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A Highly Reduced Cyanogen Ligand Derived from the Reductive Coupling of Cyanide*

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Contents

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1 Synthetic Procedures

1.1 General Considerations

All manipulations were carried out at room temperature (23 °C) under an atmosphere of purified dinitrogen in a Vacuum Atmospheres MO-40M glove box or with a vacuum manifold using standard Schlenk techniques. Celite 545 (EM Science) and 4 Å molecular sieves were dried *via* storage in a 225 °C oven for 24 h followed by complete desiccation under dynamic vacuum at 210 °C for 48 h prior to use. Solvents were purified using a commercial Glass Contour solvent purification system constructed by SG Water USA (Nashua, NH USA), and were stored over activated 4 Å molecular sieves prior to use. Benzene-d_6 and chloroform-*d* were obtained from Cambridge Isotope Laboratories, Inc. (Andover, MA USA). Prior to use, benzene-d_6 and chloroform-*d* were distilled from CaH_2, degassed with two freeze-pump-thaw cycles, and stored over activated 4 Å molecular sieves. NaCN was obtained from Aldrich; $NaC^{15}N$ and $K^{13}CN$ was obtained from Cambridge Isotopes Laboratory (Andover, MA USA). All three salts were dried at 80 °C under dynamic vacuum for 24 h prior to use. The niobium(IV) triflate complex (TfO)Nb(N[Np]Ar)$_3$ (**1**; Np = CH_2-*t*-Bu; Ar = 3,5-$Me_2C_6H_3$) was prepared according to published methods.[1] All glassware was oven-dried at a temperature of 225 °C prior to use.

Solution ^{1}H, ^{13}C{^{1}H}, and ^{15}N NMR spectra were recorded on Varian Mercury-300 or Varian Inova-500 spectrometers at 20 °C. ^{1}H and ^{13}C{^{1}H} NMR spectra were referenced internally to residual solvent ($C_6D_5\mathit{H}$ in C_6D_6, 7.16 ppm; C_6D_6, 128.29 ppm; $C\mathit{H}Cl_3$ in $CDCl_3$, 7.27 ppm; $\mathit{C}DCl_3$, 77.23 ppm). ^{15}N NMR spectra were referenced externally to neat $PhC^{15}N$ (258.4 ppm). Raman spectra were collected using laser excitation at 785 nm and 180° reflectance through the 10× objective of a Kaiser Optics Raman microscope. Combustion analyses were performed by Columbia Analytical Laboratory (Santa Fe, NM USA).

1.2 Synthesis of $(\mu,\eta^1{:}\eta^1$-NCCN)[Nb(N[Np]Ar)$_3$]$_2$ (2)

A solution of **1** (0.257 g, 0.316 mmol, 1 equiv) in THF (8 mL) was added to a suspension of NaCN (0.016 g, 0.33 mmol, 1 equiv) in THF (2 mL). The resulting mixture was stirred for *ca*. 18 h, during which time the color changed from purple-brown to orange-brown. The mixture was filtered through a plug of Celite and the volatile materials were removed from the filtrate under reduced pressure. Et_2O (8 mL) was added and subsequently removed under reduced pressure. The orange solids that remained were suspended in Et_2O (4 mL) and the resulting mixture was cooled to −35 °C minimize dissolution of the solids. The solids were then separated from the supernatant solution by filtering the mixture through a medium frit. The retained solids were washed with Et_2O (2 mL) and dried under reduced pressure, yielding the product **2** as an orange powder (0.199 g, 0.144 mmol, 91%). ^{1}H NMR (300 MHz, benzene-d_6): δ = 6.58 (s, 12H, *o*-Ar*H*), 6.50 (s, 6H, *p*-Ar*H*), 4.24 (s, 12H, NCH_2C(CH$_3$)$_3$), 2.10 (s, 36H, *m*-ArCH_3), 1.14 (s, 54H, NCH$_2$C(CH_3)$_3$) ppm. ^{13}C{^{1}H} NMR (126 MHz, chloroform-*d*): δ = 152.24 (s, Ar), 138.73 (s, Ar), 124.47 (s, Ar), 120.10 (s, Ar), 70.23 (s, NCH_2C(CH$_3$)$_3$), 35.46 (s, NCH$_2$*C*(CH$_3$)$_3$), 26.61 (s, *m*-Ar*C*H$_3$), 21.59 (s, NCH$_2$C(*C*H$_3$)$_3$) ppm. Raman (785 nm, solid sample): ν = 1132, 2060 cm^{-1}. Anal. Calcd. for $C_{80}H_{120}N_8Nb_2$: C, 69.65; H, 8.77; N, 8.12%. Found: C, 69.22; H, 7.94; N, 8.37%.

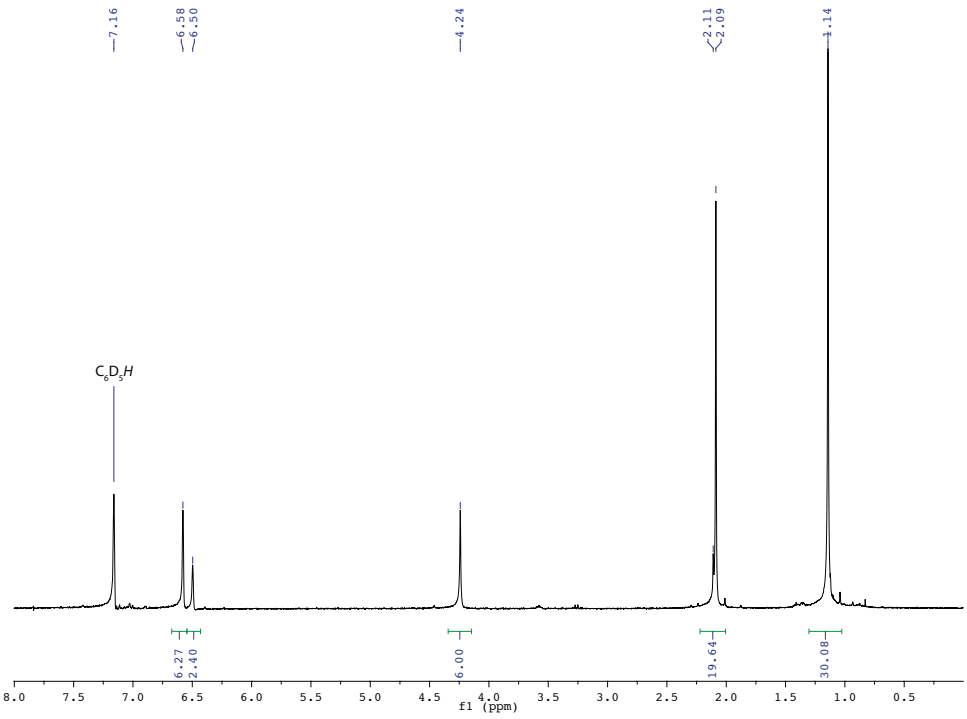

Figure 1: ^{1}H NMR spectrum (300 MHz, benzene-d_6) of **2**.

1.3 Synthesis of $(\mu,\eta^1{:}\eta^1$-^{15}NCC^{15}N)[Nb(N[Np]Ar)$_3$]$_2$ (**2**-^{15}N)

A solution of **1** and 15-crown-5 in THF (6 mL) was transferred onto solid NaC^{15}N. The resulting mixture was stirred for 3 d, during which time the color changed from purple/brown to orange/brown. The mixture was filtered through a plug of Celite and the volatile materials were removed from the filtrate under reduced pressure. Et_2O (5 mL) was added and the volatile materials were subsequently removed under reduced pressure. The orange solids that remained were slurried in a mixture of Et_2O/*n*-pentane (2 mL / 2 mL) and were isolated by filtering the suspension through a medium frit. The isolated solids were washed with Et_2O (2 mL) and dried under reduced pressure, leaving the product **2**-^{15}N as an orange powder (0.261 g, 0.189 mmol, 94%). $^{13}C\{^1H\}$ NMR (126 MHz, chloroform-*d*): δ = 152.24 (s, Ar), 138.73 (s, Ar), 124.47 (s, Ar), 120.10 (s, Ar), 79.51 (d, $^1J_{CN}$ = 26.4 Hz, *N*CC*N*), 70.23 (s, N*C*H$_2$C(CH$_3$)$_3$), 35.46 (s, NCH$_2$*C*(CH$_3$)$_3$), 26.61 (s, *m*-Ar*C*H$_3$), 21.59 (s, NCH$_2$C(*C*H$_3$)$_3$) ppm. ^{15}N NMR (50.7 MHz, chloroform-*d*): δ = 337.1 ppm (s). Raman (785 nm, solid sample): ν = 1091, 2046 cm^{-1}.

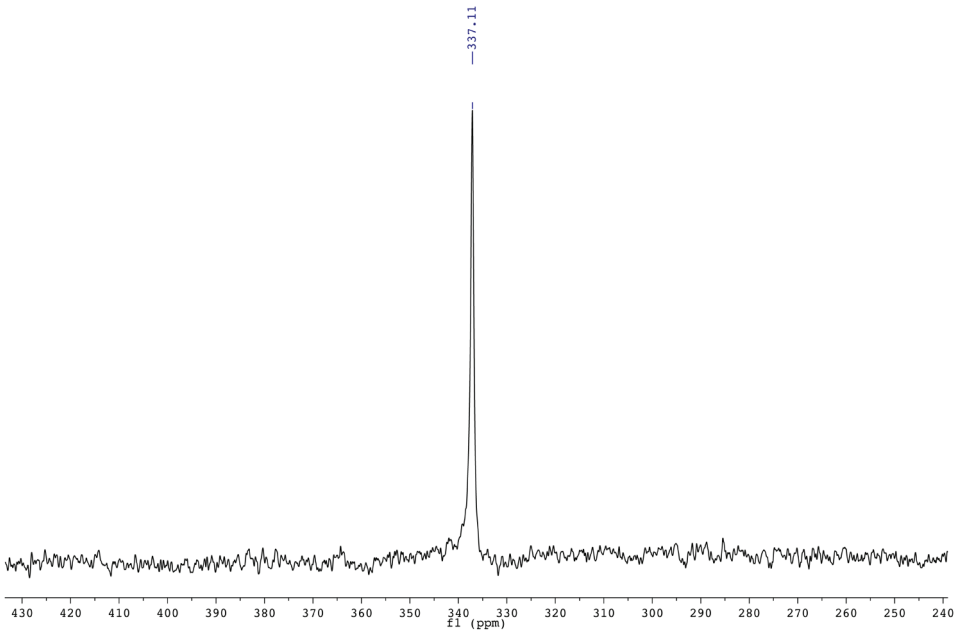

Figure 2: ^{15}N NMR spectrum (50.7 MHz, chloroform-*d*) of **2**-^{15}N.

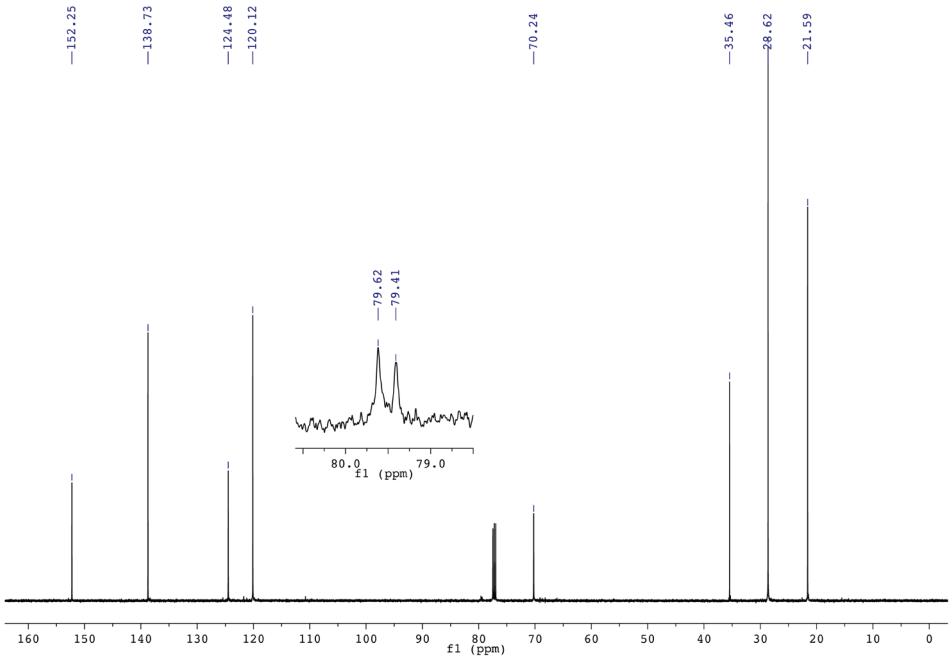

Figure 3: $^{13}C\{^{1}H\}$ NMR spectrum (126 MHz, chloroform-*d*) of **2**-^{15}N.

1.4 Synthesis of $(\mu,\eta^1{:}\eta^1$-N^{13}C^{13}CN)[Nb(N[Np]Ar)$_3$]$_2$ (2-^{13}C)

A solution of **1** in THF (10 mL) was transferred onto solid K^{13}CN. The resulting mixture was stirred for 2 d, during which time the color changed from purple/brown to orange/brown. The mixture was filtered through a plug of Celite and volatile materials were removed from the filtrate under reduced pressure. Et_2O (5 mL) was added and subsequently removed under reduced pressure. The orange solids that remained were slurried in a mixture of Et_2O/*n*-pentane (2 mL / 2 mL) and were isolated by filtering the suspension through a medium frit. The isolated solids were washed with Et_2O (2 mL) and dried under reduced pressure, leaving the product **2**-^{13}C as an orange powder (0.115 g, 0.083 mmol, 44%). $^{13}C\{^1H\}$ NMR (126 MHz, chloroform-*d*): δ = 152.24 (s, Ar), 138.73 (s, Ar), 124.47 (s, Ar), 120.10 (s, Ar), 79.49 (s, N*C*CN), 70.23 (s, N*C*H$_2$C(CH$_3$)$_3$), 35.46 (s, NCH$_2$*C*(CH$_3$)$_3$), 26.61 (s, *m*-Ar*C*H$_3$), 21.59 (s, NCH$_2$C(*C*H$_3$)$_3$) ppm. Raman (785 nm, solid sample): ν = 1129, 1983 cm^{-1}.

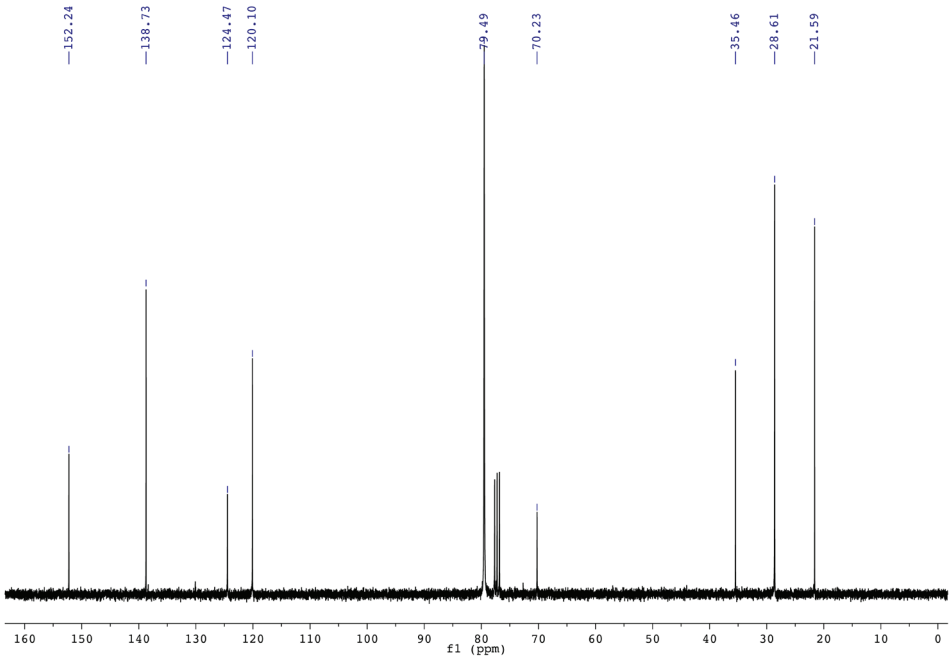

Figure 4: $^{13}C\{^{1}H\}$ NMR spectrum (126 MHz, chloroform-*d*) of **2**-^{13}C.

2 X-Ray Structure Determination

2.1 General Considerations

Low-temperature diffraction data were collected on a Siemens Platform three-circle diffractometer coupled to a Bruker-AXS Smart Apex charge-coupled device (CCD) and a graphite-monochromated Mo Kα radiation beam (0.71073 Å). Diffraction data were collected by performing ϕ- and ω-scans. All software used for diffraction data processing and crystal structure solution and refinement are contained in the SAINT+ (v6.45) and SHELXTL (v6.14) program suites.[2–5] The structure was solved using direct methods in conjunction with standard Fourier difference techniques, and refined on F^2 by full-matrix least-squares procedures. A semi-empirical absorption correction was applied to the diffraction data. All non-hydrogen atoms were refined anisotropically; all hydrogen atoms were placed at calculated positions refined isotropically using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U_{eq} value of the atoms they are linked to (1.5 times for methyl groups). Disorders were refined within SHELXL with the help of rigid bond restraints as well as similarity restraints on the anisotropic displacement parameters for neighboring atoms and on 1,2- and 1,3-distances throughout the disordered components.[6,7] The relative occupancies of disordered components were allowed to refine freely. Thermal ellipsoid plots were generated using the program PLATON.[8] Complete crystallographic data pertaining to the structure of **2** may be obtained free of charge from The Cambridge Crystallographic Data Centre (CCDC deposition number 775973) *via* the Internet at `http://www.ccdc.cam.ac.uk.data_request/cif` (or directly: Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033). A summary of the crystallographic data for the structurally characterized complex presented in this communication is given in Table 1.

Table 1: Crystallographic data for $(\mu,\eta^1{:}\eta^1$-NCCN)[Nb(N[Np]Ar)$_3$]$_2$.

	2
CCDC Deposition Number	775973
Empirical formula	$C_{80}H_{120}N_8Nb_2$
Formula weight (g mol^{-1})	1379.66
Temperature (K)	100(2)
Wavelength (Å)	0.71073
Crystal system	Orthorhombic
Space group	*Pbca*
Unit cell dimensions (Å, deg)	$a = 20.1847(14),\ \alpha = 90$
	$b = 20.4366(13),\ \beta = 90$
	$c = 20.6242(14),\ \gamma = 90$
Volume (Å^3)	8507.6(10)
Z	4
Density (calculated) (Mg m^{-3})	1.077
Absorption coefficient (mm^{-1})	0.311
$F(000)$	2952
Crystal size (mm^3)	$0.20 \times 0.20 \times 0.15$
Theta range for collection (deg)	1.73 to 29.13
Index ranges	$-27 \le h \le 27$
	$-27 \le k \le 27$
	$-27 \le l \le 28$
Reflections collected	173856
Independent reflections	11437 [$R_{(int)}$ = 0.0873]
Completeness to θ_{max} (%)	99.9%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9549 and 0.9404
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	11437 / 0 / 421
Goodness-of-fit[a]	1.089
Final R indices [$I > 2\sigma(I)$][b]	R_1 = 0.0459, wR_2 = 0.1013
R indices (all data)[b]	R_1 = 0.0672, wR_2 = 0.1091
Largest diff. peak and hole (e Å^{-3})	0.628 and −0.432

[a] GooF = $\left[\frac{\Sigma[w(F_o^2-F_c^2)^2]}{(n-p)}\right]^{\frac{1}{2}}$ [b] $R_1 = \frac{\Sigma||F_o|-|F_c||}{\Sigma|F_o|}$; $wR_2 = \left[\frac{\Sigma[w(F_o^2-F_c^2)^2}{\Sigma[w(F_o^2)^2]}\right]^{\frac{1}{2}}$; $w = \frac{1}{\sigma^2(F_o^2)+(aP)^2+bP}$; $P = \frac{2F_c^2+\max(F_o^2,0)}{3}$

2.2 Details Regarding Structural Refinement of $(\mu,\eta^1{:}\eta^1$-NCCN)[Nb(N[Np]Ar)$_3$]$_2$

The structural data refinement for **2** led to a model that was stable with respect to the diniobium μ-cyanogen complex, but additional residual electron density (max. $q > 6$ e/Å^3) was located. This residual electron density was consistent with the presence of a highly disordered solvent molecule. All attempts to model the disorder failed. The SQUEEZE routine[9] as implemented in the multi-purpose crystallographic software program PLATON[8] was employed to compensate for the contribution to the calculated structure factor imparted by the highly disordered solvent molecule.

3 Computational Details

3.1 General Considerations

Calculations on the model complex $(\mu,\eta^1{:}\eta^1$-NCCN)[Nb(NH$_2$)$_3$]$_2$ were performed using the ORCA program suite, version 2.8.[10] The calculations employed the def2-TZV basis set and the PW91 functional. No correction for relativistic effects were included in the geometry optimization calculation. Vibrational normal modes were calculated via numerical frequencies analysis. All other DFT calculations were performed using the ADF release 2009.01 program suite.[11,12] The relativistic ZORA option was employed. ZORA basis sets of triple zeta quality with two added polarization functions (TZ2P) in conjunction with large frozen core approximations were used for all atoms. Frozen core potentials were included by invoking the "`core large`" keyword in the ADF input file. Geometry optimizations were carried out and energy differences determined using the optimized Lee–Yang–Parr (OLYP) functional. The geometry optimization procedure was based on the method of Versluis and Ziegler.[13] The model complex **3** was optimized under C_i point symmetry. All other models were optimized without any symmetry constraints. Relative energies of stationary states are reported as differences in Total Bonding Energy as articulated in the ADF program suite.[12] Optimized atomic coordinates may be found below.

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Figure 5: Animation depicting the Raman-active vibrational mode at 1162 cm^{-1} in $(\mu,\eta^1{:}\eta^1\text{-NCCN})[Nb(NH_2)_3]_2$ (click image to view).

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Figure 6: Animation depicting the Raman-active vibrational mode at 2220 cm^{-1} in $(\mu,\eta^1{:}\eta^1\text{-NCCN})[Nb(NH_2)_3]_2$(click image to view).

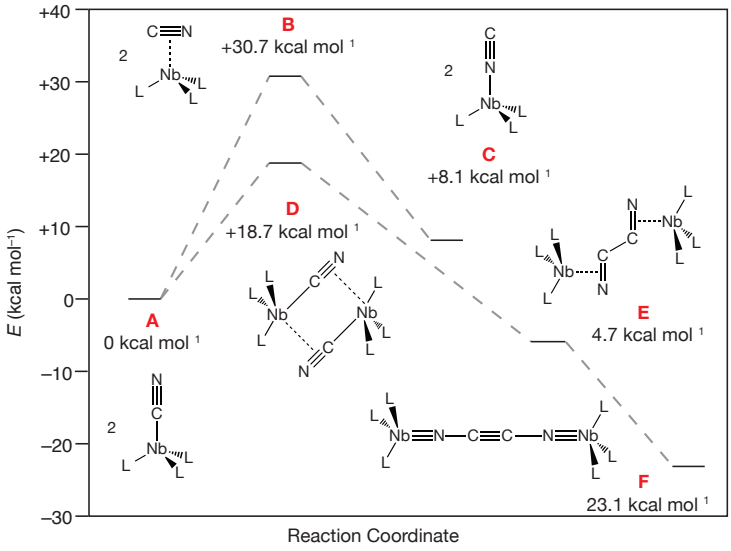

Figure 7: Relative energetics of stationary points describing the reductive coupling of Nb-bound cyanide ligands.

3.2 DFT Optimized Atomic Coordinates

Table 2: Optimized atomic coordinates (Å) of $(\mu,\eta^1{:}\eta^1\text{-NCCN})[Nb(NH_2)_3]_2$.

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Nb	0.003901	-0.009755	0.000230	N	-0.151401	0.109129	5.618265
N	0.001491	-0.005778	1.792198	N	0.751312	-1.655181	7.757006
N	1.973769	-0.051195	-0.396220	H	1.260099	-2.167145	7.035447
H	2.685057	0.149781	0.307705	H	0.623236	-2.259229	8.572049
H	2.421922	-0.460125	-1.219621	N	-2.123680	0.154546	7.806685
N	-1.038595	-1.702093	-0.396458	H	-2.834971	-0.046428	7.102762
H	-1.252583	-2.394197	0.322586	H	-2.571830	0.563475	8.630089
H	-1.602739	-1.895673	-1.227137	N	0.888687	1.805443	7.806914
N	-0.901221	1.758531	-0.346541	H	1.102686	2.497536	7.087863
H	-1.409998	2.270503	0.375018	H	1.452827	1.999027	8.637594
H	-0.773146	2.362574	-1.161589	C	-0.109579	0.071154	4.313710
Nb	-0.153819	0.113102	7.410234	C	-0.040330	0.032197	3.096753

Table 3: Optimized atomic coordinates (Å) of (μ,η^1:η^1-NCCN)[Nb(N[Me]Ph)$_3$]$_2$.

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Nb	8.209826	2.175216	7.932849	N	11.158387	−1.099563	11.428625
N	8.927519	4.039885	8.378580	C	10.497785	−0.357159	10.624162
C	8.222675	5.232609	8.039576	Nb	12.11191	−2.172349	12.552613
C	8.105521	5.635954	6.701279	N	11.392486	−4.036111	12.106418
H	8.580282	5.043592	5.926576	C	12.091377	−5.231781	12.447873
C	7.397988	6.788734	6.360309	C	12.198033	−5.638413	13.786191
H	7.319856	7.075331	5.314715	H	11.721065	−5.045603	14.559192
C	6.808999	7.574283	7.347891	C	12.898702	−6.794801	14.129363
H	6.266775	8.477977	7.082074	H	12.968868	−7.083511	15.174966
C	6.925816	7.189449	8.685664	C	13.491141	−7.580605	13.143967
H	6.465509	7.790159	9.466581	H	14.028067	−8.487041	13.411847
C	7.618975	6.032841	9.028560	C	13.384637	−7.192616	11.806086
H	7.682133	5.732410	10.071039	H	13.847156	−7.793805	11.026877
C	10.133945	4.276238	9.180538	C	12.697932	−6.032686	11.461199
H	10.595083	3.327895	9.457391	H	12.641609	−5.730330	10.418853
H	9.917537	4.827692	10.105801	C	10.188139	−4.268148	11.299996
H	10.871316	4.862649	8.612578	H	9.729887	−3.317924	11.024371
N	6.275958	1.815183	8.501083	H	10.406377	−4.817512	10.373872
C	5.168476	2.127241	7.657945	H	9.447808	−4.854750	11.864262
C	4.800903	3.462258	7.430203	N	14.045715	−1.810043	11.986745
H	5.352310	4.254640	7.925097	C	15.153502	−2.126819	12.828672
C	3.734003	3.778162	6.589045	C	15.535812	−3.461780	13.030042
H	3.474077	4.821399	6.428400	H	14.992635	−4.249862	12.519373
C	2.998453	2.769259	5.972106	C	16.604792	−3.782292	13.866946
H	2.160553	3.015677	5.325010	H	16.877361	−4.825205	14.007193
C	3.347406	1.435450	6.197144	C	17.326913	−2.777356	14.505825
H	2.785847	0.638029	5.716202	H	18.166564	−3.027226	15.149319
C	4.419613	1.116690	7.024983	C	16.962815	−1.443345	14.307541
H	4.694401	0.075696	7.172645	H	17.514342	−0.649473	14.805427
C	5.908703	1.066112	9.708581	C	15.888895	−1.120553	13.483306
H	6.792612	0.882834	10.319283	H	15.602245	−0.080120	13.354638
H	5.453632	0.092632	9.478248	C	14.418663	−1.063283	10.779661
H	5.186503	1.633581	10.312832	H	13.537053	−0.871854	10.168681
N	8.704342	1.452897	6.081997	H	14.881848	−0.093876	11.012007
C	8.528504	2.218233	4.891467	H	15.137316	−1.635584	10.175358
C	7.241756	2.502172	4.409579	N	11.617699	−1.452253	14.403623
H	6.379885	2.107718	4.936551	C	11.786556	−2.218701	15.594284
C	7.060736	3.272818	3.261128	C	13.070884	−2.510774	16.077591
H	6.051875	3.480076	2.913484	H	13.935742	−2.121684	15.551569
C	8.158806	3.759581	2.556618	C	13.245669	−3.282327	17.226363
H	8.016888	4.350151	1.655195	H	14.252913	−3.495738	17.575262
C	9.446243	3.475994	3.019123	C	12.143743	−3.762673	17.929363
H	10.312875	3.854249	2.482049	H	12.281028	−4.354659	18.830553
C	9.630569	2.719565	4.172559	C	10.85876	−3.471778	17.464683
H	10.637069	2.525814	4.533842	H	9.989086	−3.845944	17.999814
C	9.382701	0.169552	5.866665	C	10.680471	−2.713718	16.311365
H	9.523479	−0.346166	6.816382	H	9.675628	−2.514794	15.948309
H	10.370047	0.291031	5.401257	C	10.943112	−0.166201	14.613881
H	8.786318	−0.480529	5.209116	H	10.816455	0.350077	13.662311
N	9.164799	1.101997	9.055310	H	9.949236	−0.283126	15.067830
C	9.842205	0.359747	9.845715	H	11.535174	0.479359	15.279148

Table 4: Optimized atomic coordinates (Å) of (κC-CN)Nb(N[Me]Ph)$_3$.

Atom	***x***	***y***	***z***	**Atom**	***x***	***y***	***z***
Nb	5.922622	3.783558	4.937964	C	3.593346	0.390024	2.727185
C	5.840205	4.573351	2.921003	C	3.802855	1.620212	3.350471
N	6.659513	5.371611	5.912877	H	3.911158	2.521470	2.755411
C	8.092721	5.651876	6.027830	H	3.562386	0.341546	1.642026
H	8.415249	5.711298	7.074147	H	3.237503	−1.720289	3.000886
H	8.345753	6.599750	5.538088	H	3.301112	−1.568411	5.484969
H	8.665076	4.854696	5.550575	H	3.711178	0.583816	6.591780
C	5.774634	6.308383	6.517954	N	7.309106	2.302508	5.124631
C	4.880387	7.036645	5.715746	C	7.922129	1.755431	3.913755
C	3.961943	7.913241	6.292801	H	7.803784	2.466455	3.093497
C	3.930049	8.091860	7.674229	H	8.997866	1.586912	4.055871
C	4.827318	7.385482	8.478780	H	7.463255	0.808962	3.599209
C	5.741152	6.502850	7.910923	C	7.471517	1.580334	6.316413
H	6.421789	5.946247	8.549656	C	8.001495	0.273277	6.365821
H	4.807858	7.515760	9.557899	C	8.109704	−0.411338	7.574279
H	3.216310	8.777724	8.122677	C	7.694026	0.167678	8.772100
H	3.279040	8.467071	5.654098	C	7.178255	1.464952	8.741296
H	4.924585	6.921333	4.636360	C	7.081206	2.160892	7.543860
N	4.140814	2.965814	5.362226	H	6.717713	3.183712	7.562509
C	3.254663	3.402076	6.440476	H	6.863910	1.949386	9.662816
H	2.220605	3.475858	6.080144	H	7.779221	−0.373297	9.710168
H	3.267293	2.721777	7.300817	H	8.524210	−1.416717	7.572594
C	3.851082	1.714311	4.750477	H	8.326812	−0.219133	5.456917
C	3.659032	0.543948	5.508476	N	5.754096	5.072391	1.863122
C	3.437258	−0.675307	4.880093	H	3.558246	4.389845	6.792727
C	3.406864	−0.762683	3.486023				

Table 5: Optimized atomic coordinates (Å) of (κN-CN)Nb(N[Me]Ph)$_3$.

Atom	***x***	***y***	***z***	**Atom**	***x***	***y***	***z***
C	7.085221	2.166354	7.555878	C	3.279302	3.390922	6.455538
C	7.473764	1.584196	6.328886	H	8.408145	5.725678	7.061768
C	7.999909	0.275421	6.377684	H	8.320303	6.593720	5.514130
C	8.106256	−0.409808	7.585826	H	8.647623	4.849697	5.549192
C	7.695712	0.172037	8.784048	H	6.427995	5.954574	8.552993
C	7.184886	1.471487	8.753578	H	4.829684	7.536136	9.567250
N	7.311479	2.305115	5.137038	H	3.224712	8.790694	8.140777
C	7.926429	1.754148	3.927906	H	3.261140	8.461755	5.673301
Nb	5.927629	3.787620	4.905764	H	4.890643	6.909485	4.650334
N	4.158535	2.959977	5.368897	H	2.242384	3.466118	6.103361
C	3.855946	1.713118	4.751102	H	3.298400	2.705692	7.311790
C	3.658170	0.539997	5.503209	H	3.911678	2.527547	2.757889
C	3.424758	−0.674611	4.869347	H	3.540141	0.358754	1.636827
C	3.387180	−0.755061	3.475255	H	3.209523	−1.709043	2.985938
C	3.576934	0.400817	2.722176	H	3.284476	−1.56988	5.470069
C	3.798586	1.626015	3.351101	H	3.712342	0.573651	6.586343
N	5.855801	4.534796	2.953803	H	7.804981	2.458112	3.102254
C	5.759202	5.059065	1.894740	H	9.003043	1.592156	4.069882
N	6.641935	5.360623	5.923097	H	7.473632	0.802885	3.618991
C	5.761246	6.303053	6.526437	H	6.719954	3.188366	7.571205
C	4.860689	7.029377	5.729401	H	6.873705	1.957309	9.675471
C	3.949894	7.911806	6.309202	H	7.780146	−0.369281	9.722099
C	3.932049	8.100182	7.689697	H	8.514739	−1.417742	7.583605
C	4.836234	7.397388	8.489074	H	8.321343	−0.219110	5.468594
C	5.741564	6.508059	7.917655	H	3.585551	4.376150	6.811175
C	8.074888	5.651171	6.019504				

Table 6: Optimized atomic coordinates (Å) of $[(\mu,\eta^2{:}\eta^1\text{-CN})\text{Nb}(\text{N[Me]Ph})_3]_2$.

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Nb	−0.581117	−4.466614	−3.446716	C	0.827641	−7.786994	−7.698851
Nb	1.789252	−5.141221	−6.181867	H	0.191654	−7.841741	−6.817600
H	0.698836	−6.048514	−0.364663	H	1.439522	−8.700738	−7.743779
C	0.698145	−2.042829	−1.825842	H	0.177100	−7.798795	−8.586741
H	0.418515	−1.174320	−1.219653	C	2.477190	−6.558589	−8.857220
H	1.592646	−2.489798	−1.366409	C	3.704716	−7.237319	−8.899499
H	0.998986	−1.680147	−2.807614	C	4.462278	−7.285190	−10.069222
C	−1.248030	−2.970359	−0.790088	C	4.012747	−6.649515	−11.225442
C	−0.718926	−2.845371	0.515619	C	2.797646	−5.965316	−11.195975
C	−1.546431	−2.805774	1.633269	C	2.038902	−5.923492	−10.028690
C	−2.933777	−2.880921	1.499983	H	1.091390	−5.395500	−10.019434
C	−3.474255	−3.001919	0.220202	H	2.435968	−5.460510	−12.088276
C	−2.649503	−3.046670	−0.899819	H	4.599708	−6.689565	−12.139350
H	−3.090981	−3.099515	−1.884921	H	5.402675	−7.831344	−10.076810
H	−4.552971	−3.042622	0.085700	H	4.054761	−7.750994	−8.010357
H	−3.577559	−2.835757	2.373706	N	3.376307	−5.914123	−5.188021
H	−1.099428	−2.713520	2.620674	C	3.458785	−7.362012	−4.965175
H	0.355288	−2.784380	0.657564	H	3.593916	−7.573457	−3.895569
N	−2.226286	−3.727177	−4.367771	H	2.546725	−7.864743	−5.288545
C	−2.312824	−2.277741	−4.593671	H	4.308400	−7.809002	−5.500302
H	−0.438433	−8.550307	−3.033238	C	4.556405	−5.229962	−4.742835
H	−1.453229	−1.768023	−4.157232	C	5.632139	−5.007571	−5.613305
H	−3.220353	−1.858467	−4.138175	C	6.786630	−4.363451	−5.169995
C	−3.345614	−4.454459	−4.885105	C	6.890983	−3.935530	−3.848162
C	−3.540426	−4.594026	−6.269534	C	5.830970	−4.162894	−2.970834
C	−4.623859	−5.311754	−6.768763	C	4.677378	−4.806075	−3.411522
C	−5.543879	−5.899493	−5.899159	H	3.853296	−4.968561	−2.725591
C	−5.366140	−5.758018	−4.525244	H	5.897345	−3.828042	−1.938452
C	−4.280311	−5.042284	−4.023191	H	7.787668	−3.425334	−3.505024
H	−4.155510	−4.944329	−2.951105	H	7.605545	−4.193680	−5.864528
H	−6.074066	−6.207695	−3.833382	H	5.561926	−5.341898	−6.643396
H	−6.386656	−6.464084	−6.289530	C	2.360406	−1.220391	−7.725810
H	−4.742764	−5.423827	−7.843723	N	1.673733	−3.590460	−7.511748
H	−2.823474	−4.159090	−6.958678	H	1.378705	−0.870894	−7.422321
H	−2.339592	−2.041331	−5.665183	C	0.293144	−3.336107	−7.895560
N	−0.468257	−5.995992	−2.141820	H	−0.309844	−4.234834	−7.727815
C	0.816744	−6.095635	−1.455420	H	−0.176219	−2.525130	−7.324487
N	−0.430697	−2.981983	−1.937724	H	0.215882	−3.089807	−8.962628
H	1.474146	−5.271473	−1.752382	C	3.353743	−0.285657	−8.004973
H	1.338582	−7.028909	−1.709767	H	3.123208	0.773968	−7.924642
C	−1.408348	−7.028361	−1.849999	C	4.637681	−0.693365	−8.368736
C	−1.268773	−8.324722	−2.371249	C	3.924491	−2.996400	−8.187051
C	−2.204136	−9.312174	−2.070211	H	5.409490	0.040581	−8.585056
C	−3.293424	−9.030027	−1.244302	H	5.898672	−2.396118	−8.766869
C	−3.434442	−7.748569	−0.715705	H	4.135245	−4.051120	−8.316632
C	−2.498818	−6.758758	−1.011395	C	2.631352	−2.601678	−7.800002
H	−2.601219	−5.768562	−0.584295	C	4.912313	−2.056959	−8.460015
H	−4.271997	−7.512246	−0.063367	C	−0.007391	−5.934092	−5.378876
H	−4.023048	−9.802714	−1.014653	N	−1.043872	−6.349181	−4.962386
H	−2.085662	−10.307169	−2.491860	C	1.216610	−3.668949	−4.259161
N	1.663742	−6.578426	−7.677047	N	2.229360	−3.230638	−4.708056

Table 7: Optimized atomic coordinates (Å) of (μ,η^2:η^2)-NCCN)[Nb(N[Me]Ph)$_3$]$_2$.

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
C	1.331440	−5.399111	−5.974680	C	4.784073	−7.171425	−12.354767
C	0.825382	−4.691799	−4.788901	C	4.959506	−8.047958	−11.283763
N	1.227584	−3.661443	−4.190840	C	4.106931	−7.995870	−10.183701
Nb	−0.545822	−4.366190	−3.254782	H	−2.532920	−5.692203	−0.648229
N	0.947774	−6.435465	−6.574473	H	−4.440413	−9.468879	−1.410220
Nb	2.671540	−5.653337	−7.551001	H	−0.701503	−8.523621	−3.311643
N	2.179881	−7.029046	−8.989577	H	1.237530	−7.423462	−2.098626
C	0.962205	−7.810416	−9.210568	H	0.825253	−6.602705	−0.575693
N	−0.413107	−6.075792	−2.211398	H	−1.583208	−5.738276	−5.973493
C	0.881123	−6.480625	−1.665161	H	−5.552335	−7.345241	−6.295054
N	−2.163892	−3.753789	−4.285759	H	−4.828330	−3.906968	−3.818483
C	−2.342481	−2.357204	−4.675677	H	−2.223927	−2.225583	−5.759971
N	−0.085422	−2.897761	−1.841331	H	−3.333273	−1.973212	−4.399139
C	1.218332	−2.264014	−1.626999	H	0.597889	−2.972808	0.806188
C	−1.487968	−6.993615	−2.006673	H	−3.409277	−2.833157	2.337628
C	−2.549968	−6.649259	−1.158882	H	−2.733447	−2.710115	−1.899498
C	−3.608551	−7.531796	−0.952872	H	1.677853	−2.047147	−2.588511
C	−3.618436	−8.778774	−1.576547	H	1.102075	−1.327828	−1.067958
C	−2.560712	−9.131438	−2.418760	H	1.638714	−5.720135	−1.874572
C	−1.507369	−8.248911	−2.636436	H	−4.421819	−7.245080	−0.290810
C	−3.086463	−4.696772	−4.828844	H	−2.564123	−10.097091	−2.917837
C	−2.631162	−5.702637	−5.696439	H	−1.597671	−1.734356	−4.174743
C	−3.511105	−6.652667	−6.212208	H	−3.129739	−7.421916	−6.879351
C	−4.865253	−6.608120	−5.888480	H	−6.383334	−5.571020	−4.761554
C	−5.330917	−5.606810	−5.032334	H	1.925207	−2.895781	−1.066990
C	−4.453980	−4.663804	−4.503382	H	−0.946215	−2.955479	2.700232
C	−0.938850	−2.872144	−0.721037	H	−4.279218	−2.709595	0.000764
C	−0.467414	−2.916735	0.612132	H	4.694745	−4.360175	−9.905221
C	−1.347475	−2.908044	1.690297	H	6.568329	−0.533918	−9.351046
C	−2.727007	−2.845824	1.491366	H	2.739631	−1.323907	−7.568741
C	−3.210231	−2.783920	0.185720	H	0.837387	−2.528636	−8.273020
C	−2.335730	−2.791591	−0.897120	H	1.145303	−3.093732	−9.927810
N	2.497875	−3.864793	−8.489556	H	3.726636	−4.370077	−4.874194
C	1.169939	−3.386896	−8.869752	H	7.679790	−2.759234	−4.430879
N	4.339455	−6.295582	−6.615134	H	7.017639	−6.112011	−7.038325
C	4.612900	−7.711125	−6.383943	H	4.675661	−7.929496	−5.309773
C	3.575285	−2.964568	−8.704425	H	5.550495	−8.040170	−6.851045
C	4.686680	−3.369913	−9.463534	H	2.076655	−5.475272	−11.193010
C	5.755744	−2.504839	−9.686729	H	5.453061	−7.205466	−13.209789
C	5.738017	−1.211770	−9.169061	H	4.242813	−8.688508	−9.359386
C	4.640462	−0.796250	−8.413764	H	0.369581	−7.831957	−8.297295
C	3.572791	−1.657998	−8.179496	H	1.206414	−8.843058	−9.499262
C	5.250491	−5.365873	−6.034859	H	0.429801	−4.178688	−8.730225
C	4.776772	−4.389952	−5.141200	H	6.598050	−2.844185	−10.28451
C	5.642373	−3.454252	−4.578481	H	4.618606	0.205719	−7.991462
C	7.002929	−3.483591	−4.876330	H	3.806094	−8.315633	−6.802116
C	7.487317	−4.454561	−5.756424	H	5.244839	−2.709137	−3.893957
C	6.625373	−5.381925	−6.335114	H	8.545447	−4.480065	−6.006215
C	3.055478	−7.066358	−10.124203	H	0.343378	−7.389192	−10.018904
C	2.882353	−6.202125	−11.216348	H	3.592311	−5.554828	−13.139361
C	3.737952	−6.248111	−12.315558	H	5.765105	−8.778752	−11.306058

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