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"Bent-Sandwich" Derivatives of Tantalum Bearing One or Two Pentamethylcyclopentadienyl Ligands†

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The compounds $(\eta^5\text{-}C_5Me_5)_2TaCl_2$ and $(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_5H_5)TaCl_2$ are prepared in good yield by treatment of the trimethylphosphine adduct $(\eta^5\text{-}C_5Me_5)TaCl_3(PMe_3)$ with potassium pentamethylcyclopentadienide or sodium cyclopentadienide in toluene. Reaction of $(\eta^5\text{-}C_5Me_2)_2TaCl_2$ with Grignard reagents, RMgX (R = Et, *n*-Pr), affords the olefin complexes $(\eta^5\text{-}C_5Me_5)_2TaH(C_2H_3R')$ (R′ = H, Me). Treatment of $(\eta^5\text{-}C_5Me_5)_2TaCl_2$ or $(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_5H_5)TaCl_2$ with $LiAlH_4$ in diethyl ether, followed by aqueous workup, gives $(\eta^5\text{-}C_5Me_5)_2TaH_3$ and $(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_5H_5)TaH_3$, respectively, which react with two-electron donor ligands (L = CO, olefin) at elevated temperature to give compounds of general formulas $(\eta^5\text{-}C_5Me_5)_2TaH(L)$ and $(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_5H_5)TaH(L)$.

Introduction

Permethylmetallocene derivatives offer a number of advantages over their $(\eta^5\text{-}C_5H_5)$ analogues. Generally they exhibit higher thermal stability and are less prone to undergo oligomerization through single atom bridges. Such properties have facilitated the development of a rich and diverse reaction chemistry for compounds of the early transition metals with pentamethylcyclopentadienyl as ancillary ligands.[1]

Recently a route to permethylniobocene derivatives was developed which utilizes the convenient starting material $(\eta^5\text{-}C_5Me_5)_2NbBH_4$, obtained in 30–40% yield from the reaction of $NbCl_5$ with LiC_5Me_5 and $NaBH_4$ in dimethoxyethane.[2] Since the third-row (5d) derivatives generally offer greater thermal stability than the second-row (4d) analogues, we anticipated that permethyltantalocene derivatives would be sufficiently stable to allow us to examine structures and mechanisms inaccessible with $[(\eta^5\text{-}C_5H_5)_2Ta]$ or $[(\eta^5\text{-}C_5Me_5)_2Nb]$ systems. Despite our continuing interest and a long term concerted effort to prepare compounds of tantalum bearing two $(\eta^5\text{-}C_5Me_5)$ ligands, we were previously unsuccesful in gaining a synthetic entry to permethyltantalocene derivatives.

Here we report a convenient synthesis of $(\eta^5\text{-}C_5Me_5)_2TaCl_2$ and its mixed-ring analogue $(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_5H_5)TaCl_2$ together with some preliminary studies of their reactivity.

Results and Discussion

Following a previously reported procedure[3] with minor modifications, a suspension of tantalum pentachloride in toluene reacts with $(C_5Me_5)SnBu_3$ (Bu = $CH_2CH_2CH_2CH_3$) over a period of 20 h to give yellow Cp^*TaCl_4 (Cp^* = $\eta^5\text{-}C_5Me_5$).

$$TaCl_5 + Cp^*SnBu_3 \xrightarrow[\text{toluene}]{25\ ^\circ\text{C}} Cp^*TaCl_4 \qquad (1)$$

Reduction of Cp^*TaCl_4 by stirring with 0.5 equiv of magnesium in tetrahydrofuran in the presence of PMe_3 affords the trimethylphosphine adduct $Cp^*TaCl_3(PMe_3)$ (1). Treatment of 1 with KCp^* in toluene at 100 °C

$$Cp^*TaCl_4 + PMe_3 \xrightarrow[25\ ^\circ\text{C, THF}]{\text{Mg}} \underset{\mathbf{1}}{Cp^*TaCl_3(PMe_3)} \qquad (2)$$

affords the paramagnetic tantalum(IV) compound $Cp^*_2TaCl_2$ (2). Typical overall yields are in the range

$$\underset{\mathbf{1}}{Cp^*TaCl_3(PMe_3)} + KCp^* \xrightarrow[\text{toluene}]{100\ ^\circ\text{C}} \underset{\mathbf{2}}{Cp^*_2TaCl_2} \qquad (3)$$

50–60%. The mixed-ring compound $Cp^*CpTaCl_2$ (3, Cp = $\eta^5\text{-}C_5H_5$) is readily prepared in similar yield by substituting NaCp for KCp^* in eq 3. Both compounds 2 and 3 may be crystallized as dark brown needles by slow cooling of hot toluene solutions. When powdered, 2 and 3 take on a green appearance.

Attempts to prepare 2 by a route analogous to that developed for permethylniobocene dichloride[2] were unsuccessful: reaction of $TaCl_5$ with an excess of $LiCp^*$ and $NaBH_4$ in dimethoxyethane gave none of the monomeric compound $Cp^*_2TaBH_4$, although at elevated reaction temperatures a purple compound with the formula $[Cp^*Ta(B_2H_6)]_2$ could be isolated.[4] Spectroscopic data suggest that this product is isostructural with the dimeric niobium species which has been shown to possess novel bridging diborane units.[5] Other attempts to prepare 2 directly from $TaCl_5$ by reaction with excess MCp^* (M = Li, Na, K) and metal reductants such as Al and Zn were also unsuccessful, as were attempts to attach a second ring to Cp^*TaMe_3Cl, $Cp^*TaH_3Cl(PMe_3)_2$, or $Cp^*TaH_4(PMe_3)_2$,[6] by reaction with MCp^* (M = Li, Na).

Treatment of 2 or 3 with lithium aluminum hydride in diethyl ether over a period of several hours affords a yellow suspension which, on hydrolysis, gives the trihydride complexes $Cp^*_2TaH_3$ (4) and Cp^*CpTaH_3 (5) in high yields

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[1] See, for example: (a) Wolczanski, P. T.; Bercaw, J. E. *Acc. Chem. Res.* **1980**, *13*, 121. (b) Thompson, M. E.; Bercaw, J. E. *Pure Appl. Chem.* **1984**, *56*, 1. (c) Hillhouse, G. L.; Bercaw, J. E. *J. Am. Chem. Soc.* **1985**, *106*, 5474.

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[5] See "Comprehensive Organometallic Chemistry"; Pergamon Press: New York, 1982; Vol. 3, p 765.

[6] (a) Mayer, J. M. Bercaw, J. E. *J. Am. Chem. Soc.* **1982**, *104*, 2157. (b) Mayer, J. M.; Wolczanski, P. T.; Santarsiero, B. D.; Olson, W. A.; Bercaw, J. E. *Inorg. Chem.* **1983**, *22*, 1149.

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(eq 4 and 5). The intermediate yellow compound is also seen in the formation of Cp_2MH_3 (M = Nb, Ta) and has been shown, in the case of niobium, to be the tetrahydridoaluminato species $Cp_2NbH_2AlH_2$.[7]

$$\underset{\mathbf{2}}{Cp^*_2TaCl_2} \xrightarrow[2.\ H_2O]{1.\ LiAlH_4} \underset{\mathbf{4}}{Cp^*_2TaH_3} \tag{4}$$

$$\underset{\mathbf{3}}{Cp^*CpTaCl_2} \xrightarrow[2.\ H_2O]{1.\ LiAlH_4} \underset{\mathbf{5}}{Cp^*CpTaH_3} \tag{5}$$

Unlike Cp_2TaH_3,[8] **4** and **5** do not sublime cleanly. Dihydrogen is lost, consistent with the observed ions in the mass spectra at *m/e* 450 and 380, respectively, corresponding to loss of 2 equiv of dihydrogen/molecule. Such facile loss of two H_2 molecules may reflect a propensity for intramolecular activation of a C–H bond of a ring methyl group, a process which has been shown to be facile for group 4 transition-metal permethylmetallocene complexes.[9] Like Cp_2TaH_3 ^1H NMR spectra of **4** and **5** reveal AX_2 patterns for the hydride hydrogens, although shifts to lower field are observed for the pentamethylcyclopentadienyl derivatives.

Simple adducts may be prepared by thermolysis of **4** or **5** in hydrocarbon solvent in the presence of two-electron donor ligands. For example, when **4** or **5** is heated at 140 and 110 °C, respectively, under an atmosphere of carbon monoxide, the carbonyl adducts **6** and **7** are formed (eq 6 and 7).

$$\underset{\mathbf{4}}{Cp^*_2TaH_3} + CO \xrightarrow{140\ °C} \underset{\mathbf{6}}{Cp^*_2TaH(CO)} + H_2 \tag{6}$$

$$\underset{\mathbf{5}}{Cp^*CpTaH_3} + CO \xrightarrow{110\ °C} \underset{\mathbf{7}}{Cp^*CpTaH(CO)} + H_2 \tag{7}$$

Both **6** and **7** display characteristic CO stretching frequencies at 1865 and 1863 cm^{-1}, respectively, consistent with considerable back-donation from tantalum to carbon monoxide. These values are expectedly lower than the band observed for $Cp_2TaH(CO)$ ($\nu(CO) = 1885\ cm^{-1}$),[10] reflecting an increase in electron density on the metal center in the pentamethylcyclopentadienyl compounds.

The η^2-olefin compound $Cp^*_2TaH(C_2H_4)$ (**8**) is formed with concomitant formation of ethane on prolonged thermolysis (10 days at 140 °C) of $Cp^*_2TaH_3$ under excess ethylene. The quantitative yield (NMR) of this reaction points out the tremendous thermal stability of **4**, **8**, and indeed most $[Cp^*_2Ta]$ derivatives we have prepared. A more convenient route involves reaction of **2** with excess EtMgX (eq 8), a reactivity mode first reported by Teuben and co-workers for the preparation of $Cp_2NbH(C_2H_4)$.[11] Interestingly, **8** and its niobium analogue[2b,c] show no tendency to form the ethylene–ethyl derivatives $Cp^*_2M(C_2H_5)(C_2H_4)$ (M = Nb, Ta) with excess ethylene, as has been reported for the (η^5-C_5H_5) compounds.[10]

$$\underset{\mathbf{2}}{Cp^*_2TaCl_2} \xrightarrow{C_2H_5MX} \underset{\mathbf{8}}{Cp^*_2TaH(C_2H_4)} \tag{8}$$

$$X = Br, Cl$$

The ^1H NMR spectrum of **8** reveals a small (2.7-Hz) coupling between the endo ethylenic hydrogens and the metal-bound hydrogen nucleus. The upfield ^{13}C NMR shifts for the ethylenic carbons at δ 14.86 and 20.27 and the intermediate $^1J_{CH}$ values (145 and 141 Hz) are indicative of significant π back-bonding, such that the tantalacyclopropane formalism[12] contributes significantly to the bonding of ethylene to tantalum for **8**.

The propene adduct (η^5-$C_5Me_5)_2TaH(CH_2CHMe)$ (**9**) may be prepared by a similar procedure: reaction of **2** with *n*-PrMgX (X = Br, Cl) affords a single isomer of **9**, which, by comparison with the niobium analogue,[2b] is assigned as the endo form in which the methyl substituent occupies the sterically less hindered central position. In contrast, $Cp_2TaH(CH_2CHMe)$ exists in roughly equal proportions of endo and exo forms.[11] It has not proven possible to prepare **9** by thermolysis of (η^5-$C_5Me_5)_2TaH_3$ in the presence of excess propene. Rather, at 140 °C formation of propane and H/D exchange are observed between ring methyls and deuterobenzene solvent. The lower stability of the propene adduct probably reflects an increase in the unfavorable steric interaction between the olefin substituents and (η^5-C_5Me_5) groups.

Other η^2-olefin complexes and compounds of internal acetylenes can be prepared by heating **4** or **5** with 2 equiv of the unsaturated hydrocarbon. For example, the compounds $Cp^*_2TaH(MeC{\equiv}CMe)$, $Cp^*CpTaH(MeC{\equiv}CMe)$, and $Cp^*_2TaH(CH_2{=}CHPh)$ may be synthesized cleanly by heating **4** or **5** with 2-butyne or styrene at 80 °C in benzene. Although we have not isolated these adducts, their ^1H NMR data are entirely analogous to those for the permethylniobocene derivatives.[2b,13] Reactions with terminal acetylenes have not afforded tractable products, possibly due to the greater acidity of the acetylene proton.

Conclusions

The difficulties we encountered in our early attempts to prepare bis(pentamethylcyclopentadienyl)tantalum derivatives were certainly frustrating. While there could be a number of contributing factors which prevent straghtforward metathesis of chloride and a second equivalent of pentamethylcyclopentadienide for Cp^*TaCl_4, Cp^*TaMe_3Cl, or $Cp^*TaH_3Cl(PMe_3)_2$, the procedure reported herein for $Cp^*TaCl_3(PMe_3)$ does indeed afford $Cp^*_2TaCl_2$ in good yield. We presume that MCp^* (M = Li, Na, K) are sufficiently powerful reductants to effect reduction of the Ta(V) compounds and that the resulting Ta(IV) species undergo decomposition much faster than addition of the second bulky Cp* ring. Trimethylphosphine appears to coordinate only weakly to $[Cp^*TaCl_3]$ but nonetheless does prevent oligomerization and/or disproportionation of this reactive fragment. Moreover, the present procedure allows the synthesis of mixed ring bent sandwich compounds of tantalum as illustrated by $Cp^*CpTaCl_2$. Unfortunately, the method appears to be tantalum specific, since several attempts to prepare $Cp^*_2NbCl_2$[2] by an analogous sequence have failed.

By adopting procedures previously reported for Cp_2TaCl_2, we have successfully prepared $Cp^*_2TaH_3$, Cp^*CpTaH_3, $Cp^*_2TaH(L)$, and $Cp^*CpTaH(L)$ (L = CO, olefin). The tremendous thermal stability of the permethyltantalocene derivatives exceeds even our expectations and augurs well for the organometallic chemistry of this new class of sterically encumbered compounds of tantalum.

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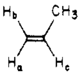
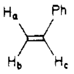
Table I. NMR and IR Data

compd	IR, cm^{-1}	type	chem shift, δ	assignment	coupling, Hz
$\mathrm{Cp^*TaCl_3(PMe_3)}$ (**1**)	965 (ν(P–C))				
$\mathrm{Cp^*_2TaCl_2}$ (**2**)					
$\mathrm{Cp^*CpTaCl_2}$ (**3**)					
$\mathrm{Cp_2^*TaH_3}$ (**4**)	1790 (ν(Ta–H))	$^{1}\mathrm{H}^{a}$	2.00 (s)	$\mathrm{C_5(C\mathit{H}_3)_5}$	
	1750		1.11 (t)	Ta–H	$^2J_{\mathrm{HH}} = 13.0$
			−0.91 (d)	Ta–H	$^2J_{\mathrm{HH}} = 13.0$
$\mathrm{Cp^*CpTaH_3}$ (**5**)	1750 (ν(Ta–H))	$^{1}\mathrm{H}^{a}$	1.99 (s)	$\mathrm{C_5(C\mathit{H}_3)_5}$	
	1720		4.72 (s)	$\mathrm{C_5\mathit{H}_5}$	
			0.07 (t)	Ta–H	$^2J_{\mathrm{HH}} = 11.8$
			−1.53 (d)	Ta–H	$^2J_{\mathrm{HH}} = 11.8$
$\mathrm{Cp^*_2TaH(CO)}$ (**6**)	1865 (ν(CO))	$^{1}\mathrm{H}^{a}$	1.84 (s)	$\mathrm{C_5(C\mathit{H}_3)_5}$	
	1725 (ν(Ta–H))		5.15 (s)	Ta–H	
$\mathrm{Cp^*CpTaH(CO)}$ (**7**)	1863 (ν(CO))	$^{1}\mathrm{H}^{a}$	1.87 (s)	$\mathrm{C_5(C\mathit{H}_3)_5}$	
	1740 (ν(Ta–H))		4.40 (s)	$\mathrm{C_5\mathit{H}_5}$	
			5.48 (s)	Ta–H	
$\mathrm{Cp^*_2TaH(C_2H_4)}$ (**8**)	1765 (ν(Ta–H))	$^{1}\mathrm{H}^{a}$	1.69 (s)	$\mathrm{C_5(C\mathit{H}_3)_5}$	
			0.34 (td)	$\mathrm{H_a}$	$J_{\mathrm{ab}} = 10.9$ $J_{\mathrm{Ha}} = 2.7$
			−0.60 (t)	$\mathrm{H_b}$	$J_{\mathrm{ba}} = 10.9$
			−2.84 (t,bd)	Ta–H	
		$^{13}\mathrm{C}^{b}$	11.83 (q)	$\mathrm{C_5(\mathit{C}H_3)_5}$	$J = 126$
			102.13 (s)	$\mathit{C}_5\mathrm{(CH_3)_5}$	
			14.86 (t)	$\mathrm{CH_2}$	$J = 145$
			20.57 (t)	$\mathrm{CH_2}$	$J = 141$
$\mathrm{Cp^*_2TaH(C_2H_3Me)}$ (**9**)	1700, 1773 (ν(Ta–H))	$^{1}\mathrm{H}^{a}$	1.96 (s)	$\mathrm{C_5(C\mathit{H}_3)_5}$	
			1.83 (s)	$\mathrm{C_5(C\mathit{H}_3)_5}$	
			0.19 (dd)	$\mathrm{H_a}$	$J_{\mathrm{ab}} = 6.6$ $J_{\mathrm{ac}} = 12.0$
			−0.20 (dd)	$\mathrm{H_b}$	$J_{\mathrm{ba}} = 6.6$ $J_{\mathrm{bc}} = 12.6$
			0.72 (dqd)	$\mathrm{H_c}$	$J_{\mathrm{ca}} = 12.0$ $J_{\mathrm{cb}} = 12.6$ $J_{\mathrm{H_c\text{-}Me}} = 7.2$
			2.50 (d)	Me	$J_{\mathrm{Me\text{-}H_c}} = 7.2$
			−2.17 (s)	Ta–H	
		$^{13}\mathrm{C}^{b}$	103.87	$\mathit{C}_5\mathrm{(CH_3)_5}$	
			103.16	$\mathit{C}_5\mathrm{(CH_3)_5}$	
			31.52 (d)	$\mathrm{C_{en}}$	$J_{\mathrm{C\text{-}H}} = 139$
			25.69 (q)	Me	$J_{\mathrm{C\text{-}H}} = 116$
			25.04 (t)	$\mathrm{C_{exo}}$	$J_{\mathrm{C\text{-}H}} = 135$
			12.59	$\mathrm{C_5(\mathit{C}H_3)_5}$	
			11.82	$\mathrm{C_5(\mathit{C}H_3)_5}$	
$\mathrm{Cp^*_2TaH(MeC{\equiv}CMe)}$		$^{1}\mathrm{H}^{c}$	1.80 (s)	$\mathrm{C_5(C\mathit{H}_3)_5}$	
			2.77 (s)	$\mathrm{CH_3C{\equiv}CCH_3}$	
			2.52 (s)		
			0.47 (s)	Ta–H	
$\mathrm{Cp^*CpTaH(MeC{\equiv}CMe)}$		$^{1}\mathrm{H}^{c}$	1.72 (s)	$\mathrm{C_5(C\mathit{H}_3)_5}$	
			4.82 (s)	$\mathrm{C_5\mathit{H}_5}$	
			2.68 (s)	$\mathrm{CH_3C{\equiv}CCH_3}$	
			2.48 (s)		
			0.23 (s)	Ta–H	
$\mathrm{Cp^*_2TaH(CH_2{=}CHPh)}$		$^{1}\mathrm{H}^{c}$	1.70 (s)	$\mathrm{C_5(C\mathit{H}_3)_5}$	
			1.55 (s)	$\mathrm{C_5(CH_3)_5}$	
			0.12 (m)	$\mathrm{H_a}$	
			1.05 (m)	$\mathrm{H_b}$	
			2.42 (m)	$\mathrm{H_c}$	
			1.23 (s)	Ta–H	

^{a}Bruker WM 500. ^{b}JEOL GX400Q. ^{c}Varian EM 390. All spectra recorded in benzene-d_6.

Experimental Section

General Considerations. All manipulations of air- and/or moisture-sensitive materials were carried out on a conventional vacuum line using standard Schlenk or cannula techniques or in a drybox under an atmosphere of dinitrogen or argon.

Solvents were dried and purified by prolonged reflux under a suitable drying agent followed by distillation under an atmosphere of dinitrogen. Ethereal solvents were stored over sodium benzophenone ketyl, and hydrocarbon solvents were stored over titanocene. Elemental analyses and mass spectral data were provided by the Caltech microanalytical service. Nuclear magnetic resonance spectra were recorded on Varian EM 390, JEOL FX90Q, Bruker WM 500, or JEOL GX400Q spectrometers. Infrared spectra were recorded on a Beckman 4240 spectrometer. Relative intensities are abbreviated as follows: vs (very strong), s (strong), m (medium), w (weak), bd (broad), sh (shoulder). $\mathrm{Cp^*SnBu_3}$[3] and $\mathrm{PMe_3}$[14] were prepared according to previously reported procedures. KCp* was prepared by the reaction of Cp*H with KH in tetrahydrofuran at room temperature.

(η^5-$\mathrm{C_5Me_5}$)$\mathrm{TaCl_4}$. $\mathrm{Cp^*SnBu_3}$ (49.9 g, 0.116 mol) was added slowly to a stirred suspension of $\mathrm{TaCl_5}$ (35.0 g, 0.098 mol) in

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toluene (400 cm^3) over a period of 30 min. A mildly exothermic reaction ensued. Stirring was continued for a further 20 h to give a copious yellow suspension, which was collected, filtered, and washed with petroleum ether (3 × 50 ml). The residue was dried in vacuo to yield 43.6 g (97%) of Cp*$TaCl_4$.

(η^5-C_5Me_5)$TaCl_3$(PMe_3) (1). Cp*$TaCl_4$ (43.6 g, 0.095 mol) was weighed into a 500-mL round-bottomed flask along with magnesium turnings (1.15 g, 0.047 mol). THF (300 mL) was condensed onto the mixture at −78 °C followed by trimethylphosphine (7.60 g, 0.10 mol), and the mixture was allowed to warm to room temperature with stirring. The solution rapidly took on a red coloration, and stirring was continued until all the magnesium turnings were consumed (~6 h). The volatiles were then removed under reduced pressure, and the residue was dried in vacuo. An analytically pure sample may be obtained by extraction with toluene (200 cm^3) containing a small amount of PMe_3 (irreversible PMe_3 dissociation occurs in the absence of PMe_3). The red toluene/PMe_3 extract was concentrated and cooled (to −78 °C) to afford red crystals of Cp*$TaCl_3$(PMe_3). However, for the purpose of the Cp*$_2TaCl_2$ preparation there is no need to purify the crude Cp*$TaCl_3$(PMe_3) residue. Anal. Calcd for $C_{13}H_{24}Cl_3PTa$: C, 31.48; H, 4.82. Found: C, 31.29; H, 4.81. IR (cm^{-1}, Nujol): 2725 (w), 1307 (w), 1290 (m), 1260 (w), 1025 (m, b d), 965 (s), 950 (m), 740 (w), 732 (w).

(η^5-C_5Me_5)$_2TaCl_2$ (2). KCp* (13.0 g, 0.075 mol) was weighed into a 500-mL round-bottomed flask along with 40 g of the Cp*$TaCl_3$(PMe_3) residue. PMe_3 (0.5 mL) was condensed onto the mixture at −78 °C, and toluene (~250 mL) was introduced under a counterflow of argon. After being allowed to warm to room temperature, the mixture was stirred and heated slowly to 100 °C. This temperature was maintained for 24 h after which large quantities of brown crystals were in evidence. The volatiles were removed under reduced pressure, and the residue was dried in vacuo. Purification was achieved by toluene Soxhlet extraction, followed by very slow cooling to afford large dark brown needle crystals of Cp*$_2TaCl_2$ (28.5 g, overall yield from $TaCl_5$, 55.9%). Anal. Calcd for $C_{20}H_{30}Cl_2Ta$: C, 46.10; H, 5.80. Found: C, 45.98; H, 5.75. Mass spectrum: *m/e* 521.

(η^5-C_5Me_5)(η^5-C_5H_5)$TaCl_2$ (3). NaCp (0.75 g, 8.5 mol) and Cp*$TaCl_3$(PMe_3) (5 g of crude residue) were stirred in toluene (50 mL) at 100 °C in the presence of PMe_3 (0.3 mL) for 18 h. The volatiles were than removed under reduced pressure, and the residue was dried in vacuo. Toluene soxhlet extraction followed by slow cooling of the toluene extract afforded dark brown needle crystals of 2, yield, 2.3 g (60.7%). Anal. Calcd for $C_{15}H_{20}Cl_2Ta$: C, 39.83; H, 4.43. Found: C, 39.82; H, 4.42. Mass spectrum: *m/e* 451. IR (cm^{-1}, Nujol): 3130 (w), 3080 (w), 2720 (w), 1260 (w), 1080 (m), 1022 (s), 1015 (s), 915 (s), 855 (w), 840 (s), 825 (s).

(η^5-C_5Me_5)$_2TaH_3$ (4). Diethyl ether (30 mL) was transferred onto a weighed mixture of 2 (0.5 g, 0.96 mmol) and $LiAlH_4$ (0.25 g, 6.6 mmol) at −78 °C. The mixture was warmed to room temperature with stirring to give a yellow suspension, which was stirred for a further 12 h. After the mixture was cooled to 0 °C, degassed H_2O (1.0 mL) was added dropwise to give a colorless solution. Removal of the volatiles under reduced pressure followed by extraction with petroleum ether (50 mL) gave a colorless solution which on concentration and cooling afforded white crystals of 4 (0.4 g, 92%). Anal. Calcd for $C_{20}H_{33}Ta$: C, 53.09; H, 7.14. Found: C, 52.86; H, 7.27. Mass spectrum: *m/e* 380. IR (cm^{-1}, Nujol): 2720 (w), 1790 (s, b d), 1750 (s, b d), 1490 (m), 1030 (s), 907 (s), 840 (m), 800 (w).

(η^5-C_5Me_5)(η^5-C_5H_5)TaH_3 (5). A stirred solution of 3 (1.5 g, 3.3 mmol) and $LiAlH_4$ (0.75 g, 19.8 mmol) in diethyl ether at −78 °C was slowly warmed to room temperature. After 12 h, the resulting yellow solution, supporting a white solid, was cooled to 0 °C and treated dropwise with H_2O (1.0 mL). The solvent was then removed under reduced pressure, and the residue was dried in vacuo overnight. Extraction with petroleum ether (80 mL) followed by concentration and cooling to −78 °C afforded white crystals of 5, yield 0.9 g (70.4%). Anal. Calcd for $C_{15}H_{23}Ta$: C, 47.15; H, 6.01. Found: C, 46.88; H, 5.99. Mass spectrum: *m/e* 380. IR (cm^{-1}, Nujol): 2725 (w), 1750 (s, b d, sh), 1720 (s, b d), 1490 (m), 1115 (w), 1070 (w), 1035 (m), 1020 (m), 1005 (m), 890 (m), 855 (m), 830 (m), 800 (s).

(η^5-C_5Me_5)$_2$TaH(CO) (6). A thick-walled glass reaction vessel (50 mL) fitted with a Teflon needle valve was charged with Cp*$_2TaH_3$ (0.5 g, 1.10 mmol), toluene (20 mL), and excess carbon monoxide (2 atm). The mixture was stirred at 140 °C for 4 days to give a purple solution which was filtered and pumped to dryness in vacuo. Extraction of the residue with octane (15 mL) gave a purple solution which was filtered and cooled slowly to −50 °C. The resulting purple crystals of 6 were collected and dried in vacuo to yield 0.4 g (86%). Anal. Calcd for $C_{21}H_{30}OTa$: C, 52.48; H, 6.40. Found: C, 52.50; H, 6.46. Mass spectrum: *m/e* 480. IR (cm^{-1}, Nujol): 2720 (w), 1865 (vs), 1725 (m), 1025 (s).

(η^5-C_5Me_5)(η^5-C_5H_5)TaH(CO) (7). In a manner analogous to 6, Cp*CpTaH_3 (0.53 g, 1.20 mmol), toluene (20 mL), and carbon monoxide were stirred at 110 °C for 24 h to give a dark blue solution. The volatiles were removed under reduced pressure, and the residue was extracted with petroleum ether (20 mL). The resulting blue solution was filtered and cooled to −78 °C to afford purple crystals of 7, yield 0.4 g (82%). Anal. Calcd for $C_{16}H_{20}OTa$: C, 47.09; H, 5.26. Found: C, 46.83; H, 5.12. Mass spectrum: *m/e* 410. IR (cm^{-1}, Nujol): 3090 (w), 2720 (w), 1863 (vs), 1740 (s), 1385 (s), 1105 (m), 1065 (w), 1035 (m), 1110 (m), 995 (w), 810 (s).

(η^5-C_5Me_5)$_2$TaH(C_2H_4) (8). EtMgCl (5.4 mL of 2.85 M Et_2O solution, 15.4 mmol) was added to a stirred suspension of Cp*$_2TaCl_2$ (2.0 g, 3.8 mmol) in diethyl ether (20 ml) at −78 °C. The mixture was warmed to room temperature and stirred for 12 h to give a clear orange solution. After removal of the volatile components, the residue was extracted with petroleum ether (80 mL) to give a yellow solution, which was filtered, concentrated, and cooled to −78 °C to afford pale yellow crystals of 8, yield 0.76 g (41.3%). Anal. Calcd for $C_{22}H_{35}Ta$: C, 54.93; H, 7.16. Found: C, 55.0; H, 7.29. Mass spectrum: *m/e* 480. IR (cm^{-1}, Nujol): 2720 (w), 1763 (s), 1490 (m), 1170 (w), 1110 (s), 1028 (s), 905 (m), 765 (m).

(η^5-C_5Me_5)$_2$TaH(CH_2CHMe) (9). In a similar manner to 8, *n*-PrMgCl (1.35 mL of 2.0 M solution in Et_2O) was treated with Cp*$_2TaCl_2$ (0.35 g, 0.67 mmol) in diethyl ether (15 mL). Extraction of the residue with petroleum ether (50 mL) gave an orange solution which was concentrated and cooled to −78 °C. The resulting yellow crystals of 9 were collected, washed with petroleum ether (2 × 5 mL), and dried in vacuo to afford 0.23 g (69.5%) of 9. Anal. Calcd for $C_{23}H_{39}Ta$: C, 55.82; H, 7.55. Found: C, 55.87; H, 7.49. IR (cm^{-1}, Nujol): 2720 (w), 1773 (s), 1700 (m), 1485 (m), 1185 (m), 1060 (w), 1020 (s), 870 (m), 745 (m).

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