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New Approach to the Chemistry of Technetium(V) and Rhenium(V) Phenylimido Complexes: Novel $[M(NPh)PNP]^{3+}$ Metal Fragments (M = Tc, Re; PNP = Aminodiphosphine) Suitable for the Synthesis of Stable Mixed-Ligand Compounds

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Ligand-exchange reactions of the aminodiphosphine ligand bis[(2-diphenylphosphino)ethyl]amine hydrochloride (PNHP·HCl) with labile $M(NPh)Cl_3(PPh_3)_2$ precursors (M = Re, Tc) in the presence of triethylamine yield monocationic phenylimido *mer,cis*-$[M(NPh)Cl_2(PNHP)]Cl$ (M = Re, **1**; Tc, **2**) intermediate complexes. X-ray analyses show that in both compounds the aminodiphosphine acts as a tridentate ligand dictating a mer,cis arrangement. Two chloride ligands, respectively in an equatorial and in the axial position trans to the linear M–NPh moiety, fill the remaining positions in a distorted-octahedral geometry. The chloride trans to the metal–imido core is labile, and is replaced by an alcoholate group, without affecting the original geometry, as established in *mer,cis*-[Re(NPh)(OEt)Cl(PNHP)]-Cl **4**. Otherwise, ligand-exchange reactions involving the aminodiphosphine bis[(2-diphenylphosphino)ethyl]methylamine (PNMeP), in which the central secondary amine has been replaced by a tertiary amine function, or its hydrochloride salt (PNMeP·HCl) give rise to three different species, depending on the experimental conditions: *fac,cis*-[Re(NPh)-Cl_2(PNMeP)]Cl **3a**, *cis,fac*-$Re(NPh)Cl_3$(PNMeP)·HCl **3b**, and *mer,trans*-$[Re(NPh)Cl_2(PNMeP)]Cl$ **3c**, which are characterized in solution by multinuclear NMR studies. The monodentate groups incorporated in these intermediate compounds, either halides and/or ethoxide, undergo substitution reactions with bidentate donor ligands such as catechol, ethylene glycol, and 1,2-aminophenol to afford stable mixed ligand complexes of the type [M(NPh)(O,O-cat)(PNP)]Cl [PNP = PNHP M = Re **5**, Tc **6**; PNP = PNMeP M = Re **7**], [Re(NPh)(O,O-gly)(PNP)]Cl [PNP = PNHP **8**, PNMeP **9**] and [Re(NPh)(O,N-ap)(PNMeP)]Cl **10**. X-ray diffraction analyses of the representative compounds **5** and **8** reveal that the aminodiphosphine switches from the meridional to the facial coordination mode placing the heteroatom of the diphosphine trans to the phenylimido unit and the bidentate ligand in the equatorial plane. Solution-state NMR studies suggest an analogous geometry for **6**, **7**, **9**, and **10**. Comparison with similar mixed ligand complexes including the terminal nitrido group is discussed.

Introduction

The search for substitution-inert rhenium and technetium compounds to be exploited as potential radiopharmaceuticals recently led to the design of new molecules whose main feature is the presence of both a stable building-block, which includes the metal and suitable ancillary ligand(s), and a coordinated chelating ligand eventually coupled to a biomolecule.[1,2] The building-block comprises the metal ion, or a particular metal core, stabilized by a suitable framework of mono or polydentate ligands, whereas the coordination sphere of the metal is completed by labile monodentate ligands such as water molecules or halide groups. The latter can be easily replaced by small chelating ligands, either bidentate or tridentate, which in turn can be coupled to a specific pharmacophore. The generality and the potentiality of this synthetic approach is well described by two recent prototypes, the tricarbonyl moiety, $[Tc^{I}(CO)_3]^{+}$,[3] and the "supernitrido" moiety $[Tc^{V}(N)(PNP)]^{2+}$ (Scheme 1).[4] Despite

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(1) Jurisson, S.; Lydon, J. D. *Chem. Rev.* **1999**, *99*, 2205−2218.
(2) Liu, S.; Edwards, D. S. *Chem. Rev.* **1999**, *99*, 2235−2268.

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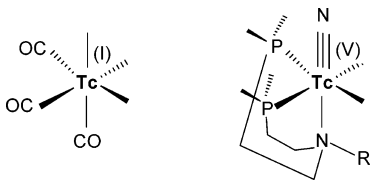
Scheme 1



the striking differences in the main features of the synthons (i.e., metal oxidation state and electronic configuration, type of ancillary ligands, molecular weight and lipophilicity, etc.), the ability to obtain stable mixed-ligands complexes confirms the correctness of this design.

In more detail, in the case of $[Tc^{I}(CO)_3(OH_2)_3]^+$, the Tc(I) ion is stabilized by the carbonyl ligands arranged in a facial fashion, thereby labilizing the trans positioned water molecules, and making them susceptible for exchange with a tridentate ligand such as histidine.[5] Several biomolecules including biotin, enkephalin, and vitamin B12 conjugates have been inserted at the N^{ϵ}-position of the imidazolic heterocycle of histidine[6] providing further support of the efficacy of the approach.

In the case of $[Tc^{V}(N)(PNP)]^{2+}$, the distinctive $[Tc(N)]^{2+}$ core is stabilized by a particular diphosphine ligand (having a five-member spacer including the nitrogen atom of a tertiary amine (PN(R)P)), adopting again a facial arrangement. The equatorially and cis-positioned phosphorus donors trans labilize the chloride groups in the intermediate species $Tc(N)(PNP)Cl_2$, making possible a straightforward formation of mixed heterocomplexes of the type *fac*-$[M(N)(PN(R)P)(X-Y)]^{+/0}$, where X−Y is a bidentate ligand like S,O-cysteine or S,N-cysteine,[7] and S,S-dithiolate.[8] Representative biomolecules such as 2-methoxyphenyl piperazines[9] or benzodiazepine analogues[10] have been incorporated into the cysteine framework giving stable metal conjugates.

In principle, in addition to the already investigated $[M(N)]^{2+}$ core, further moieties including metal nitrogen multiple bonds, i.e., metal−imido, −hydrazido, and −diazenido could be envisaged in order to exploit a synthetic strategy comprising a substitution-inert metal fragment. Our first effort in this direction was aimed at the study of a stable metal fragment including the phenylimido core $[M{=}NPh]^{3+}$ (M = Tc, Re) for the following reasons. Despite several Tc−imido complexes reported in the literature, the transfer of this chemistry at non-carrier-added (nca) level, trying to mimic the rich substitution reactivity exhibited by the oxo core, has always met severe obstacles. So far, the ^{99m}Tc−imido core has been claimed only among a series of cores suitable for the development of new radiopharmaceuticals in a patent report.[11] As far as rhenium is concerned, a few examples of nca ^{188}Re species are reported as potential target-specific radiopharmaceuticals. For instance, compounds of general formula $^{188}Re(NC_6H_4\text{-}X)Cl_3(PPh_3)_2$ contain a para-substituted phenylimido ligand functionalized with a carboxylic group conjugated to various cholesterol derivatives[12] or to a chlorambucil analogue.[13] Further studies on the rhenium phenylimido chemistry have been focused on the derivatization of the phenylimido group only,[14] or the replacement of aryl for alkyl substituents at the imido unit.[15,16] However, these compounds are hydrolytically unstable under biological conditions. In our opinion, this instability could arise from the presence of several monodentate ligands in the coordination sphere. We thought, conversely, that the phenylimido core would be stabilized by substitution of monodentate for particular polydentate ligands. Taking into account that imido−Tc and −Re derivatives strongly prefer the presence of phosphine ligands (analogously to all other compounds containing metal−nitrogen multiple bonds), we investigated the possibility of introducing a aminodiphosphines (PNP) in the phenylimido metal fragment $[M(NPh)(PNP)]^{3+}$ using a synthetic approach already successfully utilized in the case of the "supernitrido" moiety.

In this study we report on a series of cationic complexes of the type $[M(NPh)X_2(PNP)]^+$ (**1**−**4**), in which the relevant aminodiphosphine predominantly adopts a meridional coordination. In the case of rhenium, further substitution of monodentate halide and/or ethoxide groups for bidentate chelating ligand (H_2L-L) yield dissymmetric mixed-ligand complexes of the general formula *fac*-$[Re(NPh)(L-L)(PNP)]^+$ (**5**−**10**), via rearrangement of the aminodiphosphine into a facial configuration. Comparison of phenylimido $[Re(NPh)(L-L)(PNP)]^+$ with previously synthesized nitrido derivatives Re(N)(L−L)(PNP) is discussed.

Experimental Section

Caution! ^{99}Tc is a weak β-emitter ($E_\beta = 0.292$ MeV, $t_{1/2} = 2.12 \times 10^5$ years). All manipulations were carried out in laboratories approved for low-level radioactivity using monitored hoods and

(3) Alberto, R.; Schibli, R.; Waibel, R.; Abram, U.; Schubiger, A. P. *Coord. Chem. Rev.* **1999**, *190*−*192*, 901−919 and references therein.
(4) Bolzati, C.; Boschi, A.; Uccelli, L.; Tisato, F.; Refosco, F.; Cagnolini, A.; Duatti, A.; Prakash, S.; Bandoli, G.; Vittadini, A. *J. Am. Chem. Soc.* **2002**, *124*, 11468−11479.
(5) Egli, A.; Alberto, R.; Tannahill, L.; Schibli, R.; Abram, U.; Schaffland, R.; Tourwe, D.; Jeannin, K.; Iterbeke, K.; Schubiger, P. A. *J. Nucl. Med.* **1999**, *40*, 1913−1917.
(6) Van Staveren, D. R.; Mundwiler, S.; Hoffmanns, U.; Pak, J. K.; Spingler, B.; Metzler-Nolte, N.; Alberto, R. *Org. Biomol. Chem.* **2004**, *2*, 2593−2603.
(7) Bolzati, C.; Benini, E.; Cazzola, E.; Jung, C.; Tisato, F.; Refosco, F.; Spies, H.; Uccelli, L.; Duatti, A. *Bioconjugate Chem.* **2004**, *15*, 628−637.
(8) Boschi, A.; Bolzati, C.; Benini, E.; Malagò, E.; Uccelli, L.; Duatti, A.; Piffanelli, A.; Refosco, F.; Tisato, F. *Bioconjugate Chem.* **2001**, *12*, 1035−1042.
(9) Bolzati, C.; Mahmood, A.; Malagò, E.; Uccelli, L.; Boschi, A.; Jones, A. G.; Refosco, F.; Duatti, A.; Tisato F. *Bioconjugate Chem.* **2003**, *14*, 1231−1242.
(10) Boschi, A.; Uccelli, L.; Duatti, A.; Bolzati, C.; Refosco, F.; Tisato, F.; Romagnoli, R.; Baraldi, P.; Varani, K.; Borea, P. *Bioconjugate Chem.* **2003**, *14*, 1279−1288.
(11) Archer, C. M.; Dilworth, J. R.; Jobanputra, P.; Thomson, R. M. Patent n. WO 91/03262, 1991.
(12) Arterburn, J. B.; Hall, K. A.; Fogarty, I. M.; Goreham, D. M.; Bryan, J. C.; Ott, K. C. *Radiochim. Acta* **1997**, *79*, 119−121.
(13) Arterburn, J. B.; Fogarty, I. M.; Hall, K. A.; Ott, K. C.; Bryan, J. C. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2877−2878.
(14) Arterburn, J. B.; Venketeswara Rao, K.; Goreham, D. M.; Valenzuela, M. V.; Holguin, M. S.; Hall, K. A.; Ott, K. C.; Bryan, J. C. *Organometallics* **2000**, *19*, 1789−1795.
(15) Chatt, J.; Dilworth, J. R.; Leigh, G. J. *J. Chem. Soc. A* **1970**, 2239−2243.
(16) (a) Chatt, J.; Dosser, R. J.; King, F.; Leigh, G. J. *J. Chem. Soc., Dalton Trans.* **1976**, 2435−2440. (b) Ondraceck, A. L.; Fanwick, P. E.; Walton, R. A. *Inorg. Chim. Acta* **1998**, *278*, 245−249.

gloveboxes. When handled in milligram amounts, ^{99}Tc does not present a serious health hazard because common laboratory glassware provides adequate shielding. Bremsstrahlung is not a significant problem due to the low energy of the β-particles. However, normal radiation safety procedures must be used at all times, especially with solid sample, to prevent contamination and inhalation.

Materials. All solvents and commercially available substances were of reagent grade and used without further purification. Tetrahydrofuran was distilled under dinitrogen from the potassium ketyl of benzophenone. The complexes $Re(NPh)Cl_3(PPh_3)_2$[17] and $^{99}Tc(NPh)Cl_3(PPh_3)_2$[18] were prepared according to literature methods.

Instrumentation. Elemental analyses were performed on a Carlo Erba 1106 elemental analyzer. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on a Bruker AMX-300 instrument, using $SiMe_4$ as internal reference (^{1}H, ^{13}C) and 85% aqueous H_3PO_4 as external reference (^{31}P).

Synthesis of the Ligands. Bis[(2-diphenylphosphino)ethyl]amine hydrochloride (PNHP·HCl) was prepared according to the literature method.[19]

Bis[(2-diphenylphosphino)ethyl]methylamine (PNMeP). Diphenylphosphine (5.0 g, 26.9 mmol) was transferred into a two-necked round-bottom flask containing tetrahydrofuran (50 mL) under dinitrogen, and *n*-buthyllithium (2.5 M) in *n*-hexane (11 mL, 27 mmol) was slowly added to the solution giving rise to an orange color. The mixture was cooled to −78 °C in an acetone/liquid nitrogen slurry. *N*-Methylbis(2-chloroethyl)amine hydrochloride (2.6 g, 16.6 mmol), dissolved in tetrahydrofuran (50 mL), was neutralized by adding *n*-buthyllithium (6 mL, 15.6 mmol) dropwise and added to the reaction mixture using a pressure-equalizing funnel. The addition was done quite rapidly to avoid decomposition of the neutralized amine. The reaction mixture was allowed to warm to room temperature, over a period of at least 2 h, and then stirred overnight at room temperature. The resulting colorless solution was cooled to 0 °C and degassed water (50 mL) was added dropwise. The mixture was transferred into a separating funnel and treated with freshly distilled (under dinitrogen) diethyl ether (2 × 50 mL). The collected organic phases were rotoevaporated until an oil was obtained, which, by treatment with degassed methanol, separated a white solid. The product was recovered, washed with methanol, and dried in a vacuum pump. Yield: 68%. In the case that no white solid formed by addition of methanol, chromatographic purification was necessary (silica gel column, chloroform/diethyl ether 1:1). The desired product was eluted first and concentration of the first fractions led to an oil, which was treated again following the above procedure.^{1}H NMR ($CDCl_3$, ppm): 7.40−7.20 (m, 20H, H_{arom}), 2.93 (m, 4H, CH_2−CH_2), 2.68 (s, 3H, CH_3), 2.42 (m, 4H, CH_2−CH_2). ^{31}P{H} NMR ($CDCl_3$, ppm): −19.1. ^{13}C{H}($CDCl_3$, ppm): 22.1 (d, $^1J_{C-P}$ = 15 Hz, CH$_2$−PPh$_2$), 39.6 (s, N−CH$_3$), 52.4 (d, $^2J_{C-P}$ = 29 Hz, CH$_2$−CH$_2$−PPh$_2$), aromatic *C*: 128.9(d, J_{C-P} = 7 Hz), 129.5, 130.5 and 132.7 (d, J_{C-P} = 19 Hz).

Bis[(2-diphenylphosphino)ethyl]methylamine hydrochloride (PNMeP·HCl). The synthesis procedure is analogous to that reported above for PNMeP, but the workup of the product is different. After the reaction quenching with degassed water and extraction with *n*-hexane, hydrochloric acid (2 N, 50 mL) was added under vigorous stirring. A milky oil was formed which was collected and dried in a vacuum pump. The oily residue was dissolved in the minimum amount of dichloromethane, ethanol was added, and the mixture was refrigerated overnight at 4 °C. A white precipitate was formed which was filtered and dried under vacuum. Yield: 65%. ^{1}H NMR ($CDCl_3$, ppm): 7.40−7.20 (m, 20H, H_{arom}), 2.95 (m, 4H, CH_2−CH_2), 2.68 (s, 3H, CH_3), 2.42 (m, 4H, CH_2−CH_2). ^{31}P{H} NMR ($CDCl_3$, ppm): −20.0 (s). ^{13}C{H}($CDCl_3$, ppm): 22.2 (d, $^1J_{C-P}$ = 15 Hz, CH$_2$−PPh$_2$), 39.6 (s, N-CH$_3$), 52.6 (d, $^2J_{C-P}$ = 29 Hz, CH$_2$−CH$_2$−PPh$_2$), aromatic *C*: 128.9(d, J_{C-P} = 7 Hz), 129.5, 130.7 and 132.7 (d, J_{C-P} = 19 Hz).

Synthesis of the Complexes. *mer,cis*-[Re(NPh)Cl$_2$(PNHP)]Cl, 1. To a suspension of $Re(NPh)Cl_3(PPh_3)_2$ (104 mg, 0.11 mmol) in dichloromethane (15 mL) an excess of PNHP·HCl (75 mg, 0.16 mmol) dissolved in dichloromethane (3 mL) with 50 μL of triethylamine (0.38 mmol) was added dropwise. The reaction mixture was refluxed for 2 h and then stirred overnight at room temperature. The resulting solution was olive-green. The solvent was removed and the green solid was washed with diethyl ether and water, and dried under vacuum. The ^{31}P NMR spectrum of such solid in $CDCl_3$ showed two peaks at 4.3 and 8.4 ppm, which suggested the presence of two products. A pure product was obtained from a 1:2 dichloromethane/*n*-hexane mixture. Grey-blue crystals of **1** were obtained (final yield 50%). **1** is stable in air and soluble in dichloromethane and chloroform, quite soluble in ethanol and methanol, and insoluble in water, *n*-hexane, and diethyl ether. Anal. calcd. for $ReN_2C_{34}H_{34}P_2Cl_3$: C, 49.5; N, 3.4; H, 4.1. Found: C, 50.9; N, 3.4; H, 5.1. ^{1}H NMR ($CDCl_3$, ppm): 10.06 (b, 1H, NH), 8.07 (m, 4H, PPh_2), 7.74 (d, 2H, *o*-NPh), 7.50 (m, 11H, PPh_2+ *p*-NPh), 7.02 (m, 6H, PPh_2) 6.87 (t, 2H, *m*-NPh), 4.01 (bt, 2H, CH_2), 3.39 (bm, 2H, CH_2), 3.22 (bm, 4H, CH_2). ^{31}P{H} NMR ($CDCl_3$, ppm): 8.5 (s). ^{13}C{H} NMR ($CDCl_3$, ppm): 32.00 (d, $^1J_{CP}$ = 30 Hz; >P−CH$_2$−), 58.13 (s, −CH$_2$−NH−). 12 aromatic carbons: 125.5, 127.7, 128.1, 128.2, 128.5, 128.7, 129.6, 130.1, 131.0, 131.2, 133.2, 153.5 (s, ipso-C_{NPh}).

***mer,cis*-[^{99}Tc(NPh)Cl$_2$(PNHP)]Cl, 2.** To a solution of $Tc(NPh)Cl_3(PPh_3)_2$ (45 mg, 0.05 mmol) in dichloromethane/methanol (5 mL/2 mL) a 1:1 equivalent of PNHP·HCl (29 mg, 0.06 mmol) and 20 μL of triethylamine (0.15 mmol) was added under stirring. The brown mixture turned brown-green in 2 min. After 3 h the solution was taken to dryness with a flow of dinitrogen. The oily residue was treated with diethyl ether and the resulting brown-green solid was filtered. The crude solid was washed on the filter with acetone (2 mL). The resulting light green solid was dried under dinitrogen (yield 22 mg, 60%). The product is soluble in chlorinated solvents and acetonitrile, slightly soluble in alcohols, insoluble in diethyl ether. Crystals suitable for X-ray diffraction studies were collected from a 1:1 dichloromethane/*n*-hexane mixture. Anal. Calcd. for $TcN_2C_{34}H_{34}P_2Cl_3$: C, 55.5; N, 3.8; H, 4.6. Found: C, 54.6; N, 3.6; H, 4.8. ^{1}H NMR ($CDCl_3$, ppm): 9.70 (bs, 1H, NH), 8.06 (m, 6H, PPh_2+ *o*-NPh), 7.51 (m, 11H, PPh_2 + *p*-NPh), 7.02 (m, 6H, PPh_2), 6.86 (t, 2H, *m*-NPh), 3.97 (bt, 2H, CH_2), 3.34 (bm, 6H, CH_2). ^{31}P-{H} NMR ($CDCl_3$, ppm): 31.6 (bs).

***fac,cis*-[Re(NPh)Cl$_2$(PNMeP)]Cl, 3a.** To a suspension of $Re(NPh)Cl_3(PPh_3)_2$ (145 mg, 0.16 mmol) in dichloromethane (15 mL) a slight excess of PNMeP (86 mg, 0.17 mmol) was added. The reaction mixture was refluxed for 24 h. The volume of the resulting green-yellow solution was reduced to 3−4 mL and diethyl ether (10 mL) was added. A TLC analysis of the precipitate showed a mixture of different products, so separation by means of a chromatographic column was performed (silica gel, chloroform/ethanol 3:2). Two yellow fractions and a green fraction were collected. The green product was identified as [Re(NPh)Cl$_2$-(PNMeP)]Cl (yield 47%). Anal. Calcd. for $ReN_2C_{35}H_{36}P_2Cl_3$: C,

(17) La Monica, G.; Cenini, S. *Inorg. Chim. Acta* **1978**, *29*, 183−187.
(18) Nicholson, T.; Davison, A.; Jones, A. G. *Inorg. Chim. Acta* **1991**, *187*, 51−57.
(19) Wilson, M. E.; Nuzzo, R. G.; Whitesides G. M. *J. Am. Chem. Soc.* **1978**, *100*, 2269−2270.

50.1; N, 3.3; H. 4.3. Found: C. 49.6; N, 3.3; H. 4.4. ^{1}H NMR ($CDCl_3$, ppm): 7.93 (t, 1H, *p*-N*Ph*), 7.78 (d, 2H, *o*-N*Ph*), 7.51−7.31 (m, 12H, P*Ph*$_2$), 7.17(m, 8H, P*Ph*$_2$, 6.96 (m, 6H, P*Ph*$_2$ + *m*-N*Ph*), 4.08(m, 2H C*H*$_2$), 3.45 (m, 2H C*H*$_2$), and 2.95 (m, 4H C*H*$_2$), 2.61 (s, 3H, C*H*$_3$). ^{31}P{H} NMR ($CDCl_3$, ppm): 19.9 (s).

***cis,fac*-Re(NPh)Cl$_3$(PNMeP)·HCl, 3b.** In acetonitrile (15 mL), $Re(NPh)Cl_3(PPh_3)_2$ (100 mg, 0.11 mmol) and PNMeP·HCl (86 mg, 0.17 mmol) were mixed. After refluxing for 15 min the reaction mixture became clear light green, but with continued reflux a green solid started to precipitate. After 4 h the mixture was allowed to return to room temperature and filtered. The green powder was washed with diethyl ether and resulted soluble in dichloromethane, quite soluble in chloroform, and almost insoluble in diethyl ether and benzene. NMR analysis evidenced the presence of two isomers in solution (total yield 70%). Anal. calcd. for $ReN_2C_{35}H_{37}P_2Cl_4$: C, 48.0; N, 3.2; H, 4.3. Found: C, 47.7; N, 3.3; H, 4.1. ^{1}H NMR (CD_2Cl_2, ppm): 7.96 (m, 2H, P*Ph*$_2$), 7.85 (m, 2H, P*Ph*$_2$), 7.70 (m, 2H, P*Ph*$_2$), 7.55(m, 2H, P*Ph*$_2$), 7.45 (t, 1H, *p*-N*Ph*), 7.37 (m, 4H, P*Ph*$_2$), 7.21 (m, 4H, P*Ph*$_2$), 7.10 (m, 4H, P*Ph*$_2$), 6.73 (t, 2H, *m*-N*Ph*), 6.59 (d, 2H, *o*-N*Ph*), 3.37 (m, 6H, *CH*$_2$), 3.07 (m, 2H, *CH*$_2$), 2.99 (d, 1.5 H, *CH*$_3$), 2.68 (d, 1.5H, *CH*$_3$).^{31}P{H} NMR (300 MHz,CD_2Cl_2, ppm): −25.1 (s); −26.9 (s).

***mer,trans*-[Re(NPh)Cl$_2$(PNMeP)]Cl, 3c.** Dissolution of *cis,fac*-[Re(NPh)Cl$_3$(PNMeP)]·HCl **3b** in dichloromethane in the presence of triethylamine gave quantitatively the deprotonated species *mer,trans*-[Re(NPh)Cl$_2$(PNMeP)]Cl. Compound **3c** was identified in solution and not isolated. ^{1}H NMR ($CDCl_3$, ppm): 7.76 (m, 8H, P*Ph*$_2$); 7.42 (t, 1H, *p*-N*Ph*), 7.19 (m, P*Ph*$_2$, 12H), 6.71 (m, 4H, N*Ph*), 3.25 (m, 8H, C*H*$_2$−C*H*$_2$), 2.00 (s, 3H, N−C*H*$_3$). ^{31}P {H} NMR ($CDCl_3$, ppm): −24.4 (s).

***mer,cis*-[Re(NPh)(OEt)Cl(PNHP)]Cl, 4.** To a suspension of $Re(NPh)Cl_3(PPh_3)_2$ (52 mg, 0.06 mmol) in ethanol (15 mL), an excess of PNHP·HCl (43 mg, 0.089 mmol) dissolved in ethanol (3 mL) with 25 μL of triethylamine (0.19 mmol) was added dropwise. The reaction mixture was refluxed for 4 h giving a green-yellow solution. The volume was reduced under a dinitrogen stream and diethyl ether was added; after a few hours large bright blue crystals of **4** had formed. Yield: 40%. Anal. calcd. for $ReN_2C_{36}H_{39}P_2Cl_2O$: C, 51.8; N, 3.4; H, 4.7. Found: C, 52.0; N, 3.2; H, 4.8. ^{1}H NMR ($CDCl_3$, ppm): 9.59 (b, 1H, N*H*), 8.00 (m, 4H, P*Ph*$_2$), 7.53 (m, 13H, P*Ph*$_2$ + N*Ph*), 7.07 (m, 6H, P*Ph*$_2$), 6.87(t, 2H, *m*-N*Ph*), 3.99 (bt, 2H, C*H*$_2$), 3.41(bm, 2H, C*H*$_2$), 3.18 (bm, 4H, C*H*$_2$), 2.64 (q, 2H, O−C*H*$_2$−CH$_3$), −0.13 (t, 3H, O−CH$_2$−C*H*$_3$). ^{31}P{H} NMR ($CDCl_3$, ppm): −0.2 (s).

***fac*-[Re(NPh)(O,O-cat)(PNHP)]Cl, 5.** To a bluish solution of **1** (40 mg, 0.05 mmol) in dichloromethane (10 mL), catechol (5 mg, 0.045 mmol) and 20 μL of triethylamine (0.15 mmol) were added at room temperature. The reaction mixture immediately turned red. The solution was stirred overnight at room temperature. Then the solvent was removed, the residue was treated with diethyl ether, and the resulting red-brown solid was filtered and washed several times with *n*-hexane, diethyl ether, and water. **5** was obtained with a final yield of 53%. Anal. calcd. for $ReN_2C_{40}H_{38}O_2P_2Cl·2H_2O$: C, 53.5; N, 3.1; H, 4.7. Found: C, 53.8; N, 3.2; H, 4.6. ^{1}H NMR ($CDCl_3$, ppm): 7.81 (m, 4H, N*Ph* and P*Ph*$_2$), 7.46 (m, 7H, N*Ph* and P*Ph*$_2$), 7.20 (m, 4H, P*Ph*$_2$), 7.05 (m, 10H, N*Ph* and P*Ph*$_2$),6.94 (dd, 2H, catechol), 6.71 (dd, 2H, catechol), 3.68 (m, 6H, C*H*$_2$C*H*$_2$), 3.68 (bs, 1H, N*H*), 2.95 (m, 2H, C*H*$_2$C*H*$_2$).^{31}P{H} NMR ($CDCl_3$, ppm) 19.5 (s). A stoichiometric amount of NBu_4BF_4 was added to a dichloromethane solution of **5** and by addition of *n*-hexane a red-orange product quantitatively precipitated characterized as [Re(NPh)(PNHP)(O,O-cat)]BF_4. Anal. calcd. for $ReN_2C_{40}H_{38}O_2P_2BF_4$: C, 52.6; N, 3.1; H, 4.2. Found: C, 52.9; N, 3.2; H, 5.1. ^{31}P {H} NMR ($CDCl_3$, ppm) 19.52 (s). ^{13}C{H} NMR ($CDCl_3$, ppm): 29.72 (d, $^1J_{CP}$ = 32 Hz; >P−*C*H$_2$−), 47.53 (s, −*C*H$_2$−NH−), 15 aromatic carbons: 115.4, 120.4, 122.3, 128.8, 128.9, 129.1, 129.3, 129.5, 130.8, 131.1, 131.3, 131.5, 131.7, 134.3, 160.9 (s, ipso-C_{NPh}).

***fac*-[^{99}Tc(NPh)(O,O-cat)(PNHP)]ClO$_4$, 6.** To a solution of **2** (26 mg, 0.04 mmol) in methanol (5 mL), catechol (5.2 mg, 0.047 mmol) and triethylamine (10 μL, 0.08 mmol) were added. The mixture immediately turned deep purple. The solution was stirred for 4 h at room temperature and then concentrated to 2 mL by a dinitrogen flow. A drop of saturated $NaClO_4$ solution in methanol was added to the solution. After 1 day, dark-grey crystals were formed; they were collected on a filter and washed with a 1 × 2 mL of methanol. Yield 63%. Anal. calcd. for $TcN_2C_{40}H_{38}O_2P_2ClO_4$: C, 57.3; N, 3.3; H, 4.6. Found: C, 57.0; N, 3.1; H, 4.8. ^{1}H NMR ($CDCl_3$, ppm): 7.77 (m, 4H, N*Ph* and P*Ph*$_2$), 7.49 (t, 3H, N*Ph* and P*Ph*$_2$), 7.37 (m, 4H, P*Ph*$_2$), 7.22 (m, 4H, P*Ph*$_2$), 7.14 (m, 2H, P*Ph*$_2$), 7.01 (m, 8H, N*Ph* and P*Ph*$_2$), 6.81 (dd, 2H, catechol), 6.71 (dd, 2H, catechol), 3.5−2.7 (m, 8H, C*H*$_2$C*H*$_2$), 3.13 (bs, 1H, N*H*). ^{31}P{H} NMR ($CDCl_3$, ppm) 46.5 (bs). ^{13}C{H} NMR ($CDCl_3$, ppm): 28.85 (d, $^1J_{CP}$ = 29 Hz; >P−*C*H$_2$−), 46.54 (s, −*C*H$_2$−NH−), 15 aromatic carbons: 114.9, 120.0, 124.0, 128.6, 128.8, 129.2, 129.4, 129.7, 130.5, 130.9, 131.1, 131.8, 134.1, 134.3, 159.7 (s, ipso-C_{NPh}).

***fac*-[Re(NPh)(O,O-cat)(PNMeP)]Cl, 7.** To a suspension of $Re(NPh)Cl_3(PPh_3)_2$ (90 mg, 0.1 mmol) in dichloromethane (10 mL) PNMeP (53 mg, 0.11 mmol) was added at room temperature. After 5 min, catechol (15 mg, 0.14 mmol) and 30 μL of triethylamine (0.23 mmol) were added and the reaction mixture was refluxed for 30 min. The resulting solution was dark brown and was stirred at room temperature for further 2 h. The solvent was removed under vacuum and the brown residue was washed with diethyl ether. The brown solid was purified by means of a SiO_2 column using a chloroform/methanol 85:15 mixture as eluant. Three main fractions were separated: a dark brown, a green-yellow, and a red one (the most intense). The last was identified as **7**. Yield 30%. Anal. calcd. for $ReN_2C_{41}H_{40}P_2O_2Cl$: C, 56.2; N, 3.2; H, 4.6. Found: C, 56.5; N, 3.3; H, 4.6. ^{1}H NMR ($CDCl_3$, ppm): 7.77 (m, 4H, N*Ph* and P*Ph*$_2$), 7.47 (m, 9H, N*Ph* and P*Ph*$_2$), 7.05 (m, 12H, N*Ph* and P*Ph*$_2$), 6.88 (2H, dd, cat), 6.71 (dd, 2H, cat), 3.73 (b, 4H, C*H*$_2$C*H*$_2$), 3.41-(b, 2H, C*H*$_2$C*H*$_2$), 2.85 (b, 2H, C*H*$_2$C*H*$_2$), 2.1 (s, 3H, C*H*$_3$).^{31}P {H} ($CDCl_3$, ppm) = 16.3 (s).

***fac*-[Re(NPh)(O,O-gly)(PNHP)]Cl, 8.** To a bluish solution of **1** (40 mg, 0.05 mmol) in dichloromethane (15 mL) ethylene glycol (30 μL, 0.54 mmol) and triethylamine (20 μL, 0.15 mmol) were added at room temperature. The reaction mixture was refluxed for 1 h and then stirred at room temperature for 24 h. The solution became gray. After removal of the solvent with a flow of dinitrogen, the oily residue was treated with diethyl ether and the resulting gray solid was filtered. The crude solid was purified by washing, on the filter, with *n*-hexane and water. Gray crystals of [Re(NPh)-(O,O-gly)(PNHP)]Cl, suitable also for X-ray analysis, were obtained by crystallization from a dichloromethane/*n*-hexane solution. Yield 60%. Anal. calcd. for $ReN_2C_{36}H_{38}O_2P_2Cl·2H_2O$: C, 50.8; N, 3.3; H, 5.0. Found: C, 50.6; N, 3.3; H, 5.2. ^{1}H NMR ($CDCl_3$, ppm): 7.74−6.91 (m, 25H, N*Ph* and P*Ph*$_2$), 5.11 (bs, 1H, N*H*), 4.78 (d, 2H, OC*H*$_2$C*H*$_2$O), 4.60 (d, 2H, OC*H*$_2$C*H*$_2$O), 3.80 (m, 2H; PCH$_2$C*H*$_2$N), 3.16 (m, 2H; PCH$_2$C*H*$_2$N), 3.06 (m, 2H; PC*H*$_2$CH$_2$N), 2.90 (m, 2H; PC*H*$_2$CH$_2$N).^{31}P{H} NMR ($CDCl_3$, ppm) 17.3. ^{13}C-{H} NMR ($CDCl_3$, ppm): 28.78 (d, $^1J_{CP}$ = 32 Hz; >P−*C*H$_2$−), 47.70 (s, −*C*H$_2$−NH−), 78.85 (s, O−*C*H$_2$−), 122.24 (s, *o*-C_{NPh}), 127.46 (s, *p*-C_{NPh}) 128.64 (d, $^3J_{CP}$ = 11 Hz; *m*-C_{PPhexo}) 128.92 (d, $^3J_{CP}$ = 10 Hz; *m*-$C_{PPhendo}$) 129.37 (s, *m*-C_{NPh}) 130.39 (s, *p*-$C_{PPhendo}$)

Table 1. X-ray Crystal Data, Data Collection Parameters, and Refinement Parameters of **1**·$^1/_2CH_2Cl_2$, **2**·$^1/_2CH_2Cl_2$, **4**, **5**·$2H_2O$, and **8**·$2H_2O$

	1·$^1/_2CH_2Cl_2$	**2**·$^1/_2CH_2Cl_2$	**4**	**5**·$2H_2O$	**8**·$2H_2O$
formula	$C_{34}H_{34}Cl_3N_2P_2Re$·$^1/_2CH_2Cl_2$	$C_{34}H_{34}Cl_3N_2P_2T$·$^1/_2CH_2Cl_2$	$C_{36}H_{39}Cl_2N_2OP_2Re$	$C_{40}H_{42}ClN_2O_4P_2Re$	$C_{36}H_{42}ClN_2O_4P_2Re$
fw	867.58	779.38	834.73	898.34	850.31
cryst syst	monoclinic	monoclinic	triclinic	monoclinic	triclinic
space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$C2/c$	$P\bar{1}$
a, (Å)	15.081(3)	15.106(3)	11.752(2)	34.801(7)	12.733(3)
b, (Å)	12.146(2)	12.117(2)	12.519(3)	24.782(5)	17.032(3)
c, (Å)	20.418(3)	20.481(4)	15.482(3)	10.671(2)	18.806(4)
α, (deg)			75.97(3)		107.01(3)
β, (deg)	107.05(3)	107.25(3)	68.90(3)	103.84(3)	90.85(3)
γ, (deg)			64.96(3)		98.11(3)
V, (Å^3)	3576(1)	3580(1)	1914.4(7)	8936(3)	3854(1)
Z	4	4	2	8	4
ρ_{calcd} (g cm^{-3})	1.612	1.446	1.448	1.335	1.465
μ, mm^{-1}	3.814	0.817	3.425	2.887	3.343
λ source (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
$R(F)^a$ [$I > 2\sigma(I)$]	0.043	0.058	0.042	0.060	0.064
$R_w(F)^b$ [$I > 2\sigma(I)$]	0.081	0.156	0.100	0.171	0.158
GOF^c	0.702	0.879	0.886	0.820	0.822

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_w = \{\sum[w(|F_o^2| - |F_c^2|)^2]/\sum[w(|F_o^2|)^2]\}^{1/2}$. ^{c} GOF $= \{\sum[w(|F_o^2| - |F_c^2|)^2]/(n_{data} - n_{var})\}^{1/2}$.

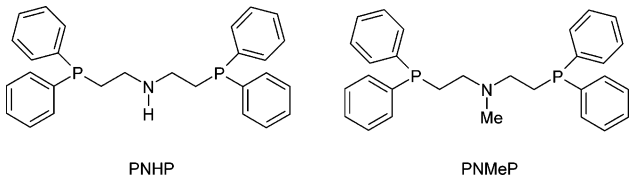
130.84 (d, $^2J_{CP} = 8$ Hz; *o*-$C_{PPhendo}$) 131.18 (s, *p*-C_{PPhexo}) 132.89 (s, ipso-$C_{PPhendo}$) 133.58 (s, ipso-C_{PPheso}) 134.21 (d, $^2J_{CP} = 8$ Hz; *o*-C_{PPhexo}) 158.07 (s, ipso-C_{NPh}).

***fac*-[Re(NPh)(O,O-gly)(PNMeP)]Cl, 9.** To a 20-mL solution of **3a** in acetonitrile (50 mg, 0.06 mmol) ethylene glycol (30 μL, 0.54 mmol) and triethylamine (20 μL, 0.15 mmol) were added. The reaction mixture was refluxed for 24 h. After that the solvent was evaporated and the dark green oily residue was dissolved in dichloromethane. The excess of ethylene glycol was removed by water extraction. The organic phase was dried and a green powder, characterized as **9**, was recovered (yield 43%). Anal. calcd. for $ReN_2C_{37}H_{40}O_2P_2Cl$: C, 53.6; N, 3.4; H, 4.9. Found: C, 53.9; N, 3.4; H, 4.7. ^{1}H NMR ($CDCl_3$, ppm): 7.48−6.98 (m, 25H, N*Ph* and P*Ph*$_2$); 4.91−4.76 (m, 4H, OC*H*$_2$C*H*$_2$O), 3.58 (m, 2H, *CH*$_2$), 3.27 (m, 2H, *CH*$_2$), 2.34 (s, 3H, N−C*H*$_3$), 2.47 (m, 4H, *CH*$_2$). ^{31}P-{H}NMR ($CDCl_3$, ppm) 24.3 (s).

***fac*-[Re(NPh)(O,N-ap)(PNMeP)]Cl, 10.** To a suspension of Re(NPh)$Cl_3(PPh_3)_2$ (90 mg, 0.1 mmol) in dichloromethane (15 mL), PNMeP (53 mg, 0.11 mmol) was added at room temperature. After 5 min 1,2 aminophenol (17 mg, 0.16 mmol) and 20 μL of triethylamine were added and the reaction mixture was refluxed and over 10 min the solution turned from green to dark brown. Then it was refluxed for 30 min and stirred overnight at room temperature. The solvent was removed and the residue was treated with diethyl ether. The red-brown solid was filtered and redissolved in dichloromethane. Elution from a silica column with chloroform/methanol 85:15 separated a yellow uncharacterized byproduct and the red *fac*-[Re(NPh)(O,N-ap)(PNMeP)]Cl. (Yield 38%). Anal. calcd. for $ReN_3C_{42}H_{40}P_2ClO$: C, 56.9; N, 4.7; H, 4.5. Found: C, 57.2; N, 4.5; H, 4.6. ^{1}H NMR ($CDCl_3$, ppm): 7.8−6.9 (m, 25H, N*Ph* and P*Ph*$_2$); 6.80 (1H, dd, O,N-ap), 6.55 (m, 3H, O,N-ap), 3.74−2.72 (b, 8H, PC*H*$_2$C*H*$_2$N), 2.0 (s, 3H, C*H*$_3$).^{31}P{H} ($CDCl_3$, ppm) = 17.8 (d), 10.1 (d).

X-ray Structure Determinations and Refinements. For the five complexes **1**·$^1/_2CH_2Cl_2$, **2**·$^1/_2CH_2Cl_2$, **4**, **5**·$2H_2O$, and **8**·$2H_2O$ intensity data were obtained at room temperature on a Siemens Nicolet R3m/V four-circle diffractometer using the $\omega - 2\theta$ scan technique with Mo Kα radiation from a graphite monochromator. Intensities were corrected for Lorentz and polarization effects. Equivalent reflections were merged, and absorption corrections were made using the ψ-scan method. Space groups, lattice parameters, and other relevant information are given in Table 1.

Scheme 2



Structures were solved by Patterson syntheses and all nonhydrogen atoms were taken from a series of full-matrix least-squares refinement cycles based on F^2 with the program system SHELXTL,[20] followed by difference Fourier syntheses. All nonhydrogen atoms were refined with anisotropic thermal parameters, while hydrogen atoms, except those of the CH_2Cl_2 and H_2O of crystallization, were placed at calculated positions and allowed to ride on their corresponding carbon atoms with isotropic thermal parameters 1.2 times the value for U_{eq} of the bonding atom. Final difference maps contained no features of chemical significance.

Results

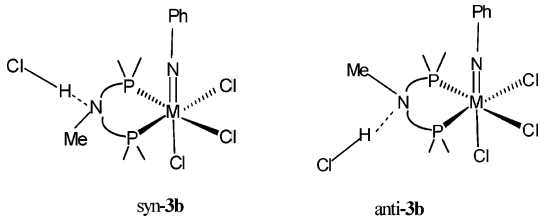
Synthesis. The aminodiphosphine ligand PNHP·HCl was prepared according to the literature,[19] whereas PNMeP·HCl (see Scheme 2) was obtained by alkylation of diphenylphosphine lithium salt with the appropriate dihalide *N*-methylbis(2-chloroethyl)amine hydrochloride.

In the case of PNMeP, better yields were achieved by addition of a neutralized batch of *N*-methylbis(2-chloroethyl)-amine hydrochloride at low temperature (−78 °C). Low amounts of unidentified impurities or of amine decomposition species may prevent the precipitation of the final product from the reaction mixture, and purification via column chromatography on silica was necessary to recover pure PNMeP.

Ligand-exchange reactions of PNHP·HCl with M(NPh)$Cl_3(PPh_3)_2$ precursors in dichloromethane solutions, in the presence of triethylamine, gave the intermediate complexes *mer,cis*-[M(NPh)Cl_2(PNHP)]Cl, (M = Re, **1**; M = Tc, **2**) in moderate yields. The reaction mixture, from which the

(20) Sheldrick, G. M. SHELXTL − NT V5.1. Program package for Crystal Structure Refinement; Bruker AXS, Inc.: Madison, WI, 1999.

Scheme 3



rhenium complex **1** was collected, showed the presence of a persistent contaminant formulated as *mer*-[Re(NPh)(OH)Cl(PNHP)]Cl on the basis of NMR spectroscopy.[21] Recrystallization of **1** from dichloromethane/ethanol mixtures afforded the ethoxide derivative *mer*-[Re(NPh)(OEt)Cl(PNHP)]Cl, **4**. Obtaining both trans imido−hydroxo and trans imido−ethoxo derivatives indicated that the halide group located trans to the phenylimido unit in the intermediate complex *mer,cis*-[Re(NPh)Cl_2(PNHP)]Cl, is labile.

The substitution reactions with the tertiary aminodiphosphine PNMeP were less clean and reproducible. A mixture of products was always detected in dichloromethane solutions, from which the *fac,cis*-[Re(NPh)Cl_2(PNMeP)]Cl, **3a** was isolated after purification via column chromatography. By using the hydrochloride salt of PNMeP and without addition of triethylamine, a mixture of *syn*- and *anti*-Re(NPh)Cl_3(PNMeP)·HCl, **3b**, was collected from acetonitrile solutions (Scheme 3). Addition of triethylamine to a dichloromethane solution of **3b** yielded quantitatively the *mer,trans*-[Re(NPh)Cl_2(PNMeP)]Cl complex **3c**.

Halides and/or ethoxide (or hydroxide) groups incorporated in *mer,cis*-[M(NPh)Cl_2(PNHP)]Cl, **1** and **2**, *mer*-[Re(NPh)(OEt)Cl(PNHP)]Cl, **4**, and *mer*-[Re(NPh)(OH)Cl(PNHP)]Cl were readily substituted with di-negative bidentate ligands (H_2L−L) in dichloromethane solutions to afford stable mixed ligand compounds of the type *fac*-[M(NPh)(L−L)(PNHP)]Cl, **5**, **6**, and **8**. In contrast, mixed ligand complexes incorporating the PNMeP ligand (**7**, **9**, and **10**) were obtained only in poor yields (30−50%) starting from the intermediate facial complex **3a**. The yield of the latter could be improved via a direct reaction starting from Re(NPh)Cl_3(PPh_3)$_2$ with sequential addition of PNMeP and H_2L−L. Analogous direct reaction was successfully utilized in the synthesis of **5** and **8**.

Characterization. Complexes **1**−**10** have been characterized by (i) elemental analyses, which are in good agreement with the proposed formulations (see Experimental Section), (ii) multinuclear NMR spectroscopy, (iii) X-ray structure analyses of selected compounds, and (iv) comparison with strictly analogous nitrido−Re and −Tc species synthesized previously.[4,8,22]

The diamagnetism shown by this class of mixed-ligand complexes is in agreement with low-spin d^2 distorted octahedral geometries typical of M(V) species including a phenylimido unit (vide infra, X-ray description). Thus, the combination of proton and phosphorus NMR signals allows a complete characterization of the complexes in solution. In the case of technetium compounds **2** and **6** ^{31}P NMR signals show broad profiles at ambient temperature. Such behavior was previously attributed to the coupling of the ^{31}P nuclei with the quadrupolar ^{99}Tc (I = 9/2) center.[23] In any case, ^{31}P NMR is a powerful tool for a rapid evaluation of the course of the reactions, as the signals of the various species are spread over a wide range (roughly from −30 to +50 ppm, see Table 2), thus recognizing the presence of the starting product, uncoordinated ligand, and compounds formed. The characteristic singlet of magnetically equivalent diphosphine phosphorus moves downfield from ca. −20 ppm (uncoordinated P) to positive values (in the range 4−46 ppm), the only exception being complexes **3b** and **3c**, for which a slightly upfield shift is observed (two singlets at −25.1 and −26.9 ppm, respectively for the mixture syn or anti **3b** (see Scheme 3), and one singlet at −24.4 ppm for **3c**). The presence of the dissymmetric aminophenolate ligand in complex **10** removes the magnetic equivalence of the diphosphine phosphorus giving rise to two doublets.

In the proton spectra of all complexes, the signals due to the phenyl rings of the diphosphine present a characteristic pattern, depending on the geometry of the complex, and can be considered a kind of fingerprint of different isomers. Mer,-cis species (**1**, **2**, and **4**) show three distinct multiplets (counting for 4H, 10H, and 6H, respectively), fac,cis species (**3a**, **3b**, and mixed complexes **5**−**10**) exhibit a more complicated pattern, whereas the mer,trans isomer **3c** provides the simplest spectrum of the series with only two multiplets (counting for 8 and 12 H). The bridging methylene protons of the PNP backbone show a series of multiplets spread over the 4.0−2.5 ppm region. In PNHP containing complexes, no coupling of the N−H protons with either methylene protons and/or phosphorus is detected, the signal being a temperature-independent broad singlet ($\gamma_{1/2}$ = ca. 20 Hz) in the −50 to 50 °C range in chloroform-*d* solutions. The >N−H signal in equatorially coordinated mer-complexes (Table 3) experiences a significant downfield shift (δ in the range 9.59−10.06 ppm) compared to the corresponding signal in fac-complexes (δ in the range 3.13−5.11 ppm). In the latter the important shielding is likely provided by electron density coming from the trans positioned phenylimido group, and enhanced by π-contribution in catecholate containing compounds.

As a general feature, it is important to note that, due to the greater acidity of Tc(V) compared to Re(V), both ^{31}P and ^{1}H signals experience larger downfield shift in technetium complexes.

^{13}C{^{1}H} spectra of uncoordinated aminodiphosphines exhibit carbon−phosphorus couplings for both ethylene

(21) ^{31}P{H} NMR ($CDCl_3$, 300 MHz) δ ppm 4.3. ^{1}H NMR ($CDCl_3$, 300 MHz) δ ppm: 7.95 (m, 4H, PPh_2), 7.59 (m, 6H, PPh_2 + NPh), 7.47 (m, 7H, PPh_2 + NPh), 7.10 (m, 6H, PPh_2 + NPh), 6.92 (t, 2H, NPh). The OH signal is not detected. The formulation of the complex is based on the strict similarity of the aromatic protons pattern with that exhibited by the *mer,cis*-ethoxide analogue **4**.

(22) Bolzati, C.; Refosco, F.; Cagnolini, A.; Tisato, F.; Boschi, A.; Duatti, A.; Uccelli, L.; Dolmella, A.; Marotta, E.; Tubaro, E. *Eur. J. Inorg. Chem.* **2004**, 1902−1913.

(23) Abram, U.; Lorenz, B.; Kaden, L.; Scheller, D. *Polyhedron* **1988**, *7*, 285−291.

Table 2. Comparison of ^{31}P Chemical Shift of Reagents and Products of This Study

class of compounds	compound	^{31}P chemical shift (ppm)	compound	^{31}P chemical shift (ppm)
ligands	PNHP	−20.3	PNMeP	−19.3
precursors	$Re(NPh)Cl_3(PPh_3)_2$	−19.6	$Re(NPh)Cl_3(PPh_3)_2$	−19.6
	$Tc(NPh)Cl_3(PPh_3)_2$	12.2		
	$Re(NPh)Cl(OEt)(PPh_3)_2$	−9.9	$Re(NPh)Cl(OEt)(PPh_3)_2$	−9.9
intermediates	*mer,cis*-[Re(NPh)(OEt)Cl(PNHP)Cl **4**	−0.2	*fac,cis*-[Re(NPh)Cl_2(PNMeP)]Cl **3a**	19.9
	mer,cis-[Re(NPh)(OH)Cl(PNHP)Cl **1a**	4.3	*cis,fac*-Re(NPh)Cl_3(PNMeP)·HCl **3b** (*syn and anti*)	−25.1; −26.9
	mer,cis-[Re(NPh)Cl_2(PNHP)]Cl **1**	8.3	*mer,trans*-[Re(NPh)Cl_2(PNMeP)]Cl **3c**	−24.4
	mer,cis-[Tc(NPh)Cl_2(PNHP)]Cl **2**	31.6		
mixed products	[Re(NPh)(O,O-cat)(PNHP)]Cl **5**	19.5	[Re(NPh)(O,O-cat)(PNMeP)]Cl **7**	16.3
	[Tc(NPh)(O,O-cat)(PNHP)]ClO_4 **6**	46.5		
	[Re(NPh)(O,O-gly)(PNHP)]Cl **8**	17.3	[Re(NPh)(O,O-gly)(PNMeP)]Cl **9**	24.3
			[Re(NPh)(O,N-ap)(PNMeP)]Cl **10**	17.8; 10.1

Table 3. Summary of Selected Structural and NMR Data

compound	Re═NPh (Å)	$H_{orto-NPh}$ (ppm)	>N−*H* (ppm)	ipso-C_{NPh}	ref
$Re(NPh)Cl_3$(pbo)[a]	1.698(9)	7.74			27
mer,cis-[Re(NPh)Cl_2(PNHP)]Cl **1**	1.702(6)	7.74	10.06	153.5	this work
fac-[Re(NPh)(O,O-gly)(PNHP)]Cl **8**	1.72(1)	7.42	5.11	158.1	this work
fac-[Re(NPh)(O,O-cat)(PNHP)]Cl **5**	1.72(1)	7.50	3.55	160.9	this work
$Re(NPh)Cl_3(PPh_3)_2$	1.726(6)	7.22			29
trans-[Re(NPh)(OH)(cyclam)]$(ClO_4)_2$[b]	1.731(9)	7.41			26
trans-[Re(NPh)$(bpy)_2$(OEt)]$(PF_6)_2$[c]	1.740(6)	7.18			25
mer,cis-[Re(NPh)(OEt)Cl(PNHP)]Cl **4**	1.743(5)	7.15	9.59	153.8	this work

[a] pbo = 2-(2-pyridyl)benzoxazole. [b] cyclam = 1,4,8,11-tetraazacyclotetradecane. [c] bpy = 2,2′-bipyridine.

bridging carbons and orto-, meta-, and ipso-phenyl ones, as detailed in the Experimental Section. Upon coordination, some of these couplings are burnt, presumably due to the quadrupolar relaxation induced by the metal on neighboring atoms, as assessed by the appearance of singlet signals for H−N[*C*H_2−CH_2−P<]$_2$ and for quaternary phenyl carbons. ^{1}H−^{13}C two-dimensional HMQC and HMBC experiments on the representative *fac*-[Re(NPh)(O,O-gly)(PNHP)]Cl complex allow the complete assignment of the signals including the ipso-carbon of the phenylimido group. The latter is by far the most downfield shifted signal in the carbon spectrum and appears as a singlet. As reported in Table 3, this signal falls in the 158−161 ppm region in fac-type complexes, and it is slightly upfield shifted in mer-type ones.

The five complexes whose crystal structures are described in this work (**1**·$^1/_2CH_2Cl_2$, **2**·$^1/_2CH_2Cl_2$, **4**, **5**·$2H_2O$, and **8**·$2H_2O$) are all monocationic species containing the [M(NPh)(PNHP)]$^{3+}$ synthon (M = Re in **1**·$^1/_2CH_2Cl_2$, **4**, **5**·$2H_2O$, and **8**·$2H_2O$; M = Tc in **2**·$^1/_2CH_2Cl_2$), where the aminodiphosphine acts as a tridentate ligand. In all the compounds, the metal shows a somewhat distorted octahedral coordination environment. The arrangement of the phosphorus atoms around the core metal is such that the conformation of the complexes **1**·$^1/_2CH_2Cl_2$, **2**·$^1/_2CH_2Cl_2$ and **4** (Figures 1 and 2) is mer,cis, while it is fac in **5**·$2H_2O$ and **8**·$2H_2O$ (Figures 3 and 4). **1**·$^1/_2CH_2Cl_2$ and **2**·$^1/_2CH_2Cl_2$ show isomorphous structures and, as a consequence, the most relevant bond distances and angles are virtually identical (Table 4).

Unlike the other molecules here reported, two distinct crystallographic complexes have been found in the unit cell of **8**·$2H_2O$. The two items have different orientation in the lattice, yet retain comparable bond distances and angles, with the only change being the conformation assumed by the two five-membered rings formed upon coordination by the neutral aminodiphosphine ligand. These rings are found almost

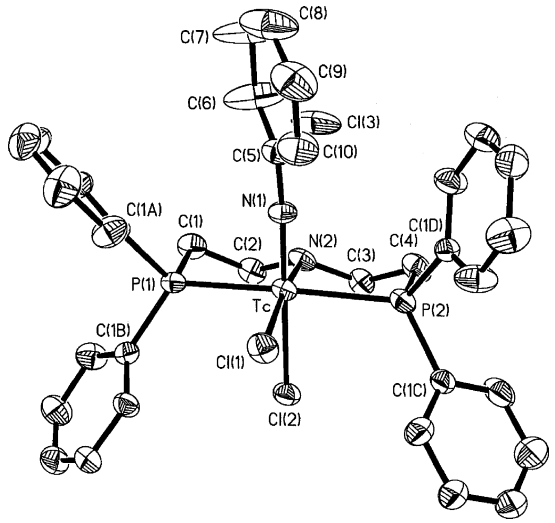


Figure 1. ORTEP representation of *mer,cis*-[Tc(NPh)Cl_2(PNHP)]Cl **2** showing 40% probability thermal ellipsoids. Hydrogen atoms and CH_2Cl_2 hemimolecule are omitted for clarity. The cation *mer,cis*-[Re(NPh)Cl_2(PNHP)]$^+$ **1** is isostructural with **2**.

invariably in the *twist-envelope* (C_2) conformation, but for the second orientation of **8**·$2H_2O$, in which one of the rings assumes the *envelope* (C_s) pucker. In all the structures, the orientation of the phenylimido ligand is roughly orthogonal to the equatorial mean plane, with the dihedral angles being 96.9° for **1**·$^1/_2CH_2Cl_2$, 96.4° for **2**·$^1/_2CH_2Cl_2$, 90.2° for **4**, 79.0° for **5**·$2H_2O$, and 78.6 and 84.6° for the two orientations of **8**·$2H_2O$.

In mer,cis complexes **1**·$^1/_2CH_2Cl_2$, **2**·$^1/_2CH_2Cl_2$, and **4**, the metal lies off the P_2NCl mean plane toward N(1) by 0.18 Å; the displacement grows to 0.40 Å in the fac complexes **5**·$2H_2O$ and **8**·$2H_2O$, where the equatorial plane is represented by the P_2O_2 donor set. The remaining two positions in the coordination sphere of the mer,cis complexes are filled

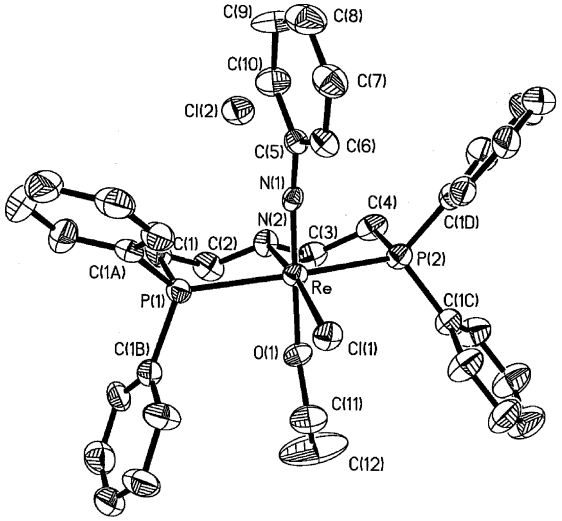


Figure 2. ORTEP representation of the cation in **4** showing 40% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity.

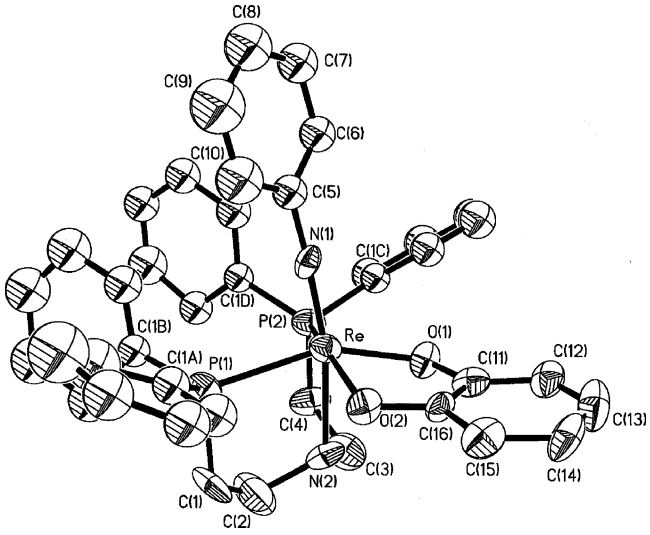


Figure 3. ORTEP representation of the cation in **5** showing 40% probability thermal ellipsoids. Chloride counteranion, hydrogen atoms, and the two water molecules are omitted for clarity.

by a couple of chloride ligands, but for complex **4**, where an ethoxide group replaces one of such chlorides. The substitution causes the Re−N(1) distance to grow to 1.743-(5) Å (Table 4), due to the strong trans effect of the ethoxide residue.

In the fac complexes **5**·2H_2O and **8**·2H_2O, the mean plane of the O,O bidentate ligand is nearly perpendicular (77.4°) to that of the phenylimido moiety. The latter is also almost orthogonal to the glycolate ligand of **8**·2 H_2O (79.4 and 84.2° for the two orientations). Oppositely, the O,O bidentate mean plane is more or less coplanar with the ReP_2 plane, with the dihedral angle being 16.7° in **5**·2H_2O, and 15.4 and 16.3° for the two orientations of **8**·2H_2O. The Re−N(2) bond distance in the fac molecules is more than 0.10 Å longer than that in the mer,cis complexes. A contribution to crystal stability in fac complexes is provided by $\pi-\pi$ interaction of two phenyl rings incorporated in cis-positioned phosphorus donors (Figures 3 and 4). This feature had already been observed in similar nitrido complexes.[4] Structural data listed

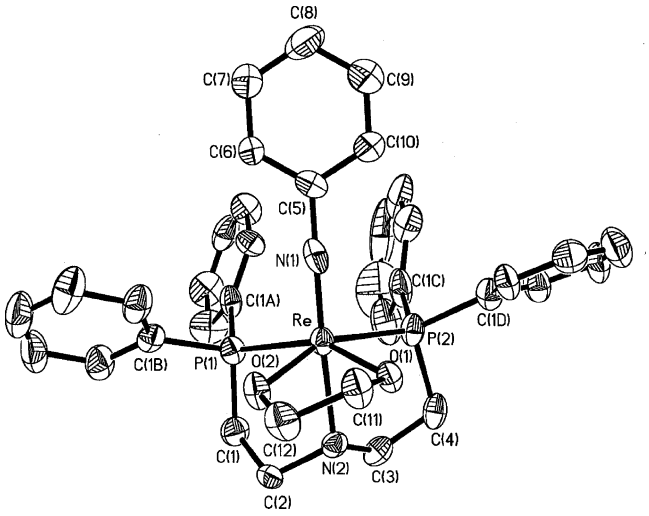


Figure 4. ORTEP representation of a cation in **8** showing 40% probability thermal ellipsoids. Chloride counteranion, hydrogen atoms, and the two water molecules are omitted for clarity.

in Table 4 indicate that fac complexes **5**·2H_2O and **8**·2H_2O show some severe distortions in the coordination environment of the metal. In fact, cis angles range from 76.4 to 110.9°, whereas the trans angles go as low as 154.7°. In our opinion, such values far from the ideality are due to the restraints imposed by the contemporary presence of two chelate ligands, both of them making, upon coordination, five-membered rings of narrow "bite" angles (ca. 80°).

Relevant nonbonding interactions have been detected only in mer,cis complexes. In **1**·$^1/_2CH_2Cl_2$ and **2**·$^1/$ CH_2Cl_2 the H atom of N(2) is hydrogen bonded to Cl(3), with bond distances of 2.17 and 2.19 Å and pertinent angles of 161°; in **4**, the same H atom interacts with the Cl(2) atom, with a bond distance of 2.22 Å and pertinent angle of 158°.

Discussion

It is worth noting that the few examples of structurally authenticated technetium phenylimido compounds reported so far comprise only phosphine and halide ligands, as illustrated by the $Tc(NPh)Cl_3(PPh_3)_2$ starting material.[17] Attempts to replace monodentate groups with tetradentate ligands, trying to mimic the rich substitution chemistry exhibited by oxo-containing precursors, have produced poor results. This behavior is likely determined by the strong preference for π-acceptor ligands exhibited by the $[Tc(NPh)]^{3+}$ core, and the consequent reluctance to release P-based donors such as triphenylphosphine. Instead, rhenium phenylimido chemistry appears to be more flexible, and examples of phosphine-free compounds are reported. These species generally contain other π-acceptor ligands, including nitrogen-based aromatic heterocycles.[24−27] The crucial pres-

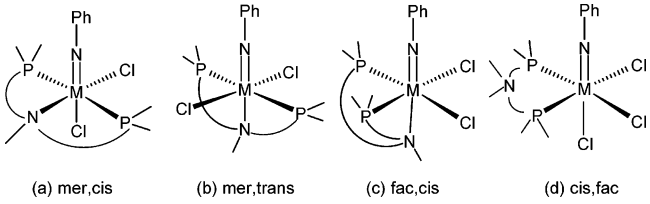
(24) Masood, Md. A.; Sullivan, B. P.; Hodgson, D. J. *Inorg. Chem.* **1994**, *33*, 5360−5362.
(25) Bakir, M.; Paulson, S.; Goodson, P.; Sullivan, B. P. *Inorg. Chem.* **1992**, *31*, 1127−1129.
(26) Wang, Y.-P.; Che, C.-M.; Wong, K.-Y.; Peng, S.-M. *Inorg. Chem.* **1993**, *32*, 5827−5832.
(27) Gangopadhyay, J.; Sengupta, S.; Bhattacharyya, S.; Chakraborty, I.; Chakravorty, A. *Inorg. Chem.* **2002**, *41*, 2616−2622.

Table 4. Selected Bond Distances (Å) and Bond Angles (deg) of **1**·$^1/_2CH_2Cl_2$, **2**·$^1/_2CH_2Cl_2$, **4**, **5**·$2H_2O$, and **8**·$2H_2O$

	1·$^1/_2CH_2Cl_2$	**2**·$^1/_2CH_2Cl_2$	**4**	**5**·$2H_2O$	**8**·$2H_2O$
M[a]−P(1)	2.427(2)	2.437(2)	2.440(2)	2.422(4)	2.448(3); 2.421(4)
M−P(2)	2.422(2)	2.424(2)	2.456(2)	2.435(4)	2.423(3); 2.410(4)
M−N(1)	1.702(6)	1.699(4)	1.743(5)	1.72(1)	1.70(1); 1.736(8)
M−N(2)	2.169(5)	2.148(4)	2.161(5)	2.26(1)	2.293(9); 2.304(9)
M−Cl(1)	2.415(2)	2.415(2)	2.415(2)		
M−Cl(2)	2.379(2)	2.413(2)			
M−O(Et)			1.934(5)		
M−O(1)				1.975(9)	1.996(7); 1.983(9)
M−O(2)				2.061(8)	1.984(7); 1.984(9)
P(1)−M−P(2)	162.3(1)	162.0(1)	162.9(1)	99.8(1)	101.9(1); 103.9(1)
Cl(2)−M−N(1)	179.3(3)	179.9(2)			
Cl(1)−M−N(2)	169.2(2)	170.0(1)	168.9(2)		
P(1)−M−N(2)	81.6(2)	81.6(1)	81.4(2)	79.0(4)	76.4(2); 78.9(3)
P(2)−M−N(2)	82.1(2)	81.9(1)	82.1(2)	78.3(7)	77.0(3); 78.0(3)
N(1)−M−O(1)				110.9(4)	106.6(4); 108.2(5)
N(1)−M−O(2)				106.2(4)	110.6(4); 110.2(5)
N(1)−M−O(Et)			178.6(2)		
N(1)−M−N(2)	97.5(3)	97.4(2)	96.9(2)	168.0(5)	165.5(4); 165.5(4)
P(1)−M−O(1)				155.5(3)	154.7(2); 155.9(3)
P(2)−M−O(2)				157.4(3)	156.3(3); 157.3(3)
O(1)−M−O(2)				80.0(4)	80.1(3); 82.1(5)

[a] M = Re; M = Tc only for **2**·$^1/_2CH_2Cl_2$.

Scheme 4

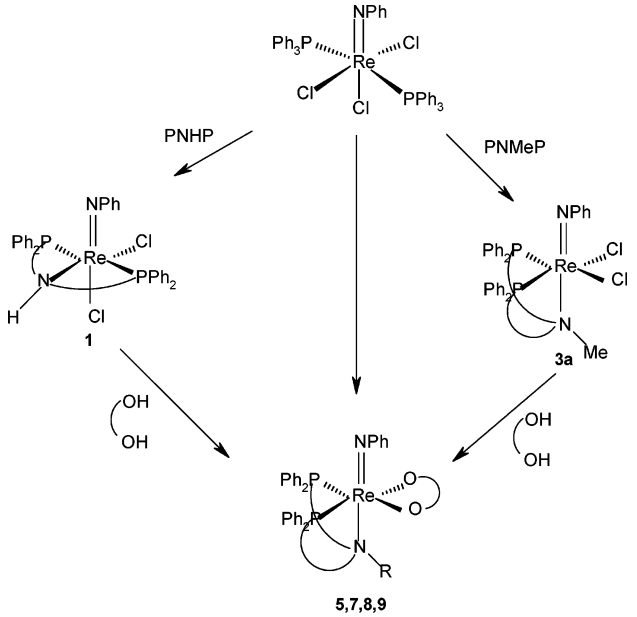


ence of π-acceptor ligands in the phenylimido coordination sphere resembles the behavior of Tc− and Re−nitrido cores, whereas the ability of coordinating nitrogen-based ligand in octahedral geometries is similar to the behavior of the oxo-core, thereby confirming the nature of the phenylimido unit to be intermediate between oxo and nitrido groups.

With the aim at maintaining the essential contribution of π-acceptor ligands in the metal phenylimido coordination sphere, we thought to substitute monodentate with particular polydentate ligands. Thus, aminodiphosphines PNHP and PNMeP were used to replace triphenylphosphine in the $M(NPh)Cl_3(PPh_3)_2$ precursors. If we rule out the trans PhN−M−P configuration, which has never been observed so far, the molecular structure of the reaction products is comprised among isomeric species (a), (b), and (c) depicted in Scheme 4. When the hydrochloric salt of PNMeP was utilized, an additional neutral compound (d) was isolated.

Analyzing in detail the reactivity of rhenium complexes (see Scheme 5), we observed that the stereochemistry of intermediate compounds was determined by the nature of the amine group inserted in the diphosphine backbone. A secondary amine function (PNHP) promoted the formation of the mer,cis isomer only, as established by the X-ray structure of **1**, whereas a tertiary amine group (PNMeP) privileged the formation of the fac,cis form **3a**, and, under specific reaction conditions, of the mer,trans isomer **3c**. Similar arrangements of the aminodiphosphine were recently observed in the corresponding nitrido complexes *fac,cis*-Tc(N)Cl_2(PNHP) and *mer,cis*-Re(N)Cl_2(PNMeP), and explained in terms of different nucleophilicity of the amine group.[28]

Scheme 5



Both mer,cis and fac,cis intermediate complexes **1** and **3a** underwent further substitution of cis positioned halides with bidentate ligands, such as catechol, ethylene glycol, and 1,2-aminophenol, to give mixed ligand complexes $[Re(NPh)(L-L)(PNP)]^+$ (**5**, **7**, **8**, and **9**), in which the aminodiphosphine were invariably facially arranged. Thus, an isomerization of PNHP from the meridional into the facial form occurred from **1** to **5**, **6**, and **8**. A cis halide arrangement was found to be an essential prerequisite for substitution, because the trans halide alignment shown in the mer,trans species **3c** gave rise to negligible amounts of mixed complexes. Obtaining stable *fac*-$[Re(NPh)(L-L)(PNP)]^+$ mixed ligand complexes again parallels the substitution chemistry exhibited by aminodiphosphine containing nitrido complexes.[4] A major

(28) Tisato, F.; Refosco, F.; Porchia, M.; Bolzati, C.; Dolmella, A.; Duatti, A.; Boschi, A.; Jung, C. M.; Pietzsch, H.-J.; Kraus, W. *Inorg. Chem.* **2004**, *43*, 8617−8625.

Table 5. Structural Data of Selected Nitrido and Phenylimido Technetium and Rhenium Complexes[a]

compound	$M-N_{core}$ (Å)	$M-X_{N-trans}$		$N-M-X_{N-trans}$ (deg)		ref
		X = N	X = Cl	X = N	X = Cl	
fac-[Tc(N)(PNP)(L)][b,c]	1.61	2.81		161.8		4
mer,cis-[Tc(N)Cl_2(PNHP)]	1.61		2.65		170.2	28
fac-[Re(N)(dedc)(PNP)]Cl[b,d]	1.66	2.73		164.4		22
fac,cis-Re(N)Cl_2(PNP)[b]	1.67	2.64		164.2		4
mer,cis-[Tc(NPh)Cl_2(PNHP)]Cl **2**	1.70		2.41		179.9	this work
mer,cis-[Re(NPh)Cl_2(PNHP)]Cl **1**	1.70		2.38		179.3	this work
fac-[Re(NPh)(O,O-gly)(PNHP)]Cl **8**	1.72	2.30		165.5		this work
fac-[Re(NPh)(O,O-cat)(PNHP)]Cl **5**	1.72	2.26		168.0		this work

[a] Estimated average standard deviations of 0.01 Å for bond lengths and 0.4 deg for angles. [b] PNP = bis[(2-diphenylphosphino)ethyl]methoxy-ethylamine. [c] H_2L = S-methyl 2-methyldithiocar-bazate. [d] dedc = diethyldithiocarbamate.

difference is constituted by the nature of the bidentate donor atoms: the $[Re(NPh)(PNP)]^{3+}$ moiety results best stabilized by oxygen-based donors, whereas the nitrido moiety $[Re(N)(PNP)]^{2+}$ prefers sulfur-based donors.

The analysis of NMR and structural data evidences a correlation between the Re═NPh bond length and the $H_{orto-NPh}$ chemical shift of the phenylimido group. Table 3 comprises parameters of the complexes reported in this work combined with those of some derivatives described in the literature. A shortening of the metal nitrogen multiple bond causes a decreasing of the electron density at the neighbor phenylimido orto proton (downfield shift), irrespective of the overall charge of the complex and nature of the coordinating atom set. On this basis, qualitative speculations on the Re═NPh bond length may be envisaged from known H_{orto} chemical shifts. For example, if we consider the H_{orto} chemical shift of compounds **3a**, **3b**, and **3c** (7.60, 6.59, and 6.73 ppm, respectively) such values could correspond to Re═NPh distances of ca. 1.71 Å for **3a** and >1.75 Å for **3b** and **3c**.

Comparison of the structural data of technetium and rhenium phenylimido complexes described in this work and in the literature[16,24−26,29−39] (no substituted phenylimido or alkylimido compounds are surveyed) reveals some common features. The six reported technetium derivatives, which include only phosphine and halide donors, exhibit $Tc-N_{imido}$ and $Tc-Cl_{trans}$ distances centered at 1.70 and 2.42 Å, respectively, and nearly linear X−Tc−NPh units. Analogous phosphine/halide rhenium complexes exhibit similar values. The coordination of an alkoxide residue trans to the phenylimido group lengthens the $Re-N_{imido}$ distance by ca. 0.04 Å, without affecting other parameters, whereas the coordination of trans N donors produces $Re-N_{imido}$ distances in the range 1.69−1.73 Å.

Further comparison of selected structural data in similar nitrido and phenylimido complexes synthesized in our laboratory is shown in Table 5, which is organized according to the increasing values of $M-N_{core}$ distances. In particular, the data suggest that the lengthening of the $M-N_{core}$ distance is matched by the shortening of the $M-X_{N-trans}$ bond, a result in accordance with the expected trans labilizing effect operated by the $[M(N)]^{2+}$ and $[M(NPh)]^{3+}$ cores. As a general feature, the $N-M-X_{N-trans}$ angle widens as the $M-N_{core}$ distance increases: fac arranged complexes ($X_{N-trans}$ = N) show narrower angles in the range 161.8−168.0°, while mer-species ($X_{N-trans}$ = Cl) show larger angles in the range 170.2−179.9°. The displacement of the metal from the mean equatorial plane depends on the PNP assembly as well, being 0.39−0.43 Å in fac-species and 0.18−0.19 Å in mer-ones.

As outlined in Scheme 5, syntheses of mixed-ligand compounds can be performed using a one-step procedure at room temperature. Since the nca synthesis of $^{188}Re(NPh)Cl_3(PPh_3)_2$ is known from the literature,[40] this method might constitute a good start for the preparation of stable ^{188}Re mixed-ligand complexes. Moreover, the incorporation of biologically active fragments onto para-substituted phenylhydrazines, which is already a known technology,[11,12] and the possibility to incorporate further functions onto the 1,2-ethylene glycol and catechol frameworks are the basis for the design of target-specific rhenium radiopharmaceuticals.[40]

Conclusions

Analogously to what was previously observed for nitrido technetium and rhenium cores, phenylimido $[M(NPh)]^{3+}$ groups also can be stabilized with suitable aminodiphosphines (PNP) leading to novel metal fragments of the type *fac*- or *mer*-$[M(NPh)(PNP)]^{3+}$. These complexes are useful intermediates for the synthesis of a new class of dissymmetric mixed-ligand *fac*-$[M(NPh)(L-L)(PNP)]^{+}$ phenylimido species.

(29) Forsellini, E.; Casellato, U.; Graziani, R.; Carletti, M. C.; Magon, L. *Acta Crystallogr*. **1984**, *C40*, 1795−1797.
(30) Rochon, F. D.; Melanson, R.; Kong, P.-C. *Inorg. Chem*. **1995**, *34*, 2273−2277.
(31) Nicholson, T.; Davison, A.; Zubieta, J. A.; Chen, Q.; Jones, A. G. *Inorg. Chim. Acta* **1995**, *230*, 205−208.
(32) Nicholson, T.; Storm, S. L.; Davis, W. M.; Davison, A.; Jones, A. G. *Inorg. Chim. Acta* **1992**, *196*, 27−34.
(33) Lee, S. W.; Choi, N.-S. *Acta Crystallogr*. **1999**, *C55*, 2018−2020.
(34) Clark, G. R., Nielson, A. J.; Rickard, C. E. F. *Polyhedron* **1988**, *7*, 117−128.
(35) Refosco, F.; Bolzati, C.; Tisato, F.; Bandoli, G. *J. Chem. Soc., Dalton Trans*. **1998**, 923−929.
(36) Bakir, M.; McKenzie, J. A. M.; Sullivan, B. P. *Inorg. Chim. Acta* **1997**, *254*, 9−17.
(37) Archer, C. M.; Dilworth, J. R.; Jobanputra, P.; Harman, M. E.; Hursthouse, M. B.; Karaulov, A. *Polyhedron* **1991**, *10*, 1539−1543.
(38) Ahmet, M. T.; Coutinho, B.; Dilworth, J. R.; Miller, J. R.; Parrott, S. J.; Zheng, Y.; Harman, M.; Hursthouse, M. B.; Malik, A. *J. Chem. Soc., Dalton Trans*. **1995**, 3041−3048.
(39) Fung, W.-H.; Cheng, W.-C.; Peng, S.-M.; Che, C.-M. *Polyhedron* **1995**, *14*, 1791−1794.
(40) Lisic, E. C.; Mierzadeh, S.; Knapp, F. F., Jr. *J. Labelled Compd. Radiopharm.* **1993**, *33*, 65−75.

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Supporting Information Available: Crystallographic data in CIF format, and tables of crystal data and structure solution and refinement details, atomic coordinates, bond lengths and angles, and anisotropic thermal parameters for complexes **1**·$^1/_2CH_2Cl_2$, **2**·$^1/_2CH_2Cl_2$, **4**, **5**·$2H_2O$, and **8**·$2H_2O$. This material is available free of charge via the Internet at http://pubs.acs.org.

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