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Synthesis and Characterization of New Technetium(I) and Rhenium(I) Schiff Base Complexes. Crystal Structure of $[M(PPh_3)_2(CO)_2\{(C_3H_2NS)N{=}CHC_6H_4O\}]$ (M = Tc, Re; C_3H_2NS = Thiazol-2-yl)

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Abstract

$[M(PPh_3)_2(CO)_3Cl]$ (M = Tc, Re) reacts with the lithium salt of the Schiff base *N*-orthohydroxybenzylidene-2-thiazolylimine in boiling THF to yield $[M(PPh_3)_2(CO)_2\{(C_3H_2NS)N{=}CHC_6H_4O\}]$. The structure of the two isomorphous complexes has been determined by X-ray crystallography based on single-crystal diffractometer data and refined to the final *R* factor of 0.039 for the Re complex and 0.059 for the Tc complex. The compounds are monoclinic, space group $P2_1/n$, with $Z = 4$. Crystal data are: $[Re(PPh_3)_2(CO)_2(L)]$ (L = Schiff base ligand), $a = 17.875(5)$, $b = 24.948(4)$, $c = 9.279(5)$ Å, $\beta = 102.39(3)°$; $[Tc(PPh_3)_2(CO)_2(L)]$, $a = 17.905(5)$, $b = 24.895(4)$, $c = 9.285(6)$ Å, $\beta = 102.63(3)°$. The metal ions are six-coordinate distorted octahedral, with *trans* PPh_3, *cis* CO groups, and one chelate bidentate anion. Structural details compare very favourably in the two complexes. Selected bond lengths are: Re–P (mean) 2.44, Re–C (mean) 1.89, Re–O 2.157(5), Re–N 2.211(6); Tc–P (mean) 2.44, Tc–C (mean) 1.89, Tc–O 2.164(5), Tc–N 2.210(7) Å.

Introduction

Studies of the inorganic chemistry of technetium are currently of importance in supporting the design of new ^{99m}Tc radiopharmaceuticals suitable for monitoring the metabolic function of the brain and heart because of the ideal nuclear properties and availability of this isotope [1]. At the same time the chemistry of congener third row rhenium has attracted increasing attention because of its chemical behaviour very similar to Tc and synthetic routes tested with Re may be usefully transferred in preparing analogous radiactive ^{99}Tc or ^{99m}Tc compounds [3–6].

Schiff base ligands possess good coordination properties toward both Re and Tc in their various V, IV, III or I oxidation states and several compounds, mainly involving the M^{5+} centre [7–9], were characterized by physico-chemical measurements and X-ray crystallography. The large number of recent reports focused on complexes containing the Tc^{5+} centre stems from the advent of a convenient synthesis of $TcOCl_4^-$ as valuable synthetic materials for the development of technetium radiopharmaceuticals via simple ligand substitution reactions. On the contrary, the chemistry of Tc(I) is relatively unexplored and only recently complexes with π-acceptor isonitrile and pseudoallyl ligands [2–4] have received some attention.

We report here the preparation and structure of the isomorphous pair $[M(PPh_3)_2(CO)_2(L)]$ (M = Tc, Re; L = the anion of the Schiff base *N*-orthohydroxybenzylidene-2-thiazolylimine).

Results and Discussion

The new complexes $[M(PPh_3)_2(CO)_2\{(C_3H_2NS)N{=}CHC_6H_4O\}]$ (M = Tc, Re) were obtained by adding $[M(PPh_3)_2(CO)_3Cl]$ as a solid to a boiling tetrahydrofuran (THF) solution of the lithium salt of the ligand generated *in situ* by treating LH with n-BuLi. The complexes have been characterized by

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elemental analysis, IR and ^{1}H NMR. The IR spectra are very similar and show the presence of the phosphine and of two *cis* terminal carbonyl groups at the expected frequencies [5]; moreover the C–N stretching absorptions are in the region 1610–1525 cm^{-1}, indicating partial double-bond character of the $\mathrm{C}\overset{\cdots}{-}\mathrm{N}$ group as a consequence of the chelating behaviour of the ligand. The ^{1}H NMR spectra ($CDCl_3$) show the two CH protons of the thiazole ring as doublets centered at higher field as in the free ligand, reflecting a decrease in aromaticity of the ring upon coordination.

X-ray Structure of [M(PPh$_3$)$_2$(CO)$_2${(C$_3$H$_2$NS)-N=CHC$_6$H$_4$O}] (M = Tc, Re)

The overall configuration of the isomorphous compounds [M(PPh_3)$_2$(CO)$_2$(L)] (M = Tc, Re) is shown in Figs. 1 and 2 together with the adopted numbering scheme. The metal atoms are six-coordinate octahedral, with *trans* PPh_3, *cis* CO, and one chelate bidentate ligand. Distortions from the idealized geometry are mainly localized in the base plane owing to the constraints imposed by the structure of the organic ligand which subtends angles of only 83° to the metal ions (the adjacent C(38)–M–N(1) angle is 98° in both compounds). Re–P, Re–C and C–O bond lengths compare well with the values found in other similar compounds and need no comment. The Re–O and Re–N bonds, which are *trans* with respect to the strong Re–CO bonds, are significantly longer than the atomic radii sum [10]. It is noteworthy that the corresponding bond distances involving Tc are comparable and almost identical to those involving Re, which is not surprising if one considers that their atomic radii have the same value [10]. Mean planes calculations show that the atoms of the base plane, including the metal, are strictly coplanar. The chelate ligand forms with this plane dihedral angles of 21.5° (Re) and 21.0° (Tc); in its turn the thiazolic ring is inclined by 40.1° (Re) and by 38.6° (Tc) with respect to the base plane and by 59.0° (Re) and 56.7° (Tc) with respect to the ligand plane. The chelate anion forms with the metal a hexa-atomic planar ring whose bond distances indicate the presence of some electronic delocalization through the ligand atoms. The bond length sequence in the thiazolic ring reflects the conjugated nature of this system, with localized C(46)=N(2) and C(47)=C(48) double bonds. The S–C bonds (mean 1.71 Å) are only slightly shorter than expected for a $C_{(sp^2)}$–S single bond (1.75 Å [11]). The bridging C(46)–N(1) bond is single.

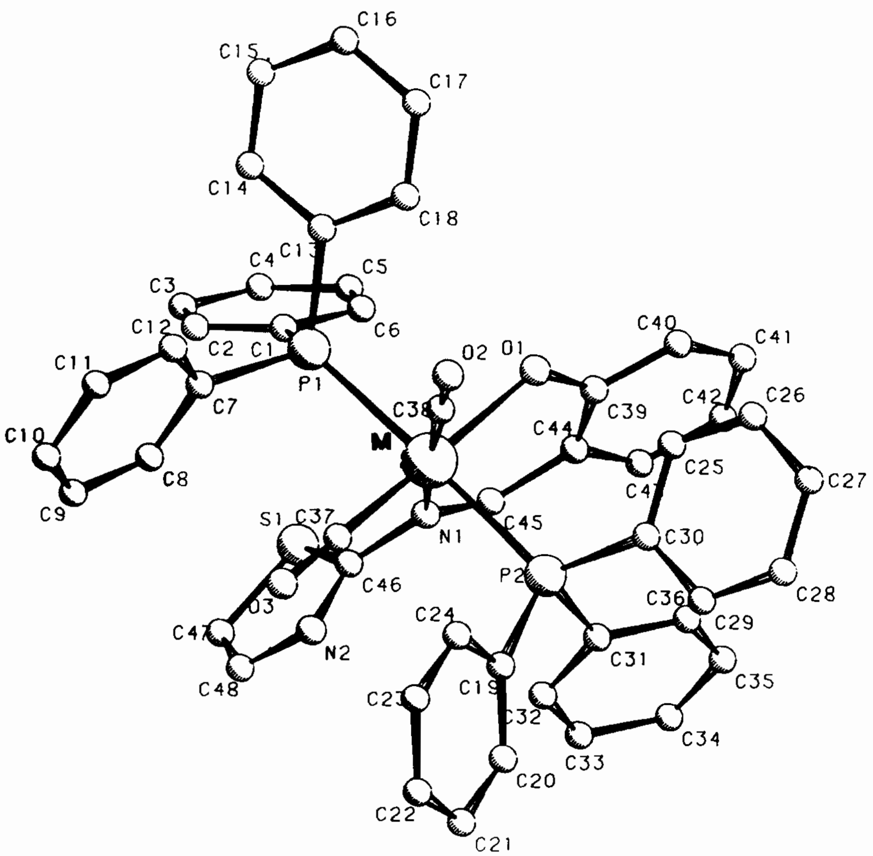

Fig. 1. The crystal structure for the isomorphous pair [M(PPh_3)$_2$(CO)$_2${(C_3H_2NS)N=CHC_6H_4O}] (M = Tc, Re).

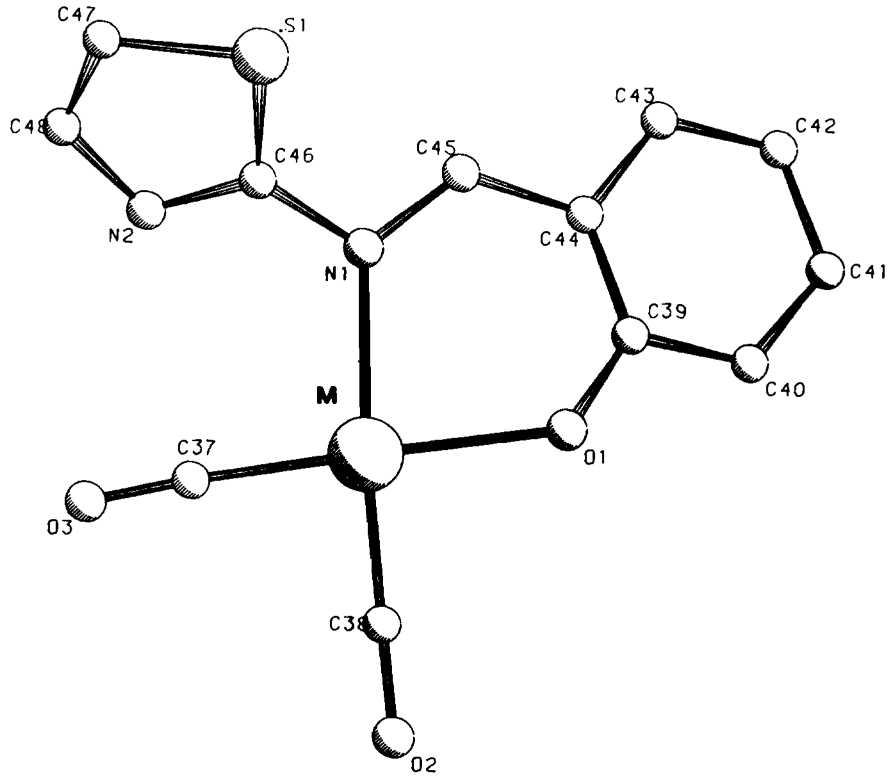

Fig. 2. Projection of the structure along the P(1)–P(2) direction. For clarity the *trans* PPh_3 groups are omitted.

Experimental

Solvents were purified and dried before use. All the syntheses were performed under argon. The starting compounds $[M(PPh_3)_2(CO)_3Cl]$ (M = Tc, Re) were prepared by the literature methods [3, 12]. Aqueous NH_4 $[^{99}TcO_4]$ was obtained from Radiochemical Centre Ltd., Amersham, U.K. Solid samples were obtained by concentration and filtration of its ammonia solutions. ^{99}Tc is a weak emitter (0.292 keV, $t_{1/2} = 2.12 \times 10^5$ years). All manipulations were carried out in a laboratory approved for low-level radioactivity with monitored hoods and glove-boxes. Other materials used were commercially available reagent grade chemicals. The Schiff base *N*-orthohydroxybenzylidene-2-thiazolylimine was prepared by mixing stoichiometric quantities of salicylaldehyde and 2-amminothiazole in EtOH. Elemental analyses were performed on a Carlo Erba elemental analyzer, model 1106. IR and ^1H NMR spectra were recorded on Perkin-Elmer 577 and on Varian Gemini 300 spectrometers, respectively.

Synthesis of the Complexes $[M(PPh_3)_2(CO)_2\{(C_3H_2NS)N{=}CHC_6H_4O\}]$ *(M = Tc, Re)*

The same procedure was followed for both complexes. A solution of n-butyllithium in hexane (0.24 ml, *c*. 2 M, 0.48 mmol) was added to a dried THF solution of the ligand (25 ml, 0.48 mmol) at room temperature. Solid $[M(PPh_3)_2(CO)_3Cl]$ (0.24 mmol) was added to the solution, and the mixture was heated to boiling point, yielding a red solution. The solution was refluxed for 1 h. The mixture was then concentrated to one third of its volume and filtered. A red–violet powder was obtained by adding EtOH to the solution. The solid was washed with H_2O, EtOH and EtOEt. The product was crystallized from CH_2Cl_2/EtOH (7:3 vol./vol.).

$[Tc(PPh_3)_2(CO)_2\{(C_3H_2NS)N{=}CHC_6H_4O\}]$

Red–violet, yield 85%. *Anal.* Found: C, 65.5; H, 4.3; N, 3.0; S, 3.2. Calc. for $C_{48}H_{37}N_2O_3P_2TcS$: C, 65.3; H, 4.2; N, 3.2; S, 3.6%. IR data (cm^{-1}, Nujol): ν(CO) 1940s, 1855s; ν(chelate ligand) 1610m, 1582m, 1525m, ^1H NMR ($CDCl_3$): δ, (masked by aryl protons), 6.85 (1H, d, CH).

$[Re(PPh_3)_2(CO)_2\{(C_3H_2NS)N{=}CHC_6H_4O\}]$

Red–violet, yield 90%. *Anal.* Found: C, 59.6; H, 3.9; N, 2.7; S, 3.0. Calc. for $C_{48}H_{37}N_2O_3P_2ReS$: C, 59.4; H, 3.9; N, 2.8; S, 3.3%. IR data (cm^{-1}, Nujol): ν(CO) 1932s, 1848s; ν(chelate ligand) 1608m, 1578m, 1535m. ^1H NMR ($CDCl_3$): δ, 7.8 (1H, s, CH), 7.73, 7.33 (2H, d, CH).

TABLE 1. Crystal and experimental data[a]

Compound	$C_{48}H_{37}N_2O_3P_2ReS$		$C_{48}H_{37}N_2O_3P_2TcS$
Formula weight	969		880
System		monoclinic	
Space group		$P2_1/n$	
General positions		$\pm(x, y, z; 1/2 + x, 1/2 - y, 1/2 + z)$	
Z		4	
a (Å)	17.875(5)		17.905(5)
b (Å)	24.948(4)		24.895(4)
c (Å)	9.279(6)		9.285(6)
β (°)	102.39(3)		102.63(3)
V (Å^3)	4041		4039
Density (g cm^{-3})	1.59		1.45
Radiation		Mo Kα (λ = 0.7107 Å)	
Absorption coefficient (cm^{-1})	35		5
Technique and geometry		Four-circle diffractometry; $\theta/2\theta$ scan mode; scan rate 2° min^{-1}	
No. independent reflexions recorded	6987		6518
No. observed reflexions $I > 3\sigma(I)$	5334		4664
Corrections applied		Lp, absorption [13]	
Parameters refined		scale factor, atomic coordinates temperature factors	
No. reflexions per parameter refined	24 (the ring carbon atoms were refined as rigid bodies with isotropic temper. factors)		11 (the ring carbon atoms were refined as rigid bodies with anisotropic temp. factors)
Weighting scheme		$w = 1$	
Final R factor for observed reflexions	0.039		0.059
Programs used		SHELX [14]	

[a] Crystal and experimental data are reported for the technetium complex only if they are different from those of the isomorphous rhenium complex.

TABLE 2. Atomic coordinates for the Re complex

Atom	x/a	y/b	z/c
Re	0.80277(2)	0.10915(1)	0.85125(3)
S	0.69285(15)	0.12843(11)	0.35249(29)
P1	0.70489(10)	0.04099(8)	0.77983(21)
P2	0.89841(11)	0.17957(8)	0.92518(21)
O1	0.89078(28)	0.05260(19)	0.82835(56)
O2	0.81699(39)	0.08049(26)	1.17419(65)
O3	0.68029(33)	0.18908(25)	0.89425(74)
N1	0.80028(32)	0.12431(23)	0.61550(64)
N2	0.70679(49)	0.19509(32)	0.56648(84)
C1	0.68395(21)	0.01682(22)	0.58779(49)
C2	0.74714(21)	0.00029(22)	0.53335(49)
C3	0.73670(21)	−0.02129(22)	0.39174(49)
C4	0.66306(21)	−0.02634(22)	0.30457(49)
C5	0.59986(21)	−0.00982(22)	0.35901(49)
C6	0.61031(21)	0.01176(22)	0.50062(49)
C7	0.61375(32)	0.06664(21)	0.81276(55)
C8	0.59087(32)	0.05362(21)	0.94303(55)
C9	0.52734(32)	0.07881(21)	0.97781(55)
C10	0.48669(32)	0.11703(21)	0.88231(55)
C11	0.50957(32)	0.13005(21)	0.75204(55)
C12	0.57310(32)	0.10486(21)	0.71727(55)
C13	0.71605(25)	−0.02456(22)	0.87151(58)
C14	0.65738(25)	−0.06223(22)	0.83488(58)
C15	0.66694(25)	−0.11360(22)	0.89544(58)
C16	0.73518(25)	−0.12730(22)	0.99263(58)
C17	0.79386(25)	−0.08962(22)	1.02927(58)
C18	0.78430(25)	−0.03826(22)	0.96871(58)
C19	0.86050(31)	0.23920(21)	1.00325(53)
C20	0.86393(31)	0.29092(21)	0.94784(53)
C21	0.82990(31)	0.33345(21)	1.00745(53)
C22	0.79245(31)	0.32427(21)	1.12245(53)
C23	0.78902(31)	0.27256(21)	1.17786(53)
C24	0.82304(31)	0.23002(21)	1.11825(53)
C25	0.94138(27)	0.20485(22)	0.77566(53)
C26	1.01660(27)	0.19191(22)	0.76982(53)
C27	1.04604(27)	0.20752(22)	0.64868(53)
C28	1.00026(27)	0.23607(22)	0.53337(53)
C29	0.92505(27)	0.24901(22)	0.53921(53)

(continued)

TABLE 2. *(continued)*

(continued)

TABLE 2. *(continued)*

Atom	*x/a*	*y/b*	*z/c*
C30	0.89561(27)	0.23340(22)	0.66035(53)
C31	0.98285(26)	0.16393(17)	1.07008(54)
C32	1.00448(26)	0.11061(17)	1.09886(54)
C33	1.07278(26)	0.09851(17)	1.19802(54)
C34	1.11944(26)	0.13973(17)	1.26839(54)
C35	1.09781(26)	0.19305(17)	1.23962(54)
C36	1.02952(26)	0.20515(17)	1.14046(54)
C37	0.81143(40)	0.09228(28)	1.05102(89)
C38	0.72609(43)	0.15918(29)	0.87379(88)
C39	0.93924(27)	0.05616(20)	0.73899(43)
C40	1.00885(27)	0.02941(20)	0.78434(43)
C41	1.06257(27)	0.02988(20)	0.69525(43)
C42	1.04667(27)	0.05710(20)	0.56080(43)
C43	0.97705(27)	0.08384(20)	0.51545(43)
C44	0.92334(27)	0.08337(20)	0.60454(43)
C45	0.85349(39)	0.11228(28)	0.54325(79)
C46	0.73695(46)	0.15175(31)	0.52560(87)
C47	0.63085(60)	0.18101(47)	0.33479(127)
C48	0.64864(65)	0.21172(49)	0.45471(121)

TABLE 3. Atomic coordinates for the Tc complex

Atom	*x/a*	*y/b*	*z/c*
Tc1	0.30256(2)	0.39112(1)	0.85018(10)
N1	0.2992(3)	0.3744(3)	0.6150(8)
O1	0.3903(3)	0.4482(2)	0.8268(6)
C45	0.3527(4)	0.3885(3)	0.5406(9)
C46	0.2360(5)	0.3498(3)	0.5219(10)
C47	0.1298(6)	0.3184(5)	0.3313(14)
C48	0.1460(7)	0.2899(5)	0.4552(14)
S1	0.1939(2)	0.3709(1)	0.3497(3)
N2	0.2048(5)	0.3065(4)	0.5671(10)
C40	0.5095(3)	0.4698(2)	0.7851(5)
C41	0.5635(3)	0.4689(2)	0.6972(5)
C42	0.5472(3)	0.4422(2)	0.5619(5)
C43	0.4769(3)	0.4164(2)	0.5144(5)
C44	0.4229(3)	0.4174(2)	0.6023(5)
C39	0.4392(3)	0.4441(2)	0.7377(5)
O2	0.3183(4)	0.4207(3)	1.1736(8)
O3	0.1812(3)	0.3117(3)	0.8990(9)
C38	0.2264(5)	0.3415(3)	0.8757(10)
C37	0.3117(4)	0.4094(3)	1.0495(12)
P1	0.2040(1)	0.4592(1)	0.7776(3)
C1	0.1833(2)	0.4837(2)	0.5860(6)
C2	0.1100(2)	0.4883(2)	0.4970(6)
C3	0.0999(2)	0.5096(2)	0.3551(6)
C4	0.1633(2)	0.5263(2)	0.3022(6)
C5	0.2367(2)	0.5217(2)	0.3911(6)
C6	0.2467(2)	0.5004(2)	0.5330(6)
C7	0.1133(3)	0.4337(2)	0.8110(6)
C8	0.0721(3)	0.3960(2)	0.7141(6)
C9	0.0089(3)	0.3704(2)	0.7487(6)
C10	−0.0131(3)	0.3826(2)	0.8801(6)
C11	0.0281(3)	0.4204(2)	0.9770(6)
C12	0.0913(3)	0.4459(2)	0.9424(6)
C13	0.2147(3)	0.5250(2)	0.8694(7)
C14	0.1555(3)	0.5624(2)	0.8348(7)
C15	0.1651(3)	0.6139(2)	0.8958(7)
C16	0.2339(3)	0.6278(2)	0.9913(7)
C17	0.2930(3)	0.5904(2)	1.0259(7)
C18	0.2835(3)	0.5390(2)	0.9650(7)
P2	0.3977(1)	0.3205(1)	0.9257(3)
C19	0.3602(4)	0.2608(2)	1.0050(6)
C20	0.3618(4)	0.2091(2)	0.9478(6)
C21	0.3274(4)	0.1667(2)	1.0072(6)
C22	0.2915(4)	0.1760(2)	1.1239(6)
C23	0.2899(4)	0.2277(2)	1.1811(6)
C24	0.3243(4)	0.2701(2)	1.1217(6)
C25	0.4408(3)	0.2949(2)	0.7766(7)
C26	0.5161(3)	0.3080(2)	0.7726(7)
C27	0.5458(3)	0.2930(2)	0.6517(7)
C28	0.5003(3)	0.2648(2)	0.5348(7)
C29	0.4251(3)	0.2517(2)	0.5388(7)
C30	0.3953(3)	0.2668(2)	0.6597(7)
C31	0.4822(3)	0.3362(2)	1.0712(7)
C32	0.5039(3)	0.3897(2)	1.0984(7)
C33	0.5722(3)	0.4021(2)	1.1974(7)
C34	0.6188(3)	0.3610(2)	1.2694(7)
C35	0.5971(3)	0.3075(2)	1.2422(7)
C36	0.5288(3)	0.2951(2)	1.1432(7)

TABLE 4. Bond distances (Å)[a]

Bond	Re complex	Tc complex
M–P(1)	2.428(2)	2.432(2)
M–P(2)	2.445(2)	2.443(2)
M–O(1)	2.157(5)	2.164(5)
M–N(1)	2.211(6)	2.210(7)
M–C(37)	1.875(8)	1.88(1)
M–C(38)	1.898(7)	1.89(1)
C(37)–O(2)	1.164(9)	1.17(1)
C(38)–O(3)	1.153(9)	1.15(1)
O(1)–C(39)	1.324(6)	1.334(7)
N(1)–C(45)	1.311(9)	1.34(1)
N(1)–C(46)	1.429(9)	1.40(1)
C(44)–C(45)	1.448(8)	1.452(9)
S–C(46)	1.73(1)	1.70(1)
S–C(47)	1.70(1)	1.72(1)
N(2)–C(46)	1.30(1)	1.32(1)
N(2)–C(48)	1.37(1)	1.37(1)
C(47)–C(48)	1.33(2)	1.33(2)
P(1)–C(1)	1.842(5)	1.841(6)
P(1)–C(7)	1.836(6)	1.832(6)
P(1)–C(13)	1.835(6)	1.838(6)
P(2)–C(19)	1.846(6)	1.849(6)
P(2)–C(25)	1.836(5)	1.838(7)
P(2)–C(31)	1.835(5)	1.837(7)

[a] e.s.d.s given in parentheses. The phenyl rings were refined as rigid bodies with fixed C–C (1.395 Å) and C–H (1.08 Å) distances.

TABLE 5. Selected bond angles (°)[a]

Angle	Re complex	Tc complex
P(1)–M–P(2)	178.3(1)	177.8(1)
N(1)–M–C(37)	175.3(3)	175.3(3)
O(1)–M–C(38)	179.3(3)	178.6(3)
O(1)–M–N(1)	82.8(2)	83.6(2)
C(37)–M–C(38)	87.0(3)	97.9(3)
O(1)–M–C(37)	92.5(2)	91.7(3)
N(1)–M–C(38)	97.7(3)	97.9(3)
M–O(1)–C(39)	127.3(4)	127.0(4)
M–N(1)–C(45)	127.2(5)	126.2(5)
M–C(37)–O(2)	178.3(7)	179.3(7)
M–C(38)–O(3)	176.9(7)	176.5(9)
M–P(1)–C(1)	118.6(2)	118.7(2)
M–P(1)–C(7)	108.9(2)	109.2(2)
M–P(1)–C(13)	119.8(2)	119.8(2)
M–P(2)–C(19)	113.3(2)	113.6(2)
M–P(2)–C(25)	114.6(2)	114.5(2)
M–P(2)–C(31)	117.9(2)	117.9(2)
M–N(1)–C(46)	120.3(5)	122.2(5)
C(44)–C(45)–N(1)	124.9(6)	125.4(7)
C(45)–N(1)–C(46)	112.5(6)	111.5(7)
N(1)–C(46)–S	121.8(6)	125.3(6)
C(46)–S–C(47)	89.3(5)	90.5(5)
S–C(47)–C(48)	109.2(8)	107.8(8)
C(47)–C(48)–N(2)	117.8(9)	118.7(9)
C(46)–N(2)–C(48)	109.1(8)	108.2(9)
C(1)–P(1)–C(7)	105.8(2)	106.2(2)
C(1)–P(1)–C(13)	97.8(3)	97.5(3)
C(7)–P(1)–C(13)	104.2(2)	103.6(3)
C(19)–P(2)–C(25)	105.5(2)	105.7(3)
C(19)–P(2)–C(31)	101.4(2)	101.0(3)
C(25)–P(2)–C(31)	102.4(2)	102.4(3)

[a] e.s.d.s given in parentheses. M = Re or Tc.

X-ray Structure Determination

Crystals of maximum dimensions 0.2 mm were selected for the X-ray measurements. Data collection was made on a Philips diffractometer with the monochromatized Mo Kα radiation. Cell dimensions were determined by least-squares refinement of 25 medium-angle settings. Crystal and experimental data are reported in Table 1. The crystals are stable under irradiation. Solution of the structures was achieved by standard Patterson and Fourier methods alternated with cycles of least-squares refinement of the atomic parameters. The full-matrix refinement was proceeded minimizing the function $\Sigma w(\Delta F)^2$ with $w = 1$. At convergence, the largest parameter shift of the non-hydrogen atoms was less than 0.3σ for the rhenium and less than 0.1σ for the technetium compound. No significant residual of electronic density was observed in the final Fourier-difference maps apart from some ripples around the Re position. Scattering factors for neutral atoms were taken from ref. 15, and those of Re and Tc were corrected for anomalous dispersion [16]. Final atomic parameters are listed in Tables 2 and 3. Bond distances and angles are reported in Tables 4 and 5.

Supplementary Material

Tables of anisotropic thermal parameters, hydrogen atom coordinates and a listing of observed and calculated structure factors for both compounds are available from U.C. on request.

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