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Utility of hydridotributyltin as both reductant and hydride transfer reagent in organotransition metal chemistry I. A convenient synthesis of the organoditantalum(IV) hydrides $(\eta\text{-}C_5Me_4R)_2Ta_2(\mu\text{-}H)_2Cl_4$ (R = Me, Et) from $(\eta\text{-}C_5Me_4R)TaCl_4$, and probes of the possible reaction pathways

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Abstract

The reaction of $(\eta\text{-}C_5Me_4R)TaCl_4$ (R = Me, Cp*; Et) with two equivalents of Bu_3SnH in toluene at 25°C yields $(\eta\text{-}C_5Me_4R)_2Ta_2(\mu\text{-}H)_2Cl_4$ in 92% yield (R = Me) or 63% (R = Et) along with Bu_3SnCl and H_2. The μ-H group is derived from the tin reagent, as shown by a deuterium labelling study. UV/vis spectra of the reaction mixture exhibit several isosbestic points during the reaction which are consistent with the absence of significant concentrations of intermediate(s). The ditantalum(IV) halide $(\eta\text{-}C_5Me_4R)_2Ta_2Cl_6$ is not a major species on the pathway from $(\eta\text{-}C_5Me_4R)TaCl_4$ to $(\eta\text{-}C_5Me_4R)_2Ta_2(\mu\text{-}H)_2Cl_4$, since the reaction of $(\eta\text{-}C_5Me_4R)_2Ta_2Cl_6$ with two equivalents of Bu_3SnH to form $(\eta\text{-}C_5Me_4R)_2Ta_2(\mu\text{-}H)_2Cl_4$ is significantly slower. Possible pathways for the formation of $(\eta\text{-}C_5Me_4R)_2Ta_2(\mu\text{-}H)_2Cl_4$ from $(\eta\text{-}C_5Me_4R)TaCl_4$ are discussed. © 1998 Elsevier Science S.A.

Keywords: Tantalum; Organodimetallics; Hydride; Peralkylcyclopentadienyl; Hydridotri(butyl)tin

1. Introduction

Hydridotri(butyl)tin is an effective but underutilized reagent in early transition metal chemistry, as opposed to its widespread use in organic synthesis. It has been used in the reduction of (cyclopentadienyl)Ti diolate/dithiolates [1], reduction of NbX_5 to $NbX_3(MeOCH_2CH_2OMe)$ (X = Cl, Br) [2,3], reduction of $TaCl_5$ to $Ta_3Cl_9(thf)_4$ and $Sn(Ta_2Cl_9)_2$ [4], reduction of mono(cyclopentadienyl)oxo(chloro)titanium clusters [5], and reduction of $ZrCl_4$ to hexazirconium clusters [6]. Bu_3SnH is also an effective hydride transfer agent, having been used in the synthesis of (cyclopentadienyl)Mo hydrides [7] (interestingly, the product also contains a $SnBu_3$ ligand) and in the synthesis of (aryloxide)tantalum(V) hydrides [8,9]. The mechanisms of these inorganic/organometallic hydride transfers and reductions with Bu_3SnH have not been examined.

During the course of our studies to evaluate hydridotri(butyl)tin as a reagent for synthesis of mid-valent organoditantalum hydride complexes, we examined the reaction of Bu_3SnH with the four-legged piano-stool, organotantalum(V) compound [10–15] $(\eta\text{-}C_5Me_4R)TaCl_4$ (**1**; R = Me, Cp*; Et) and have found it to be a convenient route for the one-step preparation of the organoditantalum(IV) hydride $(\eta\text{-}C_5Me_4R)_2Ta_2(\mu\text{-}H)_2Cl_4$ (**2**) [16]. Compound **2** is important in the history of organotransition metal chemistry because it was the first transition metal hydride to yield a formyl ligand by migratory insertion of carbon monoxide [17,18]. [1] Compound **2** was first prepared via hydrogenation of the propylene complex [19,10] $(\eta\text{-}C_5Me_4R)Ta(MeCH{=}CH_2)Cl_2$, in an overall yield of 49% based on $TaCl_5$, and via hydrogenation of the bis(neopentyl) complex

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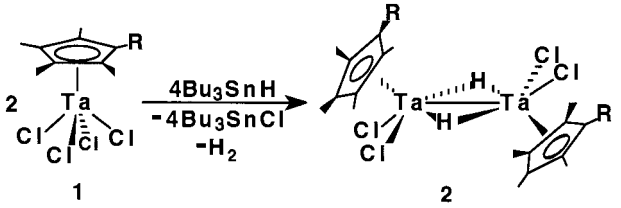
[1] Compound **2** also reacts with nitriles to give related products [18].

[20,21] $(\eta\text{-}C_5Me_4R)Ta(CH_2CMe_3)_2Cl_2$, in an overall yield of 48%. It was later obtained [22] from oxidative addition of H_2 to the organoditantalum(III) compound $(\eta\text{-}C_5Me_4R)_2Ta_2(\mu\text{-}Cl)_4$ [2] (**3**) [23], which itself is prepared in two steps from $TaCl_5$ via reduction of **1**; the overall yield of **2** based on $TaCl_5$ is 56%. Hydrogenation of **3** may play a role in the mechanism of formation of **2** in the reported routes [16] from $(\eta\text{-}C_5Me_4R)Ta(MeCH=CH_2)Cl_2$ or $(\eta\text{-}C_5Me_4R)Ta(CH_2CMe_3)_2Cl_2$ because the hydrogenation of either compound could yield, after reductive elimination, $(\eta\text{-}C_5Me_4R)TaCl_2$(solvate) and then **3** by subsequent dimerization.

2. Results and discussion

2.1. Preparation of $(C_5Me_4R)_2Ta_2(\mu\text{-}H)_2Cl_4$

The reaction of **1** with slightly greater than two equivalents of Bu_3SnH in toluene at 25° (Eq. (1)) yields the bis(μ-hydride) $(C_5Me_4R)_2Ta_2(\mu\text{-}H)_2Cl_4$ (**2**) in 92% yield (R = Me) based on **1**, along with H_2 and two equivalents of Bu_3SnCl as the only tin-containing by-product. Bu_3SnCl and H_2 are formed in stoichiometric amounts as depicted in Eq. (1).



(1)

This was shown by ^1H NMR integration (ratio of number of equivalents for $(C_5Me_5)_2Ta_2(\mu\text{-}H)_2Cl_4$:$H_2$:$Bu_3SnCl$:residual Bu_3SnH = 1.0:1.0:4.5: < 0.01 vs. a theoretical ratio of 1.0:1.0:4.0:0.0) of the reaction run in situ in a valved NMR tube which was completely filled with C_6D_6 (in order to keep the H_2, δ4.52, dissolved). The by-products were verified by comparison to ^1H NMR spectra of authentic Bu_3SnCl and H_2. The absence of $Bu_3SnSnBu_3$ was demonstrated by comparison to a ^1H NMR spectrum of authentic material.

We see no evidence for formation, during reaction of **1** with two equivalents of Bu_3SnH, of the known reduction products of **1**, the Ta(IV) dinuclear compound [24] $(C_5Me_4R)_2Ta_2Cl_6$ nor the dinuclear Ta(III) compound $(C_5Me_4R)_2Ta_2(\mu\text{-}Cl)_4$ (**3**). In the small-scale, NMR tube reaction of $(C_5Me_5)TaCl_4$ with two equivalents of Bu_3SnH in C_6D_6, resonances associated with minor amounts of a diamagnetic compound (δ2.08 and δ6.06, ratio 30:1; vide infra) and a paramagnetic species (δ22.3, broad) are observed at intermediate stages. These resonances disappear at reaction completion, with the former yielding **2**. The spectra are inconclusive on whether the latter, minor paramagnetic species is converted to **2** or to another unobserved species.

Several isosbestic points (at 340 nm, 414 nm and 478 nm; Fig. 1) are observed by UV/vis spectrophotometry during the course of the reaction of $(C_5Me_5)TaCl_4$ with two equivalents of Bu_3SnH in toluene at $\sim$0°C, consistent with the absence of any appreciable concentration of intermediate(s).

The μ-hydride ligands in **2** are derived from Bu_3SnH and not from solvent or C_5Me_4R ligand, as the reaction of $(C_5Me_5)TaCl_4$ with two equivalents of Bu_3SnD gave $(C_5Me_5)_2Ta_2(\mu\text{-}D)_2Cl_4$ with IR and ^2H NMR spectra identical to literature values [16] and to values for $(C_5Me_5)_2Ta_2(\mu\text{-}D)_2Cl_4$ prepared by addition of D_2 to **2**. The by-products dideuterium (δ4.525 in C_6H_5Me) and Bu_3SnCl were verified by ^2H NMR and ^1H NMR spectroscopies, respectively.

2.2. Examination of possible pathways for formation of $(C_5Me_4R)_2Ta_2(\mu\text{-}H)_2Cl_4$

Scheme 1 depicts several possible radical and non-radical pathways for the formation of **2** from **1**, using R = Me (Cp^*) for simplicity. The presence of isosbestic points rules out appreciable concentrations of the potential intermediates depicted in Scheme 1. A formal reduction from Ta(V) (**1**) to Ta(IV) (**2**) by Bu_3SnH occurs with formation of H_2, with the dihydrogen-evolving step presently unknown.

Several of the possible steps in Scheme 1 are based on H–$SnBu_3$ bond homolysis to give $H^\bullet$ and $Bu_3Sn^\bullet$, which then abstracts $Cl^\bullet$ from the organotantalum reactant. Chlorine atom abstraction from **1** by Bu_3SnH could form $H^\bullet$ and the Ta(IV) radical $(C_5Me_4R)TaCl_3$. The latter could then dimerize to $(C_5Me_4R)_2Ta_2Cl_6$, followed by reaction with two equivalents of Bu_3SnH to give **2** and Bu_3SnCl. We see no evidence for formation of free $H^\bullet$ during the reaction. If $H^\bullet$ were formed, it would dimerize to H_2 (with no activation barrier, limited only by diffusion) or abstract $H^\bullet$ from toluene to give H_2 and 1,2-diphenylethane by intermolecular coupling of the relatively stable benzyl radicals. 1,2-Diphenylethane is not observed by ^1H NMR spectroscopy when the reaction of **1** and Bu_3SnH (2 equiv.) is run under dilute conditions in toluene, at a concentration which would favor 1,2-diphenylethane formation over hydrogen radical dimerization. In addition, the reaction of Bu_3SnH (2 equiv.) with **1** in

[2] We have recently determined that $(\eta\text{-}C_5Me_4Et)_2Ta_2(\mu\text{-}Cl)_4$ has a tetra(μ-chloro) structure [23] similar to that previously reported [22] for the bromo analog.

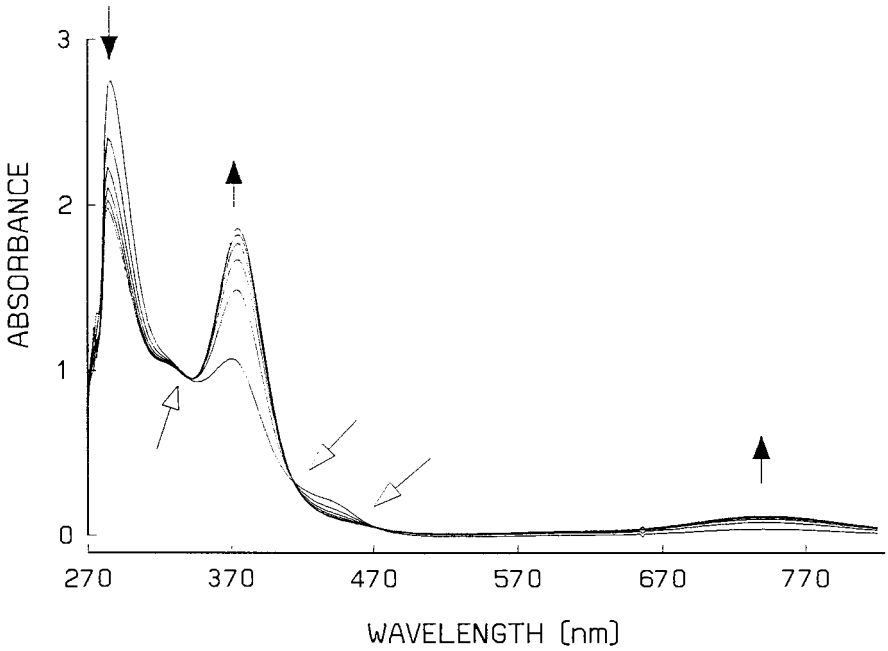
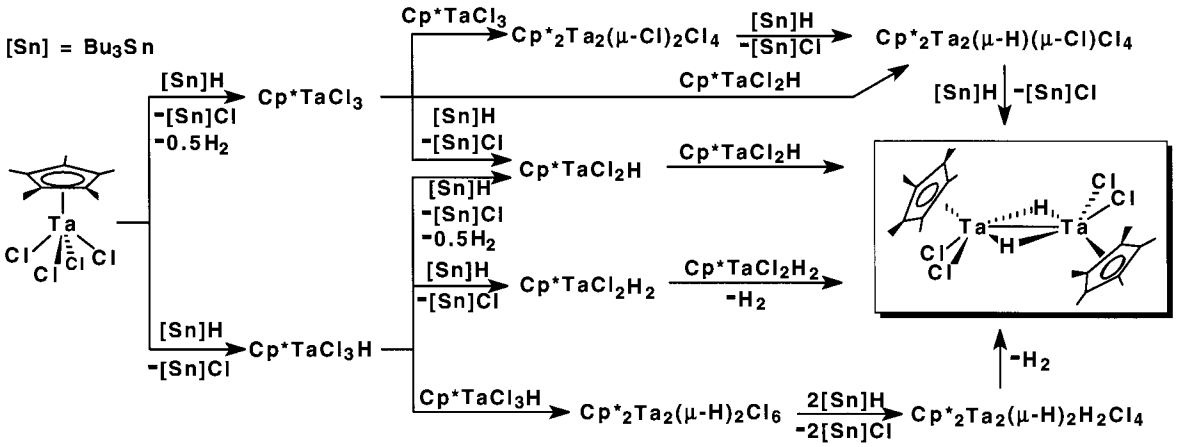


Fig. 1. UV–vis spectrum of the reaction of **1** with Bu_3SnH. The solid arrows show the direction of change of spectral maxima during the reaction. The open arrows show the isosbestic points.

$C_6D_5CD_3$ shows that HD is not formed (as determined by ^1H NMR spectroscopy with comparison to the spectrum of authentic HD). In organic synthetic applications of Bu_3SnH, homolysis of the H–$SnBu_3$ bond is seen only at elevated temperatures (such as in refluxing toluene), so we believe that it is less likely in the reactions of **1** with Bu_3SnH. Since there is no evidence for the formation of free $H^{\bullet}$, dihydrogen must be formed from intra- or intermolecular reductive elimination from tantalum or ditantalum hydrides. We therefore favor σ-bond metathesis as the route for Cl/H exchange in Scheme 1 between the various organotantalum and organoditantalum chlorides and Bu_3SnH.

In order to further exclude this radical pathway from the organometallic perspective, we examined the reaction of $(C_5Me_4R)_2Ta_2Cl_6$ with two equivalents of Bu_3SnH. This reaction yields **2** in 28% yield, but requires several days for completion by NMR spectroscopy, whereas the reaction of **1** with two equivalents of Bu_3SnH is complete within 1–2 h under the same conditions. We therefore conclude that reduction of **1** to $(C_5Me_4R)_2Ta_2Cl_6$ prior to hydride/chloride exchange does not contribute significantly to the formation of **2** from **1**. Since the reaction of $(C_5Me_4R)_2Ta_2Cl_6$ and Bu_3SnH (2 equiv.) to give **2** must proceed via two steps, possibly through an intermediate such as



Scheme 1.

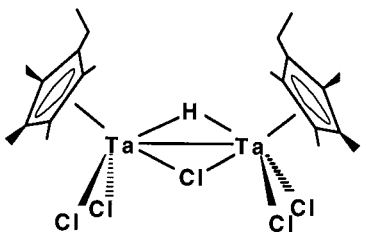
$(C_5Me_4R)_2Ta_2(\mu\text{-H})(\mu\text{-Cl})Cl_4$ [3], the slowness of this reaction suggests that either the first or second hydride/chloride exchange must be rate-limiting.

2.3. Attempted syntheses of reaction intermediates

We attempted to synthesize a possible intermediate, $(C_5Me_4R)_2Ta_2(\mu\text{-H})(\mu\text{-Cl})Cl_4$, in Scheme 1 by addition of one equivalent of either LiH or Bu_3SnH to $(C_5Me_4R)_2Ta_2Cl_6$. The reaction with LiH gives a mixture of products, none of which corresponded by ^1H NMR spectroscopy to species present in the reactions of **1** or $(C_5Me_4R)_2Ta_2Cl_6$ with Bu_3SnH. The reaction of $(C_5Me_5)_2Ta_2Cl_6$ with Bu_3SnH in toluene gives a significant amount of a product (**4**) with proton NMR signals at δ2.08 and δ6.06, in an integration ratio of 30:1. The resonance for **4** at δ6.06 is absent when Bu_3SnD is used as reactant, suggesting that it corresponds to a hydride ligand. Product **4** constitutes about 60% of the mixture after 15 min of reaction time, along with **2** (from which it cannot be easily separated) and a paramagnetic species with a broad resonance at δ38.1. The latter resonance, for a presently unidentified product, is associated with a C_5Me_5 group since it splits into resonances at δ40.6, δ34, and δ16.7 for the C_5Me_4Et analog (the fourth resonance is obscured by other resonances). This paramagnetic species is not evident in in situ reactions of **1** with two equivalents of Bu_3SnH.

Compound **4** possesses a mirror plane through both equivalent cyclopentadienyl groups as shown by ^1H NMR spectroscopy, as the reaction mixture from $(C_5Me_4Et)_2Ta_2Cl_6$ and Bu_3SnH (1 equiv.) shows a resonance pattern with two cyclopentadienyl ring methyl resonances, in addition to the Et resonances, as opposed to four ring methyl resonances. Infrared spectra of **4** which was isolated from reaction of $(C_5Me_4R)_2Ta_2Cl_6$ with one equivalent of either Bu_3SnH or Bu_3SnD are identical to one another and exhibit no discernible absorption consistent with a terminal or bridging hydride. Compound **4** slowly converts over several days to **2** in solution.

The hydride (δ 6.02) and ring methyl (δ 2.18, δ 2.09) resonances for the C_5Me_4Et analog of **4** correspond approximately but not completely with those reported for the compound $(C_5Me_4Et)_2Ta_2HCl_5$ (δ 6.08, μ-H; δ 2.2, δ 2.15, Me and Me′) [3], though the ethyl methylene resonance for **4** (δ 2.36) differs substantially from the published value for $(C_5Me_4Et)_2Ta_2HCl_5$ (δ 2.6). [3] The integration ratio of 30:1 for C_5Me_5 vs. H for the C_5Me_5 analog is consistent with a dinuclear compound (as opposed to a mononuclear tantalocene complex since there is no plausible route to the latter under the reaction conditions), and the magnetic equivalence of the C_5Me_5 groups suggests that the hydride must occupy a bridging position. The equivalence of the cyclopentadienyl groups and the mirror plane symmetry exhibited by the ^1H NMR resonances for the C_5Me_4Et analog suggests (1) a distinctly different structural type from that found for derivatives [16] of **2**, or (2) a rapid fluxional process which places the C_5Me_4Et centroids in the $Ta_2(\mu\text{-H})(\mu\text{-Cl})$ plane. One possible fluxional process would involve rotation of the $(C_5Me_4Et)TaCl_2$ group in a turnstile fashion to exchange a terminal chlorine with the μ-chlorine. The C_{2v} intermediate (**5**) in this fluxional process would possess a mirror plane containing the C_5Me_4Et centroids, the two Ta's, the μ-H, and the μ-Cl, with the terminal Cl's above and below the mirror plane. The C_5Me_4Et groups would have to be cisoid with respect to each other in order to preserve the cyclopentadienyl magnetic equivalence.



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This description is speculative, as we have no evidence which supports this fluxional process. Nonetheless, it is difficult to envision another explanation for the NMR data for **4**.

There are other, more complex pathways (not depicted in Scheme 1) which could lead to **2**. For example, disproportionation of $(C_5Me_5)_2Ta_2(\mu\text{-H})(\mu\text{-Cl})Cl_4$ (via intermolecular hydride/chloride exchange) could yield 0.5 equiv. of $(C_5Me_5)_2Ta_2(\mu\text{-Cl})_2Cl_4$ and 0.5 equiv. of **2**. $(C_5Me_5)TaCl_2H_2$ (Scheme 1) could reductively eliminate H_2 and yield solvated $(C_5Me_5)TaCl_2$, which could then dimerize to $(C_5Me_5)_2Ta_2(\mu\text{-Cl})_4$ (**3**). Oxidative addition of H_2 to **3** would then yield **2**. We believe that these more elaborate pathways do not contribute significantly to the formation of **2** from **1** but cannot exclude them. Other pathways shown in Scheme 1 involve dinuclear Ta(V) intermediates. The known dinuclear Ta(V) hydride complex [25] $(C_5Me_5)_2Ta_2(\mu\text{-H})_2(OCMe_3)_3Cl_3$, with a postulated structure with two bridging hydride ligands, could serve as a model for dinuclear intermediates such as $(C_5Me_5)_2Ta_2(\mu\text{-H})_2Cl_6$ (Scheme 1).

[3] Belmonte et al. [16] reported a small yield of a compound identified as $(C_5Me_4Et)_2Ta_2HCl_5$ on the basis of elemental analysis and ^1H NMR spectroscopy (μ-H at δ6.08 in C_6D_6) from the large scale hydrogenolysis of $(C_5Me_4Et)Ta(CH_2CMe_3)_2Cl_2$. It was also obtained in ~20% yield from the hydrogenolysis of a mixture of $(C_5Me_4Et)Ta(CH_2CMe_3)_2Cl_2$ and $(C_5Me_4Et)Ta(CH_2CMe_3)Cl_3$ [16]. A distinct IR stretch for the μ-H or terminal hydride ligand of $(C_5Me_4Et)_2Ta_2HCl_5$ was not observed [16].

3. Conclusion

Bu_3SnH serves as an effective combination reagent for reduction and hydride transfer in early transition metal chemistry. The reaction of two equivalents of Bu_3SnH with $(\eta\text{-}C_5Me_4R)TaCl_4$ constitutes a convenient, high yield synthetic route to the organoditantalum(IV) hydride complex $(\eta\text{-}C_5Me_4R)_2Ta_2(\mu\text{-}H)_2Cl_4$, with the hydrides derived from the tin reagent.

4. Experimental section

4.1. General procedures

Compounds were manipulated under a prepurified dinitrogen/helium atmosphere in a Vacuum Atmospheres glove box (helium present to assist cooling of the recirculation system blower) or on an argon Schlenk line of local design. A low temperature ($-35°$) glove box refrigerator was used for compound crystallization. Reagent grade toluene was thoroughly degassed with a stream of argon and distilled under argon in greaseless stills from sodium benzophenone ketyl. Hexane was washed several times with 5% nitric/sulfuric acid followed by water, dried over $CaCl_2$, and then distilled from sodium/potassium benzophenone ketyl solubilized by tetraglyme. Methylene chloride was rigorously degassed and then distilled from granular P_2O_5.

Tantalum pentachloride (Cerac; Pressure Chemical), hexabutylditin (Aldrich), Bu_3SnH (Fluka), and Bu_3SnD (Aldrich) were used as received. Perdeuterobenzene (Isotec) was stored over freshly cut sodium prior to use. Dideuterium (Air Products) and high-purity dihydrogen (Air Products) were used as received. Chlorotri(butyl)tin (Aldrich) was fractionally distilled in vacuo prior to use. 2,3-Dibromobutane was prepared by passing gaseous *cis/trans*-2-butene directly into water-cooled bromine until decolorization was noted. 2-Bromo-2-butene [26], 1,2,3,4,5-pentamethylcyclopentadiene [27], 1,2,3,4-tetramethyl-5-ethylcyclopentadiene [28], (1,2,3,4,5-pentamethylcyclopentadienyl)tri(butyl)tin, [8] and (1,2,3,4-tetramethyl-5-ethylcyclopentadienyl)tri(butyl)tin [29] were prepared by literature procedures. $(C_5Me_4R)SnBu_3$ (R = Me, Et) reagents were assayed after vacuum fractional distillation by gas chromatography and the resulting purities used to adjust the stoichiometry.

All ^1H NMR spectra were obtained in the internal deuterium-locked mode, and all chemical shifts are reported in ppm with positive chemical shifts representing resonances at lower field strength than that of the standard. Proton NMR spectra were obtained on a Bruker AMX-360 (360 MHz for ^1H) NMR spectrometer; spectra were internally referenced to the residual protio solvent impurity (e.g., C_6D_5H, $\delta \equiv 7.150$ for TMS with $\delta \equiv 0.000$). Deuterium NMR spectra (55.288 MHz) were obtained on the AMX-360 NMR spectrometer by first shimming the field on a standard deuterated sample via the deuterium channel, then running the instrument in unlocked mode during data acquisition using the lock channel probe coil as observation channel. Deuterium chemical shifts were referenced to the natural abundance deuterium signal for the methyl resonance of toluene ($C_6H_5CH_2D$, δ 2.103) or benzene (C_6H_5D, δ 7.151), which were referenced separately to internal tetramethylsilane (Me_3SiCH_2D, δ 0.000) at natural deuterium abundance. Reactions which were followed in situ by proton NMR spectroscopy were studied in J. Young Teflon stopcock valved, 5 mm OD NMR tubes (Brunfeldt, Bartlesville, OK) with the entire tube filled with solvent and reactants in order to facilitate approximate integration of the dihydrogen by-product signal. Infrared spectra were obtained as either Nujol mulls or KBr pellets on a Mattson Cygnus 25 spectrophotometer. UV/vis spectra were obtained on a Hewlett-Packard 8452A diode-array spectrophotometer with IBM PC data station in quartz cells of 10 mm pathlength with gas-tight Fisher–Porter Solv–Seal joints; the spectrometer cell holder was thermostatted with an external constant temperature water bath. An angled side tube with well, attached to the UV/vis cell via a Solv–Seal joint, was used to add reagents prior to UV/vis data acquisition.

4.2. Preparation of $(C_5Me_5)_2Ta_2(\mu\text{-}H)_2Cl_4$

$(C_5Me_5)TaCl_4$ (3.01 g, 6.57 mmol) was suspended in toluene (25 ml) and stirred during the addition over 10 min of a solution of Bu_3SnH (4.50 g, 15.5 mmol, 2.3 equiv.) in toluene (10 ml). The solution color changed from yellow to greenish yellow to green during the addition. The reaction mixture was stirred for 20 h and then filtered. The green precipitate was washed with toluene (20 ml) and dried in vacuo; weight 1.17 g. The filtrate was concentrated by rotary evaporation, cooled to $-35°$ overnight, then filtered and the green solid washed with hexane and dried in vacuo; weight 1.07 g. Additional crops of 0.06 g and 0.04 g were isolated by concentration of the filtrate, cooling to $-35°$, filtering and then washing with hexane. Total = 2.34 g (92% yield based on $(C_5Me_5)TaCl_4$). Both proton NMR and IR spectra matched literature [16] values as well as those for **2** obtained by hydrogenation of **3**. ^1H NMR (δ, 360 MHz, 25°C, C_6D_6): 10.402 (s, 2, μ-H), 2.025 (s, 30, C_5Me_5). IR (Nujol, cm^{-1}): 1588, medium, μ-H. IR (KBr, cm^{-1}): 1591, medium, μ-H. UV/vis (λ, nm, toluene): 286, 374 (λ_{max}), 738. MS (EI, 50 eV, m/e): 773, $(M\text{-}1)^+$ for ^{35}Cl isotopomer; 772, $(M\text{-}2)^+$ for ^{35}Cl isotopomer.

4.3. Monitoring of the reaction of $(C_5Me_5)TaCl_4$ and two equivalents of Bu_3SnH by UV/vis spectrophotometry

Two milliliters of a solution of $(C_5Me_5)TaCl_4$ (0.011 g, 0.024 mmol) dissolved in toluene (25 ml) were

placed into the UV/vis cell. An angled adapter containing 2 ml of a solution of Bu_3SnH (0.014 g, 0.048 mmol) dissolved in toluene (25 ml) was then attached via Solv–Seal joints. The cell was placed into the cell holder, precooled by a flowing ice-cooled water stream, and the well portion of the angled adapter containing the Bu_3SnH solution was cooled in ice water. The cell was removed, shaken to mix solutions, and then returned to the spectrometer. The wavelength scan range was 190 to 820 nm, and data was acquired at 3-s intervals over 150 s. Isosbestic points were observed at 340 nm, 414 nm and 478 nm.

4.4. Monitoring of the reaction of $(C_5Me_5)TaCl_4$ and two equivalents of Bu_3SnH by ^1H NMR spectroscopy

$(C_5Me_5)TaCl_4$ (0.014 g, 0.031 mmol) was partially dissolved in C_6D_6. Bu_3SnH (0.020 g, 0.069 mmol) was dissolved in a minimal amount of C_6D_6. The solution and suspension were mixed (the solution soon became homogeneous) and transferred to a 5 mm, valved NMR tube which was completely filled to the valve seat. ^1H NMR spectra were taken at five intervals over one day. The spectra showed growth of resonances associated with **2**, H_2, and Bu_3SnCl, and loss of resonances associated with $(C_5Me_5)TaCl_4$ and Bu_3SnH. A minor resonance of an unidentified and presumably paramagnetic species (δ22.3, broad), along with a small C_5Me_5 resonance at δ2.08, were noted at intermediate time points in the reaction; both resonances disappeared by completion of the reaction. Integration of the final spectrum showed the ratio $(C_5Me_5)_2Ta_2(\mu\text{-}H)_2Cl_4$:$H_2$:$Bu_3SnCl$:residual Bu_3SnH = 1.0:1.0:4.5: < 0.01.

4.5. Preparation of $(C_5Me_4Et)_2Ta_2(\mu\text{-}H)_2Cl_4$

An analogous procedure to that for preparation of $(C_5Me_5)_2Ta_2(\mu\text{-}H)_2Cl_4$ was employed, starting with 0.10 g (0.21 mmol) $(C_5Me_4Et)TaCl_4$ in toluene (10 ml) and 0.13 g Bu_3SnH (0.45 mmol, 2.1 equiv.) in toluene (5 ml). The mixture was stirred overnight and filtered to give the green product, which was washed with hexane and dried in vacuo. Weight = 0.053 g (63% yield).

^1H NMR (δ, 360 MHz, 25°C, C_6D_6): 10.439 (s, 2, μ-H), 2.569 (q, 4, $^3J_{HH}$ = 7.6 Hz, $C_5Me_4CH_2Me$), 2.132 (s, 12, $C_5Me_2Me_2Et$), 2.006 (s, 12, $C_5Me_2Me_2Et$), 0.795 (t, 6, $^3J_{HH}$ = 7.6 Hz, $C_5Me_4CH_2CH_3$).

4.6. Reaction of Bu_3SnD (2 equiv.) with $(C_5Me_5)TaCl_4$: Preparation of $(C_5Me_5)_2Ta_2(\mu\text{-}D)_2Cl_4$

An analogous procedure to that for the preparation of $(C_5Me_5)_2Ta_2(\mu\text{-}H)_2Cl_4$ was employed, starting with 0.23 g (0.50 mmol) $(C_5Me_5)TaCl_4$ in toluene (10 ml) and 0.31 g Bu_3SnD (1.1 mmol, 2.2 equiv.) in toluene (3 ml). After stirring overnight, a small first crop (0.01 g) was isolated by filtration and dried in vacuo. Concentration and cooling of the filtrate yielded 0.14 g of product after washing with hexane and drying in vacuo. Total = 0.15 g (77% yield).

^1H NMR (δ, 360 MHz, 25°C, C_6D_6): 2.023 (s, C_5Me_5). ^2H NMR (δ, 55.288 MHz, 25°C, C_6H_6): 10.226 (s, μ-D). ^2H NMR (δ, $C_6H_5CH_3$, 55.288 MHz): 10.138 (s, μ-D). IR (KBr, cm^{-1}): 1142, medium, μ-D.

4.7. Reaction of $(C_5Me_5)_2Ta_2Cl_6$ with Bu_3SnH (1 equiv.) by ^1H NMR spectroscopy

Stoichiometric amounts of both reactants were combined in C_6D_6 and spectra recorded after mixing. After 15 min, the spectrum showed approximately 60% of the diamagnetic region C_5Me_5 intensity was found at δ2.08, which was associated with a resonance at δ6.06 in a 30:1 integration ratio. Along with resonances associated with **2**, a broad resonance at δ38.1 was observed. Over the course of 2.5 days, both species converted to **2**.

4.8. Reaction of $(C_5Me_4Et)_2Ta_2Cl_6$ with Bu_3SnH (1 equiv.) by ^1H NMR spectroscopy

Using an identical procedure to that above, ^1H NMR resonances for a diamagnetic species were observed at δ 6.02 (hydride), δ 2.18 and δ 2.09 (ring methyls), and δ 2.36 (ethyl methylene); the methyl resonance of the ethyl group was obscured by the corresponding resonance for $(C_5Me_4Et)_2Ta_2(\mu\text{-}H)_2Cl_4$. The paramagnetic compound exhibited resonances at δ40.6, δ34, and δ16.7; the methyl resonance for the ring ethyl was obscured by other resonances.

4.9. Reaction of $(C_5Me_5)_2Ta_2Cl_6$ with Bu_3SnH (2 equiv.)

$(C_5Me_5)_2Ta_2Cl_6$ (0.047 g, 0.056 mmol) was dissolved in toluene (10 ml). Bu_3SnH (0.037 g, 0.13 mmol, 2.2 equiv.) in toluene (4 ml) was added and the mixture stirred overnight. The reaction mixture was filtered and the filtrate dried in vacuo. The residue was washed with hexane and dried to give 0.012 g of dark green solid (28% yield of **2**).

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