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# THE PREPARATION OF MONO($\eta^5$-PENTAMETHYLCYCLOPENTADIENYL) COMPOUNDS OF TANTALUM(V)

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## Summary

The synthesis and characterization of ($\eta^5$-$C_5Me_5$)$TaCl_4$, ($\eta^5$-$C_5Me_5$)$TaCl_4L$ (L = $PMe_3$, $P(OMe)_3$, $Ph_2PCH_2CH_2PPh_2$), ($\eta^5$-$C_5Me_5$)$TaMe_4$, and ($\eta^5$-$C_5Me_5$)$Ta(CH_2Ph)_2(CHPh)$ is described. NMR studies of the bis(1,2-diphenylphosphino)ethane (dppe) adduct show exchange of free and ligated dppe, possibly via dissociation of the ligand from a monodentate compound.

## Introduction

Recent publications [1–4] have reported the synthesis of $[CpMCl_4]_n$ (M = Nb, Ta and $n > 1$) from $MCl_5$ but the products were difficult to characterize due to their insolubility in common organic solvents. Additionally, their reluctance to sublime made it impossible to obtain a parent ion in the mass spectra of the complexes. In an effort to obtain well-characterized starting materials for our studies of mono-ring complexes of niobium and tantalum, we have explored the use of pentamethylcyclopentadiene as a ligand. Previous workers [5,6] have found that in addition to the steric and electronic differences between the normal and pentamethyl rings, methylation often leads to the formation of soluble monomeric crystalline products. Our results indicate that mono($\eta^5$-pentamethylcyclopentadienyl)tantalum(V) complexes are indeed soluble and readily characterized.

## Results and discussion

### *Synthesis of ($\eta^5$-$C_5Me_5$)$TaCl_4$*

Our source of the pentamethylcyclopentadienyl ligand in these investigations was ($C_5Me_5$)Sn-n-$Bu_3$, prepared by a modification of the procedure published [7] for ($C_5H_5$)Sn-n-$Bu_3$ (see Experimental Section). Dropwise addition of ($C_5Me_5$)Sn-n-$Bu_3$ to a methylene chloride suspension of $TaCl_5$ led to the formation of ($\eta^5$-$C_5Me_5$)$TaCl_4$ in 95% yield. The yellow crystalline product displays a singlet in the $^1H$ NMR ($CDCl_3$) at $\delta$ 2.73 ppm. A solution of equimolar quantities of ferrocene and

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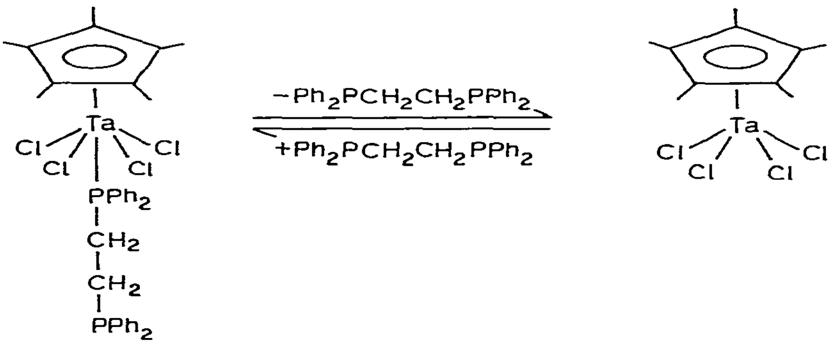
($\eta^5$-$C_5Me_5$)$TaCl_4$ yields a respective 10/15 integrated intensity ratio, supportive of the mono-ring nature of the tantalum complex. The proton-decoupled $^{13}C$ NMR spectrum ($CDCl_3$) exhibits singlets at δ 14.2 ($C_5(CH_3)_5$) and δ 133 ($C_5Me_5$) ppm. Mass spectral data are in accord with a monomeric product, showing a parent peak at $m/e = 456$–$460$ followed by successive loss of chloride ligands.

*Synthesis of ($\eta^5$-$C_5Me_5$)$TaCl_4L$ and ligand exchange studies*

We anticipate the synthesis of mono-ring hydride complexes but feel that the 14-electron ($\eta^5$-$C_5Me_5$)$MH_4$ systems will probably be unstable. We thus set out to prepare the ($\eta^5$-$C_5Me_5$)$TaCl_4L$ phosphine and phosphite adducts as a preliminary step to the hydride reactions. Treatment of a methylene chloride solution of ($\eta^5$-$C_5Me_5$)$TaCl_4$ with excess trimethylphosphine formed ($\eta^5$-$C_5Me_5$)$TaCl_4(PMe_3)$ in 71% yield. The $^1H$ NMR ($CDCl_3$) of this yellow compound shows a singlet at δ 2.50 ppm (15H, assigned to $C_5(CH_3)_5$) and a doublet ($^2J$(P–H) 11 Hz) at δ 1.73 ppm (9H, $P(CH_3)_3$). The mass spectrum is supportive of a monomeric product, displaying a parent peak at $m/e = 532$–$536$ with lower mass peaks corresponding to loss of chloride and trimethylphosphine ligands. Addition of trimethylphosphite to ($\eta^5$-$C_5Me_5$)$TaCl_4$ produced ($\eta^5$-$C_5Me_5$)$TaCl_4[P(OMe)_3]$ in 40% yield. $^1H$ NMR spectroscopy ($CDCl_3$) of this complex reveals resonances at δ 2.57 (15H, $C_5(CH_3)_5$) and δ 3.78 ppm (doublet, $^3J$(P–H) 9 Hz, 9H, $P(OCH_3)_3$). We were unable to find a parent peak in the mass spectrum, the highest mass occurring at $m/e = 456$–$460$ ($[(C_5Me_5)TaCl_4]^+$). Attempts at the preparation of ($\eta^5$-$C_5Me_5$)$TaCl_4(PPh_3)$ were unsuccessful, with no reaction observed between triphenylphosphine and ($\eta^5$-$C_5Me_5$)$TaCl_4$.

Our investigations with the potentially bidentate phosphine bis(1,2-diphenylphosphino)ethane (dppe) gave rather surprising results. The yellow crystalline product, ($\eta^5$-$C_5Me_5$)$TaCl_4$(dppe), was prepared in 81% yield from dppe and ($\eta^5$-$C_5Me_5$)$TaCl_4$. We assumed that only one phosphorus atom of the dppe ligand would bind to the metal, in analogy to the monosubstituted phosphine and phosphite adducts described above. Although we were unable to observe a parent ion in the mass spectrum of the dppe adduct, a peak was seen at $m/e = 821$ corresponding to $[(C_5Me_5)TaCl_3(dppe)]^+$. Other major peaks include $[(C_5Me_5)TaCl_4]^+$ at 456–460 and $(Ph_2PCH_2CH_2PPh_2)^+$ at 398. The $^1H$ NMR ($CDCl_3$) of ($\eta^5$-$C_5Me_5$)-$TaCl_4$(dppe) displays a singlet at δ 2.58 ppm ($C_5(CH_3)_5$, a triplet ($J$(P–H) 17 Hz) at δ 2.61 ppm ($Ph_2PCH_2CH_2PPh_2$), and a broad resonance centered at δ 7.6 ppm ($(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$). The integrated intensities from the NMR are consistent only with one dppe ligand per metal atom. The observation of a triplet due to the equivalent methylenes of the dppe moiety (as in uncomplexed dppe) is indicative of either a bidentate dppe ligand with equivalent phosphorus atoms or a monodentate ligand which is exchanging bound phosphorus atoms. Supporting the proton data is the $^{13}C$ NMR ($CDCl_3$) which possesses a single resonance for the equivalent methylene carbon atoms at δ 29.7 ppm. Other peaks in the spectrum appear at δ 13.5 ($C_5(CH_3)_5$), 133 ($C_5Me_5$) ppm, and two groups of peaks at δ 133–134 and 128–131 ppm assigned to the phenyl carbons in the dppe. In order to determine whether the equivalence of the methylenes was due to a static bidentate dppe or a fluxional process involving monodentate bonding, we undertook a $^{31}P$ NMR study of the system. ($\eta^5$-$C_5Me_5$)$TaCl_4$(dppe) in $CDCl_3$ exhibited a single broad resonance at δ − 6.30 ppm (downfield relative to $H_3PO_4$ standard) while the free ligand showed a sharp singlet at $\delta$ 12.57 ppm. A sample prepared by adding free dppe to the tantalum complex displayed a broad resonance at $\delta$ 3.83 ppm, indicative of exchange between free and bound dppe. Although we cannot rule out an associative process (proceeding through a $(C_5Me_5)TaCl_4(dppe)_2$ intermediate), we favor a dissociative process as shown in Scheme 1. Our failure to observe any $(\eta^5\text{-}C_5Me_5)TaCl_4L_2$ (L = $PMe_3$ or $P(OMe)_3$) complexes makes it seem unlikely that the associative pathway is operative here.

Scheme 1



The observation of exchange involving free and bound phosphorus is not confined to ligands containing two phosphorus atoms, however. The monophosphorus ligands we employed ($PMe_3$ and $P(OMe)_3$) also displayed this behavior. Thus, $(\eta^5\text{-}C_5Me_5)TaCl_4[P(OMe)_3]$ in chloroform-$d_1$ shows a signal at $\delta - 113.6$ ppm in the proton-decoupled $^{31}P$ NMR spectrum. The spectrum of trimethylphosphite recorded under identical conditions exhibits a resonance at $\delta - 141.0$ ppm. When $P(OMe)_3$ is added to a solution of the phosphite complex, the phosphorus peak shifts to a position between free and complexed trimethylphosphite, at $\delta - 134.4$ ppm, again suggestive of ligand exchange.

### *Synthesis of mono-ring alkyl complexes*

We set out to synthesize mono-ring alkyl complexes of Group V metals as a preliminary step in our investigations into the photochemistry of early transition metal alkyl compounds. We have examined the reactions of $(\eta^5\text{-}C_5Me_5)TaCl_4$ with alkylating agents in this effort. Addition of methyllithium to a diethyl ether solution of $(\eta^5\text{-}C_5Me_5)TaCl_4$ results in the formation of the tetramethyl complex $(\eta^5\text{-}C_5Me_5)TaMe_4$ in 85% yield. An analogous reaction of $(\eta^5\text{-}C_5Me_5)TaCl_4$ with $(PhCH_2)MgCl$ produces the dibenzylbenzylidene compound $(\eta^5\text{-}C_5Me_5)Ta(CH_2Ph)_2(CHPh)$ in 97% yield. Both of these compounds have been synthesized by Schrock and co-workers [8,9] via different routes although no spectroscopic characterization was reported for the tetramethyl complex. We find the $^1H$ NMR ($C_6D_6$) for $(\eta^5\text{-}C_5Me_5)TaMe_4$ has singlets at $\delta$ 1.68 (15H, $C_5(CH_3)_5$) and 0.67 ppm (12H, $Ta(CH_3)_4$).

Current synthetic work in our laboratory is focused on the preparation of $(\eta^5\text{-}C_5Me_5)NbCl_4$, $(\eta^5\text{-}C_5Me_5)_2NbCl_2$, and $(\eta^5\text{-}C_5Me_5)_2TaCl_2$ to be used as starting materials in the synthesis of early transition metal alkyl and hydride compounds.

## Experimental

All manipulations were carried out using either a high-vacuum system or a Vacuum Atmospheres nitrogen glovebox. Toluene, benzene, petroleum ether, and diethyl ether were purified by vacuum transfer first from 4Å molecular sieves and then from titanocene [10]. Chloroform and methylene chloride were purified by acid washing with concentrated sulfuric acid followed by drying over $CaCl_2$, distillation from $P_2O_5$, and vacuum transfer from 4Å molecular sieves. Tetrahydrofuran was purified by distillation from sodium benzophenone ketyl after refluxing overnight.

Trimethylphosphine (Strem) and trimethylphosphite (Aldrich) were stored over 4Å molecular sieves. Triphenylphosphine (Strem) and tantalum pentachloride (Alfa) were sublimed prior to use. 1,2,3,4,5-Pentamethylcyclopentadiene [11] and sodium pentamethylcyclopentadienide [12] were prepared according to the literature procedures. Tri-n-butyltin chloride (Aldrich), bis(1,2-diphenylphosphino)ethane (Strem), and methyllithium (Alfa) were used as received.

$^1H$ NMR spectra were recorded with Varian T-60 or XL-100 spectrometers. $^{13}C$ and $^{31}P$ NMR spectra were obtained with a Bruker WH-90 spectrometer. Mass spectra were measured with a Finnigan MAT-312 spectrometer. Elemental analyses were performed by Galbraith Laboratories.

### $(n\text{-}Bu)_3Sn(C_5Me_5)$

7.9 g (50 mmol) of sodium pentamethylcyclopentadienide and 16.3 g (50 mmol) of $n\text{-}Bu_3SnCl$ were added to 400 ml of toluene in the glovebox. This mixture was stirred at 20°C for 4 days followed by filtration to yield a light yellow-orange filtrate. The solid remaining on the filter was washed with three 50 ml portions of toluene and all filtrates were combined. The toluene was removed on the vacuum line to give a slightly viscous yellow-orange liquid. Distillation of this liquid at 0.005 torr with collection of the fraction between 115 and 120°C yielded 16.7 g (78%) of the light yellow-orange air-sensitive product. The $^1H$ NMR of this compound shows a singlet at $\delta$ 1.86 ppm (assigned to $C_5(CH_3)_5$) with satellite peaks due to coupling with $^{117}Sn$ and $^{119}Sn$ ($J(Sn-H)$ 17 Hz). Additionally, multiplets centered at $\delta$ 0.92 and 1.38 ppm (both due to $C_4H_9$) are found.

### $(\eta^5\text{-}C_5Me_5)TaCl_4$

4.30 g (10.1 mmol) of $n\text{-}Bu_3Sn(C_5Me_5)$ was added to a stirred suspension of 3.2 g (8.9 mmol) of $TaCl_5$ in 100 ml $CH_2Cl_2$ maintained at −78°C. The mixture was allowed to warm to room temperature and stirred at 20°C for 24 h. During this time, the color changed from light orange-yellow to deep red-brown. The reaction was then filtered to yield a red-brown solid and dark brown filtrate. The $CH_2Cl_2$ was removed in vacuo and the red-brown solid was washed several times with light petroleum ether (30–60°C) to remove all organotin compounds. The product was recrystallized from chloroform and petroleum ether to yield 3.9 g (95%) of bright yellow crystalline product. The mass spectrum exhibits peaks assigned to $[(C_5Me_5)TaCl_4]^+$, $m/e = 456\text{–}460$; $[(C_5Me_5)TaCl_3]^+$, 421–425; $[(C_5Me_5)TaCl_2]^+$, 386–388. Anal. Found: C, 25.86; H, 3.23; Cl, 29.36. $C_{10}H_{15}Cl_4Ta$ calcd.: C, 26.20; H, 3.28; Cl, 31.00%.

*($\eta^5$-$C_5Me_5$)$TaCl_4$($PMe_3$)*

400 mg (5.3 mmol) of trimethylphosphine was added to 200 mg (0.44 mmol) of ($\eta^5$-$C_5Me_5$)$TaCl_4$ in 25 ml $CH_2Cl_2$. After 24 h of stirring the solvent and excess $PMe_3$ were removed under vacuum. The resultant yellow solid was washed with light petroleum ether and dried to yield 165 mg (71%) of product. The mass spectrum shows peaks assigned to $[(C_5Me_5)TaCl_4(PMe_3)]^+$, $m/e$ = 532–536; $[(C_5Me_5)TaCl_3(PMe_3)]^+$, 497–501; $[(C_5Me_5)TaCl_4]^+$, 456–460; $[(C_5Me_5)TaCl_3]^+$, 421–425; $[(C_5Me_5)TaCl_2]^+$, 386–388. Anal. Found: C, 29.22; H, 4.65; Cl, 26.63; P, 5.88. $C_{13}H_{24}Cl_4PTa$ calcd.: C, 29.23; H, 4.53; Cl, 26.55; P, 5.80%.

*($\eta^5$-$C_5Me_5$)$TaCl_4$[P(OMe)$_3$]*

162 mg (1.3 mmol) of trimethylphosphite was added to 200 mg (0.44 mmol) of ($\eta^5$-$C_5Me_5$)$TaCl_4$ in 25 ml $CH_2Cl_2$. The solvent and excess $P(OMe)_3$ were removed in vacuo after 24 h of stirring. The crude product was washed with petroleum ether and 98 mg (40%) of the yellow product was obtained.

*($\eta^5$-$C_5Me_5$)$TaCl_4$(dppe)*

25 ml of tetrahydrofuran was vacuum transferred to a flask containing 180 mg (0.39 mmol) of ($\eta^5$-$C_5Me_5$)$TaCl_4$ and 235 mg (0.59 mmol) of $Ph_2PCH_2CH_2PPh_2$. The reaction was stirred for 17 h and then filtered. The filtrate was reduced to ca. 15 ml and an equivalent amount of petroleum ether was added causing the precipitation of a yellow product. This compound was isolated and washed with pure petroleum ether to yield 270 mg (81%) of the yellow crystalline complex.

*($\eta^5$-$C_5Me_5$)$TaMe_4$*

30 ml of diethyl ether was vacuum transferred to a Schlenk flask containing 500 mg (1.09 mmol) of ($\eta^5$-$C_5Me_5$)$TaCl_4$. This solution was maintained at −78°C while 3.0 ml of a methyllithium solution (1.6 *M* in $Et_2O$) was syringed into the flask under argon purge. The reaction mixture was allowed to warm to room temperature and the solvent was removed after stirring for 1 h at 20°C. 30 ml of petroleum ether was added to dissolve the product and the mixture was filtered to give a light yellow solution. Removal of solvent yielded 350 mg (85%) of a yellow crystalline compound.

*($\eta^5$-$C_5Me_5$)Ta(CHPh)($CH_2Ph$)$_2$*

30 ml of diethyl ether was vacuum distilled into a Schlenk flask containing 100 mg (0.218 mmol) of ($\eta^5$-$C_5Me_5$)$TaCl_4$. While this solution was maintained at −78°C, 0.8 ml of benzylmagnesium chloride solution (1.6 *M* in $Et_2O$) was syringed into the flask under argon flow. The solution immediately turned from yellow to brown. As the reaction mixture warmed from −78°C the solution became red with a light colored precipitate. After 1.5 h at room temperature the ether was removed and 30 ml of toluene was added. The solution was filtered, the filtrate volume reduced to ca. 5 ml, and 15 ml of petroleum ether was added to precipitate the product. This bright red solid was isolated and washed with pure petroleum ether to yield 100 mg (97%) of crystalline compound.

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