

Nucleophilic attack on coordinated CO in $[\text{Tc}(\text{CO})_4(\text{PPh}_3)_2]\text{BF}_4$

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Abstract

Several new technetium nucleophile–carbonyl adducts have been synthesized and characterized. Treatment of the Tc^{I} cation, *trans*- $[\text{Tc}(\text{CO})_4(\text{PPh}_3)_2]\text{BF}_4$ (**1**) with LiEt_3BH affords the Tc formyl complex $\text{Tc}(\text{CO})_3(\text{C}(\text{O})\text{H})(\text{PPh}_3)_2$ (**2**) in 76% yield. Reaction of **2** with 1 equiv. of $\text{CH}_3\text{SO}_3\text{CF}_3$ in toluene produces the Fischer carbene $[\text{Tc}(\text{CO})_3(=\text{C}(\text{OMe})\text{H})(\text{PPh}_3)_2]\text{SO}_3\text{CF}_3$ (**3**). The nucleophile OH^- reacts with **1** to give the hydroxycarbonyl complex $\text{Tc}(\text{CO})_3(\text{C}(\text{O})\text{OH})(\text{PPh}_3)_2$ (**4**). If this reaction is carried out in the presence of alkyl alcohols, ROH [R = Me (**5**), Et (**6**)] the corresponding alkoxy carbonyl complexes $\text{Tc}(\text{CO})_3(\text{C}(\text{O})\text{OR})(\text{PPh}_3)_2$ are obtained. The aryloxy carbonyl complex $\text{Tc}(\text{CO})_3(\text{C}(\text{O})\text{OR})(\text{PPh}_3)_2$ (**7**) (where R = $\text{C}_6\text{H}_4\text{CH}_3$) was prepared from the reaction of **4** with excess KOR in THF. Treatment of **1** with NaN_3 gives the isocyanate complex $\text{Tc}(\text{CO})_3(\text{NCO})(\text{PPh}_3)_2$ (**8**).

Keywords: Technetium

1. Introduction

Transition metal nucleophile–carbonyl adducts have received considerable attention because they have been shown to be intermediates in many important processes including the water–gas shift reaction, hydroformylation, the carboalkoxylation of olefins and the carbonylation of alcohols [1,2]. For the Group VII metals Mn and Re, a wide variety acyl [3,4], formyl [5,6], hydroxycarbonyl [7] and alkoxy carbonyl [8] complexes have been synthesized and characterized. Similar chemistry with Tc however has not yet been explored.

We have recently reported a simple synthesis of the cation *trans*- $[\text{Tc}(\text{CO})_4(\text{PPh}_3)_2]\text{BF}_4$ (**1**) from the neutral Tc^{I} monohydride complex $\text{HTc}(\text{CO})_3(\text{PPh}_3)_2$ [9]. The carbonyl ligands in **1** are susceptible to attack by a variety of nucleophiles. Herein we wish to report the synthesis and characterization of a number of neutral Tc^{I} nucleophile–carbonyl adducts.

2. Results and discussion

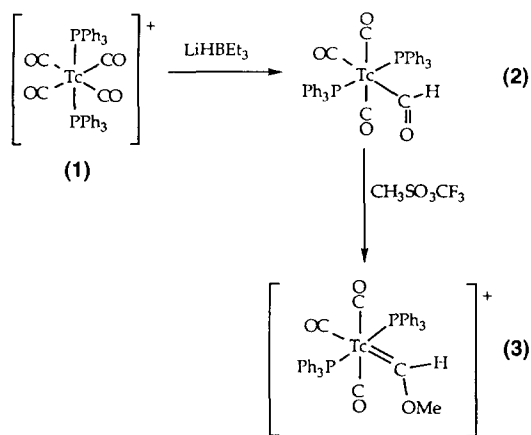
Treatment of *trans*- $[\text{Tc}(\text{CO})_4(\text{PPh}_3)_2]\text{BF}_4$ (**1**) with 1 equiv. of LiEt_3BH gives the pale yellow Tc^{I} formyl,

$\text{Tc}(\text{CO})_3(\text{C}(\text{O})\text{H})(\text{PPh}_3)_2$ (**2**), in 76% yield (see Scheme 1). Complex **2** is stable as a solid under inert atmosphere; however, it is unstable in solution. Benzene solutions of **2** show slight decomposition to the monohydride complex $\text{HTc}(\text{CO})_3(\text{PPh}_3)_2$ [10] after 12 h at room temperature. This reaction has been observed for several other Group VII formyl complexes [5].

As is characteristic of an η^1 -formyl ligand [5], the carbonyl stretching frequency of the formyl group is observed at 1581 cm^{-1} in the IR spectrum of **2**. The meridional arrangement of CO ligands is supported by the presence of two strong peaks at 1951 and 1858 cm^{-1} and one higher energy peak of lower intensity at 2035 cm^{-1} [11]. In the ^1H NMR spectrum of **2** the resonance for the formyl hydrogen atom occurs at δ 14.88 ppm. The formyl carbon atom resonance is observed as a broadened doublet at δ 279 ppm ($J_{\text{C-H}} = 105\text{ Hz}$) in the proton-coupled ^{13}C NMR spectrum of **2**. The broadening of this peak is believed to be caused by coupling between the quadrupolar ^{99}Tc nucleus ($I = \frac{9}{2}$) and the carbon nuclei. This effect is commonly observed in the $^{31}\text{P}\{\text{H}\}$ NMR and $^{13}\text{C}\{\text{H}\}$ NMR spectra of ^{99}Tc complexes where the phosphorus or carbon nuclei are bound directly to the metal center [10,12].

Addition of 1 equiv. of $\text{CH}_3\text{SO}_3\text{CF}_3$ to a toluene solution of **2** gives the Fischer carbene $[\text{Tc}(\text{CO})_3(=\text{C}(\text{OMe})\text{H})(\text{PPh}_3)_2]\text{SO}_3\text{CF}_3$ (**3**). Technetium complexes containing a $\text{Tc}=\text{C}$ bond are rare. The only two

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Scheme 1.

examples in the literature are the recently reported vinylidene complex $\text{Tc}(=\text{C}=\text{CHR})\text{Cl}(\text{dppe})_2$ [13] (where $\text{R} = \text{Ph}, \text{Me}, {}^i\text{Bu}$; $\text{dppe} = \text{bis}(\text{diphenylphosphinoethane})$) and the dimeric complex $(\text{CO})_9\text{Tc}_2\text{-C}(\text{OCH}_3)\text{R}$ [14] (where $\text{R} = \text{CH}_3, \text{C}_6\text{H}_5$). The resonance for the carbene hydrogen atom is observed in the ${}^1\text{H}$ NMR spectrum of **3** as a singlet at δ 11.8 ppm. The ${}^{13}\text{C}\{\text{H}\}$ NMR spectrum shows the signal for the carbene carbon atom as a broad singlet at δ 323 ppm. The carbonyl ligands are also broad peaks occurring at δ 203 (*cis*) and 207 (*trans*) ppm.

The reaction of $[\text{Tc}(\text{CO})_4(\text{PPh}_3)_2]\text{BF}_4$ (**1**) with excess sodium hydroxide in MeCN leads to the rapid precipitation of the hydroxycarbonyl complex $\text{Tc}(\text{CO})_3\text{-C}(\text{O})\text{OH}(\text{PPh}_3)_2$ (**4**) (see Scheme 2). This precipitate appears to contain only pure $\text{Tc}(\text{CO})_3\text{-C}(\text{O})\text{OH}(\text{PPh}_3)_2$ (**4**). In KBr, the IR spectrum of the precipitate shows $\nu(\text{C}=\text{O})$ at 1566 cm^{-1} and $\nu(\text{C}=\text{O})$ at 2052 (m) , 1954

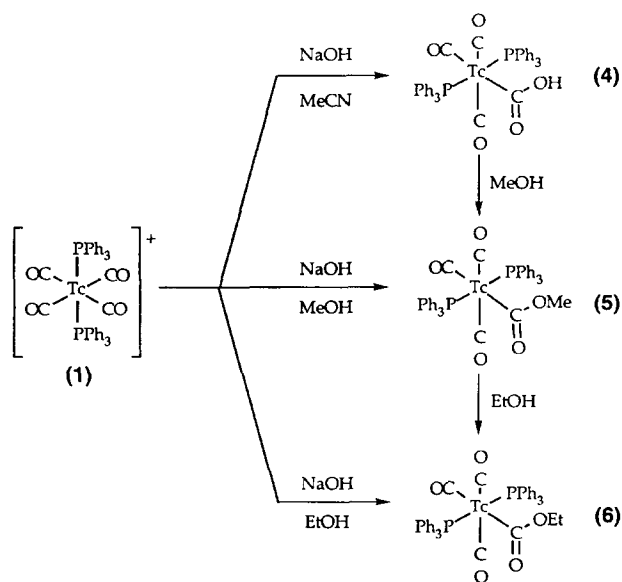
(s) and $1936\text{ (s)}\text{ cm}^{-1}$. No stretches corresponding to $\text{HTc}(\text{CO})_3(\text{PPh}_3)_2$ [10] were observed. Although an OH stretch could not be assigned in the IR spectrum of **4**, the OH proton was observed in the ${}^1\text{H}$ NMR (DMSO) spectrum as a singlet at δ 9.89 ppm. In addition to the singlet at δ 9.89 ppm the ${}^1\text{H}$ NMR spectrum of **4** shows a triplet at δ -4.25 ppm ($J_{\text{P-H}} = 19.7\text{ Hz}$) which corresponds to the monohydride $\text{HTc}(\text{CO})_3(\text{PPh}_3)_2$ [10]. The decarboxylation of **4** in DMSO solution to give $\text{HTc}(\text{CO})_3(\text{PPh}_3)_2$ occurs readily at room temperature to cleanly form the hydride after 6 h. Decarboxylation of the deuterium analog $\text{Tc}(\text{CO})_3\text{-C}(\text{O})\text{OD}(\text{PPh}_3)_2$ has proved to be convenient method of preparation for the deuteride complex $\text{DTc}(\text{CO})_3(\text{PPh}_3)_2$ [10].

The reaction of **1** with NaOH in alcohol solvents gives the corresponding ester complexes $\text{Tc}(\text{CO})_3\text{-C}(\text{O})\text{OR}(\text{PPh}_3)_2$ (**5**: $\text{R} = \text{Me}$; **6**: $\text{R} = \text{Et}$) in 84% and 59% yield. Base is necessary for the formation of **5** and **6**, since these complexes are not formed when $[\text{Tc}(\text{CO})_4\text{-}(\text{PPh}_3)_2]\text{BF}_4$ (**1**) is dissolved in alcohols.

The method employed for the preparation of complexes **5** and **6** could not be extended to phenols. The analogous aryloxy carbonyl complex $\text{Tc}(\text{CO})_3\text{-C}(\text{O})\text{-OC}_6\text{H}_4\text{CH}_3(\text{PPh}_3)_2$ (**7**) was prepared in 35% yield by treatment of **1** with the nucleophile $\text{K}[\text{OC}_6\text{H}_4\text{CH}_3]$ in THF.

The observed IR, ${}^1\text{H}$ NMR and ${}^{13}\text{C}\{\text{H}\}$ NMR data for complexes **5–7** are consistent with the formation of alkoxy carbonyl complexes [2,6–8]. The IR spectra of these complexes show $\nu(\text{C}=\text{O})$ within the expected range of $1580\text{--}1703\text{ cm}^{-1}$ [2]. Also the ${}^{13}\text{C}$ chemical shifts of the $\eta^1\text{-C}(\text{O})\text{OR}$ central carbon atom fall within the δ 158–215 ppm range observed for other $\eta^1\text{-alkoxy carbonyl}$ adducts [2]. The molecular ions for complexes **5–7** were not observed in the FAB(+) mass spectra of the complexes. In all spectra the major peak observed corresponds to the tetracarbonyl fragment, $[\text{Tc}(\text{CO})_4(\text{PPh}_3)_2]^+$.

Several Re hydroxycarbonyl and alkoxy carbonyl complexes of the type $\text{Re}(\text{CO})_3(\text{LL})\text{-C}(\text{O})\text{OR}$ (where $\text{LL} = 1,2\text{-bis}(\text{diphenylphosphinoethane}), 1,3\text{-bis}(\text{diphenylphosphinoethane})$; $\text{R} = \text{H}, \text{D}, \text{Me}, \text{Et}$) have been synthesized and characterized [7]. These complexes exhibit behavior similar to that observed for the Tc complexes **4–7**. For example, both the methyl and ethyl alkoxy carbonyl complexes are prepared readily from solutions of the hydroxycarbonyls and methanol or ethanol. These alkoxy carbonyl complexes are easily transesterified. Both $\text{Re}(\text{CO})_3(\text{dppe})\text{-C}(\text{O})\text{OMe}$ and complex **5** react with EtOH to give the corresponding ethyl ester complexes. The decarboxylation of the hydroxycarbonyl complex $\text{Tc}(\text{CO})_3\text{-C}(\text{O})\text{OH}(\text{PPh}_3)_2$ (**4**) is much faster than is observed for the similar complex $\text{Re}(\text{CO})_3\text{-C}(\text{O})\text{OH}(\text{dppe})$ [where $\text{dppe} = \text{bis}(\text{diphenylphosphinoethane})$] [7]. This is not surprising since tran-



Scheme 2.

sition metal complexes of second row metals are known to be less robust than their third row congeners.

Reaction of **1** with NaN_3 gives the isocyanate complex $\text{Tc}(\text{CO})_3(\text{NCO})(\text{PPh}_3)_2$ (**8**) in 66% yield. This reaction is believed to occur via an acyl-azide intermediate which quickly loses N_2 [8,15]. The intermediate nitrene undergoes a Curtius-like rearrangement to form the observed product. No evidence for the formation of an azide complex was observed. The IR spectrum of **8** gives two strong $\nu(\text{C}\equiv\text{O})$ stretches at 2056 and 1957 cm^{-1} and one very strong peak at 2239 cm^{-1} for $\nu(\text{NCO})$. The FAB(+) mass spectrum shows a peak at m/z 750 corresponding to the molecular ion $[\text{Tc}(\text{CO})_3(\text{NCO})(\text{PPh}_3)_2]^+$.

3. Experimental details

Caution! Technetium-99 is a weak β^- -emitter ($E = 0.292$ MeV, $t_{1/2} = 2.12 \times 10^5$ y). All work has been done in laboratories approved for the use of low levels of radioactive materials. Precautions have been detailed elsewhere [16].

All reactions were carried out under an atmosphere of $\text{N}_2(\text{g})$. Reagents and solvents were used as received unless otherwise stated. Dry box solvents (toluene, THF, pentane, Et_2O) were distilled from sodium/benzophenone. The complex $[\text{Tc}(\text{CO})_4(\text{PPh}_3)_2]\text{BF}_4$ (**1**) was prepared as described by Cook et al. [9]. The salt $\text{K}[\text{OC}_6\text{H}_4\text{CH}_3]$ was prepared by reaction of $\text{KN}[(\text{CH}_3)_3\text{Si}]_2$ with *p*-cresol in toluene. A Mattson Cynus 100 FT-IR instrument was used to record all infrared spectra. Only representative IR data are presented. Fast atom bombardment mass spectra [FAB MS(+)] were obtained using a MAT 731 mass spectrometer operating at an accelerating voltage of 8 kV and equipped with a Ion Tech B11N FAB gun. The FAB gun produces a beam of 6–8 keV xenon neutrals. All compounds were run in a matrix of neat 3-nitrobenzyl alcohol. ^1H , ^{13}C and ^{31}P NMR spectra were recorded at 300.0 MHz, 75.429 MHz and 121.421 MHz, respectively, on a Varian Unity spectrometer, unless otherwise noted. Where obtained, $^{13}\text{C}\{\text{H}\}$ NMR data was obtained on a ^{13}C labeled complex prepared from $[\text{Tc}(\text{CO})_3(^{13}\text{CO})(\text{PPh}_3)_2]\text{BF}_4$. All $^{31}\text{P}\{\text{H}\}$ NMR spectra are referenced to an external standard of 85% phosphoric acid in CDCl_3 . The elemental analyses were performed by Atlantic Microlab, Norcross, GA [17].

3.1. Preparation of $\text{Tc}(\text{CO})_3(\text{C}(\text{O})\text{H})(\text{PPh}_3)_2$ (**2**)

In the dry box a solution containing $[\text{Tc}(\text{CO})_4(\text{PPh}_3)_2]\text{BF}_4$ (**1**) (97.4 mg, 0.118 mmol) and 15 ml of toluene was treated with Super Hydride (0.12 ml of LiEt_3BH as a 1 M THF solution) and allowed to stir for 30 min. The reaction mixture was then filtered

through Celite and reduced to dryness. The remaining pale yellow solid was stirred for 30 min in 10 ml of MeCN, filtered on a fritted disk, washed with 10 ml of MeCN and Et_2O , and dried in vacuo. Yield, 59.1 mg; 76%.

Anal. Calc. for $\text{C}_{40}\text{H}_{31}\text{O}_4\text{P}_2\text{Tc}$: C, 65.23; H, 4.24%. Found: C, 64.75; H, 4.08% [17]. IR (KBr) $\nu(\text{cm}^{-1})$: 2035 (m, $\text{C}\equiv\text{O}$); 1951 (s, $\text{C}\equiv\text{O}$); 1858 (s, $\text{C}\equiv\text{O}$); 1581 (s, $\text{C}=\text{O}$). ^1H NMR (C_6D_6) δ : 7.02 [m, 18H, $\text{P}(\text{C}_6\text{H}_5)_2$]; 7.78 [m, 12H, $\text{P}(\text{C}_6\text{H}_5)_2$]; 14.88 [s, 1H, $\text{C}(\text{O})\text{H}$] ppm. ^{13}C NMR (C_6D_6) δ : 278.9 (d, $J_{\text{C-H}} = 105$ Hz, Tc-COH) ppm. $^{13}\text{C}\{\text{H}\}$ NMR (C_6D_6) δ : $[\text{P}(\text{C}_6\text{H}_5)_2]$ *ortho* or *meta* partially obscured by C_6D_6 : 130.1 [s, $\text{P}(\text{C}_6\text{H}_5)_2$ *para*]; 132.99 [t, $J_{\text{P-C}} = 5.4$ Hz, $\text{P}(\text{C}_6\text{H}_5)_2$ *ortho* or *meta*]; 136.23 [t, $J_{\text{P-C}} = 22$ Hz, $\text{P}(\text{C}_6\text{H}_5)_2$ *ipso*]; 207 [br, CO *trans* to $\text{TcC}(\text{O})\text{H}$]; 211 [br, CO *cis* to $\text{TcC}(\text{O})\text{H}$]; 280 [s, $J_{\text{P-C}} = 105.5$ Hz, $\text{TcC}(\text{O})\text{H}$] ppm. $^{31}\text{P}\{\text{H}\}$ (CD_2Cl_2 , 202.334 MHz) δ : ~ 57 (br) ppm. FAB MS(+) m/z : 707 $[\text{Tc}(\text{CO})_3(\text{PPh}_3)_2]^+$; 679 $[\text{Tc}(\text{CO})_2(\text{PPh}_3)_2]^+$.

3.2. Preparation of $[\text{Tc}(\text{CO})_3(\text{C}(\text{OMe})\text{H})(\text{PPh}_3)_2]\text{SO}_3\text{CF}_3$ (**3**)

In the dry box $\text{Tc}(\text{CO})_3(\text{C}(\text{O})\text{H})(\text{PPh}_3)_2$ (**2**) (120 mg, 0.163 mmol) was added to $\text{CH}_3\text{SO}_3\text{CF}_3$ (20 μl , 0.163 mmol) in 15 ml of toluene at 0°C . The mixture was stirred for 3 h during which time the pale yellow solid dissolved and a new white solid precipitated. The solid was collected by filtration, washed with 10 ml of Et_2O and dried in vacuo overnight. Yield, 61.6 mg; 42%.

Anal. Calc. for $\text{C}_{42}\text{H}_{34}\text{F}_3\text{O}_7\text{P}_2\text{Stc}$: C, 56.01; H, 3.80; S, 3.56%. Found: C, 55.55; H, 3.70; S, 3.41%. IR (KBr) $\nu(\text{cm}^{-1})$: 2058 (m, $\text{C}\equiv\text{O}$); 2013 (s, $\text{C}\equiv\text{O}$); 1979 (s, $\text{C}\equiv\text{O}$); 1267 (s, SO_3CF_3). ^1H NMR (CD_2Cl_2) δ : 3.58 (s, OCH_3 , 3H); 7.52 [m, 30H, $\text{P}(\text{C}_6\text{H}_5)_2$]; 11.84 [s, 1H, $\text{Tc}=\text{CH}(\text{OMe})$] ppm. $^{13}\text{C}\{\text{H}\}$ NMR (C_6D_6) δ : 77.1 (s, OCH_3); 129.63 [t, $J_{\text{P-C}} = 6.4$ Hz, $\text{P}(\text{C}_6\text{H}_5)_2$ *ortho* or *meta*]; 129.9 [s, $\text{P}(\text{C}_6\text{H}_5)_2$ *para*]; 132.87 [t, $J_{\text{P-C}} = 5.4$ Hz, $\text{P}(\text{C}_6\text{H}_5)_2$ *ortho* or *meta*]; 134.06 [t, $J_{\text{P-C}} = 22.9$ Hz, $\text{P}(\text{C}_6\text{H}_5)_2$ *ipso*]; 203 [br, CO *cis* to $\text{Tc}=\text{C}(\text{OMe})\text{H}$]; 207 [br, CO *trans* to $\text{Tc}=\text{C}(\text{OMe})\text{H}$]; 323 [br, $\text{Tc}=\text{C}(\text{OMe})\text{H}$] ppm. FAB MS(+) m/z : 723 $[\text{Tc}(\text{CO})_2(\text{C}(\text{OMe})\text{H})(\text{PPh}_3)_2]^+$; 695 $[\text{Tc}(\text{CO})_2(\text{C}(\text{OMe})\text{H})(\text{PPh}_3)_2]^+$.

3.3. Preparation of $\text{Tc}(\text{CO})_3(\text{C}(\text{O})\text{OH})(\text{PPh}_3)_2$ (**4**)

To a vigorously stirring solution of $[\text{Tc}(\text{CO})_4(\text{PPh}_3)_2]\text{BF}_4$ (**1**) (69.8 mg, 0.085 mmol) in 5 ml of MeCN was slowly added 1 equiv. of NaOH (1.5 M H_2O solution) at 0°C . The reaction mixture was allowed to warm to room temperature and then stirred for an additional 2–3 min. The white material which formed was filtered on a fritted disk, washed with 50 ml of Et_2O and dried in vacuo. Yield, 30.1 mg; 51%.

Anal. Calc. for $C_{40}H_{31}O_5P_2Tc$: C, 63.84; H, 4.15%. Found: C, 63.37; H, 4.09%. IR (KBr) $\nu(\text{cm}^{-1})$: 2052 (m, $\text{C}\equiv\text{O}$); 1954 (s, $\text{C}\equiv\text{O}$); 1936 (s, $\text{C}\equiv\text{O}$); 1566 (s, $\text{C}=\text{O}$). ^1H NMR (DMSO) δ : 7.12 [m, 12H, $\text{P}(\text{C}_6\text{H}_5)_2$]; 7.89 [m, 18H, $\text{P}(\text{C}_6\text{H}_5)_2$]; 9.79 (s, 1H, $\text{C}(\text{O})\text{OH}$) ppm. Peaks corresponding to the monohydride complex $\text{HTc}(\text{CO})_3(\text{PPh}_3)_2$ were also visible [10]. FAB MS(+) m/z : 735 [$\text{Tc}(\text{CO})_4(\text{PPh}_3)_2$]; 707 [$\text{Tc}(\text{CO})_3(\text{PPh}_3)_2$]; 679 [$\text{Tc}(\text{CO})_2(\text{PPh}_3)_2$].

3.4. Preparation of $\text{Tc}(\text{CO})_3(\text{C}(\text{O})\text{OMe})(\text{PPh}_3)_2$ (5)

Method 1

To a solution containing [$\text{Tc}(\text{CO})_4(\text{PPh}_3)_2$] BF_4 (1) (74.1 mg, 0.090 mmol) dissolved in 50 ml of MeOH was added 0.5 ml of 1 M NaOH. After stirring for 30 min, the white precipitate which had formed was collected by filtration, washed with Et_2O and dried in vacuo. This complex was recrystallized from benzene/hexane mixtures stored at 0°C overnight. Yield, 54.0 mg; 84%.

Method 2

To a round-bottom flask containing **4** (25.6 mg, 0.034 mmol) was added 15 ml of MeOH. After allowing the reaction mixture to stir overnight, the white solid was filtered on to a fritted disk, washed with Et_2O and dried in vacuo. Yield, 13.9 mg; 52%.

Anal. Calc. for $C_{41}H_{33}O_5P_2Tc$: C, 64.24; H, 4.34%. Found: C, 63.93; H, 4.16%. IR (KBr) $\nu(\text{cm}^{-1})$: 2023 ($\text{C}\equiv\text{O}$); 1957 (br, $\text{C}\equiv\text{O}$); 1623 ($\text{C}=\text{O}$). ^1H NMR (CDCl_3) δ : 2.67 [s, 3H, $\text{TcC}(\text{O})\text{OMe}$]; 7.34 [m, br, 18H, $\text{P}(\text{C}_6\text{H}_5)_2$]; 7.60 [m, br, 12H, $\text{P}(\text{C}_6\text{H}_5)_2$] ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6) δ : 48.0 [s, $\text{TcC}(\text{O})\text{OMe}$]; 126 [$\text{P}(\text{C}_6\text{H}_5)$ *ortho* or *meta*, partially obscured by C_6D_6 resonance]; 129.99 [s, $J_{\text{P-C}} = 6.5$ Hz, $\text{P}(\text{C}_6\text{H}_5)$ *ortho* or *meta*]; 134.81 [s, $\text{P}(\text{C}_6\text{H}_5)$ *para*]; 137.08 [t, $J_{\text{P-C}} = 21$ Hz, $\text{P}(\text{C}_6\text{H}_5)$ *ipso*]; 204 [br, CO *cis* to $\text{TcC}(\text{O})\text{OMe}$]; 208 (br, CO *trans* to $\text{TcC}(\text{O})\text{OMe}$]; 213 [br, $\text{TcC}(\text{O})\text{OMe}$] ppm. $^{31}\text{P}\{^1\text{H}\}$ (CD_2Cl_2 , 202.334 MHz) δ : ~ 49 (br) ppm. FAB MS(+) m/z : 735 [$\text{Tc}(\text{CO})_4(\text{PPh}_3)_2$]; 707 [$\text{Tc}(\text{CO})_3(\text{PPh}_3)_2$]; 679 [$\text{Tc}(\text{CO})_2(\text{PPh}_3)_2$].

3.5. Preparation of $\text{Tc}(\text{CO})_3(\text{C}(\text{O})\text{OEt})(\text{PPh}_3)_2$ (6)

Method 1

This complex was prepared similarly to **5** with the exception of EtOH being employed as the solvent and the length of the reaction being extended to 8 h. Yield, 43.4 mg; 59%.

Method 2

To $\text{Tc}(\text{CO})_3(\text{C}(\text{O})\text{OMe})(\text{PPh}_3)_2$ (**5**) (20.0 mg, 0.026 mmol) in 50 ml of acetone was added an equal volume of EtOH. After stirring for 24 h, the volume of the reaction mixture was reduced to 5 ml under vacuum. A white material precipitated and was filtered on to a

fritted disk, washed with Et_2O and dried in vacuo. Yield, 14.2 mg; 69%.

Anal. Calc. for $C_{42}H_{35}O_5P_2Tc$: C, 64.63; H, 4.52%. Found: C, 63.92; H, 4.51%. IR (KBr) $\nu(\text{cm}^{-1})$: 2028 (m, $\text{C}\equiv\text{O}$); 1955 (s, $\text{C}\equiv\text{O}$); 1916 (s, $\text{C}\equiv\text{O}$); 1615 (s, $\text{C}=\text{O}$). ^1H NMR (C_6D_6) δ : 0.88 (t, 3H, $J = 4.4$ Hz, OCH_2CH_3); 3.43 (q, 2H, $J = 4.1$ Hz, OCH_2CH_3); 7.05 [m, br, 18H, $\text{P}(\text{C}_6\text{H}_5)_2$]; 7.91 [m, br, 12H, $\text{P}(\text{C}_6\text{H}_5)_2$] ppm. $^{13}\text{C}\{^1\text{H}\}$ (CD_2Cl_2) δ : 14.47 (s, OCH_2CH_3); 26.20 (s, OCH_2CH_3); 128.38 [t, $J_{\text{P-C}} = 5.6$ Hz, $\text{P}(\text{C}_6\text{H}_5)$ *ortho* or *meta*]; 130.00 [s, $\text{P}(\text{C}_6\text{H}_5)$ *para*]; 133.67 [t, $J_{\text{P-C}} = 5.4$ Hz, $\text{P}(\text{C}_6\text{H}_5)$ *ortho* or *meta*]; 136.82 [t, $J_{\text{P-C}} = 20.1$ Hz, $\text{P}(\text{C}_6\text{H}_5)$ *ipso*]; 206 [br, CO *cis* to $\text{TcC}(\text{O})\text{OEt}$]; 208 [br, CO *trans* to $\text{TcC}(\text{O})\text{OEt}$]; 212 [br, $\text{TcCO}(\text{OEt})$] ppm. $^{31}\text{P}\{^1\text{H}\}$ (CD_2Cl_2 , 202.334 MHz) δ : ~ 42 (br) ppm. FAB MS(+) m/z : 735 [$\text{Tc}(\text{CO})_4(\text{PPh}_3)_2$]; 707 [$\text{Tc}(\text{CO})_3(\text{PPh}_3)_2$]; 679 [$\text{Tc}(\text{CO})_2(\text{PPh}_3)_2$].

3.6. Preparation of $\text{Tc}(\text{CO})_3(\text{C}(\text{O})\text{OC}_6\text{H}_4\text{CH}_3)(\text{PPh}_3)_2$ (7)

To a solution containing [$\text{Tc}(\text{CO})_4(\text{PPh}_3)_2$] BF_4 (1) (154 mg, 0.147 mmol) in 30 ml of THF in the dry box was added $\text{K}[\text{OC}_6\text{H}_4\text{CH}_3]$ (54 mg, 0.369 mmol). The reaction mixture was stirred for 30 min and then evaporated to dryness in vacuo. The beige colored residue was extracted into 15 ml of toluene and filtered through a bed of Celite. The toluene solution was layered with 30 ml of hexane and stored at -40°C overnight. The microcrystalline material which had formed was collected by filtration and dried in vacuo. Yield, 53.6 mg; 35%.

Anal. Calc. for $C_{47}H_{37}O_5P_2Tc$: C, 66.99; H, 4.43%. Found: C, 66.39; H, 4.39%. IR (KBr) $\nu(\text{cm}^{-1})$: 2012 (m, $\text{C}\equiv\text{O}$); 1954 (s, $\text{C}\equiv\text{O}$); 1926 (s, $\text{C}\equiv\text{O}$); 1648 (s, $\text{C}=\text{O}$). ^1H NMR (CD_2Cl_2) δ : 2.22 (s, 3H, CH_3); 6.94 (d, 2H, $J = 8.6$ Hz, C_6H_4); 6.66 (d, 2H, $J = 7.7$ Hz, C_6H_4); 7.43 [m, 18H, $\text{P}(\text{C}_6\text{H}_5)_2$]; 7.57 [m, 12H, $\text{P}(\text{C}_6\text{H}_5)_2$] ppm. $^{13}\text{C}\{^1\text{H}\}$ (CD_2Cl_2) δ : 21.43 (s, $\text{OC}_6\text{H}_4\text{CH}_3$); 125.98 (s, $\text{OC}_6\text{H}_4\text{CH}_3 \equiv \text{CH}$); 127.35 [t, $J_{\text{P-C}} = 4.9$ Hz, $\text{P}(\text{C}_6\text{H}_5)$ *ortho* or *meta*]; 129.65 [s, $\text{P}(\text{C}_6\text{H}_5)$ *para*]; 131.24 [t, $J_{\text{P-C}} = 6.9$ Hz, $\text{P}(\text{C}_6\text{H}_5)$ *ortho* or *meta*]; 132.47 (s, $\text{OC}_6\text{H}_4\text{CH}_3 \equiv \text{CH}$); 134.09 [t, $J_{\text{P-C}} = 25$ Hz, $\text{P}(\text{C}_6\text{H}_5)$ *ipso*, partially obscured]; 134.14 (s, $\text{OC}_6\text{H}_4\text{CH}_3$ *ipso* bonded to carbon); 153.15 (s, $\text{OC}_6\text{H}_4\text{CH}_3$ *ipso* bonded to oxygen); 202 [br, CO *cis* to $\text{TcC}(\text{O})\text{OC}_6\text{H}_4\text{CH}_3$]; 205 [br, CO *trans* to $\text{TcC}(\text{O})\text{OC}_6\text{H}_4\text{CH}_3$]; 214 [br, $\text{TcC}(\text{O})\text{OC}_6\text{H}_4\text{CH}_3$]. FAB MS(+) m/z : 735 [$\text{Tc}(\text{CO})_4(\text{PPh}_3)_2$]; 707 [$\text{Tc}(\text{CO})_3(\text{PPh}_3)_2$]; 679 [$\text{Tc}(\text{CO})_2(\text{PPh}_3)_2$].

3.7. Preparation of $\text{Tc}(\text{CO})_3(\text{NCO})(\text{PPh}_3)_2$ (8)

To [$\text{Tc}(\text{CO})_4(\text{PPh}_3)_2$] BF_4 (1) (76.6 mg, 0.093 mmol) dissolved in 30 ml of MeOH was added 6.9 mg of

NaN_3 . The reaction mixture was stirred for 25 h and evaporated to dryness with a stream of N_2 . The remaining solid residue was extracted into 3×15 ml portions of C_6H_6 , filtered through Celite and reduced in volume to 5 ml. The solution was then layered with 75 ml of pentane and stored at -15°C overnight. The cream colored solid which precipitated was filtered on a fritted disk, washed with 10 ml of pentane and dried in vacuo. Yield, 41.9 mg; 66%.

Anal. Calc. for $\text{C}_{40}\text{H}_{30}\text{O}_4\text{P}_2\text{Tc}$: C, 64.10; H, 4.03%. Found: C, 63.69; H, 4.00%. IR (KBr) $\nu(\text{cm}^{-1})$: 2239 (s, NCO); 2056 (w, $\text{C}\equiv\text{O}$); 1957 (s, $\text{C}\equiv\text{O}$); 1919 (s, $\text{C}\equiv\text{O}$). ^1H NMR (CDCl_3) δ : 7.34 [m, br, $\text{P}(\text{C}_6\text{H}_5)_2$]; 7.60 [m, br, $\text{P}(\text{C}_6\text{H}_5)_2$] ppm. FAB MS(+) m/z : 750 $[\text{Tc}(\text{CO})_3(\text{NCO})(\text{PPh}_3)_2]$; 721 $[\text{Tc}(\text{CO})_2(\text{N})(\text{PPh}_3)_2]$; 707 $[\text{Tc}(\text{CO})_3(\text{PPh}_3)_2]$; 693 $[\text{Tc}(\text{CO})(\text{NCO})(\text{PPh}_3)_2]$; $[\text{Tc}(\text{CO})_2(\text{PPh}_3)_2]$.

4. Conclusions

From the Tc^1 cation $[\text{Tc}(\text{CO})_4(\text{PPh}_3)_2]\text{BF}_4$ (**1**) we have synthesized and characterized new Tc formyl and alkoxy carbonyl complexes. The rich chemistry of these compounds as precursors in preparative organometallic chemistry will be investigated in the future.

References and notes

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