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Tantalum Complexes of Diphenyldipyrrolide Dianion: Partial Hydrogenation of a Phenyl Ring

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The reactivity of the pentavalent dipyrrolide complex $\{[Ph_2C(C_4H_3N)_2]_2TaCl_2\}\{Li(THF)_4\}\cdot 2THF$ was investigated. While an isostructral dimethyl derivative was readily prepared by treatment with MeLi, reaction with $NaHBEt_3$ gave a major reorganization, affording a mixture of $[Ph_2C(C_4H_3N)_2]Ta[(1,4\text{-}\eta^1{:}\eta^1\text{-}2,3\text{-}\eta^2\text{-}C_6H_7PhC(C_4H_3N)_2][Na(OEt_2)]$ and $[Ph_2C(C_4H_3N)_2]_3Ta[Na(OEt_2)]_2\cdot(OEt_2)$. The first complex arises from partial hydrogenation of one of the ligand phenyl rings performed by an intermediate Ta hydride. In the second case, ligand scrambling occurred along with reduction of the metal center.

Introduction

Recent work in this group has shown that dipyrromethane dianions provide a versatile class of supporting ligands. These species display a remarkable flexibility in terms of bonding mode (pure σ-donor, pure π-donor, and σ/π-donor).[1] At least in the case of low-valent lanthanides, these ligands may stabilize highly reactive metals yet increase the reactivity of the metal center[2] with respect to the isoelectronic cyclopentadienyl derivatives. Finally, these dianions often retain alkali cations in the molecular structure of the complex. The additional coordination of a Lewis acid to the pyrrolide ring, via either σ- or π-bonding, directly affects the metal−ligand interaction, thus allowing for the fine-tuning of the metal redox potential.[3]

Among low-valent early transition metals, niobium and tantalum occupy a special place. The few derivatives reported in the literature are able to perform a wide variety of reactions, including pyridine ring-opening,[4] pyrrole denitrogenation,[5] C−N bond cleavage,[6] C−H bond oxidative addition,[7] etc. In addition, the low oxidation state and the electron-rich electronic configuration enable other features such as cluster formation and metal−metal interactions.[8]

Given the ability of the dipyrrolide ligand to assemble large cluster structures,[9] we became interested in studying the ability of this versatile class of ligand to support low-valent tantalum. Aiming to prepare highly reactive Ta hydrides supported by this ligand system that may work as precursors for further reduction, we have now obtained a curious case of phenyl ring partial hydrogenation. In this first paper, we describe our findings.

Results and Discussion

Diphenyldipyrromethane[1a] undergoes an easy deprotonation by MeLi in ether and at room temperature,

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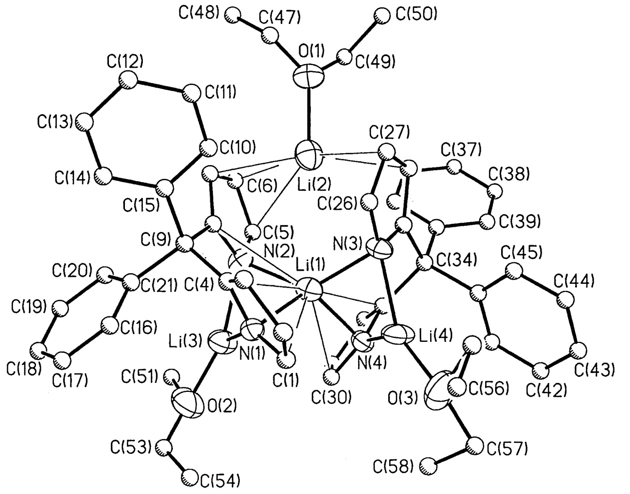


Figure 1. Thermal ellipsoid plot of **1.** Thermal ellipsoids are drawn at 30% probability.

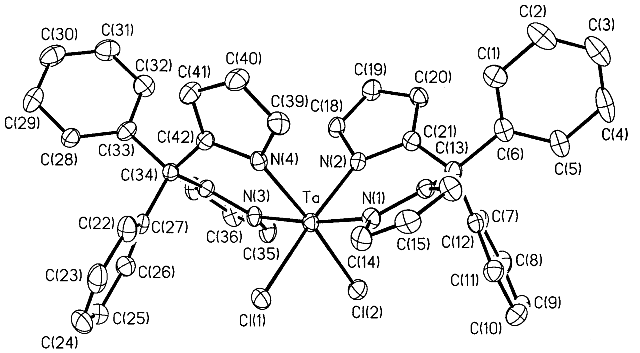
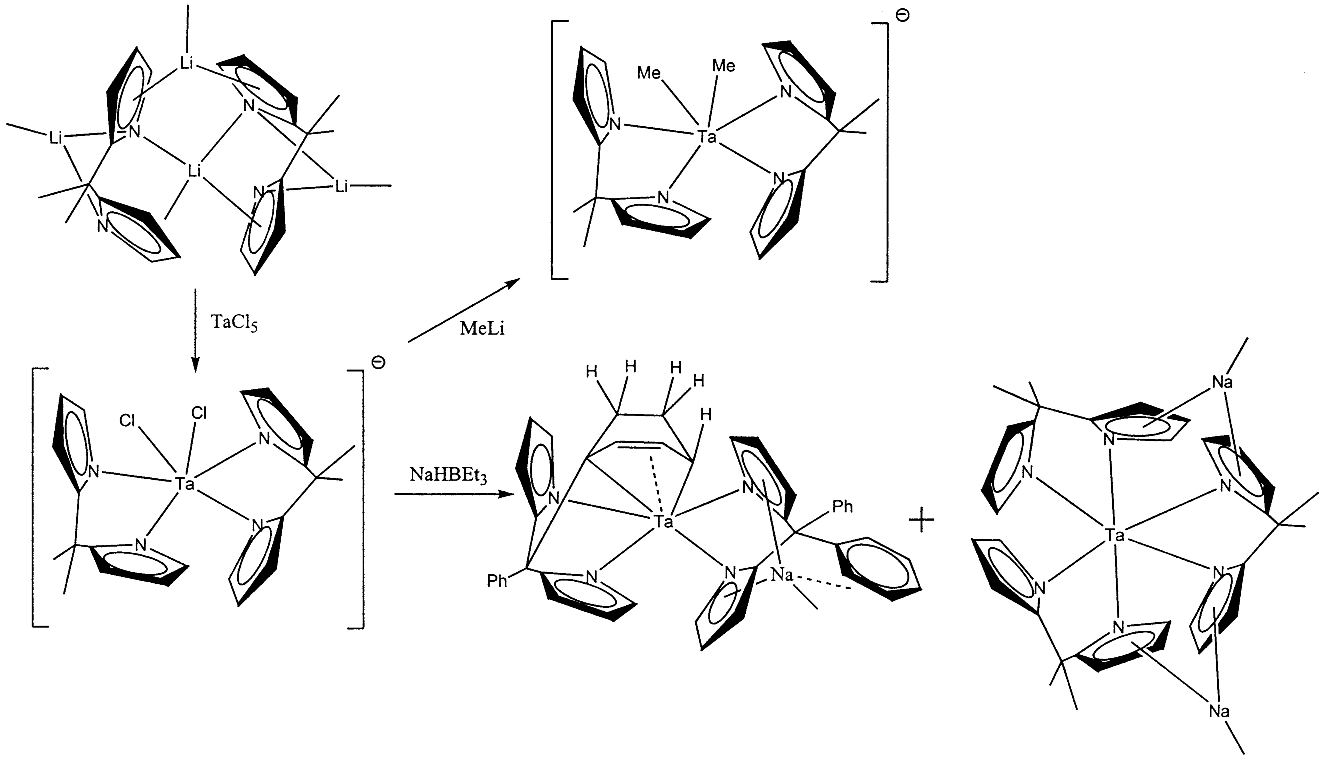


Figure 2. Thermal ellipsoid plot of **2**. Thermal ellipsoids are drawn at 30% probability.

affording the corresponding tetranuclear $[Ph_2C(C_4H_3N)_2]_2Li_4(OEt_2)_3$ (**1**). This derivative was readily isolated from an ether solution and fully characterized including by X-ray analysis (Figure 1). The structure is somewhat unusual, showing that two lithium atoms, each π-bonded to two pyrrolyl rings from two different ligands [Li(1)−N(1) = 2.034(11) Å, Li(1)−C(1) = 2.777(12) Å, Li(1)−C(4) = 2.665(12) Å, Li(1)−N(4) = 2.050(12) Å, Li(1)−C(30) = 2.777(12) Å, Li(1)−C(29) = 2.772(13) Å], hold together the dinuclear frame. Each of the other two lithium cations are instead σ-bonded to the two N atoms of each ligand [Li(3)−N(1) = 1.970(12) Å, Li(3)−N(2) = 2.051(12) Å, Li(4)−N(3) = 2.041(12) Å, Li(4)−N(4) = 1.956(12) Å]. One molecule of ether completes the coordination sphere of the two σ-bonded lithium atoms as well as that of one of the two π-bonded lithium cations. The second π-bonded lithium cation has a sort of bent-metallocene type of geometry and is also σ-bonded to two N atoms of the other two pyrrolyl rings from two different ligands [Li(1)−N(2) = 2.028(12) Å, Li(1)−N(3) = 2.033(12) Å]. The simplicity of the NMR spectra of **1**, showing only one type of pyrrolyl and phenyl rings, indicates that a rapid exchange between the nonequivalent lithium atoms occurs in solution.

The room-temperature reaction of **1** with 1 equiv of $TaCl_5$ in ether gave a green-brown solution, from which red-brown microcrystals of the diamagnetic $\{[Ph_2C(C_4H_3N)_2]_2TaCl_2\}\{Li(THF)_4\}\cdot 2THF$ (**2**) were isolated (Scheme 1). In agreement with the solid state structure (Figure 2), the NMR spectra showed two different phenyl rings and four nonequivalent pyrrolide rings. Crystals suitable for X-ray diffraction were grown from THF/hexane. The coordination sphere of the tantalum center is distorted octahedral (Figure 2) with two chloride ligands [Ta−Cl(1) = 2.3741(12) Å, Ta−Cl(2) = 2.3746(13) Å] situated *cis* to one another [Cl(1)−Ta−Cl(2) = 87.83(5)°] and the N atoms of two diphenyldipyrrolide ligands occupying the remaining four coor-

Scheme 1



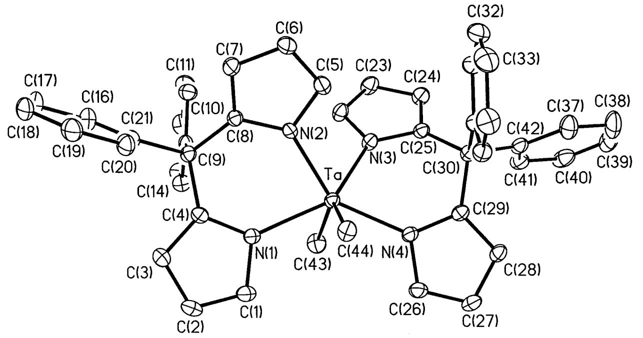


Figure 3. Thermal ellipsoid plot of **3**. Thermal ellipsoids are drawn at 30% probability.

dination sites [N(1)−Ta−Cl(1) = 89.66(10)°, N(1)−Ta−N(2) = 83.94(14)°, N(3)−Ta−N(4) = 84.43(14)°, Cl(2)−Ta−N(4) = 173.83(10)°]. The dipyrrolide ligands are σ-bound to the metal through the pyrrole nitrogen with no π-donation from the ring. The Ta−N bond lengths [Ta−N(1) = 2.094(4) Å, Ta−N(2) = 2.082(3) Å, Ta−N(3) = 2.086(3) Å, Ta−N(4) = 2.078(4) Å] are indicative of tantalum−nitrogen single bonds. A lithium cation solvated by four molecules of THF and unconnected with the anionic portion completes the structure.

Treatment of **2** with MeLi in THF afforded the expected dimethyl product $\{[Ph_2C_2(C_4H_3N)_2]_2TaMe_2\}\{Li(THF)_4\}$ (**3**) as yellow crystals. An X-ray diffraction analysis of crystals grown from THF/hexane revealed that the tantalum metal center has a trigonal prismatic geometry (Figure 3). The methyl ligands are *cis* to each other but form with the metal center an angle [C(43)−Ta−C(44) = 130.35(13)°] that is substantially larger than that formed by the chlorine atoms in the corresponding chloride derivative **2** [Cl(1)−Ta−Cl(2) = 87.83(5)°]. This is possibly the result of the fact that the Me ligand is a pure σ-donor while the Cl ligand acts additionally as a π-donor. In addition, the Ta−Me bond lengths [Ta−C(43) = 2.179(3) Å, Ta−C(44) = 2.175(3) Å], which are in the normal range of Ta−alkyl bond distances, are substantially shorter than the Ta−Cl distances of **2**. This may cause a significant increase in the steric congestion around the Ta center with consequent further distortion of the octahedral geometry. Similar to complex **2**, the Ta−N bond lengths [Ta−N(1) = 2.156(3) Å, Ta−N(2) = 2.085(2) Å, Ta−N(3) = 2.098(3) Å, Ta−N(4) = 2.130(2) Å] are essentially single bond in character.

Compound **3** is thermally robust and chemically inert toward several reagents including H_2. The alkyl signals were readily located in both the ^{1}H and ^{13}C NMR spectra at 1.36 and 95.4 ppm, respectively. In sharp contrast with the NMR spectrum of the nearly isostructural **2**, the NMR spectrum was remarkably simpler, showing only one kind of phenyl and pyrrolide ring. We speculate that the fact the structure of **3** deviates substantially from the octahedral geometry toward a trigonal prismatic coordination is possibly enhancing pseudorotation with consequent symmetrization of the NMR spectra.

Attempts to use **2** as a starting material for the preparation of highly reactive lower valent compounds were carried out with hydrides. The reaction with $NaHBEt_3$ in toluene yielded two products that have been successfully isolated and characterized by X-ray crystallography. The two complexes, separated by fractional crystallization from ether as red and yellow crystalline solids, respectively, are $[Ph_2C(C_4H_3N)_2][(1,4\text{-}\eta^1{:}\eta^1\text{-}2,3\text{-}\eta^2\text{-}C_6H_5)PhC(C_4H_3N)_2]Ta[Na(OEt_2)]$ (**4**) and $[Ph_2C(C_4H_3N)_2]_3Ta[Na(OEt_2)]_2\cdot(OEt_2)$ (**5**).

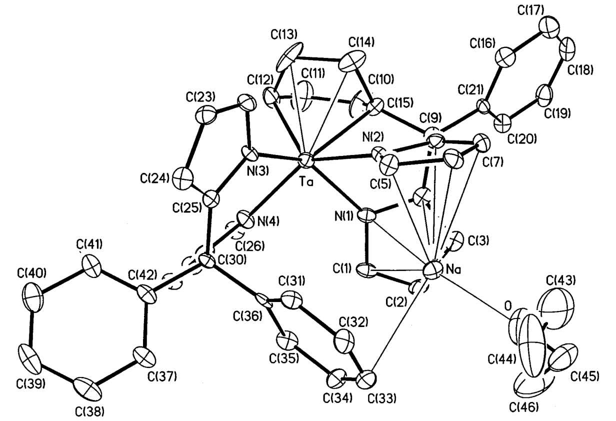


Figure 4. Thermal ellipsoid plot of **4**. Thermal ellipsoids are drawn at 30% probability.

Complex **4** is diamagnetic. Its crystal structure (Figure 4) reveals that the tantalum center is bound by two dipyrrolide ligands and one Na cation. The metal is further both σ- and π-bonded to one of the former phenyl rings from one dipyrrolide moiety that has been partly hydrogenated. As a result of the bonding interaction with the metal center and of the partial hydrogenation, the ring is severely distorted, adopting a “boat” type of conformation. The corresponding Ta−C bond distances for **4** are comparable to those observed in the structure of an arene/Ta derivative[10] and of a η^4-cyclohexadiene Nb complex previously reported in the literature.[11] The structure shows that bonding of the ring is better described in terms of both σ-bonding [Ta−C(12) = 2.222(8) Å, Ta−C(15) = 2.247(7) Å] and π-bonding [Ta−C(13) = 2.424(9) Å, Ta−C(14) = 2.506(9) Å] to the metal rather than slipped η^4-hexadienyl. The other two CH_2 groups completing the ring form long nonbonding contacts [Ta−C(11) = 3.084(8) Å, Ta−C(10) = 3.129(8) Å]. The C−C bond distances within the ring are comparable [C(11)−C(10) = 1.492(11) Å, C(12)−C(13) = 1.466(12) Å, C(12)−C(11) = 1.453(11) Å, C(15)−C(10) = 1.509(11) Å] with the exception of one [C(13)−C(14) = 1.435(12) Å] indicating a small yet significant localization of residual C−C double-bond character. Unfortunately, the hydrogen atoms could not be located. One atom of sodium is π-bonded to two pyrrolide rings from the same ligand [Na−N(1) = 2.924(6) Å, Na−C(1) = 2.984(8) Å, Na−C(2) = 2.984(8) Å, Na−C(3) = 2.914(7) Å, Na−C(4) = 2.886(7) Å, Na−N(2) = 2.802(6) Å, Na−C(5) = 2.907(7) Å, Na−C(6) = 3.045(8) Å] that has one phenyl ring bonded to tantalum. Interestingly, there is a loose π-coordination of Na to one Ph ring [Na−C(33) = 2.995(8) Å, Na−C(32) = 3.260(8) Å, Na−C(34) = 3.189(8) Å] of the second dipyrrolide ligand, probably an artifact of ligand geometry optimization. One molecule of ether completes the coordination geometry of Na.

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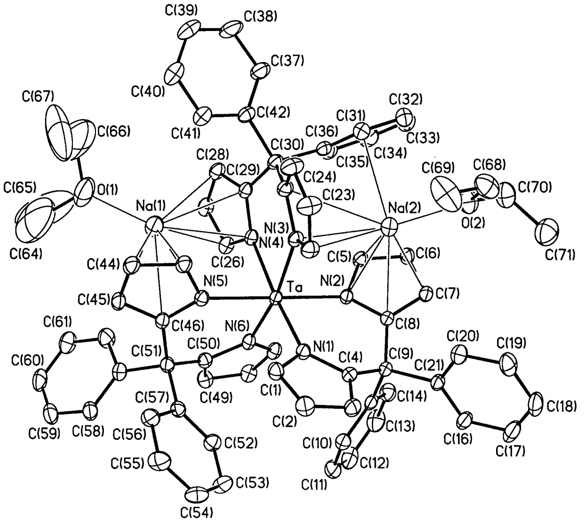

Figure 5. Thermal ellipsoid plot of **5**. Thermal ellipsoids are drawn at 30% probability.

The NMR spectra were characterized by large anisotropy, clearly showing the resonances of three distinct phenyl and four pyrrolyl rings. The partly hydrogenated ring shows the resonances of the two distinct CH_2 groups at 32.26 and 34.13 ppm of the DEPT ^{13}C NMR spectrum. The corresponding two couples of *gem*-hydrogen atoms feature four distinct well-solved multiplets at 2.27 (endo) and 3.05 ppm (exo) and at 2.88 (endo) and 3.03 (exo), respectively. The hydrogen atom at the ring *para* position that is directly bonded to Ta is present as a doublet at 2.16 ppm, while the quaternary C also bonded to Ta features a resonance at 114.05 ppm of the ^{13}C NMR spectrum. Finally, the other two hydrogen atoms attached to the two last C atoms forming the residual C−C double bond resonate at 6.51 and 6.36 ppm, and their coupling with the resonance at 2.16 ppm was clearly visible in the COSY NMR spectrum.

The structure of **5** (Figure 5) shows that the tantalum center is pseudo-octahedral and coordinated by *three* dipyrrolide ligands, two of which are in turn π-bound to the two Na atoms. The Ta−N bond lengths are similar to those already discussed for complexes **2** and **3** and warrant no further comment. Most importantly however, the metal center has undergone a one-electron reduction to the tetravalent state. The magnetic moment (1.71 μ_B) is consistent with a single unpaired electron, thus confirming the reduction to Ta(IV).

The ability of Nb and Ta hydrides to perform hydrogenation reactions and in a few cases even in catalytic fashion is documented in the literature.[12] However, the reactivity of the Ta−H function seems to be particularly sensitive to the nature of the ligand. For example, while the Cp derivatives seem to be sufficiently stable to allow full characterization,[12a,13] a more enhanced reactivity has been found for alkoxide derivatives that typically are detected as transient intermediates.[12,14] Since the formation of **4** was obtained *in the absence* of H_2, its formation is most likely the result of the intramolecular attack of the Ta-H groups of an intermediate $[H_2Ta\{Ph_2C(C_4H_3N)_2\}_2]$ anion at two contiguous *ortho* and *meta* positions of a ligand phenyl ring. The reaction is conceptually different, from the partial hydrogenation of an aromatic ring performed by a transient $(RO)_3Nb$ under H_2 atmosphere, where the reaction is triggered by oxidative addition of the metal into the C−H bond followed by hydrogenolysis.[11] Similar to the Nb case however, the two hydrogen atoms have been placed *cis* to each other. However, the hydrogenation in this particular case did not involve the *ipso* C atom but instead has directed the H atoms to the aromatic ring *ortho* and *meta* positions. Since the reaction occurred rapidly at room temperature, we believe that the hydrogenation of the ligand is an indication for a very high reactivity of Ta-H species supported by the dipyrrolide ligand system.

The formation of **5** is more difficult to rationalize, but the presence of *three* dipyrrrolide ligands around the metal center indicates that the reduction is accompanied by ligand scrambling and suggests that another product might be present in the reaction mixture.

In conclusion, it has been shown that the dipyrrolide ligand may both activate and stabilize tantalum metal complexes. The preparation of $\{[Ph_2C(C_4H_3N)_2]_2TaCl_2\}\{Li\ (THF)_4\}\cdot 2THF$ is facile and provides a promising route to tantalum−dipyrrolide chemistry. A stable bis-alkyl complex has been isolated, while attempts to form hydrides afforded both reduction of the metal center and partial hydrogenation of an aromatic ring. This confirms once again the ability of dipyrrolide ligand to increase the reactivity of the metal center and encourages further work toward the synthesis and characterization of hydride derivatives of other dipyrrolides with lower possibility of being involved in the reactivity of the metal center.

Experimental Section

General Procedures. All operations were performed under inert atmosphere by using standard Schlenk type techniques and in the drybox. $TaCl_5$ was purchased from STREM and sublimed prior to use; diphenyldipyrrolmethane was prepared by a published procedure.[1a] Methyllithium (1.4 M solution in ether) and $NaBH(C_2H_5)_3$ (1 M solution in toluene) were obtained from Aldrich and used as received. Infrared spectra were recorded on a Mattson 9000 and Nicolet 750-Magna FTIR instruments from Nujol mulls prepared in a drybox. Samples for magnetic susceptibility measurements were weighed inside a drybox equipped with an analytical balance and sealed into calibrated tubes. Magnetic measurements were carried out with a Gouy balance (Johnson Matthey) at room temperature. Magnetic moments were calculated following standard methods,[15] and corrections for underlying diamagnetism were applied to data.[16] Elemental analyses were carried out with a Perkin-Elmer 2400 CHN analyzer. Data for X-ray crystal

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Table 1. Crystal Data and Structure Analysis Results

	1	**2**	**3**	**4**	**5**
formula	$C_{54}H_{62}Li_4N_4O_3$	$C_{66}H_{80}Cl_2LiN_4O_6Ta$	$C_{60}H_{70}LiN_4O_4Ta$	$C_{46}H_{44}N_4NaOTa$	$C_{75}H_{78}N_6Na_2O_3Ta$
fw	842.84	1284.13	1099.09	872.79	1338.36
space group	monoclinic, $P2(1)/c$	monoclinic, $P2(1)/n$	monoclinic, $P2(1)/c$	triclinic, $P\bar{1}$	triclinic, $P\bar{1}$
a (Å)	14.787(5)	14.224(2)	14.570(1)	8.551(3)	13.290(1)
b (Å)	22.026(8)	32.518(4)	19.954(2)	11.671(3)	13.448(1)
c (Å)	15.134(5)	14.335(2)	18.371(1)	19.577(6)	18.868(2)
α (deg)	90	90	90	86.697(2)	81.324(1)
β (deg)	90.331(7)	112.804(9)	91.129(1)	80.432(3)	77.388(2)
γ (deg)	90	90	90	74.575(3)	85.026(1)
V (Å^3)	4929(3)	6112(1)	5339.8(7)	1857.0(9)	3248.1(5)
Z	4	4	4	2	2
radiation (Kα, Å)	0.71073	0.71073	0.71073	0.71073	0.71073
T (K)	236(2)	203(2)	203(2)	203(2)	203(2)
D_{calcd} (g cm^{-3})	1.136	1.395	1.367	1.561	1.368
μ_{calcd} (mm^{-1})	0.69	1.940	2.108	3.014	1.758
F_{000}	1800	2648	2264	880	1378
R, $R_w{}^2$ [a]	0.0711, 0.1606	0.0471, 0.0934	0.0294, 0.0633	0.0384, 0.0737	0.0340, 0.0854
GoF	1.026	1.025	1.037	0.952	1.091

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

structure determination were obtained with a Bruker diffractometer equipped with a Smart CCD area detector.

Preparation of [$Ph_2C(C_4H_3$ $N)_2]_2Li_4(OEt_2)_3$ (1). A solution of MeLi in ether (3.5 mL, 1.4 M, 5 mmol) was added to a suspension of diphenyldipyrrolmethane (0.74 g, 2.5 mmol) in ether (50 mL) cooled to 0 °C, causing a vigorous gas evolution. The solution was allowed to slowly warm to room temperature. After stirring for 24 h, the ether solution was concentrated to small volume (20 mL) and layered with hexane. Colorless crystals of **1** (0.85 g, 1.0 mmol, 78%) separated upon standing for 2 days at 4 °C. Anal. Calcd (found) for $C_{54}H_{62}Li_4N_4O_3$: C 76.95 (76.38), H 7.67 (7.51), N 6.65 (6.73). IR (Nujol mull, cm^{-1}) ν: 1596(w), 1484(m), 1421(w), 1377(m), 1274(w), 1184(w), 1153(m), 1090(m), 1067(m), 1028(m), 979(w), 960(w), 901(m), 876(w), 847(m), 785(w), 726(m), 702(m), 656(m), 625(m), 553(m). ^{1}H NMR [500 MHz, C_6D_6, 25 °C] δ: 7.0−7.2(10H, m, C*H*-Ph), 7.09(2H, s, α-C*H*-pyr), 6.35(2H, s, β-C*H*-pyr), 6.15(2H, s, γ-C*H*-pyr), 2.95(12H, q, $J_{H-H} = 7.0$ Hz, C*H*$_2$-ether), 0.95(18H, t, $J_{H-H} = 7.0$ Hz, C*H*$_3$-ether). ^{13}C{^{1}H} NMR [125.72 MHz, C_6D_6, 25 °C] δ: 150(*C*-Ph), 149(C-pyr), 130.4(*C*H-pyr), 128.8(*C*H-Ph), 127.7(*C*H-Ph), 126.2(*C*H-Ph), 110.4(*C*H-pyr), 107.3(*C*H-pyr), 59.2(*C*-ligand), 65.7 (CH$_2$ ether), 14.8(CH$_3$ ether).

Preparation of {$[Ph_2C(C_4H_3N)_2]_2TaCl_2$}{Li(THF)$_4$}·2THF (2). A solution of MeLi in ether (33 mL, 1.4 M, 46 mmol) was added to a suspension of diphenyldipyrromethane (6.8 g, 23 mmol) in ether (100 mL) at 0 °C. A clear solution was obtained by the end of the addition. The solution was allowed to warm slowly to room temperature and then transferred via cannula to a flask containing a suspension of $TaCl_5$ (4.1 g, 11.4 mmol) in ether (100 mL). The color changed immediately from yellow to green and finally to green-brown. After stirring for 24 h, a green-brown compound was precipitated. Ether was removed in vacuo, and the resulting residue was dissolved in toluene (100 mL). The dark red solution was centrifuged to remove LiCl, and toluene was removed from the dark red-brown solution in vacuo and replaced by THF (40 mL). The dark red-brown solution was layered with hexane, from which dark red crystals of **2** were obtained upon standing for a week at room temperature (10.6 g, 8.3 mmol, 72%). Anal. Calcd (found) for $C_{66}H_{80}Cl_2LiN_4O_6Ta$: C 61.73 (62.1), H 6.28 (6.35), N 4.36 (4.23). IR (Nujol mull, cm^{-1}) ν: 1595(w), 1486(m), 1423(w), 1377(m), 1260(s), 1213(m), 1109(m), 1093(m), 1075(m), 1045(s), 982(s), 886(m), 748(m), 731(m), 702(s), 654(s), 626(m), 553(m). ^{1}H NMR [500 MHz, C_6D_6, 25 °C] δ: 7.47(C*H*-Ph, dd, $J_{H-H} = 6.1$ and 1.6 Hz, 2H), 7.10(C*H*-Ph, m, 8H), 7.53(C*H*-Ph, dd, $J_{H-H} = 7.5$ Hz, 2H), 7.31(C*H*-Ph, t, $J_{H-H} = 7.5$ Hz, 4H), 7.22(C*H*-Ph, t, $J_{H-H} = 6.1$ Hz, 4H), 5.77(C*H*-pyr, br s, 1H), 5.56(C*H*-pyr, dd, $J_{H-H} = 1.3$ and 1.5 Hz, 1H), 5.49(C*H*-pyr, t, $J_{H-H} = 2.9$ Hz, 1H), 6.21(C*H*-pyr, dd, $J_{H-H} = 8.2$ Hz, 1H), 6.13(C*H*-pyr, pseudo q, $J_{H-H} = 1.3$ and 1.5 Hz, 1H), 5.65(C*H*-pyr, dd, $J_{H-H} = 1.3$ and 1.5 Hz, 1H), 8.22(C*H*-pyr, br s, 1H), 6.09(C*H*-pyr, pseudo q, $J_{H-H} = 1.4$ and 1.6 Hz, 1H), 6.05(C*H*-pyr, t, $J_{H-H} = 3.0$ Hz, 1H), 7.01 and 6.81(C*H*-pyr, overlapping m, 3H), 3.30(24H, m, C*H*$_2$-THF), 0.95(24H, m, C*H*$_2$-THF). ^{13}C{^{1}H} NMR [125.72 MHz, C_6D_6, 25 °C] δ: 159.7 and 157.5(*C*-Ph), 148.7, 147.2, 146.4, and 143.9(*C*-pyr), 128.29, 128.19, 128.00, 127.42, 127.23, and 127.16(*C*H-Ph), 147.9, 128.0, 127.1, 126.8, 126.7, 114.6, 113.86, 113.82, 113.70, 110.94, 110.83, 103.14(*C*H-pyr), 59.5 and 59.0(*C*-ligand), 67.7(*C*H$_2$-THF), 25.5(*C*H$_2$-THF).

Preparation of {$[Ph_2C(C_4H_3N)_2]_2TaMe_2$}{Li(THF)$_4$} (3). A solution of MeLi in ether (1.0 mL, 1.4 M, 1.4 mmol) was added to the dark red solution of **2** (0.9 g, 0.7 mmol) in THF (80 mL) at 0 °C. The color immediately changed from red to yellow, and the solution was allowed to warm slowly to room temperature. After stirring the reaction mixture for another 24 h, the clear yellow solution was concentrated (40 mL), layered with hexane, and allowed to stand at 4 °C for 1 week, upon which yellow crystals of **3** (0.57 g, 0.52 mmol, yield 76%) separated. Anal. Calcd (found) for $C_{60}H_{70}LiN_4O_4Ta$: C 65.57 (65.88), H 6.42 (6.35), N 5.10 (5.23). IR (Nujol mull, cm^{-1}) ν: 1593(w), 1404(m), 1282(m), 1244(w), 1223(w), 1136(m), 1109(m), 1078(s), 1078(m), 1043(s), 989(s), 887(m), 796(m), 758(m), 746(s), 719(m), 700(m), 656(w), 629(w). ^{1}H NMR [500 MHz, C_6D_6, 25 °C] δ: 7.44(4H, d, $J_{H-H} = 6.9$ Hz, C*H*-Ph), 7.10(6H, dd, $J_{H-H} = 8.4$ and 8.0 Hz, C*H*-Ph), 6.68(2H, s, α-C*H*-pyr), 6.01(2H, s, β-C*H*-pyr), 5.92(2H, s, γ-C*H*-pyr), 3.33(8H, m, C*H*$_2$-THF), 1.36(3H, s, C*H*$_3$-Ta), 1.30(8H, m, C*H*$_2$-THF). ^{13}C{^{1}H} NMR [125.72 MHz, C_6D_6, 25 °C] δ: 148.5(*C*-Ph), 147.2(*C*-pyr), 131.2(*C*H-Ph), 129.1(*C*H-pyr), 127.5(*C*H-Ph), 127.2(*C*H-Ph), 110.9(*C*H-pyr), 107.7(*C*H-pyr), 95.4(*C*H$_3$-Ta), 58.6(*C*-ligand), 68.0(*C*H$_2$-THF), 25.5(*C*H$_2$-THF).

Isolation of [Ta{$Ph_2C(C_4H_3N)_2$}{$PhC(C_4H_3N)_2$(1,4-η^1:η^1-2,3-:η^2-C_6H_7)Na(OEt$_2$)}} (4) and [Ta{$Ph_2C(C_4H_3N)_2$}$_3$[Na(OEt$_2$)]$_2$·(OEt$_2$) (5). A solution of $NaBH(C_2H_5)_3$ in toluene (1.8 mL, 1 M, 1.8 mmol) was added to a flask containing a solution of **2** (2.3 g, 1.8 mmol) in toluene (70 mL) at 0 °C. The color changed from dark red to green-brown after 3 min, and the solution was allowed to warm slowly to room temperature. After stirring for an additional 24 h, the solvent was removed in vacuo and ether (80 mL) was added to the remaining residue. The red solution was centrifuged to remove a light yellow precipitate. The ether solution was concentrated (40 mL). Red crystals of **4** separated upon standing at 4 °C for 3 days (0.35 g, 0.4 mmol, yield 22%). Anal. Calcd (found) for

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(16) Foese, G.; Gorter, C. J.; Smits, L. J. *Constantes Sélectionnées Diamagnétisme, Paramagnétisme, Relaxation Paramagnétique*; Masson: Paris, 1957.

Table 2. Selected Bond Distances (Å) and Angles (deg)

1	2	3	4	5
Li(1)−N(2) = 2.028(12)	Ta−N(2) = 2.082(3)	Ta−N(2) = 2.085(2)	Ta−N(4) = 2.067(6)	Ta−N(6) = 2.076(3)
Li(1)−N(3) = 2.033(12)	Ta−N(4) = 2.078(4)	Ta−N(3) = 2.098(3)	Ta−N(3) = 2.102(5)	Ta−N(1) = 2.093(2)
Li(1)−N(1) = 2.034(11)	Ta−N(3) = 2.086(3)	Ta−N(4) = 2.130(2)	Ta−N(1) = 2.132(5)	Ta−N(2) = 2.145(2)
Li(1)−N(4) = 2.050(12)	Ta−N(1) = 2.094(4)	Ta−N(1) = 2.156(3)	Ta−N(2) = 2.172(6)	Ta−N(3) = 2.169(2)
Li(1)−Li(3) = 2.453(16)	Ta−Cl(1) = 2.3741(12)	Ta−C(44) = 2.175(3)	Ta−C(12) = 2.223(8)	Ta−N(5) = 2.177(3)
Li(1)−Li(4) = 2.463(16)	Ta−Cl(2) = 2.3746(13)	Ta−C(43) = 2.179(3)	Ta−C(15) = 2.247(7)	Ta−N(4) = 2.224(2)
Li(1)−C(4) = 2.665(12)	Li−O(1) = 1.886(11)	Li−O(1) = 1.897(7)	Ta−C(13) = 2.426(9)	Na(1)−O(1) = 2.285(4)
Li(1)−C(33) = 2.680(12)	Li−O(2) = 1.911(12)	Li−O(3) = 1.920(8)	Ta−C(14) = 2.507(9)	Na(1)−C(27) = 2.676(4)
Li(1)−C(8) = 2.750(13)	Li−O(3) = 1.929(10)	Li−O(4) = 1.929(8)	Na−O = 2.362(8)	Na(1)−C(44) = 2.683(3)
Li(1)−C(29) = 2.772(13)	Li−O(4) =1.955(11)	Li−O(2) = 1.918(8)	Na−N(2) = 2.802(6)	Na(1)−C(45) = 2.716(3)
Li(1)−C(30) = 2.777(12)	N(2)−Ta−N(4) = 90.28(14)	N(2)−Ta−N(3) = 80.17(10)	Na−C(8) = 2.876(7)	Na(1)−C(28) = 2.717(4)
Li(1)−C(1) = 2.777(12)	N(2)−Ta−N(3) = 91.10(14)	N(2)−Ta−N(4) = 141.37(10)	Na−C(4) = 2.886(7)	Na(1)−C(26) = 2.739(3)
Li(2)−O(1) = 1.953(13)	N(4)−Ta−N(3) = 84.43(14)	N(3)−Ta−N(4) = 78.88(10)	Na−C(5) = 2.907(7)	Na(1)−C(43) = 2.747(3)
Li(2)−C(6) = 2.392(13)	N(2)−Ta−N(1) = 83.94(14)	N(2)−Ta−N(1) = 80.73(9)	Na−C(3) = 2.914(7)	Na(1)−C(29) = 2.810(3)
Li(2)−C(27) = 2.407(13)	N(4)−Ta−N(1) = 90.96(14)	N(3)−Ta−N(1) = 143.42(10)	Na−N(1) = 2.924(6)	Na(1)−C(46) = 2.818(3)
Li(2)−C(7) = 2.412(13)	N(3)−Ta−N(1) = 173.22(15)	N(4)−Ta−N(1) = 132.58(9)	Na−C(2) = 2.984(8)	Na(1)−N(5) = 2.823(3)
Li(2)−C(28) = 2.444(13)	N(2)−Ta−Cl(1) = 173.30(10)	N(2)−Ta−C(44) = 90.69(11)	Na−C(1) = 2.984(8)	Na(1)−N(4) = 2.836(3)
Li(2)−C(5) = 2.773(13)	N(4)−Ta−Cl(1) = 91.79(10)	N(3)−Ta−C(44) = 130.40(12)	Na−C(33) = 2.995(8)	Na(2)−O(2) = 2.313(3)
Li(3)−O(2) = 1.870(12)	N(3)−Ta−Cl(1) = 95.44(10)	N(4)−Ta−C(44) = 78.93(11)	Na−C(7) = 3.026(8)	Na(2)−N(3) = 2.609(3)
Li(3)−N(1) = 1.970(12)	N(1)−Ta−Cl(1) = 89.66(10)	N(1)−Ta−C(44) = 80.61(11)	Na−C(6) = 3.045(8)	Na(2)−C(6) = 2.759(4)
Li(3)−N(2) = 2.051(12)	N(2)−Ta−Cl(2) = 90.79(10)	N(2)−Ta−C(43) = 28.48(12)	N(4)−Ta−N(3) = 85.0(2)	Na(2)−C(7) = 2.797(3)
Li(4)−O(3) = 1.888(12)	N(4)−Ta−Cl(2) = 173.83(10)	N(3)−Ta−C(43) = 90.11(12)	N(4)−Ta−N(1) = 84.7(2)	Na(2)−C(22) = 2.813(4)
Li(4)−N(4) = 1.956(12)	N(3)−Ta−Cl(2) = 89.47(10)	N(4)−Ta−C(43) = 83.65(12)	N(3)−Ta−N(1) = 141.3(2)	Na(2)−C(5) = 2.816(4)
Li(4)−N(3) = 2.041(12)	N(1)−Ta−Cl(2) = 95.20(11)	N(1)−Ta−C(43) = 77.96(12)	N(4)−Ta−N(2) = 138.3(2)	Na(2)−C(8) = 2.873(3)
N(2)−Li(1)−N(3) = 131.4(5)	Cl(1)−Ta−Cl(2) = 87.83(5)	C(44)−Ta−C(43) = 130.35(13)	N(3)−Ta−N(2) = 82.7(2)	Na(2)−C(31) = 2.873(4)
N(2)−Li(1)−N(1) = 87.6(5)			N(1)−Ta−N(2) = 80.6(2)	Na(2)−N(2) = 2.882(3)
N(3)−Li(1)−N(1) = 120.2(5)			N(4)−Ta−C(12) = 90.4(3)	Na(2)−C(25) = 3.043(3)
N(2)−Li(1)−N(4) = 119.6(5)			N(3)−Ta−C(12) = 105.5(3)	N(6)−Ta−N(1) = 98.03(9)
N(3)−Li(1)−N(4) = 86.0(5)			N(1)−Ta−C(12) = 111.7(3)	N(6)−Ta−N(2) = 96.20(9)
N(1)−Li(1)−N(4) = 114.8(5)			N(2)−Ta−C(12) = 131.4(3)	N(1)−Ta−N(2) = 84.67(9)
N(2)−Li(1)−Li(3) = 53.5(4)			N(4)−Ta−C(15) = 137.5(3)	N(6)−Ta−N(3) = 169.08(8)
N(3)−Li(1)−Li(3) = 171.2(6)			N(3)−Ta−C(15) = 134.8(2)	N(1)−Ta−N(3) = 91.88(9)
N(1)−Li(1)−Li(3) = 51.1(4)			N(1)−Ta−C(15) = 71.6(2)	N(2)−Ta−N(3) = 89.24(9)
N(4)−Li(1)−Li(3) = 97.2(5)			N(2)−Ta−C(15) = 72.9(2)	N(6)−Ta−N(5) = 84.88(9)
N(2)−Li(1)−Li(4) = 169.9(6)			N(4)−Ta−C(13) = 120.5(3)	N(1)−Ta−N(5) = 94.98(9)
N(3)−Li(1)−Li(4) = 52.9(4)			N(3)−Ta−C(13) = 87.4(2)	N(2)−Ta−N(5) = 178.90(9)
N(1)−Li(1)−Li(4) = 97.2(5)			N(1)−Ta−C(13) = 129.4(2)	N(3)−Ta−N(5) = 89.72(10)
N(4)−Li(1)−Li(4) = 50.3(4)			N(2)−Ta−C(13) = 98.6(3)	N(6)−Ta−N(4) = 89.14(9)
Li(3)−Li(1)−Li(4) = 123.8(5)			N(4)−Ta−C(14) = 150.9(3)	N(1)−Ta−N(4) = 172.82(9)
N(2)−Li(1)−C(4) = 77.4(4)			N(3)−Ta−C(14) = 102.4(2)	N(2)−Ta−N(4) = 94.79(9)
N(3)−Li(1)−C(4) = 105.9(4)			N(1)−Ta−C(14) = 104.6(2)	N(3)−Ta−N(4) = 80.96(9)
N(1)−Li(1)−C(4) = 30.7(2)			O−Na−N(2) = 139.3(3)	N(5)−Ta−N(4) = 85.43(9)
N(4)−Li(1)−C(4) = 144.7(5)			O−Na−C(8) = 120.7(3)	O(1)−Na(1)−C(27) = 101.06(14)
Li(3)−Li(1)−C(4) = 66.9(4)			N(2)−Na−C(8) = 28.16(16)	O(1)−Na(1)−C(44) = 102.47(14)
Li(4)−Li(1)−C(4) = 111.1(5)			O−Na−C(4) = 127.4(2)	C(27)−Na(1)−C(44) = 156.47(12)
N(2)−Li(1)−C(33) = 105.1(4)			N(2)−Na−C(4) = 61.48(19)	O(1)−Na(1)−C(45) = 99.73(15)
N(3)−Li(1)−C(33) = 76.1(4)				C(27)−Na(1)−C(45) = 143.12(12)
N(1)−Li(1)−C(33) = 144.2(5)				C(44)−Na(1)−C(45) = 29.99(10)
N(4)−Li(1)−C(33) = 30.2(2)				O(1)−Na(1)−C(28) = 102.20(14)
Li(3)−Li(1)−C(33) = 110.7(5)				C(27)−Na(1)−C(28) = 30.13(10)
Li(4)−Li(1)−C(33) = 66.1(4)				C(44)−Na(1)−C(28) = 140.90(12)
C(4)−Li(1)−C(33) = 174.9(5)				C(45)−Na(1)−C(28) = 158.07(11)
N(2)−Li(1)−C(8) = 28.2(2)				O(1)−Na(1)−C(26) = 126.74(14)
N(3)−Li(1)−C(8) = 115.0(5)				C(27)−Na(1)−C(26) = 29.28(9)
N(1)−Li(1)−C(8) = 76.9(4)				C(44)−Na(1)−C(26) = 128.59(11)
N(4)−Li(1)−C(8) = 147.7(5)				C(45)−Na(1)−C(26) = 116.44(11)
Li(3)−Li(1)−C(8) = 65.8(4)				C(28)−Na(1)−C(26) = 48.17(10)
Li(4)−Li(1)−C(8) = 161.8(5)				
C(4)−Li(1)−C(8) = 55.9(3)				

$C_{46}H_{44}N_4NaOTa$: C 63.30 (63.71), H 5.08 (4.95), N 6.42 (6.23). IR (Nujol mull cm^{-1}) ν: 1591(w), 1313(w), 1300(w), 1259(m), 1219(w), 1182(w), 1165(w), 1140(m), 1115(m), 1093(m), 1080-(m), 1047(m), 1022(s), 981(w), 871(w), 798(s), 733(s), 719(w), 709(w), 679(w), 656(w), 509(w). ^{1}H NMR [500 MHz, THF-d_8, 25 °C] δ: *C*H-hydrogenated ring: 6.51(t, $J_{H-H} = 6.5$ Hz, 1H), 6.36(d, $J_{H-H} = 5.9$ Hz, 1H), 3.05−3.03(two m, 2H), 2.88(m, 1H), 2.27(m, 1H), 2.16(dd, 1H); *CH*-Ph: 7.95(dd, $J_{H-H} = 1.0$ and 7.1 Hz, 2H), 7.29(t, $J_{H-H} = 7.7$ Hz, 2H), 7.16(overlapping d, 1H); *CH*-Ph: 7.13(br s, 5H); *CH*-Ph: 7.04(dd, $J_{H-H} = 1.0$ and 7.1 Hz, 2H), 6.89(t, $J_{H-H} = 7.8$ Hz, 2H), 6.77(pseudo t, $J_{H-H} = 7.2$ Hz, 1H); *CH*-pyrr: 7.13(overlapping m, 1H), 5.86(t, $J_{H-H} = 2.7$ Hz, 1H), 5.34(m, 1H); *CH*-pyrr: 6.94(pseudo q, $J_{H-H} = 1.4$ Hz, 1H), 5.96(t, $J_{H-H} = 2.7$ Hz, 1H), 5.49(pseudo q, $J_{H-H} = 1.4$ Hz, 1H); *CH*-pyrr: 5.29(br s, 1H), 5.22(t, $J_{H-H} = 2.6$ Hz, 1H), 5.18(pseudo q, $J_{H-H} = 1.4$ Hz, 1H); *CH*-pyrr: 6.39(pseudo q, $J_{H-H} = 1.1$ amd 1.4 Hz, 1H), 5.78(pseudo q, $J_{H-H} = 1.1$ and 1.6 Hz, 1H), 5.34(br s, 1H); 3.41(4H, q, $J_{H-H} = 7.0$ Hz, C*H*$_2$-ether), 1.05(6H, t, $J_{H-H} = 7.0$ Hz, C*H*$_3$-ether). $^{13}C\{^1H\}$ NMR [125.72 MHz, THF-d_8, 25 °C] δ: 163.9, 152.6, and 151.0(*C*-Ph), 150.6, 148.6, 148.4, and 146.5(s, *C*-pyr), hydrogenated ring: 114.05(*C*-Ta), 130.19(*C*H═), 122.94(*C*H═), 80.47(*C*H-Ta), 34.13(*C*H$_2$), 32.26(*C*H$_2$); *C*H-Ph: 130.12, 129.09, and 12.13; *C*H-Ph: 135.95, 131.86, and 127.94; *C*H-Ph: 126.06, 126.67, and 130.52; *C*H-pyr: 103.01, 105.39, and 130.17; *C*H-pyrr: 104.79, 107.19, and 127.47; *C*H-pyrr: 112.09, 106.62, and 126.23; *C*H-pyr: 10.91, 107.99, and 125.90; *C*H$_2$-ether: 67.04; (*C*H$_3$-ether): 15.65.

After separation of **4**, the mother liquor was further concentrated (20 mL). Yellow crystals of **5** (0.45 g, 0.33 mmol, 19%) separated after upon standing 1 week at 4 °C. Anal. Calcd (found) for $C_{75}H_{78}N_6Na_2O_3Ta$: C 67.31 (67.71), H 5.87 (5.95), N 6.28 (6.23). IR (Nujol mull cm^{-1}) ν: 1650(w), 1595(w), 1261-(s), 1209(w), 1180(w), 1133(s), 1097(s), 1079(m), 1045(s), 974-(m), 899(w), 889(w), 872(w), 802(s), 746(m), 729(w), 698(s), 655(s). $\mu_{eff} = 1.71\ \mu_{BM}$.

X-ray Crystallography. Suitable crystals were selected, mounted on thin, glass fibers using paraffin oil, and cooled to the data collection temperature. Data were collected on a Bruker AXS SMART 1k CCD diffractometer using 0.3° ω-scans at 0°, 90°, and 180° in ϕ. Initial unit-cell parameters were determined from 60 data frames collected at different sections of the Ewald sphere. Semiempirical absorption corrections based on equivalent reflections were applied.[17] Systematic absences in the diffraction data and unit-cell parameters were uniquely consistent with the reported space group for **1** and **3**, $P2_1/c$, and for **2**, $P2_1/n$. No symmetry higher than triclinic was observed for **5** and **4**, and solution in the centrosymmetric space group option yielded chemically reasonable and computationally stable results of refinement. The structures were solved by direct methods, completed with difference Fourier syntheses, and refined with full-matrix least-squares procedures based on F^2. Symmetry unique solvent molecules were located cocrystallized in **5** (one diethyl ether molecule) and **2** (two tetrahydrofuran molecules). Phenyl groups in **1** were refined as idealized, flat, rigid hexagons.

All non-hydrogen atoms were refined with anisotropic displacement coefficients. All hydrogen atoms were treated as idealized contributions. All scattering factors are contained in the SHELXTL 6.12 program library (Sheldrick, G. M., Bruker AXS, Madison, WI, 2001).

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Supporting Information Available: Complete crystallographic data (CIF and PDF) for complexes **1**, **2**, **3**, **4**, and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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