Synthesis and Characterization of Technetium(III) Complexes with Schiff-base and Phosphine Ligands. Molecular Structure of (Diethylphenylphosphine)-[*N*-(2-oxidophenyl)salicylideneiminato-*NOO′*](quinolin-8-olato-*NO*)-technetium(III)†

Ulderico Mazzi,* Fiorenzo Refosco, and Francesco Tisato
Istituto di Chimica e Tecnologia dei Radioelementi del CNR, Area della Ricerca, C. so Stati Uniti 4, 35020 Padova, Italy
Giuliano Bandoli and Marino Nicolini
Dipartimento di Scienze Farmaceutiche, Università di Padova, Via Marzolo 5, 35131 Padova, Italy

The complexes [TcL(L′)L″] [L″ = PEt_2Ph, PMe_2Ph, or PPh_3; L = *N*-(2-oxidophenyl)salicylideneiminate (L^1) or *N*-(2-sulphidophenyl)salicylideneiminate (L^2); L′ = quinolin-8-olate (quin) or salicylideneiminate (L^3)] were synthesized starting from [TcO(L)(L′)] and characterized by means of physicochemical measurements and for [TcL^1(quin)(PEt_2Ph)] by means of *X*-ray analysis. The co-ordination around technetium is approximately octahedral with the phosphine ligand *trans* to the imino nitrogen of the ligand quin and the tridentate ligand L^1 on a plane orthogonal to the line P–Tc–N. The complex crystallizes in the triclinic space group $P\bar{1}$ with a = 14.196(6), b = 11.363(5), c = 9.742(4) Å, α = 68.04(3), β = 101.09(3), γ = 106.68(3)°, and Z = 2. The structure has been refined to R = 0.070 for 1 743 independent reflections.

The complexes of technetium in its low oxidation states I—III with appropriate ligands seem to be more stable, as regards substitution reactions, than those of its usual oxidation states, such as V and IV. This has prompted many researchers to prepare and study technetium complexes with π ligands (*e.g.* phosphines, isocyanides, carbon monoxide) stabilizing low oxidation states.[1–6] Phosphines are the more versatile ligands. They can also be employed as reducing agents with pertechnetate or technetium(V) complexes as the starting compounds.[1] Technetium(V) oxo-complexes are easily reduced by phosphine ligands, leading to loss of the oxo group, and formation of phosphine oxide and technetium(III) compounds.[2,3]

The present paper deals with the synthesis of technetium(III) complexes starting from [TcO(L)L′][6,7] [L = *N*-(2-oxidophenyl)salicylideneiminate (L^1) or *N*-(2-sulphidophenyl)salicylideneiminate (L^2); L′ = quinolin-8-olate (quin) or salicylideneiminate (L^3)] and tertiary phosphine to produce [TcL(L′)L″] (L″ = PPh_3, PMe_2Ph, or PEt_2Ph). The complexes were characterized by means of physicochemical measurements and the molecular structure of [TcL^1(quin)(PEt_2Ph)] is also described.

Experimental

Materials.—Technetium as [NH_4][$^{99}TcO_4$] was purchased from the Radiochemical Centre, Amersham. The starting compounds [TcO(L)L′] were prepared by methods previously reported.[6,7] The phosphines and all other materials were reagent-grade chemicals used without further purification.

Apparatus.—Elemental analyses were performed on a Carlo Erba model 1106 elemental analyser; quantitative determinations of technetium were carried out on a Rackbeta II instrument, model 1215, with Instagel (Packard Instrument International) as scintillator. Infrared spectra were recorded in the range 4 000—250 cm^{-1} on a Perkin-Elmer PE 580B spectrometer using Nujol mulls between CsI pellets. Proton n.m.r. spectra were recorded on a Varian FT80 instrument using dimethylformamide (dmf) as solvent and $SiMe_4$ as internal reference. Magnetic susceptibility measurements were performed in solution by the Evans n.m.r. method[8] using a Varian FT80 spectrometer. Conductivity measurements were made in acetonitrile at 25 °C using a Metrohm Herison conductometer, model E518. The compounds described were all non-conducting. U.v.–visible spectra were recorded in dmf as solvent with a Cary 17D spectrometer.

Technetium-99 is a weak β-emitter [$E_{\beta\max.}$ = 292 keV (*ca.* 4.7×10^{-14} J) with $t_{\frac{1}{2}} = 2.12 \times 10^5$ y]. All manipulations of it were carried out in laboratories approved for low-level radioactivity, using glove-boxes under a slight vacuum, for both the synthesis and recovery operations.

Synthesis.—All the complexes were synthesized by the procedure detailed below for [TcL^1(quin)(PEt_2Ph)].

Double the stoicheiometric amount of diethylphenylphosphine (0.108 g, 0.65 mmol) was added to a stirred solution of [TcO(L^1)(quin)] (0.153 g, 0.325 mmol) in EtOH (25 cm^3). The reaction solution slowly turned from red to deep red. After 3 h a dark red precipitate was collected by filtration and washed with Et_2O. The mother-liquor, left to evaporate for some days, yielded other crystals. The yield, based on [TcL^1(quin)(PEt_2Ph)], was 41%. The complex was recrystallized from CH_2Cl_2–EtOH.

X-Ray Analysis.—Crystals were grown by slow evaporation of EtOH solution. An irregularly shaped red crystal with approximate dimensions 0.10 × 0.25 × 0.10 mm was chosen for data collection on a Philips PW 1100 automated diffractometer, using the ω—2θ scan technique and Mo-K_α radiation (graphite monochromator, λ = 0.7107 Å).

Crystal data. $C_{32}H_{30}N_2O_3PTc$, M = 620.5, triclinic, space group $P\bar{1}$, a = 14.196(6), b = 11.363(5), c = 9.742(4) Å, α = 68.04(3), β = 101.09(3), γ = 106.68(3)°, U = 1 389.7(1.1) Å^3, D_m = 1.48 g cm^{-3} (by flotation in $CHCl_3$ at *ca.* 0 °C), Z = 2, D_c = 1.482 g cm^{-3}, μ(Mo-K_α) = 5.4 cm^{-1}. (Niggli reduced cell: a = 9.742, b = 11.363, c = 14.196 Å, α = 73.32, β = 78.91, γ = 68.04°). ψ-Scan curves at χ *ca.* 90° indicated that the absorption problems were not severe and no absorption correc-

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.

Table 1. Atomic positional parameters ($\times 10^4$) for [TcL^1(quin)(PEt$_2$Ph)][a]

Atom	x	y	z
Tc	2 230(1)	−844(2)	3 267(2)
P	3 101(4)	−900(5)	1 408(6)
O(1)	2 588(9)	1 149(11)	2 666(13)
O(2)	3 412(9)	−1 020(12)	4 700(14)
O(3)	972(9)	−937(12)	1 941(13)
N(1)	1 515(11)	−582(15)	4 853(16)
N(2)[b]	1 614(19)	−2 798(24)	3 814(27)
N(2′)[c]	2 028(37)	−2 795(49)	4 368(57)
C(1)	958(14)	−1 491(18)	5 931(21)
C(2)	576(14)	−1 105(18)	6 929(21)
C(3)	774(14)	170(18)	6 752(21)
C(4)	1 337(13)	1 170(17)	5 622(20)
C(5)	1 566(14)	2 540(19)	5 362(22)
C(6)	2 111(15)	3 368(20)	4 241(23)
C(7)	2 477(14)	2 955(19)	3 253(22)
C(8)	2 265(12)	1 604(16)	3 487(19)
C(9)	1 711(12)	739(17)	4 674(19)
C(10)	3 567(13)	−2 151(18)	5 705(20)
C(11)	4 481(15)	−2 092(20)	6 560(22)
C(12)	4 640(17)	−3 244(24)	7 659(26)
C(13)	3 923(19)	−4 428(25)	7 869(28)
C(14)	3 023(18)	−4 499(22)	6 967(26)
C(15)	2 839(16)	−3 343(20)	5 794(22)
C(16)[b]	1 941(23)	−3 754(31)	5 017(34)
C(16′)[c]	1 410(38)	−3 704(54)	4 091(60)
C(17)	718(15)	−3 232(20)	2 920(22)
C(18)	193(18)	−4 434(23)	2 831(27)
C(19)	−612(18)	−4 525(23)	1 757(27)
C(20)	−929(16)	−3 387(22)	749(24)
C(21)	−358(13)	−2 161(18)	862(20)
C(22)	446(13)	−2 102(18)	1 894(20)
C(23)	4 060(13)	−1 809(16)	2 245(19)
C(24)	4 927(14)	−1 275(17)	2 924(20)
C(25)	5 641(15)	−2 038(20)	3 709(22)
C(26)	5 423(17)	−3 310(22)	3 705(25)
C(27)	4 560(17)	−3 839(21)	3 027(24)
C(28)	3 831(15)	−3 132(19)	2 287(22)
C(29)	3 827(14)	757(18)	340(21)
C(30)	3 037(16)	1 553(21)	−657(25)
C(31)	2 331(14)	−1 620(18)	56(21)
C(32)	2 924(15)	−1 596(20)	−1 186(23)

[a] The estimated error in the last digits is given in parentheses. Numbering scheme as in Figure 1. [b] Occupancy factor: 0.7. [c] Occupancy factor: 0.3.

tions were applied. Of the 4 643 reflections collected at room temperature in the range $3 \leqslant 2\theta \leqslant 50°$, only 1 743 independent reflections with $I \geqslant 3\sigma(I)$ were selected and used in the structure analysis.

Structure determination and refinement. The positions of the Tc and P atoms were determined from a sharpened, origin-removed Patterson map, while the remaining non-hydrogen atoms were located with two Fourier syntheses. The structure was refined, using the SHELX program system,[9] by the least-squares procedure to $R = 0.075$, with $w = 1$ for each reflection and anisotropic thermal parameters for Tc, P, O, and N(1). A look at the Fourier difference map around the N(2)–C(16) bridge showed positional disorder. The occupancy factors of these atoms were refined separately, leading to $R = 0.070$, and the two orientations showed, with some degree of confidence, a population ratio of *ca.* 7:3. The present model provides an adequate answer to the structural question; owing to the low ratio of parameters (1 743) to variables (195), it was decided to carry out no further refinement. Final atomic positional parameters are found in Table 1, selected interatomic distances and angles in Table 2. Additional material available from the Cambridge Crystallographic Data Centre comprises the thermal parameters and the remaining bond lengths and angles.

Table 2. Selected bond lengths (Å) and angles (°) of [TcL^1(quin)(PEt$_2$Ph)]

Tc–P	2.41(1)	C(8)–C(9)	1.41(2)	N(2)–C(17)	1.47(3)
Tc–O(1)	2.05(1)	C(9)–N(1)	1.39(2)	C(17)–C(22)	1.40(3)
Tc–O(2)	1.97(1)	O(2)–C(10)	1.34(2)	C(22)–O(3)	1.33(2)
Tc–O(3)	1.99(1)	C(10)–C(15)	1.43(3)	P–C(23)	1.83(2)
Tc–N(1)	2.15(2)	C(15)–C(16)	1.40(3)	P–C(29)	1.88(2)
Tc–N(2)	2.04(2)	C(16)–N(2)	1.38(3)	P–C(31)	1.83(2)
O(1)–C(8)	1.30(3)				

P–Tc–N(1)	174.1(5)	Tc–O(1)–C(8)	114.9(1.1)
P–Tc–O(1)	95.3(4)	O(1)–C(8)–C(9)	120.0(1.7)
P–Tc–O(2)	89.8(4)	C(8)–C(9)–N(1)	115.8(1.6)
P–Tc–O(3)	90.8(4)	Tc–N(1)–C(9)	110.3(1.1)
P–Tc–N(2)	90.9(8)	Tc–O(2)–C(10)	124.7(1.2)
O(1)–Tc–O(2)	92.8(6)	O(2)–C(10)–C(15)	119.9(1.7)
O(1)–Tc–O(3)	95.0(5)	C(10)–C(15)–C(16)	137.8(2.2)
O(1)–Tc–N(1)	78.9(6)	C(15)–C(16)–N(2)	116.1(2.8)
O(1)–Tc–N(2)	169.5(9)	C(16)–N(2)–Tc	125.1(2.2)
O(2)–Tc–O(3)	172.0(6)	C(16)–N(2)–C(17)	116.6(2.5)
O(2)–Tc–N(1)	89.9(6)	Tc–N(2)–C(17)	118.3(1.7)
O(2)–Tc–N(2)	95.7(8)	N(2)–C(17)–C(22)	106.9(2.0)
O(3)–Tc–N(1)	90.3(6)	C(17)–C(22)–O(3)	119.1(1.8)
O(3)–Tc–N(2)	76.3(9)	C(22)–O(3)–Tc	118.6(1.2)
N(1)–Tc–N(2)	95.0(9)		

Results and Discussion

The synthesis of the technetium(III) complexes, [TcL(L′)L″], starting from the technetium(V) analogues containing the $Tc{=}O^{3+}$ core instead of the phosphine group L″, is very simple and gives the same result either using a 1:2 stoicheiometric ratio of Tc:P or an excess of phosphine. This means that the technetium(III) complex is very stable to substitution reactions with further phosphine ligands. The balanced reaction could be simply written as in equation (1), even though its mechanism, as

$$[TcO(L)L'] + 2L'' \longrightarrow [TcL(L')L''] + O{=}L'' \quad (1)$$

shown below, is more complicated.

The products are deep coloured crystals from red to violet-red. They are stable in the solid state and in solutions of CH_2Cl_2, $CHCl_3$, dmf, and Me_2CO, slightly soluble even in Et_2O, but insoluble in hydrocarbons. Elemental analyses are given in Table 3. All the complexes show very similar i.r. spectra with ν(C=N) vibrations in the 1 595—1 607 cm^{-1} region and some phosphine-sensitive absorption bands at 1 095, 695, 524, and 512 cm^{-1} for PPh$_3$, at 698, 525, and 502 cm^{-1} for PEt$_2$Ph, and at 686, 543, and 485 cm^{-1} for PMe$_2$Ph. The u.v.–visible bands in dmf, due to charge-transfer transitions as reported for other similar compounds,[10,11] follow the same pattern for all the complexes. The absorptions and the corresponding absorption coefficients ε are reported in Table 4. Magnetic susceptibility measurements in solution (Table 4) show the usual values of $\mu_{eff.} = 2.5$—2.6, in agreement with a d^4 octahedral system with two unpaired electrons.[12] The resulting paramagnetism shifts the ^{1}H n.m.r. signals of the complexes up- and down-field relative to the SiMe$_4$ reference peak and broadens

Table 3. Colours and elemental analyses of [TcL(L′)L″] complexes with calculated values in parentheses

Compound	Colour	Analysis (%) C	H	N	P	Tc
[TcL^1(quin)(PEt$_2$Ph)]	Dark red	62.4 (61.8)	5.1 (5.0)	4.4 (4.5)	5.1 (5.0)	16.1 (15.9)
[TcL^1(quin)(PMe$_2$Ph)]	Deep red	61.2 (60.8)	4.7 (4.4)	4.5 (4.7)	5.4 (5.2)	16.5 (16.7)
[TcL^1(quin)(PPh$_3$)]	Deep red	67.3 (66.9)	4.5 (4.3)	4.1 (3.9)	4.5 (4.3)	13.8 (13.8)
[TcL^2(quin)(PPh$_3$)]	Violet	63.9 (64.3)	4.2 (4.0)	5.3 (5.6)	4.4 (4.1)	13.7 (13.3)
[TcL^2(quin)(PEt$_2$Ph)]	Violet	60.1 (60.4)	4.6 (4.8)	4.2 (4.4)	4.6 (4.9)	15.4 (15.6)
[TcL^1(L^3)(PMe$_2$Ph)]	Deep red	58.9 (59.2)	4.8 (4.6)	5.0 (4.9)	5.7 (5.4)	17.0 (17.4)

Table 4. U.v.–visible (nm) and i.r. (cm^{-1}) spectral parameters and magnetic moments for [TcL(L′)L″] complexes

Compound	ν(C=N)	$\lambda_{max.}(\varepsilon)$*					$\mu_{eff.}$
[TcL^1(quin)(PEt$_2$Ph)]	1 595	290 (2 200)	382 (2 500)	408 (sh) (2 300)	465 (1 300)	570 (600)	2.6
[TcL^1(quin)(PMe$_2$Ph)]	1 601	295 (2 800)	380 (2 100)	405 (sh) (2 200)	460 (1 400)	580 (500)	2.5
[TcL^1(quin)(PPh$_3$)]	1 589	290 (2 300)	380 (2 400)	405 (sh) (1 600)	478 (1 600)	578 (600)	2.5
[TcL^2(quin)(PPh$_3$)]	1 607	290 (2 500)	380 (2 200)	400 (sh) (1 800)	470 (1 000)	570 (400)	2.5
[TcL^2(quin)(PEt$_2$Ph)]	1 605	290 (2 300)	390 (2 300)	405 (sh) (2 200)	480 (1 500)	580 (600)	2.6
[TcL^1(L^3)(PMe$_2$Ph)]	1 604	295 (2 900)	390 (2 200)	405 (sh) (2 000)	480 (1 500)	580 (500)	2.6

* ε in dm^3 mol^{-1} cm^{-1}; in dmf solutions.

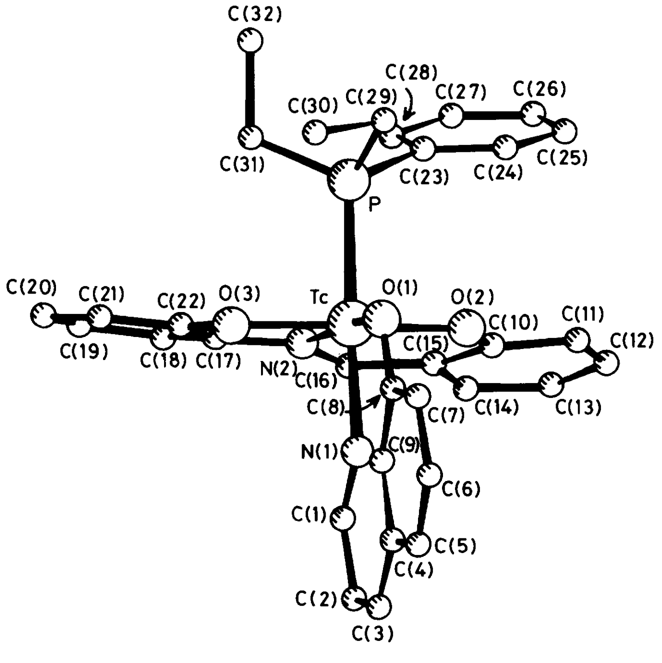


Figure 1. PLUTO drawing (W. D. S. Motherwell and W. Clegg, PLUTO 78, Program for Plotting Molecular and Crystal Structures, University of Cambridge, 1978) of [TcL^1(quin)(PEt$_2$Ph)] showing the structure and atom-labelling scheme

the linewidths, but for [TcL^1(quin)(PMe$_2$Ph)] and [TcL^1(L^3)(PMe$_2$Ph)] some assignments can be made. The linewidths (21 Hz) are in agreement with those reported in the literature for analogous technetium(III) compounds.[3,12] The resonances at $\delta = -10.40$ and -13.30 p.p.m. for [TcL^1(quin)(PMe$_2$Ph)] and $\delta = -9.00$ and -11.90 p.p.m. for [TcL^1(L^3)(PMe$_2$Ph)] were tentatively attributed to the methyl groups of the phosphine ligand.

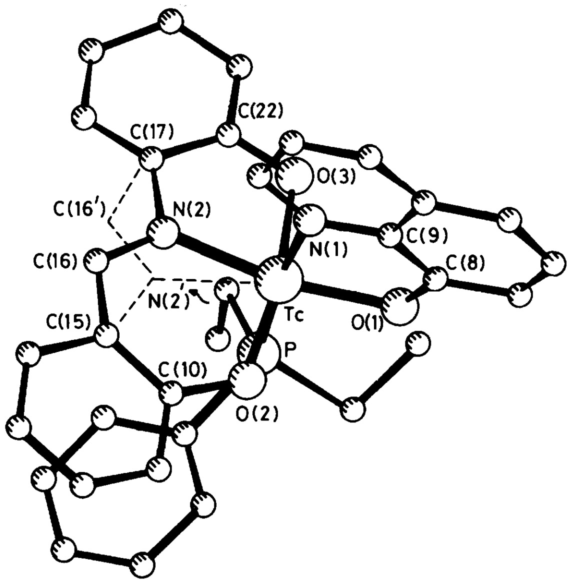
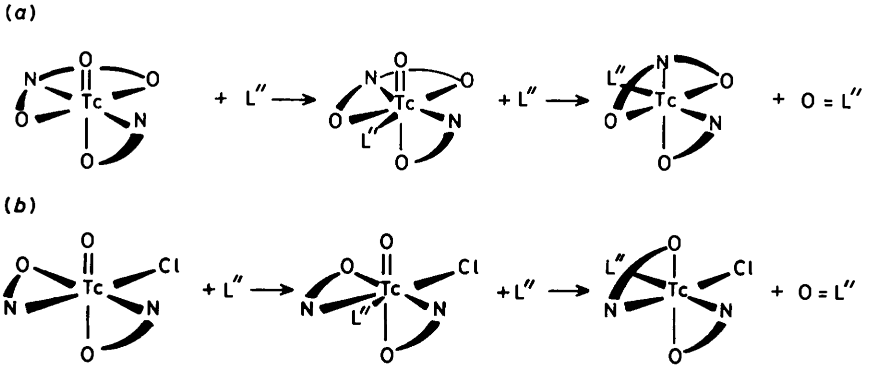


Figure 2. Perspective view of [TcL^1(quin)(PEt$_2$Ph)] showing, with dashed lines, the second orientation of the N(2)–C(16) bridge

The structure of [TcL^1(quin)(PEt$_2$Ph)] contains discrete molecules without any significant intermolecular interaction (Figure 1). The L^1 moiety acts as a tridentate O,N,O-donor ligand to the Tc atom which resides in an approximately octahedral co-ordination environment. The atoms O,N,O occupy three equatorial sites, while the fourth site is occupied by the oxygen atom of the O,N bidentate quin ligand; the apical phosphine ligand is located *trans* to the quin nitrogen atom



Scheme. Proposed mechanism for the formation of (*a*) [$TcL(L')L''$] and (*b*) [$TcCl(L^4)_2L''$] complexes

(Figure 1). The departure from an ideal octahedron is mainly ascribed to the acute bite angles O(1)–Tc–N(1) and O(3)–Tc–N(2) [78.9(6) and 76.3(9)°, respectively] (Table 2). The ligand L^1, as a whole, is roughly planar and is nearly normal to the strictly planar quin moiety [dihedral angle 94.1(4)°], as found[6] in the parent complex [$TcO(L^1)$(quin)] in which the oxygen atom of the quin is *trans* to the Tc=O bond, while the quin nitrogen resides in the equatorial plane. The Tc atom is displaced 0.04(1) Å from the mean equatorial plane toward the phosphorus atom and the P–Tc–N(1) angle is non-linear [174.1(5)°]. The Tc–N(1) distance [2.15(2) Å] is significantly longer than the 'normal' average of 2.07 Å,[13] but comparable with the reported Tc–N(quin) distances of 2.18 and 2.21 Å in [$TcO(mquin)_2Cl$][10] (mquin = 2-methylquinolin-8-olate) and 2.19 Å in [$TcO(L^1)$(quin)].[6] The remaining bond lengths and angles in the 'inner core' of the complex fall within the expected ranges,[13] even if the Tc–O(1) distance [2.05(1) Å] is somewhat longer.

The bridging mode of the L^1 moiety resembles the situation already found in [$ReO(Cl)(OH_2)(L^1)]\cdot Et_2O$,[14] [$ReO(Cl)(L^1)(PMe_2Ph)$],[14] and especially in [$TcO(L^1)$(quin)][6] and [$TcO(Cl)(L^2)$].[7] The positional disorder prevents us from determining accurately the geometry of this part of the complex. The ligand L^1 seems to have two orientations about the –C(16)=N(2)–bridge (Figure 2) with a population ratio of *ca.* 7:3, but the model derived exhibits unsatisfactory geometry and in particular for the second orientation the distance C(15)–N(2′) is unrealistic (1.65 Å).

From the structural data one can see that the mutual positions of the Schiff-base ligands are changed in respect of those of the starting complexes. In particular, the phenolic oxygen, primarily *trans* to oxo oxygen, is now *trans* to the imino nitrogen of the tridentate Schiff-base ligand. The final structure can easily be attained if the mechanism in the Scheme is operative. The formation of the final product is assumed to involve the production of a seven-co-ordinated intermediate just before the reduction of Tc^V to Tc^{III}, followed by the removal of the oxo group by means of a second phosphine molecule to form phosphine oxide and the technetium(III) complex. A similar behaviour was found in the reaction of [$TcO(Cl)(L^4)_2$] (L^4 = *N*-phenylsalicylideneniminate) with PMe_2Ph, producing [$TcCl(L^4)_2(PMe_2Ph)$].[3] The *X*-ray structure, even in this case, shows a rearrangement of the position of the ligands and the phosphine group is once more *trans* to an imine nitrogen atom. A simple displacement of a phenolate group leads to the final configuration [Scheme (*b*)]. In both cases the mechanism is supported by the impossibility of complete loss of a Schiff-base ligand.

Analogous rhenium starting complexes do not undergo reduction reactions even under reflux. The starting complexes were always recovered unchanged. This has also been observed for other similar complexes[3] and can be attributed to the higher reduction potential of rhenium(V) complexes compared to technetium(V) ones.[15]

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