Electronic Supplementary Material (ESI) for Dalton Transactions.

H/D Scrambling in a Chromium-catalyzed Dehydrocoupling Reaction of Borane–dimethylamine Adduct

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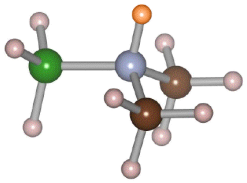
Supplementary Information

Computational Details. To obtain thermochemical parameters, frequency calculations were carried out on deuterated isotopomers of the species that participate in the dehydrocoupling reaction of $BH_3{\cdot}NHMe_2$ (**1a**), whose structures were previously optimized and reported.[1] This computation was performed at the DFT/PBE0 level of theory.[2] Chromium was described with the effective core potentials (ECP) of Hay and Wadt with a double-ζ valence basis set (LANL2DZ)[26] augmented with f-polarization functions (α = 1.941).[3] A double ζ plus polarization valence basis set augmented with diffuse functions, 6-31++G(d,p) was employed for B, N, BH, CrH and NH hydrogen atoms, which directly participated in the dehydrocoupling. For the other atoms, a standard 6-31G(d) basis set was applied. These functional and basis sets are the same as those employed for the geometry optimizations. Thermochemical parameters thus obtained, including zero point energies and Gibbs free energy contributions, were then added to the solvation free energy obtained by the SCRF (self consistent reaction field) calculations using the CPCM model.[4] As reported previously, on the SCRF calculations, Stuttgart-Dresden ECP and valence triple-ζ plus f-polarization basis set (SDD) were used for chromium,[5] and Dunning's aug-cc-pVDZ was employed to describe the other atoms.[6] The free energy values are given as those at 298 K and 1 atm in benzene. All calculations were performed with the Gaussian 03 package of programs.[7]

Cartesian coordinates, electronic energies and Gibbs free energies of the geometry-optimized species.

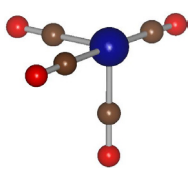


$BH_3{\cdot}NDMe_2$ (**1a-d$_N$**)

Electronic energy (CPCM) –161.5192364

Gibbs free energy (CPCM) –161.5470674

H	2.04857800	-1.01454000	-0.35358400	H	1.55169900	-0.00000500	1.33388200
H	2.04857900	1.01453900	-0.35357800	D	0.01862300	0.00000000	-1.36031200
C	-0.69884800	1.21633100	0.10120700	H	-0.17666900	2.08751500	-0.29644800
H	-1.74306500	1.21366400	-0.23113200	H	-0.65615100	1.25217300	1.19205200
C	-0.69885100	-1.21633100	0.10120700	H	-1.74306500	-1.21366500	-0.23113800
H	-0.17666800	-2.08751400	-0.29644200	H	-0.65615900	-1.25216800	1.19205300
B	1.56950300	-0.00000100	0.11655300	N	0.00328300	0.00000000	-0.34180000

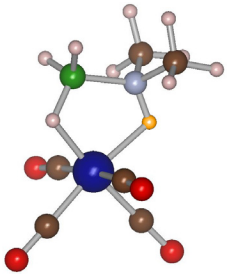


$[Cr(CO)_4]$

Electronic energy (CPCM) –539.8324284

Gibbs free energy (CPCM) –539.8683934

Cr	-0.00002600	0.00001800	-0.64421300	C	-1.88859200	0.00009100	-0.60690900
O	-3.03281300	0.00027800	-0.49475900	C	1.88847100	-0.00032700	-0.60694000
O	3.03270500	-0.00059900	-0.49491200	C	-0.00025100	-1.28351500	0.63000200
O	-0.00053200	-2.10462300	1.44405000	C	0.00033600	1.28364200	0.62989000
O	0.00074400	2.10496800	1.44372700				

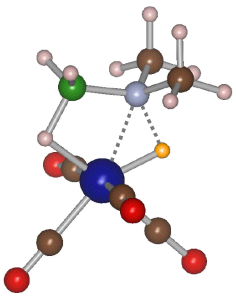


$[Cr(CO)_4(\eta^2\text{-}BH,ND\text{-}BH_3{\cdot}NDMe_2)]$ (**4-d$_N$**)

Electronic energy (CPCM) –701.3672539

Gibbs free energy (CPCM) –701.4110489

B	1.54834700	-0.16412300	-1.59154100	H	1.79277600	-1.29082500	-1.92941400
H	0.31280600	0.10112400	-1.76301200	H	2.11674000	0.68911000	-2.22514200
N	2.04099000	0.01944900	-0.02454400	D	1.30520100	0.04192600	0.73141200
C	2.89237900	-1.13249000	0.37534800	H	3.73696000	-1.18952100	-0.31318800
H	2.30769900	-2.04867500	0.30045000	H	3.25148000	-0.99310300	1.40029800
C	2.77976300	1.29598400	0.16193400	H	3.68724000	1.25648900	-0.44226600
H	3.03676600	1.43011900	1.21779900	H	2.15813600	2.12158500	-0.18134200
Cr	-0.39759900	0.00124900	-0.14905400	C	-0.45607500	-1.87391500	-0.17957800
O	-0.55766300	-3.02093500	-0.18973800	C	-0.49867900	1.87032200	-0.18119200
O	-0.63589400	3.01483900	-0.19805700	C	-2.11229700	-0.01622800	-0.75683200
O	-3.19015600	-0.02818500	-1.17063000	C	-0.98784100	-0.00331000	1.57583700
O	-1.35323500	-0.00395900	2.67568900				



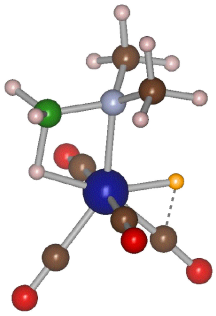
TS for the ND activation (**TS1-d$_N$**)

Electronic energy (CPCM) –701.3527503

Gibbs free energy (CPCM) –701.3949363

B	1.47452200	0.00013100	-1.65079200	H	1.81419400	1.02684100	-2.18091700
H	0.14785100	0.00001800	-1.79467200	H	1.81438100	-1.02630400	-2.18133900
N	1.84679900	-0.00017700	-0.12596200	D	0.84291100	-0.00003900	0.96106900
C	2.59540300	1.20064800	0.30223500	H	3.59877800	1.16418600	-0.13357200
H	2.09549000	2.09912900	-0.05301900	H	2.67651300	1.23171100	1.39514200
C	2.59499000	-1.20136000	0.30193800	H	3.59853400	-1.16490300	-0.13348000
H	2.67569800	-1.23296000	1.39485800	H	2.09502200	-2.09956900	-0.05392600

Cr	-0.29525900	0.00003100	-0.12405000	C	-0.37753000	1.87605700	-0.18851400
O	-0.50837100	3.01703800	-0.23827200	C	-0.37800200	-1.87597300	-0.18853900
O	-0.50917700	-3.01691600	-0.23832000	C	-2.05057500	0.00018600	-0.75185000
O	-3.12600100	0.00027800	-1.15368300	C	-0.91572400	0.00006700	1.59282900
O	-1.27954100	0.00009700	2.69079500				

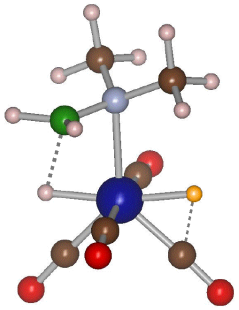


The ND-activated Intermediate (**5-d$_N$**)

Electronic energy (CPCM) –701.3733618

Gibbs free energy (CPCM) –701.4157438

B	1.58201100	0.00001300	-1.57754900	H	1.84178800	1.03235600	-2.14160600
H	0.20761200	-0.00009600	-1.67610400	H	1.84188400	-1.03228200	-2.14165700
N	1.87188500	-0.00001400	-0.08732300	D	0.05289300	0.00001000	1.56533400
C	2.55135900	1.18933300	0.44372100	H	3.62527800	1.13248000	0.21993100
H	2.16156000	2.09419700	-0.02004700	H	2.42371000	1.25365900	1.53030900
C	2.55132700	-1.18940600	0.44366900	H	3.62524400	-1.13257900	0.21986800
H	2.42368800	-1.25377200	1.53025700	H	2.16149100	-2.09423900	-0.02013100
Cr	-0.22633200	0.00002300	-0.02982200	C	-0.27235200	1.88726900	-0.08450000
O	-0.38683600	3.02720200	-0.13728200	C	-0.27232400	-1.88722700	-0.08423300
O	-0.38679000	-3.02717000	-0.13685900	C	-1.80135100	-0.00018800	-1.01813100
O	-2.76923200	-0.00034700	-1.63188500	C	-1.30423000	0.00018300	1.42601300
O	-2.03976700	0.00031300	2.32969300				

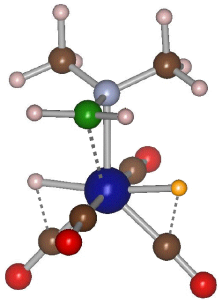


TS for the BH activation of (**TS2-d$_N$**)

Electronic energy (CPCM) –701.3532987

Gibbs free energy (CPCM) –701.3945107

B	-1.51898100	-1.40429400	-1.08411900	H	-1.39855200	-2.54041400	-0.73446000
H	0.13899300	0.09697400	-1.64302100	H	-1.58946500	-1.11411600	-2.24220000
N	-1.92585600	-0.42579100	-0.09722300	D	0.08455900	-0.12893300	1.61817500
C	-2.41612700	-0.92327000	1.19659500	H	-3.46218600	-1.24508000	1.09939300
H	-1.81236400	-1.77267300	1.51817400	H	-2.36059700	-0.13481000	1.95316900
C	-2.75510900	0.69117000	-0.56995600	H	-3.78489000	0.34544000	-0.72983200
H	-2.77345100	1.49885300	0.16755100	H	-2.35957400	1.07226100	-1.51270000
Cr	0.25684600	0.02095500	-0.01478100	C	0.84510700	-1.76326800	-0.12008800
O	1.33373200	-2.80329900	-0.14758800	C	-0.18189400	1.84265500	0.16425300
O	-0.38579700	2.96568800	0.28885600	C	1.47626200	0.49258900	-1.25027200
O	2.28822100	0.82000800	-2.01462900	C	1.43711900	0.18960400	1.33774800
O	2.23846600	0.29819000	2.17485700				

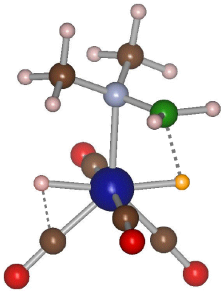


$[Cr(CO)_4(H)(D)(BH_2NMe_2)]$ (**6-d$_{Cr}$**)

Electronic energy (CPCM) –701.3573498

Gibbs free energy (CPCM) –701.3993728

B	1.18059400	1.92621900	-0.00003700	H	1.09604200	2.50132500	1.04637900
D	-0.12791400	0.03892400	-1.64479600	H	1.09606100	2.50127000	-1.04648300
N	1.83235600	0.62316500	-0.00000900	H	-0.12782700	0.03886700	1.64481700
C	2.56990700	0.22194400	1.20613800	H	3.57340400	0.66775700	1.18903600
H	2.04359900	0.56923700	2.09559300	H	2.67395600	-0.86673800	1.25189900
C	2.56997200	0.22195400	-1.20613000	H	3.57342000	0.66787200	-1.18903600
H	2.67414800	-0.86671900	-1.25183500	H	2.04363600	0.56913900	-2.09560900
Cr	-0.24366100	-0.02507300	-0.00000600	C	-1.08315200	1.65342400	0.00001000
O	-1.74616100	2.59383900	-0.00006500	C	0.42984100	-1.78515700	-0.00009000
O	0.82333000	-2.86301900	-0.00017500	C	-1.37780400	-0.49181100	-1.31847000
O	-2.15042600	-0.81435900	-2.12773100	C	-1.37759000	-0.49182600	1.31863100
O	-2.15013800	-0.81441200	2.12795800				

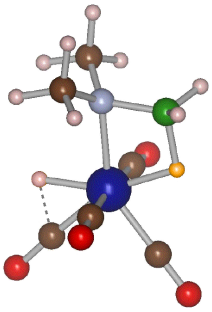


TS for the BD activation (**TS2-d$_{B(b)}$**)

Electronic energy (CPCM) –701.3532207

Gibbs free energy (CPCM) –701.3944577

B	1.51898100	-1.40429400	-1.08411900	H	1.39855200	-2.54041400	-0.73446000
D	-0.13899300	0.09697400	-1.64302100	H	1.58946500	-1.11411600	-2.24220000
N	1.92585600	-0.42579100	-0.09722300	H	-0.08455900	-0.12893300	1.61817500
C	2.41612700	-0.92327000	1.19659500	H	3.46218600	-1.24508000	1.09939300
H	1.81236400	-1.77267300	1.51817400	H	2.36059700	-0.13481000	1.95316900
C	2.75510900	0.69117000	-0.56995600	H	3.78489000	0.34544000	-0.72983200
H	2.77345100	1.49885300	0.16755100	H	2.35957400	1.07226100	-1.51270000
Cr	-0.25684600	0.02095500	-0.01478100	C	-0.84510700	-1.76326800	-0.12008800
O	-1.33373200	-2.80329900	-0.14758800	C	0.18189400	1.84265500	0.16425300
O	0.38579700	2.96568800	0.28885600	C	-1.47626200	0.49258900	-1.25027200
O	-2.28822100	0.82000800	-2.01462900	C	-1.43711900	0.18960400	1.33774800
O	-2.23846600	0.29819000	2.17485700				

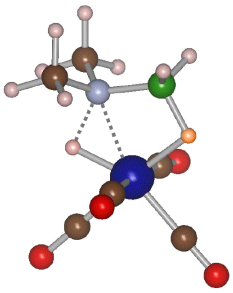


The NH-activated Intermediate (**5-$d_{B(b)}$**)

Electronic energy (CPCM) –701.3736038

Gibbs free energy (CPCM) –701.4159548

B	-1.58201100	0.00001300	-1.57754900	H	-1.84178800	1.03235600	-2.14160600
D	-0.20761200	-0.00009600	-1.67610400	H	-1.84188400	-1.03228200	-2.14165700
N	-1.87188500	-0.00001400	-0.08732300	H	-0.05289300	0.00001000	1.56533400
C	-2.55135900	1.18933300	0.44372100	H	-3.62527800	1.13248000	0.21993100
H	-2.16156000	2.09419700	-0.02004700	H	-2.42371000	1.25365900	1.53030900
C	-2.55132700	-1.18940600	0.44366900	H	-3.62524400	-1.13257900	0.21986800
H	-2.42368800	-1.25377200	1.53025700	H	-2.16149100	-2.09423900	-0.02013100
Cr	0.22633200	0.00002300	-0.02982200	C	0.27235200	1.88726900	-0.08450000
O	0.38683600	3.02720200	-0.13728200	C	0.27232400	-1.88722700	-0.08423300
O	0.38679000	-3.02717000	-0.13685900	C	1.80135100	-0.00018800	-1.01813100
O	2.76923200	-0.00034700	-1.63188500	C	1.30423000	0.00018300	1.42601300
O	2.03976700	0.00031300	2.32969300				

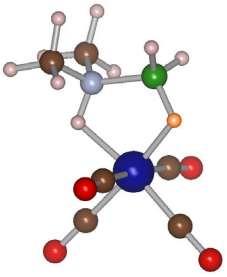


TS for the NH activation (**TS1-$d_{B(b)}$**)

Electronic energy (CPCM) –701.3534743

Gibbs free energy (CPCM) –701.3956693

B	-1.47452200	0.00013100	-1.65079200	H	-1.81419400	1.02684100	-2.18091700
D	-0.14785100	0.00001800	-1.79467200	H	-1.81438100	-1.02630400	-2.18133900
N	-1.84679900	-0.00017700	-0.12596200	H	-0.84291100	-0.00003900	0.96106900
C	-2.59540300	1.20064800	0.30223500	H	-3.59877800	1.16418600	-0.13357200
H	-2.09549000	2.09912900	-0.05301900	H	-2.67651300	1.23171100	1.39514200
C	-2.59499000	-1.20136000	0.30193800	H	-3.59853400	-1.16490300	-0.13348000
H	-2.67569800	-1.23296000	1.39485800	H	-2.09502200	-2.09956900	-0.05392600
Cr	0.29525900	0.00003100	-0.12405000	C	0.37753000	1.87605700	-0.18851400
O	0.50837100	3.01703800	-0.23827200	C	0.37800200	-1.87597300	-0.18853900
O	0.50917700	-3.01691600	-0.23832000	C	2.05057500	0.00018600	-0.75185000
O	3.12600100	0.00027800	-1.15368300	C	0.91572400	0.00006700	1.59282900
O	1.27954100	0.00009700	2.69079500				

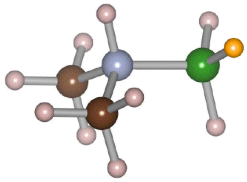


$[Cr(CO)_4(\eta^2\text{-}BD,NH\text{-}BH_2D{\cdot}NHMe_2)]$ (**4-d$_{B(b)}$**)

Electronic energy (CPCM) –701.3664219

Gibbs free energy (CPCM) –701.4102779

B	-1.54834700	-0.16412300	-1.59154100	H	-1.79277600	-1.29082500	-1.92941400
D	-0.31280600	0.10112400	-1.76301200	H	-2.11674000	0.68911000	-2.22514200
N	-2.04099000	0.01944900	-0.02454400	H	-1.30520100	0.04192600	0.73141200
C	-2.89237900	-1.13249000	0.37534800	H	-3.73696000	-1.18952100	-0.31318800
H	-2.30769900	-2.04867500	0.30045000	H	-3.25148000	-0.99310300	1.40029800
C	-2.77976300	1.29598400	0.16193400	H	-3.68724000	1.25648900	-0.44226600
H	-3.03676600	1.43011900	1.21779900	H	-2.15813600	2.12158500	-0.18134200
Cr	0.39759900	0.00124900	-0.14905400	C	0.45607500	-1.87391500	-0.17957800
O	0.55766300	-3.02093500	-0.18973800	C	0.49867900	1.87032200	-0.18119200
O	0.63589400	3.01483900	-0.19805700	C	2.11229700	-0.01622800	-0.75683200
O	3.19015600	-0.02818500	-1.17063000	C	0.98784100	-0.00331000	1.57583700
O	1.35323500	-0.00395900	2.67568900				

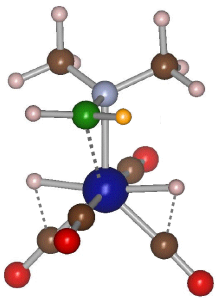


$BH_2D{\cdot}NHMe_2$ (**1a-d$_B$**)

Electronic energy (CPCM) –161.5180644

Gibbs free energy (CPCM) –161.5460124

H	2.04857800	-1.01454000	-0.35358400	H	1.55169900	-0.00000500	1.33388200
D	2.04857900	1.01453900	-0.35357800	H	0.01862300	0.00000000	-1.36031200
C	-0.69884800	1.21633100	0.10120700	H	-0.17666900	2.08751500	-0.29644800
H	-1.74306500	1.21366400	-0.23113200	H	-0.65615100	1.25217300	1.19205200
C	-0.69885100	-1.21633100	0.10120700	H	-1.74306500	-1.21366500	-0.23113800
H	-0.17666800	-2.08751400	-0.29644200	H	-0.65615900	-1.25216800	1.19205300
B	1.56950300	-0.00000100	0.11655300	N	0.00328300	0.00000000	-0.34180000



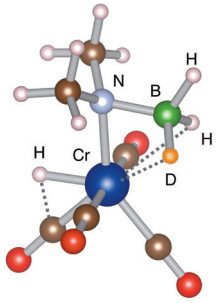
$[Cr(CO)_4(H)_2(BHDNMe_2)]$ (**6-d$_B$**)

Electronic energy (CPCM) –701.3578608

Gibbs free energy (CPCM) –701.3998918

B	1.18059400	1.92621900	-0.00003700	H	1.09604200	2.50132500	1.04637900
H	-0.12791400	0.03892400	-1.64479600	D	1.09606100	2.50127000	-1.04648300
N	1.83235600	0.62316500	-0.00000900	H	-0.12782700	0.03886700	1.64481700
C	2.56990700	0.22194400	1.20613800	H	3.57340400	0.66775700	1.18903600

H	2.04359900	0.56923700	2.09559300	H	2.67395600	-0.86673800	1.25189900
C	2.56997200	0.22195400	-1.20613000	H	3.57342000	0.66787200	-1.18903600
H	2.67414800	-0.86671900	-1.25183500	H	2.04363600	0.56913900	-2.09560900
Cr	-0.24366100	-0.02507300	-0.00000600	C	-1.08315200	1.65342400	0.00001000
O	-1.74616100	2.59383900	-0.00006500	C	0.42984100	-1.78515700	-0.00009000
O	0.82333000	-2.86301900	-0.00017500	C	-1.37780400	-0.49181100	-1.31847000
O	-2.15042600	-0.81435900	-2.12773100	C	-1.37759000	-0.49182600	1.31863100
O	-2.15013800	-0.81441200	2.12795800				

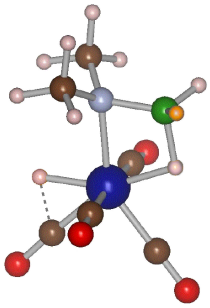


TS for BH exchange of the amidoborane intermediate (**TS3**)

Electronic energy (CPCM) –701.3427085

Gibbs free energy (CPCM) –701.3848915

B	-1.5669000	0.0000100	-1.5810500	D	-0.9613400	1.0282100	-1.8682900
H	-2.5607400	0.0000300	-2.2756400	H	-0.9613300	-1.0281600	-1.8683300
N	-1.8452100	-0.0000200	-0.0492500	H	0.0171800	0.0000400	1.5566100
C	-2.5618000	-1.1879800	0.4247000	H	-3.6213300	-1.1202000	0.1423300
H	-2.1531400	-2.0889200	-0.0337600	H	-2.4947800	-1.2746200	1.5157100
C	-2.5618100	1.1879200	0.4247400	H	-3.6213500	1.1201300	0.1424000
H	-2.4947700	1.2745400	1.5157600	H	-2.1531700	2.0888800	-0.0337000
Cr	0.2117600	0.0000100	-0.0291500	C	0.2778900	-1.9010200	-0.0003500
O	0.4204000	-3.0374800	0.0405900	C	0.2778600	1.9010300	-0.0002900
O	0.4203400	3.0375000	0.0406900	C	1.7378000	0.0000500	-1.1432500
O	2.6641700	0.0000800	-1.8128900	C	1.3848800	-0.0000400	1.3462200
O	2.1631800	-0.0000900	2.2123200				



The NH-activated Intermediate (**5-d$_{B(b)}$**)

Electronic energy (CPCM) –701.3738158

Gibbs free energy (CPCM) –701.4162018

B	-1.58201100	0.00001300	-1.57754900	H	-1.84178800	1.03235600	-2.14160600
H	-0.20761200	-0.00009600	-1.67610400	D	-1.84188400	-1.03228200	-2.14165700
N	-1.87188500	-0.00001400	-0.08732300	H	-0.05289300	0.00001000	1.56533400
C	-2.55135900	1.18933300	0.44372100	H	-3.62527800	1.13248000	0.21993100
H	-2.16156000	2.09419700	-0.02004700	H	-2.42371000	1.25365900	1.53030900
C	-2.55132700	-1.18940600	0.44366900	H	-3.62524400	-1.13257900	0.21986800
H	-2.42368800	-1.25377200	1.53025700	H	-2.16149100	-2.09423900	-0.02013100
Cr	0.22633200	0.00002300	-0.02982200	C	0.27235200	1.88726900	-0.08450000
O	0.38683600	3.02720200	-0.13728200	C	0.27232400	-1.88722700	-0.08423300
O	0.38679000	-3.02717000	-0.13685900	C	1.80135100	-0.00018800	-1.01813100
O	2.76923200	-0.00034700	-1.63188500	C	1.30423000	0.00018300	1.42601300
O	2.03976700	0.00031300	2.32969300				

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