

Preparation, Structure, and Property of $\text{Re}(\text{NAr})(\text{PR}_3)_2\text{Cl}_3$, ($\text{PR}_3 = \text{PMe}_3, \text{PEt}_3, \text{P}(\text{OMe})_3$; $\text{Ar} = \text{C}_6\text{H}_5, 2,6\text{-}i\text{-Pr}_2\text{-C}_6\text{H}_3$)

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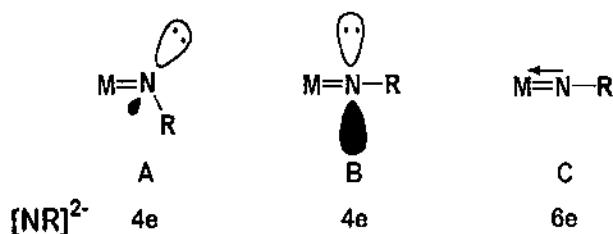
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Several bisphosphine- and bisphosphite-substituted Re-imido complexes have been prepared from $\text{Re}(\text{NPh})(\text{PPh}_3)_2\text{Cl}_3$, **1**, and $\text{Re}(\text{N-C}_6\text{H}_3\text{-}i\text{-Pr}_2)\text{Cl}_3(\text{py})$, **4**. Compound **1** reacted with trimethyl phosphite ($\text{P}(\text{OMe})_3$) to give a mixture of two isomers, *mer,trans*- $\text{Re}(\text{NPh})(\text{P}(\text{OMe})_3)_2\text{Cl}_3$, **2**, and *fac,cis*- $\text{Re}(\text{NPh})(\text{P}(\text{OMe})_3)_2\text{Cl}_3$, **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*- $\text{Re}(\text{NPh})(\text{PEt}_3)_2\text{Cl}_3$, **3**. Compound **4** reacted with trimethylphosphine (PMe_3) to give *mer,trans*- $\text{Re}(\text{N-C}_6\text{H}_3\text{-}i\text{-Pr}_2)(\text{PMe}_3)_2\text{Cl}_3$, **5**, which was converted to *mer*- $\text{Re}(\text{N-C}_6\text{H}_3\text{-}i\text{-Pr}_2)(\text{PMe})(\text{OPMe}_3)\text{Cl}_3$, **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, $\beta = 101.43(2)^\circ$, $Z = 4$, $R(wR_2) = 0.0521(0.1293)$. 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

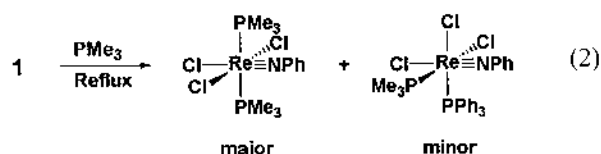
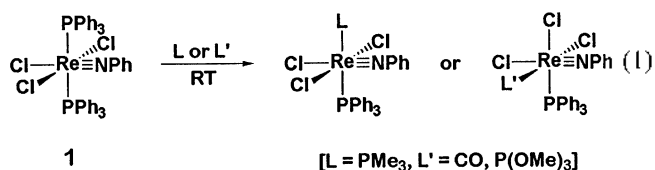
Transition-metal imido complexes have been of continuous interest.¹⁻⁶ Three general types of imido complexes are now known,¹ although Cundari's theoretical studies led to a conclusion that a minimum of eight resonance structures are required to describe the metal imido linkage.⁷ The imido ligand can 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 $\text{M}=\text{N}$ double bond ($1\sigma, 1\pi$) and a bent $\text{M}-\text{N}-\text{R}$ linkage with the lone pair in an $\text{N}(sp^2)$ hybrid orbital. In the closed-shell formalism, the imido dianion $[\text{NR}]^{2-}$ 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 $\text{M}-\text{N}$ 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 $\text{N}(p)$ atomic orbital that does not participate in the sp hybridization. In **B**, the $\text{M}=\text{N}$ double bond ($1\sigma, 1\pi$) 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 $\text{M}=\text{N}$ triple bond ($1\sigma, 2\pi$) and a linear $\text{M}-\text{N}-\text{R}$ linkage, where the nitrogen lone pair $p(\pi)$ to $\text{M}(d\pi)$ donation is very effective. In **C**, the imido ligand 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 $\text{Re}(\text{NPh})\text{Cl}_3(\text{PPh}_3)\text{L}$ or $\text{Re}(\text{NPh})\text{Cl}_3\text{L}_2$ from the reactions of $\text{Re}(\text{NPh})(\text{PPh}_3)_2\text{Cl}_3$ with small, strongly coordinating ligands ($\text{L} = \text{CO}, \text{P}(\text{OMe})_3, \text{PMe}_3$) (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 $\text{Re}(\text{NAr})(\text{PR}_3)_2\text{Cl}_3$ ($\text{PR}_3 = \text{PMe}_3, \text{PEt}_3, \text{P}(\text{OMe})_3$; $\text{Ar} = \text{C}_6\text{H}_5, 2,6\text{-}i\text{-Pr}_2\text{-C}_6\text{H}_3$).



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 ($\text{H}_2\text{N}-\text{C}_6\text{H}_3-2,6-i\text{-Pr}_2$) was distilled over CaH_2 . CO (99.9%) was purchased from Union Gas company and used as received. Re metal, trimethylphosphine (PMe_3 , 1 M in toluene), trimethyl phosphite ($\text{P}(\text{OMe})_3$), triethylphosphine (PEt_3 , 1 M in THF), triphenylphosphine (PPh_3), sodium cyclopentadienylide (NaCp ; $\text{Cp} = \text{C}_5\text{H}_5$, 2 M in THF), thallium cyclopentadienylide (TlCp), sodium pentamethylcyclopentadienylide (NaCp^* ; $\text{Cp}^* = \text{C}_5\text{Me}_5$, 0.5 M in THF), LiBEt_3H , and LiBEt_3D were purchased from Aldrich company and used as received. $\text{Re}(\text{NPh})(\text{PPh}_3)_2\text{Cl}_3$, **1**,²⁰ and $\text{Re}(\text{N}-\text{C}_6\text{H}_3-i\text{-Pr}_2)_2\text{Cl}_3$ (**py**), **4**,^{21,22} were prepared by the literature methods.

^1H - and $^{13}\text{C}\{^1\text{H}\}$ -NMR spectra were recorded with a Bruker AMX 500 MHz spectrometer with reference to internal solvent resonances and reported relative to tetramethylsilane. $^{31}\text{P}\{^1\text{H}\}$ -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 $\text{Re}(\text{NPh})(\text{P}(\text{OMe})_3)_2\text{Cl}_3$, **2 and **2a**.** Heating (30 min) 2.0 g (2.2 mmol) of **1** with 1.10 mL of $\text{P}(\text{OMe})_3$ (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*- $\text{Re}(\text{NPh})(\text{P}(\text{OMe})_3)_2\text{Cl}_3$, **2**, and *fac,cis*- $\text{Re}(\text{NPh})(\text{P}(\text{OMe})_3)_2\text{Cl}_3$, **2a**. This product mixture conveniently recrystallized from acetone-hexane. ^1H NMR (CDCl_3): δ 7.804–7.277 (5H, m, phenyl), 3.954 (18H, t, $J_{\text{P-H}} = 5.3$ Hz, $\text{P}(\text{OMe})_3$ for **2a**), 3.879 (18H, d, $J_{\text{P-H}} = 10.6$ Hz, $\text{P}(\text{OMe})_3$ for **2**). $^{13}\text{C}\{^1\text{H}\}$ -NMR (CDCl_3): δ 130.2–124.1 (phenyl), 54.4 (t, $J_{\text{P-C}} = 54.4$ Hz, for **2**), 50.9 (d, $J_{\text{P-C}} = 80.5$ for **2a**). $^{31}\text{P}\{^1\text{H}\}$ -NMR (CDCl_3): δ 81.7 (**2a**), 72.1 (**2**). Anal. Calcd for $\text{C}_{12}\text{H}_{23}\text{NO}_6\text{-P}_2\text{Cl}_3\text{Re}$: C, 22.81; H, 3.67; N, 2.22. Found: C, 23.12; H, 3.97; N, 1.87. Mp (decomp.): 126–128 °C. IR (KBr): 2955, 1178, 1050, 1024, 807, 779, 767, 750, 684, 527 cm^{-1} .

Preparation of *mer,trans*- $\text{Re}(\text{NPh})(\text{PEt}_3)_2\text{Cl}_3$, **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 vac-

uum to give 0.45 g (0.73 mmol, 83%) of **3**. This product conveniently recrystallized from benzene-hexane. ^1H 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). $^{13}\text{C}\{^1\text{H}\}$ -NMR (CDCl_3): δ 130.2–119.8 (phenyl), 14.8 (t, $J_{\text{P-C}} = 14.3$ Hz, PCH_2CH_3), 7.4 (s, PCH_2CH_3). $^{31}\text{P}\{^1\text{H}\}$ -NMR (CDCl_3): δ -23.3 (s). Anal. Calcd for $\text{C}_{18}\text{H}_{35}\text{NP}_2\text{Cl}_3\text{Re}$: C, 34.87; H, 5.69; N, 2.26. Found: C, 35.38; H, 5.76; N, 2.02. Mp (decomp.): 117–119 °C. IR (KBr): 2970, 2935, 2907, 1475, 1455, 1420, 1259, 1162, 780, 762, 732, 716, 691 cm^{-1} .

Preparation of *mer,trans*- $\text{Re}(\text{N}-\text{C}_6\text{H}_3-i\text{-Pr}_2)(\text{PMe}_3)_2\text{Cl}_3$, **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. ^1H NMR (CDCl_3): δ 7.647–7.069 (3H, m, phenyl), 3.917 (2H, m, CHMe_2), 1.642 (18H, t, $J_{\text{P-H}} = 4.6$ Hz, PMe_3), 1.148 (12H, d, $J = 6.8$ Hz, CHMe_2). $^{13}\text{C}\{^1\text{H}\}$ -NMR (CDCl_3): δ 152.2–125.2 (phenyl), 28.1 (CHMe_2), 24.3 (CHMe_2), 12.8 (t, $J_{\text{P-C}} = 16.8$ Hz, PMe_3). $^{31}\text{P}\{^1\text{H}\}$ -NMR (CDCl_3): δ -40.7 (s). Anal. Calcd for $\text{C}_{13}\text{H}_{35}\text{NP}_2\text{Cl}_3\text{Re}$: C, 34.87; H, 5.69; N, 2.26. Found: C, 34.94; H, 5.75; N, 1.83. Mp (decomp.): 207–209 °C. IR (KBr): 2955, 2912, 2867, 1587, 1414, 1359, 1284, 954, 856, 804, 762, 745, 675 cm^{-1} .

Formation of *mer*- $\text{Re}(\text{N}-\text{C}_6\text{H}_3-i\text{-Pr}_2)(\text{PMe}_3)(\text{OPMe}_3)\text{Cl}_3$, **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**. ^1H -NMR (CDCl_3): δ 7.583–7.026 (3H, m, phenyl), 3.926 (2H, m, CHMe_2), 1.709 (9H, d, $J_{\text{P-H}} = 13.0$ Hz, OPMe_3), 1.547 (9H, $J_{\text{P-H}} = 16.0$ Hz, PMe_3), 1.165 (12H, d, $J = 6.8$ Hz, CHMe_2). $^{13}\text{C}\{^1\text{H}\}$ -NMR (CDCl_3): δ 140.1–124.7 (phenyl), 28.1 (CHMe_2), 24.3 (CHMe_2), 16.4 (d, $J_{\text{P-C}} = 71.1$ Hz, OPMe_3), 15.3 (d, $J_{\text{P-C}} = 35.5$ Hz, PMe_3). $^{31}\text{P}\{^1\text{H}\}$ -NMR (CDCl_3): δ 65.3 (d, $J_{\text{P-P}} = 8.5$ Hz, OPMe_3), -39.5 (d, $J_{\text{P-P}} = 8.5$ Hz, PMe_3). Anal. Calcd for $\text{C}_{18}\text{H}_{35}\text{NOP}_2\text{Cl}_3\text{Re}$: C, 33.99; H, 5.55; N, 2.20. Found: C, 33.91; H, 5.78; N, 1.94. Mp (decomp.): 127–129 °C. 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 I. The orientation matrix and unit cell parameters were determined by least-squares analyses of the setting angles of 25 reflections in the range $20.0^\circ < 2\theta < 30.0^\circ$. Three check reflections were measured every 100 reflections throughout data collection and showed no significant variations in intensity. Intensity data were corrected for Lorentz 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 ₆ P ₂ ·Cl ₃ Re	C ₁₈ H ₃₅ NP ₂ ·Cl ₃ Re	C ₁₈ H ₃₅ NOP ₂ ·Cl ₃ Re
fw	631.80	619.96	635.96
temperature, K	293	293	293
crystal system	monoclinic	orthorhombic	orthorhombic
space group	<i>P</i> 2 ₁ / <i>m</i>	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>P</i> 2 ₁ 2 ₁ 2 ₁
<i>a</i> , Å	8.870(2)	11.307(1)	14.036(4)
<i>b</i> , Å	14.393(3)	11.802(1)	16.486(5)
<i>c</i> , Å	17.114(4)	19.193(2)	11.397(3)
β, deg	101.43(2)		
<i>V</i> , Å ³	2141.5(8)	2561.2(4)	2637(1)
<i>Z</i>	4	4	4
<i>d</i> _{calc} , g cm ⁻³	1.960	1.608	1.602
μ, mm ⁻¹	6.224	5.185	5.041
<i>F</i> (000)	1224	1224	1256
No. of unique reflns	3552	2472	2058
No. of reflns with <i>I</i> > 2σ(<i>I</i>)	3355	2428	2030
No. of params refined	227	226	236
2θ range (°)	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
<i>GOF</i> on <i>I</i> ²	1.086	1.046	1.008
<i>R</i>	0.0521	0.0250	0.0261
<i>wR</i> ₂ ^a	0.1293	0.0593	0.0630

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

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 × 0.3 × 0.4 mm³, was used for crystal and intensity data collection. The unit cell parameters and systematic absences, *h*0*l* (*h* + *l* = 2*n* + 1) and 0*k*0 (*k* = 2*n* + 1), unambiguously indicated *P*2₁/*m* 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 × 0.3 × 0.5 mm³, was used for crystal and intensity data collection. The unit cell parameters and systematic absences, *h*00 (*h* = 2*n* + 1), 0*k*0 (*k* = 2*n* + 1), and 00*l* (*l* = 2*n* + 1), unambiguously indicated *P*2₁2₁2₁ 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 (×10⁴) and equivalent isotropic displacement parameters (Å²×10³) for **2**

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (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 × 0.4 × 0.4 mm³, was used for crystal and intensity data collection. The unit cell parameters and systematic absences, *h*00 (*h* = 2*n* + 1), 0*k*0 (*k* = 2*n* + 1), and 00*l* (*l* = 2*n* + 1), unambiguously indicated *P*2₁2₁2₁ 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)₂Cl₃, **2**, and *fac,cis*-Re(NPh)(P(OMe)₃)₂Cl₃, **2a**, approximately in a ratio of 9 : 1 on the basis of ¹H NMR peak intensities (eq 3). This reaction is therefore more stereoselective, compared to that employed for preparation of a PMe₃ analogue, in which the corresponding product ratio is

Table 3. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^3 \times 10^3$) 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.

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*- $\text{Re}(\text{NPh})(\text{P}(\text{OMe})_3)_2\text{Cl}_3$ (**2**). Variable-temperature (20, 30, 40, 50 °C in CDCl_3) ^1H -NMR spectra of **2** show that the intensity ratio of 9:1 remains intact and there is almost no change in chemical shifts of $\text{P}(\text{OMe})_3$ protons.

In ^1H NMR spectra, methyl protons of $\text{P}(\text{OMe})_3$ 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

Table 4. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^3 \times 10^3$) 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.

coupled *trans* phosphorus nuclei ($J_{\text{P-H}} = 5.3$ Hz).²⁵ ^1H NMR spectra of **2a** show a sharp doublet at δ 3.879 ($J_{\text{P-H}} = 10.6$ Hz), which indicates a *cis*-orientation of the two $\text{P}(\text{OMe})_3$ ligands.

Compound **1** also reacts with PEt_3 in a refluxing benzene to exclusively give *mer,trans*- $\text{Re}(\text{NPh})(\text{PEt}_3)_2\text{Cl}_3$, **3** in 83% yield (eq 4). $^{13}\text{C}\{^1\text{H}\}$ -NMR spectra of **3** exhibit a triplet at δ 14.8 ($J_{\text{P-C}} = 14.3$ Hz), owing to the virtual coupling of the carbon nucleus to the two *trans* phosphorus nuclei.²⁵⁻³¹ ^1H -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*- $\text{Re}(\text{N-C}_6\text{H}_3\text{-}i\text{-Pr}_2)(\text{PMe}_3)_2\text{Cl}_3$, **5**, in moderate yield (eq 5). The Re metal has been formally

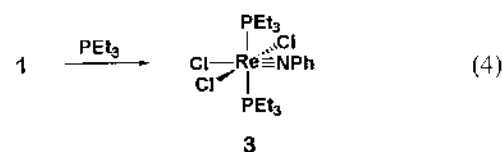
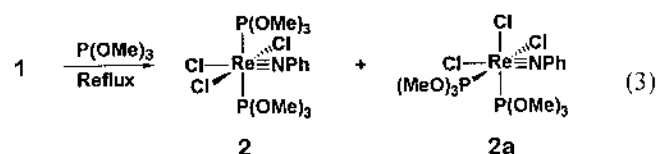


Table 5. Selected bond distances (Å) and bond angles (°) in **2**

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)				

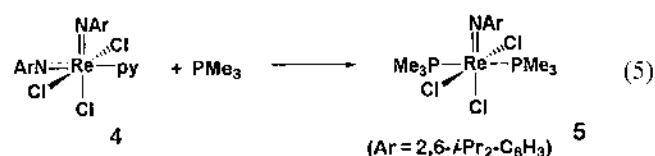
Table 6. Selected bond distances (Å) and bond angles (°) in **5** and **6**

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-C₆H₃-i-Pr₂) has been replaced during the reaction. Unfortunately, we cannot

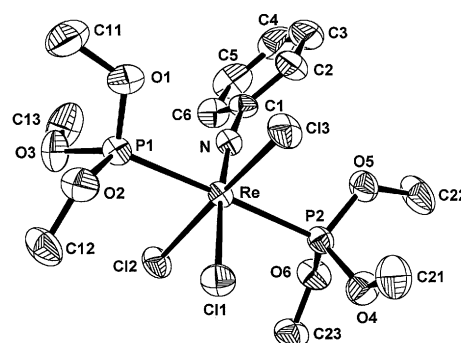
give an explanation for these reactivities, the imido abstraction and the Re metal reduction.

In ¹H NMR spectra of **5**, methyl protons of PMe₃ exhibit a triplet at δ 1.642 (*J*_{P-H} = 4.6 Hz), because of their virtual coupling to the two *trans* phosphorus nuclei. ¹³C{¹H}-NMR spectra of **5** exhibit a triplet at δ 12.8 (*J*_{P-C} = 66.8 Hz), also because of the virtual coupling of the carbon nucleus to the



two phosphorus nuclei.²⁵ As expected, ³¹P{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 drawing²⁸ of **2** showing the atom-labeling scheme and 50% probability thermal ellipsoids.

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)(PPh₃)₂Cl₃, **1**, and Re(N-C₆H₃-*i*-Pr₂)₂Cl₃(py), **4**. Vigorous reaction conditions (refluxing benzene solutions) are required for reactions of **1** with P(OMe)₃ or PEt₃, whereas mild conditions (room-temperature benzene solutions) for reactions of **4** with PMe₃. 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 (ZnR₂; R = Me, Et; AlR₃; R = Me, Et; RMgBr; R = Me, Et; MCp; M = Li, Na, Ti; NaCp*) and hydrides (LiBEt₃H, LiBEt₃D).

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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.

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