Preparation and Properties of the d^0 $(\eta^5\text{-}C_5Me_5)Ta({=}NR)_2$ Functional Group

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The reaction of 2 equiv of LiNHAr ($Ar = 2,6\text{-}C_6H_3{}^iPr_2$) with Cp^*TaCl_4 ($Cp^* = \eta^5\text{-}C_5Me_5$) in THF affords the imido compound $Cp^*Ta({=}NAr)Cl_2$ (**1**). Upon reaction of Cp^*TaCl_4 with 4 equiv of LiNHAr in Et_2O, the bis(imido) complex $[Li(OEt_2)][Cp^*Ta({=}NAr)_2Cl]$ (**2**) is isolated. The THF adduct $[Li(THF)][Cp^*Ta({=}NAr)_2Cl]$ (**3**) is formed when this reaction is carried out in THF or when **1** is reacted with 2 equiv of LiNHAr in THF. $[Li(OEt_2)][Cp^*Ta({=}NAr)_2Cl]$ (**2**) crystallizes in the monoclinic space group $P2_1/n$ (No. 14) with $a = 13.108(3)$ Å, $b = 17.998(5)$ Å, $c = 16.919(4)$ Å, $\beta = 96.69(1)°$, and $V = 3964\ (3)$ Å^3 with $Z = 4$ and $\rho_{calcd} = 1.31$ g cm^{-3}. The molecular structure of **2** is characterized as containing a $\mu\text{-}[Li(OEt_2)]^+$ moiety bridging the imide nitrogens. In solution the imido ligands are equivalent with restricted rotation about $Ta\text{–}N\text{–}C_{ipso}$, implying an intact $[Li(OEt_2)]^+$ bridge. $Cp^*Ta({=}NAr)(NEt_2)Cl$ (**5**; prepared from $Ta({=}NAr)(NEt_2)Cl_2(THF)_2$ (**4**) and $Li[C_5Me_5]$) reacts with LiNHAr (in refluxing THF) to afford $[Li(THF)][Cp^*Ta({=}NAr)_2Cl]$ (**3**) only very slowly.

Introduction

Organoimido ligands have been widely employed as ancillary groups to support high-oxidation-state metal centers.[1] Recent advances in transition metal–imido chemistry include the generation of reactive M=NR ligands which can serve as sites for C—H bond activation,[2] cycloaddition chemistry,[2c,3] or imido-transfer reactions.[3d,4] Such reactive compounds are often coordinated by *more than one* π-donor ligand, a feature which has prompted investigations into multiple imido chemistry.[5–8] On the basis of the synthesis and reactivity of the d^0 group 6 complexes $Cp^*M({=}NR)_2X$ (M = Mo,[9] W;[7,10,11] $Cp^* = \eta^5\text{-}C_5Me_5$), some derivatives of which activate C—H bonds,[7] their group 5 analogs were judged worthy of investigation. We now report routes to the pentamethylcyclopentadienyl bis(imido) complex of tantalum $[Cp^*Ta({=}NAr)_2Cl]^-$, which is isoelectronic with its d^0 group 6 congeners. These compounds constitute the intermediate (n = 1) member of the series of d^0 tantalum–imido "functional groups" $[(\eta^5\text{-}C_5R_5)_nTa({=}NR)_{3-n}]^{n-1}$ (n = 0[8] or 2[12]) related by the formal 1σ,2π donor analogy[7,13] between $[NR]^{2-}$ and $[\eta^5\text{-}C_5R_5]^-$ ligands.

Results

Upon treatment of an Et_2O solution of Cp^*TaCl_4 with 2 equiv of LiNHAr ($Ar = 2,6\text{-}C_6H_3{}^iPr_2$), yellow-orange crystals of $Cp^*Ta({=}NAr)Cl_2$ (**1**) are formed in high yield (Scheme I). The preparation and structure of this complex were recently reported by Gibson and co-workers.[14] Upon reaction of an Et_2O solution of Cp^*TaCl_4 with 4 equiv of LiNHAr, a pale yellow-green complex is obtained which can be formulated as "$Cp^*Ta({=}NAr)_2(OEt_2)$" by NMR but which elemental analysis and an X-ray structure determination reveal to be the chloride complex $[Li(OEt_2)][Cp^*Ta({=}NAr)_2Cl]$ (**2**) (Scheme I). When a THF solution of Cp^*TaCl_4 is treated with 4 equiv of LiNHAr or when $Cp^*Ta({=}NAr)Cl_2$ is reacted with 2 equiv of LiNHAr (in THF), yellow-green crystals of **3** are obtained after appropriate workup. The NMR spectra and elemental analysis of **3** are consistent with its formulation as $[Li(THF)][Cp^*Ta({=}NAr)_2Cl]$ (**3**) (Scheme I). These complexes are analogs of our previously reported niobium species $(\eta^5\text{-}C_5H_5)Nb({=}NAr)_2(pyridine)$, prepared from $Nb({=}NAr)_2Cl(pyridine)_2$ and $Na[C_5H_5]$.[6]

Unlike the spectra of the neutral tungsten analog $Cp^*W({=}NAr)_2Cl$, which contains equivalent imido ligands with free rotation about $W\text{—}N\text{—}C_{ipso}$ (established by the single $C\mathit{H}Me_2$ resonance and two $CH\mathit{Me}_2$ environments), the ^1H and ^{13}C NMR spectra of **2** and **3** reveal *inequivalent* $C\mathit{H}Me_2$ environments and *four* $CH\mathit{Me}_2$ signals (at probe temperature). These data imply either restricted rotation about the $Ta\text{—}N\text{—}C_{ipso}$ moiety or inequivalent imido ligands. The single C_{ipso} and C_{para} resonances observed in the ^{13}C NMR spectra of **2** and **3** secure the equivalence of the imido ligands and imply *restricted rotation about* $Ta\text{—}N\text{—}C_{ipso}$ brought about by the presence of the intact $[\mu\text{-}Li(OEt_2)]^+$ moiety, which bridges the imido nitrogens (*vide infra*).

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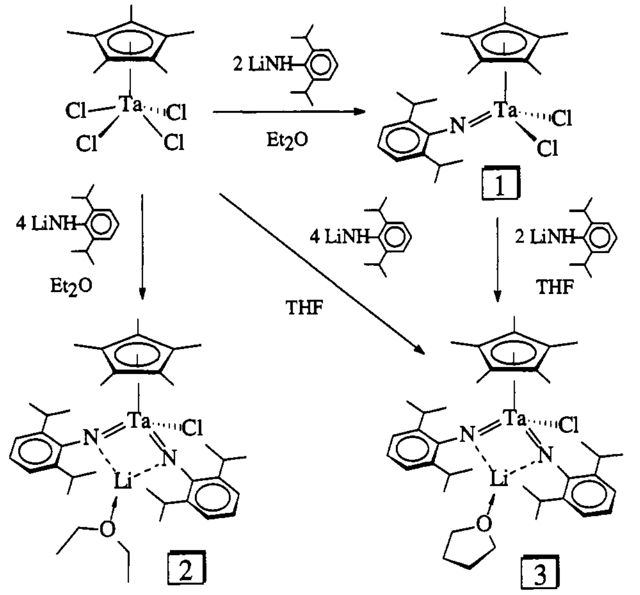
Scheme I



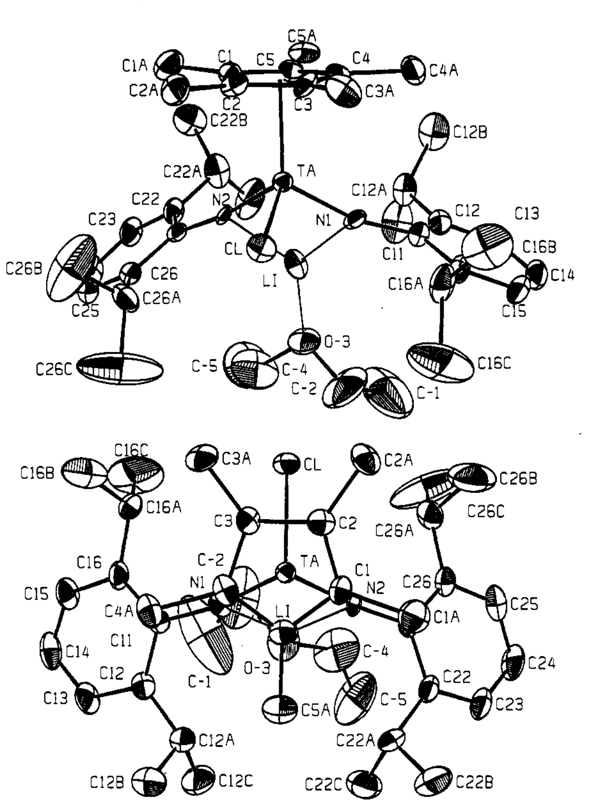


Figure 1. Molecular structure of $[Li(OEt_2)][(\eta^5\text{-}C_5Me_5)Ta({=}NAr)_2Cl]$ (Ar = 2,6-diisopropylphenyl) in two projections.

Consistent with this analysis are the ^1H and ^{13}C NMR spectra of $Cp^*W({=}NAr)_2Cl$,[7] $(\eta^5\text{-}C_5H_5)Nb({=}NAr)_2(pyridine)$,[6] and $Cp^*W({=}NPh)_2Me$,[11] all of which require free rotation about $M{-}N{-}C_{ipso}$, as indicated by the single C_{ortho} and C_{meta} resonances in their ^{13}C NMR spectra.

Yellow-green crystals of **2** were obtained from Et_2O/pentane at −35 °C. Figure 1 shows the approximately tetrahedral local geometry of $[Cp^*Ta({=}NAr)_2Cl]^-$, and Tables I and II summarize crystal and structural data. As in $Cp^*W({=}NAr)_2Cl$, the planes of the NAr phenyl groups are turned roughly parallel to the Cp* plane, rather than perpendicular, to minimize steric repulsion between the Cp* methyl and NAr isopropyl groups, a feature which is also manifested in the deviations from idealized tetrahedral geometry about the metal. The Ta—Cp* ring carbon distances (Table II) reveal an abnormally short Ta—C(5) bond (2.39(1) Å), while the other four Ta—Cp* ring carbon distances fall in the range between 2.46(1) and 2.52(1) Å. This structural feature has been noted in the $\eta^5\text{-}C_5Me_5$ ligands of the oxo compounds $Cp^*W(O)_2(OC_5Me_5)$[15] and $Cp^*W(O)_2(\eta^1\text{-}C_5Me_5)$[16] and the imido species $Cp^*W({=}NAr)_2Cl$[7] and $Cp^*W({=}NC_6H_4\text{-}4\text{-}Me)_2(CH_2SiMe_3)$[10] and has been attributed to the strong trans influence of these π-donor ligands. The orientation of the Cp* ligand in **2** places the short Ta—C(5) bond trans to the Ta—Cl bond, also suggesting the trans influence of the $[NR]^{2-}$ ligand. However, in each of these other complexes, a small measure of 1,3-diene type π-electron localization is observed in their $\eta^5\text{-}C_5Me_5$ ligands with the shorter C—C bonds located trans to the oxo or imido ligands. The level of precision in the structure of **2** does not substantiate such a "η^1,η^4"-C_5Me_5 ligand on the basis of anything other that Ta—C distances.

The arylimido moieties of **2** are equivalent in the solid state, since the extent of association of the $[\mu\text{-}Li(OEt_2)]^+$ ion with N(1) and N(2) is comparable. Accordingly, the Ta—N bond distances (Ta—N(1) = 1.862(9) Å and Ta—N(2) = 1.86(1) Å) are identical although their corresponding $Ta{-}N{-}C_{ipso}$ angles (161(1) and 170.5(8)°, respectively) show some difference. These $Ta{-}N_{imido}$ distances are ca. 0.1 Å longer than most d^0 Ta=NR bonds[1] and imply a dimished π donation to the metal, probably arising from Li^+ coordination. The long $Ta{-}N_{imido}$ bond in $Cp^*_2Ta({=}NPh)H$[12] (1.831(10) Å) compares to those in **2** and reflects a Ta=N bond order between 2 and 3, as must also be the case in $[Li(OEt_2)][Cp^*Ta({=}NAr)_2Cl]$.[17] Finally, the Li atom in **2** is displaced 0.21(1) Å from the TaN_2 plane, presumably to position itself in the cavity lined by the NAr methyl groups and the chloride ligand.

In the formation of $[Cp^*Ta({=}NAr)_2Cl]^-$ from $Cp^*Ta({=}NAr)Cl_2$, one can envision the d^0 $Cp^*Ta({=}NR)_2$ "functional group" arising *via* either an *inter*molecular deprotonation of "$Cp^*Ta({=}NAr)(NHAr)Cl$" or an *intra*molecular α-H abstraction from nascent "$Cp^*Ta({=}NAr)(NHAr)_2$".[18] Such processes may often be examined by the *in situ* generation of species in which intramolecular α-H transfer from a $[NHAr]^-$ ligand is *favored* by a proximate *di*alkylamido ligand; Scheme II summarizes our attempt to do so in this system. The reaction of $[Ta(NEt_2)_2Cl_3]_2$ with 1 equiv of LiNHAr (per tantalum) in THF forms $Ta({=}NAr)(NEt_2)Cl_2(THF)_2$ (**4**); we have previously communicated the preparation of this complex by another route.[6] When **4** reacts with LiCp* in refluxing THF, $Cp^*Ta({=}NAr)(NEt_2)Cl$ (**5**) can be isolated in 95% yield. Upon reaction of **5** with 1 equiv of LiHNAr (refluxing THF, 48 h), $[Li(THF)][Cp^*Ta({=}NAr)_2Cl]$ (**3**) forms only very slowly. Thus, under these conditions, **3** is observed in only ca. 5% yield while the solution largely contains unreacted starting material (by ^1H NMR). $Cp^*Ta({=}NAr)(NHAr)(NEt_2)$ has not been identified in this reaction; therefore, this result is not subject to definitive interpretation, since **3** could arise by $[NHAr]^-$ displacement of $[NEt_2]^-$ which then deprotonates the primary amide *inter*molecularly or **3** could arise by displacement of Cl^- to form Cp*Ta-

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(17) These Ta—N distances are more consistent with an *imide* rather than a "lithio*amide*" ligand, a feature which has been described for $[Li(THF)_2]_2[Nb({=}Nmes)_3(n\text{-}Bu)]$ (mes = 2,4,6-$C_6Me_3H_2$) and its associated $[Li(THF)_2]^+$ ions.[8] While Li^+ coordination is expected to lengthen Ta—N bonds, so is 3-fold 1σ,2π orbital symmetry, which results in Ta—N bond orders lower than 3 (see Discussion).

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Table I. Details of the X-ray Diffraction Study of $[Li(OEt_2)][(\eta^5\text{-}C_5Me_5)Ta({=}NAr)_2Cl]$

mol formula	$C_{38}H_{59}ClLiN_2OTa$
mol wt	783.25
crystal color	yellow
space group	$P2_1/n$ (No. 14)
unit cell vol, Å^3	3964(3)
a, Å	13.108(3)
b, Å	17.998(5)
c, Å	16.919(4)
β, deg	96.69(1)
Z	4
calcd density, g cm^{-3}	1.31
cryst dimens, mm	0.25 × 0.25 × 0.58
data collcn temp, °C	22 ± 1
Mo Kα radiation, λ, Å	0.710 73
monochromator	graphite
abs coeff, cm^{-1}	28.4
2θ range, deg	0–50
total no. of reflns measd	7568 (6979 unique)
no. of reflns measd with $I > 3\sigma(I)$	3862
scan type	ω–2θ
scan speed, deg min^{-1}	4.5
no. of params refined	397
R^a	0.054
$R_w{}^b$	0.067

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2}$.

Table II. Selected Interatomic Distances (Å) and Bond Angles (deg) in $[Li(OEt_2)][\eta^5\text{-}C_5Me_5)Ta({=}NAr)_2Cl]$[a,b]

	Interatomic Distances		
Ta–N(1)	1.862(9)	C(1)–C(2)	1.38(2)
Ta–N(2)	1.86(1)	C(2)–C(3)	1.42(2)
Ta–Cl	2.398(3)	C(3)–C(4)	1.43(2)
Ta–Li	2.63(3)	C(4)–C(5)	1.39(2)
Ta–Cp$^*_{cent}$	2.16	C(1)–C(5)	1.41(2)
Ta–C(1)	2.46(1)	N(1)–Li	1.99(3)
Ta–C(2)	2.50(1)	N(2)–Li	2.03(3)
Ta–C(3)	2.52(1)	Li–O(3)	1.92(3)
Ta–C(4)	2.48(1)	N(1)–C(11)	1.43(1)
Ta–C(5)	2.39(1)	N(2)–C(21)	1.37(2)
	Bond Angles		
Cl–Ta–N(1)	101.7(3)	Ta–N(2)–Li	84.7(7)
Cl–Ta–N(2)	101.2(3)	N(1)–Li–N(2)	90(1)
Cl–Ta–Cp$^*_{cent}$	107.0	N(1)–Li–O(3)	129(2)
N(1)–Ta–N(2)	99.1(4)	N(2)–Li–O(3)	135(1)
N(1)–Ta–Cp$^*_{cent}$	122.6	C(1)–C(2)–C(3)	107(1)
N(2)–Ta–Cp$^*_{cent}$	121.8	C(2)–C(3)–C(4)	107(1)
Ta–N(1)–C(11)	161(1)	C(3)–C(4)–C(5)	109(1)
Ta–N(2)–C(21)	170.5(8)	C(4)–C(5)–C(1)	107(1)
Ta–N(1)–Li	86.0(9)	C(5)–C(1)–C(2)	110(1)

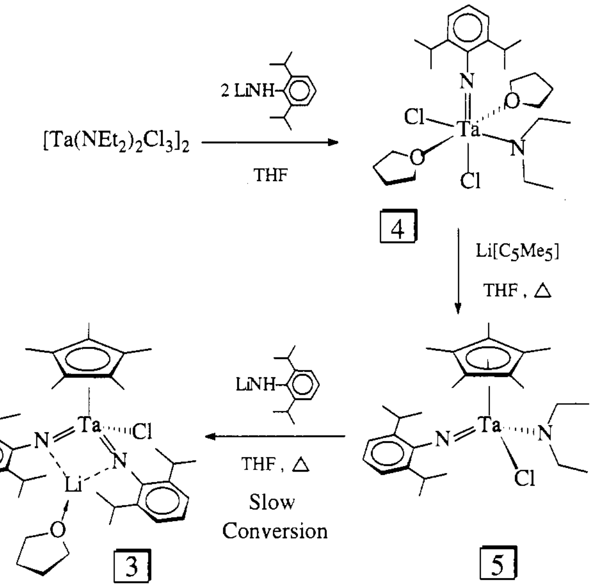
[a] Numbers in parentheses are estimated standard deviations in the least significant digits. [b] Cp$^*_{cent}$ represents the average of the *x*, *y*, and *z* coordinates of the η^5-C_5Me_5 ring carbons; uncertainties are not included on distances and angles involving this point.

(=NAr)(NHAr)(NEt$_2$), which loses HNEt$_2$ *intra*molecularly. We prefer the former, *inter*molecular, deprotonation pathway for the generation of **3** in the reactions of Schemes I and II, supported the following observations: (i) Cp*Ta(=NPh)(NHPh)$_2$ was recently prepared and, upon thermolysis, was *not* observed to form a bis(imido) complex in the presence of σ-donor ligands;[18] (ii) [Cp*W(=NPh)(NHPh)Me]PF$_6$ readily undergoes deprotonation by an external reagent (NEt$_3$) to form Cp*W(=NPh)$_2$Me in 94% yield (along with [HNEt$_3$]PF$_6$).[11]

Discussion

Considerable evidence has been presented to suggest that the 3-fold orbital symmetry of M(1σ,2π)$_3$ complexes like "Cp*Ta(=NAr)$_2$" leads to the *combination* of these 1σ,2π ligands contributing 2 electrons *less* than the maximum possible.[5,7,13] This notion has been formalized in Re(=NAr)$_n$(RC≡CR)$_{3-n}$X complexes[13a] (the acetylene dianion [RC=CR]$^{2-}$ is a 1σ,2π donor) and in Os(=NAr)$_3$,[3e] where extended Hückel studies demonstrate the occupation of a ligand-centered, nonbonding MO. Thus, the Cp*Ta(=NAr)$_2$ moiety is expected to behave as a formal 16-electron fragment, just like "W(=NAr)$_3$",[5] "[Cp*W(=NAr)$_2$]$^+$",[7] and "[Ta(=NAr)$_3$]$^-$",[8] none of which has been isolated without being coordinated by a 2-electron σ donor.

Scheme II



In the formation of [Cp*Ta(=NAr)$_2$Cl]$^-$ from Cp*Ta(=NAr)Cl$_2$ and LiNHAr, we suggest the principal mechanism involves the intermediacy of "Cp*Ta(=NAr)(NHAr)Cl", which is deprotonated intermolecularly by the second equivalent of LiNHAr. The fact that Cp*Ta(=NPh)(NHPh)$_2$ does not undergo α-hydrogen transfer upon thermolyis to form "Cp*Ta(=NPh)$_2$",[18] and the facile deprotonation of [Cp*W(=NPh)(NHPh)Me]PF$_6$ with NEt$_3$,[11] support this proposal. The generation of the "third" 1σ,2π ligand in M(1σ,2π)$_3$ complexes (e.g. [Ta(=NAr)$_3$(NHAr)]$^{2-}$ [8] and [W(=NAr)$_3$Cl]$^-$ [5]) by intermolecular processes has been suggested before. For example, th e formation of [W(=NAr)$_3$Cl]$^-$ from W(NAr)$_2$Cl$_2$(THF)$_2$ and 2 equiv of LiNHAr appears to proceed *via* nascent "W(NAr)$_2$(NHAr)Cl", which is deprotonated intermolecularly by the second equivalent of LiNHAr.[5] The synthesis and reactivity of related "π-loaded" metal centers are areas of our continued interest.

Experimental Section

General Details. All experiments were performed under a nitrogen atmosphere, either by standard Schlenk techniques[19] or in a Vacuum Atmospheres HE-493 drybox, at room temperature (unless otherwise indicated). Cp*TaCl$_4$,[20] [Ta(NEt$_2$)$_2$Cl$_3$]$_2$,[21] LiNHAr,[22] and LiCp*[23] were prepared by the literature procedures. Solvents were distilled under N$_2$ from an appropriate drying agent[24] and were transferred to the drybox without exposure to air. The "cold" solvents used to wash isolated solid products were typically cooled to ca. −30 °C before use. ^{1}H (250 MHz) and ^{13}C (62.9 MHz) NMR spectra were recorded at probe temperature (unless otherwise specified) on a Bruker WM-250 spectrometer in C$_6$D$_6$ solvent (which was passed down a 5–6-cm column of activated alumina

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prior to use). Chemical shifts are referenced to protio impurities (δ 7.15) or the solvent ^{13}C resonance (δ 128.0) and are reported downfield of Me_4Si. Microanalytical samples were handled under N_2, stored cold, and combusted with WO_3 (Texas Analytical Laboratories, Inc., Stafford, TX, or Desert Analytics, Tucson, AZ). Abbreviations: Ar = 2,6-$C_6H_3{}^i$-Pr_2; Cp* = $[C_5Me_5]^-$.

Preparations. Cp*Ta(=NAr)Cl_2 (1). Gibson and co-workers recently reported this complex.[14] A solution of LiNHAr (0.81 g, 4.42 mmol) in 40 mL of Et_2O was added dropwise to a rapidly stirred solution of Cp*$TaCl_4$ (1.00 g, 2.18 mmol) in 50 mL of Et_2O. During the addition, the orange tantalum solution became pale yellow-orange. This solution was stirred at room temperature for 24 h, after which time it was filtered through Celite and the solvent was removed from the filtrate in vacuo to afford a pale orange powder. This product was collected on a frit, washed with cold pentane (3 × 15 mL), and dried in vacuo; yield 0.79 g, 1.40 mmol (64%). Analytically pure samples were obtained by recrystallization from Et_2O/pentane solutions at −35 °C. ^1H NMR (C_6D_6): δ 7.18–6.88 (A_2B mult, 3 H, H_{aryl}), 3.52 (spt, 2 H, $C\mathit{H}Me_2$), 1.86 (s, 15 H, $C_5\mathit{Me}_5$), 1.33 (d, 12 H, $CH\mathit{Me}_2$). ^{13}C NMR (C_6D_6): δ 148.3 (C_{ipso}), 145.4 (C_o), 124.9 (C_p), 122.2 (C_m), 121.4 (C_5Me_5), 28.1 ($\mathit{C}HMe_2$), 24.4 ($CH\mathit{Me}_2$), 11.2 ($C_5\mathit{Me}_5$). These data are identical to those reported.[14] Anal. Calcd for $C_{22}H_{32}Cl_2NTa$: C, 46.98; H, 5.73; N, 2.49. Found: C, 46.84; H, 5.78; N, 2.53.

[Li(OEt_2)][Cp*Ta(=NAr)$_2$Cl] (2). A solution of LiNHAr (1.68 g, 9.17 mmol) in 40 mL of Et_2O was added dropwise to a rapidly stirred slurry of Cp*$TaCl_4$ (1.00 g, 2.18 mmol) in 20 mL of Et_2O. During the addition, the orange tantalum solution became yellow-green with the formation of a white precipitate. The reaction mixture was allowed to stir at room temperature overnight (ca. 12 h), the solvent was removed in vacuo, and the product was extracted from the resulting solid with minimal toluene. Filtration of the extract through Celite, followed by removal of the toluene from the filtrate (in vacuo), afforded a pale yellow-green solid. This solid was recrystallized from Et_2O/pentane solutions (−35 °C) to afford 1.05 g (1.34 mmol, 62%) of large yellow-green cubic crystals. ^1H NMR (C_6D_6): δ 7.17–6.82 (mult, 6 H total, H_{aryl}), 3.90 and 3.57 (spt, 2 H each, $C\mathit{H}Me_2$), 2.79 (q, 4 H, $OC\mathit{H}_2CH_3$), 1.95 (s, 15 H, $C_5\mathit{Me}_5$), 1.43, 1.41, 1.29, and 1.19 (d, 6 H each, $CH\mathit{Me}_2$), 0.49 (t, 6 H, $OCH_2C\mathit{H}_3$). ^{13}C NMR (C_6D_6): δ 153.2 (C_{ipso}), 143.1 and 137.7 (C_o), 122.3 and 120.3 (C_m), 116.9 (C_5Me_5), 123.3 (C_p), 65.2 ($O\mathit{C}H_2CH_3$), 27.7 and 26.7 ($\mathit{C}HMe_2$), 26.8, 25.2, 25.1, and 24.5 ($CH\mathit{Me}_2$), 11.0 ($C_5\mathit{Me}_5$), 13.8 ($OCH_2\mathit{C}H_3$). Anal. Calcd for $C_{38}H_{59}ClLiN_2OTa$: C, 58.27; H, 7.59; N, 3.58; Cl, 4.53. Found: C, 58.53; H, 7.76; N, 3.50, Cl, 4.58.

[Li(THF)][Cp*Ta(=NAr)$_2$Cl] (3). This compound was prepared by a procedure analogous to that described for [Li(OEt_2)][Cp*Ta(=NAr)$_2$Cl] (**2**) above, except that both LiNHAr and Cp*$TaCl_4$ solutions were prepared in THF. Removal of the toluene from the extract (in vacuo) afforded a pale orange solid, which was washed with cold pentane and dried in vacuo; yield 68%. Recrystallization from THF/pentane solutions (−35 °C) provided pale green needles of analytically pure compound. ^1H NMR (C_6D_6): δ 7.20–6.86 (mult, 6 H total, H_{aryl}), 3.91 and 3.60 (spt, 2 H each, $C\mathit{H}Me_2$), 2.93 (br, 4 H, H_α, THF), 1.94 (s, 15 H, $C_5\mathit{Me}_5$), 1.47, 1.44, 1.30, and 1.20 (d, 6 H each, $CH\mathit{Me}_2$), 0.89 (br, 4 H, H_β, THF). ^{13}C NMR (C_6D_6): δ 153.1 (C_{ipso}), 143.1 and 137.6 (C_o), 123.1 and 122.2 (C_m), 120.3 (C_p), 116.7 (C_5Me_5), 68.4 (C_α, THF), 27.9 and 27.0 ($\mathit{C}HMe_2$), 25.6 (C_β, THF), 26.9, 24.9, 23.7, and 23.6 ($CH\mathit{Me}_2$), 10.9 ($C_5\mathit{Me}_5$). Anal. Calcd for $C_{38}H_{57}ClLiN_2OTa$: C, 58.42; H, 7.36; N, 3.59; Cl, 4.54. Found: C, 58.14; H, 7.54; N, 3.49; Cl, 5.08.

Ta(=NAr)(NEt_2)Cl_2(THF)$_2$ (4). A solution of LiNHAr (2.12 g, 11.57 mmol) in 40 mL of THF was added dropwise to a stirred solution of $[Ta(NEt_2)_2Cl_3]_2$ (5.00 g, 5.79 mmol) in 40 mL of THF. This mixture was allowed to stir ca. 24 h, over which time the orange solution slowly turned pale yellow-orange. The solvent was then removed in vacuo and the product extracted from the residue with Et_2O. Filtration of the extract through Celite, followed by removal of the solvent from the filtrate (in vacuo), afforded the product as a yellow solid. This solid was collected on a frit, washed with cold pentane (2 × 15 mL), and dried in vacuo; yield 4.52 g (7.02 mmol, 61%). Analytically pure samples were obtained from Et_2O/pentane solutions at −35 °C. ^1H NMR (C_6D_6): δ 7.19–6.88 (A_2B mult, 3 H, H_{aryl}), 4.43 (spt, 2 H, $C\mathit{H}Me_2$), ca. 3.90 (br, 4 H, $NC\mathit{H}_2CH_3$), 3.84 (mult, 8 H, H_α, THF), 1.43 (d, 12 H, $CH\mathit{Me}_2$), 1.24 (mult, 8 H, H_β, THF), 1.08 (t, 6 H, $NCH_2C\mathit{H}_3$). ^{13}C NMR (C_6D_6): δ 150.7 (C_{ipso}), 146.0 (C_o), 124.9 (C_p), 122.6 (C_m), 71.6 (C_α, THF), 45.3 ($N\mathit{C}H_2CH_3$), 27.9 and 25.4 (C_β, THF and $\mathit{C}HMe_2$), 24.3 ($CH\mathit{Me}_2$), 14.2 ($NCH_2\mathit{C}H_3$). The equivalence of the THF ligands in **4** most likely reflects a structure similar to that of Ta(=NAr)(O-2,6-$C_6H_3{}^iPr_2$)Cl_2(THF)$_2$,[21] viz. with *cis* NAr and NEt_2 ligands and *trans* THF ligands, as indicated in Scheme II. Anal. Calcd for $C_{24}H_{43}Cl_2N_2O_2Ta$: C, 44.80; H, 6.74; N, 4.35. Found: C, 44.49; H, 6.57; N, 4.36.

Table III. Positional Parameters and Their Estimated Standard Deviations for [Li(OEt_2)][(η^5-C_5Me_5)Ta(=NAr)$_2$Cl[a]

atom	x	y	z	B, Å^2
Ta	0.23300(4)	0.16361(3)	0.05158(3)	3.338(8)
Cl	0.0836(3)	0.1323(2)	−0.0379(2)	5.32(8)
N(1)	0.3293(7)	0.1822(6)	−0.0187(5)	4.0(2)
N(2)	0.2033(6)	0.2613(5)	0.0777(5)	3.1(2)
Li	0.295(2)	0.289(1)	−0.007(2)	5.4(6)
O-3	0.296(1)	0.3681(7)	−0.0829(7)	9.5(3)
C-1	0.360(3)	0.355(2)	−0.194(3)	36(2)
C-2	0.274(3)	0.337(2)	−0.171(1)	22(1)
C-4	0.248(2)	0.441(1)	−0.071(2)	17(1)
C-5	0.295(3)	0.500(2)	−0.042(2)	22(2)
C(1)	0.2266(9)	0.1178(7)	0.1882(7)	4.3(3)
C(2)	0.161(1)	0.0716(8)	0.1409(7)	4.7(3)
C(3)	0.2225(9)	0.0296(7)	0.0931(7)	4.4(3)
C(4)	0.326(1)	0.0543(7)	0.1126(8)	4.8(3)
C(5)	0.3275(9)	0.1115(7)	0.1678(7)	4.5(3)
C(1A)	0.196(1)	0.169(1)	0.2529(8)	8.0(5)
C(2A)	0.0485(9)	0.0587(8)	0.1437(9)	6.3(4)
C(3A)	0.188(1)	−0.0330(7)	0.0362(9)	6.5(4)
C(4A)	0.4179(9)	0.0226(8)	0.0734(8)	6.3(4)
C(5A)	0.424(1)	0.1438(8)	0.2114(8)	6.3(4)
C(11)	0.4062(9)	0.1706(7)	−0.0706(7)	4.4(3)
C(12)	0.506(1)	0.2022(8)	−0.0518(8)	5.3(3)
C(12A)	0.540(1)	0.2385(9)	0.0253(9)	7.1(4)
C(12B)	0.627(1)	0.194(1)	0.075(1)	10.5(6)
C(12C)	0.578(1)	0.315(1)	0.015(1)	12.0(7)
C(13)	0.575(1)	0.195(1)	−0.1080(9)	7.4(4)
C(14)	0.547(1)	0.1604(9)	−0.1805(9)	7.6(4)
C(15)	0.453(1)	0.134(1)	−0.1971(8)	7.0(4)
C(16)	0.380(1)	0.1347(9)	−0.1447(8)	5.9(4)
C(16A)	0.278(1)	0.095(1)	−0.1665(9)	7.6(4)
C(16B)	0.285(1)	0.014(1)	−0.172(1)	13.2(8)
C(16C)	0.220(2)	0.129(2)	−0.242(2)	20(1)
C(21)	0.1719(9)	0.3277(7)	0.1056(6)	3.9(3)
C(22)	0.239(1)	0.3732(8)	0.1600(8)	5.3(3)
C(22A)	0.346(1)	0.3485(9)	0.189(1)	7.9(4)
C(22B)	0.367(1)	0.350(1)	0.279(1)	9.6(6)
C(22C)	0.426(1)	0.399(1)	0.157(1)	13.6(8)
C(23)	0.204(1)	0.4411(8)	0.1813(9)	6.8(4)
C(24)	0.110(1)	0.4681(9)	0.155(1)	8.2(5)
C(25)	0.045(1)	0.4223(9)	0.1084(9)	7.6(4)
C(26A)	−0.005(1)	0.307(1)	0.0311(9)	7.0(4)
C(26B)	−0.080(2)	0.275(2)	0.076(1)	22(1)
C(26C)	−0.055(2)	0.342(1)	−0.038(1)	26(1)
C(26)	0.072(1)	0.3540(8)	0.0813(7)	5.2(3)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

Cp*Ta(=NAr)(NEt_2)Cl (5). An ampule (Teflon stopcock) was charged with 5.00 g (7.77 mmol) of Ta(=NAr)(NEt_2)Cl_2(THF)$_2$ (**4**), 1.21 g (8.51 mmol) of LiCp*, and ca. 80 mL of THF. The reaction vessel was closed and placed in an oil bath maintained at ca. 130 °C, and the mixture was allowed to stir at reflux for 48 h. Over this time, the reaction slowly proceeded, as noted by the slow dissolution of the suspended LiCp* and the gradual darkening of the solution from orange to brown. The reaction volatiles were then removed in vacuo, and the product was extracted from the residue with toluene/Et_2O. The extract was filtered through Celite and the solvent removed from the filtrate in vacuo to afford the product as a yellow-orange solid. This solid was washed with pentane (2 × 15 mL) and dried in vacuo to afford 4.42 g (7.37 mmol, 95%) of product. Analytically pure samples were obtained by recrystallization from Et_2O/pentane solutions at −35 °C. ^1H NMR (C_6D_6, 55 °C): δ 8.21–7.86 (A_2B mult, 3 H, H_{aryl}), 3.79 (spt, 2 H, $C\mathit{H}Me_2$), 3.68 (q, 4 H, $NC\mathit{H}_2CH_3$), 1.96 (s, 15 H, $C_5\mathit{Me}_5$), 1.38 and 1.30 (d, 6 H each, $CH\mathit{Me}_2$), 1.06 (t, 6 H, $NCH_2C\mathit{H}_3$). ^{13}C NMR (C_6D_6, 55 °C): δ 149.9 (C_{ipso}), 144.3 (C_o), 123.3 (C_p), 122.6 (C_m), 117.9 (C_5Me_5), 50.7 ($N\mathit{C}H_2CH_3$), 27.5 ($\mathit{C}HMe_2$), 25.3 and 24.5 ($CH\mathit{Me}_2$), 13.8 ($NCH_2\mathit{C}H_3$), 11.1 ($C_5\mathit{Me}_5$). Anal. Calcd for $C_{26}H_{42}ClN_2Ta$: C, 52.13; H, 7.07; N, 4.68. Found: C, 52.04; H, 6.98; N, 4.72.

Structural Determination of [Li(OEt_2)][Cp*Ta(=NAr)$_2$Cl] (2). A yellow irregular crystal of **2**, crystallized from Et_2O/pentane (−35 °C), was mounted in a glass capillary in a random orientation. Preliminary examinations and data collection were performed at ambient temperature with Mo Kα radiation (λ = 0.710 73 Å) on a Syntex P2_1 diffractometer equipped with a Crystal Logics data collection control system and with a graphite crystal incident beam monochromator. Additional crystal data are recorded in Table I. From the systematic absences of $h0l$ ($h + l = 2n + 1$) and $0k0$ ($k = 2n + 1$) and from subsequent least-squares refinement, the space group was determined to be $P2_1/n$ (No. 14). A total of 7568 reflections were collected in the $+h,+k,\pm l$ octants (6979 unique) in the range $2° \leq \theta \leq 50.0°$, with 3862 reflections having $I \geq 3\sigma(I)$. (Only those reflections with $I \geq 3\sigma(I)$ were used in the refinements.) Two representative check reflections were measured after every 98 data reflections and remained constant within experimental error throughout data collection. Hydrogen atoms were placed in calculated positions and included in the refinement. Lorentz and polarization corrections were applied to the data, and an empirical absorption correction was attempted but yielded no improvement in the structure. The agreement factors for the 383 observed and accepted reflections was 8.8% based upon I and 5.2% based on F_o. The structure was solved using the Patterson heavy-atom method to locate the Ta atom, and the remaining atoms were located in succeeding difference Fourier syntheses. The structure was refined by full-matrix least-squares procedures for final R = 0.054 and R_w = 0.067. The largest peak in the final difference Fourier map was 2.06(15) e/Å^3. All calculations were performed on a VAX computer using MolEN/VAX.[25] Table III lists atomic coordinates and their estimated standard deviations for $[Li(OEt_2)][Cp^*Ta(=NAr)_2Cl]$.

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Supplementary Material Available: A full report of the structure solution and refinement, tables of crystal data, data collection parameters, hydrogen positional and thermal parameters, bond distances, bond angles, and least-squares planes, and ORTEP figures for $[Li(OEt_2)][Cp^*Ta(=NAr)_2Cl]$ (Ar = 2,6-diisopropylphenyl) (16 pages). Ordering information is given on any current masthead page.

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[25] *MolEN, An Interactive Structure Solution Procedure*; Enraf-Nonius: Delft, The Netherlands, 1990.