Articles

Synthesis and Crystal Structures of (Phosphine)technetium(V) Complexes with Phenylimido and Phenyldiazenido Ligands Using the Precursor PhNHNHCOCH$_3$

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The reaction of of NH$_4$[TcO$_4$] with PhNHNHCOCH$_3$, PMePh$_2$, and HX in methanol gave the compound Tc(NPh)(PMePh$_2$)$_2$X$_3$. The crystal structures of the compounds with X = Cl (**I**) and Br (**II**) were determined by X-ray diffraction methods. The results have shown that the two phosphine ligands are in *trans* position to each other, with Tc−P distances of 2.467(2), 2.473(2) Å for **I** and 2.481(5), 2.487(5) Å for **II**. The Tc−N bond distances are 1.695(3) and 1.711(11) Å, with angles Tc−N−C of 175.9(2) and 176.3(11)° for **I** and **II**, respectively. A similar reaction with a less bulky phosphine, dimethylphenylphosphine, and HBr produced the compound Tc(NNPh)(PMe$_2$Ph)$_3$Br$_2$. The organodiazenido unit was obtained from the cleavage of the NH−C bond of the hydrazine derivative. No such rearrangement has been reported before. The compound was studied by crystallographic methods. The results have shown that the three phosphine ligands are in a *mer* geometry and the −NNPh is in *trans* position to one of the Br ligands. The *trans* Tc−P bonds are 2.458(5) Å, while the third bond (*trans* to Br) is shorter, 2.409(5) Å. The Tc−Br bond *trans* to −NNPh is 2.603(3)Å, while the one *trans* to a phosphine is 2.635(3) Å. The Tc−N bond distance is 1.770(11) Å and the angles Tc−N−N = 171.9(11)° and N−N−Ph = 122.1(12)°.

Introduction

The chemistry of technetium is now developing very rapidly, especially in relation to the use of the isotope ^{99m}Tc in nuclear medicine. The search for new technetium complexes, which will image a specific organ, is an active area of research.

Organoimido ligands (−NR) may prove to be very useful for the radiopharmaceutical field. The physical and chemical properties can be altered by varying the organic substituent −R on the ligand. The linear organoimido core M═N−R is formally isoelectronic with the M═O unit, which is present in several Tc radiopharmaceuticals.[1,2] Phenylimido complexes might become versatile and useful synthetic precursors for Tc chemistry.

Most organoimido Tc complexes have been synthesized from [Tc(O)Cl$_4$]$^-$.[3,4] These methods are not very useful for the synthesis of ^{99m}Tc compounds, since "one-pot" syntheses are usually required for use in nuclear medicine. Recently, a simpler method was reported[5] for the preparation of Tc(NPh)(PPh$_3$)$_2$Cl$_3$ from the reaction of ammonium pertechnetate with PPh$_3$, PhNHNHCOCH$_3$, and HCl in methanol. The phenylimido unit was generated through the cleavage of the N−N bond in the hydrazine derivative.

Organohydrazine ligands display an extensive coordination chemistry. Monosubstituted derivatives often react to give metallic complexes containing other nitrogen ligands, including dinitrogen.[6] The organodiazenido unit (−NNR) is isoelectronic with the ligand nitrosyl, and the diazenide group (−NNH) may be a possible intermediate in the conversion of dinitrogen to ammonia. Crystal structure studies of several Tc and Re complexes have shown that the organodiazenido ligand can exhibit different types of geometry where the M−N−N unit can be linear or bent.[7−9]

We recently started a study on the synthesis of Tc compounds containing the ligand −NPh, using the precursor PhNHNHCOCH$_3$ and phosphine ligands less bulky than PPh$_3$. The first results of this study are described in this paper.

Experimental Section

Ammonium pertechnetate (NH$_4{}^{99}$TcO$_4$) was obtained from Oak Ridge National Laboratory. It was recrystallized in nitric acid (caution: ammonium pertechnetate in acid medium will produce some radioactive volatile compound) and dissolved in water. A solution 0.286 M was prepared. All manipulations were made in a laboratory approved for low-level radioactive material (^{99}Tc is a β-emitter with a particle energy of 0.292 MeV and a half-life of 2.13 × 10^5 years). Dimethylphenylphosphine and PhNHNHCOCH$_3$ were bought from Aldrich.

Tc(NPh)(PMePh$_2$)$_2$X$_3$. The chloro compound (**I**) was synthesized according to the published method for the synthesis of the PPh$_3$ analog.[5]

[⊗] Abstract published in *Advance ACS Abstracts,* March 15, 1995.

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Table 1. Crystal Data and Experimental Details of the X-ray Diffraction Studies

	I	II	III
formula	$C_{32}H_{31}NCl_3P_2Tc \cdot {}^1/_2CH_3OH$	$C_{32}H_{31}NP_2Br_3Tc$	$C_{30}H_{38}N_2P_3Br_2Tc$
MW	711.9	829.2	777.4
crystalline system	triclinic	monoclinic	orthorhombic
space group	$P\bar{1}$	$P2_1/c$	$P2_12_12_1$
a (Å)	11.265(5)	11.623(6)	8.475(4)
b (Å)	12.412(5)	18.924(20)	12.633(4)
c (Å)	13.849(6)	14.813(7)	31.171(14)
α (deg)	65.67(3)	90	90
β (deg)	69.21(4)	100.28(2)	90
γ (deg)	77.80(1)	90	90
V (Å^3)	1644.7(13)	3206(4)	3337(2)
Z	2	4	4
$F(000)$	726	1632	1560
ϱ_{calcd} (Mg m^{-3})	1.438	1.718	1.547
λ(Mo Kα) (Å)	0.710 69	0.710 69	0.710 69
μ(Mo Kα) (mm^{-1})	0.803	4.311	2.991
size of crystal (mm)	0.19 × 0.23 × 0.29	0.19 × 0.27 × 0.29	0.10 × 0.15 × 0.35
2θ max (deg)	55	55	45
quadrants measured	$h,\pm k,\pm l$	$h,k,\pm l$	$h,k,\pm l$
h,k,l	$0 \rightarrow 14, -15 \rightarrow 16, -16 \rightarrow 18$	$0 \rightarrow 15, 0 \rightarrow 24, -19 \rightarrow 18$	$0 \rightarrow 9, 0 \rightarrow 13, -33 \rightarrow 33$
scan technique	$2\theta/\theta$	$2\theta/\theta$	ω
std reflns	4 every 96	3 every 97	3 every 97
$T(K)$	294	294	294
weighting scheme	$1/w = \sigma^2(F) + 0.0001F^2$	$1/w = \sigma^2(F) + 0.0015F^2$	$1/w = \sigma^2(F) + 0.001F^2$
no. of ind reflns (R_{int})	7592 (0.014)	7357(0.028)	4364 (0.047)
no. of obs reflns	5370 $F > 4.8\sigma(F)$	3590 $F > 5.8\sigma(F)$	2743 $F > 4.4\sigma(F)$
$R = \sum\lvert F_o - F_c\rvert/\sum F_o$	0.041	0.075	0.061
mean xc6/σ	0.007	0.024	0.023
$R_w = \sum w(\lvert F_o - F_c\rvert)/\sum(wF_o)$	0.036	0.078	0.056
largest diff peak (e Å^{-3})	0.80	1.28	0.94
goodness-of-fit	1.64	1.95	1.14

The bromo complex (**II**) was prepared by substituting HCl by HBr. The compounds were recrystallized in a mixture of dichloromethane and methanol.

$Tc(NNPh)(PMe_2Ph)_3Br_2$. A 0.5 mL sample of an aqueous solution of $NH_4[TcO_4]$ (0.143 mmol) was evaporated to dryness and then dissolved in 12 mL of methanol. $PhNHNHCOCH_3$ (0.038 g (0.25 mmol)) dissolved in 10 mL of methanol) and 0.2 mL (1.40 mmol) of dimethylphenylphosphine were added to the pertechnetate solution. The mixture was placed in an oil bath and heated at 58 °C with stirring during 30 min. The color of the solution turned from green to almost black. The mixture was cooled to room temperature and 4 drops of HBr (4%) were added. The volume of the solution was reduced to about half on a rotary evaporator. The solution was left standing overnight. The next day, the precipitate was collected by filtration and washed with methanol. Yield: 30%. Crystals adequate for crystallographic methods were obtained by slow evaporation of a $CH_2Cl_2-C_2H_5OH$ solution.

Crystallographic Measurements and Structure Resolution. The crystals were selected after examination under a polarizing microscope for homogeneity. The unit cell parameters were obtained by least-squares refinement of the angles 2θ (16−30°), ω, and χ for 25 well-centered reflections on a Siemens P4 diffractometer using graphite-monochromatized Mo Kα radiation. Corrections were made for Lorentz−polarization effects, and the anomalous dispersion terms of Tc, Br, P, and Cl were included in the calculations.[10]

The coordinates of the Tc atom were determined from direct methods, and the positions of all the other non-hydrogen atoms were found by the usual Fourier methods. Two residual peaks were observed close to an inversion center for crystal **I**. These were assigned to half of a molecule of methanol. The refinement of the structure was done by full-matrix least-squares analysis. The H atoms were fixed at their calculated positions (riding model) with U_{eq} = 0.08 Å^2. Isotropic secondary-extinction corrections were included in the calculations.[10] The refinement of the enantiomorphic structure for crystal **III** resulted in significantly higher R factors. The scattering curves were taken from ref 10. The calculations were done on a SHELXTL system.[11]

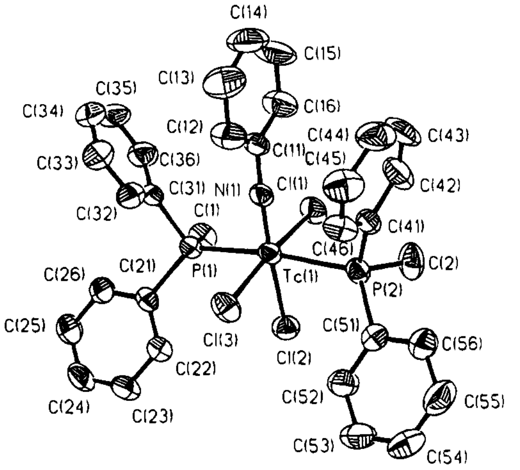

Figure 1. Labeled diagram of $Tc(NPh)(PMePh_2)_2Cl_3$, **I** (ellipsoids represent 50% probability).

Results and Discussion

The reaction of $NH_4[TcO_4]$ with $PhNHNHCOCH_3$, $PMePh_2$, and HCl in methanol gave the compound $Tc(NPh)(PMePh_2)_2Cl_3$ (**I**) as reported for PPh_3.[5] The organoimido ligand was formed from the cleavage of the N−N bond of the hydrazine derivative. A similar reaction with HBr produced the corresponding bromo analog, $Tc(NPh)(PMePh_2)_2Br_3$ (**II**). The crystal structures of the two compounds were determined by X-ray diffraction methods. The results have shown that the two phosphine ligands are in *trans* positions to each other. Labeled diagrams of the molecules are shown in Figures 1 and 2. The chloro compound crystallized with molecules of methanol.

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(10) *International Tables for X-ray Crystallography*; Kynoch Press: Birmington, England, 1974; Vol. IV, pp 55, 99, 149.

(11) SHELXTL PLUS (PC version, 1990−3), Siemens Analytical Instruments Inc., Madison, WI.

Table 2. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Temperature Factors ($Å^2 \times 10^3$)

atom	x	y	z	U_{eq}[a]	atom	x	y	z	U_{eq}[a]
Tc(NPh)(PMePh$_2$)$_2$Cl$_3$·$^1/_2$CH$_3$OH (**I**)									
Tc(1)	1636(1)	1760(1)	1891(1)	35(1)	C(31)	1136(3)	−945(3)	1877(3)	42(2)
Cl(1)	1647(1)	2905(1)	−30(1)	54(1)	C(32)	490(4)	−1423(3)	3007(3)	56(2)
Cl(2)	3865(1)	2173(1)	1193(1)	51(1)	C(33)	−509(4)	−2116(4)	3397(4)	72(2)
Cl(3)	1795(1)	683(1)	3746(1)	53(1)	C(34)	−903(5)	−2321(4)	2656(5)	82(3)
P(1)	2441(1)	−40(1)	1443(1)	38(1)	C(35)	−291(5)	−1853(5)	1540(5)	84(3)
P(2)	1143(1)	3624(1)	2249(1)	42(1)	C(36)	730(4)	−1168(4)	1153(4)	65(2)
N(1)	82(3)	1535(2)	2234(2)	38(1)	C(41)	−551(3)	3713(3)	2961(3)	43(2)
C(1)	3189(4)	276(3)	−29(3)	55(2)	C(42)	−1442(4)	4385(4)	2422(4)	67(2)
C(2)	1419(5)	4979(3)	1018(3)	70(2)	C(43)	−2723(5)	4343(5)	2981(5)	83(3)
C(11)	−1189(3)	1415(3)	2442(3)	43(2)	C(44)	−3140(4)	3636(5)	4078(5)	77(3)
C(12)	−1891(4)	764(4)	3496(3)	63(2)	C(45)	−2280(4)	2956(4)	4628(4)	69(3)
C(13)	−3163(4)	666(5)	3696(5)	87(3)	C(46)	−998(4)	2988(4)	4071(3)	54(2)
C(14)	−3715(5)	1201(5)	2871(6)	91(4)	C(51)	1862(3)	3864(3)	3131(3)	46(2)
C(15)	−3009(5)	1848(5)	1821(6)	96(4)	C(52)	2931(4)	3186(4)	3406(3)	60(2)
C(16)	−1738(4)	1974(4)	1595(4)	70(3)	C(53)	3470(4)	3431(4)	4046(4)	74(3)
C(21)	3607(3)	−1112(3)	2075(3)	42(2)	C(54)	2958(5)	4342(4)	4405(4)	73(3)
C(22)	4329(3)	−835(3)	2560(3)	50(2)	C(55)	1903(5)	5015(4)	4157(4)	74(3)
C(23)	5265(4)	−1662(4)	2951(3)	60(2)	C(56)	1347(4)	4784(4)	3522(3)	61(2)
C(24)	5470(4)	−2744(4)	2865(4)	70(2)	O(1)	4892(29)	5150(27)	482(24)	353(27)
C(25)	4762(4)	−3028(4)	2389(4)	77(3)	C(3)	5617(18)	5170(13)	841(11)	205(13)
C(26)	3821(4)	−2215(3)	1996(4)	63(2)					
Tc(NPh)(PMePh$_2$)$_2$Br$_3$ (**II**)									
Tc(1)	2626(1)	927(1)	2308(1)	24(1)	C(26)	401(12)	−109(8)	3597(10)	45(2)
Br(1)	1977(2)	622(1)	599(1)	51(1)	C(31)	2876(9)	−617(7)	2952(9)	27(2)
Br(2)	3294(1)	1279(1)	3996(1)	47(1)	C(32)	2232(12)	−1155(8)	2488(10)	42(2)
Br(3)	2405(3)	2207(1)	1905(2)	102(1)	C(33)	2308(13)	−1841(8)	2858(10)	47(2)
P(1)	536(3)	1006(2)	2453(2)	28(1)	C(34)	3055(13)	−1984(8)	3640(10)	47(2)
P(2)	4694(3)	1094(2)	2125(2)	26(1)	C(35)	3783(13)	−1439(8)	4122(11)	49(2)
N(1)	2774(8)	60(6)	2637(7)	29(2)	C(36)	3651(12)	−742(7)	3765(10)	37(2)
C(1)	−436(13)	1287(9)	1403(10)	51(2)	C(41)	5103(10)	1221(7)	1004(9)	29(2)
C(2)	5361(11)	1868(7)	2695(9)	36(2)	C(42)	4454(11)	1576(8)	372(9)	36(2)
C(11)	16(10)	1567(7)	3308(8)	26(2)	C(43)	4838(12)	1888(8)	−386(10)	43(2)
C(12)	637(13)	2159(8)	3675(10)	44(2)	C(44)	5818(13)	1601(8)	−613(10)	51(2)
C(13)	151(13)	2607(8)	4269(11)	53(2)	C(45)	6470(11)	1107(7)	−44(9)	38(2)
C(14)	−874(12)	2432(9)	4511(10)	54(2)	C(46)	6104(11)	930(8)	769(10)	41(2)
C(15)	−1507(12)	1867(8)	4129(10)	46(2)	C(51)	5554(10)	363(7)	2673(8)	25(2)
C(16)	−1054(12)	1437(8)	3530(10)	41(2)	C(52)	5487(11)	−315(8)	2219(9)	38(2)
C(21)	28(10)	131(7)	2726(9)	32(2)	C(53)	6039(14)	−882(9)	2629(11)	55(2)
C(22)	−628(12)	−286(8)	2051(13)	58(2)	C954)	6682(13)	−807(9)	3565(11)	59(2)
C(23)	−879(14)	−979(12)	2317(16)	92(2)	C(55)	6747(12)	−176(8)	3993(10)	49(2)
C(24)	−584(15)	−1196(9)	3149(16)	89(2)	C(56)	6207(11)	388(8)	3556(10)	42(2)
C(25)	63(15)	−789(9)	3821(14)	75(2)					
Tc(NNPh)(PMe$_2$Ph)$_3$Br$_2$ (**III**)									
Tc(1)	4741(1)	6173(1)	8791(1)	33(1)	C(16)	3842(17)	4402(12)	9864(5)	56(1)
Br(1)	6568(2)	6955(2)	8199(1)	55(1)	C(21)	2927(14)	3762(12)	8308(5)	43(1)
Br(2)	7316(2)	5589(2)	9202(1)	59(1)	C(22)	1687(16)	3805(13)	8578(5)	56(1)
P(3)	5172(5)	7812(3)	9200(1)	46(1)	C(23)	288(17)	3286(12)	8490(6)	60(1)
P(1)	4784(5)	4396(4)	8470(1)	43(1)	C(24)	135(17)	2713(12)	8116(6)	63(2)
P(2)	2649(5)	6782(4)	8330(1)	40(1)	C(25)	1339(18)	2665(13)	7851(7)	71(2)
N(1)	3342(13)	5777(10)	9181(4)	41(1)	C(26)	2712(16)	3118(12)	7923(6)	54(1)
N(2)	2271(13)	5603(11)	9427(4)	50(1)	C(31)	2213(16)	6050(12)	7828(5)	48(1)
C(1)	5471(16)	3390(12)	8838(6)	63(1)	C(32)	713(17)	5598(13)	7759(6)	66(2)
C(2)	6140(15)	4200(13)	8025(5)	61(2)	C(33)	470(19)	5084(13)	7366(6)	80(2)
C(3)	2786(16)	8106(12)	8106(5)	59(2)	C(34)	1670(19)	5034(14)	7066(6)	85(2)
C(4)	759(14)	6810(13)	8597(5)	53(1)	C(35)	3087(19)	5476(15)	7130(7)	96(2)
C(5)	4949(16)	7545(13)	9775(4)	61(1)	C(36)	3332(17)	5992(13)	7521(5)	62(1)
C(6)	7125(15)	8398(12)	9173(6)	65(2)	C(41)	3862(15)	8923(12)	9125(4)	45(1)
C(11)	2371(17)	4815(12)	9747(4)	48(1)	C(42)	2326(17)	8881(14)	9287(5)	65(2)
C(12)	986(18)	4502(14)	9928(6)	69(2)	C(43)	1312(19)	9646(14)	9206(7)	92(2)
C(13)	1032(19)	3725(15)	10240(7)	89(2)	C(44)	1760(19)	10505(15)	8941(6)	87(2)
C(14)	2477(20)	3273(15)	10352(6)	96(2)	C(45)	3183(18)	10599(14)	8793(7)	89(2)
C(15)	3794(19)	3600(14)	10175(7)	91(2)	C(46)	4251(17)	9786(13)	8884(6)	65(2)

[a] U_{eq} is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

When a similar reaction was done with dimethylphenylphosphine, a brownish oil was obtained. The product could not be purified. The method was slightly modified (less solvent was added and the proportions of PhNHNHCOCH$_3$ and PMe$_2$Ph were increased), and eventually an orange compound was obtained from the reaction with HBr, with a yield of about 30%. After recrystallization in CH$_2$Cl$_2$−C$_2$H$_5$OH, orange crystals suitable for X-ray diffraction were obtained. The results of the crystallographic study have shown that the product was quite different. It contained an organodiazenido unit and three PMe$_2$Ph ligands. A labeled diagram of the molecule formed, Tc(NNPh)(PMe$_2$-Ph)$_3$Br$_2$ (**III**) is shown in Figure 3. Several Re and Tc organodiazenido complexes have been reported, but they were all synthesized from organohydrazine RNHNH$_2$ deriva-

Table 3. Selected Bond Distances (Å) and Angles (deg)

$Tc(NPh)(PMePh_2)_2Cl_3 \cdot {}^1/_2CH_3OH$ (**I**)			
Tc(1)−Cl(1)	2.442(1)	Tc(1)−Cl(2)	2.433(1)
Tc(1)−Cl(3)	2.412(1)	Tc(1)−P(1)	2.467(2)
Tc(1)−P(2)	2.473(2)	Tc(1)−N(1)	1.695(3)
P(1)−C(1)	1.811(4)	P(1)−C(21)	1.838(4)
P(1)−C(31)	1.815(4)	P(2)−C(2)	1.820(3)
P(2)−C(41)	1.815(4)	P(2)−C(51)	1.829(5)
N(1)−C(11)	1.385(5)		
Cl(1)−Tc(1)−Cl(2)	84.4(1)	Cl(1)−Tc(1)−Cl(3)	175.3(1)
Cl(2)−Tc(1)−Cl(3)	91.0(1)	Cl(1)−Tc(1)−P(1)	90.2(1)
Cl(2)−Tc(1)−P(1)	84.8(1)	Cl(3)−Tc(1)−P(1)	90.2(1)
Cl(1)−Tc(1)−P(2)	89.2(1)	Cl(2)−Tc(1)−P(2)	87.1(1)
Cl(3)−Tc(1)−P(2)	89.7(1)	P(1)−Tc(1)−P(2)	172.0(1)
Cl(1)−Tc(1)−N(1)	89.6(1)	Cl(2)−Tc(1)−N(1)	173.9(1)
Cl(3)−Tc(1)−N(1)	95.0(1)	P(1)−Tc(1)−N(1)	94.3(1)
P(2)−Tc(1)−N(1)	93.7(1)	Tc(1)−P(1)−C(1)	113.3(1)
Tc(1)−P(1)−C(21)	120.1(2)	C(1)−P(1)−C(21)	103.1(2)
Tc(1)−P(1)−C(31)	110.0(1)	C(1)−P(1)−C(31)	106.7(2)
C(21)−P(1)−C(31)	102.5(2)	Tc(1)−P(2)−C(2)	115.5(2)
Tc(1)−P(2)−C(41)	106.7(1)	C(2)−P(2)−C(41)	105.6(2)
Tc(1)−P(2)−C(51)	121.1(1)	C(2)−P(2)−C(51)	102.8(2)
C(41)−P(2)−C(51)	103.6(2)	Tc(1)−N(1)−C(11)	175.9(2)
$Tc(NPh)(PMePh_2)_2Br_3$ (**II**)			
Tc(1)−Br(1)	2.574(3)	Tc(1)−Br(2)	2.571(3)
Tc(1)−Br(3)	2.498(4)	Tc(1)−P(1)	2.481(5)
Tc(1)−P(2)	2.487(5)	Tc(1)−N(1)	1.711(11)
P(1)−C(1)	1.831(14)	P(1)−C(11)	1.835(13)
P(1)−C(21)	1.827(14)	P(2)−C(2)	1.797(14)
P(2)−C(41)	1.823(14)	P(2)−C(51)	1.811(12)
N(1)−C(31)	1.362(17)		
Br(1)−Tc(1)−Br(2)	177.8(1)	Br(1)−Tc(1)−Br(3)	89.0(1)
Br(2)−Tc(1)−Br(3)	88.9(1)	Br(1)−Tc(1)−P(1)	88.8(1)
Br(2)−Tc(1)−P(1)	91.7(1)	Br(3)−Tc(1)−P(1)	84.3(1)
Br(1)−Tc(1)−P(2)	92.3(1)	Br(2)−Tc(1)−P(2)	86.7(1)
Br(3)−Tc(1)−P(2)	84.9(1)	P(1)−Tc(1)−P(2)	169.1(1)
Br(1)−Tc(1)−N(1)	93.6(4)	Br(2)−Tc(1)−N(1)	88.5(4)
Br(3)−Tc(1)−N(1)	177.2(4)	P(1)−Tc(1)−N(1)	94.8(4)
P(2)−Tc(1)−N(1)	95.9(4)	Tc(1)−P(1)−C(1)	114.1(5)
Tc(1)−P(1)−C(11)	122.9(4)	C(1)−P(1)−C(11)	100.9(6)
Tc(1)−P(1)−C(21)	108.9(4)	C(1)−P(1)−C(21)	106.0(7)
C(11)−P(1)−C(21)	102.3(6)	Tc(1)−P(2)−C(2)	113.4(5)
Tc(1)−P(2)−C(41)	122.0(4)	C(2)−P(2)−C(41)	99.2(6)
Tc(1)−P(2)−C(51)	108.7(4)	C(2)−P(2)−C(51)	104.7(6)
C(41)−P(2)−C(51)	107.2(6)	Tc(1)−N(1)−C(31)	176.3(10)
P(1)−C(11)−C(12)	121.6(10)	P(1)−C(11)−C(16)	119.3(10)
$Tc(NNPh)(PMe_2Ph)_3Br_2$ (**III**)			
Tc(1)−Br(1)	2.603(3)	Tc(1)−Br(2)	2.635(3)
Tc(1)−P(3)	2.458(5)	Tc(1)−P(1)	2.458(5)
Tc(1)−P(2)	2.409(5)	Tc(1)−N(1)	1.770(11)
P(3)−C(5)	1.835(15)	P(3)−C(6)	1.815(14)
P(3)−C(41)	1.804(15)	P(1)−C(1)	1.809(16)
P(1)−C(2)	1.818(15)	P(1)−C(21)	1.837(14)
P(2)−C(3)	1.815(16)	P(2)−C(4)	1.805(14)
P(2)−C(31)	1.854(15)	N(1)−N(2)	1.208(16)
N(2)−C(11)	1.413(19)		
Br(1)−Tc(1)−Br(2)	87.6(1)	Br(1)−Tc(1)−P(3)	87.7(1)
Br(2)−Tc(1)−P(3)	82.0(1)	Br(1)−Tc(1)−P(1)	92.8(1)
Br(2)−Tc(1)−P(1)	86.0(1)	P(3)−Tc(1)−P(1)	168.0(2)
Br(1)−Tc(1)−P(2)	83.9(1)	Br(2)−Tc(1)−P(2)	171.4(1)
P(3)−Tc(1)−P(2)	98.6(2)	P(1)−Tc(1)−P(2)	93.4(2)
Br(1)−Tc(1)−N(1)	172.9(4)	Br(2)−Tc(1)−N(1)	98.2(4)
P(3)−Tc(1)−N(1)	89.0(4)	P(1)−Tc(1)−N(1)	91.8(4)
P(2)−Tc(1)−N(1)	90.4(4)	Tc(1)−P(3)−C(5)	109.6(5)
Tc(1)−P(3)−C(6)	117.1(6)	C(5)−P(3)−C(6)	102.3(7)
Tc(1)−P(3)−C(41)	119.8(5)	C(5)−P(3)−C(41)	101.9(7)
C(6)−P(3)−C(41)	103.8(7)	Tc(1)−P(1)−C(1)	112.8(5)
Tc(1)−P(1)−C(2)	116.4(6)	C(1)−P(1)−C(2)	100.6(7)
Tc(1)−P(1)−C(21)	119.9(5)	C(1)−P(1)−C(21)	98.2(7)
C(2)−P(1)−C(21)	105.8(7)	Tc(1)−P(2)−C(3)	118.4(5)
Tc(1)−P(2)−C(4)	112.6(5)	C(3)−P(2)−C(4)	102.5(7)
Tc(1)−P(2)−C(31)	119.4(5)	C(3)−P(2)−C(31)	98.6(7)
C(4)−P(2)−C(31)	102.8(7)	Tc(1)−N(1)−N(2)	171.9(11)
N(1)−N(2)−C(11)	122.1(12)		

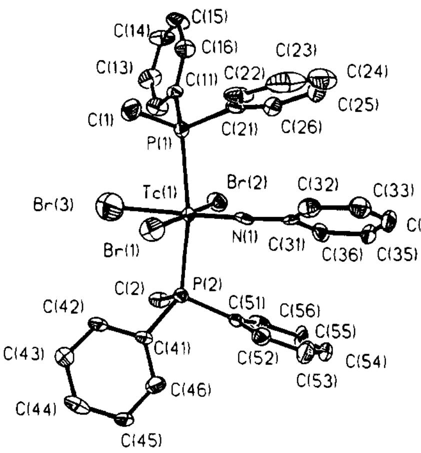

Figure 2. Labeled diagram of $Tc(NPh)(PMePh_2)_2Br_3$, **II** (ellipsoids represent 50% probability).

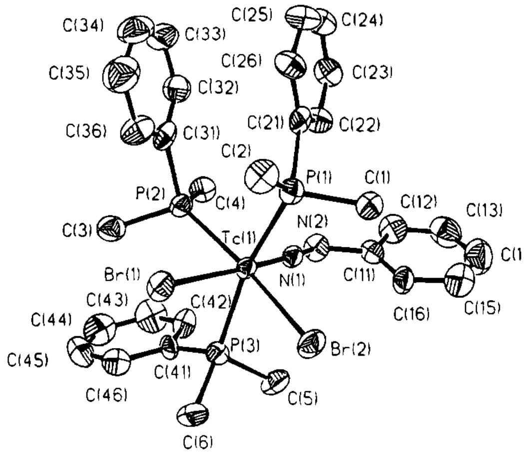

Figure 3. Labeled diagram of $Tc(NNPh)(PMePh_2)_3Br_2$, **III** (ellipsoids represent 50% probability).

tives. To our knowledge, this reaction is the first example of the formation of a Tc−NNR complex, using the precursor $PhNHNHCOCH_3$ or a similar reagent. In this case, the N−C bond is cleaved instead of the N−N bond of the hydrazine molecule. A reaction mechanism was proposed by Nicholson, Davison, and Jones[5] for the incorporation of the phenylimino unit into the Tc−NPh complex. The first step involved the formation of a Tc−N bond with the N in α position to the phenyl group ($Tc-NH(Ph)NHCOCH_3$). In our reaction, the first step must be the formation of a Tc−N bond with the N atom in β position to Ph ($Tc-NH(COCH_3)NHPh$). No such rearrangement of the precursor $PhNHNHCOCH_3$ has been reported in the literature. The compound *trans*-$Tc(PMe_2Ph)_2Br_4$ might be an intermediate in the formation of the diazenido compound, since a green solution was first observed. It has been shown that $Tc(PPh_3)_2Cl_4$ is not an intermediate in the formation of the phenylimido compound $Tc(NPh)(PPh_3)_2Cl_3$,[5] but several diazenido complexes of the type $TcCl(PPh_3)_2(NNPh)$ were prepared from $Tc(PPh_3)_2Cl_4$.[7]

The difference in behavior could be due to the smaller size of the phosphine ligand $PMePh_2$ compared to PPh_3, which would allow the hydrazine derivative to approach better the Tc atom. Since the yield of the reaction is relatively low (30%), we believe that the phenylimido compound was also formed but did not precipitate as with more bulky phosphines. Contrary to bulkier PR_3 ligands, the Tc atom can bind more than two PMe_2Ph ligands, and in this case, the ionic compound $[Tc(NPh)(PMe_2Ph)_3X_2]^+$ could be formed and would stay in solution. With a bulky phosphine like PPh_3, it is not possible to bind three of these ligands to Tc. For example, the reaction of $[TcO_4]^-$ with benzoylhydrazine and PPh_3 will form the pentacoordinate compound[5,12] $Tc(N)(PPh_3)_2Cl_2$, while a similar reaction with PMe_2Ph will produce the hexacoordinated complex $Tc(N)(PMe_2Ph)_3Cl_2$.[13] Preliminary results in our laboratories have shown that, under similar conditions, $PMePh_2$ also forms the pentacoordinate compound. Furthermore, the reaction of $[TcO_4]^-$ in HCl solution with a large excess of PPh_3 produces *trans*-$Tc(PPh_3)_2Cl_4$ while the same reaction with PMe_2Ph will form $Tc(PMe_2Ph)_3Cl_3$.[14]

Selected bond distances and angles are shown in Table 3. For the two compounds with $PMePh_2$, the geometry around the Tc atom is a slightly distorted octahedron. For crystals **I** and **II**, the Tc−P bond distances are 2.467(2), 2.473(2) Å and 2.481(5), 2.487(5) Å respectively. These values are close to those reported for Tc(V)−P bonds located in *trans* position to a second phosphine ligand (average 2.489 Å).[12,13,15,16] The Tc−Cl(2) bond, in *trans* position to the −NPh ligand, is not different (2.433(1)Å) from the two bonds in *trans* position to each other (2.412(2) and 2.442(1) Å) as observed for the PPh_3 analog (2.414(2) vs 2.404(2) and 2.416(2) Å).[5] For the bromo analog, the Tc−Br(3) bond located in *trans* position to the organoimido ligand is significantly shorter, 2.498(4) Å, than the two others (2.574(3) and 2.571(3) Å). The Tc−N bonds are quite short, 1.695(3) Å for **I** and 1.711(11) Å for **II**, but longer than those in Tc(V)−nitrido complexes (about 1.62 Å[17−19]). The angle Tc−N−C(11) is almost linear, 175.9(2)° for **I** and 176.3(10)° for **II**. For the chloro analog with PPh_3 the reported Tc−N is 1.704(4) Å and the angle Tc−N−C is 171.8(4)°.[5] These values confirm the linear coordination of the triply-bonded phenylimido ligand.

The compound obtained with a less bulky phosphine, $Tc(NNPh)(PMe_2Ph)_3Br_2$ (**III**), has a distorted octahedral geometry. The three PMe_2Ph ligands are in *mer* positions with the two *trans* Tc−P distances of 2.458(5) Å. The third bond which is located in *trans* position to Br(2) seems shorter, 2.409(5) Å. The *trans* influence of phosphines is larger than the one of halides. The Tc−Br bonds are 2.603(3) (*trans* to −NNPh) and 2.635(3) Å (*trans* to P). The Tc−N bond is slightly longer (1.753(13) Å) than in compounds **I** and **II** as observed for similar complexes.[7−9] The Tc−N−N segment is linear (172(1)°), but the N−N−Ph angle is bent (121(1)°). The similar reported Tc[4,7,9] and Re[8] compounds were all obtained from the reaction with the precursor $RNHNH_2$. The geometry of the segment M−N−N−R can vary depending on the presence of absence of H atoms on the ligand (see refs 7 and 8). The formal charge on the −NNPh ligand in our complex is −3 and the oxidation state of Tc is V. The N−N bond distance is 1.208(16) Å, close to those reported for similar compounds.[7,9]

The average P−C distances are 1.821(4) for I, 1.821(13) for **II**, and 1.821(15) Å for **III**. The $Tc-P-CH_3$ angles (average 114.4(1) for **I**, 113.8(5) for **II**, and 114.5(5)° for **III**) and the Tc−P−C(phenyl) angles (114.5(1), 115.6(4), and 119.7(5)° respectively) are larger than normal tetrahedral angles. All the C−P−C bond angles are smaller than the tetrahedral value with average angles of 104.0(2), 103.4(6) and 101.8(7)°. These angular values confirm the multiple nature of the Tc−P bonds (multiple bonds occupy more space than single bonds).

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Supplementary Material Available: Packing diagrams of the three structures and lists of anisotropic temperature factors (Table S1), hydrogen coordinates (Table S2), and bond distances and angles (Table S3) (12 pages). Ordering information is given on any current masthead page.

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