Syntheses and Structural Characterizations of Six-Coordinate Oxo−M(V) Complexes (M = Tc, Re) Containing a Tetradentate P₂N₂-Phosphino−Amido Ligand

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Reaction of the potentially tetradentate ligand *N,N'*-bis[2-(diphenylphosphino)phenyl]propane-1,3-diamine (H₂dppd) with [MO₄]⁻ (M = Tc, Re) (*via* reduction-substitution) or [ReOCl₄]⁻ (*via* ligand-exchange) produces neutral and stable six-coordinate oxo−M(V) complexes of the type [TcO(dppd)X] (X = Cl (**1**), OH (**2**), OMe (**3**), OEt (**4**), O₂CCF₃ (**5**)) and [ReO(dppd)X] (X = Cl (**6**), OH (**7**), OMe (**8**), OEt (**9**), O₂CCF₃ (**10**)). The P₂N₂ donor atoms of dppd coordinate in the equatorial plane orthogonal to the M = O linkage; a mononegative unidentate nucleophile completes the distorted octahedral geometry. Compound **3** crystallizes in the monoclinic space group $P2_1/m$ with cell constants $a = 9.157(2)$ Å, $b = 20.391(3)$ Å, $c = 9.948(1)$ Å, $\beta = 114.76(1)°$, and $Z = 2$. Refinement of 3224 observed reflections and 221 parameters yields $R = 0.033$ and $R_w = 0.041$. Compound **8** crystallizes in the monoclinic space group $P2_1/m$ with cell constants $a = 9.175(1)$ Å, $b = 20.415(3)$ Å, $c = 9.946(2)$ Å, $\beta = 114.84(1)°$, and $Z = 2$. Refinement of 2176 observed reflections and 221 parameters yields $R = 0.053$ and $R_w = 0.062$. Compound **10** crystallizes in the monoclinic space group $P2_1/c$ with cell constants $a = 12.866(3)$ Å, $b = 31.416(6)$ Å, $c = 9.729(2)$ Å, $\beta = 111.53(3)°$, and $Z = 4$. The refinement converges to a conventional R of 0.030 and R_w of 0.043 for 3070 observations with 350 parameters.

Introduction

In the last decade the continuing study of the coordination chemistry of technetium[1] and its third row congener rhenium has played a fundamental role in the development of new technetium-based radiopharmaceuticals.[2] In addition, the knowledge of the detailed molecular structure of many ⁹⁹ᵐTc-agents has allowed the design of "more sophisticated" radiomolecules the biological distribution of which is determined not only by perfusion but also by receptor binding interactions.[3] Tetradentate ligands provide the basic framework of the majority of these technetium agents because their intrinsic chelate effect produces a clean reaction to a (usually) substitution-inert product. Among such polydentate ligands N₄-hexamethylpropylene amine oxime (HM-PAO),[4] N₃S-mercaptoacetyltriglycyl (MAG₃),[5] N₂S₂-ethyl cysteine dimer (ECD)[6] and other diamino− or diamido−

dithiols,[7] and N₃O-mixed Schiff base (MRP20)[8] constitute the essential skeleton of five-coordinate oxo−Tc(V) complexes in
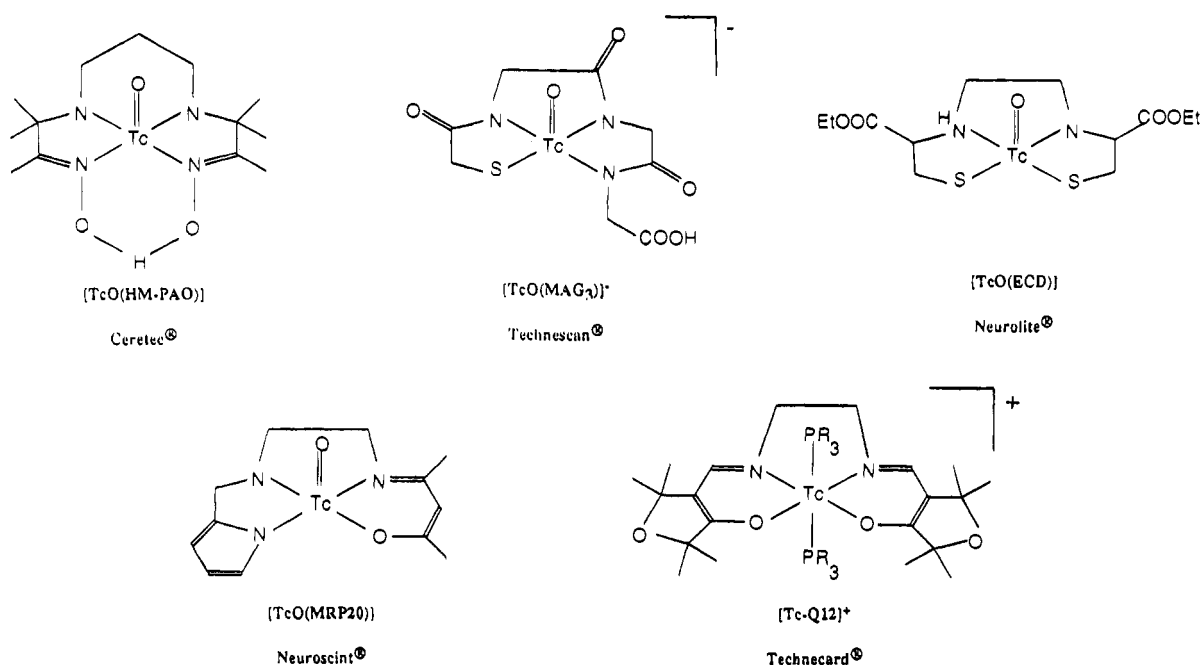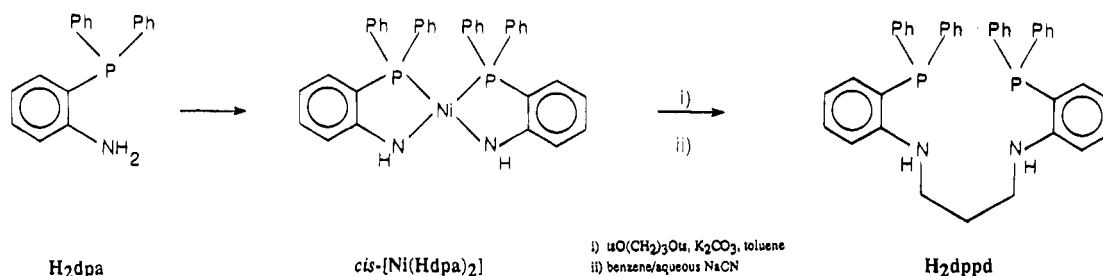
(1) (a) Bandoli, G.; Mazzi, U.; Roncari, E.; Deutsch, A. E. *Coord. Chem. Rev.* **1982,** *44,* 57. (b) Melnik, M.; Van Lier, G. *Coord. Chem. Rev.* **1987,** *77,* 275. (c) Tisato, F.; Refosco, F.; Bandoli, G. *Coord. Chem. Rev.* **1994,** *135/136,* 325. (d) Baldas, J.; *Advances in Inorganic Chemistry*; Sykes, A. G., Ed.; Academic Press: San Diego, CA, 1994; Vol. 41, pp 1−123.

(2) (a) Deutsch, A. E.; Libson, K.; Jurisson, S.; Lindoy, L. F. *Prog. Inorg. Chem.* **1983,** *30,* 75. (b) Verbruggen, A. *Eur. J. Nucl. Med.* **1990,** *17,* 346. (c) Nowotnik, D.; Nunn, A. *Drug News Persp.* **1991,** *5,* 174. (d) Eckelman, W. *The Chemistry of Technetium in Medicine,* National Academy Press: Washington, DC, 1992.

(3) (a) Nicolini, M., Bandoli, G., Mazzi, U., Eds. *Technetium in Chemistry and Nuclear Medicine-3*; Raven Press: New York. (b) Jurisson, S.; Berning, D.; Wei Ja; Danghse Ma *Chem. Rev.* **1993,** *93,* 1137.

(4) (a) Jurisson, S.; Schlemper, E.; Troutner, D.; Canning, L.; Nowotnik, D.; Neirinckx, R. *Inorg. Chem.* **1986,** *25,* 543. (b) Jurisson, S.; Aston, K.; Kay Fair, C.; Schlemper, E.; Sharp P.; Troutner, D. *Inorg. Chem.* **1987,** *26,* 3576.

(5) (a) Fritzberg, A. R.; Kasina, S.; Eshima, D.; Johnson, D. L. *J. Nucl. Med.* **1986,** *27,* 111. (b) Nosco, D.; Tofe, A.; Dunn, T.; Lyle, L.; Wolfangel, R.; Bushman, M.; Grummon, G.; Helling, D.; Marmion, M.; Miller, K.; Pipes, D.; Strubel, T.; Wester, D. In *Technetium in Chemistry and Nuclear Medicine-3*; Nicolini, M., Bandoli, G., Mazzi, U., Eds.; Raven Press: New York, 1990; p 381.

(6) (a) Edwards, D.; Cheesman, E.; Watson, M.; Maheu, L.; Nguyen, S.; Dimitre, L.; Nason, T.; Watson, A.; Walovitch, R. C. In *Technetium in Chemistry and Nuclear Medicine-3*; Nicolini, M., Bandoli, G., Mazzi, U., Eds.; Raven Press: New York, 1990; p 433. (b) Walovitch, R. C.; Hill, T. C.; Garrity, S. T.; Cheesman, E.; Burgess, B. A.; O'Leary, D. H.; Watson, A.; Ganey, M. V.; Morgan, R. A.; Williams, S. J. *J. Nucl. Med.* **1989,** *30,* 1892. (c) Leveille, J.; Demonceau, G.; DeRoo, M.; Morgan, R. A.; Kupranick, D.; Walovitch, R. C. *Nucl. Med. Biol.* **1987,** *14,* 59.

(7) (a) Efange, S. M. N.; Kung, H. F.; Billings, J.; Guo, Y. Z.; Blau, M. *J. Nucl. Med.* **1987,** *28,* 1012. (b) Kung, H. F.; Guo, Y. Z.; Yu, C. C.; Billings, J.; Subraman, V.; Calabrese, J. C. *J. Med. Chem.* **1989,** *32,* 433. (c) Epps, L. A.; Burns, H. D.; Lever, S. Z.; Goldfarb, H. W.; Wagner, H. N., Jr. *Int. J. Appl. Radiat. Isot.* **1987,** *38,* 661. (d) Lever, S. Z.; Burns, H. D.; Kervitsky, T. M.; Goldfarb, H. W.; Woo, D. V.; Wong, D. F.; Epps, L. A.; Kramer, A. V.; Wagner, H. N., Jr. *J. Nucl. Med.* **1985,** *26,* 1287. (e) Lever, S. Z.; Baidoo, K. E.; Mahmood, A. *Inorg. Chim. Acta* **1990,** *176,* 183.

(8) (a) Morgan, G.; Abram, U.; Evrard, G.; Durant, M.; Deblaton, M.; Clemens, P.; Van der Broeck, J.; Thornback, J. *J. Chem. Soc., Chem. Commun.* **1990,** 1772. (b) Morgan, G.; Deblaton, M.; Hussein, W.; Thornback, J.; Evrard, G.; Durant, M.; Stach, J.; Abram, U.; Abram, S. *Inorg. Chim. Acta* **1991,** *190,* 257.

Chart 1

[TcO(HM·PAO)]
Ceretec®

[TcO(MAG₃)]⁻
Technescan®

[TcO(ECD)]
Neurolite®

[TcO(MRP20)]
Neuroscint®

[Tc-Q12]⁺
Technecard®

Scheme 1

H₂dpa

cis-[Ni(Hdpa)₂]

i) uO(CH₂)₃Ou, K₂CO₃, toluene
ii) benzene/aqueous NaCN

H₂dppd

which the ligand is completely ligated to the basal plane of a square pyramid bearing the oxo group at the apex (Chart 1).

In addition, another N₂O₂-Schiff base tetradentate chelate (H₂Y) coordinates on the equatorial sites of an octahedron in [⁹⁹ᵐTcᴵᴵᴵY(PR₃)₂]⁺ (Y = 1,2-bis(((dihydro-2,2,5,5-tetramethyl-3(2H)-furanonato-4)methylene)imino)ethene; R = (CH₂)₃OMe), which bears two *trans*-axial monotertiary ether-substituted alkylphosphines.[9] Polydentate ligands can also be advantageously and conveniently derivatized with appropriate linkers which may, in turn, form stable conjugates with receptor binding moieties. In this field, and remaining with the systems briefly described above, functionalized N₂S₂-diamino—dithiols represent a prototypical example of small molecule radiopharmaceuticals the biodistribution of which is driven by either specific biochemical interactions or metabolism.[10] Since nitrogen and phosphorus are known to be suitable donor atoms for technetium[1c] (and rhenium), we have investigated the reactivity of another potentially tetradentate P₂N₂-chelate toward the group 7 metals relevant to nuclear medicine. The only reported descriptions of H₂dppd reactivity involve (i) its coordination with the group 10 metals,[11] which produces neutral square-planar complexes

of the type [M(dppd)] (M = Ni, Pd, Pt) together with the unique *trans*-spanned [Rhᴵ(CO)Cl(H₂dppd)] complex[11] and (ii) the utilization of the chelate as neutral extractant of Cu²⁺ ions across a water/1,2-DCE interface.[12] This work is part of a more extensive study we have been pursuing on the reactivity of technetium and rhenium with heterofunctionalized phosphines[13] and, in particular, with the bidentate P,N-phosphino—amine ligand (H₂dpa) which is the precursor for the synthesis of H₂dppd[14] (Scheme 1).

Acronyms and Abbreviations

FAB = fast atom bombardment; EI = electron impact; NBA = nitrobenzyl alcohol; 1,2-DCE = 1,2-dichloroethane; H₂dppd = N,N'-bis[2-(diphenylphosphino)phenyl]propane-1,3-diamine; H₂dpa = (2-diphenylphosphino)benzenamine; rms = root mean square; H₂eg = ethylene glycol.

(9) DeRosch, M. A.; Brodack, J. W.; Grummon, G. D.; Marmion, M. E.; Nosco, D. L.; Deutsch, K. F.; Deutsch, E. *J. Nucl. Med.* **1992**, *33*, 850.

(10) Lever, S. Z.; Wagner, H. N., Jr. In *Technetium in Chemistry and Nuclear Medicine-3*; Nicolini, M., Bandoli, G., Mazzi, U., Eds.; Raven Press: New York, 1990; p 649.

(11) Cooper, M. K.; Duckworth, P. A.; Hambley, T. W.; Organ, G. S.; Henrick, K.; McPartlin, M.; Parek, A. *J. Chem. Soc., Dalton Trans.* **1989**, 1067.

(12) Cheng, Y.; Schiffrin, D. J.; Guerriero, P.; Vigato, P. A. *Inorg. Chem.* **1994**, *33*, 765.

(13) (a) Refosco, F.; Bandoli, G.; Mazzi, U.; Tisato, F.; Dolmella, A.; Nicolini, M. *Inorg. Chem.* **1990**, *29*, 2179. (b) Bolzati, C.; Refosco, F.; Tisato, F.; Bandoli, G.; Dolmella, A. *Inorg. Chim. Acta* **1992**, *201*, 7. (c) Refosco, F.; Tisato, F.; Bandoli, G.; Deutsch, E. *J. Chem. Soc., Dalton Trans.* **1993**, 2901. (d) Tisato, F.; Refosco, F.; Bandoli, G.; Bolzati, C.; Moresco, A. *J. Chem. Soc., Dalton Trans.* **1994**, 1453.

(14) (a) Refosco, F.; Bolzati, C.; Moresco, A.; Bandoli, G.; Dolmella, A.; Mazzi, U.; Nicolini, M. *J. Chem. Soc., Dalton Trans.* **1991**, 3043. (b) Bandoli, G.; Dolmella, A.; Tisato, F.; Refosco, F. *Acta Crystallogr.* **1994**, *C50*, 530. (c) Refosco, F.; Tisato, F.; Bandoli, G.; Bolzati, C.; Dolmella, A.; Moresco, A.; Nicolini, M. *J. Chem. Soc., Dalton Trans.* **1993**, 605.

Experimental Section

Caution! Technetium-99 emits a low energy β-particle (0.292 MeV) with half-life of 2.12×10^5 years. When handled in milligram amounts, it does not present a serious health hazard since common laboratory materials provide adequate shielding. Bremsstrahlung is not a significant problem due to the low energy of the β-particle emission, but normal radiation safety procedures must be used at all times to prevent contamination. All operations were performed in a laboratory approved for low-level radioactivity with monitored hoods and gloveboxes.

Reagents. Unless otherwise noted, all chemicals were of reagent grade and were used without further purification. Technetium-99 as [NH$_4$][TcO$_4$] was purchased from the Radiochemical Centre, Amersham, England. The crystalline salt [NBu$_4$][TcO$_4$] was obtained by metathesis, by addition of excess of [NBu$_4$]Cl to aliquots of ammonia solutions of [NH$_4$][TcO$_4$]. The salts [NBu$_4$][MOCl$_4$] and [NBu$_4$]-[MO(eg)$_2$] (M = Tc, Re) were prepared as reported previously.[15] Rhenium as a fine metal powder was obtained as a gift from H. C. Starck GmbH, Postfach, Germany. It was oxidized to suitable Re(V) and perrhenate precursors prior to use.[16] The ligand H$_2$dppd was prepared according to the method reported by Cooper *et al.*[11]

Measurements. Elemental analyses were performed on a Carlo Erba Model 1106 elemental analyzer. Infrared spectra were recorded in the range 4000–400 cm^{-1} on a Mattson 3030 Fourier-transform spectrometer using KBr pellets for rhenium compounds or Nujol mulls between CsI disks for technetium ones. ^{1}H and ^{31}P NMR spectra were collected on a Bruker AC-200 instrument, using SiMe$_4$ as internal reference (^{1}H) and 85% aqueous H$_3$PO$_4$ as external reference (^{31}P). The UV–visible spectra were recorded in CH$_2$Cl$_2$ using a Cary 17D spectrometer (700–220 nm). Conductivity measurements were made in acetonitrile at 25 °C using a Metrohm Herison E518 conductometer. EI and ion positive FAB mass spectra were recorded by using a NBA matrix on a VG 30–250 spectrometer (VG Instrument) at the probe temperature. For FAB measurements Xe was used as the primary beam gas, and the ion gun was operated at 8 keV (*ca.* 1.28×10^{-15} J) and 100 μA. Data were collected over the range 100–1000 at 0.7 s per scan. The SEM measurement was obtained as previously reported.[14c]

Syntheses of Technetium Complexes. [TcO(dppd)Cl], 1. Solid H$_2$dppd (0.057 g, 0.01 mmol) and [NBu$_4$]Cl (0.134 g, 4.8 mmol) were added to a solution of [NBu$_4$][TcO$_4$] (0.059 g, 0.015 mmol) dissolved in acetonitrile (10 mL) under stirring, and the mixture was then refluxed for 3 h. The initial colorless solution slowly turned blue as the ligand dissolved. The resulting solution was cooled and evaporated to dryness under a gentle stream of dinitrogen. The blue oil was extracted several times with Et$_2$O, and the combined ether phases were reduced again to dryness and treated with EtOH (5 mL). Upon standing, a blue microcrystalline solid precipitated; the precipitate was filtered off, washed with ethanol (5 mL), and dried under vacuum pump (yield 48%). **1** is soluble in dichloromethane, chloroform, and acetonitrile and insoluble in alcohols. Anal. Calcd for C$_{39}$H$_{34}$N$_2$P$_2$OClTc: C, 63.03; H, 4.61; N, 3.77. Found: C, 63.61; H, 4.50; N, 4.27. IR (KBr, cm^{-1}): 895 (s) [v(Tc=O)]. UV–vis [CH$_2$Cl$_2$, nm (ϵ)]: 620 (6700), 530 (8100), 340 (sh), 270 (50300). Λ_M (CH$_3$CN): 13.50 Ω^{-1} cm^2 mol^{-1} (neutral). ^{1}H NMR (CDCl$_3$, ppm): δ 2.52 (m, 2H), 3.95 (m, 4H), 6.75–7.80 (28H).

[TcO(dppd)(OH)], 2. In a test tube **3** (*vide infra*) (0.045 g, 0.06 mmol) was dissolved in a 1:1 (v/v) dichloromethane/acetone mixture (10 mL) and two drops of water were added to the red-brown solution. The reaction mixture was left to concentrate to about 3 mL until a red-brown powder appeared. The solid was filtered off and washed with few drops of diethyl ether (yield 38%). **2** is soluble in chlorinated solvents, slightly soluble in acetonitrile, and insoluble in alcohols. Anal. Calcd for C$_{39}$H$_{35}$N$_2$P$_2$O$_2$Tc: C, 64.63; H, 4.87; N, 3.87. Found: C, 65.12; H, 5.01; N, 3.71. IR (KBr, cm^{-1}): 3566 (sharp) [v(O–H)] 888 (s) [v(Tc=O)]. Λ_M (CH$_3$CN): 8.70 Ω^{-1} cm^2 mol^{-1} (neutral). UV–vis [CH$_2$Cl$_2$, nm (ϵ)]: 590 (6700), 515 (7400), 335 (6400), 270 (sh).

^{1}H NMR (CDCl$_3$, ppm): δ 0.04 (s, 1H), 2.54 (mult, 2H), 4.01 (mult, 4H), 6.65–7.85 (28H).

[TcO(dppd)(OR)] (R = Me, (3), Et (4)). Solid H$_2$dppd (0.107 g, 0.18 mmol) was added to a solution of [NBu$_4$][TcO$_4$] (0.049 g, 0.12 mmol) in methanol (or ethanol) (10 mL) under stirring. The reaction mixture was gently warmed at 40 °C for 24 h. The colorless solution slowly changed to red-brown and deposited a red-brown crystalline powder. The precipitate was filtered off, washed with methanol (or ethanol), and dried under vacuum. (yield 82 and 71% for **3** and **4**, respectively). **3** and **4** are soluble in chlorinated solvents, slightly soluble in acetonitrile and acetone, and insoluble in alcohols and diethyl ether. Anal. Calcd for C$_{40}$H$_{37}$N$_2$P$_2$O$_2$Tc (**3**): C, 65.09; H, 4.97; N, 3.80. Found: C, 66.04; H, 5.21; N, 3.62. IR (KBr, cm^{-1}): 882 (s) [v(Tc=O)]. Λ_M (CH$_3$CN): 10.05 Ω^{-1} cm^2 mol^{-1} (neutral). UV–vis [CH$_2$Cl$_2$, nm (ϵ)]: 570 (7000), 505 (8500), 345 (7900), 270 (sh). ^{1}H NMR (CDCl$_3$, ppm): δ 2.36 (t, 3H) 2.53 (mult, 2H), 3.90 (mult, 4H), 6.70–7.80 (28H). Anal. Calcd for C$_{41}$H$_{39}$N$_2$P$_2$O$_2$Tc (**4**): C, 65.41; H, 5.22; N, 3.72. Found: C, 65.94; H, 5.25; N, 3.65. IR (KBr, cm^{-1}): 879 (s) [v(Tc=O)]. Λ_M (CH$_3$CN): 12.30 Ω^{-1} cm^2 mol^{-1} (neutral). UV–vis [CH$_2$Cl$_2$, nm (ϵ)]: 560 (5700), 490 (7000), 350 (6700), 270 (sh). ^{1}H NMR (CDCl$_3$, ppm): δ 0.12 (t, 3H), 2.52 (m, 2H), 2.60 (m, 2H) 3.88 (mult, 4H), 6.70–7.80 (28H).

[TcO(dppd)(O$_2$CCF$_3$)], 5. In a round bottom flask **3** (0.066 g, 0.09 mmol) was dissolved in dichloromethane (5 mL), and an equal volume of methanol was added to the red-brown solution. Then five drops of neat trifluoroacetic acid were added to the mixture and the solution was left to evaporate at room temperature until a blue solid appeared. The precipitate was filtered off and washed with few drops of diethyl ether (yield 52%). **5** is soluble in chlorinated solvents, slightly soluble in acetonitrile and acetone, and insoluble in alcohols. Anal. Calcd for C$_{41}$H$_{34}$N$_2$P$_2$O$_3$F$_3$Tc: C, 60.00; H, 4.17; N, 3.41. Found: C, 59.43; H, 3.99; N, 3.86. IR (KBr, cm^{-1}): 1704 [v(C=O)], 905 (s) [v(Tc=O)]. Λ_M (CH$_3$CN): 6.50 Ω^{-1} cm^2 mol^{-1} (neutral). UV–vis [CH$_2$Cl$_2$, nm (ϵ)]: 625 (8600), 525 (9200), 320 (sh), 265 (sh). ^{1}H NMR (CDCl$_3$, ppm): δ 2.54(m, 2H), 3.93 (mult, 4H), 6.75–7.80 (28H).

Synthesis of Rhenium Complexes. [ReO(dppd)Cl], 6. Method a. Solid H$_2$dppd (0.144 g, 0.24 mmol) was added to a solution of [NBu$_4$][ReOCl$_4$] (0.142 g, 0.24 mmol) in methanol (20 mL) while the solution was stirred at room temperature. The reaction mixture suddenly turned from light green to brown as the ligand dissolved. After the solution was stirred for an additional 30 min at room temperature a brown solid appeared. After 1 h, the precipitate was filtered off, washed with small volumes of methanol and a few drops of diethyl ether (in which the brown solid is sparingly soluble), and dried under vacuum (yield 89%). **6** is soluble in dichloromethane and chloroform, slightly soluble in acetonitrile, and insoluble in alcohols and acetone. Anal. Calcd for C$_{39}$H$_{34}$N$_2$P$_2$OClRe: C, 56.41; H, 4.13; N, 3.37. Found: C, 56.92; H, 4.37; N, 3.51. SEM Re/P/Cl ratio: 1/2/1. IR (KBr, cm^{-1}): 925 (s) [v(Re=O)]. EI mass (*m/z*, relative intensity): 830 (M, 100), 795 (M − Cl, 84), 718 (M − Cl − Ph, 14), 641 (M − Cl − 2Ph, 96). UV–vis [CH$_2$Cl$_2$, nm (ϵ)]: 545 (sh), 450 (12 000), 345 (8700), 260 sh). Λ_M (CH$_3$CN): 13.50 Ω^{-1} cm^2 mol^{-1} (neutral). ^{1}H NMR (CDCl$_3$, ppm): δ 2.56 (mult, 2H), 4.05 (mult, 4H), 6.70–7.70 (28H). ^{31}P{^{1}H} NMR (CDCl$_3$, ppm): δ 6.43 (s). Analogous reactants in acetonitrile also gave a brown powder whose spectrochemical properties are identical to those of **6** in solution, while the infrared spectrum exhibits a Re=O stretching vibration at 937 cm^{-1}.

Method b. Solid H$_2$dppd (0.075 g, 0.12 mmol) and five drops of concentrated HCl were added to a solution of [NBu$_4$][ReO$_4$] (0.041 g, 0.08 mmol) in ethanol (10 mL) under stirring. The initial colorless solution was then refluxed for 0.5 h resulting in a brown solution and a dark precipitate after cooling. The solid was filtered off and washed with ethanol (5 mL) and diethyl ether (2 mL) (yield 40%). IR and ^{1}H NMR spectra are identical to those reported for the complex synthesized in methanol with the method described above.

[ReO(dppd)(OH)], 7. Five drops of 5% NaOH were added to a dispersion of **6** (0.052 g, 0.06 mmol) in 10 mL of acetone. The reaction mixture was refluxed overnight resulting in a brilliant red solution with a red brick microcrystalline precipitate. The precipitate was filtered off and washed with aliquots (2 × 1 mL) of water, 3 mL of acetone, and diethyl ether (yield 56%). **7** is soluble in chlorinated solvents, benzene, and acetonitrile, slightly soluble in acetone and alcohols, and

(15) (a) Davison, A.; Trop, H. S.; DePamphilis, B. V.; Jones, A. G. *Inorg. Synth.* **1982**, *21*, 160. (b) Lis, T.; Jezowska-Trzebiatowska, B. *Acta Crystallogr. Sect. B* **1977**, *133*, 1249. (c) Johnson, N. P.; Lock, C. J. L.; Wilkinson, G. *J. Chem. Soc.* **1964**, 1054.
(16) Rouschias, G. *Chem. Rev.* **1974**, *74*, 531.

insoluble in diethyl ether. Anal. Calcd for $C_{39}H_{35}N_2P_2O_2Re$: C, 57.69; H, 4.34; N, 3.45. Found: C, 58.05; H, 4.52; N, 3.47. IR (KBr, cm^{-1}): 3590 (sharp) [v(O−H)], 918 (s) [v(Re=O)]. EI mass (*m/z*, relative intensity): 812 (M, 70), 795 (M − OH, 100), 718 (M − OH − Ph, 14), 641 (M − OH − 2Ph, 92). Λ_M (CH$_3$CN): 9.80 Ω^{-1} cm^2 mol^{-1} (neutral). UV−vis [CH$_2$Cl$_2$, nm (ϵ)]: 510 (sh), 410 (9600), 345 (9900), 245 (25 700). ^{1}H NMR (CDCl$_3$, ppm): δ 0.05 (s, 1H) 2.60 (mult, 2H), 3.97 (mult, 4H), 6.60−7.90 (28H). ^{31}P{^{1}H} NMR (CDCl$_3$, ppm): δ 6.34 (s).

[ReO(dppd)(OR)] (R = Me (8), Et (9)). In a test tube **6** (0.050 g, 0.06 mmol) is dissolved in the minimum amount of dichloromethane (4 mL) and layered with methanol (or ethanol) (8 mL) containing 2 drops of 25% methanol solution of sodium methoxide (or 21% ethanol solution of sodium ethoxide). Light brown crystals of **8** (or **9**) deposited from the solution. They were filtered off, washed with methanol (or ethanol), and dried overnight in a vacuum (yield 75−80%). **8** and **9** are soluble in chlorinated solvents, slightly soluble in acetonitrile, and insoluble in alcohols. Anal. Calcd for $C_{40}H_{37}N_2P_2O_2Re$ (**8**): C, 58.21; H, 4.45; N, 3.39. Found: C, 57.84; H, 4.40; N, 3.52. IR (KBr, cm^{-1}): 915 (s) [v(Re=O)]. EI mass (*m/z*, relative intensity): 826 (M, 46), 811 (M − Me, 78), 795 (M − OMe, 100), 718 (M − OMe − Ph, 15), 641 (M − OMe − 2Ph, 97). Λ_M (CH$_3$CN): 5.90 Ω^{-1} cm^2 mol^{-1} (neutral). UV−vis [CH$_2$Cl$_2$, nm (ϵ)]: 500 (sh), 410 (9000), 345 (6500), 245 (sh). ^{1}H NMR (CDCl$_3$, ppm): δ 2.46 (s, 3H) 2.55 (mult, 2H), 3.90 (mult, 4H), 6.70−7.70 (28H). ^{31}P{^{1}H} (CDCl$_3$, ppm): δ 6.59 (s). Anal. Calcd for $C_{41}H_{39}N_2P_2O_2Re$ (**9**): C, 58.62; H, 4.68; N, 3.34. Found: C, 58.54; H, 4.52; N, 3.45. IR (KBr, cm^{-1}): 892 (s) [v(Re=O)]. EI mass (*m/z*, relative intensity): 840 (M, 32), 811 (M − Et, 80), 795 (M − OEt, 100), 718 (M − OEt − Ph, 12), 641 (M − OEt − 2Ph, 94). Λ_M (CH$_3$CN): 9.10 Ω^{-1} cm^2 mol^{-1} (neutral). UV−vis [CH$_2$Cl$_2$, nm (ϵ)]: 500 (sh), 410 (9000), 345 (7500), 245 (21 400). ^{1}H NMR (CDCl$_3$, ppm): δ 0.15 (t, 3H), 2.56 (m, 4H) 4.01 (mult, 4H), 6.60−7.80 (28H). ^{31}P{^{1}H} NMR (CDCl$_3$, ppm): δ 6.24 (s).

[ReO(dppd)(O$_2$CCF$_3$)], 10. Two drops of neat trifluoroacetic acid were added to **6** (0.075 g, 0.09 mmol) dissolved in dichloromethane (5 mL) in a test tube. The solution was then layered with methanol (10 mL). Dark brown crystals of **10** subsequently formed which were filtered off and washed with methanol and few drops of diethyl ether (yield 82%). **10** is soluble in chlorinated solvents, slightly soluble in acetonitrile and acetone, and insoluble in alcohols. Anal. Calcd for $C_{41}H_{34}N_2P_2O_3F_3Re$: C, 54.23; H, 3.77; N, 3.09. Found: C, 54.71; H, 3.91; N, 2.96. IR (KBr, cm^{-1}): 1711 [v(C=O)], 892 (s) [v(Re=O)]. FAB$^+$ mass (*m/z*, relative intensity): 838 (M, 4), 811 (M − OCCF$_3$, 18), 795 (M − O$_2$CCF$_3$, 100), 718 (M − O$_2$CCF$_3$ − Ph, 5), 641 (M − O$_2$CCF$_3$ − 2Ph, 100). Λ_M (CH$_3$CN): 9.10 Ω^{-1} cm^2 mol^{-1} (neutral). UV−vis [CH$_2$Cl$_2$, nm (ϵ)]: 545 (sh), 445 (12 200), 345 (8800), 260 (sh). ^{1}H NMR (CDCl$_3$, ppm): δ 2.58 (m, 2H) 4.05 (mult, 4H), 6.70−7.70 (28H). ^{31}P{^{1}H} NMR (CDCl$_3$, ppm): δ 6.65 (s).

H$_2$dppd. See ref 11 for preparation. ^{1}H and ^{31}P{^{1}H} NMR (CDCl$_3$) of H$_2$dppd are as follows. ^{1}H (ppm): δ 1.57 (quintet, 2H), 2.88 (mult, 4H), 4.40 (broad s, 2H), 6.35−7.20 (28H). ^{31}P{^{1}H} (ppm): δ −22.9 (s).

Crystallographic Data Collection and Refinement. Single crystals of **3, 8**, and **10** suitable for X-ray analysis were grown from CH$_2$Cl$_2$/MeOH solutions upon slow evaporation. The diffraction data were collected using a Nicolet Siemens R3m/V diffractometer. Cell parameters were determined from 50 high-angle data ($2\theta > 23°$). Crystallographic summary data are reported in Table 1, while other experimental parameters have been deposited. Absorption corrections were empirical based on the Ψ-scans of six reflections. Structure solution proceeded from Patterson syntheses. The hydrogens were included in calculated positions and held fixed. Fractional atomic coordinates and thermal parameters for **3, 8**, and **10** are reported in Table 2. Table 3 reports some relevant interatomic distances and angles. The SHELXTL-PLUS package of computer programs[17] was employed for the solution and refinement of the structures.

(17) Sheldrick, G. M. SHELXTL-PLUS. An Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data for Nicolet R3m/V, University of Gottingen, 1987.

Table 1. Crystallographic Data for **3, 8**, and **10**

	3	8	10
empirical formula	$C_{40}H_{37}N_2O_2P_2Tc$	$C_{40}H_{37}N_2O_2P_2Re$	$C_{41}H_{34}N_2O_3F_3P_2Re$
fw	737.7	825.8	907.8
cryst syst	monoclinic	monoclinic	monoclinic
space group	$P2_1/m$	$P2_1/m$	$P2_1/c$
a, Å	9.157(2)	9.175(1)	12.866(3)
b, Å	20.391(3)	20.415(3)	31.416(6)
c, Å	9.948(1)	9.946(2)	9.729(2)
β, deg	114.76(1)	114.84(1)	111.53(3)
V, Å^3	1684.8(8)	1690.7(4)	3658(1)
Z	2	2	4
D_{calc}, g/cm^3	1.45	1.62	1.65
μ, cm^{-1} (Mo Kα)	5.5	37.3	34.7
I(max)/I(min)	1.0/0.76	1.0/0.62	1.0/0.81
T, °C	21	21	21
residuals, %: R; R_w	3.3; 4.1	5.3; 6.2	3.1; 4.3
goodness-of-fit^a	0.93	0.83	0.72

$^a\langle\sum w(|F_o - |F_c|)^2/(N_o - N_v)\rangle^{1/2}$ (N_o = observation no.; N_v = variable no.).

Results

Synthesis of Tc Complexes. Oxo−alkoxo−Tc(V) and oxo−chloro−Tc(V) phosphino−amido complexes, [TcO(dppd)(OR)] (R = Me, Et) and [TcO(dppd)Cl] can be prepared by reduction-substitution reactions of [TcO$_4$]$^-$ with the heterodonor H$_2$dppd ligand in alcohols or acetonitrile under mild conditions (40 °C). In these syntheses, described for the alkoxo species by the eq 1, the phosphine functions both as reductant (0.5 mol is consumed in the reduction of Tc(VII) to Tc(V) with the concomitant production of phosphineoxide) and a coordinating agent

$$[NBu_4][TcO_4] + 1.5H_2dppd + ROH \rightarrow$$
$$[TcO(dppd)(OR)] + 0.5H_2dppdO_2 + [NBu_4]OH + H_2O$$
$$(1)$$
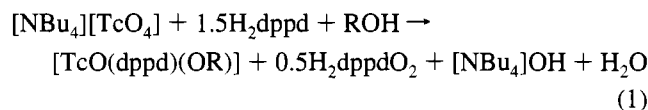
It has to be noted that the use of a large excess of phosphino−amine up to 10:1 ligand to metal ratio does not affect the reaction pathway and always Tc(V) complexes are recovered. Other oxo−Tc(V) phosphino−amido derivatives can be synthesized by ligand exchange, *e.g.* by dissolving the labile methoxo complex [TcO(dppd)(OMe)] in dichloromethane/methanol mixtures followed by the addition of aqueous sodium hydroxide or neat trifluoroacetic acid, to form [TcO(dppd)(OH)] and [TcO-(dppd)(O$_2$CCF$_3$)], respectively.

Synthesis of Re Complexes. The oxo−chloro−Re(V) phosphino−amido complex [ReO(dppd)Cl] can be prepared in high yield (90%) by ligand-exchange reactions of [ReOCl$_4$]$^-$ with equimolar amount of H$_2$dppd in acetonitrile or alcohols at room temperature according to the stoichiometry outlined in eq 2.

$$[NBu_4][ReOCl_4] + H_2dppd \rightarrow$$
$$[ReO(dppd)Cl] + [NBu_4]Cl + 2HCl \quad (2)$$
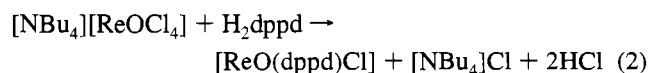
The same oxo−chloro−Re(V) complex can also be synthesized from [ReO$_4$]$^-$ in refluxing methanol, but the yield is somewhat reduced (*ca.* 40%). [ReO(dppd)Cl] is the ideal precursor for the synthesis of other oxo−Re(V) phosphino−amido species which can be prepared by dissolving **6** in dichloromethane and layering the solution with appropriate alkaline solutions of ROH (R = H, Me, Et)/NaOR. Similar exchange reactions can be performed also in acid media, as in the case of **10**, where the dissolution of the chloro complex is followed by the addition of a methanolic solution of trifluoroacetic acid.

Table 2. Fractional Coordinates and Thermal Parameters for **3**, **8**, and **10**.

	x/a	y/b	z/c	U_{eq},[a] Å^2		x/a	y/b	z/c	U_{eq},[a] Å^2
					Compound **3**				
Tc	0.0329(1)	0.2500	0.3469(1)	0.023(1)	C(9)	0.2759(3)	0.3434(1)	0.1823(3)	0.029(1)
P(1)	0.1084(1)	0.3440(1)	0.2361(1)	0.025(1)	C(10)	0.2514(3)	0.3446(2)	0.0356(3)	0.048(1)
O(1)	−0.1506(3)	0.2500	0.2031(3)	0.032(1)	C(11)	0.3821(4)	0.3444(2)	−0.0020(4)	0.060(2)
O(2)	0.2771(3)	0.2500	0.4436(2)	0.030(1)	C(12)	0.5355(4)	0.3436(2)	0.1059(4)	0.052(1)
N(1)	0.0324(2)	0.3219(1)	0.4893(2)	0.030(1)	C(13)	0.5617(3)	0.3432(2)	0.2510(4)	0.050(1)
C(1)	0.1642(3)	0.3993(1)	0.3895(3)	0.030(1)	C(14)	0.4326(3)	0.3425(2)	0.2913(3)	0.044(1)
C(2)	0.2482(3)	0.4574(2)	0.3998(3)	0.042(1)	C(15)	−0.0580(3)	0.3827(1)	0.0820(3)	0.030(1)
C(3)	0.2820(3)	0.5002(2)	0.5167(3)	0.046(1)	C(16)	−0.1441(3)	0.3459(2)	−0.0452(3)	0.045(1)
C(4)	0.2291(3)	0.4844(2)	0.6234(3)	0.046(1)	C(17)	−0.2782(4)	0.3720(2)	−0.1609(3)	0.058(1)
C(5)	0.1464(3)	0.4272(2)	0.6173(3)	0.040(1)	C(18)	−0.3295(4)	0.4335(2)	−0.1511(4)	0.062(1)
C(6)	0.1120(3)	0.3817(1)	0.4998(3)	0.030(1)	C(19)	−0.2469(4)	0.4702(2)	−0.0272(4)	0.064(2)
C(7)	−0.0263(3)	0.3119(2)	0.6039(3)	0.039(1)	C(20)	−0.1108(3)	0.4458(2)	0.0894(3)	0.046(1)
C(8)	−0.1244(5)	0.2500	0.5793(4)	0.039(2)	C(21)	0.3686(5)	0.2500	0.5993(4)	0.046 (2)
					Compound **8**				
Re	0.0365(1)	0.2500	0.3465(1)	0.024(1)	C(9)	0.2750(11)	0.3439(5)	0.1799(11)	0.026(4)
P(1)	0.1091(3)	0.3444(2)	0.2363(3)	0.028(1)	C(10)	0.2527 14)	0.3459(8)	0.0353(14)	0.054(6)
O(1)	−0.1508(11)	0.2500	0.2062(11)	0.032(4)	C(11)	0.3835(16)	0.3462(9)	−0.0017(16)	0.067(7)
O(2)	0.2779(11)	0.2500	0.4430(11)	0.029(4)	C(12)	0.5322(15)	0.3437(7)	0.1047(17)	0.056(6)
N(1)	0.0368(9)	0.3220(5)	0.4901(9)	0.032(3)	C(13)	0.5588(13)	0.3422(7)	0.2501(16)	0.051(5)
C(1)	0.1630(12)	0.3998(6)	0.3888(11)	0.034(4)	C(14)	0.2750(11)	0.3427(7)	0.2896(13)	0.047(5)
C(2)	0.2474(14)	0.4585(7)	0.3990(15)	0.049(6)	C(15)	−0.0579(11)	0.3817(5)	0.0801(12)	0.028(4)
C(3)	0.2792(14)	0.5018(7)	0.5142(15)	0.048(5)	C(16)	−0.1425(13)	0.3463(7)	−0.0441(14)	0.046(5)
C(4)	0.2318(15)	0.4846(7)	0.6275(14)	0.052(6)	C(17)	−0.2775(14)	0.3716(9)	−0.1622(15)	0.064(6)
C(5)	0.1452(13)	0.4262(7)	0.6141(12)	0.042(5)	C(18)	−0.3284(15)	0.4325(9)	−0.1512(18)	0.065(7)
C(6)	0.1121(11)	0.3810(6)	0.4992(11)	0.030(4)	C(19)	−0.2485(17)	0.4689(7)	−0.0289(19)	0.067(7)
C(7)	−0.0244(12)	0.3123(7)	0.6039(12)	0.041(5)	C(20)	−0.1105(14)	0.4439(7)	0.0880(14)	0.047(5)
C(8)	−0.1167(19)	0.2500	0.5846(18)	0.037(7)	C(21)	0.3685(20)	0.2500	0.5996(18)	0.054(8)
					Compound **10**				
Re	0.2364(1)	0.1549(1)	0.1362(1)	0.025(1)	C(16)	0.2400(8)	0.0673(3)	0.2875(11)	0.039(4)
P(1)	0.0731(2)	0.1309(1)	−0.0764(3)	0.030(1)	C(17)	0.2702(10)	0.0197(3)	0.2944(12)	0.051(5)
P(2)	0.3970(2)	0.1329(1)	0.0712(2)	0.027(1)	C(18)	0.0069(8)	0.1691(3)	−0.2256(10)	0.036(2)
F(1)	0.2358(7)	0.0001(2)	0.1696(7)	0.094(4)	C(19)	0.0581(11)	0.2054(4)	−0.2444(14)	0.070(3)
F(2)	0.2324(7)	−0.0011(2)	0.3843(8)	0.096(4)	C(20)	0.0059(11)	0.2332(5)	−0.3660(14)	0.075(4)
F(3)	0.3787(7)	0.0158(3)	0.3499(10)	0.115(5)	C(21)	−0.0962(11)	0.2237(4)	−0.4651(15)	0.077(4)
O(1)	0.2380(5)	0.2029(2)	0.0606(7)	0.032(2)	C(22)	−0.1479(13)	0.1856(5)	−0.4566(17)	0.094(4)
O(2)	0.2391(5)	0.0865(2)	0.1715(6)	0.032(2)	C(23)	−0.0937(11)	0.1583(5)	−0.3365(14)	0.075(4)
O(3)	0.2268(8)	0.0822(3)	0.3944(9)	0.077(5)	C(24)	0.0779(7)	0.0824(3)	−0.1727(10)	0.030(2)
N(1)	0.1176(6)	0.1583(2)	0.2260(8)	0.034(3)	C(25)	0.1064(9)	0.0833(3)	−0.3006(12)	0.051(3)
N(2)	0.3615(6)	0.1564(3)	0.3374(7)	0.033(3)	C(26)	0.1137(9)	0.0462(4)	−0.3668(13)	0.058(3)
C(1)	−0.0226(7)	0.1228(3)	0.0167(11)	0.037(4)	C(27)	0.0914(10)	0.0078(4)	−0.3217(13)	0.061(3)
C(2)	−0.1261(8)	0.1012(3)	−0.0475(12)	0.053(5)	C(28)	0.0633(9)	0.0060(3)	−0.1989(12)	0.053(3)
C(3)	−0.1966(8)	0.0980(4)	0.0284(13)	0.060(5)	C(29)	0.0567(8)	0.0431(3)	−0.1246(11)	0.042(2)
C(4)	−0.1637(10)	0.1138(4)	0.1687(15)	0.066(6)	C(30)	0.4627(7)	0.1778(3)	0.0142(10)	0.036(2)
C(5)	−0.0619(9)	0.1329(4)	0.2402(13)	0.055(5)	C(31)	0.5727(9)	0.1892(4)	0.0979(12)	0.054(3)
C(6)	0.0111(8)	0.1381(3)	0.1608(11)	0.037(4)	C(32)	0.6219(12)	0.2228(5)	0.0456(17)	0.088(4)
C(7)	0.1374(8)	0.1764(3)	0.3702(10)	0.042(4)	C(33)	0.5611(10)	0.2452(4)	−0.0807(13)	0.066(3)
C(8)	0.2438(8)	0.2018(3)	0.4278(11)	0.048(4)	C(34)	0.4536(9)	0.2340(3)	−0.1583(12)	0.054(3)
C(9)	0.3477(8)	0.1743(3)	0.4679(10)	0.040(4)	C(35)	0.4025(8)	0.2001(3)	−0.1151(10)	0.039(2)
C(10)	0.4921(7)	0.1183(3)	0.2519(10)	0.032(3)	C(36)	0.4023(7)	0.0904(3)	−0.0526(9)	0.028(2)
C(11)	0.5864(7)	0.0946(3)	0.2791(10)	0.035(4)	C(37)	0.4461(9)	0.0952(4)	−0.1600(12)	0.054(3)
C(12)	0.6596(8)	0.0869(3)	0.4214(11)	0.044(4)	C(38)	0.4536(9)	0.0605(4)	−0.2461(14)	0.065(3)
C(13)	0.6347(8)	0.1033(4)	0.5383(11)	0.053(4)	C(39)	0.4155(9)	0.0220(3)	−0.2259(12)	0.050(3)
C(14)	0.5405(8)	0.1276(3)	0.5114(10)	0.039(4)	C(40)	0.3699(9)	0.0161(4)	−0.1197(12)	0.053(3)
C(15)	0.4621(7)	0.1342(3)	0.3702(9)	0.029(3)	C(41)	0.3649(8)	0.0496(3)	−0.0330(11)	0.047(3)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij}.

Characterization. Elemental analyses, as given in the Experimental Section, are in good agreement with the proposed formulations. The IR spectra of all oxo−M(V) complexes exhibit the characteristic M=O stretching vibration in the range 879−908 cm^{-1} for technetium and 892−937 cm^1 for rhenium. The complexes possess IR absorptions typical of the coordinated phosphine ligand, and lack the ν(N−H) vibration characteristic of the free ligand. Additionally there is a sharp band attributable to ν(O−H) beyond 3550 cm^{-1} in the hydroxo derivatives and an intense band around 1700 cm^{-1} characteristic of the C=O vibration in the trifluoroacetato species. EI and FAB$^+$ mass spectra of the rhenium compounds demonstrate the presence of the parent molecules along with the [ReO(dppd)]$^+$ moiety

as the major fragment, consistent with the lability of the unidentate ligand coordinated *trans* to the Re=O group.

All of the oxo−M(V) phosphino−amido complexes are nonconducting in acetonitrile solutions and exhibit well-defined, intense absorption bands in the visible and UV regions. Re(V) complexes exhibit longest visible bands at higher energy than Tc(V) ones; this implies that the charge transfers occur from the ligand to the metal (LTMCT) since Tc(V) is a stronger oxidant than is Re(V).

NMR data are reported for all 10 complexes in the Experimental Section. The ^{31}P{^{1}H} singlet due to the equivalent coordinated phosphorus atoms moves significantly downfield from −22.9 (in the free ligand) to *ca.* 6.50 ppm in all rhenium

Table 3. Selected Bond Distances (Å) and Angles (deg) for **3** (M = Tc), **8** (M = Re), and **10**

	3	8
M—P(1)	2.450(1)	2.444(3)
M—O(1)	1.691(2)	1.699(8)
M—O(2)	2.030(2)	2.011(9)
M—N(1)	2.040(2)	2.05(1)
P(1)—C(1)	1.791(3)	1.79(1)
P(1)—C(9)	1.824(3)	1.83(1)
P(1)—C(15)	1.828(2)	1.829(9)
N(1)—C(6)	1.402(3)	1.37(2)
N(1)—C(7)	1.464(4)	1.47(2)
C(1)—C(6)	1.414(4)	1.41(2)
C(7)—C(8)	1.509(4)	1.50(2)
P(1)—M—O(1)	89.2(1)	90.2(3)
P(1)—M—O(2)	75.6(1)	76.2(2)
O(1)—M—O(2)	155.2(1)	157.5(5)
P(1)—M—N(1)	80.4(1)	80.0(3)
O(1)—M—N(1)	107.3(1)	106.1(3)
O(2)—M—N(1)	89.6(1)	89.3(3)
P(1)—M—P(1A)	102.9(1)	104.1(2)
N(1)—M—N(1A)	91.9(1)	91.6(5)
M—P(1)—C(1)	98.2(1)	98.6(4)
M—P(1)—C(9)	123.9(1)	123.5(3)
M—P(1)—C(15)	115.0(1)	114.9(4)
C(6)—N(1)—C(7)	114.4(2)	114.3(1.0)
P(1)—C(1)—C(6)	115.7(2)	115.1(9)
N(1)—C(6)—C(1)	119.8(2)	120.5(1.0)
N(1)—C(7)—C(8)	112.2(3)	113.2(1.2)
C(7)—C(8)—C(7A)	113.6(4)	116.6(1.5)

Distances for **10**

Re—P(1)	2.463(2)	F(1)—C(17)	1.29(1)
Re—P(2)	2.471(3)	F(2)—C(17)	1.32(2)
Re—O(1)	1.682(6)	F(3)—C(17)	1.30(1)
Re—O(2)	2.174(6)	O(2)—C(16)	1.27(1)
Re—N(1)	2.023(9)	O(3)—C(16)	1.21(1)
Re—N(2)	2.028(6)	N(1)—C(6)	1.43(1)
P(1)—C(1)	1.80(1)	N(1)—C(7)	1.45(1)
P(1)—C(18)	1.84(1)	N(2)—C(9)	1.46(1)
P(1)—C(24)	1.80(1)	N(2)—C(15)	1.40(1)
P(2)—C(10)	1.80(1)	C(7)—C(8)	1.50(1)
P(2)—C(30)	1.83(1)	C(8)—C(9)	1.51(1)
P(2)—C(36)	1.82(1)	C(16)—C(17)	1.54(1)

Angles for **10**

P(1)—Re—P(2)	103.6(1)	C(18)—P(1)—C(24)	103.7(4)
P(1)—Re—O(1)	92.9(2)	Re—P(2)—C(10)	98.9(4)
P(2)—Re—O(1)	89.6(2)	Re—P(2)—C(30)	112.6(3)
P(1)—Re—O(2)	77.9(1)	C(10)—P(2)—C(30)	105.6(4)
P(2)—Re—O(2)	78.4(2)	Re—P(2)—C(36)	127.8(3)
O(1)—Re—O(2)	162.5(3)	C(10)—P(2)—C(36)	106.4(4)
P(1)—Re—N(1)	80.4(2)	C(30)—P(2)—C(36)	103.4(5)
P(2)—Re—N(1)	163.9(2)	Re—O(2)—C(16)	126.9(6)
O(1)—Re—N(1)	105.9(3)	Re—N(1)—C(6)	122.5(7)
O(2)—Re—N(1)	87.5(3)	Re—N(1)—C(7)	123.2(6)
P(1)—Re—N(2)	161.4(2)	C(6)—N(1)—C(7)	113.8(9)
P(2)—Re—N(2)	79.1(2)	Re—N(2)—C(9)	122.9(6)
O(1)—Re—N(2)	105.5(3)	Re—N(2)—C(15)	123.2(6)
O(2)—Re—N(2)	84.8(3)	C(9)—N(2)—C(15)	113.1(6)
N(1)—Re—N(2)	92.3(3)	P(1)—C(1)—C(2)	123.5(8)
Re—P(1)—C(1)	98.7(3)	P(1)—C(1)—C(6)	116.2(7)
Re—P(1)—C(18)	118.0(3)	N(1)—C(7)—C(8)	112.4(9)
C(1)—P(1)—C(18)	106.7(5)	C(7)—C(8)—C(9)	113.1(8)
Re—P(1)—C(24)	121.0(3)	N(2)—C(9)—C(8)	111.9(7)
C(1)—P(1)—C(24)	107.6(5)		

complexes, while the phosphorus signal is not detectable in the technetium complexes. Proton NMR spectra for both technetium and rhenium complexes show the disappearance of the broad N—H singlet and a significant downfield shift of *ca.* 1 ppm for all the protons of the propylic chain, when compared to the corresponding signals in the free ligand. In addition, where available, the spectra exhibit proton signals arising from the aliphatic residue of the monodentate ligand coordinated *trans* to the oxo group. These data confirm the coordination of the

doubly deprotonated tetradentate ligand and the presence of the 6th ligand in solution, which is consistent with the structure investigated in the solid state by X-ray crystallography.

The labeling and geometry of the atoms in the crystal structures of **3** and **8** are shown in the thermal ellipsoid drawing of Figure 1. These two isomorphous structures contain discrete monomeric neutral complex units, and the weighted rms of 0.027 Å, derived from the BMFIT program,[18] confirms that the two structures are superimposable (maximum deviation of 0.047 Å at C(3)). The tetradentate P₂N₂-ligand occupies the four equatorial positions of a distorted octahedron around the metal atom; the axial positions are occupied by an oxo atom (O(1)) and by a methoxo ligand (O(2)), with an O(1)—Tc—O(2) angle of only 155.2° (the corresponding value in **8** is 157.5°). The metal atoms are displaced from the equatorial P₂N₂ plane by 0.31 Å in **3** and 0.30 Å in **8** toward O(1), a situation reminiscent of 5-coordinate Tc=O structures and similarly encountered in the analogous complex [TcO(Hdpa)₂(OMe)].[14c] However, other structures such as [TcOBr₂(Npy)₂(OEt)][19] (Npy = 4-nitropyridine) contain a technetium atom which is not substantially displaced from the equatorial plane. Around the metal atoms, the 5,6,5 ring systems have conformations most nearly described as a twist-envelope (C_2) for the 5-membered rings and a boat (C_{2v}) for the six-membered one (Figure 2). A comparison of **3** with the [TcO(Hdpa)₂(OMe)] complex shows that the two structures are not superimposable (Figure 3), the weighted rms being of 0.21 Å, when the fitting is performed using the "inner core" octahedron atoms. In particular, the major differences between **3** and the "bis-Hdpa complex" reside in an opening of the P—Tc—P angle (from 102.9(1)° of **3** to 111.2(1)°) along with a lengthening of the Tc—P bond distance (from 2.450(1) of **3** to 2.507(3) Å) and in a contraction of the N—Tc—N angle (from 91.9(1)° of **3** to 87.1(4)°), while the "bite" P—Tc—N angles do not change (mean value of 80°). The gross result is a more bent character for the complex containing the quadridentate ligand; the dihedral angle between the two aminophenyl moieties (wings) is 56.5° in **3** and only 20° in [TcO(Hdpa)₂-(OMe)]. Distances and angles are in the expected range.[1c] No intermolecular bonding of significance occurs in the crystals. The substitution of the trifluoroacetato for the methoxo group (Figure 4) does not modify the stereochemistry of the structure. The structures of **8** and **10** differ significantly only in the orientation of a phenyl ring [C(36)—40)], as evidenced in Figure 5, to accommodate the trifluoroacetate ligand.

Discussion

In a previous paper we have described the synthesis of oxo—M(V) (M = Tc, Re) compounds containing the bidentate P,N-chelate H₂dpa.[14c] The resulting [MO(Hdpa)₂X] complexes (X = uninegative monodentate ligand coordinated *trans* to the oxo group) contain the bidentate ligands equatorially coordinated with a *cis*-P orientation. They appear to be sensitive to further metal reduction when M = Tc. For instance, methanolic solutions of [TcO(Hdpa)₂(OMe)] undergo facile cleavage of the oxo group in presence of a noncoordinating acid and excess H₂dpa to give tris-substituted [Tcᴵᴵᴵ(H₂dpa)(Hdpa)₂]⁺.[14a] In coordinating acid media (*i.e.* hydrochloric acid) the equivalent reactants yield the mixed halo—phosphino complex [Tcᴵᴵᴵ(H₂-dpa)₂Cl₂]⁺.[20] Conversely, the isostructural [ReO(Hdpa)₂(OMe)] complex is harder to reduce and instead rearranges in hydrochloric acid solutions to another thermodinamically stable Re(V)

(18) Nyburg, S. C. *Acta Crystallogr.* **1974**, *B30*, 251.
(19) Fackler, P. H.; Kastner, M. E.; Clarke, M. J. *Inorg. Chem.* **1984**, *23*, 3968.
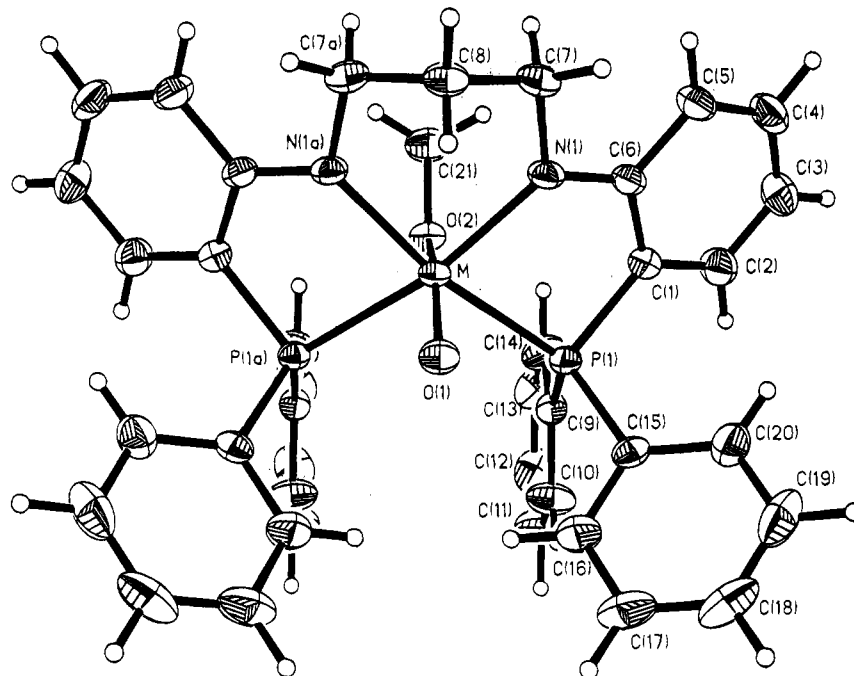(20) Refosco, F.; Tisato, F. Unpublished results.

Figure 1. Perspective view of **3** (M = Tc) and **8** (M = Re) with atom contours at 50% probability. The atom-numbering scheme is shown.
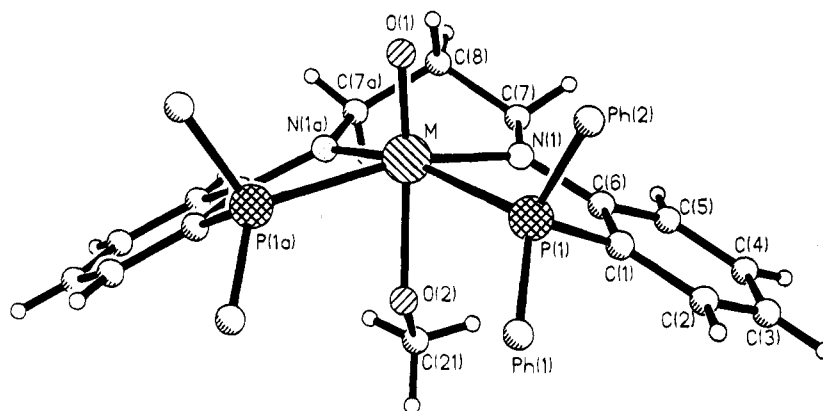

Figure 2. Another view of **3** and **8**, in which the phenyl rings (Ph) are omitted for clarity.
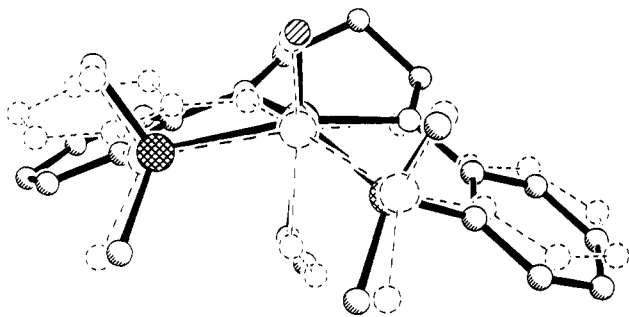

Figure 3. Superimposition of **3** (—) and [TcO(Hdpa)₂(OMe)] (- - -).

"twisted" species [ReOCl(Hdpa)₂], which contains the bidentate ligands orthogonally coordinated.[14c] In order to ensure the formation of a single product and, eventually, to increase the stability of oxo—M(V) derivatives, the tetradentate H₂dppd ligand was synthesized by joining the amino groups of two bidentate H₂dpa with a propylic chain.[11] The molecule H₂dppd readily reacts with [MO₄]⁻ (M = Tc, Re) in alcoholic solutions, acting both as ligand and reductant to give neutral oxo—M(V) derivatives of the type [MO(dppd)X]. While the reduction of perrhenate requires drastic conditions (refluxing methanol), the conversion of pertechnetate to oxo—Tc(V) phosphino—amido complexes requires only gentle heating at 40 °C, consistent with

the fact that technetium is significantly easier to reduce than is rhenium.[21] [MO(dppd)X] complexes are remarkably more stable toward further reduction than the corresponding bis-bidentate [MO(Hdpa)₂X] compounds. On the other hand, the monodentate ligand coordinated *trans* to the oxo group remains labile. The strong chelate effect imposed by the tetradentate ligand onto the M=O core forces the complex to retain its square-pyramidal coordination environment during the exchange of the monodentate group. The X ligand appears to be more readily exchanged in [TcO(dppd)X] complexes than in the isostructural rhenium species. In fact, a simple mass effect obtained by dissolving, for example, the methoxo complex in ethanol allows the replacement of the methoxo for the ethoxo group (or vice versa) in technetium derivatives, whereas the use of sodium ethoxide in ethanol is required to obtain a similar replacement in rhenium analogs. It is worth noting the wide range of acid—base stability of the [ReO(dppd)]⁺ moiety, which is able to exchange the monodentate group either in strong alkaline (by sodium hydroxide) or in strong acid (by trifluoro-acetic acid) conditions to give the octahedral [ReO(dppd)OH] and [ReO(dppd)(O₂CCF₃)] complexes, respectively. The stabil-

(21) Deutsch, E. A.; Libson, K.; Vanderheyden, J.-L. In *Technetium in Chemistry and Nuclear Medicine-3*; Nicolini, M., Bandoli, G., Mazzi, U., Eds.; Raven Press: New York, 1990; p 13.
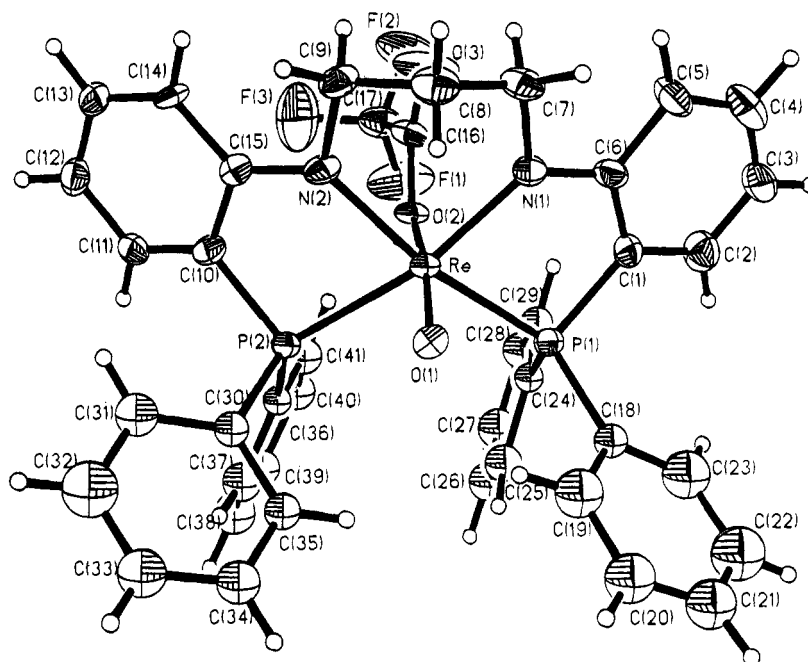
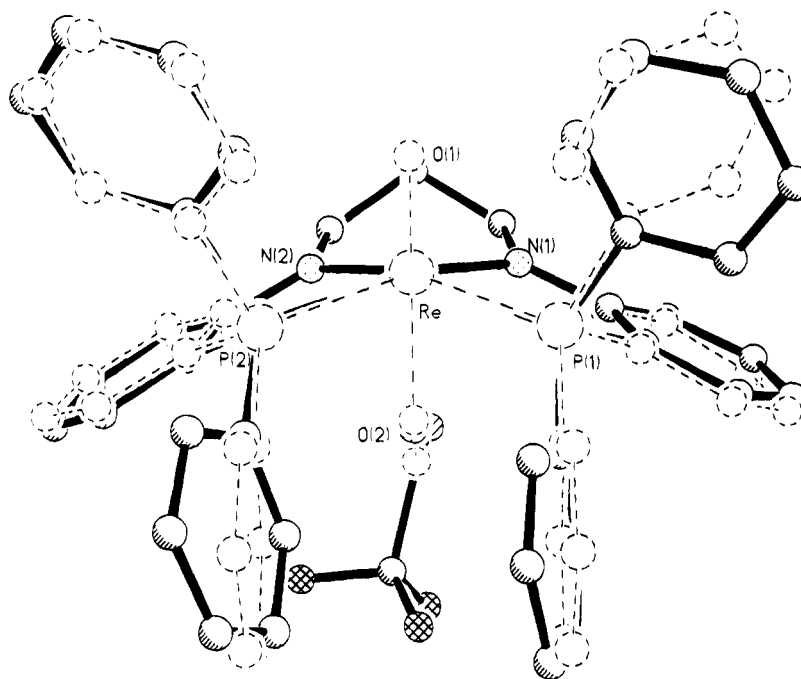**Figure 4.** Perspective view of **10**. Vibrational ellipsoids are drawn at the 50% probability level.

Figure 5. Superimposition of **10** (—) and **8** (- - -).

ity of the [ReO(dppd)]⁺ moiety can be seen in the peaks of the mass spectra, which invariably show the cluster assignable to this formulation as the most intense peak with detectable fragmentation corresponding to the loss of one and two phenyl groups without disruption of the backbone ligand framework. Effective control of the coordination of the site *trans* to the oxo group is desirable and appears to be the next step to be investigated. Work is in progress to synthesize a potentially pentadentate ligand by incorporating a pendant group that would hold a terminal hydroxyl or acid function onto the PNNP framework.

The literature on technetium coordination chemistry offers many examples of reduction of pertechnetate, as well as oxo— Tc(V) species, by tertiary phosphines through repeated extraction of oxygen atoms mediated by P(III) in acid media.[22] In spite of this general behavior, some stable Tc(V) complexes retain

tertiary phosphines in their coordination sphere. A survey of the Cambridge Crystallographic Data base[23] reveals that 12 X-ray structures of Tc(V)—P complexes are reported (Table 4).

(22) (a) Golowin, M.; Rahman, M.; Belmonte, J.; Giering, W. P. *Organometallics* **1985**, *4*, 1981. (b) Rahman, M.; Liu, H. Y.; Prock, A.; Giering, W. P. *Organometallics* **1987**, *6*, 650.

(23) (a) Allen, F. H.; Kennard, O.; Taylor, R. *Acc. Chem. Res.* **1983**, *16*, 146. (b) Allen, F. H.; Davies, J. E.; Galloy, J. J.; Johnson, O.; Kennard, O.; Macrae, C. F.; Mitchell, E. M.; Mitchell, G. F.; Smith, J. M.; Watson, D. G. *J. Chem. Inf. Comput. Sci.* **1987**, *31*, 187.

(24) Vanderheyden, J.-L.; Ketring, A. R.; Libson, K.; Heeg, M. J.; Roecker, L.; Motz, P.; Whittle, R.; Elder, R. C.; Deutsch, E. A. *Inorg. Chem.* **1984**, *23*, 3184

(25) Nicholson, T.; Davison, A.; Jones, A. G. *Inorg. Chim. Acta* **1991**, *187*, 51.

(26) Abrams, M. J.; Larsen, S. K.; Shaikh, S. N.; Zubieta, J. *Inorg. Chim. Acta* **1991**, *185*, 7.

(27) Archer, C. M.; Dilworth, J. R.; Griffiths, D. V.; McPartlin, M.; Kelly, J. D.; *J. Chem. Soc., Dalton Trans.* **1992**, 183.

Table 4. Technetium—Phosphorus Bond Lengths in Tc(V) Complexes

compd^a	CN^b	Tc(V)—P, Å	*trans*-atom	ref
[TcO(OH)(dmpe)$_2$]$^+$	6	2.473, 2.480	P, P	24
[TcO(OMe)(Hdpa)$_2$]	6	2.511, 2.503	N$_{amido}$, N$_{amido}$	14c
[TcO(OMe)(dppd)]	6	2.450	N$_{amido}$	this work
[Tc(NPh)Cl$_3$(PPh$_3$)$_2$]	6	2.489, 2.517	P, P	25
[Tc(C$_8$H$_5$N$_4$)Cl$_2$(PPh$_3$)$_2$]	6	2.490, 2.477	P, P	26
[TcNCl(dmpe)$_2$]$^+$	6	2.447, 2.443, 2.448, 2.453	P, P, P, P	27
[TcNCl$_2$(PMe$_2$Ph)$_3$]	6	2.444, 2.486	Cl, P	28
[TcN(NCS)$_2$(MeCN)(PPh$_3$)$_2$]	6	2.494, 2.524	P, P	29
[TcNCl$_2$(PPh$_3$)$_2$]	5	2.464, 2.462	P, P	26
[TcN(dtcbz-*ONS*)(PPh$_3$)]	5	2.419	N$_{imino}$	30
[TcNCl(ptcb-*NS*)(PPh$_3$)]	5	2.429	N$_{imino}$	31
[TcN(ecbap-*ONO*)(PPh$_3$)]	5	2.398	N$_{imino}$	32

^{a} dmpe = 1,2-bis(dimethylphosphino)ethane; NPh = phenylimido; C$_8$H$_5$N$_4$ = hydrazidophthalazine; dtcbz-*ONS* = *S*-methyl-3-salicylidene-dithiocarbazoato; ptcb-*NS* = *O*-ethyl(phenylimino)thiocarbonato; ecbap-*ONO* = *N*-(2-ethoxycarbonyl-3-oxobutenyl)-2-aminophenolato. ^{b} CN = coordination number.

These compounds are all stabilized by the presence of a characteristic Tc=N or Tc=O core. The majority (nine) bears a Tc—nitrogen multiple bond (seven compounds contain a nitrido core and two an imido one), while only three exhibit the more common Tc—oxo group. The existence of several nitrido—Tc(V) species is interpretable on the basis of their redox properties which exhibit a wide range of stability in the cathodic region, making lower oxidation states not easily accessible.[33] On the contrary, oxo—Tc(V) derivatives are generally easy to reduce, except in those complexes wherein a particular combination of the remaining donor atoms induces an overall stability of the Tc(V) moiety, as in the case of oxo—Tc(V) phosphino—amido complexes. The Tc(V)—P bond distance appears to be only slightly affected by coordination number, occurring in the 2.398—2.464 Å range for five-coordinate species and 2.443—2.524 Å for six-coordinate ones; the overall average distance is 2.480(0.025) Å. The *trans*-substituent does not seem to influence significantly the Tc(V)—P distance. The

equatorially coordinated tetradentate PNNP system utilized in this work imposes a *cis*-P configuration, which is exhibited also by the bis-substituted [MO(Hdpa)$_2$X] complexes. This behavior can be explained in terms of electronic factors which primarily govern the metal—donor interactions. Steric factors alone would favor a *trans*-P configuration by placing the encumbered phenyl rings attached to the phosphorus atoms on opposite sites. Consequently, the two amido nitrogens would face each other, but the strong donating property of this donor group induces a rearrangement of the bis-bidentate complex to the more thermodinamically stable *cis*-P configuration which places an electron acceptor (P) *trans* to an electron donor (N$_{amido}$) and diminishes competition.

Conclusion

The tetradentate P$_2$N$_2$-phosphinoamine H$_2$dppd reacts with [MO$_4$]$^-$ (M = Tc, Re) as both a ligand and reducing agent, to give six-coordinate neutral oxo—M(V) phosphino—amido complexes of general formula [MO(dppd)X]. The chelate ligates on the equatorial plane orthogonal to the M=O linkage and the distorted octahedral coordination sphere is completed by a monodentate ligand, which readily exchanges with other nucleophiles without affecting the remaining [MO(dppd)]$^+$ moiety. Despite the presence of two P(III) donors in the inner core, this class of complexes seems to be resistant to further reduction of the metal center. This fact is quite common for Re derivatives and rare for Tc ones. The reason for such a stability appears to be ascribed primarily to the chelation effect imposed by the polydentate ligand, since the corresponding bis-bidentate complexes [Tc^{V}O(Hdpa)$_2$X], in which the phosphino—amido ligands are not joined to each other, are easily reduced to Tc(III) species. Work is in progress to further stabilize oxo—M(V) phosphino—amido derivatives by controlling the coordination site *trans* to the oxo group.

(28) Batsanov, A. S.; Struchkov, Y. T.; Lorenz, B.; Olk, B. *Z. Anorg. Allg. Chem.* **1988**, *564*, 129.
(29) Baldas, J.; Bonnyman, J.; Williams, G. A. *J. Chem. Soc., Dalton Trans.* **1984**, 833.
(30) Marchi, A.; Duatti, A.; Rossi, R.; Magon, L.; Pasqualini, R.; Bertolasi, V.; Ferretti, V.; Gilli, G. *J. Chem. Soc., Dalton Trans.* **1988**, 1743.
(31) Rossi, R.; Marchi, A.; Aggio, S.; Magon, L.; Duatti, A.; Casellato, U.; Graziani, R. *J. Chem. Soc., Dalton Trans.* **1990**, 477.
(32) Abram, U.; Abram, S.; Munze, R.; Jager, E. G.; Stach, J.; Kirmse, R.; Admiraal, G.; Beurskens, P. T. *Inorg. Chim. Acta* **1991**, *182*, 233.
(33) Pasqualini, R.; Duatti, A. *J. Chem. Soc., Chem. Commun.* **1992**, 1354.