Inorg. Chem. **2005**, *44*, 3172–3180

Inorganic Chemistry
Article

Rhenium(V) and Technetium(V) Complexes with Phosphoraneimine and Phosphoraneiminato Ligands

Maren Hecht, Sonia Saucedo Anaya, Adelheid Hagenbach, and Ulrich Abram*

Freie Universität Berlin, Institute of Chemistry, Fabeckstrasse 34-36, D-14195 Berlin, Germany

Received December 17, 2004

Air-stable rhenium(V) nitrido complexes are formed when $[ReOCl_3(PPh_3)_2]$, $[NBu_4][ReOCl_4]$, or $[NBu_4][ReNCl_4]$ are treated with an excess of silylated phosphoraneiminates of the composition $Me_3SiNPPh_3$ or $Ph_2P(NSiMe_3)CH_2PPh_2$ in CH_2Cl_2. Complexes of the compositions $[ReNCl(Ph_2PCH_2PPh_2NH)_2]Cl$ (**1**), $[ReN(OSiMe_3)(Ph_2PCH_2PPh_2NH)_2]Cl$ (**2**) or $[ReNCl_2(PPh_3)_2]$ (***3***) were isolated and structurally characterized. The latter compound was also produced during a reaction of the rhenium(III) precursor $[ReCl_3(PPh_3)_2(CH_3CN)]$ and $Me_3SiNPPh_3$. Nitrogen transfer from the phosphorus to the rhenium atoms and the formation of nitrido ligands were observed in all examples. All products of reactions with an excess of the potentially chelating phosphoraneiminate $Me_3SiNP(Ph_2)CH_2PPh_2$ contain neutral $Ph_2PCH_2PPh_2NH$ ligands. The required protons are supplied by a metal-induced decomposition of the solvent dichloromethane. The Re–N(imine) bond lengths (2.055–2.110 Å) indicate single bonds, whereas the N–P bond with lengths between 1.596 Å and 1.611 Å reflect considerable double bond character. An oxorhenium(V) phosphoraneiminato complex, the dimeric compound $[ReOCl_2(\mu\text{-}N\text{-}Ph_2PCH_2PPh_2N)]_2$ (**4**), is formed during the reaction of $[NBu_4][ReOCl_4]$ with an equivalent amount of $Ph_2P(NSiMe_3)CH_2PPh_2$ in dry acetonitrile. The blue neutral complex with two bridging phosphoraneiminato units is stable as a solid and in dry solvents. It decomposes in solution, when traces of water are present. The rhenium–nitrogen distances of 2.028(3) and 2.082(3) Å are in the typical range of bridging phosphoraneiminates and an almost symmetric bonding mode. Technetium complexes with phosphoraneimine ligands were isolated from reactions of $[NBu_4][TcOCl_4]$ with $Me_3SiNPPh_3$, and $[NBu_4][TcNCl_4]$ with $Me_3SiNP(Ph_2)CH_2PPh_2$. Nitrogen transfer and the formation of a five-coordinate nitrido species, $[TcNCl_2(HNPPh_3)_2]$ (**5**), was observed in the case of the oxo precursor, whereas reduction of the technetium(VI) starting material and the formation of the neutral technetium(V) complex $[TcNCl_2(Ph_2PCH_2PPh_2NH)]$ (**6**) or $[TcNCl(Ph_2PCH_2PPh_2NH)_2]Cl$ (**7**) was observed in the latter case. Both technetium complexes are air stable and X-ray structure determinations show bonding modes of the phosphoraneimines similar to those in the rhenium complexes.

Introduction

Phosphoraneimine and phosphoraneiminato complexes are known for a large number of main group and transition metals.[1−3] Since discrete R_3PN^- anions are hitherto unknown and even alkali metal derivatives are built of multinuclear molecular aggregates,[4] frequently trimethylsilylated phosphoraneimines are used for the synthesis of the transition metal complexes. The driving force of the reactions is the high stability of the formed trimethylchlorosilane or hexamethyldisiloxane. Depending on the oxidation state of the transition metal, the phosphoraneiminato ligands coordinate linear, bent, or as bridging ligands.[2] Electron-rich metal ions prefer the formation of μ-N-bridged dimers or multinuclear aggregates of heterocubane (four metal atoms) or partially face-centered octahedral (six metal atoms) structures both containing μ_3-bonded phosphoraneiminato ligands. Com-

---

* To whom correspondence should be addressed. Tel. (#49) 30 83854002, FAX (#49) 30 83852676, e-mail: abram@chemie.fu-berlin.de.

(1) Dehnicke, K.; Weller, F. *Coord. Chem. Rev.* **1997**, *158*, 103.

(2) Dehnicke, K.; Krieger, M.; Massa, W. *Coord. Chem. Rev.* **1999**, *182*, 19 and references therein.

(3) Dehnicke, K. *Z. Anorg. Allg. Chem.* **2003**, *629*, 729.

(4) (a) Batsanov, A. S.; Davidson, M. G.; Howard, J. A. K.; Lamb, S.; Lustig, C.; Price, R. D. *J. Chem. Soc., Chem. Commun.* **1997**, 1211. (b) Anfang, S.; Seybert, G.; Harms, K.; Geiseler, G.; Massa, W.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **1998**, *624*, 1187. (c) Chitsaz, S.; Neumüller, B.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **1999**, *625*, 9. (d) Chitsaz, S.; Neumüller, B.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **2003**, *629*, 592.

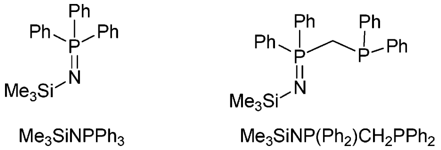
10.1021/ic048210q CCC: $30.25

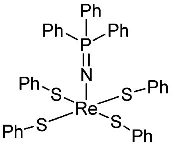
plexes with linear or slightly bent nitrogen-bridges between the metal and the phosphorus atoms are formed by metals in high formal oxidation states, as has been demonstrated for Os(VIII)[5] or Re(VII) compounds.[6]

Stable donor−acceptor complexes with trimethylsilylated phosphoraneimines or ligands of the type $R_3P{=}NH$ are well established for a series of metal(II) halides[2,7] and group IV and group V metals.[2,8] Only a few structurally characterized examples are known for metals of the groups VI−VIII.[6e,9]

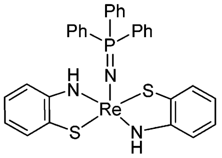
Surprisingly less is known about phosphoraneimine and phosphoraneiminato complexes of rhenium and technetium. Some pioneering work in this field has been done by Katti et al. They isolated $[H_2NPPh_3][ReO_4]$ as the product of a reaction between $Me_3SiNPPh_3$ and ammonium perrhenate and reported the formation of the rhenium(VII) phosphoraneiminate $O_3ReN{=}PPh_3$ by dehydration of the ion pair.[10] The extension of this approach to technetium gave similar results, when the 'carrier-free' ^{99m}Tc was used.[11] Our recent attempts, to perform reactions between ^{99}Tc-pertechnetate and $Me_3SiNPPh_3$ on a milligram scale, however, exclusively gave $[H_2NPPh_3][TcO_4]$, a compound the structure of which has been elucidated before.[11c] Thermal dehydration did not proceed on this concentration level. The same holds true for the claimed synthesis of the neutral $O_3Tc{=}NPPh_3$ from $(NH_4)TcO_4$ and $Me_3SiNPPh_3$ in dry toluene.[11c] A series of oxo complexes with phosphoraneiminates have been described as products of the reaction between Re_2O_7 and bifunctional ligands on the basis of spectroscopical data, but no X-ray structural data of any of these complexes could be provided.[12] Thus, only a few structurally fully characterized rhenium(V) and rhenium(VI) phosphoraneiminato complexes are documented. Two of them, tetrakis(thiophenolato)-triphenylphosphoraneiminatorhenium(VI)[13] (**I**) and bis(2-aminothiophenolato-N,S)triphenylphosphoraneiminatorhenium(V)[14] (**II**), are formed during reactions of nitrido complexes with triphenylphosphine, whereas a dimeric rhenium(VI) complex with a metal−metal bond (**III**) is the product of the reaction of $ReNCl_4$ with $Me_3SiNPPh_3$.[15]

Chart 1. Phosphoraneiminates Used

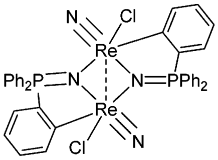




(**I**)



(**II**)



(**III**)

Here, we present further studies of the reactions of trimethylsilylated phosphoraneiminates (see Chart 1) with common rhenium and technetium precursors such as $[NBu_4][MOCl_4]$, $[NBu_4][MNCl_4]$, $[ReOCl_3(PPh_3)_2]$, and $[MCl_3(PPh_3)_2(CH_3CN)]$ (M = Re, Tc) including the X-ray crystal structures of prototype products.

Experimental Section

General Considerations. Solvents were dried and used freshly distilled unless otherwise stated. $[NBu_4][ReOCl_4]$,[16] $[NBu_4][ReNCl_4]$,[17] $[ReOCl_3(PPh_3)_2]$,[18] $[ReCl_3(PPh_3)_2(CH_3CN)]$,[19] $[NBu_4][TcOCl_4]$,[20] $[NBu_4][TcNCl_4]$,[21] $[TcCl_3(PPh_3)_2(CH_3CN)]$,[22] and

---

(5) Katti, K. V.; Roesky, H. W.; Rietzel, M. *Z. Anorg. Allg. Chem.* **1987**, *553*, 123.

(6) (a) Roesky, H. W.; Hesse, D.; Rietzel, M.; Noltemeyer, M. *Z. Naturforsch.* **1990**, *45b*, 72. (b) Roesky, H. W.; Hesse, D.; Noltemeyer, M.; Sheldrick, G. M. *Chem. Ber.* **1991**, *124*, 757. (c) Weller, F.; Kang, H.-C.; Massa, W.; Rübenstahl, T.; Kunkel, F.; Dehnicke, K. *Z. Naturforsch.* **1995**, *50b*, 1050. (d) Leichtweis, I.; Hasselbring, R.; Roesky, H. W.; Noltemeyer, M.; Herzog, A. *Z. Naturforsch.* **1993**, *48b*, 1234. (e) Schlecht, S.; Deubel, D. V.; Frenking, G.; Geiseler, G.; Harms, K.; Magull, J.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **1999**, *625*, 887.

(7) Cambridge Crystal Structure Database, Vers. 5.25, update 2, April 2004, Cambridge.

(8) (a) Grob, T.; Geiseler, G.; Harms, K.; Greiner, A.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **2002**, *628*, 217. (b) Grob, T.; Harms, K.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **2001**, *627*, 1801. (c) Schrumpf, F.; Roesky, H. W.; Noltemeyer, M. *Z. Naturforsch.* **1990**, *45b*, 1600. (d) Stahl, M.; Faza, N.; Massa, W.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **1997**, *623*, 1855. (e) Grun, M.; Harms, K.; Meyer zu Köcker, R.; Dehnicke, K.; Goesmann, H. *Z. Anorg. Allg. Chem.* **1996**, *622*, 1091. (f) Rübenstahl, T.; Weller, F.; Dehnicke, K. *Z. Kristallogr.* **1995**, *210*, 537. (g) Sarsfield, M. J.; Thornton-Pett, M.; Bochmann, M. *J. Chem. Soc., Dalton Trans.* **1999**, 3329. (h) Cavell, R. C.; Babu, R. P. K.; Kasani, A.; McDonald, R. *J. Am. Chem. Soc.* **1999**, *121*, 5805. (i) Gamer, M. T.; Rastätter, M.; Roesky, P. W. *Z. Anorg. Allg. Chem.* **2002**, *628*, 2269. (j) Babu, R. P. K.; McDonald, R.; Cavell, R. G. *Chem. Commun.* **2000**, 481. (k) Aparna, K.; Babu, R. P. K.; McDonald, R.; Cavell, R. G. *Angew. Chem.* **2001**, *113*, 4535; *Angew. Chem., Int. Ed.* **2001**, *40*, 4400. (l) Babu, R. P. K.; McDonalds, R.; Cavell, R. G. *Organometallics* **2000**, *19*, 3462. (m) Grun, M.; Weller, F.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **1997**, *623*, 224. (n) Sarsfield, M. J.; Said, M.; Thornton-Pett, M.; Gerrard, L. A.; Bochmann, M. *J. Chem. Soc., Dalton Trans.* **2001**, 822. (o) Aharonian, G.; Feghali, K.; Gambarotta, S.; Yap, G. P. A. *Organometallics* **2001**, *20*, 2616. (p) Aharonian, G.; Feghali, K.; Gambarotta, G.; Yap, G. P. A. *Organometallics* **2001**, *20*, 5008. (q) Wang, Z.-X.; Li, Y.-X. *Inorg. Chem.* **2002**, *41*, 5934.

(9) (a) Leung, W.-P.; So, C.-W.; Wang, J.-Z.; Mak, T. C. W. *Chem. Commun.* **2003**, 248. (b) Kasani, A.; McDonald, R.; Cavell, R. G. *Chem. Commun.* **1999**, 1993. (c) Pingrong, W.; Stephan, D. W. *Organometallics* **2002**, *21*, 1308. (d) Miller, J. S.; Miller, M. O.; Caulton, K. G. *Inorg. Chem.* **1974**, *13*, 1632. (e) Abram, U.; Hagenbach, A. *Z. Anorg. Allg. Chem.* **2002**, *628*, 1719. (f) Bennett, B. K.; Saganic, E.; Lovell, S.; Kaminsky, W.; Samuel, A.; Mayer, J. M. *Inorg. Chem.* **2003**, *42*, 4127.

(10) Katti, K. V.; Singh, P. R.; Barnes, C. L.; Katti, K. K.; Kopocka, K.; Ketring, A. R.; Volkert, W. A. *Z. Naturforsch.* **1993**, *48b*, 1381.

(11) (a) Katti, K. V.; Singh, P. R.; Katti, K. K.; Volkert, W. A.; Ketring, A. R. *Radiochim. Acta* **1994**, *66/67*, 129. (b) Katti, K. K.; Singh, P. R.; Volkert, W. A.; Anderson, C. J.; Welch, M. J.; Hoffman, T.; Katti, K. V.; Ketring, A. R.; Wang, M. *Appl. Radiat. Isot.* **1995**, *46*, 53.

(12) Katti, K. V.; Cavell, R. G. *Inorg. Chem.* **1989**, *28*, 3033.

(13) Dilworth, J. R.; Neaves, B. D.; Hutchinson, J. P.; Zubieta, J. A. *Inorg. Chim. Acta* **1982**, *65*, L223.

(14) Tsang, B. W.; Reibenspies, J.; Martell, A. E. *Inorg. Chim. Acta* **1993**, *211*, 23.

(15) Nusshär, D.; Weller, F.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **1993**, *619*, 1121.

(16) Alberto, R.; Schibli, R.; Egli, A.; Schubiger, P. A.; Hermann, W. A.; Artus, G.; Abram, U.; Kaden, T. A. *J. Organomet. Chem.* **1995**, *493*, 119.

(17) Abram, U.; Braun, M.; Abram, S.; Kirmse, R.; Voigt, A. *J. Chem. Soc., Dalton Trans.* **1998**, 231.

(18) Johnson, N. P.; Lock, C. J. L.; Wilkinson, G. *Inorg. Synth.* **1967**, *9*, 145.

(19) Rouschias, G.; Wilkinson, G. *J. Chem. Soc. A* **1967**, 993.

(20) Preetz, W.; Peters, G. *Z. Naturforsch.* **1980**, *35b*, 1355.

(21) Baldas, J.; Boas, J. F.; Bonnyman, J.; Williams, G. A. *J. Chem. Soc., Dalton Trans.* **1998**, 231.

(22) Pearlstein, R. M.; Davis, W. M.; Jones, A. G.; Davison, A. *Inorg. Chem.* **1989**, *28*, 3332.

$Me_3SiNPPh_3$[23] were prepared by standard procedures. $Me_3SiNP(Ph_2)CH_2PPh_2$ was synthesized by a modification of the general route previously published by Appelt and Ruppert.[24]

Radiation Precautions. ^{99}Tc is a weak β^--emitter. All manipulations with this isotope were performed in a laboratory approved for the handling of low-level radioactive materials. Normal glassware provides adequate protection against the low-energy beta emission of the technetium compounds. Secondary X-rays (bremsstrahlung) play an important role only when larger amounts of ^{99}Tc are used.

Infrared spectra were measured as KBr pellets on a Shimadzu FTIR-spectrometer. FAB$^+$ mass spectra were recorded with a TSQ (Finnigan) instrument using a nitrobenzyl alcohol matrix (results are given in the form: *m/z*, % of base peak (B), assignment). Elemental analysis of carbon, hydrogen, nitrogen, and sulfur were determined using a Heraeus vario EL elemental analyzer. The technetium analyses were done by liquid scintillation counting. NMR-spectra were taken with a JEOL 400 MHz multinuclear spectrometer.

[ReNCl($Ph_2PCH_2PPh_2NH)_2$]Cl (1). $Ph_2P(NSiMe_3)CH_2PPh_2$ (104 mg, 0.22 mmol) was dissolved in 5 mL of acetonitrile and added to $[NBu_4][ReNCl_4]$ (58 mg, 0.1 mmol) in a small amount of acetonitrile. The color of the solution turned brown upon stirring at room temperature for 30 min. Yellow columns of $[ReNCl(Ph_2PCH_2PPh_2NH)_2]Cl\cdot 3CH_3CN$ precipitated from this solution after standing overnight in a refrigerator. Yield: 83 mg (78%). Elemental analysis. Calcd for $C_{56}H_{55}N_6Cl_2P_4Re$ C: 56.3, H: 4.6, N: 7.0. Found C: 56.2, H: 4.5, N: 6.8%. IR: NH 3050 (m), M−N−P 1114 (m), Re≡N 1065 (m), N═P 991 cm^{-1}. ^{1}H NMR (CD_3CN): $\delta = 8.3-6.9$ (m, 20H, phenyl), 6.35 (s, 1H, NH), 3.13 (tr, J_{P-H} 12 Hz, 2H, CH_2) ppm. ^{31}P NMR (CD_3CN): $\delta = 59.39$ d (N*P*Ph_2CH_2), 18.14 d (CH_2*P*Ph_2). FAB$^+$ MS: *m/z* = 1034, 12% B, ($[ReNCl(Ph_2CH_2PPh_2NH)_2]^+$); 998, 25% B, ($[ReN(Ph_2CH_2PPh_2NH)_2]^+$); 400, 15% B, ($[Ph_2CH_2PPh_2NH]^+$).

[ReN(OSiMe$_3$)($Ph_2PCH_2PPh_2NH)_2$]Cl (2). $Ph_2P(NSiMe_3)CH_2PPh_2$ (236 mg, 0.25 mmol) and $[NBu_4][ReOCl_4]$ (59 mg, 0.1 mmol) were dissolved each in 1 mL of acetonitrile, and the ligand was slowly added to the rhenium precursor. The color of the solution changed from yellow to blue and slowly turned to brown when the addition was finished. The solution was stored in a refrigerator overnight. This resulted in deposition of yellow needles of $[ReN(OSiMe_3)(Ph_2PCH_2PPh_2NH)_2]Cl\cdot H_2O$. Yield: 64 mg (57%). Elemental analysis. Calcd for $C_{53}H_{55}N_3ClO_2P_4ReSi$ C: 55.8, H: 4.8, N: 3.7. Found C: 56.0, H: 4.9, N: 3.8%. IR: NH 2858 (m), M−N−P 1119 (m), Re≡N 1060 (m), N═P 964 cm^{-1}. ^{1}H NMR (CD_3CN): $\delta = 8.5-6.7$ (m, 40H, phenyl), 6.25 (s, 2H, NH), 3.14 (tr, J_{P-H} 12 Hz, 4H, CH_2), 0.02 (s, 9H, CH_3) ppm. ^{31}P NMR (CD_3CN): $\delta = 37.51$ d (N*P*Ph_2CH_2), 25.54 d (CH_2*P*Ph_2). FAB$^+$ MS: *m/z* = 1089, 10% B, ($[ReN(OSiMe_3)(Ph_2CH_2PPh_2NH)_2]^+$); 999, 70% B, ($[ReN(Ph_2CH_2PPh_2NH)_2]^+$); 400, 40% B, ($[Ph_2CH_2PPh_2NH]^+$).

[ReNCl$_2$(PPh$_3$)$_2$] (3). (a) $[ReOCl_3(PPh_3)_2]$ (83 mg, 0.1 mmol) was suspended in CH_2Cl_2 or acetonitrile (20 mL), and $Me_3SiNPPh_3$ (70 mg, 0.2 mmol) was added. The solid slowly dissolved upon heating under reflux to give a clear, dark-brown solution. Cooling overnight resulted in the precipitation of red crystals of $[ReNCl_2(PPh_3)_2]$. More product was obtained by concentration and cooling of the mother liquor. Yield: 65%. (b) $[ReCl_3(PPh_3)_2(CH_3CN)]$ (87 mg, 0.1 mmol) was suspended in acetonitrile, $Me_3SiNPPh_3$ (70 mg, 0.2 mmol) was added, and the mixture was heated to reflux to give a pale orange-red solution from which slowly deposited hexagonal plates of $[ReNCl_2(PPh_3)_2]$. More product could be obtained as a brick-red powder by concentrating the mother liquor. Yield: 90%. Elemental analysis. Calcd for $C_{36}H_{30}NP_2Cl_2Re$ C: 54.3, H: 3.8, N: 1.8. Found C: 54.5, H: 3.6, N: 1.8%. The infrared spectrum of the compound and the unit cell dimensions of the single-crystals were identical with those published previously.[26]

[ReOCl$_2$($Ph_2PCH_2PPh_2N$)]$_2$ (4). $Ph_2P(NSiMe_3)CH_2PPh_2$ (47 mg, 0.1 mmol) and $[NBu_4][ReOCl_4]$ (59 mg, 0.1 mmol) were dissolved each in 1 mL of absolutely dry acetonitrile, and the ligand was added dropwise to the rhenium precursor. The color of the solution changed to blue and light blue crystals of $[ReOCl_2(Ph_2PCH_2PPh_2N)]_2\cdot 2\ CH_3CN$ slowly separated upon storing at −20 °C. Yield: 56 mg (83%). Elemental analysis. Calcd for $C_{54}H_{50}N_4Cl_4O_2P_4Re_2$ C: 45.5, H: 3.5, N: 3.9. Found C: 45.3, H: 3.5, N: 3.8%. IR: M−N−P 1117 (m), N═P 986 (m), Re═O 943 cm^{-1} (m). ^{1}H NMR (CD_3CN): $\delta = 8.5-6.9$ (m, 20H, phenyl), 3.3 (tr, J_{P-H} 12 Hz, 2H, CH_2) ppm. ^{31}P NMR (CD_3CN): $\delta = 81.7$ d (N*P*Ph_2CH_2), 21.3 d (CH_2*P*Ph_2) ppm. The dimeric complex did not give satisfactory mass spectra.

[TcNCl$_2$(HNPPh$_3$)$_2$] (5). $[NBu_4][TcOCl_4]$ (50 mg, 0.1 mmol) was dissolved in 2 mL of CH_2Cl_2 and mixed with $Me_3SiNPPh_3$ (140 mg, 0.4 mmol) in 1 mL of CH_2Cl_2. The solution was stirred at room temperature for 30 min. During this time, the color changed to yellow-brown. Large yellow crystals of $[TcNCl_2(HNPPh_3)_2]$ deposited together with a small amount of colorless $HNPPh_3$ and a blue, technetium-containing oil after overlayering with 5 mL of *n*-hexane. The side products could be removed by rinsing with a small amount of cold CH_2Cl_2. Yield: 37 mg (50%). Elemental analysis. Calcd for $C_{36}H_{34}N_3Cl_2OP_2Tc$: Tc 13.1. Found Tc: 13.2%. IR: NH 3025 (m), M−N−P 1135 (m), Tc≡N 1070 (m), N═P 940 cm^{-1}. The solubility of the complex prevented the detection of NMR spectra of sufficient quality.

[TcNCl$_2$($Ph_2PCH_2PPh_2NH$)] (6). $Ph_2P(NSiMe_3)CH_2PPh_2$ (70 mg, 0.15 mmol) in 1 mL of THF was added to a solution of $[NBu_4][TcNCl_4]$ (50 mg, 0.1 mmol) in 2 mL of THF. The color of the solution changed to dark brown upon stirring at room temperature for 30 min. Standing overnight in a refrigerator resulted in an orange-red solution, from which an orange-red solid deposited. Recrystallization from acetonitrile gave orange plates. Yield: 30 mg (52%). Elemental analysis. Calcd for $C_{25}H_{23}N_2Cl_2P_2Tc$: Tc 17.0. Found Tc: 17.1%. IR: NH 3485 (m), M−N−P 1115 (m), Tc≡N 1085 (m), N═P 970 cm^{-1}. ^{1}H NMR (CD_3CN): $\delta = 8.0-6.6$ (m, 20H, phenyl), 6.4 (s, 1H, NH), 3.98 (tr, J_{P-H} 12 Hz, 2H, CH_2) ppm. ^{31}P NMR (CD_3CN): $\delta = 60.3$ d (N*P*Ph_2CH_2), 31.7 broad (CH_2*P*Ph_2).

[TcNCl($Ph_2PCH_2PPh_2NH)_2$]Cl (7). $Ph_2P(NSiMe_3)CH_2PPh_2$ (104 mg, 0.22 mmol) in 1 mL of acetonitrile was added to a solution of $[NBu_4][TcNCl_4]$ (50 mg, 0.1 mmol) in 5 mL of the same solvent. The solution was stirred at room temperature for 30 min, and the volume was reduced in a vacuum to about 1 mL. Yellow crystals of $[TcNCl(Ph_2PCH_2PPh_2NH)_2]Cl\cdot 2CH_3CN$ deposited upon standing overnight. Yield: 85 mg (80%). Elemental analysis. Calcd for $C_{54}H_{52}N_5Cl_2P_4Tc$: Tc 9.3. Found Tc: 8.5%. IR: NH 3051 (s), M−N−P 1115 (m), Tc≡N 1050 (m), N═P 995 cm^{-1}. ^{1}H NMR (CD_3CN): $\delta = 8.0-6.8$ (m, 20H, phenyl), 6.3 (s, 1H, NH), 3.12 (tr, J_{P-H} 12 Hz, 2H, CH_2) ppm. ^{31}P NMR (CD_3CN): $\delta = 52.1$ d (N*P*Ph_2CH_2), 37.8 very broad (CH_2*P*Ph_2).

---

(23) Birkhofer, L.; Ritter, A.; Kim, S. M. *Chem. Ber.* **1963**, *96*, 3099.
(24) Appel, R.; Ruppert, I. *Z. Anorg. Allg. Chem.* **1974**, *406*, 131.
(25) G. M. Sheldrick, SHELXS-97 and SHELXL97 − programs for the solution and refinement of crystal structures. Göttingen, Germany, 1997.
(26) Doedens, R. J.; Albers, J. *Inorg. Chem.* **1967**, *6*, 204.

Table 1. X-ray Structure Data Collection and Refinement Parameters

	(**1**)·3CH$_3$CN	(**2**)·H$_2$O	(**4**)·2CH$_3$CN	(**5**)	(**6**)·H$_2$O	(**7**)·2CH$_3$CN
formula	$C_{56}H_{55}Cl_2N_6P_4Re$	$C_{53}H_{55}Cl\ N_3O_2P_4ReSi$	$C_{54}H_{50}Cl_4N_4O_2P_4Re_2$	$C_{25}H_{23}Cl_2N_2P_2Tc$	$C_{36}H_{34}Cl_2N_3OP_2Tc$	$C_{54}H_{52}Cl_2N_5P_4Tc$
M_w	1193.04	1139.62	1425.1	582.29	755.50	1063.79
crystal system	monoclinic	orthorhombic	triclinic	monoclinic	monoclinic	monoclinic
a/Å	18.104(5)	15.041(1)	10.783(1)	19.476(5)	25.666(5)	12.487(3)
b/Å	15.186(5)	16.791(1)	11.320(2)	16.582(5)	9.236(1)	17.115(4)
c/Å	19.813(5)	21.456(4)	11.939(2)	16.227(5)	31.073(4)	25.060(7)
α/°	90	90	76.52(1)	90	90	90
β/°	96.72(1)	90	73.63(1)	100.48(1)	102.28(1)	98.36(1)
γ/°	90	90	77.43(1)	90	90	90
V/Å^3	5410(3)	5419(1)	1341.6(3)	5153(3)	7197(2)	5299(2)
space group	$P2_1/n$	$P2_12_12_1$	$P\bar{1}$	$P2_1/c$	$C2/c$	$P2_1/n$
Z	4	4	1	8	8	4
D_{calc}/g cm^{-3}	1.465	1.397	1.764	1.501	1.394	1.333
μ/mm^{-1}	2.506	2.473	4.871	0.906	0.669	0.533
no. of reflections	66109	13256	6777	36192	8926	31775
no. independent	16465	11743	5831	8040	7790	12184
no. parameters	633	586	317	595	420	855
R1/wR2[a]	0.0265/0.0632	0.0434/0.1091	0.0289/0.0692	0.0671/0.1432	0.0549/0.1359	0.0410/0.0823
GOF	1.029	1.128	1.080	1.104	0.987	0.901
device/temp/K	Bruker Smart/193	CAD4/293	CAD4/293	Bruker Smart/293	CAD4/293	Bruker Smart/193

[a] $R1 = |F_o - F_c|/|F_o|$; $wR2 = [w(F_o^2 - F_c^2)^2/(wF_o^2)]^{-1/2}$.

[TcNCl$_2$(PPh$_3$)$_2$] (8). [TcCl$_3$(PPh$_3$)$_2$(CH$_3$CN)] (77 mg, 0.1 mmol) was suspended in acetonitrile, Me$_3$SiNPPh$_3$ (70 mg, 0.2 mmol) was added, and the mixture was heated to reflux for 30 min to give a pale orange-red solution from which hexagonal plates of [TcNCl$_2$(PPh$_3$)$_2$] slowly deposited. More of the sparingly soluble product could be obtained as a brick-red powder by concentrating the mother liquor. Yield: 90%. Elemental analysis. Calcd for $C_{36}H_{30}NP_2Cl_2Tc$ Tc: 14.0. Found C: Tc: 14.2%. The infrared spectrum was identical with that published previously.[27]

X-ray Crystallography. The intensities for the X-ray determinations were collected on an automated single-crystal diffractometer of the type CAD4 (Enraf Nonius) or on a SMART CCD (Bruker) with Mo Kα radiation ($\lambda = 0.71073$ Å). Standard procedures were applied for data reduction and absorption correction. Structure solutions and refinements were performed with SHELXS97 and SHELXL97.[25] Hydrogen atom positions were calculated for idealized positions and treated with the 'riding model' option of SHELXL, except of those H-atoms, which are bonded to nitrogen atoms and/or involved in hydrogen bonds. Their positions were derived from the final Fourier maps and refined. More details on data collections and structure calculations are contained in Table 1.

Additional information on the structure determinations have been deposited with the Cambridge Crystallographic Data Centre.

Results and Discussion

Trimethylsilylphosphoraneiminates are excellent starting materials for the preparation of metal complexes containing phosphoraneiminato ligands. This has been demonstrated for a large number of main group and transition metals.[1,2] The ready formation of trimethylchlorosilane or hexamethyldisiloxane is regarded as the driving force of these reactions when they start from appropriate chloro or oxo complexes. Surprisingly, this general route does not fully apply for rhenium and technetium compounds. Despite the fact, that there exist some rare examples of rhenium phosphoraneiminato complexes containing the metal in the oxidation states "+7", "+6", and "+5", reactions of common rhenium and technetium precursors such as [ReOCl$_3$(PPh$_3$)$_2$], [MOCl$_4$]$^-$, or [MCl$_3$(PPh$_3$)$_2$(CH$_3$CN)] (M = Re, Tc) with an excess of trimethylsilylphosphoraneiminates result in cleavage of the P=N bond and the formation of nitrido complexes.

[ReOCl$_3$(PPh$_3$)$_2$] dissolves in solutions of Me$_3$SiNPPh$_3$ in dichloromethane or acetonitrile, and red crystals of the nitrido species [ReNCl$_2$(PPh$_3$)$_2$] deposit after cooling and concentration of the reaction mixture. The reaction follows the general route given in eq 1.

$$[ReOCl_3(PPh_3)_2] + Me_3SiNPPh_3 \rightarrow [ReNCl_2(PPh_3)_2] + OPPh_3 + Me_3SiCl \quad (1)$$

The formation of OPPh$_3$ and CH$_3$SiCl was detected by ^{31}P and ^{1}H NMR, and the resulting [ReNCl$_2$(PPh$_3$)$_2$] was characterized by elemental analysis, IR-spectra, and X-ray crystallography. Surprisingly, the same product was isolated from reactions of the rhenium(III) complex [ReCl$_3$(PPh$_3$)$_2$(CH$_3$CN)] with Me$_3$SiNPPh$_3$. Obviously, oxidation of the metal atom is performed by the (reductive) release of PPh$_3$ from the phosphoraneiminate. This is strongly suggested by the detection of uncoordinated PPh$_3$ in the reaction mixture after precipitation of the sparingly soluble [ReNCl$_2$(PPh$_3$)$_2$] when the reaction is carried out in dry solvents and under exclusion of air. The same type of reaction proceeds when the analogous technetium precursor, [TcCl$_3$(PPh$_3$)$_2$(CH$_3$CN)], is used, and [TcNCl$_2$(PPh$_3$)$_2$] can be isolated in good yields. The identity of the product was confirmed by its infrared spectrum and an X-ray structure analysis, which was identical with that previously determined.[28] The high stability of the triple bonds between nitrogen and technetium or rhenium is most probably the driving force for the decomposition of the phosphoraneiminate and the formation of nitrido ligands. Similar formations of M≡N bonds (M = Re, Tc) have been observed during the decomposition of other nitrogen-containing species such as dithiocarbazates,[29] benzamidines,[30]

---

(27) Kaden, L.; Lorenz, B.; Schmidt, K.; Sprinz, H.; Wahren, M. *Isotopenpraxis* **1981**, *17*, 174. (b) Baldas, J.; Bonnyman, J.; Williams, G. A. *J. Chem. Soc., Dalton Trans*. **1984**, 833.

(28) Gernert, M. B.; Hiller, W.; Dilworth, J. R.; Parrott, S. J. *Z. Kristallogr.* **1995**, *210*, 961.

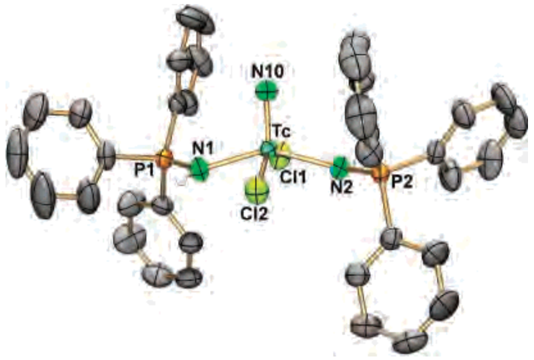


Figure 1. Ellipsoid representation[36] of [TcNCl$_2$(HNPPh$_3$)$_2$] (**5**). Thermal ellipsoids represent 50% probability. Hydrogen atoms at carbon atoms are omitted for clarity.

Table 2. Selected Bond Lengths (Å) and Angles (deg) in [TcNCl$_2$(HNPPh$_3$)$_2$] (**5**)

Tc−N10	1.589(4)	Tc−Cl1	2.389(1)
Tc−Cl2	2.388(1)	Tc−N1	2.078(4)
Tc−N2	2.102(4)	N1−P1	1.601(4)
N2−P2	1.593(4)		
N10−Tc−Cl1	105.0(2)	N10−Tc−Cl2	106.2(2)
N10−Tc−N1	104.4(2)	N10−Tc−N2	105.4(2)
Cl1−Tc−Cl2	148.81(5)	Cl1−Tc−N1	89.2(1)
Cl1−Tc−N2	82.5(1)	Cl2−Tc−N1	82.5(1)
Cl2−Tc−N2	89.9(1)	N1−Tc−N2	150.2(2)
Tc−N1−P1	133.7(3)	Tc−N2−P2	134.8(3)

phenylhydrazine,[31] azides,[17,32] and isothiocyanato or thionitrosyl ligands.[33,34]

We were not able to isolate products that are formed by ligand exchange of triphenylphosphine by triphenylphosphoraneiminate or triphenylphosphoraneimine during the above-mentioned attempts. The reaction of [NBu$_4$][TcOCl$_4$] with Me$_3$SiNPPh$_3$ in CH$_2$Cl$_2$, however, forms the technetium(V) nitrido complex [TcNCl$_2$(HNPPh$_3$)$_2$] (**5**) in reasonable yields as has been reported previously in a short communication.[35] More detailed studies of the course of the reaction and a comparison with reactions of [ReOCl$_4$]$^-$ with Me$_3$SiNP(Ph$_2$)CH$_2$PPh$_2$ (vide infra) suggest that the first step is the coordination of a phosphoraneiminato ligand that rapidly loses PPh$_3$ and converts to a nitrido species. This is clearly indicated by the formation of the paramagnetic [NBu$_4$][TcNCl$_4$]. This compound is isolated as orange red crystals as the sole product when the reaction is performed in carefully dried acetonitrile. It can doubtlessly be identified by its EPR and IR spectra. No other product could be isolated from such reaction mixtures as long as moisture was carefully excluded. Standing of such reaction mixtures, that contain an excess of Me$_3$SiNPPh$_3$ for a prolonged time, however, results in the formation of the triphenylphosphoraneimine technetium(V) complex (**5**). The rate of this reaction and the yield of **5** can be increased by the addition a small amounts of water. Compound **6** is formed as the major product of the reaction of [NBu$_4$][TcOCl$_4$] with Me$_3$SiNPPh$_3$ when dichloromethane is used as solvent. Decomposition of the solvent is the source of the protons in such reactions as has been checked by a corresponding reaction in CD$_2$Cl$_2$.

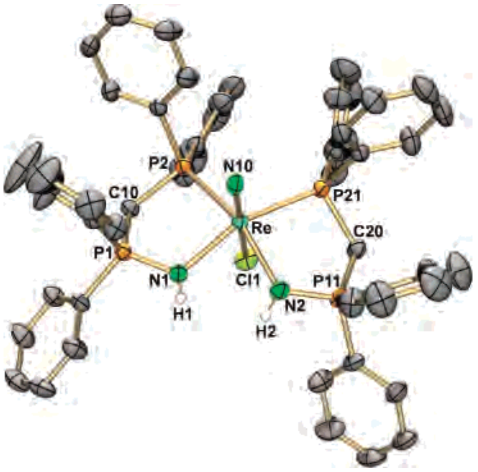


Figure 2. Ellipsoid representation[36] of the complex cation of **1**. Thermal ellipsoids represent 50% probability. Hydrogen atoms at carbon atoms are omitted for clarity.

[TcNCl$_2$(HNPPh$_3$)$_2$] is an air-stable yellow solid, which is only sparingly soluble in organic solvents. Therefore, no NMR spectra of reasonable quality could be obtained. The Tc≡N vibration in the IR spectrum of the compound is clearly resolved at 1070 cm^{-1}. Figure 1 shows the molecular structure of **5**, selected bond lengths are contained in Table 2. The technetium atom is five-coordinate, and its coordination sphere can best be described as a square pyramid with the nitrido nitrogen atom as apex. The basal plane of the pyramid is formed by the chloro ligands and the nitrogen atoms of the phosphoraneimines. They are coplanar within 0.053(2) Å (rms 0.0536). The Tc atom is displaced from this plane by 0.589(2) Å toward N10. This contrasts the bonding situation of [TcNCl$_2$(PPh$_3$)$_2$], where the coordination sphere of the metal is strongly distorted toward a trigonal bipyramid with the phosphines as axial ligands.[28] The Tc−N10 bond length of 1.589(4) Å belongs to the shortest technetium−nitrogen triple bonds that have been observed.[7] Shorter Tc≡N bonds were only observed for two [TcNCl$_4$]$^-$ salts,[37] a dithiocarbamato/dithiooxalato mixed-ligand complex[38] and a complex cation with 1,4,8,11-tetrathiacyclodecadecane (1.581 Å).[39] The phosphoraneimine ligands in **5** are in trans-arrangement, and the corresponding Tc−N bond lengths indicate single bonds as is observed for other donor−acceptor complexes of the same type.[9] The spectroscopically detected protonation of N1 and N2 is supported by Tc−N−P angles of 133.7(3) and 134.8(3)° and the localization of the corresponding hydrogen atom positions in the final Fourier maps.

An excess of the chelating phosphoraneimine Me$_3$SiNP(Ph$_2$)CH$_2$PPh$_2$ readily reacts with [NBu$_4$][ReOCl$_4$] and [NBu$_4$][ReNCl$_4$] under exchange of the equatorial chloro ligands and formation of air-stable, cationic rhenium(V)

---

(29) Duatti, A.; Marchi, A.; Pasqualini, R. *J. Chem. Soc., Dalton Trans.* **1990**, 3729.

(30) Abram, U.; Wollert, R. *Radiochim. Acta* **1993**, *63*, 149.

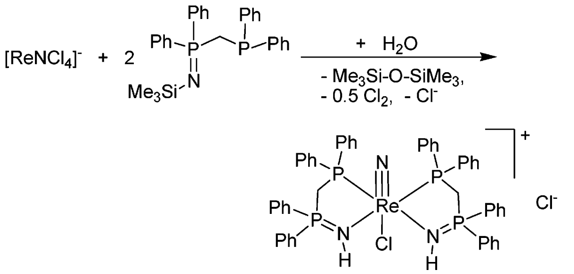
(31) (a) Chatt, J.; Falk, C. D.; Leigh, G. J.; Paske, R. J. *J. Chem. Soc. A* **1969**, 2288. (b) Baldas, J.; Bonnyman, J.; Pojer, P. M.; Williams, G. A.; Mackay, M. F. *J. Chem. Soc., Dalton Trans.* **1981**, 1798.

(32) (a) Baldas, J.; Bonnyman, J.; Williams, G. A. *J. Chem. Soc., Dalton Trans.* **1984**, 2395. (b) Abram, U.; Köhler, K.; Kirmse, R.; Kalinochenko, N. B.; Marov, I. N. *Inorg. Chim. Acta*, **1990**, *176*, 139.

(33) Bonfada, E.; Abram, U.; Strähle, J. *Z. Anorg. Allg. Chem*. **1998**, *624*, 757.

complexes. The products contain $Ph_2PCH_2PPh_2NH$ ligands when moisture is not carefully excluded during the entire reaction, and the replacement of the oxo ligand of $[ReOCl_4]^-$ by an "N^{3-}" ligand is obtained as has been observed for the reaction of $[ReOCl_4]^-$ with $Me_3SiNPPh_3$. The isolation of an oxo complex, however, is successful when equimolar amounts of $[NBu_4][ReOCl_4]$ and $Me_3SiNP(Ph_2)CH_2PPh_2$ and absolutely dry solvents are used.

The rhenium(VI) center is reduced during reactions with $[NBu_4][ReNCl_4]$, and the formation of the rhenium(V) complex $[ReNCl(Ph_2PCH_2PPh_2NH)_2]Cl$ (**1**) can be described by eq 2.



(2)

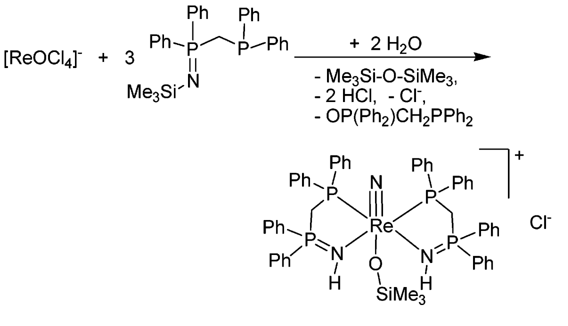
Attempted reactions of $[ReNCl_4]^-$ in dry acetonitrile do not give the same product. No reaction was observed at ambient conditions or with slight heating, and prolonged heating under reflux results in decomposition of the phosphoraneimine and the formation of a variety of rhenium(VI) species, as determined by EPR spectroscopy of the reaction mixtures. We were not able to isolate and characterize defined products from the resulting dark brown solutions.

Single crystals of an acetonitrile solvate of **1** are obtained by slow evaporation of a CH_3CN solution of the complex. They decompose slowly by the loss of solvent to give a yellow powder. NMR and IR spectroscopic results confirm the diamagnetism of the product and the protonation of the nitrogen atoms. The coordination environment of rhenium in the $[ReNCl(Ph_2PCH_2PPh_2NH)_2]^+$ cation is a distorted octahedron with the $Ph_2PCH_2PPh_2NH$ igands in cis-arrangement (Figure 2). Selected bond lengths and angles are summarized in Table 3. The Re−Cl bond of 2.715(1) Å is markedly elongated by the considerable trans influence of the strong σ-donor "N^{3-}" ligand. Two different angles between the nitrido nitrogen atom and the equatorial donor atoms are observed (92.92(7) and 94.29(7)° to the phosphine donors, 102.35(9) and 106.34(9)° to the imine nitrogen atoms). This may not primarily be attributed to different sterical requirements of these moieties, but to the fact that the imine hydrogen atoms H1 and H2 are involved in hydrogen bonds to the counterion Cl^-. More details are contained in Figure S1 and Table S1 of the Supporting Information. The Re−N1 and Re−N2 bond lengths of 2.110(2) and 2.084(2) Å clearly indicate a rhenium−nitrogen single bond and the presence of a donor−acceptor type complex. This is also supported by the Re−N−P angles, which are close to 120°. Whereas the P2−C10 and P21−C20 bond lengths are in the typical range, the P1−C10 and P11−C20 bonds (1.793(2) and 1.805(3) Å) are slightly shortened. This indicates some delocalization of electron density over the phosphoraneimine phosphorus atoms.

Table 3. Selected Bond Lengths (Å) and Angles (deg) in the Rhenium Nitrido Complexes (**1**), (**2**) and Their Technetium Analogue (**7**)

	(**1**)	(**2**)	(**7**)
M−N10	1.666(2)	1.690(4)	1.620(3)
M−Cl1/O	2.715(1)	1.952(4)	2.715(1)
M−N1	2.110(2)	2.071(5)	2.103(3)
M−N2	2.084(2)	2.055(5)	2.106(3)
M−P2	2.432(1)	2.496(2)	2.417(1)
M−P21	2.432(1)	2.485(2)	2.462(1)
N1−P1	1.596(2)	1.598(5)	1.586(3)
N2−P11	1.605(2)	1.611(6)	1.587(3)
P1−C10	1.793(2)	1.796(6)	1.808(3)
P2−C10	1.840(2)	1.828(6)	1.846(3)
P11−C20	1.805(3)	1.795(7)	1.794(3)
P21−C20	1.848(2)	1.823(7)	1.838(3)
N10−M−Cl/O	168.69(7)	165.6(2)	164.1(1)
N10−M−N1	102.35(9)	98.3(2)	105.8(1)
N10−M−N2	106.34(9)	99.3(2)	104.3(1)
N10−M−P2	92.92(7)	86.9(2)	91.9(1)
N10−M−P21	94.29(7)	89.7(2)	91.7(1)
M−N1−P1	120.1(1)	125.2(3)	127.6(2)
M−N2−P11	125.4(1)	126.2(3)	125.9(2)
N1−P1−C10	105.3(1)	105.6(3)	106.2(2)
P1−C10−P2	108.3(1)	110.0(3)	107.0(2)
C10−P2−M	103.38(8)	102.0(2)	103.9(1)
N1−M−P2	84.69(6)	83.6(1)	79.30(8)
N2−P11−C20	105.8(1)	105.3(3)	106.2(2)
P11−C20−P21	108.0(1)	108.7(3)	110.8(2)
C20−P21−M	102.84(8)	99.7(2)	101.5(1)
N2−M−P21	83.56(6)	82.3(2)	83.30(8)
N1−M−N2	81.73(8)	84.9(2)	83.6(1)

A similar bonding situation is found in the $[ReN(OSiMe_3)(Ph_2PCH_2PPh_2NH)_2]^+$ cation, which is formed when $[NBu_4][ReOCl_4]$ reacts with an excess of $Ph_2P(NSiMe_3)CH_2PPh_2$ according to eq 3.



(3)

The trimethylsiloxo ligand is product of the attack of a released $\{Me_3Si\}$ residue to the oxo ligand of the starting complex. Figure 3 depicts an ellipsoid representation of the cation. Selected bond lengths and angles are compared with the corresponding values in $[ReNCl(Ph_2PCH_2PPh_2NH)_2]^+$ in Table 3. Similar to the situation in the chloro derivative, the N10−Re−N(imine) bond angles are larger than the N10−Re−P angles and some delocalization of electron

---

(34) Abram, U.; Hübner, R.; Wollert, R.; Kirmse, R.; Hiller, W. *Inorg. Chim. Acta* **1993**, *206*, 9.

(35) Abram, U.; Hagenbach, A. *Z. Anorg. Allg. Chem.* **2002**, *628*, 1719.

(36) Farrugia, L. J. *J. Appl. Crystallogr.* **1997**, *30*, 565.

(37) Baldas, J.; Colmanet, S. F.; Williams, G. A. *Chem. Commun.* **1991**, 954.

(38) Baldas, J.; Boas, J. F.; Colmanet, S. F.; Williams, G. A. *J. Chem. Soc. Dalton Trans.* **1992**, 2845.

(39) Pietzsch, H.-J.; Spies, H.; Leibnitz, P.; Reck, G. *Polyhedron* **1993**, *12*, 2995.

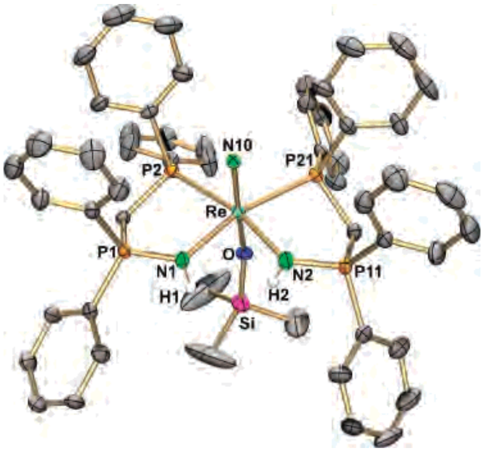


Figure 3. Ellipsoid representation[36] of the complex cation of **2**. Thermal ellipsoids represent 30% probability. Hydrogen atoms at carbon atoms are omitted for clarity.

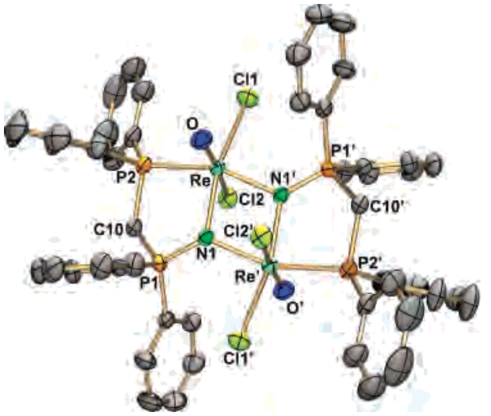


Figure 4. Ellipsoid representation[36] of **4**. Thermal ellipsoids represent 50% probability. Hydrogen atoms are omitted for clarity.

density from the P═N double bonds to the P−C10 and P−C20 bonds is observed. The imine nitrogen atoms and the chloride counterion are linked by hydrogen bonds as has been observed for **1**. Details are given in Fig. S2 and Table S2.

A remarkable feature is the Re−N10 bond length of 1.690(4) Å, which is somewhat longer than in $[ReNCl(Ph_2PCH_2PPh_2NH)_2]^+$, and the fact that the Re−O bond of 1.952(4) Å is shorter than expected for a rhenium−oxygen single bond despite the expected lengthening by the well-documented trans-influence of nitrido ligands (see also the discussion vide supra concerning the unexceptionally long Re−Cl bond in **1**). This indicates partial double bond character and transfer of π-electron density from the Re≡N bond to the trans-situated Re−O bond. This has previously been observed for a number of oxorhenium complexes with trans-bonded alkoxo ligands[40] and a few examples of imido complexes.[41] For nitrido species, however, it is without precedent.

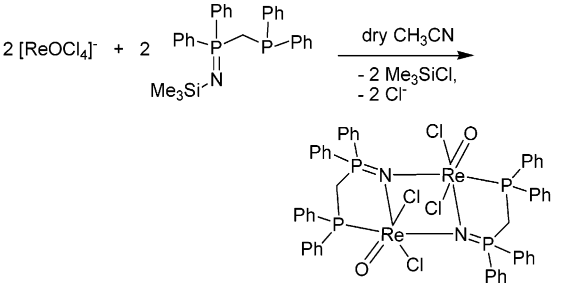
The presence of a nitrido ligand, which cannot doubtlessly be derived from the X-ray structural data, is concluded from the spectroscopic results and the elemental analysis of the product. The Re≡N frequency in the IR spectrum of the compound can be assigned at 1060 cm^{-1}, the diamagnetism of the complex indicates the presence of an "N^{3-}" ligand rather than an "O^{2-}" one, and the molecular ion of the complex cation could be detected at $m/z = 1089$ in the FAB^+ mass spectrum.

Table 4. Selected Bond Lengths (Å) and Angles (deg) in $[ReOCl_2(\mu N-Ph_2PCH_2PPh_2N)]_2$ (**4**)[a]

Re−O	1.679(3)	Re−Cl1	2.422(1)
Re−Cl2	2.546(1)	Re−P2	2.446(1)
Re−N1	2.028(3)	Re−N1′	2.081(3)
N1−P1	1.612(3)	P1−C10	1.817(4)
P2−C10	1.835(4)		
O−Re−Cl1	94.7(1)	O−Re−Cl2	167.5(1)
O−Re−P2	92.5(1)	O−Re−N1	102.4(2)
O−Re−N1′	103.9(2)	Re−N1−Re′	103.9(2)
Re−N1−P1	122.6(2)	N1−P1−C10	108.0(2)
P1−C10−P2	109.1(2)	Re−P2−C10	100.8(1)
N1−Re−P2	87.0(1)	Re......Re′	3.235(1)

[a] Symmetry operation: (′) $1 - x, 2 - y, 2 - z$.

A rhenium(V) complex with an oxo ligand can be isolated when equimolar amounts of $[NBu_4][ReOCl_4]$ and $Ph_2P(NSiMe_3)CH_2PPh_2$ are used and the reaction is performed in carefully dried acetonitrile (eq 4).



(4)

The color of the solution then turns blue and bright blue crystals of $[ReOCl_2(\mu-N-Ph_2PCH_2PPh_2N)]_2$ (**4**) precipitate upon concentration. The solid product is stable on air after isolation and can be redissolved in dry solvents without decomposition. Access of moisture to the reaction mixture, however, results in an immediate change of color and the formation of various phosphoraneimine products. This is indicated by the appearance of various ^{31}P NMR signals in the range between 35 and 45 ppm in such reaction mixtures, whereas the phosphoraneiminato phosphorus atom in **4** shows a resonance at 81.7 ppm. The oxo band in the infrared spectrum of the dimeric complex can be assigned at 943 cm^{-1}, which is in the typical range of monooxo rhenium(V) complexes.

An X-ray structure analysis of $[ReOCl_2(\mu-N-Ph_2PCH_2PPh_2N)]_2$ confirms the dimeric character of the complex (Figure 4). The rhenium atoms are linked by two phosphoraneiminato functionalities in an almost symmetric fashion with Re−N1 bond lengths of 2.028(3) and 2.081(6) Å. The molecular structure has inversion symmetry with the center of inversion in the center of the resulting four-membered $\{Re_2N_2\}$ ring. Selected bond lengths and angles are summarized in Table 4. There are no significant differences in

---

(40) Abram, S.; Abram, U.; Schulz Lang, E.; Strähle, J. *Acta Crystallogr.* **1995**, *C51*, 1078 and references therein.

(41) (a) Witter, U.; Strähle, J.; Abram, U. *Z. Anorg. Allg. Chem.* **1995**, *621*, 1338. (b) Witter, U.; Strähle, J.; Abram, U. *Z. Anorg. Allg. Chem.* **1997**, *623*, 218. (c) Yam, W.-W. V.; Tam, K.-K.; Cheung, K.-K. *J. Chem. Soc., Dalton Trans.* **1995**, 2779.

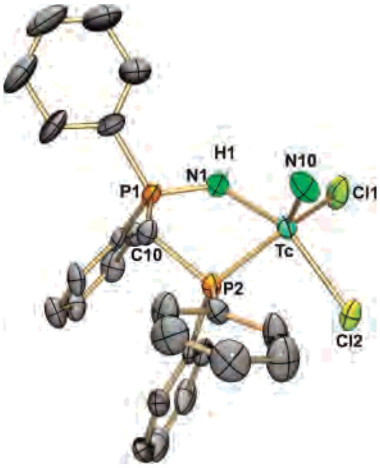


Figure 5. Ellipsoid representation[36] of **6**. Thermal ellipsoids represent 50% probability. Hydrogen atoms of carbon atoms are omitted for clarity.

Table 5. Selected Bond Lengths (Å) and Angles (deg) in $[TcNCl_2(Ph_2PCH_2PPh_2NH)]$ (**6**) (values for two crystallographically independent species)

Tc−N10	1.612(7)/1.620(8)	Tc−Cl1	2.411(2)/2.405(2)
Tc−Cl2	2.409(2)/2.413(2)	Tc−N1	2.077(7)/2.095(7)
Tc−P2	2.372(2)/2.364(2)	N1−P1	1.606(7)/1.608(7)
P1−C10	1.804(7)/1.811(8)	P2−C10	1.838(7)/1.826(8)
N10−Tc−Cl1	109.9(3)/102.3(3)	N10−Tc−Cl2	106.1(3)/114.8(3)
N10−Tc−N1	107.0(4)/104.8(4)	N10−Tc−P2	93.8(3)/96.2(3)
Tc−N1−P1	126.5(4)/124.6(4)	N1−P1−C10	104.9(4)/105.6(4)

the Re−N(imine) bond lengths in **1** and **2** and the Re−N1 bond length in **4**, although the latter one belongs to a phosphoraneiminato unit. However, the values are in the range of the M−N bond lengths in the other structurally characterized osmium and rhenium complexes with bridging phosphoraneiminates.[5,6]

Our attempts to isolate crystalline products from reactions of $[NBu_4][TcOCl_4]$ with $Ph_2P(NSiMe_3)CH_2PPh_2$ failed up to now. Independent of the solvents and the ratios of the reactants only mixtures of different complexes are formed. The EPR spectroscopic detection of $[TcNCl_4]^-$ after addition of 1 equiv of phosphoraneimine confirms the formation of nitrido species. This technetium(VI) species, however, disappears after addition of an excess of $Ph_2P(NSiMe_3)CH_2PPh_2$, and a mixture of various diamagnetic Tc(V) complexes is formed as can be concluded from the ^{31}P NMR spectra of the resulting solutions. This led us to study the ligand exchange reaction starting from $[NBu_4][TcNCl_4]$.

When $[NBu_4][TcNCl_4]$ is mixed with equimolar amounts or a slight excess of $Ph_2P(NSiMe_3)CH_2PPh_2$, only an intermediate color change is observed. But no more EPR signal can be detected in the finally obtained orange-red solution. This indicates reduction or dimerization of the technetium complex. Orange-red crystals of $[TcNCl_2(Ph_2PCH_2PPh_2NH]$ (**6**) deposit upon cooling. The compound is soluble in organic solvents such as $CHCl_3$ or acetonitrile and stable in air. Figure 5 is an ellipsoid representation of the structure of one of two crystallographically independent molecules of **6** in its unit cell. Selected bond lengths and angles are summarized in Table 5. The technetium atom is five-coordinate with the atoms Cl1, Cl2, P2, and N1 as the basal plane of an irregular square pyramid and the nitrido nitrogen atom as its apex. The metal is located approximately 0.56 Å above the basal plane. The bonding situation inside the chelate ring is similar to those described previously for the rhenium complexes. The imine nitrogen atoms in both independent molecules are protonated and form hydrogen bonds to each one chloro ligand of a neighboring molecule. This results in the formation of H-bonded dimeric units in the solid-state structure of the compound. Details are contained in Table S3 and Figure S3.

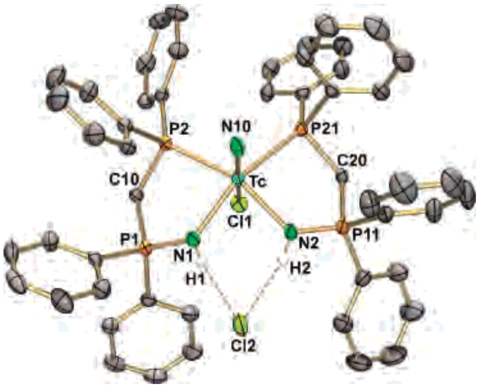


Figure 6. Ellipsoid representation[36] of the complex cation of **7** with the hydrogen bonds between the nitrogen atoms and the chloride counterion (N1−H1 0.86, H1−Cl2 2.51, N1−Cl2 3.322(3) Å, N1−H1−Cl2 157.7°; N2−H2 0.86, H2−Cl2 2.38, N2−Cl2 3.225(3) Å, N2−H2−Cl2 167.4°). Thermal ellipsoids represent 50% probability. Hydrogen atoms of carbon atoms are omitted for clarity.

Further ligand exchange and the formation of $[TcNCl(Ph_2PCH_2PPh_2NH)_2]Cl$ (**7**) is observed when $[NBu_4][TcNCl_4]$ reacts with a large excess of $Ph_2P(NSiMe_3)CH_2PPh_2$. This is indicated by a change of the color of the reaction mixture from orange-red to yellow-brown. Yellow needles of $[TcNCl(Ph_2PCH_2PPh_2NH)_2]Cl\cdot 2\ CH_3CN$ precipitate from such solutions upon standing and cooling overnight. The $\nu(Tc\equiv N)$ band in this product is observed at 1050 cm^{-1}, and the ^{31}P NMR shows the phosphoraneimine signal as a doublet at 52.1 ppm and a very broad signal at 37.8 ppm. The latter one has been assigned to the phosphine site of the chelating ligand. The broadening of ^{31}P NMR signals of phosphorus atoms directly coordinated to technetium in diamagnetic nitridotechnetium(V) complexes seems to be typical. It is temperature-dependent and has been attributed to a scalar coupling of the ^{31}P nucleus with the quadrupole moment of ^{99}Tc in a previous paper.[42]

The structure of the $[TcNCl(Ph_2PCH_2PPh_2NH)_2]^+$ cation is very similar to that of the corresponding rhenium complex. The technetium−nitrogen triple bond causes a strong trans-influence, which results in a very long Tc−Cl bond of 2.715(1) Å. Delocalization of electron density from the P═N bonds to the neighboring P−C bonds is indicated by two sets of bond lengths of the P−C10 and P−C20 bonds (1.794(3) and 1.808(3) Å from the P(V) atoms and 1.838(3) and 1.846(3) Å from the P(III) atoms). More bond lengths and angles are contained in Table 3 and can easily compared there with the corresponding values in the $[ReNCl(Ph_2PCH_2$-

---

(42) Abram, U.; Lorenz, B.; Kaden, L.; Scheller, D. *Polyhedron* **1988**, *7*, 285.

$PPh_2NH)_2]^+$ and $[ReN(OSiMe_3)(Ph_2PCH_2PPh_2NH)_2]^+$ cations. The nitrogen atoms of the ligands are linked with the chloride counterion by hydrogen bonds as is shown in Figure 6.

Conclusions

The examples in the present paper show that common rhenium and technetium complexes readily react with trimethylsilylated phosphoraneimines and that non-nitrido starting materials are easily converted into nitrido complexes by cleavage of P═N bonds. Access of moisture or protons from other sources (e.g. decomposition of solvents) results in protonation of $\{R_3P{=}N\}^-$ units and coordination of the resulting neutral phosphoraneimines in donor−acceptor complexes. The stability of the products is increased when the phosphoraneimine units are constituents of chelating systems.

Phosphoraneiminato complexes are formed under exclusion of moisture and strict control of the reaction.

Acknowledgment. We thank the Hermann-Starck AG, Goslar, for providing us with rhenium metal, and Prof. R. Kirmse, Leipzig, for EPR measurements. S.S.A thanks CONACYT (Mexico) for financial support.

Supporting Information Available: Tables and illustrations of hydrogen bonds in compounds **1**, **2**, and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

IC048210Q