Supporting Information

Reaction of $[\eta^1:\eta^5\text{-}(Me_2NCH_2CH_2)C_2B_9H_{10}]TaMe_3$ with aryl isonitriles: tantallacarborane-mediated facile cleavage of C-N multiple bond

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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 by working in an argon-filled 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 the Shanghai Institute of Organic Chemistry, CAS, China. All organic solvents were freshly distilled from sodium benzophenone ketyl immediately prior to use. Complexes $TaMe_3Cl_2$,[1] 2,6-diisopropylphenyl isonitrile[2] and 7-$Me_2NHCH_2CH_2$-7,8-$C_2B_9H_{11}$[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^1:η^5-($Me_2NCH_2CH_2$)$C_2B_9H_{10}$]$TaMe_3$ (1). To a THF solution (20 mL) of 7-$Me_2NHCH_2CH_2$-7,8-$C_2B_9H_{11}$ (103 mg, 0.5 mmol) was added an excess amount of NaH (36 mg, 1.5 mmol), and the reaction mixture was heated to reflux for 6 h. After removal of the 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 ^{o}C with stirring. The mixture was stirred at room temperature for 3 h and filtered. The filtrate was concentrated to about 3 mL, from which complex **1** was isolated as yellow crystals after this solution stood at -30 ^{o}C overnight (200 mg, 93%). ^{1}H NMR (400 MHz, C_6D_6): δ 3.11 (s, 1H) (cage *H*), 2.11 (m, 1H) (NCH*H*), 2.06 (s, 3H) (TaCH_3), 1.79 (s, 3H) (NMe(CH_3)), 1.64 (m, 4H) (NMe(CH_3) and CH*H*), 1.50 (m, 4H) (TaCH_3 and CH*H*), 1.37 (m, 1H) (NCH*H*), 1.05 (s, 3H) (TaCH_3). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): δ 85.7, 83.3, 81.5 (Ta*C*H_3), 65.8 (N*C*H_2), 56.7 (cage *C*),

52.7, 49.8 (NMe(CH_3)), 35.4 (CH_2). $^{11}B\{^1H\}$ NMR (128 MHz, C_6D_6): δ 15.6 (1B), 7.9 (1B), 0.5 (1B), -3.0 (1B), -5.2 (2B), -6.2 (1B), -10.0 (1B), -13.4 (1B). ^{11}B NMR (128 MHz, C_6D_6): δ 15.6 (d, J_{BH} = 127 Hz, 1B), 7.9 (d, J_{BH} = 150 Hz, 1B), 0.5 (d, J_{BH} = 150 Hz, 1B), -3.0 (d, J_{BH} = 142 Hz, 1B), -5.2 (d, J_{BH} = 120 Hz, 2B), -6.2 (d, J_{BH} = 105 Hz, 1B), -10.0 (d, J_{BH} = 169 Hz, 1B), -13.4 (d, J_{BH} = 147 Hz, 1B). IR (KBr, cm^{-1}): ν_{BH} 2543 (vs). Anal. Calcd for $C_9H_{29}B_9NTa$ (**1**): C, 25.04; H, 6.78; N, 3.25. Found: C, 25.01; H, 6.75; N, 3.32.

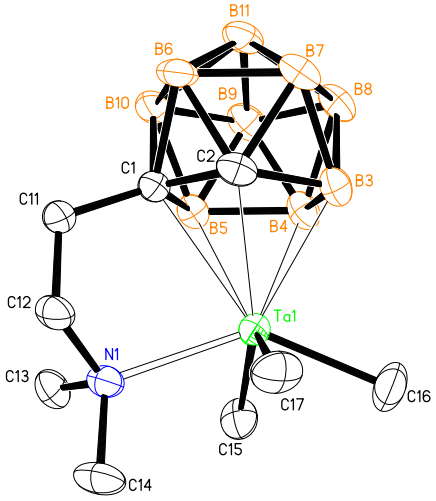

Figure S1. Molecular Structure of **1**. Selected bond lengths (Å) and angels (deg): Ta-cent: 2.046, Ta-N1 2.369(3), Ta-C15 2.184(4), Ta-C16 2.198(5), Ta-C17 2.192(4), C15-Ta-N1 82.2(1), C15-Ta-C16 79.9(2), C16-Ta-C17 78.9(2), C17-Ta-N1 79.8(2). cent represents the centroid of the C_2B_3 ring.

Preparation of {σ:η^1:η^5-[MeN(CH_2)CH_2CH_2]($CHMe_2$)$C_2B_9H_9$}Ta[=N(2,6-$Me_2C_6H_3$)](THF) (2). To a THF solution (10 mL) of [η^1:η^5-($Me_2NCH_2CH_2$)$C_2B_9H_{10}$]$TaMe_3$ (**1**; 107 mg, 0.25 mmol) was slowly added a THF (3 mL) solution of 2,6-dimethylphenyl isocyanide (33 mg, 0.25 mmol) at -30 ^oC, resulting in an immediate color change from yellow to dark purple and finally to orange. The reaction mixture was warmed to room temperature. After filtration, the clear orange solution was concentrated to about 2 mL. Complex **2** was isolated as yellow crystals after this solution stood at

room temperature for 3 days (114 mg, 74%). ^{1}H NMR (400 MHz, d_5-pyridine) for **2a** and **2b**: δ 7.14 (d, J = 7.6 Hz, 4H) (Ar-*H*), 6.78 (t, J = 7.6 Hz, 2H) (Ar-*H*), 4.03 (s, 2H) (cage *H*), 3.63 (m, 8H) (THF), 3.50 (d, J = 8.4 Hz, 2H) (N(CH*H*)Ta), 3.35 (m, 2H) (N(CH*H*)), 3.18 (m, 2H) (N(CH*H*), 2.90 (m, 2H) (N(CH*H*)Ta), 2.64 (s, 6H) (NCH_3), 2.57 (s, 12H) (Ar-CH_3), 2.40 (m, 2H) (CH*H*), 2.32 (m, 2H) (CH*H*), 2.21 (m, 2H) (BC*H*Me$_2$), 1.59 (m, 8H) (THF), 1.05 (d, J = 6.8 Hz, 6H) (BCH(CH_3)Me), 0.78 (d, J = 7.2 Hz, 6H) (BCH(CH_3)Me). ^{1}H NMR (400 MHz, d_5-pyridine) for **2c**: δ 7.10 (d, J = 7.2 Hz, 2H) (Ar-*H*), 6.84 (t, J = 7.6 Hz, 1H) (Ar-*H*), 3.63 (m, 4H) (THF), 3.35 (m, 1H) (N(CH*H*)), 3.26 (s, 1H) (cage *H*), 3.09 (m, 1H) (N(CH*H*)), 2.90 (s, 3H) (NCH_3), 2.61 (s, 6H) (Ar-CH_3), 2.50 (d, J = 9.2 Hz, 1H) (N(CH*H*)Ta), 2.32 (m, 1H) (CH*H*), 2.21 (m, 1H) (N(CH*H*)Ta), 2.15 (m, 1H) (CH*H*), 1.59 (m, 4H) (THF), 0.96 (d, J = 7.2 Hz, 3H) (BCH(CH_3)Me), 0.33 (d, J = 7.2 Hz, 3H) (BCH(CH_3)Me), -0.01 (m, 1H) (BC*H*Me$_2$). ^{13}C{^{1}H} (100 MHz, d_5-pyridine) for **2a** and **2b**: δ 153.3, 129.4, 128.2, 123.1 (Ar-*C*), 69.6 (cage *C*), 67.8 (THF), 67.7 (N*C*H$_2$Ta), 63.4 (N*C*H$_2$), 59.1 (cage *C*), 50.8 (N*C*H$_3$), 36.4 (*C*H$_2$), 26.2 (BCH(*C*H$_3$)Me), 25.8 (THF), 23.1 (BCH(*C*H$_3$)Me), 19.7 (Ar-*C*H$_3$), 16.3 (br, B*C*HMe$_2$). ^{13}C{^{1}H} (100 MHz, d_5-pyridine) for **2c**: δ 154.3, 128.7, 128.3, 122.8 (Ar-*C*), 69.4 (cage *C*), 67.8 (THF), 63.5 (N*C*H$_2$Ta), 62.4 (N*C*H$_2$), 60.0 (cage *C*), 54.3 (N*C*H$_3$), 37.3 (*C*H$_2$), 27.4 (BCH(*C*H$_3$)Me), 25.8 (THF), 24.7 (BCH(*C*H$_3$)Me), 20.6 (Ar-*C*H$_3$), 15.5 (br, B*C*HMe$_2$). ^{11}B{^{1}H} NMR (128 MHz, d_5-pyridine) for **2**: δ 3.7 (2B), 2.2 (4B), -5.1 (6B), -6.9 (2B), -8.4 (1B), -10.7 (6B), -14.0 (2B), -17.7 (4B). ^{11}B NMR (128 MHz, d_5-pyridine) for **2**: δ 3.7 (s, 2B), 2.2 (d, J_{BH} = 95 Hz, 4B), -5.1 (d, J_{BH} = 116 Hz, 6B), -6.9 (br, unresolved, 2B), -8.4 (br, unresolved, 1B), -10.7 (br, unresolved, 6B), -14.0 (d, J_{BH} = 150 Hz, 2B), -17.7 (d, J_{BH} = 142 Hz, 4B). IR (KBr, cm^{-1}): ν_{BH} 2554 (vs). Anal. Calcd for $C_{19}H_{38}B_9N_2O_{0.5}Ta$ (**2** - 0.5THF): C, 39.29; H, 6.60; N, 4.82. Found: C, 38.99; H, 6.46; N, 4.55.

Preparation of [η^1:η^5-(Me$_2$NCH$_2$CH$_2$)(CHMe$_2$)C$_2$B$_9$H$_9$]Ta[=N(2,6-Me$_2$C$_6$H$_3$)][η^2-*C*,*N*-MeC=N(2,6-Me$_2$C$_6$H$_3$)

(3). This complex was prepared as orange crystals from [η^1:η^5-($Me_2NCH_2CH_2$)$C_2B_9H_{10}$]$TaMe_3$ (**1**; 107 mg, 0.25 mmol) and 2,6-dimethylphenyl isocyanide (66 mg, 0.50 mmol) in THF (15 mL) at -30 ^oC using the same procedures reported for **2**: yield 117 mg (68%). ^1H NMR (400 MHz, d_5-pyridine): δ 7.27 (m, 2H) (Ar-*H*), 7.16 (m, 1H) (Ar-*H*), 7.10 (d, J = 7.2 Hz, 2H) (Ar-*H*), 6.75 (t, J = 7.2 Hz, 1H) (Ar-*H*), 4.12 (m, 1H) (NCH*H*), 3.09 (s, 3H) (N=CCH_3), 3.05 (s, 1H) (cage *H*), 2.86 (s, 3H) (Ar-CH_3), 2.84 (s, 3H) (Ar-CH_3), 2.76 (m, 7H) (N(CH_3)$_2$ and NCH*H*), 2.63 (m, 1H) (CH*H*), 2.50 (m, 1H) (CH*H*), 2.12 (s, 3H) (Ar-CH_3), 2.06 (s, 3H) (Ar-CH_3), 1.28 (d, J = 6.8 Hz, 3H) (BCHMe(CH_3)), 1.16 (m, 1H) (BC*H*Me_2), 0.94 (d, J = 6.4 Hz, 3H) (BCHMe(CH_3)). $^{13}C\{^1H\}$ (100 MHz, d_5-pyridine): δ 155.8 (N=*C*CH_3), 141.7, 132.9, 131.0, 130.4, 130.3, 129.9, 129.4, 128.7, 128.6, 127.8, 125.8, 122.9 (Ar-*C*), 72.4 (cage *C*), 66.9 (N*C*H_2), 57.2 (N=C*C*H_3), 53.1 (cage *C*), 49.0 (N(*C*H_3)$_2$), 38.5 (*C*H_2), 27.1, 25.6 (BCH(*C*H_3)Me), 22.5, 22.0 (Ar-*C*H_3), 19.0, 17.4 (Ar-*C*H_3), 17.3 (br, B*C*HMe_2). $^{11}B\{^1H\}$ NMR (128 MHz, d_5-pyridine): δ 2.6 (1B), 0.8 (2B), -7.6 (1B), -9.5 (2B), -11.4 (2B), -18.1 (1B). ^{11}B NMR (128 MHz, d_5-pyridine): δ 2.6 (s, 1B), 0.8 (d, J_{BH} = 118 Hz, 2B), -7.6 (br, unresolved, 1B), -9.5 (br, unresolved, 2B), -11.4 (br, unresolved, 2B), -18.1 (d, J_{BH} = 125 Hz, 1B). IR (KBr, cm^{-1}): ν_{BH} 2535 (vs). Anal. Calcd for $C_{27}H_{47}B_9N_3Ta$ (**3**): C, 46.87; H, 6.85; N, 6.07. Found: C, 47.26; H, 6.91; N, 5.69.

Preparation of {η^1:η^5-($Me_2NCH_2CH_2$)$C_2B_9H_{10}$}Ta[=N(2,6-^{i}Pr$_2$C$_6$H$_3$)][η^2-*C*,*N*-MeC=N(2,6-^{i}Pr$_2$C$_6$H$_3$) (4). This complex was prepared as yellow crystals form [η^1:η^5-($Me_2NCH_2CH_2$)$C_2B_9H_{10}$]$TaMe_3$ (**1**; 107 mg, 0.25 mmol) and 2,6-diisopropylphenyl isocyanide (140 mg, 0.75 mmol) in THF (15 mL) at -30 ^oC using the same procedures reported for **2**: yield 103 mg (54%). ^1H NMR (400 MHz, d_5-pyridine): δ 7.45 (m, 2H) (Ar-*H*), 7.33 (d, J = 7.6 Hz, 1H) (Ar-*H*), 7.23 (m, 2H) (Ar-*H*), 6.99 (d, J = 7.6 Hz, 1H) (Ar-*H*), 4.31 (m, 2H) (Ar-C*H*Me_2), 4.11 (m, 1H) (NC*H*H), 3.63 (s, 1H) (cage *H*), 3.31 (s, 3H) (N=CCH_3), 3.12 (m, 1H) (Ar-C*H*Me_2), 3.03 (m, 1H) (NC*H*H), 2.98 (s, 3H) (NMeCH_3), 2.93 (m, 1H)

(Ar-C*H*Me$_2$), 2.75 (s, 3H) (NC*H*$_3$Me), 2.62 (m, 2H) (C*H*$_2$), 1.32 (m, 12H) (Ar-CH(C*H*$_3$)$_2$), 1.10 (m, 12H) (Ar-CH(C*H*$_3$)$_2$). ^{13}C NMR (100 MHz, d_5-pyridine): δ 152.2 (N=*C*CH$_3$), 144.2, 142.3, 142.2, 142.1, 141.9, 141.8, 138.7, 138.3, 128.9, 128.8, 125.7, 125.6 (Ar-*C*), 74.0 (cage *C*), 67.4 (N*C*H$_2$), 56.4 (N=C*C*H$_3$), 50.4 (N*C*H$_3$), 50.0 (cage *C*), 38.0 (*C*H$_2$), 28.0, 27.9, 27.5, 27.0 (Ar-*C*HMe$_2$), 25.6, 25.2, 23.5, 23.4 (Ar-CH(*C*H$_3$)$_2$), 22.0 (N*C*H$_3$). ^{11}B{^{1}H} NMR (128 MHz, d_5-pyridine): δ 1.7 (2B), 0.6 (1B), -6.58 (1B), -9.1 (2B), -9,7 (2B), -16.3 (1B). ^{11}B NMR (128 MHz, d_5-pyridine): δ 1.7 (d, J = 113 Hz, 2B), 0.6 (br, unresolved, 1B),-6.58 (br, unresolved, 1B), -9.1 (br, unresolved, 2B), -9,7 (br, unresolved, 2B), -16.3 (d, J = 126 Hz, 1B). IR (KBr, cm^{-1}): ν_{BH} 2537 (vs). Anal. Calcd for $C_{32}H_{57}B_9N_3Ta$ (**4**): C, 50.81; H, 7.62; N, 5.39. Found: C, 50.43; H, 7.54; N, 5.51.

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.[4] 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.[5] All hydrogen atoms were geometrically fixed using the riding model. Crystal data and details of data collection and refinement are given in Tables S1.

CCDC 943870 - 943873 for complexes **1** – **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	**2a**	**3a**·0.5C_7H_8	**4**·0.25THF
formula	$C_2H_{29}B_9NTa$	$C_{21}H_{42}B_9N_2OTa$	$C_{30.5}H_{51}B_9N_3Ta$	$C_{33}H_{59}B_9N_3O_{0.25}Ta$
crystal size (mm)	0.40x0.30x0.20	0.40x0.30x0.20	0.50x0.40x0.30	0.50x0.40x0.30
fw	429.57	616.81	737.98	780.07
crystal system	monoclinic	orthorhombic	triclinic	monoclinic
space group	$P2_1/c$	*P*bca	*P*(-1)	$P2_1/c$
a, Å	12.998(1)	14.759(2)	8.896(1)	22.280(2)
b, Å	17.412(1)	18.933(3)	10.812(1)	20.164 (2)
c, Å	18.024(1)	19.809(3)	18.188(1)	20.630(2)
α, deg	90	90	92.057(2)	90
β, deg	98.188(2)	90	100.241(1)	111.047(2)
γ, deg	90	90	90.513(1)	90
V, $Å^3$	4037.5(5)	5534.9(13)	1720.2(2)	8649.6(14)
Z	8	8	2	8
D_{calcd}, Mg/m^3	1.413	1.480	1.425	1.198
radiation (λ), Å	0.71073	0.71073	0.71073	0.71073

2θ range, deg	3.2 to 50.5	4.0 to 50.5	3.8 to 50.5	2.8 to 50.5
μ, mm^{-1}	5.429	3.989	3.221	2.566
$F(000)$	1664	2464	746	3184
no. of obsd reflns	7254	5010	6161	15568
no. of params refnd	361	307	397	856
goodness of fit	1.057	1.086	1.080	1.010
R1	0.025	0.050	0.034	0.053
wR2	0.059	0.130	0.087	0.154