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Multiple Bonds between Main Group Elements and Transition Metals. 95.[1] Synthesis and Reactivity of $TcCl(CO)_3[P(C_6H_5)_3]_2$: Novel Technetium Complexes of 1,4,7-Triazacyclononane and Hydridotris(pyrazolyl)borate

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trans-$TcCl(CO)_3[P(C_6H_5)_3]_2$ (**2**) is accessible in 95% yield by treatment of the easily available Tc(V) ionic precursor $[TcOCl_4]^-$ (**1**) with triphenylphosphine in an atmosphere of carbon monoxide (1 atm). **2** is recognized as a useful starting material for subsequent substitution reactions, especially with tridentate nitrogen ligands. Thus, the compounds $[(C_6H_{15}N_3)Tc(CO)_2\{P(C_6H_5)_3\}]Cl$ (**5**) and $[HB(C_3H_3N_2)_3]Tc(CO)_2\{P(C_6H_5)_3\}]$ (**6**) were synthesized in good yields. The structures of compounds **2**, **5**, and **6** were determined by single-crystal X-ray diffraction techniques. **2** crystallizes in the triclinic space group $P\bar{1}$ (No. 2) with $a = 10.245$ (1) Å, $b = 12.744$ (1) Å, $c = 14.423$ (1) Å, $\alpha = 69.42$ (1)°, $\beta = 74.89$ (1)°, $\gamma = 81.51$ (1)°, $R = 0.029$, and $R_w = 0.025$. Compound **5** crystallizes in the monoclinic space group $P2_1/c$ (No. 14) with $a = 12.997$ (5) Å, $b = 8.680$ (1) Å, $c = 25.189$ (5) Å, $\beta = 101.13$ (4)°, $R = 0.059$, and $R_w = 0.037$. Compound **6** crystallizes in the monoclinic space group $C2/c$ (No. 15) with $a = 31.191$ (8) Å, $b = 9.7252$ (6) Å, $c = 18.818$ (5) Å, $\beta = 93.36$ (1)°, $R = 0.045$, and $R_w = 0.033$.

Introduction

Although the chemistry of the artificial element technetium has received enormous interest within the last two decades, owing to its importance in radiodiagnostics,[2,3] many aspects of its chemistry are as yet hardly understood. Due to applications in nuclear medicine, the chemistry of the oxidation states +IV and +V is best developed. These oxidation states are easily accessible by reduction of the pertechnetate ion $[TcO_4]^-$ with divalent tin in aqueous systems.[4]

The behavior of the lower oxidation states between +II and −I, the traditional field of organometallic chemistry, is not systematically explored. Lack of suitable precursor compounds and/or scarce knowledge about reactivity of the known species are responsible for this underdevelopment.[5,6] Typically, precursor compounds such as $Tc_2(CO)_{10}$, $TcX(CO)_5$ (X = halogen), and $[Tc(CO)_6]^+$ are not easily available.[7-9] These compounds are known, but they cannot be synthesized readily due to radiation safety problems associated with high-pressure reactions. Another reason may arise from the attitude that organotechnetium compounds are not suited for applications in nuclear medicine, an assessment which was convincingly contradicted by Davison's cationic isonitrile complexes of the formula $[Tc(CNR)_6]^+$.[10,11]

We now wish to report a new, easy synthesis of the useful starting material *trans*-$TcCl(CO)_3[P(C_6H_5)_3]_2$, (**2**) from $[TcOCl_4]^-$ (**1**; tetrakis(*n*-butyl)ammonium salt). We also describe the synthesis and full characterization of the novel technetium(I) complexes $[(TAN)Tc(CO)_2\{P(C_6H_5)_3\}]Cl$ (**5**) and $[\{HB(pyz)_3\}]Tc(CO)_2[P(C_6H_5)_3]$ (**6**) [$HB(pyz)_3$ = hydridotris(pyrazolyl)borate; TAN = 1,4,7-triazacyclononane].

Experimental Section

Caution! Since ^{99}Tc is a weak β^--emitter ($\beta_{max} = 0.29$ MeV, $T_{1/2} = 2.12 \times 10^5$ y), all manipulations were carried out in a low-pressure glovebox. No volatile technetium complexes could be detected during the syntheses.

$NH_4[TcO_4]$ was obtained as a gift from the Paul Scherrer Institut (Würenlingen, Switzerland). Carbon monoxide was purchased as proanalysi quality from Linde GmbH. All other chemicals were received from Aldrich Co. and were used without further purification. Technetium analysis was done by liquid scintillation counting. A known amount of a complex was dissolved in the scintillation cocktail, and the decays were counted on a Beckman LS 6300 counter.

$[N(n\text{-}C_4H_9)_4][TcO_4]$ was prepared by precipitation of an aqueous solution of $[NH_4][TcO_4]$ with $[N(n\text{-}C_4H_9)_4]Cl$. The starting complex $[N(n\text{-}(C_4H_9)_4][TcOCl_4]$ (**1**) was prepared in over 90% yield from $[N(n\text{-}C_4H_9)_4][TcO_4]$ and concentrated HCl according to a described protocol.[12,13] However, $TcCl(CO)_3[P(C_6H_5)_3]_2$ (**2**) was not prepared by a standard protocol.[14,15] With the following method we achieved yields better than 90% for this particular compound.

Preparation of $TcCl(CO)_3[P(C_6H_5)_3]_2$ (2). A 25-mL two-necked round-bottom flask equipped with a reflux condenser was flushed three times with CO. Under a stream of CO, 435 mg (0.87 mmol) of $[N(n\text{-}C_4H_9)_4][TcOCl_4]$ (**1**), 12 mL of toluene, and 2 mL of CH_3CN were transferred into the flask. A 714-mg (2.7-mmol) amount of triphenylphosphine was then added under vigorous stirring, before the system was tightly closed. The solution was very dark, but no precipitation took place. The reaction mixture was kept for 4 h at 110 °C, during which period the solution turned colorless and a white precipitate formed. No intermediate color could be observed. The suspension was then cooled, and the solvent was removed in vacuo. The remaining white powder was washed three times with cold methanol (0 °C) and recrystallized from CH_2Cl_2/*n*-hexane by the slow diffusion technique. Long, white needles of X-ray quality were formed. The compound is soluble in methylene chloride and THF, slightly soluble in methanol and acetone, and insoluble in nonpolar organic solvents and water. Yield: 1.20 g (95%).

Anal. Calcd for $C_{39}H_{30}ClP_2O_3Tc$: Tc, 13.31. Found: Tc, 13.47. IR (KBr, cm^{-1}): 2057 (w), 1962 (vs), 1919 (s). ^1H-NMR ($CDCl_3$, 25 °C, δ in ppm): 7.72 [CH, (m)]. ^{99}Tc-NMR ($CDCl_3$, 25 °C, δ in ppm vs $\delta(TcO_4^-) = 0$ ppm): $\delta(Tc) = -1645$.

Preparation of $[(C_6H_{15}N_3)Tc(CO)_2\{P(C_6H_5)_3\}]Cl$ (5). A 190-mg (0.27-mmol) amount of **2** dissolved in 4 mL of warm THF (Schlenk tube) under N_2. A 37-mg (0.29-mmol) amount of 1,4,7-triazacyclononane was then added under stirring. Small amounts of a white precipitate formed quickly. The temperature was increased to 70 °C. Evolution of CO was observed while more precipitate formed. After 2 h, the reaction was complete and the white precipitate was filtered off. Some 3% of the total activity (Tc) remained in solution. The filtrate was washed with cold THF and was dried in vacuo. Recrystallization from CH_3OH/CH_2Cl_2/*n*-hexane by the slow diffusion technique gave 136 mg (92%) of **5** as white needles. Anal. Calcd for $C_{26}H_{30}ClPO_2N_3Tc$: Tc, 17.00. Found: Tc, 17.12. IR (KBr, cm^{-1}): 1936 (vs), 1849 (vs), 1481 (w), 1454 (w), 1433 (m), 1092 (w), 752 (m), 699 (m), 664 (w), 633 (w), 568 (w), 515 (m). ^{99}Tc-NMR (CD_3OD, 25 °C, δ in ppm vs $[TcO_4^-] = 0$ ppm): $\delta(Tc) = -934$.

Preparation of $[HB(pyz)_3]Tc(CO)_2[P(C_6H_5)_3]$ (6). A 53-mg (0.07-mmol) amount of **2** and 18 mg (0.07 mmol) of $K[HB(pyz)_3]$ were dis-

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Table I. Crystallographic Data for the Technetium(I) Complexes **2**, **5**, and **6**

compd	**2**	**5**	**6**
formula	$C_{39}H_{30}ClO_3P_2Tc$	$C_{26}H_{30}ClN_3O_2PTc{\cdot}CH_3OH$	$C_{29}H_{25}BN_6O_2PTc$
fw	742.1	580.9	629.3
space group	$P\bar{1}$, No. 2	$P2_1/c$, No. 14	C_2/c, No. 15
cryst system	triclinic	monoclinic	monoclinic
a, Å	10.245 (1)	12.997 (5)	31.191 (8)
b, Å	12.744 (1)	8.680 (1)	9.7252 (6)
c, Å	14.423 (1)	25.189 (5)	18.818 (5)
α, deg	69.42 (1)		
β, deg	74.89 (1)	101.13 (4)	93.36 (1)
γ, deg	81.51 (1)		
V, Å^3	1698	2788	5699
Z	2	4	8
ρ_{calcd}, g·cm^{-3}	1.45	1.46	1.47
R^a	0.029	0.059	0.045
$R_w{}^b$	0.025	0.037	0.033
GOF^c	2.305	1.990	2.461

$^a R = \sum(||F_o| - |F_c||)/\sum|F_o|$. $^b R_w = [\sum_w(|F_o| - |F_c|)^2/\sum_w|F_o|^2]^{1/2}$. $^c \mathrm{GOF} = [\sum_w(|F_o| - |F_c|)^2/(\mathrm{NO} - \mathrm{NV})]^{1/2}$.

solved in 10 mL of THF, and the solution was heated for 5 h at 70 °C. Small amounts of a white precipitate were formed slowly, and the color of the solution turned yellowish. The solution was cooled to room temperature and filtered. The solvent was removed in vacuo, and the slightly yellow powder was washed twice with diethyl ether. The residue was dissolved in a mimimum amount of CH_2Cl_2. Slow diffusion of *n*-hexane into the methylene chloride induced the formation of 41 mg (91%) of **6** as yellowish blocks. Anal. Calcd for $C_{29}H_{25}BN_6O_2PTc$: Tc, 15.98. Found: Tc, 15.69. IR (KBr, cm^{-1}): 3082 (w), 3056 (w), 1937 (s), 1856 (s), 1436 (m), 1407 (m), 1309 (m), 1210 (m), 1114 (m), 1050 (m), 764 (m), 695 (m), 618 (m), 530 (m). ^{1}H-NMR ($CDCl_3$, 25 °C, δ in ppm): 7.78 (d, 1 H, CH), 7.60 (d, 2 H, CH), 7.54 (d, 1 H, CH), 7.31 (m, 3 H, CH), 7.25 (m, 6 H, CH), 7.12 (m, 6 H, CH), 6.67 (d, 2 H, CH), 6.12 (t, 1 H, CH), 5.80 (t, 2 H, CH). ^{99}Tc-NMR ($CDCl_3$, 25 °C, δ in ppm vs $\delta[TcO_4^-] = 0$ ppm): $\delta(Tc) = -1198$.

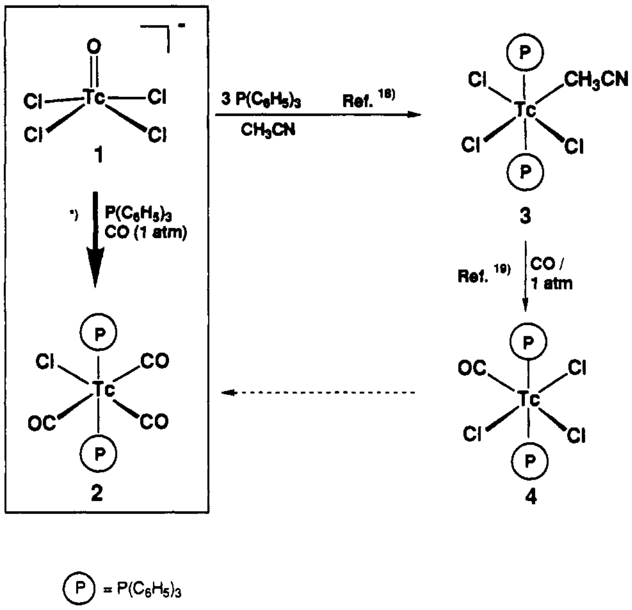
Crystallography and Refinement of Structures. The data related to the crystallographic studies of **2**, **5**, and **6** were collected on CAD-4 diffractometers (Enraf-Nonius) with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at ambient temperature. All computations were carried out on a MicroVAX-3100 computer with the program systems STRUX-III and SDP. The structures were solved by Patterson methods (SHELXS-86) and refined by subsequent least-squares and difference-Fourier techniques. Correction for Lorentz and polarization effects were applied. Hydrogen atoms were inserted for both structures at calculated positions but were not refined (d(C–H), d(B–H) and d(N–H) = 95 pm). Scattering factors were taken from ref 16, and anomalous scattering factors, from ref 17. Crystallographic details for **2**, **5**, and **6** are summarized in Table I.

Results and Discussion

I. Preparative Results. The Tc(I) complex $TcCl(CO)_3[P(C_6H_5)_3]_2$ (**2**) was synthesized in 95% yield, starting from the easily available precursor species $[TcOCl_4]^-$ (**1**) according to Scheme I. **2** is stable under atmospheric conditions and can be used as a convenient starting material for subsequent ligand substitution reactions. Addition of acetonitrile to the reaction mixture results in an increased reaction rate. This effect is not only due to the better solubility of **1** in the solvent but also for some stabilization of reduced Tc(I) intermediates by acetonitrile ligands before carbon monoxide can substitute these ligands.

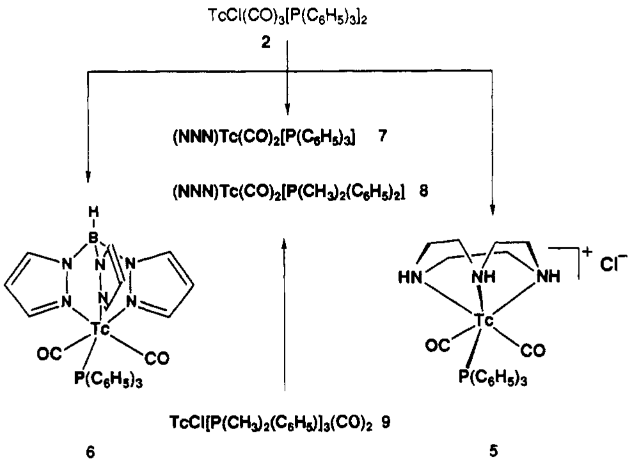
If methanol is used instead of acetonitrile, the reaction time is twice as long and yields are much lower. In the course of the reaction it is not important whether CO is bubbled through the solution or if there is just a CO atmosphere in a closed system. We could not observe either one of the two recently reported species $TcCl_3[P(C_6H_5)_3]_2(CH_3CN)$ (**3**) or $TcCl_3[P(C_6H_5)_3]_2(CO)$ (**4**).[18,19] We had expected both species to be stable intermediates during the reduction step. **3** is insoluble and should thus precipitate; **4** has an intense wine-red color. Nevertheless, we observed neither one of these characteristics. If these species are formed at all, they can only be present in very low steady-state concen-

Scheme I. Reaction Pathway to Compound **2** and Possible Intermediates **3** and **4**^{a}



^{a} **1** is present as the $[N(n\text{-}C_4H_9)_4]^+$ salt. An asterisk indicates the present work as reference.

Scheme II. Substitution Reactions of Compound **1** with the Tridentate Cyclic Amines TAN and $(HB(pyz)_3)^-$



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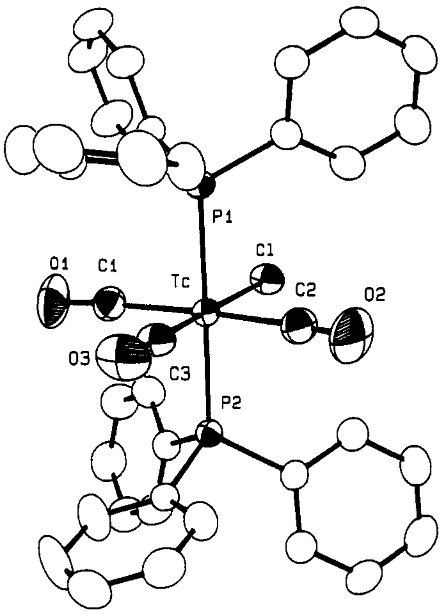

Figure 1. ORTEP drawing of *trans*-$TcCl(CO)_3[P(C_6H_5)_3]_2$ (**2**). Hydrogen atoms are omitted for clarity. Thermal ellipsoids are at the 50% probability level.

Table II. Selected Bond Lengths (Å) and Angles (deg) of the Tc(I) Complex $TcCl(CO)_3[P(C_6H_5)_3]_2$ (**2**) with Estimated Standard Deviations in Parentheses

	Bond Lengths		
Tc–Cl	2.5055 (4)	Tc–C3	1.887 (2)
Tc–P1	2.4404 (5)	C1–O1	1.126 (3)
Tc–P2	2.4454 (5)	C2–O2	1.121 (2)
Tc–C1	1.979 (2)	C3–O3	1.145 (2)
Tc–C2	1.983 (2)		
	Bond Angles		
Cl–Tc–P1	88.51 (1)	P1–Tc–P2	174.59 (2)
Cl–Tc–P2	87.34 (1)	P1–Tc–C1	88.35 (5)
Cl–Tc–C1	92.60 (6)	P1–Tc–C2	91.89 (5)
C3–Tc–Cl	178.84 (6)	P1–Tc–C3	91.38 (5)

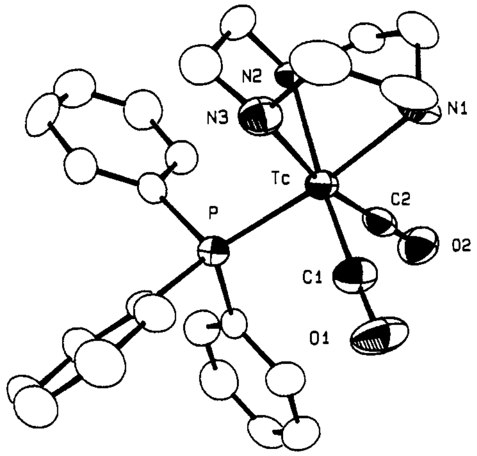

Figure 2. ORTEP drawing of the cation $[(TAN)Tc(CO)_2\{P(C_6H_5)_3\}]^+$ of complex **5**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are at the 50% probability level.

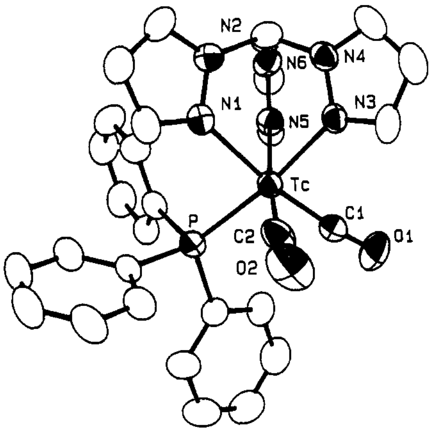

Figure 3. ORTEP representation of $[HB(pyz)_3]Tc(CO)_2[P(C_6H_5)_3]$ (**6**). Hydrogen atoms are omitted for clarity. Thermal ellipsoids are at the 50% probability level.

trations (Scheme I), and spectroscopic experiments should be performed to prove their existance. Furthermore, a carbonylation experiment on compound **4** and **3** under our conditions would induce **2** if these species were present.

2 is a useful starting material for subsequent substitution reactions by a variety of ligands. We especially concentrated on tridentate amines 1,4,7-triazacyclononane (TAN) and hydridotris(pyrazolyl)borate ($[HB(pyz)_3]^-$). According to Scheme II, one chloride, one carbon monoxide, and one triphenylphosphine are readily displaced by the incoming N,N,N-amines. The resulting complexes **5** and **6** are stable against oxygen and water, respectively. Even under severe reaction conditions, we did not succeed in substituting either one of the remaining CO or triphenylphosphine ligands. If compound **6** is refluxed in a mixture of 30% H_2O_2 and methanol, even after 5 h over 90% of the starting material is still present (no decomposition). No specific oxidation product was isolated.

It is interesting that mainly the products **5** and **6** were formed but not, for example, an analogous tricarbonyl compound of the form $[(TAN)Tc(CO)_3]^+$. The trans influence phenomenon is clearly responsible for this result. Since the amine ligands are only able to coordinate in a facial geometry, one phosphine must consequently be replaced. This is supported kinetically by the trans influence of the phosphines and the thermodynamic (entropic) stabilization of the resulting complex by a chelating effect. Other authors found similar effects when they used bidentate *pseudo*-allyl ligands such as triazenido and formamidinato (e.g. $p\text{-}CH_3C_6H_4N\text{-}N\text{-}NC_6H_4\text{-}p\text{-}CH_3$).[20] Compounds **7** and **8** (Scheme II) are also a result of trans influence. If one starts from compound **9**, one chloride and one phosphine are released; starting with **2**, one chloride and one carbon monoxide are substituted. These results are in good agreement with our observations.

II. Structural Results. (1) The Technetium(I) Complex *mer*-$TcCl(CO)_3[P(C_6H_5)_3]_2$ (2). Compound **2** has an almost undistorted octahedral core geometry with a meridional substitution pattern of the carbonyl ligands (Figure 1). The phosphines are located in trans positions to each other. The technetium–phosphorus distances differ only slightly [Tc–P1 = 2.4404 (5) Å and Tc–P2 = 2.4454 (5) Å]. They are in the usual range for low-valent complexes of technetium and rhenium.[21] It is noteworthy that the carbonyl group which is located trans to the chloro ligand has a shorter distance to technetium and a longer $C\equiv O$ distance than the others (Table II). This is an indication of stronger backbonding of this carbonyl group C3–O3 due to the trans influence of the chloride ligand.

(2) The Technetium(I) Complexes of 1,4,7-Triazacyclononane and Hydridotris(pyrazolyl)borate. Both compounds have an octahedral core geometry, with the three nitrogen atoms adopting facial positions of the polyhedron (Figures 2 and 3). The 1,4,7-triazacyclononane complex **5** has a shorter Tc–P bond than observed in compound **2**, shorter Tc–CO distances, and longer $C\equiv O$ bonds (Table IV). This observation corresponds to the IR data that also indicate weaker $C\equiv O$ bonds (ν(CO) stretch). The nitrogen atom N1 which is located in trans position to the phosphine ligand has a bond to the metal atom which is shortened by 0.05 Å as compared with the other nitrogen atoms.

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Table III. Final Fractional Atomic Coordinates and Equivalent Isotropic Displacement Parameters for **2** (Estimated Standard Deviations in Parentheses)[a]

atom	x/a	y/b	z/c	B_{eq}, Å^2
Tc	0.18307 (2)	0.01918 (2)	0.22772 (1)	2.143 (4)
Cl	0.42492 (6)	−0.03783 (5)	0.16298 (5)	3.18 (1)
P1	0.25458 (6)	0.20473 (5)	0.19845 (4)	2.35 (1)
P2	0.12647 (6)	−0.16651 (5)	0.24198 (4)	2.27 (1)
O1	0.0918 (2)	0.1166 (2)	0.0238 (1)	6.43 (6)
O2	0.2034 (3)	−0.0625 (2)	0.4533 (1)	7.44 (7)
O3	−0.1084 (2)	0.0882 (2)	0.3094 (2)	5.63 (6)
C1	0.1339 (3)	0.0794 (2)	0.0940 (2)	3.45 (6)
C2	0.2025 (3)	−0.0344 (2)	0.3705 (2)	3.73 (7)
C3	0.0016 (2)	0.0614 (2)	0.2791 (2)	3.30 (6)
C11	0.3762 (2)	0.2147 (2)	0.2688 (2)	2.55 (5)
C12	0.3939 (3)	0.3148 (2)	0.2806 (2)	3.26 (6)
C13	0.4941 (3)	0.3201 (2)	0.3278 (2)	3.74 (7)
C14	0.5761 (2)	0.2269 (2)	0.3634 (2)	3.80 (7)
C15	0.5587 (3)	0.1273 (2)	0.3531 (2)	4.05 (7)
C16	0.4598 (2)	0.1209 (2)	0.3059 (2)	3.34 (6)
C21	0.3324 (2)	0.2847 (2)	0.0669 (2)	2.55 (5)
C22	0.3901 (3)	0.2297 (2)	−0.0034 (2)	3.48 (7)
C23	0.4524 (3)	0.2895 (2)	−0.1015 (2)	4.26 (7)
C24	0.4585 (3)	0.4035 (2)	−0.1312 (2)	4.25 (8)
C25	0.4028 (3)	0.4593 (2)	−0.0628 (2)	4.07 (7)
C26	0.3399 (3)	0.4007 (2)	0.0358 (2)	3.48 (6)
C31	0.1088 (2)	0.2975 (2)	0.2314 (2)	2.57 (5)
C32	0.0332 (3)	0.3595 (2)	0.1611 (2)	3.77 (7)
C33	−0.0837 (3)	0.4210 (2)	0.1891 (2)	4.86 (8)
C34	−0.1270 (3)	0.4217 (2)	0.2871 (2)	4.98 (8)
C35	−0.0546 (3)	0.3589 (2)	0.3576 (2)	5.04 (8)
C36	0.0625 (3)	0.2971 (2)	0.3306 (2)	4.03 (7)
C41	0.1959 (2)	−0.2918 (2)	0.3304 (2)	2.44 (5)
C42	0.3149 (3)	−0.2871 (2)	0.3587 (2)	3.55 (7)
C43	0.3684 (3)	−0.3821 (2)	0.4233 (2)	4.63 (8)
C44	0.3060 (3)	−0.4812 (2)	0.4606 (2)	4.36 (8)
C45	0.1894 (3)	−0.4874 (2)	0.4330 (2)	3.85 (7)
C46	0.1346 (2)	−0.3931 (2)	0.3688 (2)	3.29 (6)
C51	0.1666 (2)	−0.2026 (2)	0.1244 (2)	2.63 (5)
C52	0.1154 (3)	−0.2966 (2)	0.1210 (2)	3.80 (7)
C53	0.1462 (3)	−0.3219 (2)	0.0317 (2)	4.45 (7)
C54	0.2276 (3)	−0.2555 (2)	−0.0543 (2)	4.42 (7)
C55	0.2805 (3)	−0.1643 (2)	−0.0517 (2)	4.25 (7)
C56	0.2512 (3)	−0.1381 (2)	0.0374 (2)	3.36 (6)
C61	−0.0557 (2)	−0.1800 (2)	0.2900 (2)	2.42 (5)
C62	−0.1114 (2)	−0.1946 (2)	0.3921 (2)	3.53 (7)
C63	−0.2492 (3)	−0.1928 (2)	0.4295 (2)	4.25 (8)
C64	−0.3344 (3)	−0.1752 (2)	0.3664 (2)	4.67 (8)
C65	−0.2816 (3)	−0.1587 (3)	0.2652 (2)	5.77 (9)
C66	−0.1427 (3)	−0.1614 (2)	0.2269 (2)	4.46 (7)

[a] B values for anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter $B_{eq} = (4/3)[a^2B(1,1) + ... + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ... + bc(\cos\alpha)B(2,3)]$.

Table IV. Selected Bond Lengths (Å) and Angles (deg) for $[(C_6H_{15}N_3)Tc(CO)_2\{P(C_6H_5)_3\}]Cl$ (**5**) with Estimated Standard Deviations in Parentheses

	Bond Lengths		
Tc–N1	2.192 (3)	Tc–C1	1.862 (6)
Tc–N2	2.242 (4)	Tc–C2	1.856 (6)
Tc–N3	2.246 (4)	C1–O1	1.171 (5)
Tc–P1	2.388 (1)	C2–O2	1.183 (5)
	Bond Angles		
N1–Tc–N2	79.6 (1)	N1–Tc–C1	94.8 (2)
N1–Tc–N3	78.7 (7)	N1–Tc–C2	92.8 (2)
N2–Tc–N3	78.3 (1)	N1–Tc–P	174.1 (1)

The hydridotris(pyrazolyl)borate complex **6** has bonding properties similar to those of **5**. The carbonyl groups again indicate a stronger π back-donation from the metal atom compared with compound **2**. The trans ligand of phopshorus, N3, is much closer to technetium than the two others, N1 and N5, which may derive from the trans influence of the carbonyl ligands (Table VI).

Table V. Final Fractional Atomic Coordinates and Equivalent Isotropic Displacement Parameters for **5** (Estimated Standard Deviations in Parentheses)[a]

atom	x/a	y/b	z/c	B_{eq}, Å^2
Tc	0.12608 (4)	0.06619 (7)	0.13249 (2)	2.336 (9)
Cl	0.7367 (1)	0.7503 (2)	0.19434 (7)	4.59 (5)
P	0.2665 (1)	0.1657 (2)	0.09397 (6)	2.45 (4)
O1	0.0699 (4)	0.3867 (5)	0.1653 (2)	5.2 (1)
O2	−0.0317 (3)	0.1373 (5)	0.0299 (2)	4.6 (1)
N1	0.0065 (4)	−0.0499 (6)	0.1686 (2)	3.3 (1)
N2	0.1566 (4)	−0.1800 (6)	0.1135 (2)	2.9 (1)
N3	0.2193 (4)	−0.0165 (6)	0.2118 (2)	3.7 (1)
C1	0.0938 (5)	0.2629 (7)	0.1538 (2)	3.4 (2)
C2	0.0325 (4)	0.1065 (7)	0.0685 (2)	2.9 (1)
C3	−0.0020 (5)	−0.2213 (8)	0.1541 (2)	3.9 (2)
C4	0.0502 (5)	−0.2559 (7)	0.1064 (2)	3.3 (2)
C5	0.2348 (5)	−0.2559 (8)	0.1569 (3)	4.1 (2)
C6	0.2912 (5)	−0.1353 (8)	0.1987 (3)	4.5 (2)
C7	0.1510 (6)	−0.0813 (9)	0.2480 (2)	5.1 (2)
C8	0.0391 (5)	−0.0320 (8)	0.2279 (2)	4.8 (2)
C11	0.2318 (4)	0.2851 (7)	0.0333 (2)	2.3 (1)
C12	0.2704 (5)	0.2686 (8)	−0.0134 (2)	3.4 (2)
C13	0.2416 (5)	0.3659 (8)	−0.0568 (2)	4.3 (2)
C14	0.1735 (5)	0.4859 (7)	−0.0541 (2)	3.8 (2)
C15	0.1345 (5)	0.5071 (8)	−0.0071 (3)	4.2 (2)
C16	0.1625 (5)	0.4081 (8)	0.0362 (2)	3.5 (2)
C21	0.3456 (4)	0.0117 (7)	0.0717 (2)	2.8 (1)
C22	0.2992 (4)	−0.0829 (8)	0.0283 (2)	3.1 (1)
C23	0.3529 (5)	−0.2066 (8)	0.0135 (3)	4.8 (2)
C24	0.4534 (5)	−0.2399 (8)	0.0415 (3)	5.3 (2)
C25	0.4986 (5)	−0.1496 (9)	0.0845 (3)	5.2 (2)
C26	0.4457 (5)	−0.0240 (7)	0.0989 (3)	3.8 (2)
C31	0.3637 (5)	0.2921 (7)	0.1344 (2)	2.9 (2)
C32	0.3548 (5)	0.3330 (8)	0.1863 (2)	3.7 (2)
C33	0.4246 (5)	0.4354 (9)	0.2164 (2)	4.8 (2)
C34	0.5044 (5)	0.4999 (8)	0.1943 (3)	5.1 (2)
C35	0.5162 (5)	0.4595 (9)	0.1433 (3)	4.9 (2)
C36	0.4459 (5)	0.3569 (8)	0.1129 (2)	4.1 (2)
O42	0.1995 (4)	0.5801 (7)	0.3239 (3)	9.9 (2)
C41	0.2669 (7)	0.638 (1)	0.3660 (3)	10.7 (3)

[a] B values for anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter $B_{eq} = (4/3)[a^3B(1,1) + ... + c^2\mathrm{B}(3,3) + ab(\cos\gamma)B(1,2) + ... + bc(\cos\alpha)B(2,3)]$.

Table VI. Selected Bond Lengths (Å) and Angles (deg) for $[HB(C_3H_3N_2)_3]Tc(CO)_2[P(C_6H_5)_3]$ (**6**) with Estimated Standard Deviations in Parentheses

	Bond Lengths		
Tc–N1	2.219 (1)	Tc–C1	1.867 (3)
Tc–N3	2.166 (2)	Tc–C2	1.870 (3)
Tc–N5	2.215 (2)	C1–O1	1.154 (3)
Tc–P	2.402 (1)	C2–O2	1.151 (3)
	Bond Angles		
N1–Tc–N3	82.02 (7)	N1–Tc–C1	172.50 (9)
N1–Tc–N5	84.38 (7)	P–Tc–N1	91.33 (5)
N3–Tc–N5	83.93 (5)	P–Tc–N3	172.86 (5)
N3–Tc–C1	91.09 (8)	P–Tc–N5	92.86 (5)

Scheme III. Description of the Transition Metal–CO Bond as a Resonance Hybride

$$\mathrm{M-C\equiv O} \longleftrightarrow \mathrm{M^{+}=C=O^{-}}$$

III. ^{99}Tc-NMR Spectroscopy. ^{99}Tc-NMR spectroscopy is a useful tool to study the electronic properties of metal centers. Elements in the neighborhood of Tc in the periodic table can not be observed in this easy way. Correlation between the chemical shift of the technetium nucleus and the oxidation state has been proposed.[22] Most of the known complexes of this element fall inside these defined ranges; i.e., the chemical shifts are in good agreement with the oxidation states derived traditionally from the type of the ligand and charge of the complex. For Tc(I) complexes we find the typical range −1400 to 3500 ppm relative to $\delta([TcO_4]^-) = 0$ ppm. The presented compounds **5** and **6** and a recently prepared cluster $Na[Tc_3(CO)_9(OCH_3)_4]$ (**10**)[23] resonate *far*

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(22) O'Connell, L. A.; Pearlstein, R. M.; Davison, A.; Thornback, J. R.; Kronauge, J. F.; Jones, A. G. *Inorg. Chim. Acta* **1989**, *161*, 39.

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Table VII. Final Fractional Atomic Coordinates and Equivalent Isotropic Displacement Parameters for **6** (Estimated Standard Deviations in Parentheses)[a]

atom	x/a	y/b	z/c	B_{eq}, Å^2
Tc	0.38869 (1)	0.29953 (3)	0.44414 (1)	2.681 (5)
P	0.34277 (3)	0.10497 (8)	0.41949 (5)	2.89 (2)
O1	0.4111 (1)	0.2374 (3)	0.5990 (1)	6.74 (8)
O2	0.32029 (8)	0.4843 (3)	0.4988 (2)	7.54 (8)
N1	0.38205 (8)	0.3659 (2)	0.3312 (1)	2.89 (5)
N2	0.41829 (8)	0.3977 (3)	0.2973 (1)	3.04 (6)
N3	0.43145 (8)	0.4751 (2)	0.4523 (1)	2.96 (5)
N4	0.46043 (7)	0.4959 (3)	0.4019 (1)	3.21 (6)
N5	0.44636 (8)	0.1895 (2)	0.4109 (1)	3.10 (6)
N6	0.47223 (8)	0.2517 (3)	0.3650 (1)	3.29 (6)
C1	0.4012 (1)	0.2557 (3)	0.5397 (2)	3.81 (8)
C2	0.3443 (1)	0.4092 (4)	0.4756 (2)	4.21 (9)
C11	0.4074 (1)	0.4357 (4)	0.2293 (2)	3.82 (8)
C12	0.3639 (1)	0.4294 (4)	0.2192 (2)	4.02 (7)
C13	0.3489 (1)	0.3854 (3)	0.2833 (2)	3.68 (8)
C21	0.4823 (1)	0.6124 (4)	0.4176 (2)	4.30 (8)
C22	0.4680 (1)	0.6682 (4)	0.4779 (2)	4.76 (9)
C23	0.4357 (1)	0.5796 (4)	0.4981 (2)	3.88 (7)
C31	0.5048 (1)	0.1666 (4)	0.3514 (2)	4.47 (8)
C32	0.5002 (1)	0.0468 (4)	0.3887 (2)	4.34 (9)
C33	0.4630 (1)	0.0647 (3)	0.4255 (2)	3.54 (7)
C41	0.3265 (1)	0.0008 (4)	0.4947 (2)	3.36 (6)
C42	0.2843 (1)	−0.0422 (3)	0.5010 (2)	3.93 (8)
C43	0.2745 (1)	−0.1245 (4)	0.5583 (2)	5.1 (1)
C44	0.3056 (1)	−0.1668 (4)	0.6073 (2)	5.0 (1)
C45	0.3479 (1)	−0.1263 (4)	0.6009 (2)	5.15 (9)
C46	0.3581 (1)	−0.0427 (4)	0.5451 (2)	4.24 (8)
C51	0.29131 (9)	0.1432 (3)	0.3703 (2)	2.91 (7)
C52	0.2639 (1)	0.2392 (3)	0.3976 (2)	3.96 (8)
C53	0.2252 (1)	0.2730 (4)	0.3610 (2)	5.11 (9)
C54	0.2143 (1)	0.2130 (5)	0.2971 (2)	5.38 (9)
C55	0.2409 (1)	0.1166 (5)	0.2688 (2)	5.5 (1)
C56	0.2795 (1)	0.0798 (4)	0.3056 (2)	4.35 (8)
C61	0.3665 (1)	−0.0238 (3)	0.3623 (2)	2.92 (6)
C62	0.3664 (1)	−0.1645 (3)	0.3780 (2)	3.74 (7)
C63	0.3861 (1)	−0.2569 (3)	0.3344 (2)	4.31 (8)
C64	0.4050 (1)	−0.2115 (4)	0.2750 (2)	4.37 (7)
C65	0.4047 (1)	−0.0744 (4)	0.2584 (2)	4.30 (8)
C66	0.3860 (1)	0.0180 (4)	0.3016 (2)	3.85 (7)
B	0.4625 (1)	0.3982 (4)	0.3387 (2)	3.60 (9)

[a] B values for anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter $B_{eq} = (4/3)[a^2B(1,1) + ... + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ... + bc(\cos\alpha)B(2,3)]$.

outside of this range: **5** at −934 ppm, **6** at −1198 ppm, and **8** at −621 ppm.

The compounds $[Tc(CNR)_4(NN)]^+$ (with NN = bidentate aromatic amine, e.g. 4,4′-dimethyl-2,2′-bipyridine) as recently reported by Davison et al. display a similar behavior.[24] They resonate at ca. −850 ppm, again outside of the "Tc(I) region". It is thus once again necessary to consider the specific electronic properties of the ligands. If good σ-donor ligands such as amines or alcoholates (in case of **10**) are present in the ligand sphere, the ground-state resonance contribution M═C═O becomes more important (Scheme III). For this reason, the nucleus is deshielded and therefore mimics a nucleus in a higher oxidation state; i.e., the resonance is displaced toward lower field. Parallel to this effect the M–C bonding is expected to be very strong, so that no further reactions occur even if extreme conditions are employed. Although it is known from the literature[22] that Tc(I) as a d^6 low-spin center exhibits Tc–P coupling, we were not able to detect any. The reason may be that for radiation safety considerations we had to work with very diluted solutions.

Conclusion

Low-valent technetium complexes of the carbonyl series have become available from the now easily accessible precursor *trans*-$TcCl(CO)_3[P(C_6H_5)_3]_2$ (**2**), which is conveniently synthesized from $[N(n\text{-}C_4H_9)_4][TcOCl_4]$ (**1**) and triphenylphosphine in an atmosphere of carbon monoxide at 110 °C. The ionic complex $[(C_6H_{15}N_3)Tc(CO)_2\{P(C_6H_5)_3\}]Cl$ (**5**) and the neutral derivative $[HB(pyz)_3]Tc(CO)_2[P(C_6H_5)_3]$ (**6**) hardly differ in their ^{99}Tc-NMR and IR data (ν(CO)), thus reflecting almost identical ligating properties of the two N,N,N-ligands 1,4,7-triazacyclononane (TAN) and hydridotris(pyrazolyl)borate $[HB(pyz)_3]^-$. ^{99}Tc-NMR spectroscopy is a good tool to determine the electronic properties at the metal center and is in good agreement with the structural data (carbonyl bonding) and the IR Data (C≡O stretching vibrations).

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Supplementary Material Available: For all structures, a complete table of crystallographic data and tables of atom positions, anisotropic displacement parameters, and bond distances and angles for all atoms (45 pages); listings of calculated and observed structure factors (75 pages). Ordering information is given on any current masthead page.

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