2760 *Organometallics* **1997,** *16,* 2760−2762

# $Tp^*Sn(Cl)Bu_2$ as a Convenient Reagent for the Preparation of Hydrotris(3,5-dimethylpyrazolyl)borate Complexes of Niobium, Tantalum, and Zirconium

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*Received February 18, 1997*[⊗]

*Summary: Organotin complexes bearing a Tp* ligand, $Tp^*Sn(Cl)_nBu_{3-n}$ (**1**, n = 1; **2**, n = 2; Tp* = hydrotris(3,5-dimethylpyrazolyl)borate), were found to be useful reagents for introducing a Tp* ligand on niobium and tantalum as well as zirconium. The reactivities of these organotin compounds together with $Tp^*SnCl_3$ (**3**) were compared directly by using the reaction with $ZrCl_4$, which affords $Tp^*ZrCl_3$ (**4**), as a test case. The reaction rate was in the order **1** > **2** ≫ **3**. Thus, complex **1** was used for the preparation of $Tp^*NbCl_3$ (**5**) and $[Tp^*TaCl_3][TaCl_6]$ (**6**), whose structures were confirmed by X-ray analysis. X-ray analysis of **1** indicated that one of the three Sn−N bonds in **1** was cleaved and that the Sn atom adopted a five-coordinate square pyramidal geometry that made complex **1** more reactive than the six-coordinate complexes **2** and **3**.*

Since hydrotris(pyrazolyl)borate (Tp) and its derivatives typically serve as tridentate, anionic, six-electron donor ligands similar to the well-known cyclopentadienyl ligands, investigations of organometallic and inorganic chemistry using this type of ligand have developed rapidly.[1−3] A variety of transition metal complexes bearing a Tp ligand and their derivatives have been synthesized mainly by using alkali-metal Tp compounds such as NaTp as reagents. However, this method sometimes has a disadvantage for the preparation of mono-Tp complexes of early transition metals because of the contamination with byproducts and the unexpected reduction of the metal halides.[1−3] Although the reactions of $TaCl_3({=}CH^tBu)(thf)_2$, $TaMe_3Cl_2$, and $NbCl_3(alkyne)$ with Tp* (Tp* = hydrotris(3,5-dimethylpyrazolyl)borate) and/or Tp ligands afforded $Tp^*TaCl_2({=}CH^tBu)(thf)_2$,[4] $TpTaMe_3Cl$,[5,6] and $TpNbCl_2(alkyne)$,[7−9] respectively, crystallographically-characterized halo complexes of niobium and tantalum of the type $TpMCl_n$ have never been prepared.[10,11] In view of the known versatility of (cyclopentadienyl)trialkylsilane[12,13] and (cyclopentadienyl)trialkyltin[14,15] as reagents for the preparation of mono-Cp complexes of niobium and tantalum, we were interested in an analogous approach to introduce a Tp* ligand onto niobium and tantalum. Here, we report the preliminary results of our finding that an organotin complex $Tp^*Sn(Cl)Bu_2$ is a very useful starting compound.

In order to find the best reagent suitable for introducing a Tp* ligand onto niobium and tantalum, we examined the reaction of equimolar amounts of $ZrCl_4$ and $Tp^*Sn(Cl)_nBu_{3-n}$ (**1**, n = 1; **2**, n = 2; **3**, n = 3) to afford $Tp^*ZrCl_3$ (**4**) as a test case. Organotin reagents **1**−**3** were readily prepared by the reaction of KTp* with $Sn(Cl)_{n+1}Bu_{3-n}$,[16] and **4**, a known compound, has been synthesized by the reaction of KTp* with 2 equiv of $ZrCl_4$.[17] Reactions of **1** and **2** with 1 molar equiv of $ZrCl_4$ in dichloromethane at room temperature for 10 min afforded **4** in a quantitative yield, and the same reactions of **1** and **2** at −10 °C for 10 min gave **4** in 65% and 38% yield, respectively (eq 1). Reaction of **3** with $ZrCl_4$ at room temperature did not proceed at all. It is notable that 2 equiv of $ZrCl_4$ were essential in order to obtain a high yield in the reaction of $ZrCl_4$ with KTp*, and thus, the maximum yield based on $ZrCl_4$ would be less than 50%[17] in sharp contrast to the stoichiometric reaction of $ZrCl_4$ and the Tp*−organotin compounds. The reactivity of these organotin complexes depends on the number of the alkyl substituents on tin; the more highly alkylated organotin complexes exhibited higher reactivity. $Tp^*SnBu_3$ was expected to be the most reactive but was thermally unstable and gradually decomposed at room temperature. Organosilane derivatives of Tp* might serve our purpose, but such compounds have not been isolated to date.[18] Thus, we finally chose complex

$$\underset{\substack{\mathbf{1}\ (n=1)\\ \mathbf{2}\ (n=2)}}{ZrCl_4 + Tp^*Sn(Cl)_nBu_{3-n}} \xrightarrow[CH_2Cl_2]{\text{room temperature}} \underset{\mathbf{4}}{Tp^*ZrCl_3} \qquad (1)$$

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[†] Research Fellow of the Japan Society for the Promotion of Science, 1996−1997.

[⊗] Abstract published in *Advance ACS Abstracts,* May 15, 1997.

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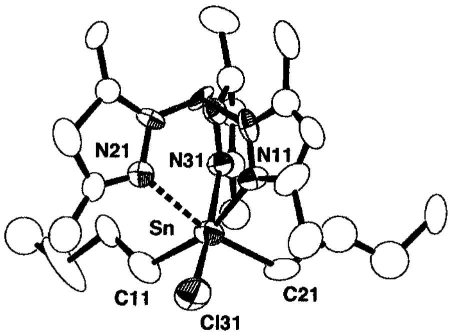

**Figure 1.** ORTEP drawing of complex **1** with the numbering scheme. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Sn−N(11) 2.22(2), Sn−N(21) 2.46(2), Sn−N(31) 2.294(4), Sn−C(11) 2.32(2), Sn−C(21) 2.07(3), Sn−Cl(31) 2.492(2); N(11)−Sn−N(21) 74.4(2), N(11)−Sn−N(31) 82.3(6), N(11)−Sn−C(11) 161.5(8), N(11)−Sn−C(21) 87.7(8), N(11)−Sn−C(31) 82.3(6), N(21)−Sn−N(31) 83.6(6), N(21)−Sn−C(11) 88.9(8), N(21)−Sn−C(21) 162.0(8), N(21)−Sn−C(31) 86.7(4), N(31)−Sn−C(11) 88.3(8), N(31)−Sn−C(21) 95.2(4), N(31)−Sn−Cl(31) 168.6(1), C(11)−Sn−C(21) 109.0(3), C(11)−Sn−C(31) 97.6(6), C(21)−Sn−C(31) 92.1(6).

**1** as the reagent to prepare mono-Tp* complexes of niobium and tantalum.

The crystal structure of complex **1** was determined by X-ray analysis (Figure 1).[19] The bond distances of Sn−N(11) (2.22(2) Å) and Sn−N(31) (2.294(4) Å) are longer than that found for $\mathrm{TpSnCl_3}$ (2.234(7) Å),[20] while the distance of Sn−N(21) (2.46(2) Å) is larger by ca. 0.2 Å. The bond angles N(11)−Sn−C(11) (161.5(8)°), N(21)−Sn−C(21) (162.0(8)°), and N(31)−Sn−Cl(31) (168.6(1)°) deviate significantly from 180°. This deformation from octahedral geometry around the tin atom might be due to the strong *trans* influence of the butyl ligands. Thus, the tin atom of **1** adopts a five-coordinate square pyramidal geometry, which may account for the higher reactivity of **1** compared with those of the six-coordinate complexes **2** and **3**.

Reaction of $\mathrm{NbCl_4{\cdot}2THF}$ with a stoichiometric amount of **1** in toluene at −78 °C to room temperature gave a Tp* complex of niobium $\mathrm{Tp^*NbCl_3}$ (**5**) as orange crystals in 41% yield (eq 2).[21] Figure 2 shows the crystal structure of **5**.[22] The niobium atom in **5** is coordinated by one Tp* and three chloride ligands with octahedral geometry. The average distances of the Nb−N (2.20 Å) and Nb−Cl (2.342 Å) are normal for Nb−N bond distances.

$$\mathrm{NbCl_4{\cdot}(THF)_2} + \underset{\mathbf{1}}{\mathrm{Tp^*Sn(Cl)Bu_2}} \xrightarrow[\text{toluene}]{-78\ ^\circ\text{C to room temperature}} \underset{\mathbf{5}}{\mathrm{Tp^*NbCl_3}} \quad (2)$$

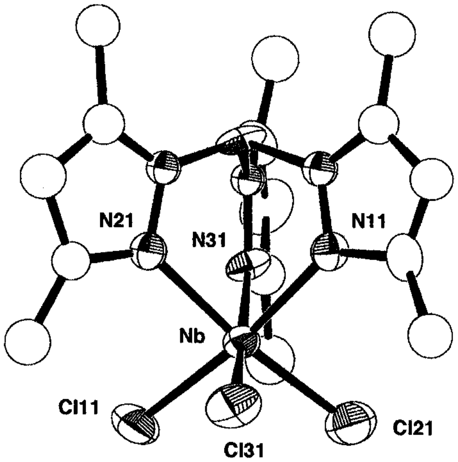

**Figure 2.** ORTEP drawing of complex **5** with the numbering scheme. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Nb−N(11) 2.204(4), Nb−N(21) 2.18(1), Nb−N(31) 2.22(1), Nb−Cl(11) 2.353(5), Nb−Cl(21) 2.320(4), Nb−Cl(31) 2.350(3); N(11)−Nb−N(21) 83.6(5), N(11)−Nb−N(31) 84.9(5), N(11)−Nb−Cl(11) 172.4(2), N(11)−Nb−Cl(21) 91.5(4), N(11)−Nb−Cl(31) 88.8(4), N(21)−Nb−N(31) 83.5(1), N(21)−Nb−Cl(11) 89.4(4), N(21)−Nb−Cl(21) 171.8(4), N(21)−Nb−Cl(31) 90.3(4), N(31)−Nb−Cl(11) 91.4(4), N(31)−Nb−Cl(21) 89.6(4), N(31)−Nb−Cl(31) 171.6(4), Cl(11)−Nb−Cl(21) 95.2(2), Cl(11)−Nb−Cl(31) 94.1(2), Cl(21)−Nb−Cl(31) 89.6(4).

Complex **1** also is a useful reagent for introducing a Tp* ligand onto a Ta(V) metal center. Treatment of $\mathrm{TaCl_5}$ with 1 molar equiv of **1** in toluene at 60 °C afforded a cationic complex **6** as an orange powder in 54% yield (eq 3).[23] The structure of complex **6**, determined by X-ray analysis, is comprised of a discrete $\mathrm{Tp^*TaCl_3^+}$ cation and a $\mathrm{TaCl_6^-}$ anion.[24] The cationic portion of **6** is shown in Figure 3. The tantalum atom is coordinated by three nitrogen atoms of the Tp* ligand and three chloro ligands in an octahedral fashion. The average Ta−N bond distance (2.17 Å) is slightly shorter than that of the niobium analog **5** (2.20 Å), the observed

$$\mathrm{2TaCl_5} + \underset{\mathbf{1}}{\mathrm{Tp^*Sn(Cl)Bu_2}} \xrightarrow[\text{toluene}]{\text{room temperature }-60\ ^\circ\text{C}} \underset{\mathbf{6}}{\mathrm{[Tp^*TaCl_3][TaCl_6]}} \quad (3)$$

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[19] Crystallographic data for **1**: $\mathrm{C_{23}H_{40}N_6BClSn}$, $fw = 565.56$, monoclinic, space group $P2_1$ (No. 4), $a = 8.360(2)$ Å, $b = 18.329(3)$Å, $c = 9.400(2)$ Å, $\beta = 104.45(1)°$, $V = 1394.8(4)$ Å$^3$, $Z = 2$, $d_{\mathrm{calcd}} = 1.346$ g cm$^{-3}$, 1989 reflections ($I > 3\sigma(I)$, $2\theta_{\max} = 55.1°$, $2\theta-\omega$ scan, 20 °C), $R = 0.039$ and $R_w = 0.022$ for 237 variables.

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[21] Procedure for **5**: To a deep red solution of $\mathrm{NbCl_4{\cdot}(THF)_2}$ (91.3 mg, 0.241 mmol) in toluene (10 mL) at −78 °C was added dropwise a solution of **1** (136.5 mg, 0.241 mmol) in toluene (5 mL). The reaction mixture was stirred at −78 °C for 5 min and then was allowed to warm to room temperature. The mixture was stirred at room temperature for 12 h and gave **5** as a dark red suspension. All volatiles were removed under reduced pressure, and the residue was washed with hexane (20 mL × 2). The product was extracted with dichloromethane; recrystallization from a mixture of dichloromethane and hexane at room temperature afforded **5** (48.9 mg, 41% yield) as orange crystals, mp 278−284 °C (dec). IR (Nujol/CsI): 2560 ($\nu_{\mathrm{B-H}}$) cm$^{-1}$. Anal. Calcd for $\mathrm{C_{15}H_{22}N_6BCl_3Nb}$: C, 36.29; H, 4.47; N, 16.93. Found: C, 36.13; H, 4.42; N, 16.82.

[22] Crystallographic data for **5**: $\mathrm{C_{15}H_{22}N_6BNbCl_3}$, $fw = 496.45$, monoclinic, space group $P2_1$ (No. 4), $a = 8.135(1)$ Å, $b = 14.181(2)$ Å, $c = 9.1455(9)$ Å, $\beta = 100.166(9)°$, $V = 1038.4(2)$ Å$^3$, $Z = 2$, $d_{\mathrm{calcd}} = 1.588$ g cm$^{-3}$, 2114 reflections ($I > 3\sigma(I)$, $2\theta_{\max} = 55.0°$, $2\theta-\omega$ scan, 20 °C), $R = 0.040$ and $R_w = 0.032$ for 153 variables.

[23] Spectroscopic and analytical data for **6**: Mp 187−213 °C (dec). IR (Nujol/KBr): 2560 ($\nu_{\mathrm{B-H}}$) cm$^{-1}$. Complex **6** was found to be a 2:1 mixture of two isomers. $\mathrm{[Tp^*TaCl_3]^+}$: $^1$H NMR (CDCl$_3$) $\delta$ 2.64 (s, 9H), 2.79 (s, 9H), 6.20 (s, 3H). $\mathrm{[(HB(pzMe_2\text{-}3,5)(\eta^1\text{-}pzMe_2\text{-}3,5)_2)TaCl_3]^+}$ or $\mathrm{(HB(pzMe_2\text{-}3,5)(\eta^1\text{-}pzMe_2\text{-}3,5)_2)TaCl_4}$: $^1$H NMR (CDCl$_3$) $\delta$ 2.42 (s, 3H), 2.49 (s, 6H), 2.70 (s, 3H), 2.85 (s, 6H), 5.97 (s, 1H), 6.02 (s, 2H). Anal. Calcd for $\mathrm{C_{15}H_{22}N_6BCl_{10}Ta_2}$: C, 18.42; H, 2.27; N, 8.59. Found: C, 18.70; H, 2.30; N, 8.31.

[24] Crystallographic data for **6**: $\mathrm{C_{15}H_{22}N_6BTa_2Cl_9}$, $fw = 978.16$, orthorhombic, space group *Pbcn* (No. 60), $a = 20.716(5)$ Å, $b = 11.927(3)$ Å, $c = 23.403(8)$ Å, $V = 5782(2)$ Å$^3$, $Z = 8$, $d_{\mathrm{calcd}} = 2.247$ g cm$^{-3}$, 3709 reflections ($I > 3\sigma(I)$, $2\theta_{\max} = 55.0°$, $2\theta-\omega$ scan, 20 °C), $R = 0.041$ and $R_w = 0.024$ for 298 variables.

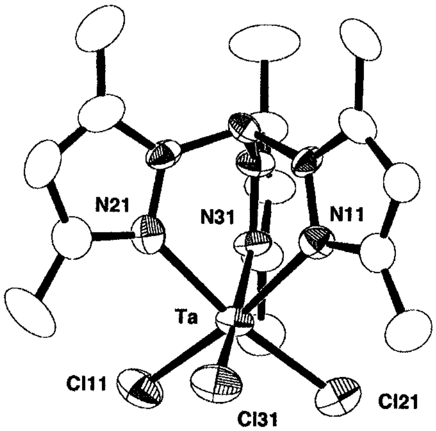

**Figure 3.** ORTEP drawing of the cation Tp*$TaCl_3^+$ in complex **6** with the numbering scheme. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ta–N(11) 2.171(8), Ta–N(21) 2.153(8), Ta–N(31) 2.149(7), Ta–Cl(11) 2.281(3), Ta–Cl(21) 2.273(3), Ta–Cl(31) 2.278(2); N(11)–Ta–N(21) 84.2(3), N(11)–Ta–N(31) 83.0(3), N(11)–Ta–Cl(11) 171.9(2), N(11)–Ta–Cl(21) 89.8(2), N(11)–Ta–Cl(31) 89.1(2), N(21)–Ta–N(31) 83.2(3), N(21)–Ta–Cl(11) 89.4(2), N(21)–Ta–Cl(21) 171.5(2), N(21)–Ta–Cl(31) 89.8(2), N(31)–Ta–Cl(11) 91.4(2), N(31)–Ta–Cl(21) 90.1(2), N(31)–Ta–Cl(31) 170.0(2), Cl(11)–Ta–Cl(21) 96.1(1), Cl(11)–Ta–Cl(31) 95.77(10), Cl(21)–Ta–Cl(31) 96.1(1).

difference reflecting the difference in the ionic radii of tantalum and niobium, *i.e.*, $Ta^{5+} = 0.64$ Å, $Nb^{4+} = 0.74$ Å. In solution, **6** was observed by NMR spectroscopy to be a mixture of a complex [Tp*$TaCl_3$]$^+$ and a dissymmetric one coordinated by two nitrogen atoms of the Tp* ligand, *i.e.*, a five-coordinate species [(HB($pzMe_2$-3,5)($\eta^1$-$pzMe_2$-3,5)$_2$)$TaCl_3$]$^+$ or a six-coordinated species (HB($pzMe_2$-3,5)($\eta^1$-$pzMe_2$-3,5)$_2$)$TaCl_4$. The $^1H$ NMR spectrum of **6** in $CDCl_3$ at 35 °C displayed three singlets at $\delta$ 2.64, 2.49, and 2.42 in a 6:2:1 ratio due to the three kinds of magnetically nonequivalent $CH_3$ protons of the pyrazolyl rings. The largest peak at $\delta$ 2.64 is assigned to a hexacoordinated species [Tp*$TaCl_3$]$^+$. The two singlets observed at $\delta$ 2.49 and 2.42 are assignable to the 3-$CH_3$ protons of the dissymmetric tantalum species, the former signal at $\delta$ 2.49 being due to the 3-$CH_3$ protons of two pyrazolyl rings bound to the tantalum atom and the latter at $\delta$ 2.42 due to that of the uncoordinated one.

In summary, the Tp*–organotin complex **1** proved to be a useful reagent for the preparation of mono-Tp* complexes of niobium and tantalum as well as of zirconium. Application of **1** to the preparation of the Tp* complexes of other transition metals, especially early transition metals, is our further interest.

**Acknowledgment.** We thank Professor Kitaura (Osaka Prefecture University) for fruitful discussions of the structure of **1**. K.M. acknowledges the financial support by the Grant-in-Aid for Scientific Research (Grant No. 05236106 and No. 08875178) from the Ministry of Education, Science, Sports and Culture, Japan and by the Kurata Foundation.

**Supporting Information Available:** Text giving the experimental details for the preparation of **4** and **6**, tables of final positional parameters, final thermal parameters, and bond distances and angles, and drawings showing the atom-numbering scheme for **1**, **5**, and **6** (51 pages). Ordering information is given on any current masthead page.

OM9701175