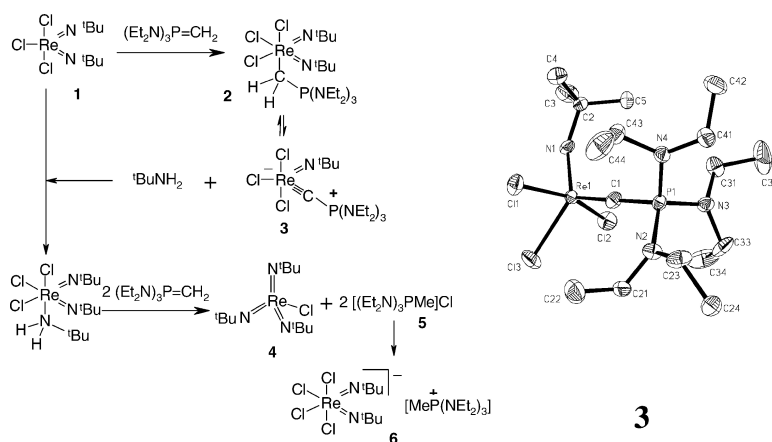


Formation of a Rhenium(VII) Phosphonio–Methylidyne Complex

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Formation of a Rhenium(VII) Phosponio–Methylidyne Complex

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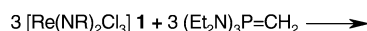
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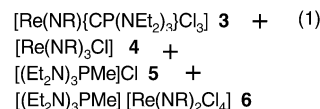
Summary: The rhenium(VII) phosponio–methylidyne complex $[\text{Re}(\text{N}^t\text{Bu})\{\text{C}-\text{P}(\text{NEt}_2)_3\}\text{Cl}_3]$ (**3**) is obtained via interaction of an imido ligand in $[\text{Re}(\text{N}^t\text{Bu})_2\text{Cl}_3]$ (**1**) with the phosphorus ylide $(\text{Et}_2\text{N})_3\text{P}=\text{CH}_2$. The isolation of all the intermediates and products of this reaction allows us to postulate a mechanism in which the amine, formally generated from the imido ligand, is trapped by the Lewis acid **1** with formation of $[\text{Re}(\text{N}^t\text{Bu})_3\text{Cl}]$ (**4**) and $[(\text{Et}_2\text{N})_3\text{P}-\text{CH}_3]^+[\text{Re}(\text{N}^t\text{Bu})_2\text{Cl}_4]^-$ (**6**). **3** and **6** have been structurally characterized.

In recent years the chemistry of phosphorus ylides has progressed intensively.¹ Tris(diethylamino)methyl-ene phosphorane is known to react with $[\text{TiCl}_4]$ and $[\text{ZrCl}_4]$ to give 1,3-dimetallacyclobutanes containing two deprotonated bridging ylide ligands $[(\text{Et}_2\text{N})_3\text{P}-\text{C}]^{2-}$.² Attempts to extend these transylidation reactions to homoleptic niobium, tungsten, and molybdenum halides failed to yield organometallic species, due to the complex redox chemistry involved.³ Therefore, despite their interesting applications in organic synthesis,⁴ the organometallic chemistry of *P*-dialkylamino phosphorus ylides with electron-poor transition metals of d^0 electron configuration has remained limited to group 4 metals.⁵ We have been interested in transylidation reactions of phosphorus ylides with more redox stable imido metal complexes leading to the phosponio–methylidene complexes $[\text{M}=\text{CH}-\text{PR}_3] \leftrightarrow [\text{M}-\text{CH}=\text{PR}_3]$.⁶ Recently, the

Scheme 1



R = *tert*-butyl



terminal phosponio–methylidyne complexes of d^0 electron configuration $[\text{M}=\text{C}-\text{PR}_3] \leftrightarrow [\text{M}=\text{C}=\text{PR}_3]$ have been obtained via a transylidation cascade.⁷ In lower metal oxidation states a few tungsten complexes with such a functional group, $[\text{M}=\text{C}-\text{PR}_3]$, are known; they are formed, however, via different mechanistic pathways.⁸

The ligands $[\text{N}-\text{CR}_3]^{2-}$ and $[\text{C}-\text{PR}_3]^{2-}$ are isoelectronic $\sigma + 2\pi$ donor groups. We found that the phosphorus ylide $[\text{H}_2\text{C}=\text{PR}_3]$ (**2**; R = NEt₂) replaces an imido ligand in $[\text{Re}(\text{N}^t\text{Bu})_2\text{Cl}_3]$ (**1**)⁹ with formation of the phosponio–methylidyne complex **3**. By careful investigation of the stoichiometry of this transformation and characterization of the intermediates and byproducts we are able to suggest a reaction scheme (Schemes 1 and 2).

The reaction proceeds via the labile classical ylide complex **2**,^{10a} which is isolated when the parent compound **1** is treated with 1 equiv of $(\text{Et}_2\text{N})_3\text{P}=\text{CH}_2$ in benzene. We assume that the ylide ligand is *cis* to both imido ligands, as found in the related and structurally characterized $\text{Pr}_3\text{P}=\text{CH}_2$ adduct.¹¹ **2** is only stable as a solid; in solution it decomposes into the products **3–6**. We suggest a mechanism with two proton-transfer steps to the nitrogen atom of an imido ligand and dissociation of free amine, which is then trapped by the Lewis acid **1** in order to shift the equilibrium to the side of complex **3**. Complex **1** reacts with *tert*-butylamine and ylide as

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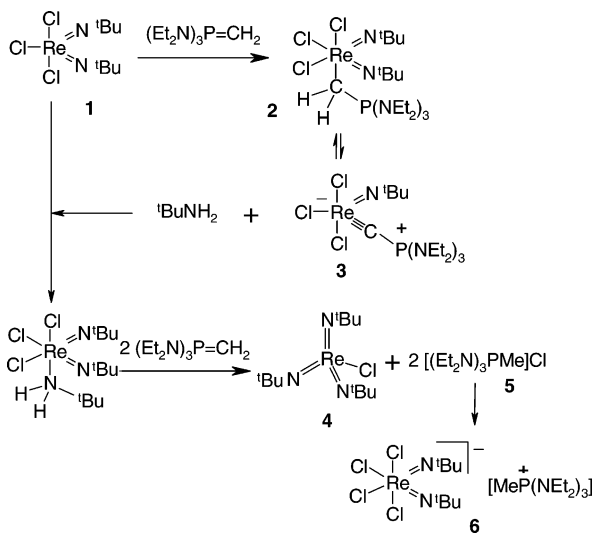
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Scheme 2. Proposed Mechanism for the Formation of Complexes 2–6


a base to give the known tris(imido) complex **4**¹² and phosphonium chloride **5**. Part of **5** is trapped by **1** to ylideate the phosphonium imidorhenate **6**. While the byproducts are known, an imido ligand transfer via the dinuclear intermediate $[\text{Re}(\mu\text{-NR})\text{Re}]$ and deprotonation of coordinated ylide by ylide as a base (transylation) cannot be excluded as an alternative mechanism at this stage.

The compounds **2**, **3**, and **6** have been characterized by elemental analyses and NMR spectroscopy. The chemical shift of the methylidene carbon atom in **3** is found at lower field (δ_{C} 293.6 ppm) in comparison to other high-valent but more π -bond-loaded complexes $[\text{W}(\text{NDip})(\text{C}-\text{PPh}_3)_2(\text{CH}-\text{PPh}_3)_2]$ (Dip = 2,6-diisopropylphenyl; δ_{C} = 213.7),⁷ and $[\text{Re}(\text{C}-\text{PPh}_3)(\text{N}^t\text{Bu})_2](\text{O}^t\text{Bu})$ (δ_{C} 216.0 ppm).^{10b} The shielding is even lower than in cationic $[\text{Tp}'\text{W}(\text{C}-\text{PMe}_3)(\text{CO})_2]^+$ (Tp' = hydridotris-(3,5-dimethylpyrazolyl)borate; δ_{C} 253.4 ppm).^{8a} By crystallization from benzene single crystals of **3** and **6** suitable for X-ray diffraction analysis were obtained.

The coordination geometry of **3** (Figure 1) can be described as a distorted trigonal bipyramid. This is similar to the geometry of the parent complex $[\text{Re}(\text{N}^t\text{Bu})_2\text{Cl}_3]$.¹¹ The two strong π -donor ligands $[\text{tBuN}]^{2-}$ and $[(\text{Et}_2\text{N})_3\text{PC}]^{2-}$ and Cl3 define the equatorial plane. The axial chloro ligands are bent toward Cl3 (Cl1–Re1–Cl2 = 163.8(6)°). The distribution of the interbond angles in the equatorial plane is interesting. The N1–Re1–C1 angle, 110.2(3)°, is smaller than the angles Cl3–Re1–N1 = 132.7(2)° and Cl3–Re1–C1 = 117.0(2)°. The same trend has been observed for $[\text{Re}(\text{N}^t\text{Bu})_2\text{Cl}_3]$ (N–Re–N = 110.7°). In most other compounds with multiply bonded cis ligands, repulsion between the π -electrons leads to an increase of the interbond angle from idealized values (120°).¹² Whereas the imido ligand in **3** is slightly bent (Re1–N1–C2 = 153.1(4)°), the phosphonio–methylidene functional group (Re1–C1–P1 = 179.3(4)°) is linear. The Re1–C1 distance, 1.758(6) Å, is more typical of a rhenium(VII)–carbon triple bond than of a double bond. In the related neopentylidene/neopentylidyne complex $[\text{Re}(\text{C}^t\text{Bu})(\text{CH}^t\text{Bu})\text{I}_2(\text{Py})_2]$, Re–C

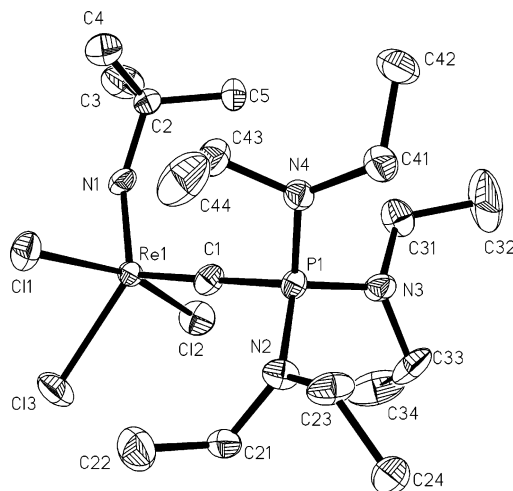


Figure 1. ORTEP diagram of **3**. Selected bond distances (Å) and angles (deg): Re1–N1, 1.735(4); Re1–Cl1, 2.380(1); Re1–Cl2, 2.370(1); Re1–Cl3, 2.395(2); Re1–C1, 1.758(6); P1–C1, 1.744(6); N1–Re1–C1, 110.2(3); Cl2–Re1–Cl1, 163.8(6); N1–Re1–Cl3, 132.7(2); P1–C1–Re1, 179.3(4); C1–Re1–Cl3, 117.0(2); C2–N1–Re1, 153.1(4).

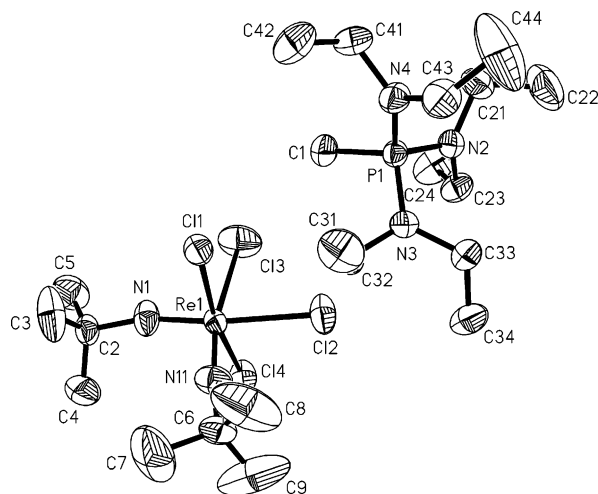


Figure 2. ORTEP diagram of **6**. Selected bond distances (Å) and angles (deg): Re1–N1, 1.717(5); Re1–N11, 1.718(5); Re1–Cl4, 2.387(1); Re1–Cl1, 2.391(1); Re1–Cl3, 2.439(2); Re1–Cl2, 2.544(2); P1–C1, 1.785(6); N1–Re1–N11, 103.4(3); N11–Re1–Cl3, 166.0(1); N1–Re1–Cl2, 170.6(2); Cl1–Re1–Cl4, 170.3(5); C2–N1–Re1, 162.4(5); C6–N11–Re1, 174.5(5).

distances of 1.742(9) Å for Re=C and 1.873(9) Å for Re=C were found.¹³ The distance C1–P1 = 1.744(6) Å is close to that of a single bond, as found in the phosphonium ion of **6** (P1–C1 = 1.785(6) Å). Furthermore, the longer Re–N bond distances in $[\text{Re}(\text{N}^t\text{Bu})_2\text{Cl}_3]$ (average 1.693 Å) in comparison to those in **3** (Re1–N1 = 1.735(4) Å) reveal that the donor strength of this new, sterically demanding terminal carbon donor $[\text{R}_3\text{P}-\text{C}]^{2-}$ (R = NEt₂) tends to be stronger than that of the isoelectronic imido nitrogen donor functional group $[\text{R}_3\text{C}-\text{N}]^{2-}$ (R = Me).

The molecular structure of **6** (Figure 2) reveals the two discrete ions $[(\text{Et}_2\text{N})_3\text{PCH}_3]^+$ and $[\text{Re}(\text{N}^t\text{Bu})_2\text{Cl}_4]^-$. It is similar to that of the related $[(\text{Et}_2\text{N})_3\text{PCH}_3]_2\text{-}[\text{ZrCl}_6]$.^{2b} However, due to the repulsion between the

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π -electrons the imidorhenate anion shows a distorted-octahedral coordination geometry with the wide angle $\text{N1-Re1-N11} = 103.4(3)^\circ$. In accord with the trans influence of the strong π donors, both bond distances trans to the imido ligand, Re-Cl2 and Re-Cl3 (2.544 and 2.439 Å, respectively), are elongated in comparison to the cis Re-Cl bond (2.387 and 2.391 Å).

Experimental Section. General Procedures and Materials. All procedures were carried out under an argon atmosphere in freshly distilled anhydrous solvents. $[\text{Re}(\text{N}^t\text{Bu})_2\text{Cl}_3]^9$ and $(\text{Et}_2\text{N})_3\text{P}=\text{CH}_2^{5b}$ were prepared by published procedures. NMR spectra were recorded on a Bruker AMX 300 spectrometer (^1H , 300.1 MHz; ^{13}C , 75.5 MHz; ^{31}P , 81.0 MHz) and on a Bruker AMX 400 spectrometer (^1H , 400.1 MHz; ^{13}C , 100.6 MHz; ^{31}P , 162.0 MHz). Elemental analyses were recorded on a Heraeus CHN-Rapid instrument. Single-crystal structures were determined with ENRAF-Nonius CAD4 and Stoe IPDS diffractometers.

Synthesis of 2. To 2.59 g (5.96 mmol) of $[\text{Re}(\text{N}^t\text{Bu})_2\text{Cl}_3]$ in 50 mL of benzene was added 1.56 g (5.96 mmol) of $(\text{Et}_2\text{N})_3\text{P}=\text{CH}_2$ in 10 mL of benzene at 0 °C. After 15 min of stirring at ambient temperature, the brown suspension was filtered, reduced in volume, layered with pentane, and stored at 4 °C. The product precipitates as a violet crystalline material. Yield: 3.0 g (72%). Anal. Calcd for $\text{C}_{21}\text{H}_{50}\text{Cl}_3\text{PN}_5\text{Re}$ (696.19): C, 36.23; H, 7.24; N, 10.06. Found: C, 36.59; H, 7.32; N, 9.87. ^1H NMR (300.1 MHz, CDCl_3): δ 1.14 (t, 18H, $\text{N}(\text{CH}_2\text{CH}_3)_2$, $^3J_{\text{HH}} = 7.1$ Hz), 1.57 (s, 18H, $\text{NC}(\text{CH}_3)_3$), 2.58 (d, 2H, ReCH_2P , $^2J_{\text{PH}} = 15.6$ Hz), 3.20 (m, 12H, $\text{N}(\text{CH}_2\text{CH}_3)_2$); ^{31}P NMR (81.0 MHz, CDCl_3): δ 67.0.

Synthesis of 3 and 6. A 3.14 g amount (7.22 mmol) of $[\text{Re}(\text{N}^t\text{Bu})_2\text{Cl}_3]$ (**1**) was dissolved in 50 mL of toluene, and 1.89 g (7.22 mmol) of $(\text{Et}_2\text{N})_3\text{P}=\text{CH}_2$ in toluene (60 mL) was added dropwise with stirring at 0 °C. The reaction mixture was stirred for 6 h at ambient temperature and turned red-brown. After removal of the solvent at reduced pressure, the solid residue was extracted first with pentane (80 mL), then with diethyl ether (80 mL), and finally with benzene (60 mL). From the pentane extract yellow crystals of $[\text{Re}(\text{N}^t\text{Bu})_3\text{Cl}]$ were obtained at -80 °C (spectroscopic features are identical with those of an authentic sample). From the diethyl ether extract colorless **5** with some minor amounts of orange **3** and purple **6** crystallized. From benzene first the main fraction of purple-black cubes **6** crystallized at 4 °C and second, after decanting and reducing in volume, the main part of orange crystalline **3**. The overall yield of recrystallized **3** is 2.1 g (3.37 mmol, 71% with respect to Scheme 1), and the yield of **6** is 0.5 g (0.68 mmol, 28%). Anal. Calcd for $\text{C}_{17}\text{H}_{39}\text{Cl}_3\text{N}_4\text{PRe}$ (623.06; **3**): C, 32.77; H, 6.31; N, 8.99; Cl, 17.07.

Found: C, 32.09; H, 6.48; N, 8.57; Cl, 17.79. ^1H NMR (400.1 MHz, CD_2Cl_2 , 213 K) δ 1.13 (t, 18H, $\text{N}(\text{CH}_2\text{CH}_3)_2$, $^3J_{\text{HH}} = 6.8$ Hz), 1.39 (s, 9H, $\text{NC}(\text{CH}_3)_3$), 3.17 (m, 12H, $\text{N}(\text{CH}_2\text{CH}_3)_2$). ^{13}C NMR (100.6 MHz, CD_2Cl_2 , 213 K): δ 13.2 (s, $\text{N}(\text{CH}_2\text{CH}_3)_2$), 28.1 (s, $\text{NC}(\text{CH}_3)_3$), 38.6 (d, $\text{N}(\text{CH}_2\text{CH}_3)_2$, $^2J_{\text{PC}} = 4.9$ Hz), 73.7 (s, $\text{NC}(\text{CH}_3)_3$), 293.6 (d, $\text{CP}(\text{NEt}_2)_3$, $^1J_{\text{PC}} = 105.1$ Hz). ^{31}P NMR (162.0 MHz, CD_2Cl_2 , 213 K): δ 39.4. Anal. Calcd for $\text{C}_{21}\text{H}_{51}\text{Cl}_4\text{N}_5\text{PRe}$ (732.82; **6**): C, 34.43; H, 7.02; N, 9.56. Found: C, 34.36; H, 6.96; N, 9.64. ^1H NMR (300.1 MHz, CD_2Cl_2): δ 1.20 (t, 18H, $\text{N}(\text{CH}_2\text{CH}_3)_2$, $^3J_{\text{HH}} = 7.1$ Hz), 1.58 (s, 18H, $\text{NC}(\text{CH}_3)_3$), 2.07 (d, 3H, PCH_3 , $^2J_{\text{PH}} = 13.6$ Hz), 3.11 (m, 12H, $\text{N}(\text{CH}_2\text{CH}_3)_2$). ^{13}C NMR (75.5 MHz, CD_2Cl_2): δ 14.2 (s, $\text{N}(\text{CH}_2\text{CH}_3)_2$), 28.0 (d, PCH_3 , $^1J_{\text{PC}} = 21.9$ Hz), 31.2 (s, $\text{NC}(\text{CH}_3)_3$), 40.5 (s, $\text{N}(\text{CH}_2\text{CH}_3)_2$), 73.8 (s, $\text{NC}(\text{CH}_3)_3$). ^{31}P NMR (81.0 MHz, CD_2Cl_2): δ 58.6.

Crystallographic Data for 3 and 6. Crystallographic data for **3**: ($\text{C}_{17}\text{H}_{39}\text{Cl}_3\text{N}_4\text{PRe}$, $M_r = 623.04$): crystal size $0.55 \times 0.55 \times 0.25$ mm³, monoclinic, space group Cc , $a = 9.419(2)$ Å, $b = 17.420(2)$ Å, $c = 15.826(2)$ Å, $\beta = 102.727(13)^\circ$, $V = 2532.9(7)$ Å³, $D_c = 1.634$ g cm⁻³ for $Z = 4$, $F(000) = 1240$, $\mu = 5.186$ mm⁻¹, Enraf-Nonius CAD4 diffractometer, $\lambda = 0.71069$ Å, $T = 203$ K, ω scans, 5077 reflections, $\theta_{\text{max}} = 31.2^\circ$, 4701 independent and 4602 observed reflections ($F \geq 4\sigma(F)$), empirical absorption correction (ψ scans), Flack parameter (absolute structure) -0.008(7), hydrogens calculated, 245 refined parameters, $R1 = 0.0266$ (observed data), $wR2 = 0.0685$ (independent data).

Crystallographic Data for **6** ($\text{C}_{21}\text{H}_{51}\text{Cl}_4\text{N}_5\text{PRe}$, $M_r = 732.64$): crystal size $0.45 \times 0.30 \times 0.30$ mm³, orthorhombic, space group $P2_12_12_1$, $a = 11.071(2)$ Å, $b = 11.932(1)$ Å, $c = 24.397(2)$ Å, $V = 3223.0(6)$ Å³, $D_c = 1.510$ g cm⁻³ for $Z = 4$, $F(000) = 1480$, $\mu = 4.169$ mm⁻¹, Enraf-Nonius CAD4 diffractometer, $\lambda = 0.71069$ Å, $T = 213$ K, ω scans, 7090 reflections, $\theta_{\text{max}} = 26^\circ$, 6296 independent and 6110 observed reflections ($F \geq 4\sigma(F)$), empirical absorption correction (ψ scans), Flack parameter (absolute structure) -0.011(7), hydrogens calculated, 314 refined parameters, $R1 = 0.0279$ (observed data), $wR2 = 0.0719$ (independent data). Cambridge database files: CCDC-171749 (**3**) and CCDC-171750 (**6**).

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Supporting Information Available: Tables containing full X-ray crystallographic data for **3** and **6**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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