Preparation, Structure, and Property of $Re(NAr)(PR_3)_2Cl_3$, (PR_3 = PMe_3, PEt_3, $P(OMe)_3$; Ar = C_6H_5, 2,6-*i*-Pr_2-C_6H_3)

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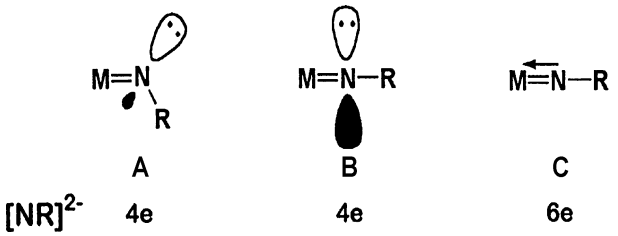
Several bisphosphine- and bisphosphite-substituted Re-imido complexes have been prepared from $Re(NPh)(PPh_3)_2Cl_3$, **1**, and $Re(N\text{-}C_6H_3\text{-}i\text{-}Pr_2)_2Cl_3(py)$, **4**. Compound **1** reacted with trimethyl phosphite ($P(OMe)_3$) to give a mixture of two isomers, *mer,trans*-$Re(NPh)(P(OMe)_3)_2Cl_3$, **2**, and *fac,cis*-$Re(NPh)(P(OMe)_3)_2Cl_3$, **2a**. In this reaction, the mer,trans-isomer is a major product. Complex **1** also reacted with triethylphosphine (PEt_3) to exclusively give *mer,trans*-$Re(NPh)(PEt_3)_2Cl_3$, **3**. Compound **4** reacted with trimethylphosphine (PMe_3) to give *mer,trans*-$Re(N\text{-}C_6H_3\text{-}i\text{-}Pr_2)(PMe_3)_2Cl_3$, **5**, which was converted to *mer*-$Re(N\text{-}C_6H_3\text{-}i\text{-}Pr_2)(PMe)(OPMe_3)Cl_3$, **6**, on exposure to air. Crystallographic data for **2**: monoclinic space group $P2_1/n$, a = 8.870(2) Å, b = 14.393(3) Å, c = 17.114(4) Å, β = 101.43(2)°, Z = 4, $R(wR_2)$ = 0.0521(0.1293). Crystallographic data for **5**: orthorhombic space group $P2_12_12_1$, a = 11.307(1) Å, b = 11.802(1) Å, c = 19.193(2) Å, Z = 4, $R(wR_2)$ = 0.0250(0.0593). Crystallographic data for **6**: orthorhombic space group $P2_12_12_1$, a = 14.036(4) Å, b = 16.486(5) Å, c = 11.397(3) Å, Z = 4, $R(wR_2)$ = 0.0261(0.0630).

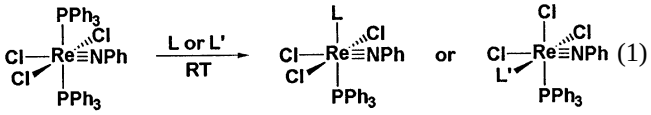
Introduction

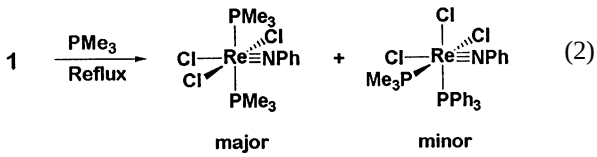
Transition-metal imido complexes have been of continuous interest.[1-6] Three general types of imido complexes are now known,[1] although Cundari's theoretical studies led to a conclusion that a minimum of eight resonance structures are required to describe the metal imido linkage.[7] The imido ligand can be considered to bond to a transition metal with one σ and either one or two π bonds. Limiting valence bond descriptions of this interaction are shown below.



Structure **A** depicts an sp^2-hybridized nitrogen leading to an M=N double bond (1σ, 1π) and a bent M-N-R linkage with the lone pair in an N(sp^2) hybrid orbital. In the closed-shell formalism, the imido dianion $[NR]^{2-}$ in **A** acts as a four-electron donor. Some zero-valent metals (Cr, W) are known to possess a bent imido ligand (**A**).[8,9] In addition, bent imido species with a formal M-N double bond are known to be more reactive than linear ones, because nucleophilic reactivity is enhanced in the bent NR ligand.[10-16] Structure **B** depicts an *sp*-hybridized nitrogen with the lone pair in an N(*p*) atomic orbital that does not participate in the *sp* hybridization. In **B**, the M=N double bond (1σ, 1π) is maintained if symmetry restrictions or an energy mismatch with available metal orbitals does not allow donation of the lone pair on the nitrogen atom to the metal. In **B**, the imido ligand acts as a formal four-electron donor. The more common complexes of metals in a high oxidation state have a linear imido ligand (**C**). Structure **C** depicts an *sp*-hybridized nitrogen leading to an M≡N triple bond (1σ, 2π) and a linear M-N-R linkage, where the nitrogen lone pair $p(\pi)$ to M(d_π) donation is very effective. In **C**, the imido liagnd acts as a formal six-electron donor. Wigley pointed out that in cases where multiple π donor ligands are present in the molecule, a molecular orbital approach is required to accurately describe imido bonding.[1]

Recently we have prepared several Re-imido complexes of the type $Re(NPh)Cl_3(PPh_3)L$ or $Re(NPh)Cl_3L_2$ from the reactions of $Re(NPh)(PPh_3)_2Cl_3$ with small, strongly coordinating ligands (L = CO, $P(OMe)_3$, PMe_3) (eq 1 and 2).[17-19] Because of our continuous interest in the complexes of this type, we tried to prepare other bisphosphine- and bisphosphite-substituted Re-imido complexes. Herein we report preparation, structure, and some properties of $Re(NAr)(PR_3)_2Cl_3$ (PR_3 = PMe_3, PEt_3, $P(OMe)_3$; Ar = C_6H_5, 2,6-*i*-Pr_2-C_6H_3).





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 manip-

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ulated 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, toluene, and tetrahydrofuran (THF) 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. 2,6-Diisopropylaniline (H_2N-C_6H_3-2,6-*i*-Pr_2) was distilled over CaH_2. CO (99.9%) was purchased from Union Gas company and use as received. Re metal, trimethylphosphine (PMe_3, 1 M in toluene), trimethyl phosphite ($P(OMe)_3$), triethylphosphine (PEt_3, 1 M in THF), triphenylphosphine (PPh_3), sodium cyclopentadienylide (NaCp; Cp = C_5H_5, 2 M in THF), thallium cyclopentadienylide (TlCp), sodium pentamethylcyclopentadienylide (NaCp*; Cp* = C_5Me_5, 0.5 M in THF), $LiBEt_3H$, and $LiBEt_3D$ were purchased from Aldrich company and used as received. Re(NPh)$(PPh_3)_2Cl_3$, **1**,[20] and Re(N-C_6H_3-*i*-$Pr_2)_2Cl_3$ (py), **4**,[21,22] were prepared by the literature methods.

^{1}H- and ^{13}C{^{1}H}-NMR spectra were recorded with a Bruker AMX 500 MHz spectrometer with reference to internal solvent resonances and reported relative to tetramethylsilane. ^{31}P{^{1}H}-NMR spectra were also recorded with a Bruker AMX 500 MHz spectrometer with reference to external 85% H_3PO_4. 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 were performed by the Korea Basic Science Center.

Preparation of Re(NPh)(P(OMe)$_3)_2Cl_3$, 2 and 2a. Heating (30 min) 2.0 g (2.2 mmol) of **1** with 1.10 mL of $P(OMe)_3$ (9.2 mmol) under reflux in benzene (60 mL) gave a green solution, and then the solvent was removed under vacuum to give green gummy solids. The resulting solids were washed with diethyl ether (2 × 25 mL) and then dried under vacuum to give 1.09 g (1.90 mmol, 87%) of a mixture of isomers, *mer,trans*-Re(NPh)$(P(OMe)_3)_2Cl_3$, **2**, and *fac,cis*-Re(NPh)-$(P(OMe)_3)_2Cl_3$, **2a**. This product mixture conveniently recrystallized from acetone-hexane. ^{1}H NMR ($CDCl_3$): δ 7.804-7.277 (5H, m, phenyl), 3.954 (18H, t, $J_{P\text{-}H}$ = 5.3 Hz, $P(OMe)_3$ for **2a**), 3.879 (18H, d, $J_{P\text{-}H}$ = 10.6 Hz, $P(OMe)_3$ for **2**). ^{13}C{^{1}H}-NMR ($CDCl_3$): δ 130.2-124.1 (phenyl), 54.4 (t, $J_{P\text{-}C}$ = 54.4 Hz, for **2**), 50.9 (d, $J_{P\text{-}C}$ = 80.5 for **2a**). ^{31}P{^{1}H}-NMR ($CDCl_3$): δ 81.7 (**2a**), 72.1 (**2**). Anal. Calcd for $C_{12}H_{23}NO_6P_2Cl_3Re$: C, 22.81; H, 3.67; N, 2.22. Found: C, 23.12; H, 3.97; N, 1.87. Mp (decomp.): 126-128 ºC. IR (KBr): 2955, 1178, 1050, 1024, 807, 779, 767, 750, 684, 527 cm^{-1}.

Preparation of mer,trans-Re(NPh)$(PEt_3)_2Cl_3$, 3. Heating (4 h) 0.80 g (0.88 mmol) of **1** with 2.0 mL (2.0 mmol) of PEt_3 (1 M in THF) under reflux in benzene (60 mL) gave a light green solution, and then the solvent was removed under vacuum to give green solids. The resulting solids were washed with hexane (3 × 25 mL) and then dried under vacuum to give 0.45 g (0.73 mmol, 83%) of **3**. This product conveniently recrystallized from benzene-hexane. ^{1}H NMR ($CDCl_3$): δ 7.738-7.263 (5H, m, phenyl), 2.210 (12H, m, PCH_2CH_3), 1.163 (18H, m, PCH_2CH_3). ^{13}C{^{1}H}-NMR ($CDCl_3$): δ 130.2-119.8 (phenyl), 14.8 (t, $J_{P\text{-}C}$ = 14.3 Hz, PCH_2CH_3), 7.4 (s, PCH_2CH_3). ^{31}P{^{1}H}-NMR ($CDCl_3$): δ -23.3 (s). Anal. Calcd for $C_{18}H_{35}NP_2Cl_3Re$: C, 34.87; H, 5.69; N, 2.26. Found: C, 35.38; H, 5.76; N, 2.02. Mp (decomp.): 117-119 ºC. IR (KBr): 2970, 2935, 2907, 1475, 1455, 1420, 1259, 1162, 780, 762, 732, 716, 691 cm^{-1}.

Preparation of mer,trans-Re(N-C_6H_3-*i*-$Pr_2)(PMe_3)_2Cl_3$, 5. To an opaque, dark green solution of benzene (60 mL) containing 0.35 g (0.48 mmol) of **4** was added 2.0 mL (2.0 mmol) of PMe_3 (1 M in toluene). The resulting solution was allowed to stir for 12 h at room temperature, and then filtered. The solvent was removed under vacuum to give yellowish green solids. The resulting solids were washed with pentane (2 × 25 mL) and then dried under vacuum to give 0.16 g (0.26 mmol, 54%) of **5**. This product mixture conveniently recrystallized from benzene-pentane. ^{1}H NMR ($CDCl_3$): δ 7.647-7.069 (3H, m, phenyl), 3.917 (2H, m, C*H*Me_2), 1.642 (18H, t, $J_{P\text{-}H}$ = 4.6 Hz, PMe_3), 1.148 (12H, d, *J* = 6.8 Hz, CH*Me*$_2$). ^{13}C{^{1}H}-NMR ($CDCl_3$): δ 152.2-125.2 (phenyl), 28.1 (*C*HMe_2), 24.3 (CH*Me*$_2$), 12.8 (t, $J_{P\text{-}C}$ = 16.8 Hz, P*Me*$_3$). ^{31}P{^{1}H}-NMR ($CDCl_3$): δ -40.7 (s). Anal. Calcd for $C_{18}H_{35}NP_2Cl_3Re$: C, 34.87; H, 5.69; N, 2.26. Found: C, 34.94; H, 5.75; N, 1.83. Mp (decomp.): 207-209 ºC. IR (KBr): 2955, 2912, 2867, 1587, 1414, 1359, 1284, 954, 856, 804, 762, 745, 675 cm^{-1}.

Formation of mer-Re(N-C_6H_3-*i*-$Pr_2)(PMe_3)(OPMe_3)Cl_3$, 6. When the solution of benzene-pentane containing **5** was allowed to be in contact with air for 72 h, **5** slowly transformed to **6.** ^{1}H-NMR ($CDCl_3$): δ 7.583-7.026 (3H, m, phenyl), 3.926 (2H, m, C*H*Me_2), 1.709 (9H, d, $J_{P\text{-}H}$ = 13.0 Hz, OP*Me*$_3$), 1.547 (9H, $J_{P\text{-}H}$ = 16.0 Hz, P*Me*$_3$), 1.165 (12H, d, *J* = 6.8 Hz, CH*Me*$_2$). ^{13}C{^{1}H}-NMR ($CDCl_3$): δ 140.1-124.7 (phenyl), 28.1 (*C*HMe_2), 24.3 (CH*Me*$_2$), 16.4 (d, $J_{P\text{-}C}$ = 71.1 Hz, OP*Me*$_3$), 15.3 (d, $J_{P\text{-}C}$ = 35.5 Hz, P*Me*$_3$). ^{31}P{^{1}H}-NMR ($CDCl_3$): δ 65.3 (d, $J_{P\text{-}P}$ = 8.5 Hz, O*P*Me_3), -39.5 (d, $J_{P\text{-}P}$ = 8.5 Hz, *P*Me_3). Anal. Calcd for $C_{18}H_{35}NOP_2Cl_3Re$: C, 33.99; H, 5.55; N, 2.20. Found: C, 33.91; H, 5.78; N, 1.94. Mp (decomp.): 127-129 ºC. IR (KBr): 2965, 2925, 2869, 1461, 1435, 1362, 1295, 1107 (P=O), 1004, 957, 866, 756, 679 cm^{-1}.

X-ray Structure Determination. All X-ray data were collected with use of either an Enraf-Nonius CAD4 diffractometer (for **2** and **6**) or an Mac Sciences MXC diffractometer (for **5**), both of which are equipped with an 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 25 reflections in the range 20.0º < 2θ < 30.0º. Three check reflections were measured every 100 reflections throughout data collection and showed no significant variations in intensity. Intensity data were corrected for Lorenz and polarization effects. Decay corrections were also made. The intensity data were empirically corrected with ψ-scan data. All calculations were

Table 1. X-ray data collection and structure refinement

	2	5	6
formula	$C_{12}H_{23}NO_6P_2Cl_3Re$	$C_{18}H_{35}NP_2Cl_3Re$	$C_{18}H_{35}NOP_2Cl_3Re$
fw	631.80	619.96	635.96
temperature, K	293	293	293
crystal system	monoclinic	orthorhombic	orthorhombic
space group	$P2_1/n$	$P2_12_12_1$	$P2_12_12_1$
a, Å	8.870(2)	11.307(1)	14.036(4)
b, Å	14.393(3)	11.802(1)	16.486(5)
c, Å	17.114(4)	19.193(2)	11.397(3)
β, deg	101.43(2)		
V, Å^3	2141.5(8)	2561.2(4)	2637(1)
Z	4	4	4
d_{cal}, g cm^{3-}	1.960	1.608	1.602
μ, mm^{-1}	6.224	5.185	5.041
F(000)	1224	1224	1256
No. of unique reflns	3552	2472	2058
No. of reflns with I > 2σ(I)	3355	2428	2030
No. of params refined	227	226	236
2θ range (º)	3-50	4-50	3-50
scan type	ω-2θ	ω-2θ	ω-2θ
Max. in Δρ (e Å^{-3})	0.98	0.88	0.98
GOF on F^2	1.086	1.046	1.008
R	0.0521	0.0250	0.0261
wR_2[a]	0.1293	0.0593	0.0630

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

carried out with use of the SHELXS-86 and SHELXL-93 programs.[23,24]

A light green crystal of **2**, shaped as a block, of approximate dimensions $0.3 \times 0.3 \times 0.4$ mm^3, was used for crystal and intensity data collection. The unit cell parameters and systematic absences, *h*0*l* ($h + l = 2n + 1$) and 0*k*0 ($k = 2n + 1$), unambiguously indicated $P2_1/n$ as a space group. The structure was solved by the heavy atom method. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were generated in idealized positions and refined using a riding model.

A green crystal of **5**, shaped as a block, of approximate dimensions $0.2 \times 0.3 \times 0.5$ mm^3, was used for crystal and intensity data collection. The unit cell parameters and systematic absences, *h*00 ($h = 2n + 1$), 0*k*0 ($k = 2n + 1$), and 00*l* ($l = 2n + 1$), unambiguously indicated $P2_12_12_1$ as a space group. The structure was solved by the heavy atom method. Five (C13-C17) out of six carbon atoms in the two trimethylphosphine ligands exhibited a structural disorder and the best fit was obtained by considering the carbon atoms to be distributed over two positions with the site occupation factors of 0.54 : 0.46 (C13-C17 : C13A-C17A). The other non-hydrogen atoms were refined anisotropically. All hydrogen atoms were generated in idealized positions and refined using a riding model.

Table 2. Atomic coordinates (×10^4) and equivalent isotropic displacement parameters (Å^3×10^3) for **2**

	x	y	z	*U*(eq)[a]
Re	222(1)	1151(1)	2490(1)	27(1)
Cl(1)	-1447(2)	740(2)	3390(1)	45(1)
Cl(2)	289(3)	2676(1)	3102(1)	45(1)
Cl(3)	29(3)	-448(1)	2067(1)	48(1)
P(1)	2455(2)	730(1)	3522(1)	34(1)
P(2)	-2117(2)	1495(1)	1525(1)	34(1)
O(1)	3403(7)	-69(5)	3232(4)	55(2)
O(2)	2143(7)	320(4)	4342(3)	47(1)
O(3)	3658(7)	1521(4)	3869(3)	51(2)
O(4)	-3741(8)	1124(4)	1631(4)	50(2)
O(5)	-1837(8)	1168(4)	692(3)	48(2)
O(6)	-2518(7)	2558(4)	1360(3)	48(1)
N	1237(7)	1489(4)	1779(3)	31(1)
C(1)	1862(8)	1745(5)	1142(4)	33(2)
C(2)	1760(13)	1123(6)	505(5)	53(2)
C(3)	2298(13)	1405(8)	-155(6)	63(3)
C(4)	2925(12)	2261(10)	-188(6)	73(3)
C(5)	3019(11)	2880(7)	429(7)	62(3)
C(6)	2511(10)	2626(6)	1124(5)	47(2)
C(11)	4830(11)	-408(8)	3708(7)	69(3)
C(12)	1695(14)	909(7)	4927(5)	59(3)
C(13)	4305(12)	2101(8)	3326(7)	75(3)
C(21)	-4100(14)	150(7)	1704(7)	67(3)
C(22)	-2856(15)	1409(8)	-51(6)	78(4)
C(23)	-3240(11)	3089(6)	1900(5)	53(2)

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

A green crystal of **6**, shaped as a block, of approximate dimensions $0.3 \times 0.4 \times 0.4$ mm^3, was used for crystal and intensity data collection. The unit cell parameters and systematic absences, *h*00 ($h = 2n + 1$), 0*k*0 ($k = 2n + 1$), and 00*l* ($l = 2n + 1$), unambiguously indicated $P2_12_12_1$ as a space group. The structure was solved by the heavy atom method. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were generated in idealized positions and refined using a riding model.

Final atomic positional parameters for non-hydrogen atoms for are shown in Tables 2-4. The selected bond distances and bond angles are shown in Tables 5 and 6.

Results and Discussion

Preparation. Compound **1** reacts with $P(OMe)_3$ in a refluxing benzene to give a mixture of two isomers, *mer,trans*-$Re(NPh)(P(OMe)_3)_2Cl_3$, **2**, and *fac,cis*-$Re(NPh)(P(OMe)_3)_2Cl_3$, **2a**, approximately in a ratio of 9 : 1 on the basis of ^{1}H NMR peak intensities (eq 3). This reaction is therefore more stereoselective, compared to that employed for preparation of a PMe_3 analogue, in which the corresponding product ration is

Table 3. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å$^3 \times 10^3$) for **5**

	x	y	z	U(eq)[a]
Re	1510(1)	636(1)	8759(1)	35(1)
Cl(1)	424(2)	2426(2)	8729(2)	64(1)
Cl(2)	231(3)	287(2)	9731(2)	81(1)
Cl(3)	2518(3)	1438(2)	7771(1)	65(1)
P(1)	2878(2)	1690(2)	9495(1)	58(1)
P(2)	-76(3)	-55(3)	8008(2)	74(1)
N(1)	2252(5)	-636(5)	8792(3)	35(1)
C(1)	2827(6)	-1690(6)	8795(4)	38(2)
C(2)	3727(7)	-1896(7)	8306(4)	45(2)
C(3)	4239(9)	-2977(9)	8311(5)	58(3)
C(4)	3944(9)	-3766(8)	8789(6)	63(2)
C(5)	3085(10)	-3548(8)	9279(6)	62(3)
C(6)	2506(8)	-2508(7)	9291(5)	49(2)
C(7)	4119(9)	-1043(9)	7787(5)	62(3)
C(8)	5463(10)	-830(9)	7832(6)	77(3)
C(9)	3746(14)	-1338(14)	7059(6)	115(5)
C(10)	1618(10)	-2281(8)	9866(5)	62(3)
C(11)	755(10)	-3256(11)	9956(7)	94(4)
C(12)	2224(13)	-2036(16)	10542(6)	121(6)
C(13)	2372(29)	2404(27)	10251(14)	93(9)
C(14)	3565(32)	2961(31)	9040(17)	115(11)
C(15)	4133(28)	809(27)	9725(16)	96(9)
C(13A)	2512(21)	1723(20)	10412(11)	81(6)
C(14A)	2986(27)	3184(24)	9307(14)	102(8)
C(15A)	4333(22)	1233(23)	9418(13)	91(7)
C(16)	349(22)	134(20)	7001(11)	53(5)
C(17)	-1607(28)	195(28)	8471(16)	102(9)
C(16A)	-181(22)	221(21)	7157(11)	80(6)
C(17A)	-1468(21)	598(19)	8058(12)	89(6)
C(18)	-226(14)	-1568(12)	8092(7)	98(4)

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

Table 4. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å$^3 \times 10^3$) for **6**

	x	y	z	*U*(eq)[a]
Re	548(1)	1243(1)	8373(1)	40(1)
Cl(1)	1014(2)	-178(2)	8570(3)	66(1)
Cl(2)	-784(2)	785(2)	7230(3)	68(1)
Cl(3)	2093(2)	1630(2)	9118(3)	63(1)
P(1)	153(2)	2586(2)	7744(2)	49(1)
P(2)	1958(2)	848(2)	5946(2)	56(1)
O(2)	1247(5)	1220(4)	6763(5)	62(2)
N(1)	12(5)	1322(4)	9687(6)	47(2)
C(1)	-389(6)	1334(6)	10826(7)	51(2)
C(2)	-108(7)	1913(7)	11651(9)	60(3)
C(3)	-464(11)	1831(10)	12769(11)	105(5)
C(4)	-1095(13)	1216(11)	13061(12)	138(7)
C(5)	-1400(11)	679(10)	12230(11)	106(5)
C(6)	-1061(8)	704(7)	11107(9)	63(3)
C(7)	-1417(8)	126(7)	10179(11)	67(3)
C(8)	-2426(12)	386(9)	9807(17)	121(6)
C(9)	-1500(12)	-729(8)	10606(14)	108(5)
C(10)	544(8)	2593(7)	11338(9)	67(3)
C(11)	69(11)	3446(7)	11534(12)	92(4)
C(12)	1462(8)	2545(9)	12049(13)	93(4)
C(13)	-963(9)	2923(7)	8354(13)	87(4)
C(14)	983(10)	3384(7)	8053(14)	94(4)
C(15)	-40(11)	2662(7)	6170(10)	82(4)
C(16)	2860(9)	268(9)	6586(13)	104(5)
C(17)	1351(12)	194(10)	5003(16)	136(7)
C(18)	2488(14)	1612(9)	5085(17)	161(10)

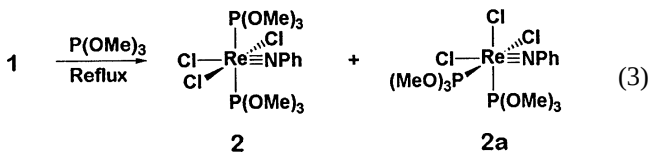
Equivalent isotropic *U* defined as one third of the trace of the orthogonalized U_{ij} tensor.

4.6 : 1.[19] Several attempts to separate **2a** from the product mixture have not been successful. This mixture, however, has crystallized only in the *mer,trans*-Re(NPh)(P(OMe)$_3$)$_2$Cl$_3$ (**2**). Variable-temperature (20, 30, 40 , 50 °C in $CDCl_3$) ^{1}H-NMR spectra of **2** show that the intensity ratio of 9:1 remains intact and there is almost no change in chemical shifts of P(OMe)$_3$ protons.

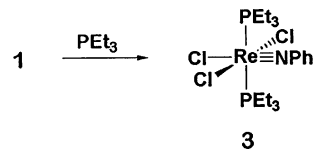
In ^{1}H NMR spectra, methyl protons of P(OMe)$_3$ in **2** exhibit a sharp triplet at δ 3.954, analogous to the PMe$_3$ analogue,[19] because of their virtual coupling to the two strongly coupled *trans* phosphorus nuclei ($J_{P\text{-}H}$ = 5.3 Hz).[25] ^{1}H NMR spectra of **2a** show a sharp doublet at δ 3.879 ($J_{P\text{-}H}$ = 10.6 Hz), which indicates a *cis*-orientation of the two P(OMe)$_3$ ligands.

Compound **1** also reacts with PEt$_3$ in a refluxing benzene to exclusively give *mer,trans*-Re(NPh)(PEt$_3$)$_2$Cl$_3$, **3** in 83% yield (eq 4). ^{13}C{^{1}H}-NMR spectra of **3** exhibit a triplet at δ 14.8 ($J_{P\text{-}C}$ = 14.3 Hz), owing to the virtual coupling of the carbon nucleus to the two *trans* phosphorus nuclei.[25-31] P{^{1}H}-NMR spectra of **3** exhibit a singlet at δ -23.3 as expected. The NMR data mentioned above indicate that the two PEt$_3$ ligands are placed *trans* to each other in **3**.

Compound **4** reacts with PMe$_3$ in benzene at room temperature to give *mer,trans*-Re(N-C$_6$H$_3$-*i*-Pr$_2$)(PMe$_3$)$_2$Cl$_3$, **5**, in moderate yield (eq 5). The Re metal has been formally



(3)



(4)

Table 5. Selected bond distances (Å) and bond angles (°) in **2**

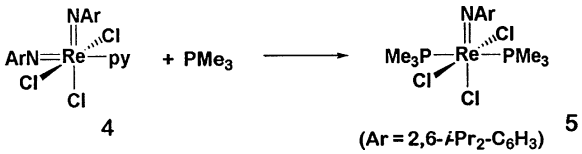
Re-N	1.721(6)	Re-Cl(3)	2.408(2)	Re-Cl(1)	2.411(2)
Re-Cl(2)	2.427(2)	Re-P(2)	2.433(2)	Re-P(1)	2.453(2)
P(1)-O(1)	1.562(6)	P(1)-O(3)	1.593(6)	P(1)-O(2)	1.597(5)
P(2)-O(5)	1.567(6)	P(2)-O(4)	1.580(7)	P(2)-O(6)	1.583(5)
N-C(1)	1.368(9)				
N-Re-Cl3	94.2(2)	N-Re-Cl1	173.72(19)	Cl3-Re-Cl1	86.68(8)
N-Re-Cl2	94.5(2)	Cl3-Re-Cl2	171.09(7)	Cl1-Re-Cl2	84.94(8)
N-Re-P2	87.6(2)	Cl3-Re-P2	89.43(7)	Cl1-Re-P2	86.22(7)
Cl2-Re-P2	93.04(7)	N-Re-P1	96.8(2)	Cl3-Re-P1	88.85(7)
Cl1-Re-P1	89.45(7)	Cl2-Re-P1	88.03(7)	P2-Re-P1	175.44(6)
O1-P1-O3	106.3(4)	O1-P1-O2	101.8(3)	O3-P1-O2	99.0(3)
O5-P2-O4	108.4(4)	O5-P2-O6	101.4(3)	O4-P2-O6	99.7(3)
C1-N-Re	172.4(5)				

Table 6. Selected bond distances (Å) and bond angles (°) in **5** and **6**

Compound **5**		Compound **6**	
Re(1)-N(1)	1.721(6)	Re(1)-N(1)	1.680(7)
Re(1)-Cl(1)	2.445(2)	Re(1)-Cl(1)	2.443(2)
Re(1)-Cl(2)	2.396(2)	Re(1)-Cl(2)	2.401(3)
Re(1)-Cl(3)	2.406(2)	Re(1)-Cl(3)	2.414(3)
Re(1)-P(1)	2.436(3)	Re(1)-P(1)	2.393(3)
Re(1)-P(2)	2.441(3)	Re(1)-O(2)	2.081(6)
N(1)-C(1)	1.403(9)	N(1)-C(1)	1.416(11)
		P(2)-O(2)	1.496(6)
N(1)-Re(1)-Cl(2)	96.6(2)	N(1)-Re(1)-Cl(2)	99.1(3)
N(1)-Re(1)-Cl(3)	98.1(2)	N(1)-Re(1)-Cl(3)	94.0(3)
Cl(2)-Re(1)-Cl(3)	165.25(8)	Cl(2)-Re(1)-Cl(3)	166.74(10)
N(1)-Re(1)-P(1)	96.6(2)	N(1)-Re(1)-P(1)	95.3(3)
Cl(2)-Re(1)-P(1)	91.11(11)	P(1)-Re(1)-Cl(2)	87.02(10)
Cl(3)-Re(1)-P(1)	87.42(10)	P(1)-Re(1)-Cl(3)	93.99(10)
N(1)-Re(1)-P(2)	95.1(2)	N(1)-Re(1)-O(2)	176.4(3)
Cl(2)-Re(1)-P(2)	87.69(13)	O(2)-Re(1)-Cl(2)	83.3(2)
Cl(3)-Re(1)-P(2)	90.80(11)	O(2)-Re(1)-Cl(3)	83.8(2)
P(1)-Re(1)-P(2)	168.36(10)	O(2)-Re(1)-P(1)	82.08(19)
N(1)-Re(1)-Cl(1)	178.7(2)	N(1)-Re(1)-Cl(1)	96.4(3)
Cl(2)-Re(1)-Cl(1)	82.15(9)	Cl(2)-Re(1)-Cl(1)	87.49(11)
Cl(3)-Re(1)-Cl(1)	83.10(9)	Cl(3)-Re(1)-Cl(1)	88.88(10)
P(1)-Re(1)-Cl(1)	83.76(9)	P(1)-Re(1)-Cl(1)	167.73(10)
P(2)-Re(1)-Cl(1)	84.61(10)	O(2)-Re(1)-Cl(1)	86.4(2)
C(1)-N(1)-Re(1)	177.5(6)	C(1)-N(1)-Re(1)	175.1(7)
		P(2)-O(2)-Re(1)	150.5(4)

reduced from Re(+7) in **4** to Re(+5) in **5**. It is worth noting that the strongly bound imido ligand (N-C_6H_3-*i*-Pr_2) has been replaced during the reaction. Unfortunately, we cannot give an explanation for these reactivities, the imido abstraction and the Re metal reduction.

In ^{1}H NMR spectra of **5**, methyl protons of PMe_3 exhibit a triplet at δ 1.642 ($J_{P\text{-}H}$ = 4.6 Hz), because of their virtual coupling to the two *trans* phosphorus nuclei. $^{13}C\{^1H\}$-NMR spectra of **5** exhibit a triplet at δ 12.8 ($J_{P\text{-}C}$ = 66.8 Hz), also because of the virtual coupling of the carbon nucleus to the



(5)

two phosphorus nuclei.[25] As expected, $^{31}P\{^1H\}$-NMR spectra of **5** exhibit a singlet at δ -40.7.

Structure. Molecular structures with their atomic numbering schemes for **2**, **5**, and **6** are shown in Figures 1-3. The coordination sphere of the Re metal in **2** can be described as a slightly distorted octahedron. Compound **2** has an NPh group, three *mer*-Cl atoms, and two *trans*-$P(OMe)_3$ ligands. The equatorial plane, defined by Re, N, Cl1, Cl2, and Cl3, is nearly planar with the average atomic displacement from the least-squares plane not exceeding 0.074 Å. The dihedral

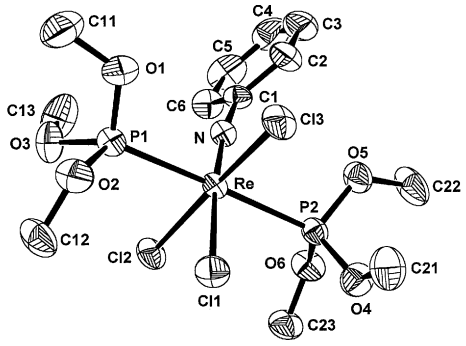


Figure 1. *ORTEP* drawing[28] of **2** showing the atom-labeling scheme and 50% probability thermal ellipsoids.

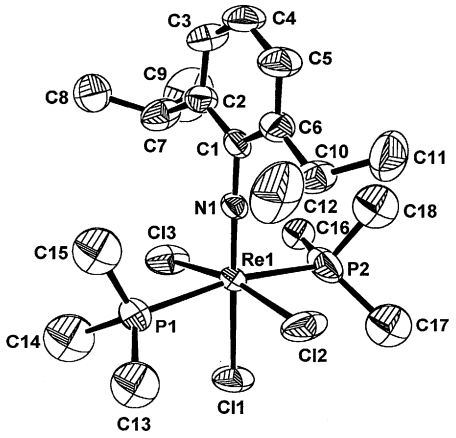


Figure 2. *ORTEP* drawing of **5**.

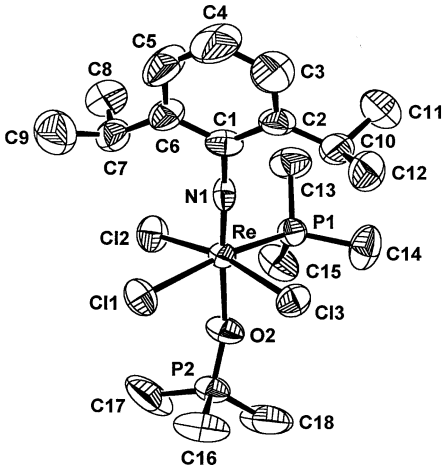


Figure 3. *ORTEP* drawing of **6**.

angle between the equatorial plane and the imido phenyl ring (C1-C6) is 19.0(4)°.

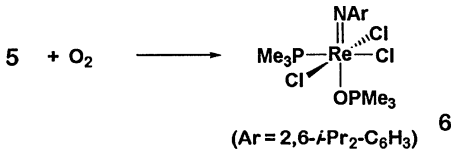
The coordination sphere of the Re metal in **5** can also be described as a slightly distorted octahedron. Compound **5** has an NAr group, three *mer*-Cl atoms, and two *trans*-PMe_3 groups. The equatorial plane, defined by Re, N1, Cl1, Cl2, and Cl3, is essentially planar with the average atomic displacement of 0.002 Å.

The coordination sphere of the Re metal in **6** can be described as a slightly distorted octahedron. Compound **6** has an NAr group, three *mer*-Cl atoms, and one PMe_3 group *trans* to Cl, and one $OPMe_3$ group *trans* to the imido ligand (NAr). The equatorial plane, defined by P1, Cl1, Cl2, and Cl3, is nearly planar with the average atomic displacement of 0.016 Å. The Re metal lies 0.258 Å above this plane.

Of particular interest are the bonding parameters of the Re-N-C bond. The Re-N-C bond angles of 172.4(5)°-177.5(6)° in **2**, **5**, and **6**, are 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.[1] These angles, therefore, indicate that the imido groups in **2**, **5**, and **6**, are linear and the Re-N bonds have a triple bond character with an *sp*-hybrid nitrogen. The Re-N bond distance of 1.680(7)-1.721(6) Å are also consistent with those found for aryl imido ligands coordinated to rhenium.[3] All the Re-P and Re-C bond distances are within the ranges for known Re(V) complexes.[26]

Property. Any sign of reaction has not been observed in reactions of **2** with mild alkylating reagents such as $ZnMe_2$, $ZnEt_2$, $AlMe_3$, and $AlEt_3$. Moreover, **2** does not react with strong carbon nucleophiles such as LiCp, NaCp, TlCp, NaCp* (Cp = C_5H_5, Cp* = C_5Me_5) and Grignard reagents (MeMgBr, EtMgBr) even under vigorous conditions (refluxing toluene). Compound **2** is also inert toward hydrides ($LiBEt_3H$, $LiBEt_3D$). In constrast to **2**, compound **5** reacts with Grignard reagents, although it does not react ZnR_2, AlR_3, MCp (M = Li, Cp, Tl), NaCp*, or hydrides. Unfortunately, reactions of **5** with RMgBr (R = Me, Et) gave too many intractable species and therefore we could not obtain meaningful spectral data.

Compound **5** is gradually oxidized to *mer*-Re(N-C_6H_3-*i*-Pr_2)(PMe_3)($OPMe_3$)Cl_3, **6**, when the recrystallization of **5** is attempted from benzene-pentane (eq 6). It is interesting to note that only one of the both PMe_3 ligands in **5** has been converted to the corresponding phosphine oxide ($OPMe_3$) and the mutual orientation of the phosphines has also been changed from *trans* to *cis*. If the Re metal is thought of as having a formal oxidation state of +5 and if the imido group is thought of as acting as a four-electron donor, then **5** can be described as a saturated, 18-electron complex, and therefore this reaction (**5** → **6**) is likely to involve a dissociative fashion. In addition, the intermediate, probably formed by PMe_3 dissociation, seems to have undergone pseudo-rotation, considering the *cis* orientation of the PMe_3 and $OPMe_3$ ligands in **6**. In order to get some insight into the mechanism for the formation of **6**, compound **5** has been treated with excess (10 fold) O=PPh_3, but no reaction has occurred.



(6)

In ^{1}H NMR spectra of **6**, methyl protons of $OPMe_3$ exhibit a doublet at δ 1.709 ($J_{P\text{-}H}$ = 13.0 Hz), and those of PMe_3 a doublet at δ 1.547 ($J_{P\text{-}H}$ = 16.0 Hz). In ^{13}C{^{1}H}-NMR spectra of **6**, the $OPMe_3$ carbons exhibit a doublet at δ 16.4 ($J_{P\text{-}C}$ = 71.1 Hz) and PMe_3 carbons also a doublet at δ 15.3 ($J_{P\text{-}C}$ = 35.5 Hz). As expected, ^{31}P{^{1}H}-NMR spectra of **6** exhibit two phosphorus resonances at δ 65.3 (d, $J_{P\text{-}P}$ = 8.5 Hz) for $OPMe_3$ and δ -39.5 (d, $J_{P\text{-}P}$ = 8.5 Hz) for PMe_3. The strong IR band at 1107 cm^{-1} is assigned to the P=O bond in $OPMe_3$.

Recently, Bergman and his coworkers reported an insertion of CO into an Ir≡N bond in Cp*Ir(≡N^{t}Bu), which is the first carbonylation of a terminal imido ligand to give an isocyanate complex.[27] These results prompted us to investigate the possibility of the CO insertion into Re-imido bonds in

our compounds. However, no reactions of **2, 3**, or **5** with CO have been observed.

In summary, several bisphosphine- and bisphosphite-substituted Re-imido complexes have been prepared from Re(NPh)-$(PPh_3)_2Cl_3$, **1**, and Re(N-C_6H_3-*i*-$Pr_2)_2Cl_3$(py), **4**. Vigorous reaction conditions (refluxing benzene solutions) are required for reactions of **1** with $P(OMe)_3$ or PEt_3, whereas mild conditions (room-temperature benzene solutions) for reactions of **4** with PMe_3. All the products are air-stable in the solid state, but they are air-sensitive in solution. For example, **5** is converted to **6** on exposure to air during recrystallization and therefore the contact of solutions of the products with air should be avoided. Compound **2** is remarkably inert to carbon nucleophiles (ZnR_2: R = Me, Et; AlR_3: R = Me, Et; RMgBr: R = Me, Et; MCp: M = Li, Na, Tl; NaCp*) and hydrides ($LiBEt_3H$, $LiBEt_3D$).

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Supplementary Material Available. Tables of bond distances and bond angles, anisotropic thermal parameters, positional parameters for hydrogen atoms (12 pages); listings of observed and calculated structure factors (19 pages). Supplementary materials are available from one of the authors (S.W. Lee) upon request.

References

1. Wigley, D. E. *Prog. Inorg. Chem.* **1994**, *42*, 239.
2. Lin, Z.; Hall, M. B. *Coord. Chem. Rev.* **1993**, *123*, 149.
3. Nugent, W. A. *Metal-Ligand Multiple Bonds*; John Wilely and Sons: New York, 1988.
4. Chisholm, M. H.; Rothwell, I. P. *Comprehensive Coordination Chemistry*; Wilkinson, G.; Gillard R. D.; McCleverty, J. A., Pergamon: Oxford, England, 1987; Vol. 2, p 161.
5. Nugent, W. A.; Haymore, B. L. *Coord. Chem. Rev.* **1980**, *31*, 123.
6. Cenini, S.; La Monica, G. *Inorg. Chim. Acta* **1976**, *18*, 279.
7. Cundari, T. R. *J. Am. Chem. Soc.* **1992**, *114*, 7879.
8. Massey, S. T.; Mansour, B.; McElwee-White, L. *J. Organomet. Chem.* **1995**, *485*, 123.
9. Arndtsen, A.; Sleiman, H. F.; Chang, A. K.; McElwee-White, L. *J. Am. Chem. Soc.* **1991**, *113*, 4871.
10. Saravanamuthu, A.; Ho, D. M.; Kerr, M. E.; Fitzgerald, C.; Bruce, M. R. M. *Inorg. Chem.* **1993**, *32*, 2202.
11. Bradley, D. C.; Hodge, S. R.; Runnacles, J. D.; Hughes, M.; Mason, J.; Richard, R. L. *J. Chem. Soc., Dalton Trans.* **1992**, 1663.
12. Minelli, M.; Carson, M. R.; Whisenhunt, D. W.; Inhof, W.; Hutter, G. *Inorg. Chem.* **1990**, *29*, 4801.
13. Sloan, O. D.; Thornton, P. *Polyhedron* **1988**, *7*, 329.
14. Goeden, G. V.; Haymore, B. L. *Inorg. Chem.* **1983**, *22*, 157.
15. Nugent, W. A.; Harlow, R. L.; McKinney, R. J. *J. Am. Chem. Soc.* **1979**, *101*, 7265.
16. Haymore, B. L.; Maatta, E. A.; Wentworth, R. A. *J. Am. Chem. Soc.* **1979**, *101*, 2063.
17. Kim, Y.-W.; Jung, J.-H.; Park, H.-S.; Lee, S. W. *Bull. Korean Chem. Soc.* **1994**, *15*, 891.
18. Kim, Y.-W.; Jung, J.-H.; Lee, S. W. *Bull. Korean Chem. Soc.* **1994**, *15*, 150.
19. Park, B.-G.; Kim, Y.-W.; Jung, G.-S.; Park, H.-S.; Lee, S. W. *Bull. Korean Chem. Soc.* **1995**, *16*, 835.
20. Jhonson, N. P.; Lock, C. J.; Wilkinson, G. *Inorg. Synth.* **1967**, *9*, 145.
21. Horton, A. D.; Schrock, R. R. *Polyhedron* **1988**, *7*, 1841.
22. Toreki, R.; Schrock, R. R.; Davis, W. M. *J. Am. Chem. Soc.* **1992**, *114*, 3367.
23. Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467.
24. Sheldrick, G. M. *SHELXL-93*; University of Göttingen: 1993.
25. Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*; 2nd ed.; John Wilely and Sons: New York, 1994; p 237.
26. Orpen, A. G.; Brammer, L.;. Allen, F. H;. Kennard, O.; Watson, D. G.; Taylor, R. *J. Chem. Soc., Dalton Trans.* **1989**, *S*1.
27. Glueck, D. S.; Wu, J.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1991**, *113*, 2041.
28. Farrugia, L. J. *ORTEP-3 for Windows*; University of Glasgow: 1997.