Supporting Information

Conversion of (η^5-$C_2B_9H_{10}R$)TaX_3 to (η^6-$C_2B_9H_{10}R$)TaX in the absence of reducing agent: synthesis and structure of tantallacarboranes incorporating an *arachno*-η^6-$C_2B_9^{4-}$ ligand

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General Procedures. All reactions and manipulations were carried out under an argon atmosphere with the rigid exclusion of air and moisture using standard Schlenk or cannula techniques, or glovebox. ^{1}H NMR spectra were recorded on a Bruker DPX 400 spectrometer at 400 MHz. ^{13}C{^{1}H} NMR spectra were recorded on a Bruker DPX 400 spectrometer at 100 MHz. ^{11}B NMR spectra were recorded on a Bruker DPX 400 spectrometer at 128 MHz. All chemical shifts were reported in δ units with references to the residual solvent resonance of the deuterated solvents for proton and carbon chemical shifts, and to external $BF_3 \cdot OEt_2$ (0.00 ppm) for boron chemical shifts. Infrared spectrum was obtained from KBr pellets prepared in the glovebox on a Perkin-Elmer 1600 Fourier transform spectrometer. Elemental analyses were performed by Shanghai Institute of Organic Chemistry, Chinese Academy of Science, China or MEDAC Ltd., U. K.. All organic solvents were freshly distilled from sodium benzophenone ketyl immediately prior to use. Complexes 7-$Me_2NHCH_2CH_2$-7,8-$C_2B_9H_{11}$,[1] $Ta(NMe_2)_5$,[2] and $TaMe_3Cl_2$,[3] were prepared according to literature procedures. All other chemicals were purchased from either Aldrich or Acros Chemical Co. and used as received unless otherwise specified.

Preparation of [η^5-($Me_2NCH_2CH_2$)$C_2B_9H_{10}$]$Ta(NMe_2)_3$ (1). To a THF solution (10 mL) of $Ta(NMe_2)_5$ (201 mg, 0.5 mmol) was slowly added a THF solution (10 mL) of 7-$Me_2NHCH_2CH_2$-7,8-$C_2B_9H_{11}$ (103 mg, 0.5 mmol) with stirring at room temperature. The reaction mixture was stirred at room temperature overnight. After filtration, the filtrate was concentrated to about 5 mL, to which was added toluene (2 mL). Slow evaporation of solvents afforded **1** as yellow crystals (214 mg, 83%). ^{1}H NMR (400 MHz, C_6D_6): δ 3.15 (s, 18H) (N(CH_3)$_2$), 3.07 (s, 1H) (cage CH), 2.35 (m, 2H) (NCH_2), 2.20 (m, 1H) (CHH), 1.96 (s, 6H) (N(CH_3)$_2$), 1.89 (m, 1H) (CHH). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): δ 67.1 (cage C), 60.0 (NCH$_2$), 57.1 (cage CH), 49.9, 46.0 (N(CH$_3$)$_2$), 36.2 (CH$_2$). ^{11}B{^{1}H} NMR (128 MHz, C_6D_6): δ 3.9 (1B), -0.2 (1B), -3.2 (1B), -6.1 (1B),

-7.6 (1B), -8.5 (1B), -9.9 (1B), -11.2 (1B), -17.3 (1B). IR (KBr, cm^{-1}): ν_{BH} 2522 (vs). Anal. Calcd for $C_{12}H_{38}B_9N_4Ta$ (**1**): C, 27.89; H, 7.41; N, 10.84. Found: C, 27.46; H, 6.92; N, 10.42.

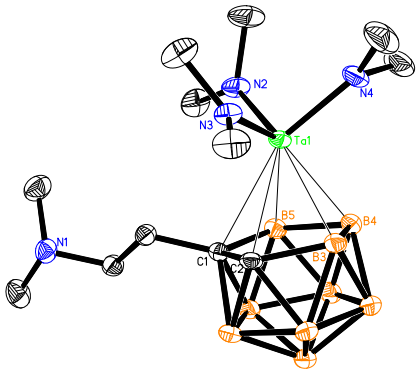

Figure S1. Molecular Structure of **1**. Selected bond lengths (Å) and angles (deg): Ta1-cent: 2.070, Ta1-C1 2.663(4), Ta1-C2 2.555(4), Ta1-B3 2.412(5), Ta1-B4 2.424(5), Ta1-B5 2.542(4), Ta1-N2 1.979(3), Ta1-N3 1.970(4), Ta1-N4 1.947(4), C1-C2 1.580(5), N2-Ta1-N3 102.4(2), N3-Ta1-N4 95.7(2), N4-Ta1-N2 96.4(2). cent represents the centroid of the C_2B_3 ring.

Preparation of [η^1:η^6-($Me_2NCH_2CH_2$)$C_2B_9H_{10}$]Ta(NMe_2)(NC_5H_5) (2). A benzene/pyridine (v/v = 10:1) solution (10 mL) of **1** (258 mg, 0.5 mmol) was heated to reflux for 1 day. After filtration, the clear orange solution was concentrated to about 3 mL. Complex **2** was isolated as yellow crystals after this solution stood at room temperature for 1 day (135 mg, 46%). ^{1}H NMR (400 MHz, d_5-pyridine): δ 8.71 (m, 2H) (Pyr-*H*), 7.56 (m, 1H) (Pyr-*H*), 7.19 (m, 2H) (Pyr-*H*), 5.64 (s, 1H) (cage C*H*), 3.50 (s, 3H) (TaN(CH_3)$_2$), 3.4 (s, 3H) (TaN(CH_3)$_2$), 2.98 (m, 2H) (NCH_2), 2.69 (s, 3H) (N(CH_3)$_2$), 2.62 (m, 1H) (CH*H*), 2.45 (m, 1H) (CH*H*), 1.69 (s, 3H) (N(CH_3)$_2$). ^{13}C{^{1}H} (100 MHz, d_5-pyridine): δ 155.0 (cage *C*), 140.3 (cage *C*H), 67.6 (N*C*H$_2$), 49.6, 49.3, 47.7, 47.5 (N(*C*H$_3$)$_2$), 46.8 (*C*H$_2$). ^{11}B{^{1}H} NMR (128 MHz, d_5-pyridine): δ 11.8 (1B), 5.0 (1B), 1.5 (2B), -0.1 (3B), -19.4 (1B), -35.2 (1B). IR (KBr, cm^{-1}): ν_{BH} 2504 (vs). Anal. Calcd for $C_{9.25}H_{27.25}B_9N_{2.25}Ta$ (**2**—0.75NC_5H_5): C, 24.78; H, 6.13; N, 7.03. Found: C, 25.12; H, 6.65; N, 6.75.

Preparation of (η^5-$C_2B_9H_{11}$)$TaMe_3$ (3). This complex was synthesized by a modified literature method.[4] To a THF solution (20 mL) of (Me_3NH)(7,8-$C_2B_9H_{12}$) (97 mg, 0.5 mmol) was added NaH (36 mg, 1.5 mmol), and the reaction mixture was heated to reflux for 3 h. After removal of excess NaH by filtration, the clear solution was added to a THF solution (10 mL) of Me_3TaCl_2 (148 mg, 0.5 mmol) at -30 ^oC with stirring. The mixture was allowed to stir at room temperature for 1 h. After removal of the solvent under vacuum, the resulting brown yellow residue was extracted with Et_2O (5 mL x 3). The combined Et_2O solutions were concentrated to about 5 mL, from which complex **3** was isolated as yellow crystals after this solution stood at -30 ^oC overnight (124 mg, 69%). ^1H NMR (400 MHz, C_6D_6): δ 2.48 (s, 2H) (cage C*H*), 1.06 (s, 9H) (TaCH_3). These data are identical to the reported ones.[4]

Preparation of (η^6-$C_2B_9H_{11}$)Ta[η^3-*C,C,N*-$CH_2C(CH_3)NAd$](DME) (4). To a DME solution (10 mL) of (η^5-$C_2B_9H_{11}$)$TaMe_3$ (**3**; 90 mg, 0.25 mmol) was slowly added a DME (5 mL) solution of adamantyl isonitrile (40 mg, 0.25 mmol) at -30 ^oC. The reaction mixture was slowly warmed to room temperature and stirred for 12 h. Slow evaporation of DME afforded the product **4** as yellow crystals (110 mg, 74%). ^1H NMR (400 MHz, d_5-pyridine): δ 6.05 (s, 2H) (cage C*H*), 4.54 (s, 2H) (NC(CH_3)=CH_2), 3.47 (s, 4H) (DME), 3.25 (s, 6H) (DME), 2.55 (s, 3H) (NC(CH_3)=CH_2), 2.02 (m, 6H) (Ad-*H*), 1.90 (m, 3H) (Ad-*H*), 1.45 (s, 6H) (Ad-*H*). $^{13}C\{^1H\}$ NMR (100 MHz, d_5-pyridine): δ 137.2 (N*C*Me=CH_2) 133.7 (cage *C*H), 88.3 (NCMe=*C*H_2), 72.1, 58.6 (DME), 46.7, 43.2, 36.2, 30.2 (Ad-*C*), 25.5 (*C*H_3). $^{11}B\{^1H\}$ NMR (128 MHz, d_5-pyridine): δ 20.2 (1B), 6.2 (1B), 2.5 (2B), 0.4 (3B), -21.3 (1B), -33.1 (1B). IR (KBr, cm^{-1}): ν_{BH} 2511 (vs). Anal. Calcd for $C_{23}H_{51}B_9NO_4Ta$ (**4** + DME): C, 40.39; H, 7.52; N, 2.05. Found: C, 40.46; H, 7.23; N, 2.19.

X-ray Structure Determination. Single crystals were immersed in Paraton-N oil and sealed under N_2 in thin-walled glass capillaries. All data were collected at 293 K on a Bruker SMART 1000 CCD

diffractometer using Mo-Kα radiation. An empirical absorption correction was applied using the SADABS program.[5] All structures were solved by direct methods and subsequent Fourier difference techniques and refined anisotropically for all non-hydrogen atoms by full-matrix least squares calculations on F^2 using the SHELXTL program package.[6] All hydrogen atoms were geometrically fixed using the riding model. Crystal data and details of data collection and structure refinement are given in Table S1.

CCDC 999578-999580 for complexes **1**, **2** and **4** contain the supplementary crystallographic data. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

References

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Table S1. Crystal Data and Summary of Data Collection and Refinement

	1	**2·C_6H_6**	**4**
formula	$C_{12}H_{38}B_9N_4Ta$	$C_{19}H_{37}B_9N_3Ta$	$C_{19}H_{41}B_9NO_2Ta$
crystal size (mm)	0.50 x 0.40 x 0.30	0.50 x 0.40 x 0.30	0.50 x 0.30 x 0.20
fw	516.70	585.76	597.77
crystal system	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/n$	$P2_1/n$
a, Å	11.080(1)	10.076(3)	9.508(1)
b, Å	16.589(1)	22.404(5)	14.026(1)
c, Å	12.214(1)	11.470(3)	21.345(2)
β, deg	97.377(1)	90.440(5)	96.654(1)
V, Å^3	2226.4(3)	2589.3(1)	2827.2(3)
Z	4	4	4
D_{calcd}, Mg/m^3	1.542	1.503	1.393
radiation (λ), Å	0.71073	0.71073	0.71073
2θ range, deg	4.2 to 50.5	3.6 to 50.5	3.8 to 50.5
μ, mm^{-1}	4.941	4.257	3.903
F(000)	1024	1160	1180
no. of obsd reflns	4024	4687	5123
no. of params refnd	238	281	293
goodness of fit	1.049	1.031	1.010
R1	0.021	0.045	0.084
wR2	0.052	0.108	0.205