clear explanation at this point. In ¹H NMR spectra, methyl protons of PMe₃ in **II** exhibit a triplet at 1.658 ppm ($J_{P-H}=4.6$ Hz), due to the virtual coupling by which methyl protons appear to be coupled both to its own and to the *trans*-phosphorus nucleus about equally.[7] The *trans* orientation of the two phosphine groups was confirmed by X-ray crystallography (*vide infra*). ¹H NMR spectra of **III** exhibit a doublet at 1.920 ppm ($J_{P-H}=10.6$ Hz), which indicates a *cis*-orientation of the two phosphine groups.

Formation of the two stereoisomers, *cis* and *trans*, arises a question as to how they are formed. In the previous paper we reported that the substitution of PPh₃ in **I** by PMe₃ at room temperature gave *mer,trans*-Re(NPh)(PPh₃)(PMe₃)Cl₃, a momophosphine substituted product.[3a] The bisphosphine substitution reactions for **II** and **III** turned out to require more severe reaction conditions (a refluxing benzene). Since the starting material **I** is a saturated 18-electron complex, the formation of **II** and **III** might be expected to proceed in a dissociative pathway. As described earlier, **II** and **III** could also be prepared from the reaction of Re(NPh)(PPh₃)(PMe₃)Cl₃ with PMe₃ in a refluxing benzene. It is therefore likely that **II** and **III** are formed from the five-coordinate intermediate, which is generated by dissociation of the remaining
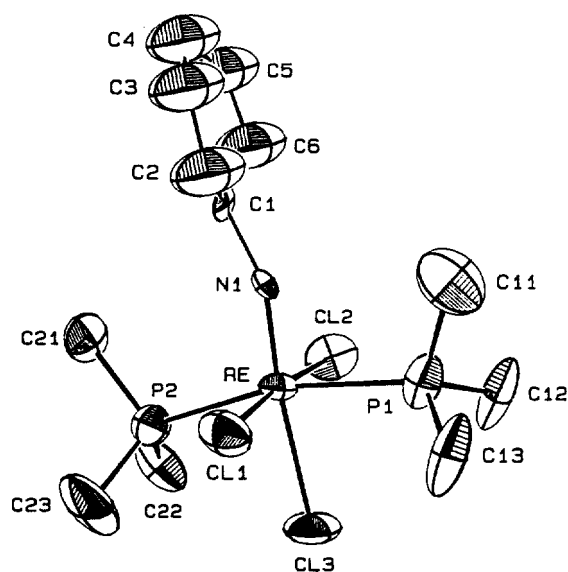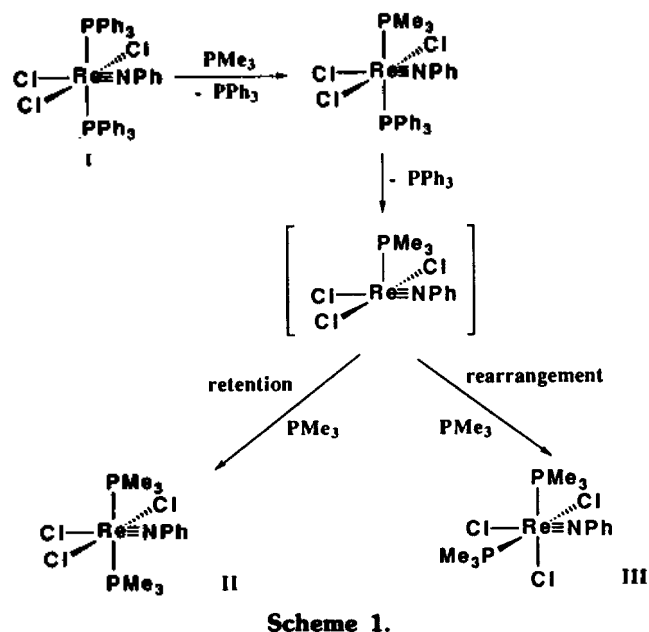
Scheme 1.

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

PPh₃ from Re(NPh)(PPh₃)(PMe₃)Cl₃. In addition, that intermediate appeared to be a little fluxional, considering the relative orientations of two phosphine ligands in **II** and **III**. In other words, **II** was formed by binding of the second PMe₃ before the intermediate rearranged and **III** was formed after the intermediate rearranged (Scheme 1). Since two PMe₃ and NPh ligands are relatively strong *trans*-influence ligands, their mutual *cis*-orientation is expected to be preferred electronically. This *cis*-preference among the three ligands maybe plays a role in determining the direction of the ligand rearrangement of the intermediate to produce the *fac*-orientation of the three Cl ligands in **III**.

Structure. Molecular structures of **II** and **III** with the atomic numbering schemes are shown in Figure 1 and 2. In both compounds the coordination sphere of the Re metal
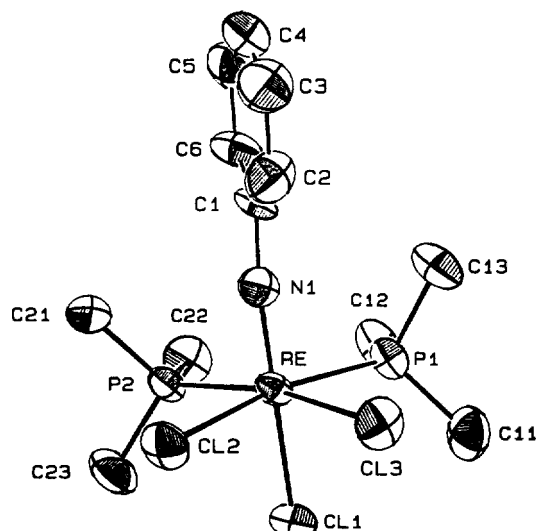

Figure 2. ORTEP drawing of III showing the atom-labeling scheme and 50% probability thermal ellipsoids.

Table 5. Bonding parameters of the Re-N-C bond

Compound	Re-N (Å)	Re-N-C (deg)	Reference
mer,trans-Re(NPh)(PPh₃)(PMe₃)Cl₃	1.711(6)	176.0(6)	3a
fac,cis-Re(NPh)(PPh₃)(P(OMe)₃)Cl₃	1.710(8)	167.9(7)	3a
mer,trans-Re(NPh)(PPh₃)₂Cl₃, **1**	1.726(6)	172.6(6)	8
mer,trans-Re(NPh)(PMe₃)₂Cl₃, **II**	1.708(7)	158(2)	this work
fac,cis-Re(NPh)(PMe₃)₂Cl₃, **III**	1.724(12)	174(1)	this work

can be described as a distorted octahedron. Compound **II** has a NPh group, three *mer*-Cl atoms and two *trans* phosphine ligands. Compound **III** has a NPh group, three *fac*-Cl atoms and two *cis*-phosphine ligands. In all compounds the equatorial plane including a Re metal is coplanar with the average displacement from the least-squares plane being less than 0.13 Å.

Of particular interest are the bonding parameters of the Re-N-C bonds. A comparison of bond distances and bond angles is given in Table 5. The Re-N bond distances appear to be relatively insensitive to the types of phosphine and to the geometries of the coordination sphere. The bond angle of Re-N-C (158(2)°) in **II** is considerably distorted from linearity, compared to other related complexes. This bond angle of Re-N-C indicates that the Re-N bond in **II** has a less triple bond character, and therefore the nitrogen atom has a less *s*-character.[1a] At this point we cannot give a clear explanation for the substantial bending of the Re-N-C bond in **II**.

In compound **III**, the Re-Cl bond (1.412(4) Å) *trans* to NPh is shorter than the other two Re-Cl bonds (1.442(4) Å) *trans* to PMe₃, which indicates that PMe₃ exerts a stronger *trans*-influence than NPh in this compound. The Re-P bond distances (2.413-2.439 Å) agree with known values (2.324-2.470 Å).[9] In addition, the bond angle (165.9(1)°) of P-Re-P in **II** also shows a severe distortion from an ideal one (180°) for a

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trans geometry.

Recently, Bergman and his coworkers reported an insertion of CO into an Ir≡N bond in Cp*Ir(≡N'Bu), (Cp*=C₅(CH₃)₅), which is the first carbonylation of a terminal imido ligand to give an isocyanate complex.[10] The results of above studies prompted us to investigate the possibility of insertion of CO into Re-nitrene bonds in our compounds. No reactions of compound II or III with CO (up to 6 atm) have been observed.

Supplementary Material Available. Tables of bond distances and bond angles, anisotropic thermal parameters, positional parameters for hydrogen atoms (6 pages); listings of observed and calculated structure factors (10 pages). Supplementary materials are available from one of the authors (S. W. Lee) upon request.

References

1. (a) Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds*; John Wiley and Sons: New York, U.S.A. 1988. (b) Chisholm, M. H.; Rothwell, I. P. In *Comprehensive Coordination Chemistry*; Wilkinson, G.; Gillard, R. D.; J. A. McCleverty, Ed.; Pergman Press: Oxford, England, 1987; Vol. 2, pp 161-188. (c) Nugent, W. A.; Haymore, B. L. *Coord. Chem. Rev.* **1980**, *31*, 123. (d) Cenini, S.; La Monica, G. *Inorg. Chim. Acta* **1976**, *18*, 279.
2. (a) Arndtsen, B. A.; Sleiman, H. F.; Chang, A. K.; McElwee-White, L. *J. Am. Chem. Soc.* **1991**, *113*, 4871. (b) Massey, S. T.; Mansour, B.; McElwee-White, L. *J. Organomet. Chem.* **1995**, *485*, 123.
3. (a) Kim, Y.-W.; Jung, J-H.; Park, H-S.; Lee, S. W. *Bull. Korean Chem. Soc.* **1994**, *15*, 891. (b) Kim, Y-W.; Jung, J-H.; Lee, S. W. *Bull. Korean Chem. Soc.* **1994**, *15*, 150.
4. Johnson, N. P.; Lock, C. J. L.; Wilkinson, G. *Inorg. Synth.* **1967**, *9*, 145.
5. Sheldrick, G. M. *Acta Cryst.* **1990**, *A46*, 467.
6. Sheldrick, G. M. *SHELXL-93*; University of Gottingen, 1993.
7. Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*; John Wiley and Sons: 2nd ed., New York, U.S.A. 1994; p 237.
8. Forellini, E.; Casellato, U. *Acta Cryst.* **1984**, *C40*, 1795.
9. Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G.; Taylor, R. *J. Chem. Soc., Dalton Trans.* **1989**, S1-S83.
10. Glueck, D. S.; Wu, J.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1991**, *113*, 2041.

Kinetics and Mechanism of Aminolysis of Phenyl Benzoates in Acetonitrile

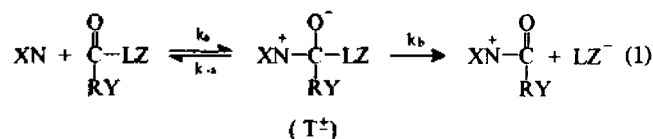**Han Joong Koh, Ho Chan Lee, Hai Whang Lee, and Ikchoon Lee**

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The kinetics and mechanism of the reactions of phenyl benzoates with benzylamines and pyrrolidine are investigated in acetonitrile. The variations of ρ_X ($\rho_{XY}>0$) and ρ_Z ($\rho_{YZ}<0$) with respect to the substituent in the substrate (σ_Y) indicate that the reactions proceed through a tetrahedral intermediate, $T^\pm$, with its breakdown in the rate determining step. The large magnitudes of ρ_Z, ρ_{XY} and ρ_{YZ} as well as the effects of secondary kinetic isotope effects involving deuterated nucleophiles are also in line with the proposed mechanism.

Introduction

The mechanism of ester aminolysis has been extensively studied. The nucleophilic reactions of a series of structurally similar amines with various esters exhibit curved Brönsted-type plots (for $\beta_{nuc}(\beta_X)$) when the basicity of the leaving group is relatively low.[1] The nonlinear plots have been interpreted in terms of a tetrahedral intermediate, $T^\pm$, along the reaction path (eq. 1 where X, Y and Z represent substituents in the nucleophile, substrate, and leaving group, respectively) and a change in the rate-limiting step from breakdown to products (k_b) of $T^\pm$ to its formation (k_a) as the amine becomes more basic.[1]

$$XN + \overset{\overset{O}{\parallel}}{\underset{\underset{RY}{|}}{C}}-LZ \underset{k_{-a}}{\overset{k_a}{\rightleftharpoons}} XN\overset{+}{-}\overset{\overset{O^-}{|}}{\underset{\underset{RY}{|}}{C}}-LZ \overset{k_b}{\longrightarrow} XN\overset{+}{-}\overset{\overset{O}{\parallel}}{\underset{\underset{RY}{|}}{C}} + LZ^- \quad (1)$$

$$(T^\pm)$$

In contrast to the generally accepted view of the past 20-30 years that the nucleophilic substitution reactions at a carbonyl group involve almost invariably the tetrahedral intermediate, it has been shown recently that some acyl transfer reactions can involve a concerted mechanism.[2] Most of these studies are, however, carried out in protic solvents, typically in aqueous solution. Recent results of aminolysis studies of esters[3] and acyl halides[4] have shown that the similar mecha-