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Reactions of the Technetium(I) Carbonyl Complexes [$Tc(PMe_2Ph)_3(CO)_2Cl$] and [$Tc(PPh_3)_2(CO)_3Cl$] toward Pseudoallyl Ligands Such as Triazenido, Formamidinato, and Acetamidinato. Crystal Structures of [$Tc(PMe_2Ph)_2(CO)_2(p\text{-}CH_3C_6H_4N\overset{\cdots}{-}N\overset{\cdots}{-}NC_6H_4CH_3\text{-}p)$] and [$Tc(PMe_2Ph)_2(CO)_2(C_6H_5N\overset{\cdots}{-}C(CH_3)\overset{\cdots}{-}NC_6H_5)$]

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Received February 27, 1985

New technetium(I) complexes of bidentate pseudoallyl ligands as triazenido, formamidinato, and acetamidinato have been synthesized and characterized. X-ray structure determinations of [$Tc(PMe_2Ph)_2(CO)_2(p\text{-}CH_3C_6H_4N\overset{\cdots}{-}N\overset{\cdots}{-}NC_6H_4CH_3\text{-}p)$] (**1a**) and [$Tc(PMe_2Ph)_2(CO)_2(C_6H_5N\overset{\cdots}{-}C(CH_3)\overset{\cdots}{-}NC_6H_5)$] (**1c**) show the technetium atom in a distorted octahedral coordination geometry with two axial PMe_2Ph and two *cis*-CO groups and the chelate ligands, which form a four-membered ring with the metal. Compound **1a** crystallizes in space group *Pbca* of the orthorhombic system with $a = 11.036$ (2) Å, $b = 14.657$ (4) Å, $c = 38.92$ (1) Å, and $R = 0.045$ for 3381 diffractometer data with $I \geq 3\sigma(I)$. Compound **1c** crystallizes in the same space group, *Pbca*, with $a = 8.954$ (3) Å, $b = 16.727$ (2) Å, $c = 41.435$ (5) Å, and $R = 0.035$ for 4108 diffractometer data with $I \geq 3\sigma(I)$.

Introduction

Within the last 10 years the chemistry of technetium has received considerable attention because of the preeminence of ^{99m}Tc in many diagnostic studies involving the imaging of internal organs by radioscintigraphic techniques.[1,2] However, the paucity of information currently available requires a deeper understanding of the basic chemistry of this element.[3] On the other hand, difficulties concerning the trace-level experiments, caused by the extremely low ^{99m}Tc concentrations (i.e. 10^{-8}–10^{-9} M) used, make imperative the use of macroscopic amounts of the long-lived ^{99}Tc ($t_{1/2} = 2.12 \times 10^5$ years).[4]

Current work on technetium compounds as new clinical diagnostic agents concerns mainly technetium(V) complexes with coordinating chelating mixed-donor-atom ligands.[5-8] On the contrary, the chemistry of Tc(I) is relatively unexplored and only recently has received some attention with π-acceptor ligands.[3,9]

We have previously reported the synthesis and characterization by X-ray diffraction of rhenium(I) complexes with π-acceptor pseudoallyl ligands such as triazenido, amidinato, and amidato of the type [$Re(PPh_3)_2(CO)_2(RN\overset{\cdots}{-}X\overset{\cdots}{-}NR)$] (X = CH or N) and [$Re(PPh_3)_2(CO)_2(ArN\overset{\cdots}{-}CH\cdot\cdot O)$)].[10] In this paper we report the preparation and characterization of the complexes of technetium(I) with the first two classes of ligands [$Tc(PMe_2Ph)_2(CO)_2(dtt)$] (**1a**), [$Tc(PMe_2Ph)_2(CO)_2(dct)$] (**1b**), [$Tc(PMe_2Ph)_2(CO)_2(dpa)$] (**1c**), [$Tc(PMe_2Ph)_2(CO)_2(dtf)$] (**1d**), and [$Tc(PPh_3)_2(CO)_2(dtt)$] (**1e**), where dtt = *N,N′*-di-*p*-tolyltriazenido, dct = *N,N′*-bis(*p*-chlorophenyl)triazenido, dpa = *N,N′*-diphenylacetamidinato, and dtf = *N,N′*-di-*p*-tolylformamidinato, and the structure determinations of the two complexes **1a** and **1c**.

Experimental Section

Aqueous $NH_4[^{99}TcO_4]$ was obtained from Radiochemical Centre Ltd., Amersham, England. 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 gloveboxes.

The literature preparation of [$Tc(PMe_2Ph)_3(CO)_2Cl$] was not followed.[11] The formation of an oily residue did not permit the recovery of the compound in good yield, and the following new method was employed: *mer*-[$TcCl_3(PMe_2Ph)_3$][12] (1.0 g) was reacted with CO and the mixture was stirred with toluene (50 mL) and an excess of PMe_2Ph at room temperature for 6 h. The final solution, when concentrated and treated with pentane, gave white crystals of $Tc(PMe_2Ph)_3(CO)_3Cl$ in 80% yield.

The preparation of $Tc(PPh_3)_2(CO)_3Cl$ was performed as described in the literature.[11] However, the addition of an excess of PPh_3 to the mixture shortens the reaction time from 20 to 8 h. Yield: >90%. Solvents were purified and dried before use. ArNHCHNAr, ArNHC(CH_3)NAr,[13] and $ArNHN_2Ar$[14] were prepared by following the literature methods.

The IR spectra of solid samples in KBr or as Nujol mulls were recorded on a Perkin-Elmer 577 spectrophotometer. ^1H NMR spectra of $CDCl_3$ solutions were collected on a WP 80-MHz Bruker instrument. Elemental analyses were performed on a Carlo Erba elemental analyzer Model 1106; the elemental analyses for the radioactive technetium compounds were carried out on a Packard liquid-scintillation instrument, Model TRI-CARB 300 C, with Insta-gel as scintillator.

Preparation of [$Tc(PR_3)_2(CO)_2(ArN\overset{\cdots}{-}X\overset{\cdots}{-}NAr)$] (1a ($PR_3$ = PMe_2Ph, X = N, Ar = p-MeC_6H_4); 1b (PR_3 = PMe_2Ph, X = N, Ar = p-ClC_6H_4); 1c (PR_3 = PMe_2Ph, X = $C(CH_3)$, Ar = C_6H_5); 1d (PR_3 =

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Table I. Crystal Data

compd	*trans*-Tc(PMe_2Ph)$_2$(CO)$_2$(dpa) (**1c**)	*trans*-Tc(PMe_2Ph)$_2$(CO)$_2$(dtt) (**1a**)
fw	639.59	654.61
cryst size, mm	0.19 × 0.24 × 0.50	0.12 × 0.33 × 0.43
space group	*Pbca*	*Pbca*
unit cell params		
a, Å	8.954 (3)	11.036 (2)
b, Å	16.727 (2)	14.657 (4)
c, Å	41.435 (5)	38.92 (1)
V, Å^3	6205 (2)	6295 (2)
Z	8	8
ρ(calcd), g cm^3	1.37	1.38
ρ(obsd), g cm^3	1.35	1.36
μ(Mo Kα), cm^{-1}	5.8	5.8
radiation	Mo Kα	Mo Kα
monocromator	graphite	graphite
θ_{min}–θ_{max}, deg	2–27	2–27
no. of std reflcns	2 (stable)	2 (stable)
temp, °C	22	22
no. of indep reflcns	6672	6845
no. of reflcns with $I > 3\sigma(I)$	4108	3381
no. of variables (last cycle)	352	361
final R_1,^{a} R_2^{a}	0.035, 0.046	0.045, 0.055
final shift/error max	0.20	0.38
largest peak (e Å^{-3}) in final difference map	0.43	0.62
weighting	$1/w^2 = 1/\sigma^2(1) + 0.04I$	$1/w^2 = 1/\sigma^2(1) + 0.04I$
error in an observn of unit weight	1.5	1.6

$^a R_1 = \sum|\Delta F_o|/\sum|F_o|$; $R_2 = (\sum w|\Delta F_o|^2/\sum w|F_o|^2)^{1/2}$.

PMe_2Ph, X = CH, Ar = *p*-MeC_6H_4); 1e (PR_3 = PPh_3, X = N, Ar = *p*-MeC_6H_4)). For both classes of complexes we followed the same procedure. A solution of *n*-butyllithium in hexane (0.24 mL, ca. 2 M, 0.48 mmol) was added to a dried PhH solution of ArNHXNAr (40 mL, 0.48 mmol) at room temperature under nitrogen atmosphere. Solid *mer*-[Tc(PMe_2Ph)$_3$(CO)$_2$Cl] (0.24 mmol) or *trans*-[Tc(PPh_3)$_2$(CO)$_3$Cl] (0.24 mmol) was added to the solution, in which it dissolved in a few minutes with heating to the boiling point, yielding a light yellow solution. The solution was refluxed for 3 h under nitrogen. The mixture was then concentratged to one-third of its volume and filtered. A yellow 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 v/v).

[Tc(PMe_2Ph)$_2$(CO)$_2$(dtt)] (**1a**): 85%; orange. Anal. Found: Tc, 14.7; C, 57.2; H, 5.0; N, 6.1. Calcd for $TcN_3P_2O_2C_{32}H_{36}$: Tc, 15.1; C, 58.6; H, 5.5; N, 6.4.

[Tc(PMe_2Ph)$_2$(CO)$_2$(dct)] (**1b**): 80%; orange-yellow. Anal. Found: Tc, 13.9; C, 51.1; H, 3.9; N, 5.5. Calcd for $TcN_3P_2O_2Cl_2C_{30}H_{30}$: Tc, 14.2; C, 51.7; H, 4.3; N, 6.0.

[Tc(PMe_2Ph)$_2$(CO)$_2$(dpa)] (**1c**): 80%; pale yellow. Anal. Found: Tc, 15.1; C, 59.3; H, 5.4; N, 4.0. Calcd for $TcN_2P_2O_2C_{32}H_{35}$: Tc, 15.4; C, 60.0; H, 5.5; N, 4.4.

[Tc(PMe_2Ph)$_2$(CO)$_2$(dtf)] (**1d**): 75%; yellow. Anal. Found: Tc, 14.6; C, 59.8; H, 5.3; N, 3.8. Calcd for $TcN_2P_2O_2C_{33}H_{37}$: Tc, 15.1; C, 60.5; H, 5.7; N, 4.3.

[Tc(PPh_3)$_2$(CO)$_2$(dtt)] (**1e**): 85%; orange. Anal. Found: Tc, 10.2; C, 68.5; H, 4.5; N, 4.1. Calcd for $TcN_3P_2O_2C_{52}H_{44}$: Tc, 10.9; C, 69.1; H, 4.9; N, 4.6.

Collection of the X-ray Data. Crystal data and other crystallographic parameters for [Tc(PMe_2Ph)$_2$(CO)$_2$(dpa)] (**1c**) and [Tc(PMe_2Ph)$_2$(CO)$_2$(dtt)] (**1a**) are given in Table I. Data were collected on an Enraf-Nonius CAD-4 diffractometer with monochromated Mo Kα radiation and $\omega/2\theta$ scan. Cell parameters were obtained by a least-squares procedure on the diffractomer positions of 25 reflections in the range 10° $< \theta <$ 13°. Intensities were corrected for Lorentz and polarization but not for absorption owing to the small absorption coefficient. Scattering factors and anomalous scattering corrections were taken from ref 20.

Solution and Refinement of Structures. In both structures the positions of the Tc atoms were located from Patterson synthesis. All other non-H atoms were located in the subsequent Fourier maps. After three cycles of isotropic refinement, both structures were refined by full-matrix least squares using anisotropic temperature factors for all the non-H atoms. H atoms were given calculated positions with C–H bond distances of 0.95 Å and fixed isotropic *B*'s of 5.0 Å^2. Weights were applied according to the scheme given in Table I. In compound **1a** the C(17)–C(22) phenyl ring turned out to be somewhat disordered, as clearly indicated by the unrealistically high values of the vibrational parameters of the C(19), C(20), C(21), and C(22) atoms. Final statistical parameters are given in Table I. Final positional and equivalent isotropic vibrational parameters[21] are reported in Table III. Tables of observed and calculated

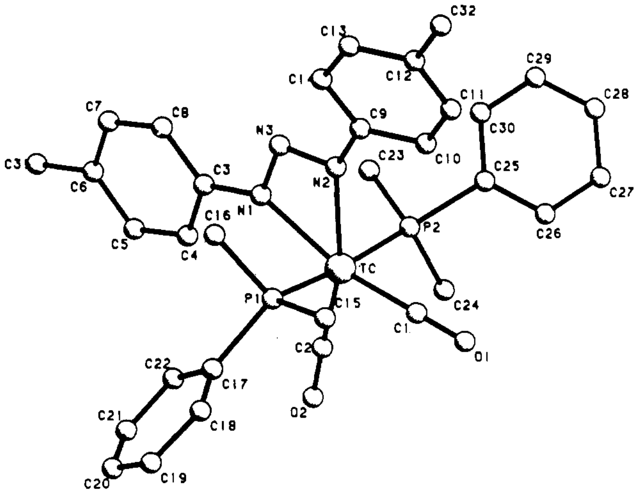

Figure 1. Crystal structure of [Tc(PMe_2Ph)$_2$(CO)$_2$(dtt)] (**1a**).

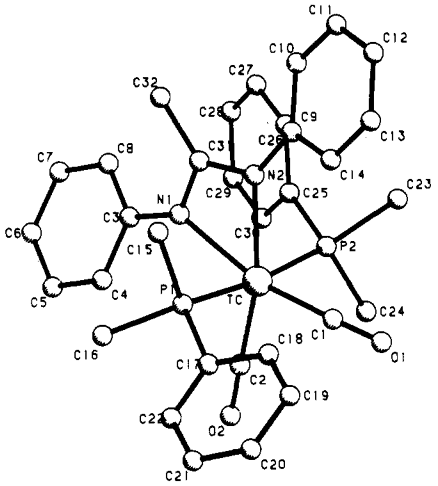

Figure 2. Crystal structure of [Tc(PMe_2Ph)$_2$(CO)$_2$(dpa)] (**1c**).

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Table II

		IR, cm^{-1} (Nujol)		^{1}H NMR, τ (CDCl$_3$)			
no.	compd[a]	ν(CO)	ν(L)	aryl	CH	Me	
1a	[Tc(PMe$_2$Ph)$_2$(CO)$_2$(dtt)]	1920, 1845	1260	2.7 (m)		7.7 (s, PhMe)	8.43 (t, PMe)
1b	[Tc(PMe$_2$Ph)$_2$(CO)$_2$(dct)]	1920, 1845	1265	2.8 (m)			8.43 (t, PMe)
1c	[Tc(PMe$_2$Ph)$_2$(CO)$_2$(dpa)]	1915, 1835	1260	2.8 (m)		8.25 (m, CMe)	8.43 (t, PMe)
1d	[Tc(PMe$_2$Ph)$_2$(CO)$_2$(dtf)]	1920, 1840	1260	3.0 (m)	1.8 (m)	7.7 (s, PMe)	8.43 (t, PMe)
1e	[Tc(PPh$_3$)$_2$(CO)$_2$(dtt)]	1920, 1845	1270	2.7 (m)		7.7 (s, PMe)	

[a] dtt = p-MeC$_6$H$_4$N$\cdots$N$\cdots$NC$_6$H$_4$Me-p]$^-$; dct = [p-ClC$_6$H$_4$N$\cdots$N$\cdots$NC$_6$H$_4$Cl-p]$^-$; dpa = [C$_6$H$_5$N$\cdots$C(Me)$\cdots$NC$_6$H$_5$]$^-$; dtf = [p-MeC$_6$H$_4$N$\cdots$CH$\cdots$NC$_6$H$_4$Me-p]$^-$.

Table III. Positional ($\times 10^4$) and Thermal (Å^2) Parameters with Esd's in Parentheses

	1c				**1a**			
	x	y	z	B_{eq}[a]	x	y	z	B_{eq}[a]
Tc	−5.1 (3)	2333.9 (2)	1219.2 (1)	2.312 (4)	139.5 (3)	1960.3 (3)	1293.2 (1)	2.993 (7)
P(1)	358 (1)	1138.2 (6)	1543.5 (2)	3.03 (2)	−661 (1)	503 (1)	1107.2 (4)	3.89 (3)
P(2)	−633 (1)	3497.2 (6)	914.5 (2)	2.93 (2)	713 (1)	3436 (1)	1497.9 (4)	3.72 (3)
N(1)	−2052 (3)	1760 (2)	1038 (1)	2.53 (6)	−927 (4)	2601 (3)	889 (1)	3.3 (1)
N(2)	−2170 (3)	2522 (2)	1461 (1)	2.57 (6)	−1774 (4)	2314 (3)	1357 (1)	3.1 (1)
N(3)					−1973 (4)	2643 (3)	1047 (1)	3.2 (1)
O(1)	2285 (3)	3379 (2)	1554 (1)	5.7 (1)	1061 (4)	1127 (3)	1962 (1)	6.6 (1)
O(2)	2430 (3)	1841 (2)	751 (1)	6.0 (1)	2684 (4)	1645 (4)	1020 (1)	8.1 (1)
C(1)	1421 (4)	2961 (2)	1432 (1)	3.3 (1)	690 (5)	1443 (4)	1702 (2)	3.9 (1)
C(2)	1494 (4)	2024 (3)	931 (1)	3.5 (1)	1694 (5)	1758 (4)	1120 (2)	4.6 (1)
C(3)	−2485 (4)	1335 (2)	763 (1)	2.7 (1)	−847 (5)	2958 (4)	558 (1)	3.3 (1)
C(4)	−1389 (4)	892 (2)	602 (1)	3.4 (1)	278 (5)	2970 (5)	403 (2)	4.6 (1)
C(5)	−1723 (5)	460 (3)	325 (1)	4.4 (1)	446 (5)	3346 (5)	84 (2)	5.1 (2)
C(6)	−3136 (6)	480 (3)	199 (1)	4.8 (1)	−486 (6)	3723 (4)	−102 (2)	4.6 (1)
C(7)	−4209 (5)	934 (2)	346 (1)	4.5 (1)	−1621 (5)	3682 (5)	52 (2)	4.7 (1)
C(8)	−3902 (4)	1365 (2)	624 (1)	3.4 (1)	−1812 (5)	3306 (4)	372 (1)	3.9 (1)
C(9)	−2696 (4)	2946 (2)	1728 (1)	2.7 (1)	−2786 (4)	2139 (3)	1651 (1)	3.1 (1)
C(10)	−4167 (4)	3229 (2)	1759 (1)	3.2 (1)	−2583 (5)	1957 (4)	1909 (1)	3.8 (1)
C(11)	−4578 (5)	3670 (3)	2026 (1)	4.2 (1)	−3545 (5)	1729 (4)	2117 (2)	4.7 (1)
C(12)	−3562 (5)	3858 (3)	2264 (1)	4.8 (1)	−4712 (5)	1675 (4)	2000 (2)	4.3 (1)
C(13)	−2099 (5)	3602 (3)	2229 (1)	4.8 (1)	−4907 (5)	1852 (4)	1655 (2)	4.1 (1)
C(14)	−1681 (4)	3159 (3)	1965 (1)	3.8 (1)	−3967 (5)	2078 (4)	1436 (1)	3.6 (1)
C(15)	−1138 (5)	909 (3)	1826 (1)	5.5 (1)	−934 (8)	−259 (5)	1465 (2)	8.3 (2)
C(16)	405 (6)	223 (2)	1311 (1)	4.9 (1)	−2110 (6)	520 (5)	895 (2)	7.3 (2)
C(17)	2009 (4)	1061 (2)	1803 (1)	3.2 (1)	171 (5)	−201 (4)	805 (2)	5.3 (1)
C(18)	2306 (5)	1664 (3)	2025 (1)	4.8 (1)	214 (9)	−1092 (5)	815 (2)	9.1 (3)
C(19)	3506 (6)	1625 (3)	2230 (1)	6.2 (1)	827 (10)	−1600 (6)	563 (3)	13.9 (3)
C(20)	4463 (6)	979 (3)	2213 (1)	6.1 (1)	1235 (9)	−1268 (7)	311 (3)	19.5 (3)
C(21)	4213 (5)	394 (3)	1994 (1)	5.5 (1)	1245 (14)	−401 (9)	309 (4)	42.0 (4)
C(22)	2992 (5)	424 (3)	1792 (1)	4.2 (1)	684 (12)	143 (6)	542 (3)	28.3 (3)
C(23)	−1089 (6)	4364 (2)	1158 (1)	4.8 (1)	349 (9)	4390 (4)	1228 (2)	7.1 (2)
C(24)	816 (5)	3906 (3)	659 (1)	6.1 (1)	2330 (6)	3619 (6)	1566 (2)	7.2 (2)
C(25)	−2235 (4)	3425 (2)	648 (1)	3.2 (1)	53 (5)	3751 (3)	1908 (2)	3.6 (1)
C(26)	−3661 (4)	3545 (3)	764 (1)	4.5 (1)	625 (6)	3537 (5)	2215 (2)	5.3 (2)
C(27)	−4872 (5)	3469 (3)	562 (2)	8.0 (2)	71 (8)	3759 (5)	2525 (2)	7.1 (2)
C(28)	−4678 (7)	3281 (3)	243 (2)	10.7 (1)	−1044 (8)	4194 (5)	2525 (2)	8.0 (2)
C(29)	−3298 (9)	3151 (4)	129 (1)	9.5 (2)	−1589 (7)	4391 (6)	2224 (2)	7.3 (2)
C(30)	−2089 (6)	3214 (3)	327 (1)	5.5 (1)	−1065 (6)	4168 (5)	1918 (2)	6.2 (2)
C(31)	−2940 (4)	2036 (2)	1269 (1)	2.6 (1)	−279 (7)	4147 (6)	−446 (2)	7.1 (2)
C(32)	−4502 (5)	1750 (2)	1334 (1)	3.7 (1)	−5755 (6)	1392 (5)	2228 (2)	6.1 (2)

[a] $B_{eq} = 8\pi^2 U_{eq}$ according to Hamilton.[21]

structure factors and anisotropic thermal parameters have been deposited as supplementary material. Relevant bond distances and angles are given in Tables IV and V, and views of the two molecules with atom-labeling schemes are shown in Figures 1 and 2. All calculations were done with the CAD-4-SDP system of programs.[22]

Results and Discussion

The new complexes [Tc(PR$_3$)(CO)$_2$(ArN$\cdots$X$\cdots$NAr)] were prepared in satisfactory yields (80%) by adding [Tc(PMe$_2$Ph)$_3$(CO)$_2$Cl] or [Tc(PPh$_3$)$_2$(CO)$_3$Cl] as a solid to a PhH solution of the lithium salt of the appropriate ligand, generated in situ by treating LH with Li(n-Bu).

The IR spectra of the starting compounds and complexes are reported in Table II. These latter complexes show two strong bands having about the same intensity in the 1920–1915- and 1845–1835-cm^{-1} ranges. From their intensity ratio and by the equation[15] $I_{asym}/I_{sym} = (1 - \cos \sigma)/(1 + \cos \sigma)$, the CO–Tc–CO bond angle (σ) is found to be about 90°, suggesting a cis structure

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Table IV. Selected Bond Distances (Å) with Esd's in Parentheses

	1c	**1a**		**1c**	**1a**
Tc–P(1)	2.431 (1)	2.432 (1)	N(1)–N(3)		1.310 (5)
Tc–P(2)	2.387 (1)	2.391 (1)	N(2)–N(3)		1.320 (4)
Tc–N(1)	2.202 (2)	2.178 (4)	N(1)–C(3)	1.396 (4)	1.393 (5)
Tc–N(2)	2.203 (2)	2.190 (3)	C(3)–C(4)	1.399 (4)	1.381 (6)
Tc–C(1)	1.874 (3)	1.872 (5)	C(4)–C(5)	1.393 (4)	1.371 (7)
Tc–C(2)	1.876 (3)	1.867 (5)	C(5)–C(6)	1.366 (5)	1.373 (7)
			C(6)–C(7)	1.373 (6)	1.390 (7)
P(1)–C(15)	1.823 (4)	1.808 (7)	C(7)–C(8)	1.385 (5)	1.377 (6)
P(1)–C(16)	1.807 (4)	1.801 (6)	C(8)–C(3)	1.395 (4)	1.387 (6)
P(1)–C(17)	1.832 (3)	1.814 (5)	N(2)–C(9)	1.394 (4)	1.393 (5)
P(2)–C(23)	1.812 (4)	1.794 (6)	C(9)–C(10)	1.407 (4)	1.396 (6)
P(2)–C(24)	1.810 (4)	1.824 (6)	C(10)–C(11)	1.383 (4)	1.378 (6)
P(2)–C(25)	1.817 (3)	1.814 (5)	C(11)–C(12)	1.378 (5)	1.369 (7)
C(1)–O(1)	1.157 (4)	1.179 (5)	C(12)–C(13)	1.389 (5)	1.383 (7)
C(2)–O(2)	1.158 (4)	1.173 (5)	C(13)–C(14)	1.372 (5)	1.382 (6)
			C(14)–C(9)	1.384 (4)	1.395 (6)
N(1)–C(31)	1.326 (3)				
N(2)–C(31)	1.331 (4)				
C(31)–C(32)	1.502 (4)				

Table V. Selected Bond Angles (deg) with Esd's in Parentheses

	1c	**1a**
P(1)–Tc–P(2)	173.97 (3)	173.80 (4)
P(1)–Tc–N(1)	86.6 (1)	88.1 (1)
P(1)–Tc–N(2)	89.1 (1)	83.8 (1)
P(1)–Tc–C(1)	96.3 (1)	90.9 (2)
P(1)–Tc–C(2)	91.7 (1)	95.0 (2)
P(2)–Tc–N(1)	88.9 (1)	89.6 (1)
P(2)–Tc–N(2)	85.2 (1)	90.2 (1)
P(2)–Tc–C(1)	87.3 (1)	89.8 (2)
P(2)–Tc–C(2)	93.3 (1)	91.2 (2)
N(1)–Tc–N(2)	59.0 (1)	57.2 (1)
N(1)–Tc–C(1)	166.5 (1)	165.4 (2)
N(1)–Tc–C(2)	105.0 (1)	107.7 (2)
N(2)–Tc–C(1)	107.8 (1)	108.2 (2)
N(2)–Tc–C(2)	163.9 (1)	164.9 (2)
C(1)–Tc–C(2)	88.1 (1)	86.9 (2)
Tc–C(1)–O(1)	176.8 (3)	178.5 (4)
Tc–C(2)–O(2)	179.2 (3)	178.0 (5)
N(1)–C(31)/N(3)–N(2)	109.4 (2)	105.4 (3)
N(1)–C(31)–C(32)	125.0 (3)	
N(2)–C(31)–C(32)	124.9 (3)	
C(31)/N(3)–N(1)–Tc	95.8 (2)	99.1 (3)
C(31)/N(3)–N(1)–C(3)	126.8 (2)	118.2 (4)
C(3)–N(1)–Tc	136.9 (2)	142.7 (3)
N(1)–C(3)–C(4)	117.8 (3)	117.8 (4)
N(1)–C(3)–C(8)	124.8 (3)	124.9 (4)
C(4)–C(3)–C(8)	117.3 (3)	117.3 (4)
C(31)/N(3)–N(2)–Tc	95.6 (2)	98.2 (2)
C(31)/N(3)–N(2)–C(9)	127.5 (2)	117.1 (4)
C(9)–N(2)–Tc	136.8 (2)	142.6 (3)
N(2)–C(9)–C(10)	124.0 (3)	117.3 (4)
N(2)–C(9)–C(14)	118.1 (3)	124.2 (4)
C(10)–C(9)–C(14)	117.7 (3)	118.4 (4)

for the complexes. Substitution of the Cl^- and PMe_2Ph ligands in $[Tc(PMe_2Ph)_3(CO)_2Cl]$ with $ArN\overset{\cdots}{-}X\overset{\cdots}{-}NAr$ causes a slight increase in $\nu(C{=}O)$, while the substitution of Cl^- and CO in $Tc(PPh_3)_2(CO)_3Cl$ exhibits a marked lowering. This trend in the $\nu(C{=}O)$ values follows the expected π-acceptor order CO ≫ pseudoallyl > phosphine. The $\nu(C{=}O)$ values reported in Table II are closely related to those of the corresponding rhenium(I) complexes $[Re(PPh_3)_2(CO)_2(ArN\overset{\cdots}{-}X\overset{\cdots}{-}NAr)]$ (1925–1893- and 1840–1815-cm^{-1} ranges)[10] as well as to those of rhenium(I) complexes with Schiff bases, $[Re(CO)_2LP_2]$ (L = *N*-methyl-, *N*-phenyl-, half *N*,*N′*-ethylenebis(salicylideneaminate) or hydroxyquinolinate; P = PMe_2Ph or PPh_3; 1915–1893- and 1834–1810-cm^{-1} ranges).[16] The high $\nu(C{=}O)$ values reported for the technetium(I) cationic complexes *cis*- or *trans*-$[Tc(P(OEt)_2Ph)_4(CO)_2]^+$ (1939 and 1933 cm^{-1} and 2028 and 1937 cm^{-1}, respectively) indicate that the positive charge inhibits the back electron shift from the metal to CO antibonding π orbitals, causing the CO frequencies to rise.[17] The triazenido complexes show a significant ligand band at about 1260 cm^{-1}, which is characteristic of the chelating ligands.[18]

The proton NMR spectra of the complexes are also reported in Table II. The methyl resonances of the two dimethylphenylphosphine are a 1:2:1 triplet at τ 8.43. This triplet arises when the complexes have a plane of symmetry passing through the technetium and phosphorus atoms.[19] It follows, therefore, that the phosphines are mutually in trans positions.

The methyne proton of complex **1d** and the protons of the corresponding methyl group in complex **1c** show a multiplet at τ 1.8 and a triplet at τ 8.25, respectively, owing to coupling with the phosphorus atoms. The methyl protons of the ligands in complexes **1a**, **1d**, and **1e** show the same resonance at τ 7.7.

Description and Discussion of the Structures

Both crystal structures consist of discrete monomeric units with no molecules of solvation. The coordination around the Tc atoms is very roughly octahedral with the two PMe_2Ph ligands in the trans apical positions, forming P–Tc–P angles of 173.97 (3)° in **1c** and 173.80 (4)° in **1a**, and the acetamidinato and triazenido ligands coordinated in a bidentate fashion. The maximum deformations from octahedral symmetry are observed in the equatorial plane as a consequence of the small bite of the bidentate ligand; the N(1)–Tc–N(2) angles are 59.0 (1)° in **1c** and 57.2 (1)° in **1a** while the N–Tc–C(cis) angles are widened in the range 105.0–108.2°. All other X–Tc–X′(cis) angles do not differ from orthogonality by more than 6.3°. The best comparison between the **1c** and **1a** coordination polyhedra is obtained by interchanging C(1) with C(2) and N(1) with N(2) in one of the two compounds, in such a case all differences between corresponding X–Tc–X′(cis) angles are smaller than 4.4°.

The conformation of PMe_2Ph ligands is somewhat different in the two compounds. In **1c** the P–C(phenyl) bonds nearly eclipse an equatorial ligand (C(1)–Tc–P(1)–C(17) = −14.1° and N(1)–Tc–P(2)–C(25) = −6.3°); the same happens in **1a** for C-

Table VI. Structural Parameters[a] for Mononuclear Triazenido $[RN\overset{\cdots}{-}N\overset{\cdots}{-}R]^-$ and Amidinato $[RN\overset{\cdots}{-}C(R')\overset{\cdots}{-}NR]^-$ Complexes[b]

complex	R′	M–N	N–M–N	N–N or N–C	N–N–N or N–C–N	N–N–C(R_1) or N–C–C(R_1)	C–C–C[c]	ref
trans-$[Tc^I(PMe_2Ph)_2(dtt)]$ (**1a**)		2.186 (6)	57.2 (1)	1.316 (5)	105.4 (3)	117.6 (6)	117.8 (5)	this work
trans-$[Ru^{II}(PPh_3)_2(H)(CO)(dtt)]$		2.164 (15)	57.7 (1)	1.314 (4)	105.2 (3)	115.6 (4)	rbr	24
$[Re^{III}(PPh_3)_2(Cl)_2(dtt)]$		2.05 (4)	58 (1)	1.31 (2)	99 (2)	115 (3)	120 (2)	25
$[Co^{III}(dpt)_3]$		1.919 (6)	65.1 (2)	1.321 (5)	102.9 (4)	119.4 (4)	120.3 (4)	26
$[Cr^{III}(dpt)_3]$		2.01 (1)	62.4 (8)	1.31 (2)	105 (1)	117.3 (9)	124.0 (6)	27
averages			58.3 (12)	1.316 (3)	104.7 (6)	117.5 (8)		
trans-$[Tc^I(PMe_2Ph)_2(CO)_2(dpa)]$ (**1c**)	Me	2.203 (1)	59.0 (1)	1.329 (3)	109.4 (2)	127.2 (4)	117.5 (2)	this work
trans-$[Ru^{II}(PPh_3)_2(H)(CO)(dtf)]$	H	2.22 (3)	59.8 (2)	1.311 (5)	114.7 (5)	123 (1)	rbr	28
trans-$[Ru^{II}(PPh_3)_2(CO)(Cl)(iif)]$	H	2.14 (9)	61.1 (4)	1.31 (1)	113 (1)			29
trans-$[Re^I(PPh_3)_2(CO)_2(dtf)]$	H	2.22 (1)	60.0 (1)	1.33 (1)	112 (1)	124 (1)	120.6 (8)	10
averages			60.0 (2)	1.314 (5)	114.0 (8)	123.5 (7)		

[a] Distances are in angstroms; angles are in degrees. [b] Values are weighted averages when more than one equivalent parameter is present; the esd's or the esd's of the weighted averages are in parentheses. [c] C–C–C = phenyl ring angle at the ipso carbon with respect to the N-substituent; rbr = rigid-body refinement; a = acetamidinato, f = formamidinato, t = triazenido; di = *N*,*N′*-diisopropyl, dp = *N*,*N′*-diphenyl, dt = *N*,*N′*-di-*p*-tolyl, ii = *N*-isopropyl-*N′*-isopropenyl.

(2)–Tc–P(1)–C(17) = −13.2°, while the P(2) phosphine ligand is slightly rotated in such a way that the P–C(methyl) bond nearly eclipses Tc–N(1) (N(1)–Tc–P(2)–C(23) = −10.7°).

Tc–P distances are similar in the two compounds (Tc–P(1) = 2.431 (1) Å in **1c** and 2.423 (1) Å in **1a**; Tc–P(2) = 2.387 (1) Å in **1c** and 2.391 (1) Å in **1a** but differ inside each complex, Tc–P(1) being on the average longer, without any apparent reason, than Tc–P(2) by 0.038 Å. In the only other P-containing complex of Tc(I) the Tc–P distances have been found to be in the range 2.38–2.44 Å.[17] Tc–CO distances of 1.87–1.88 Å compare well with those reviewed[23] in a variety of Tc(I)–Tc(III) compounds (1.86–1.90 Å). Tc–N distances are 2.202 (2) and 2.203 (2) Å in **1c** and 2.178 (4) and 2.190 (3) Å in **1a**. They are indistinguishable within each compound, which parallels the identity of the two trans CO substituents, while their average is possibly slightly shorter in the triazenido case. The structures of **1c** and **1a** permit an accurate comparison of acetamidinato and triazenido ligands in a strictly comparable molecular environment. The coordination geometries are not perfectly identical, as Tc, N(1), N(2), and N(3) lie strictly on the same plane in **1a**, while in **1c** C(31) is out of the Tc,N(1),N(2) plane by 0.055 Å. Both ligands are symmetrical as far as the pseudoallylic anion is concerned, C(31)–N(1) and C(31)–N(2) being 1.326 (4) and 1.331 (4) Å and N(1)–C(3) and N(2)–C(9) 1.396 (4) and 1.394 (4) Å in **1c** and N(3)–N(1) and N(3)–N(2) being 1.310 (5) and 1.320 (4) Å and N(1)–C(3) and N(2)–C(9) 1.393 (5) and 1.393 (5) Å in **1a**. This can be taken as the indication of a complete delocalization of the π-system in the two anions and agrees with the symmetry of the couples of Tc–N distances. The phenyl and *p*-tolyl groups are slightly out of plane with respect to the mean Tc,N(1),N(2),N(3)/C(31) plane, actual dihedral angles (τ) being 24.7 and 25.6° and 6.7 and 24.3° for the C(3)–C(8) and C(9)–C(14) planes in **1c** and **1a**, respectively. This corresponds to a substantial coupling of the π-systems on the pseudoallyl fragment and the two terminal aromatic rings. In fact, the superposition integral of two p_π atomic orbitals located on adjacent atoms decreases with the cosine of their dihedral angle τ, being 1 for $\tau = 0$ and as high as 0.90 for the maximum τ observed, which is 25.6°. Analysis of literature data shows that in such or similar ligands τ ranges from 5° ($\cos \tau = 0.996$) to 36° ($\cos \tau = 0.81$), indicating a definite tendency to planarity of the whole ligand perturbed by nonbonded interactions but not till decoupling of the π-system occurs.

Table VI collects some structural parameters of the triazenido, acetamidinato, and formamidinato anionic ligands as observed in some mononuclear transition-metal complexes. While the overall precision of the data is not sufficient to establish whether the N–C and N–N distances are different, the angular values inside the ligands seem to indicate a systematic trend. In particular, the N–(C/N)–N angle increases in the series triazenido, acetamidinato, and formamidinato, being respectively 104.7 (6), 109.4 (2), and 114.0 (8)°. It is clear that the effect runs in reverse order with respect to the putative effect of the steric hindrance of the C-substituent; it can be easily rationalized in terms of the VSEPR[30] model, the room taken by the nonbonding pair on N being greater than the room taken by the C–H and C–C bonding pairs and the room taken by the $\mathrm{C{-}CH_3}$ bonding pair being smaller than that of the C–H bond as the methyl group is less electronegative than hydrogen. The increase of the N–(C/N)–N angle is paralleled by that of the bite of the bidentate ligand (see N–M–N angles in Table VI) and by a change of the (C/N)–N–C angles, which are smaller in the triazenido case.

A last point concerns the values of the C(4)–C(3)–C(8) and C(10)–C(9)–C(14) endocyclic phenyl angles; these are, on average, 117.5 (2)° in **1c** and 117.8 (5)° in **1a**, i.e. significantly smaller than 120°. It may be of interest to compare these values with others in the literature (last column of Table VI). It is found that angles in opposite phenyl rings are always identical within 2σ but that their average value changes: for instance it is close to 120° (e.g. 120.6 (8)° in $\mathrm{Re^{I}(PPh_3)_2(CO)_2(dpf)}$[10]) or much greater than 120° (e.g. 124.0 (6)° in $\mathrm{Cr^{III}(dpt)_3}$[27]). As it is known that the endocyclic phenyl angle changes from 114 to 125° according to the nature of the ipso substituent, being respectively smaller or larger than 120° for electron-donating or electron-attracting substitutents.[31] it may be tentatively suggested that the value of this angle can be an indirect indicator of the electron density on the pseudoallylic fragment or, more generally, of the π-backbonding from the metal.

Registry No. **1a**, 99354-91-3; **1b**, 99354-92-4; **1c**, 99354-93-5; **1d**, 99354-94-6; **1e**, 99354-95-7; *mer*-$\mathrm{[Tc(PMe_2Ph)_3(CO)_2Cl]}$, 64347-48-4; *trans*-$\mathrm{[Tc(PPh_3)_2(CO)_3Cl]}$, 64396-16-3.

Supplementary Material Available: Tables of anisotropic thermal parameters, hydrogen atom positional parameters, and structure factor amplitudes for both compounds (45 pages). Ordering information is given on any current masthead page.

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Notes

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Direct Observation of the $\mathrm{HTiO_3^-}$ Ion

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Received February 11, 1985

The existence of $\mathrm{H_2TiO_3}$, sometimes called metatitanic acid, in the hydrolysis of Ti(IV) halides is supported by thermodynamic[1,2] and kinetic[3] studies. In aqueous solution it ionizes to cations containing the metal,[4] and bases derived from it that contain the metal are not well-characterized. Although the empirical formulas of some minerals of both the ilmenite and perovskite structures correspond to $\mathrm{MTiO_3}$, the $\mathrm{TiO_3^{2-}}$ ion does not occur as a discrete unit in such minerals.[5] To our knowledge no report exists of the $\mathrm{HTiO_3^-}$ ion, although a recent report on formation of calcium titanates contains results for empirical formulas suggesting the existence of the related $\mathrm{HTi_2O_5^-}$ ion.[6]

This absence of $\mathrm{HTiO_3^-}$ from the literature is vexing in view of the obvious stability of $\mathrm{HCO_3^-}$ and of numerous citations of $\mathrm{HSiO_3^-}$,[7] ions whose chemistry it could be expected to resemble

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