

Syntheses of Tantalum(V) Complexes Containing Tetramethylpyrrolyl, Pyrrolyl, and Indolyl Ligands

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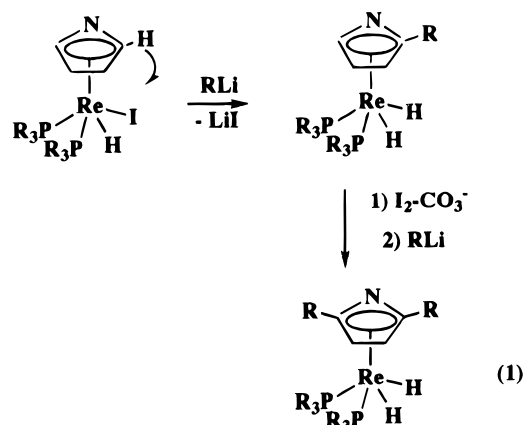
The reaction of TaMe_3Cl_2 with the lithium salt of tetramethylpyrrole (Li-TMP) led to the formation of $(\eta^5\text{-TMP})\text{TaMe}_3\text{Cl}$ (**1**). Reactions of **1** with a series of anionic ligands have been carried out to form products of the formula $(\eta^5\text{-TMP})\text{TaMe}_3\text{X}$, where $\text{X} = \text{SR}$, Me, pyrrolyl, or indolyl. Crystals of $(\eta^5\text{-TMP})\text{TaMe}_3(\text{indolyl})$ (**5**), were isolated in space group $P2_1/c$ with $a = 8.957(2)$ Å, $b = 28.540(6)$ Å, $c = 14.695(3)$ Å, $\beta = 99.40(3)^\circ$, $V = 3706.1(14)$ Å³, and $Z = 8$. The structure confirmed the η^5 -bonding mode of the tetramethylpyrrolyl ligand and the η^1 -N-coordination mode of the indolyl ligand. The derivatives $(\eta^5\text{-TMP})\text{TaMe}_3\text{X}$ showed limited stability, and decomposition products which formed in toluene solutions at room temperature have been identified in some cases. The reaction of $(\eta^5\text{-TMP})\text{TaMe}_3(\text{pyrrolyl})$ with hydrogen (2–3 atm) in benzene-*d*₆ solution at room temperature was studied. The stoichiometric formation of cyclohexane-*d*₆ by hydrogenation of an equivalent of solvent was confirmed by ¹H and ¹³C NMR and gas chromatographic/mass spectroscopic data. The characteristics and scope of the room temperature arene hydrogenation process are discussed.

Introduction

The derivatization of pyrrole and indole rings is of interest for the elaboration of the ring systems and in the synthesis of natural products,^{1,2} while the reduction and denitrogenation of such rings are problems inherent in the industrial hydrotreating process.^{3,4} The role of transition metal ions in facilitating these types of reactions has been recognized,^{2d,5,6} but considerable work remains to establish a thorough understanding of metal coordination effects on pyrrole and indole reactivity.

Many examples of transition metal complexes which contain an η^5 -pyrrole or a deprotonated η^5 -pyrrolyl ring have been reported.⁷ The majority of these complexes involve the platinum group metals (Groups 8–10). Examples of η^5 -pyrrole derivatives with early transition metals include $(\text{HNC}_4\text{H}_4)\text{Cr}(\text{CO})_3$,⁸ $(\text{C}_4\text{H}_4\text{N})\text{Mn}(\text{CO})_3$ and related derivatives,⁹ and derivatives of $\text{C}_5\text{H}_5(\text{C}_4\text{H}_4\text{N})\text{TiCl}_2$ ¹⁰ and of $(\text{C}_4\text{H}_4\text{N})\text{Re}(\text{PR}_3)_2\text{H}_2$.^{6b} In some cases, the reactivity of the heterocyclic ligand in these complexes

has been found to be significantly enhanced. For example, the pyrrolyl ligand in $(\text{C}_4\text{H}_4\text{N})\text{Re}(\text{PR}_3)_2\text{HI}$ was found to undergo nucleophilic substitution reactions at the α carbons, eq 1,^{6b-d}



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while free pyrrole does not react with nucleophiles. The topic of reactions of coordinated pyrrole ligands has been reviewed recently.^{7b,11}

Most of the previous examples of η^5 -pyrrole complexes of the early transition metals involved relatively low valent derivatives. We wished to explore the reactivity of η^5 -pyrrole ligands in coordination complexes of high-valent early transition metals. A high-valent metal ion has the potential to serve as an effective Lewis acid, enhancing the activation of the π -coordinated heterocycle toward reduction or nucleophilic addition reactions. Previous examples of η^1 -(N)-pyrrolyl complexes of Zr(IV) and Ti(IV) have been reported, $\text{Cp}_2\text{M}(\text{NC}_4\text{H}_4)_2$ and $\text{Zr}(\text{NC}_4\text{H}_2\text{Me}_2)_4$,¹² and structural studies suggested that the metal ions served as an effective Lewis acid for accepting π

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electron density from the pyrrolyl nitrogen. The bond distances in the pyrrolyl ring of the Zr complex showed a significant degree of localization of π electron density. Recently a macrocyclic tetrapyrrole ligand, meso-octaethylporphyrinogen, has been shown to undergo both η^5 - and η^1 -coordination with Zr(IV).¹³ An unusual homologation of an η^1 -pyrrolyl ligand to pyridine upon CO addition was characterized for this Zr macrocycle.

The reactions of tantalum complexes with other nitrogen heterocycles have established unusual coordination geometries and new reactivities. For example, examples of η^2 -pyridine complexes of Ta(III) have been reported,^{14,15} and the nucleophilic cleavage of a C–N bond in an η^2 -pyridine ligand has been studied mechanistically.^{16,17} In this paper we report the synthesis and characterization of a series of η^5 -tetramethylpyrrolyl (TMP) complexes of Ta(V) of the formula (TMP)TaMe₃X. The series includes derivatives where X = η^1 -bonded pyrrolyl and indolyl ligands. These were synthesized in the hope that the effects of different bonding modes on nitrogen heterocycle reactivity might be compared. These complexes appear to be the first examples of η^5 -tetramethylpyrrolyl coordination to a d⁰ metal ion.

Results and Discussion

Syntheses of (η^5 -TMP)TaMe₃Cl and (η^5 -TMP)TaMe₂Cl₂

The reaction of TaMe₃Cl₂ with (tetramethylpyrrolyl)lithium in diethyl ether proceeded at room temperature to form an orange crystalline derivative with the formula (TMP)TaMe₃Cl (**1**). We tentatively assigned a structure with a π -bonded TMP ligand by analogy to the reaction of TaMe₃Cl₂ with TiCp or LiCp* to form η^5 -Cp*TaMe₃Cl.¹⁸ The ¹H NMR spectrum of **1** at room temperature showed three methyl singlets in a ratio of 2:2:3, which corresponded to inequivalent pyrrolyl methyls and the methyl ligands on tantalum. Below –30 °C, the single tantalum–methyl resonance was split into two singlets assigned to the two methyl groups cis to the chloride ligand and one trans methyl ligand. A similar scrambling of methyl positions at room temperature by a proposed pseudorotation process has been observed previously for Cp*TaMe₃Cl.^{18a} The ΔG^\ddagger for the scrambling process in the tetramethylpyrrolyl derivative was determined from the variable temperature NMR data to be 12.3 ± 0.3 kcal/mol, similar to the value of 13.6 ± 1.4 kcal/mol for the Cp* analogue. The ¹³C NMR and mass spectral data for **1** were also consistent with the proposed formulation and structure. The compositions of **1** and of the other tantalum derivatives reported here were verified by high-resolution exact mass determinations.

Complex **1** was extremely sensitive to trace amounts of water or other proton sources which led to the dissociation of free tetramethylpyrrolyl. Reactions of **1** with hydride reagents also

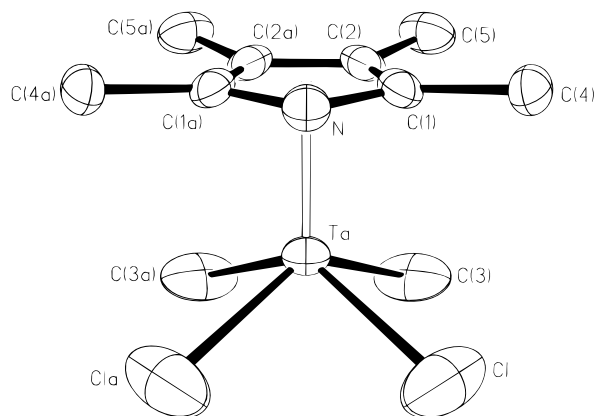


Figure 1. Perspective drawing and numbering scheme for **2**. Thermal ellipsoids are shown at 50% probability.

Table 1. Bond Lengths (Å) and Bond Angles (deg) for Ta(NC₄Me₄)Cl₂Me₂

Bond Lengths			
Ta–Cl	2.358(5)	Ta–N	2.253(14)
Ta–C(1)	2.350(9)	Ta–C(2)	2.536(11)
Ta–C(3)	2.178(15)	N–C(1)	1.373(13)
C(1)–C(2)	1.368(17)	C(1)–C(4)	1.527(13)
C(2)–C(5)	1.520(18)	C(2)–C(2A)	1.397(19)
Bond Angles			
Cl–Ta–N	96.5(3)	Cl–Ta–C(1)	92.3(3)
N–Ta–C(1)	34.6(3)	Cl–Ta–C(2)	117.9(3)
N–Ta–C(2)	56.2(4)	C(1)–Ta–C(2)	32.2(4)
Cl–Ta–C(3)	81.5(4)	N–Ta–C(3)	127.9(4)
C(1)–Ta–C(3)	93.3(4)	C(2)–Ta–C(3)	78.8(4)
Cl–Ta–ClA	81.9(2)	N–Ta–ClA	96.5(3)
C(1)–Ta–ClA	130.0(3)	C2–Ta–ClA	146.0(3)
C(3)–Ta–ClA	133.9(4)	N–Ta–C(1A)	34.6(3)
C(1)–Ta–C(1A)	54.8(4)	C(2)–Ta–C(1A)	53.7(3)
C(3)–Ta–C(1A)	130.5(5)	C(2)–Ta–C(2A)	32.0(4)
C(3)–Ta–C(2A)	99.2(5)	C(3)–Ta–C(3A)	79.9(8)
C(1)–N–C(1A)	104.0(13)	N–C(1)–C(2)	111.7(9)
C(1)–C(2)–C(2A)	106.3(6)		

led to decomposition with tetramethylpyrrolyl dissociation, perhaps through intermediate tantalum hydride formation. The facile ligand dissociation suggested that the interaction between Ta(V) and the heterocycle was quite ionic in character. Attempts were made to increase the stability of the TMP–Ta^V interaction by changing the nature of the coligand X in the complexes, and the syntheses of additional derivatives of (TMP)TaMe₃X are described below.

A minor product (about 10%) formed in the above synthesis of **1** was identified as (TMP)TaMe₂Cl₂ (**2**). It is likely that this product arises from the reaction of TaMe₂Cl₃ with pyrrolyl-lithium.¹⁹ TaMe₂Cl₃ is a potential side product which may be formed during the synthesis of TaMe₃Cl₂,^{18b} and it was detected in the NMR spectrum of the latter starting reagent in a 1:10 ratio. In the ¹H NMR spectrum of **2** three methyl singlets were observed in a 1:1:1 ratio, shifted downfield slightly relative to the resonances of **1**. In attempted crystallizations of the product mixture, single crystals of **2** were isolated from a saturated ether solution at –40 °C. This product, **2**, was characterized by an X-ray diffraction study to confirm the bonding mode of the tetramethylpyrrolyl ligand.

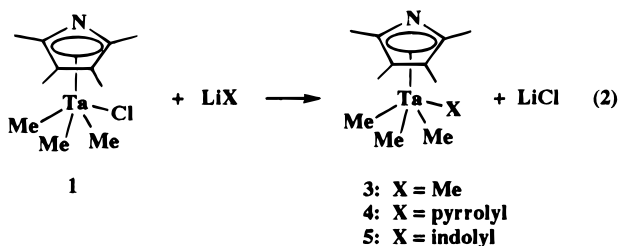
A perspective drawing and numbering scheme for the molecule are shown in Figure 1, and selected bond distances and angles are presented in Table 1. The structure confirmed a piano stool arrangement with an η^5 -TMP ligand and cis pairs

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of methyl and chloride ligands. An examination of the interactions between the metal ion and the TMP ligand shows that the Ta–N and Ta–C(1) distances are significantly shorter than the Ta–C(2) distance, suggesting some degree of ring slippage toward an η^3 -azaallyl bonding interaction. Similar differences in M–C distances for a η^5 -pyrrolyl ligand have been observed previously for the complex $(\eta^5$ -3,4-Me₂-pyrrolyl)Mn(CO)₃.^{9a} However, in both the Ta and Mn structures, comparisons of C–C bonding distances within the TMP ligand do not provide clear evidence for an allyl–ene localization of electron density.

Syntheses of $(\eta^5$ -TMP)TaMe₃X Derivatives. The reactions of **1** with a series of anionic ligands, LiX, were carried out in diethyl ether at room temperature, eq 2, and the metathesis products $(\eta^5$ -TMP)TaMe₃X, where X = Me, pyrrolyl, or indolyl, were isolated and characterized.



Reactions of **1** with potential π donor ligands such as thiolates, alkoxides, and dialkylamides were also attempted, but products appeared to be significantly less stable in these cases and were not successfully isolated. For example, in an NMR tube reaction monitored spectroscopically, the derivative $(\eta^5$ -TMP)TaMe₃(S^tBu) appeared to be formed quantitatively from the reaction of 1 equiv of lithium *tert*-butyl thiolate with **1**. NMR data for the proposed product are given in the Experimental Section. However, the product decomposed in the benzene-*d*₆ solution over a period of about 1 h with the loss of isobutene and methane, which were identified by NMR spectroscopy. Free tetramethylpyrrole was also observed in the NMR spectrum of the decomposition products. The elimination of isobutene from a *tert*-butyl thiolate ligand is a common decomposition pathway which has been used in some cases for the preparation of metal sulfido complexes.²⁰ Some Ta^V=S complexes have been reported previously,^{21,22} but attempts to trap a Ta=S intermediate in this system with phosphine or with nitrogen donor ligands were unsuccessful. The reaction of **1** with a less reactive thiolate ligand, 2,6-dimethylbenzenethiolate, also led to a thiolate complex of limited stability. The product decomposed in solution by an uncharacterized pathway.

Complexes **3–5** were isolated as orange crystalline materials and were characterized by spectroscopic techniques. Spectroscopic data for **3** are unremarkable and are presented in the

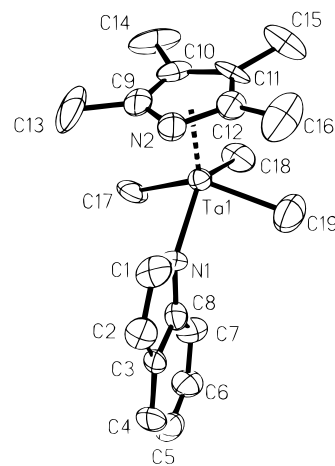


Figure 2. Perspective drawing and numbering scheme for **5**. Thermal ellipsoids are shown at 50% probability.

Experimental Section. In the ¹H NMR spectrum of $(\eta^5$ -TMP)-TaMe₃(NC₄H₄) (**4**) in benzene-*d*₆, resonances for the pyrrolyl hydrogens were observed at 7.48 and 6.60 ppm, downfield from the resonances for free pyrrole in this solvent which occur at 6.35 and 6.32 ppm. Downfield shifts for metal N-bonded derivatives of related heterocycles have been reported previously.²³ At room temperature a single broad resonance was observed for the Ta–Me groups, but in the ¹³C NMR spectrum two resonances were observed as expected for methyls cis and trans to the pyrrolyl ligand at 73.3 and 66.2 ppm. Variable temperature ¹H NMR experiments showed two resolved methyl singlets at *T* < 5 °C, and a $\Delta G^\ddagger = 14.5 \pm 0.3$ kcal/mol was determined for the fluxional process.

In the ¹H NMR spectrum of $(\eta^5$ -TMP)TaMe₃(indolyl), **5**, resonances for the hydrogens on the indolyl ligand were also shifted downfield compared to those of free indole in the same solvent. At ambient temperature the spectrum showed two broadened Ta–Me resonances in a 2:1 ratio. The resonance for the Me group trans to the indolyl ligand at 0.95 ppm was shifted slightly downfield relative to the cis Me resonance at 0.86 ppm. Variable temperature NMR data established that a fluxional process that exchanged these methyl resonances occurred at elevated temperatures (methyl peaks coalesced at *T* > 35 °C), and the ΔG^\ddagger for this process was found to be 15.5 ± 0.4 kcal/mol. The ΔG^\ddagger values for the pseudorotation process in the series of derivatives $(\eta^5$ -TMP)TaMe₃X (**1**, **4**, and **5**) increase as the steric bulk of the unique ligand X increases.

X-ray Diffraction Study of 5. Single crystals of **5** were obtained from a saturated Et₂O solution. The complex crystallized in space group *P*2₁/*c* with two independent molecules per asymmetric unit. The structural features of the two molecules are very similar, and a perspective drawing of one of these is shown in Figure 2. Selected bond distances and angles are given in Table 2. The arrangement of η^5 -TMP and η^1 -indolyl and methyl ligands gives a normal piano stool structure. The bonding distances between tantalum and the η^5 -TMP ligand in **5** are similar to those found for **2**, and the same pattern of shorter distances for the bonds to the α carbons than for those to the β carbons of the ring is observed.

The η^1 -N-bonded indolyl ligand maintains its planar character. The Ta–N(1) bond distance (2.070(11) Å) is relatively long, but still within the range of Ta–N distances in other Ta(V) amide complexes.^{24–26} Using a criterion developed by Chish-

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Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) for Ta(NC₄Me₄)Me₃(indolyl) (**5**)

Bond Lengths			
Ta(1)–N(1)	2.070(11)	Ta(1)–N(2)	2.238(11)
Ta(1)–C(9)	2.373(11)	Ta(1)–C(10)	2.552(13)
Ta(1)–C(11)	2.572(13)	Ta(1)–C(12)	2.347(13)
Ta(1)–C(17)	2.226(13)	Ta(1)–C(18)	2.19(2)
Ta(1)–C(19)	2.197(13)	N(1)–C(1)	1.42(2)
N(1)–C(8)	1.41(2)	C(1)–C(2)	1.35(2)
C(2)–C(3)	1.46(2)	C(3)–C(8)	1.39(2)
N(2)–C(9)	1.37(2)	C(9)–C(10)	1.40(2)
C(10)–C(11)	1.40(2)	C(11)–C(12)	1.35(2)
N(2)–C(12)	1.40(2)		
Bond Angles			
N(1)–Ta(1)–C(17)	86.3(5)	N(1)–Ta(1)–C(18)	131.5(5)
N(1)–Ta(1)–C(19)	84.4(6)	C(17)–Ta(1)–C(18)	76.1(6)
C(18)–Ta(1)–C(19)	78.0(6)	C(17)–Ta(1)–C(19)	135.3(6)

Table 3. Crystal Data for Compounds **2** and **5**

	2	5
formula	C ₁₀ H ₁₈ NC ₁₂ Ta	C ₁₉ H ₂₇ N ₂ Ta
fw	404.1	464.39
crystal system	orthorhombic	monoclinic
unit cell dimensions		
<i>a</i> , Å	13.102(4)	8.957(2)
<i>b</i> , Å	14.167(3)	28.540(6)
<i>c</i> , Å	6.946(2)	14.695(3)
β, deg		99.40(3)
volume, Å ³	1289.3(6)	3706.1(14)
space group	<i>Pnma</i>	<i>P2₁/c</i>
<i>Z</i>	4	8
density, calc, g/cm ³	2.082	1.665
λ(Mo Kα, Å)	0.71073	0.71073
temp, °C	–55 to –60	25(2)
scan type	2θ–θ	2θ–θ
θ range	3.0 to 50.0	1.58–22.55
independent reflections	1187	4875
reflections observed	1034	3315
absorption corr	semiempirical	XABS2
<i>R</i> ^a	0.0630	0.0477
<i>R</i> _w	0.0890 ^b	0.0915 ^c
GOF	2.00	0.968
largest peak in final diff map, e/Å ³	4.84	1.075

$$^a R = R_1 = \sum |F_o| - |F_c| / \sum |F_o|. \quad ^b R_w = [\sum w(|F_o| - |F_c|)^2] / \sum w(F_o)^2]^{1/2}. \quad ^c R_w = [\sum [w(F_o^2 - F_c^2)^2] / \sum w(F_o^2)]^{1/2}.$$

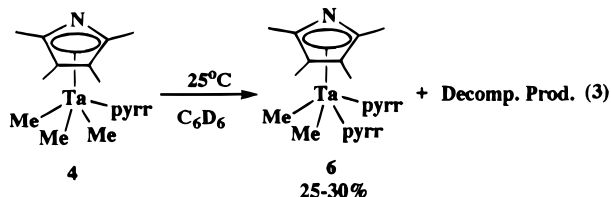
olm and co-workers,²⁶ in which Ta–N and Ta–C bond lengths within the same molecule are compared, there appears to be relatively little contribution to this bond from a N–Ta π interaction. On the basis of covalent radii, the σ-only Ta–N(sp²) bond is expected to be about 0.1 Å shorter than the Ta–C(sp³) bonds. In other Ta(V) amide complexes in which significant π bonding was proposed (e.g., Ta(NMe₂)₃(*p*-tolyl)(Br)), the Ta–N and Ta–C distances differed by 0.2 Å or more. However, in **5** a difference of only 0.13–0.14 Å is observed between these two bond types. The expected delocalization of the nitrogen lone pair in the aromatic ring system is consistent with the relatively long Ta–N bond distance.

Reactivity Studies of (TMP)TaMe₃X Derivatives. The reaction of (η⁵-TMP)TaMe₃(NC₄H₄) (**4**) with an equivalent of free pyrrole in C₆D₆ was monitored by NMR spectroscopy at room temperature. Sharp distinct resonances for free pyrrole and coordinated pyrrolyl were observed, indicating that ligand exchange was slow on the NMR time scale under these conditions. We did not observe evidence for a further reaction

involving the elimination of methane and the formation of (η⁵-TMP)TaMe₂(NC₄H₄)₂ in this system.

The thermal stabilities of **4** and **5** were also investigated. Previous well-defined decomposition pathways for high-valent Cp*metal–L complexes (L = alkyl, amide, aryl, or pyridine) include β hydrogen elimination to produce an η²-coordination mode of the ligand L–H,^{27–30} or hydrogen migration from a methyl group of the Cp* ligand to the metal ion, followed by further alkane elimination.^{31,32} We were interested in determining whether the thermal decomposition of **4** and **5** might lead to derivatives with η²-coordinated pyrrolyl and indolyl ligands or with a modified tetramethylpyrrolyl ligand. Further reactivity of such bonding modes would be of interest. However, these decomposition pathways were not identified for the present systems.

Benzene solutions of both **4** and **5** under an inert atmosphere or under vacuum underwent slow decomposition at room temperature. For example, in the NMR spectrum of **4**, the resonances of the starting reagent slowly decreased over a period of several days and a single new set of resonances grew in. The spectrum of the product showed two new pyrrolyl multiplets in the aromatic region and three new singlets in the upfield region with integrations consistent with the formulation (η⁵-TMP)TaMe₂(NC₄H₄)₂ (**6**), eq 3. The ¹³C NMR data and mass



spectral data for this product also supported the proposed formulation. Only 25–30% of **4** was accounted for by the formation of **6**, but other (TMP)Ta-containing products were not observed in the spectrum. For example, our failure to detect any (η⁵-TMP)TaMe₄ (**3**) in the decomposition solution appears to rule out the formation of **6** by a bimolecular ligand exchange, since **3** is expected to be stable under these reaction conditions.³³

Complex **5** also underwent a similar slow decomposition in toluene solution at room temperature. Spectroscopic data for the resulting product, formed in ca. 25% yield, supported the formulation (TMP)TaMe₂(indolyl)₂.

Attempts were made to prepare cationic pentamethylpyrrole derivatives by reacting **2–4** with methylating agents such as Me₃OBf₄ or MeOTf. However, these reactions led only to decomposition of the tantalum(V) derivatives. Neither the η⁵-tetramethylpyrrole ligand nor the η¹-heterocycles appeared to

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(33) Complex **6** has been found to be stable in benzene solution both at room temperature and at 50 °C over a period of 8 days.

be activated to nucleophilic attack, and reactions with reagents such as triethylborohydride, methyl lithium, or diethyl malonate also led to decomposition of the complexes.

A brief investigation of the insertion chemistry of the (TMP)-Ta^V derivatives also provided evidence that these complexes are relatively unstable relative to the Cp* analogues. Facile insertions of carbon monoxide and isocyanides into the Ta-alkyl ligands of many Cp*Ta^V derivatives have been characterized.³⁴ For example, one of the first examples of such an insertion was the reaction of Cp*TaMe₄ with carbon monoxide to form an η^2 -acetone derivative Cp*TaMe₂(η^2 -Me₂CO), which was isolated and characterized.^{34a} A similar insertion was tentatively identified for the reaction of CO (1 equiv) with (η^5 -TMP)TaMe₃(NC₄H₄) (**4**), and ¹H NMR data for (η^5 -TMP)-TaMe(NC₄H₄)(η^2 -Me₂CO) are included in the Experimental Section. However, this product was not successfully isolated because it underwent decomposition in solution in the sealed NMR tube over a period of 30 min.

Attempted Reductions of (η^5 -TMP)TaMe₃X Derivatives. Certain Cp*Ta^V derivatives have been found to react with hydrogen to form tantalum hydride complexes.^{29b} Both (η^5 -TMP)TaMe₃(NC₄H₄) (**4**) and (η^5 -TMP)TaMe₃(indolyl) (**5**) reacted with hydrogen (ca. 3.5 atm) in benzene solution at room temperature. The reactions in sealed tubes were followed by NMR spectroscopy. An interesting feature of the ¹H NMR spectrum for the reaction of **4** with hydrogen in C₆D₆ was the appearance of a strong singlet at 1.36 ppm. This resonance was assigned to deuterated cyclohexane, C₆H₆D₆, which resulted from the hydrogenation of the benzene-*d*₆ solvent. In the {¹H}¹³C NMR spectrum, a three-line pattern centered at 26.5 ppm with *J*_{C-D} = 19 Hz supported the formation of the reduced arene. The GC/mass spectrum of the volatile component of this reaction also confirmed that cyclohexane-*d*₆ was present. Approximately 1 equiv of cyclohexane per mole of starting tantalum complex was produced. Intermediate hydrogenation products such as cyclohexadiene-*d*₂ or cyclohexene-*d*₄ were not observed. No precipitate was visible in the dark brown reaction mixtures, and addition of mercury to the reaction did not affect the product formation, suggesting that the aromatic hydrogenation is a homogeneous process.³⁵

The nature of the active species in the arene reduction has not been identified. The resonances for the starting tantalum complex slowly disappeared, but no signals corresponding to new tantalum derivatives were observed in the normal diamagnetic region of the spectrum. A small amount of free tetramethylpyrrole (15%) was initially formed, but resonances for this compound did not increase in intensity as the starting material disappeared. Methane was also observed to form during the reaction and was identified by NMR spectroscopy; this product was not quantified by the NMR data because of its volatility.

The scope of the arene hydrogenation activity of **4** has been explored briefly. Toluene-*d*₈ was hydrogenated under similar reaction conditions as benzene, and the formation of methylcyclohexane-*d*₈ was confirmed by GC/MS data. A competition reaction of excess hydrogen with equimolar amounts of deuterated benzene and toluene in the presence of **4** resulted in the selective hydrogenation of toluene. Methylcyclohexane-*d*₈ was

identified, but no evidence for cyclohexane formation was observed by NMR spectroscopy or by GC/mass spectral analysis. Naphthalene was partially reduced under similar conditions to form tetrahydronaphthalene. In contrast no hydrogenation activity was observed under these conditions for an arene with an electron-withdrawing group, such as benzonitrile, or for heteroaromatics, such as thiophene.

The promotion of arene hydrogenations by metal complexes has been reported previously.^{36,37} Many of these examples involve platinum group metals, but recently, high-valent niobium and tantalum derivatives have been found to catalyze the hydrogenation of arenes under conditions of high temperature and pressure.^{36a-c} The arene hydrogenations reported here are of limited practical application because of the stoichiometric nature of the reaction, but the composition and structure of the reduction product of **4** which promotes this arene reduction under such mild conditions are of interest. Although the closely related complex **5** showed similar NMR broadening under hydrogen pressure, no arene hydrogenation products were detected in this system. Further work to identify reduced tantalum products or to trap or stabilize such products in the presence of additional donor ligands is planned.

Conclusions. A series of new Ta(V) complexes containing the η^5 -tetramethylpyrrolyl anion have been synthesized and characterized, including derivatives that also contained η^1 -pyrrolyl or indolyl ligands. Although the coordination of the nitrogen heterocycles to the Ta(V) ion has the potential for activating the rings toward further reactions, we found that the highly reactive nature of the complexes, which includes slow ligand dissociations, facile redox processes, and extreme sensitivity toward electrophiles, does not permit a detailed investigation of ligand-based reactivity in these systems.

Experimental Section

TaMe₃Cl₂^{18b} and tetramethylpyrrole³⁸ were synthesized according to literature procedures. Pyrrole was distilled from CaH₂ and stored over Linde 4A molecular sieves. Lithiated pyrroles, indoles, and thiolates were prepared by combining the appropriate compound with an equimolar amount of *n*-butyllithium in hexane and filtering off the insoluble product. Diethyl ether and benzene-*d*₆ were distilled from sodium benzophenone ketyl and stored over 4 Å molecular sieves before use. Hexane, pentane, and deuterated chloroform were distilled from CaH₂ and stored over 4 Å molecular sieves before use. All reactions were carried out under a nitrogen atmosphere using standard Schlenk techniques.

¹H NMR spectra were recorded at 300 MHz, and ¹³C NMR spectra were recorded at 75.4 MHz on a Varian VXR-300 NMR spectrometer. Chemical shifts were referenced to tetramethylsilane by using the

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deuterated solvent signal as a secondary reference. ^1H NMR chemical shifts are reported at ambient probe temperature, 18 °C, unless otherwise indicated. Mass spectra were obtained on a VG Analytical 7070 EQ-HF mass spectrometer.

Synthesis of $(\eta^5\text{-NC}_4\text{Me}_4)\text{TaMe}_3\text{Cl}$ (1). TaMe_3Cl_2 (0.945 g, 3.18 mmol) with a small impurity of TaMe_2Cl_3 (ca. 10%) was dissolved in 100 mL of diethyl ether. This solution was transferred into a suspension of (tetramethylpyrrolyl)lithium (0.406 g, 3.15 mmol) in 30 mL of diethyl ether with vigorous stirring. A rapid color change from pale yellow to orange occurred with the formation of a pale precipitate (LiCl). The solution was stirred for 1 h and filtered through a bed of Celite. The orange filtrate was then concentrated in vacuo and kept at -20 °C for 48 h giving orange crystals of **1** in 42% yield. ^1H NMR (C_6D_6): δ 2.03, 1.30 (s, 6H, TMP); 1.00 (s, 9H, TaMe). At -43 °C, two sharp Ta–Me resonances were resolved at 0.77 and 1.03 ppm. Their coalescence temperature was -17.5 °C. ^{13}C NMR (C_6D_6): δ 137.3, 132.9 (s, TMP); 71.6 (br s, TaMe); 15.0, 9.9 (TMP–Me). MS (Cl^-): m/z 383 (P). (EI^+): m/z 368 (P–Me), 353 (P–2Me). HR MS (Cl^-): Calcd m/z 383.0843. Found: m/z 383.0848.

A minor impurity in the product (ca. 10%) was identified as $(\eta^5\text{-NC}_4\text{Me}_4)\text{TaMe}_2\text{Cl}_2$ (**2**). This complex probably arises from the reaction of TaMe_2Cl_3 (vide supra) with the Li–pyrrolyl reagent. The same complex can also be prepared in about 30% yield from the reaction of TaMe_3Cl_2 with neutral tetramethylpyrrole. ^1H NMR (C_6D_6): δ 2.12, 1.36 (2 s, 6H, TMP); 1.09 (s, 6H, TaMe).

X-ray Diffraction Study of $(\eta^5\text{-NC}_4\text{Me}_4)\text{TaMe}_2\text{Cl}_2$. Orange crystals of **2** were obtained from a saturated Et_2O solution of a mixture of **1** and **2** cooled at 253 K for 48 h. A suitable crystal was coated with Apiezon T grease, and data were collected at 193 K on a Siemens P3/F diffractometer. Axial photographs indicated orthorhombic symmetry, and the centered settings of 25 intense reflections with 2θ values between 24.0° and 50.0° gave the unit cell dimensions listed in Table 5. A Patterson map gave the location of the Ta atom at a site of crystallographic mirror symmetry. Phases derived from the location of the Ta gave positions of other atoms of the structure. From differences in electron density and bond length to the Ta, it was possible to clearly differentiate between the coordinated chloro and methyl carbon atoms. ψ scans recorded at the conclusion of data collection were used to obtain an absorption profile, and an empirical correction for absorption was applied to the data. Crystal data, data collection parameters, and results of the analysis are given in Table 3.

Synthesis of $(\eta^5\text{-NC}_4\text{Me}_4)\text{TaMe}_4$ (3). Complex **1** (108 mg, 0.28 mmol) was dissolved in 10 mL of diethyl ether. 1.2 M MeLi in diethyl ether (0.235 mL, 0.28 mmol) was added dropwise with stirring. An immediate color change from orange to green with the formation of a gray precipitate (LiCl) occurred. The solution was stirred for 30 min and filtered through Celite. The dark green filtrate was concentrated in vacuo and cooled at -20 °C for 18 h giving dark green, crystalline **3** in 49% yield. ^1H NMR (C_6D_6): δ 2.00, 1.31 (s, 6H, TMP); 0.83 (s, 12H, TaMe). ^{13}C NMR (CDCl_3): δ 134.9, 132.2 (s, TMP); 73.1 (s, TaMe); 14.7, 10.2 (TMP–Me). MS (Cl^-): m/z 363 (P). (EI^+): m/z 348 (P–Me), 332 (P–2Me). HR MS (Cl^-): Calcd m/z 363.1389. Found: m/z 363.1385.

Synthesis of $(\eta^5\text{-NC}_4\text{Me}_4)\text{TaMe}_3(\text{NC}_4\text{H}_4)$ (4). Complex **1** (470 mg, 1.23 mmol) was dissolved in 100 mL of diethyl ether and added to a suspension of pyrrolyllithium (90 mg, 1.23 mmol) in 50 mL of diethyl ether with vigorous stirring. The solution was stirred at room temperature for 3.5 h and filtered through a bed of Celite. The solvent was removed from the resultant yellow filtrate in vacuo leaving a yellow oil. The oil was extracted with hexanes, and the extract was filtered and concentrated in vacuo. The solution was cooled at -78 °C for 18 h giving the yellow crystalline product **4** in 65% yield. ^1H NMR (C_6D_6): δ 7.48, 6.60 (2 m, each 2H, pyr); 1.87, 1.32 (2 s, each 6H, TMP); 0.82 (br s, 9H, TaMe). At -40 °C, two Ta–Me resonances were resolved at 0.79 and 0.67 ppm. Their coalescence temperature was 18.5 °C. ^{13}C NMR (C_6D_6): δ 135.0, 130.6 (s, TMP); 127.3, 111.6 (s, pyr); 73.3 (s, TaMe); 66.2 (s, TaMe₂); 14.6, 9.8 (TMP). MS (Cl^-): m/z 414 (P). (EI^+): m/z 399 (P–Me), 348 (P–pyr). HR MS (Cl^-): Calcd m/z 414.1498. Found: m/z 414.1507.

Synthesis of $(\eta^5\text{-NC}_4\text{Me}_4)\text{TaMe}_3(\text{indolyl})$ (5). Complex **1** (218 mg, 0.57 mmol) was dissolved in 15 mL of diethyl ether and added to a suspension of indolylithium (70 mg, 0.57 mmol) in 15 mL of diethyl

ether with vigorous stirring. An immediate color change from orange to brown with the formation of a pale precipitate (LiCl) occurred. The solution was stirred for 2.5 h and filtered through Celite. The brown filtrate was concentrated in vacuo and cooled at -20 °C for 36 h giving brown-green crystals of **5** in 29% yield. ^1H NMR with tentative assignments (C_6D_6): δ 8.20, 7.71 (2d, each 1H, $J = 8$ Hz, ind); 8.08, 6.71 (2d, each 1H, $J = 3$ Hz, ind); 7.30 (m, 2H, ind); 1.85, 1.33 (2s, each 6H, TMP); 0.95 (br s, 3H, TaMe); 0.86 (br s, 6H, TaMe₂). At -19 °C, two sharp Ta–Me resonances were observed at 0.92 and 0.79 ppm. Their coalescence temperature was 38 °C. ^{13}C NMR (C_6D_6): δ 143.8, 134.9, 134.3, 132.6, 130.7, 122.5, 121.9, 120.6, 116.7 (TMP and ind aromatics); 73.2 (s, TaMe); 64.6 (s, TaMe₂); 14.3, 9.8 (2s, TMP–Me). MS (Cl^-): m/z 464 (P). (EI^+): m/z 449 (P–Me). HR MS (Cl^-): Calcd m/z 464.1648. Found: m/z 464.1609.

X-ray Diffraction Study of $(\eta^5\text{-NC}_4\text{Me}_4)\text{TaMe}_3(\text{indolyl})$ (5). Crystals suitable for diffraction were grown from a saturated Et_2O solution of **5** cooled at 253 K for 72 h. A sample of crystals was placed under Apiezon T grease. The datum crystal was mounted on a glass fiber and quickly placed in the 233 K N_2 stream of a locally-modified Nicolet LT-2 apparatus on a Nicolet R3 diffractometer. Data were collected to a Data General Nova 4/C minicomputer.

Structure solution and refinement were performed on the DEC microVAX 3200 in the X-ray laboratory at the University of California at Davis using the SHELX suite of programs. All non-hydrogen atoms were refined with anisotropic thermal parameters. Data were corrected for absorption. Largest residuals in the final difference map were $\leq 1.075 \text{ e} \cdot \text{Å}^{-3}$ and were located unreasonably close to the two Ta centers. These were dismissed as absorption artifacts.

Hydrogen atoms were placed at calculated distances and allowed to ride on the position of the parent atom. The isotropic thermal parameter was modeled to ride as 1.2 times the equivalent isotropic thermal parameter of the parent atom. No notable intermolecular contacts were observed.

Formation of $(\eta^5\text{-NC}_4\text{Me}_4)\text{TaMe}_3(\text{S}^i\text{Bu})$. Complex **1** (12 mg, 3.1×10^{-2} mmol) and LiS^iBu (3 mg, 3×10^{-2} mmol) were placed in an NMR tube connected to a Schlenk adapter. C_6D_6 (0.8 mL) was added to the reaction vessel, the mixture was frozen at -196 °C, and the vessel was evacuated. The NMR tube was then flame sealed and thawed to room temperature. An immediate reaction occurred, and a pale precipitate (LiCl) formed. The yellow benzene-soluble product formed in quantitative yield by ^1H NMR, but all attempts to isolate and purify the compound on a larger scale led to decomposition of the product. ^1H NMR (C_6D_6): δ 2.15, 1.34 (2s, each 6H, TMP); 1.60 (s, 9H, SⁱBu); 0.95 (s, 9H, TaMe).

Formation of $(\eta^5\text{-NC}_4\text{Me}_4)\text{TaMe}_3(\text{dmpt})$ (dmpt = 2,6-dimethylbenzenethiolate). Complex **1** (10 mg, 3×10^{-2} mmol) and lithium 2,6-dimethylbenzenethiolate (4 mg, 3×10^{-2} mmol) were placed in an NMR tube connected to a Schlenk adapter. 0.8 mL of C_6D_6 was added to the reaction vessel, the mixture was frozen at -196 °C, and the vessel was evacuated. The NMR tube was then flame sealed and thawed to room temperature. An immediate color change from pale orange to red-orange occurred with the formation of a pale precipitate (LiCl). The initial conversion to $(\eta^5\text{-NC}_4\text{Me}_4)\text{TaMe}_3(\text{dmpt})$ was 71% by ^1H NMR, but the compound showed significant decomposition after 1 day in solution at room temperature. The complex decomposed when isolation and purification were attempted. ^1H NMR (C_6D_6): δ 7.08 (d, 2H, SPhMe₂); 6.90 (t, 1H, SPhMe₂); 2.85 (s, 6H, SPhMe₂); 1.91, 1.24 (2s, each 6H, TMP); 0.72 (s, 9H, TaMe).

Thermal Decomposition of $(\eta^5\text{-NC}_4\text{Me}_4)\text{TaMe}_3(\text{NC}_4\text{H}_4)$ (4). In a typical experiment complex **4** (15 mg, 0.036 mmol) was dissolved in 0.6 mL of C_6D_6 , the solution was degassed in two freeze–pump–thaw cycles, and the NMR tube was flame sealed under vacuum. The reaction was monitored by NMR at room temperature. The decomposition product $(\eta^5\text{-NC}_4\text{Me}_4)\text{TaMe}_2(\text{NC}_4\text{H}_4)_2$ (**6**) grew in slowly over the course of 44 days, and at this time the yield of **6** was 27% (by ^1H NMR). Resonances for other tantalum products were not observed. ^1H NMR (C_6D_6): δ 7.00, 6.43 (2m, each 4H, pyr); 1.73, 1.35 (2s, each 6H, TMP); 0.91 (s, 6H, TaMe). ^{13}C NMR (C_6D_6): δ 138.0, 133.5 (TMP); 130.2, 113.5 (pyr); 67.3 (TaMe); 13.4, 10.0 (TMP–Me). MS (Cl^-): m/z 465 (M).

Thermal Decomposition of $(\eta^5\text{-NC}_4\text{Me}_4)\text{TaMe}_3(\text{indolyl})$ (5). Complex **5** (15 mg, 0.032 mmol) was dissolved in 0.6 mL of C_6D_6 , the

solution was degassed in two freeze–pump–thaw cycles, and the NMR tube was flame sealed under vacuum. The reaction was monitored by NMR at room temperature. The decomposition product ($\eta^5\text{-NC}_4\text{Me}_4$)- $\text{TaMe}_2(\text{indolyl})_2$ grew in very slowly; and after 44 days, the yield was 25% (by ^1H NMR). ^1H NMR (C_6D_6): δ 7.68, 7.57 (2d, each 2H, $J = 8$ Hz, ind); 7.27 (m, 4H, ind); 6.93, 6.49 (2d, each 2H, $J = 3$ Hz, ind); 2.04, 1.78 (2s, each 6H, TMP); 1.41 (s, 6H, TaMe). ^{13}C NMR (C_6D_6): δ 145.2, 133.0 (2s, TMP); 137.6, 122.7, 122.5, 121.0, 117.2, 108.2 (6 s, ind); 125.9, 121.3 (2 s, ind quart C); 80.3 (s, TaMe); 12.2, 8.7 (2 s, TMP Me).

Formation of ($\eta^5\text{-NC}_4\text{Me}_4$)TaMe(NC_4H_4)($\eta^2\text{-Me}_2\text{CO}$). Complex **4** (10 mg, 0.024 mmol) was dissolved in 0.6 mL of C_6D_6 in an NMR tube. The yellow solution was frozen under vacuum. Carbon monoxide (243 Torr, 0.024 mmol) was added, and the tube was flame sealed. On thawing, the solution became orange at the solvent/gas interface, and upon shaking the solution became dark orange. An initial ^1H NMR spectrum showed evidence for ($\eta^5\text{-NC}_4\text{Me}_4$)TaMe(pyrr)($\eta^2\text{-Me}_2\text{CO}$). ^1H NMR (C_6D_6): δ 7.79 (m, 2H, pyrr); 6.55 (m, 2H, pyrr); 2.14 (s, 3H, $\eta^2\text{-Me}_2\text{CO}$); 1.70 (s, 3H, $\eta^2\text{-Me}_2\text{CO}$); 1.94 (s, 6H, TMP); 1.46 (s, 6H, TMP); 0.25 (s, 3H, TaMe). Within 30 min the compound had decomposed significantly. Free pyrrole and tetramethylpyrrole were observed in the spectrum at this time.

Hydrogenation of Benzene- d_6 . Complex **4** (10 mg, 0.02 mmol) was dissolved in 0.6 mL of C_6D_6 . The tube was evacuated, and H_2 (3.5 atm) was added to the tube. The tube was flame sealed, and the solution was shaken at room temperature. After 1 week the reaction appeared to be complete, and the spectrum indicated that cyclohexane- d_6 had formed in 84% yield. The tube was opened, the volatiles were transferred, and the GC/MS data were obtained. ^1H NMR (C_6D_6): δ 1.36 (s, 6H, $\text{C}_6\text{D}_6\text{H}_6$). ^{13}C NMR (C_6D_6): δ 26.5 (t, $J_{\text{C-D}} = 19$ Hz, $\text{C}_6\text{D}_6\text{H}_6$). GC/MS: m/z 90 (M).

Hydrogenation of Toluene- d_8 . Complex **4** (9 mg, 0.02 mmol) and hydrogen (2.5 atm) were combined in 0.6 mL of toluene- d_8 , and the reaction tube was flame sealed. After 2 weeks the volatiles were vacuum transferred and GC/MS data qualitatively confirmed the formation of methylcyclohexane- d_8 . The product was not successfully identified by ^1H or ^{13}C NMR. GC/MS: m/z 106 (M). In a competition experiment, 10 mg of **4** was dissolved in 0.3 mL of benzene- d_6 (3 mmol) and 0.3 mL of toluene- d_8 (3 mmol) and hydrogen (2.5 atm) were added. The reaction tube was flame sealed and maintained at room temperature for 2 weeks. The volatiles were then vacuum transferred and analyzed by GC/MS. The data established that methylcyclohexane- d_8 had formed but no cyclohexane- d_6 was detected.

Hydrogenation of Naphthalene. Complex **4** (18 mg, 0.043 mmol) and naphthalene (140 mg, 1.09 mmol) were combined in 5 mL of THF. The Schlenk reaction tube was evacuated, and 2.5 atm of H_2 was added. After 2 weeks stirring at room temperature, the solution was concentrated to ca. 2 mL in vacuo, and the GC/MS experiment was performed. The data gave evidence for the partial hydrogenation of naphthalene to tetrahydronaphthalene. No other reduced species were detected. GC/MS: m/z 132 (M).

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Supporting Information Available: Details of data collection and refinement and complete tables of bond distances and angles and positional and thermal parameters for **2** and **5** (18 pages). Ordering information is given on any current masthead page.

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