Supporting Information for

Redox Initiated Reactivity of Dinuclear β-Diketiminatoniobium Imido Complexes

Benjamin M. Kriegel, Lara C. E. Naested, Grégory Nocton, K. V. Lakshmi, Trevor D. Lohrey, Robert G. Bergman, and John Arnold*

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A. Crystallographic Data

Table S1 Crystallographic data for compounds **1 – 5**

Compound	**1·Et$_2$O**	**2**	**3**	**4a·1.5 Et$_2$O**	**5**
Empirical formula	$C_{36}H_{53}N_4OCl_2Nb$	$C_{29}H_{44}N_3Nb$	$C_{54}H_{78}N_6Nb_2$	$C_{83.75}H_{90.25}N_6O_{1.75}F_{20}BNb$	$C_{57}H_{83}N_6Nb_2$
Formula weight (amu)	721.63	527.58	997.1	1785.49	1038.11
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
Space group	*P*-1	*P*2$_1$/c	*P*2$_1$/n	*P*2$_1$/c	*P*2$_1$/c
a (Å)	9.1510(5)	11.6055(5)	12.1729(5)	29.313(2)	19.6714(6)
b (Å)	11.5419(7)	25.688(1)	15.8007(6)	16.020(1)	13.6781(4)
c (Å)	17.856(1)	9.5984(4)	13.4968(5)	27.544(1)	20.0479(6)
α (°)	87.826(1)	90	90	90	90
β (°)	77.694(1)	98.730(1)	93.481(2)	100.729(3)	92.016(2)
γ (°)	84.586(1)	90	90	90	90
V (Å^3)	1834.1(2)	2828.4(2)	2591.2(2)	8094.5(9)	5390.9(3)
Z	2	4	2	4	4
ρ_{calcd} (g/cm^3)	1.307	1.239	1.278	1.465	1.279
μ (mm^{-1})	0.506	0.445	0.482	0.380	0.466
F_{000} (e$^-$)	760	1120	1052	3663	2196
Crystal size (mm^3)	.40 x .32 x .24	.08 x .08 x .02	.06 x .04 x .04	.08 x .06 x .03	.04 x .02 x .02
Theta min / max (˚)	1.773 / 25.329	1.585 / 25.359	1.987 / 25.405	1.414 / 25.415	1.803 / 25.397
Reflections collected	88948	86456	25246	116724	29828
R_{int}	0.0408	0.0506	0.0516	0.0789	0.0718
T_{max} / T_{min}	0.7452 / 0.6826	0.7452 / 0.6573	0.7452 / 0.6696	0.7452 / 0.6997	0.7452 / 0.6327
Data / restr. / param.	6661 / 0 / 410	5183 / 0 / 311	4749 / 0 / 295	14873 / 0 / 1062	9833 / 0 / 640
GoF	1.111	1.101	1.021	1.014	1.043
R_1 / wR_2 (I>2σ(I))	0.0231 / 0.0588	0.0332 / 0.0820	0.0421 / 0.0979	0.0418 / 0.0909	0.0571 / 0.1218
R_1 / wR_2 (all data)	0.0236 / 0.0591	0.0399 / 0.0875	0.0619 / 0.1094	0.0647 / 0.1004	0.0961 / 0.1363
Res. peak / hole (e$^-$/Å^3)	0.441 / -0.446	1.183 / -0.411	1.952 / -0.379	0.821 / -0.614	0.937 / -0.824

B. Data for Density Functional Theory Calculations

Table S2 Comparison of selected experimental and computed metrical parameters for **4**.

Bond distance (Å)	XRD	B3LYP	PBE0
Nb1-Nb2	2.717	2.753	2.686
Nb1-N1(imido)	1.974	2.021	1.970
Nb2-N1(imido)	1.974	2.021	1.999
Nb1-N2(imido)	1.991	2.006	1.953
Nb2-N2(imido)	1.991	2.006	2.011
Nb1-N(BDI)	2.095	2.147	2.093
Nb1-N(BDI)	2.113	2.148	2.109
Nb2-N(BDI)	2.095	2.147	2.107
Nb2-N(BDI)	2.113	2.148	2.116
Bond angle (˚)			
N1(imido)-Nb1-N(BDI)	119.8	119.3	125.3
N1(imido)-Nb1-N(BDI)	116.4	118.6	117.0
N2(imido)-Nb2-N(BDI)	120.2	119.3	127.8
N2(imido)-Nb2-N(BDI)	117.7	118.6	118.8

Table S3 Calculated and experimental g-tensors and hyperfine coupling constants for **4**. Magnitudes of coupling constants are given in parenthesis.

	g_1, g_2, g_3	A^{93}Nb(1) (MHz)	A^{93}Nb(2) (MHz)	ΔA^{93}Nb
PBE0	1.997 1.977 1.842	38 76 187 (100)	59 98 209 (122)	22
B3LYP	1.997 1.980 1.833	73 91 226 (130)	81 100 229 (137)	7
Exp	1.996 1.968 1.908	111 48 200 (120)	115 52 234 (134)	14

Table S4 Partial atomic charges and electron spin density on selected atoms in B3LYP-optimized structures of **3** and **4** calculated using Mulliken, NPA, Hirshfeld, and QTAIM approaches.

	Atom	Mulliken Charge	NPA Charge	Hirshfeld Charge	QTAIM Charge	Mulliken Spin	Hirshfeld Spin	QTAIM Spin
3	Nb	+0.85	+1.06	+0.30	+1.87			
	N(imido)	-0.60	-0.73	-0.22	-1.20			
	N(BDI)	-0.67	-0.64	-0.16	-1.32			
	μ-H	-0.24	-0.21	-0.08	-0.48			
4	Nb	+1.10	+1.71	+0.40	+1.89	+0.57	+0.47	+0.47
	N(imido)	-0.83	-1.17	-0.23	-1.30	-0.11	-0.05	-0.06
	N(BDI)	-0.72	-0.74	-0.14	-1.33	-0.03	-0.03	0.00

Table S5 Partial atomic charges and electron spin density on selected atoms in PBE0-optimized structure of **4** calculated using Mulliken and Loewdin approaches.

	Atom	Mulliken Charge	Mulliken Spin	Loewdin Spin
4	Nb	+1.35	+0.53	+0.49
		+1.40	+0.67	+0.62
	N(imido)	-0.76	-0.13	-0.96
		-0.77	-0.14	-1.06
	N(BDI)	-0.46	-0.40	-0.26
		-0.44	-0.39	-0.25
		-0.42	-0.27	-0.16
		-0.43	-0.29	-0.18

Atom Coordinates (B3LYP)

5.3

Nb	0.0005	1.3563	-0.0553
N	0.0006	1.447	-1.8418
C	0.0003	1.4275	-3.2928
C	-1.2608	2.1428	-3.8223
H	-2.1663	1.6716	-3.4312
H	-1.2907	2.1011	-4.9173
H	-1.2646	3.1938	-3.5207
C	-0.0002	-0.0401	-3.7727
H	0.8852	-0.5645	-3.405
H	-0.0005	-0.0882	-4.8679
H	-0.8855	-0.5642	-3.4044
C	1.2615	2.1421	-3.823
H	1.2658	3.1931	-3.5217
H	1.2909	2.1001	-4.9179
H	2.167	1.6707	-3.4321
Nb	-0.0005	-1.3565	0.0555
N	-0.0006	-1.4473	1.8419
C	-0.0004	-1.4278	3.293
C	1.2605	-2.1431	3.8227
H	2.1661	-1.6721	3.4315
H	1.2904	-2.1012	4.9176
H	1.2642	-3.1941	3.5213
C	0.0001	0.0398	3.7728
H	-0.8851	0.5644	3.4047
H	0.0001	0.088	4.868
H	0.8857	0.5637	3.4048
C	-1.2617	-2.1423	3.823

5.4

Nb	-0.0461	-1.3103	-0.4197
N	-0.0313	-0.458	1.3958
N	1.468	-2.7775	-0.8265
N	-1.6344	-2.6878	-0.8616
C	-1.3853	-3.5029	-1.9131
C	3.8445	-2.0932	-0.6031
C	1.1926	-3.5936	-1.8693
C	3.7041	-1.0719	-1.7053
H	3.5069	-1.5429	-2.6759
H	4.6171	-0.4815	-1.8037
H	2.8798	-0.3772	-1.5203
C	-0.0971	-3.7886	-2.4136
H	-0.1034	-4.3971	-3.3091
C	2.7695	-2.909	-0.2026
C	5.0871	-2.2721	0.019
H	5.92	-1.6504	-0.3008
C	-2.5391	-4.2074	-2.5995
H	-2.9305	-5.0126	-1.9694
H	-2.2167	-4.6471	-3.544
H	-3.3697	-3.5236	-2.7899
C	2.3064	-4.4097	-2.4945
H	3.1874	-3.7991	-2.7042
H	1.9706	-4.878	-3.4201
H	2.6288	-5.2031	-1.8118
C	2.9495	-3.8987	0.7893
C	-1.1977	-1.9076	3.0236
H	-2.1676	-1.5227	2.6977

H	-1.2662	-3.1933	3.5216	H	-1.277	-2.1881	4.0793
H	-1.2912	-2.1004	4.918	H	-0.9846	-2.8139	2.4515
H	-2.1671	-1.6707	3.4321	C	4.2078	-4.0316	1.382
N	-1.5187	2.6838	0.9706	H	4.3458	-4.7959	2.1432
N	1.5205	2.6835	0.9701	C	-0.0847	-0.8647	2.8291
C	-2.8538	2.6963	0.4236	C	5.2928	-3.2269	1.0168
C	-3.1641	3.6375	-0.5841	C	-2.9412	-2.7782	-0.2434
C	2.8557	2.6953	0.4231	C	-3.1957	-3.8249	0.6694
C	3.1661	3.6348	-0.5857	C	-0.371	0.3596	3.7162
C	2.4308	4.2414	2.6613	H	0.4001	1.1273	3.5935
H	3.2437	3.5631	2.9311	H	-0.3796	0.0709	4.7725
H	2.0936	4.7609	3.5593	H	-1.343	0.8029	3.4832
H	2.8554	4.9832	1.9768	C	-3.9526	-1.8536	-0.5686
C	3.8427	1.8027	0.8874	C	1.2657	-1.4756	3.2474
C	5.1204	1.8587	0.3146	H	1.558	-2.2875	2.5782
H	5.8797	1.1708	0.6789	H	1.1987	-1.8769	4.2643
C	-1.2747	3.5021	2.0017	H	2.0591	-0.7251	3.2351
C	3.5634	0.8122	1.9903	C	-2.1766	-4.9007	0.9616
H	3.1845	1.3018	2.8944	H	-2.2217	-5.7052	0.2159
H	4.4723	0.2675	2.2577	H	-2.3632	-5.3587	1.9364
H	2.8101	0.082	1.6798	H	-1.155	-4.5177	0.9488
C	-3.8412	1.8043	0.8874	C	-4.4528	-3.8917	1.2781
C	2.1421	4.6417	-1.0532	H	-4.6448	-4.6957	1.9851
H	2.5279	5.2219	-1.896	C	-5.4692	-2.9749	0.9948
H	1.8733	5.3485	-0.2586	C	-3.7364	-0.7783	-1.6032
H	1.2145	4.153	-1.3637	H	-2.979	-0.0517	-1.2938
C	-5.4465	2.7671	-0.6958	H	-4.6591	-0.2231	-1.7832
C	-2.1395	4.6444	-1.0503	H	-3.4012	-1.1953	-2.5594
H	-2.5257	5.2271	-1.8913	C	-5.1982	-1.9733	0.0583
H	-1.2128	4.1555	-1.363	H	-5.9824	-1.2689	-0.209
H	-1.869	5.3491	-0.2544	C	1.8284	-4.824	1.1991
C	4.4518	3.6431	-1.1327	H	2.1719	-5.5326	1.9564
H	4.6824	4.3661	-1.913	H	1.4393	-5.403	0.3544
C	5.4479	2.7627	-0.6975	H	0.9813	-4.2723	1.6191
C	-5.1193	1.8621	0.3151	C	6.6363	-3.3857	1.6874
H	-5.8794	1.1752	0.6798	H	6.6427	-2.913	2.6771
C	0.0012	3.7849	2.5269	H	7.435	-2.9271	1.0982
H	0.0015	4.4342	3.3929	H	6.887	-4.4408	1.8342
C	-4.4499	3.6479	-1.1301	C	-6.8106	-3.0625	1.6826
H	-4.6806	4.373	-1.9084	H	-7.1005	-4.1019	1.8628
C	-2.4282	4.2416	2.6623	H	-7.5973	-2.5894	1.0883
H	-2.8526	4.984	1.9782	H	-6.789	-2.5598	2.6575
H	-2.0908	4.7606	3.5605	Nb	0.046	1.3103	0.4197
H	-3.2414	3.5635	2.9317	N	0.0313	0.458	-1.3958
C	1.277	3.5019	2.0012	N	-1.4681	2.7774	0.8265

C	-3.5627	0.8132	1.99	N	1.6344	2.6878	0.8615
H	-2.8081	0.0841	1.6803	C	1.3854	3.5029	1.913
H	-4.4714	0.2671	2.2553	C	-3.8446	2.0934	0.603
H	-3.1861	1.3025	2.8952	C	-1.1925	3.5934	1.8694
C	-6.836	2.8175	-1.2882	C	-3.7044	1.0719	1.7051
H	-7.3517	3.7485	-1.0222	H	-3.5082	1.5428	2.6759
H	-7.4523	1.987	-0.9322	H	-4.6171	0.4809	1.8027
H	-6.8082	2.7698	-2.3826	H	-2.8796	0.3777	1.5205
C	6.8398	2.816	-1.2841	C	0.0972	3.7885	2.4136
H	7.3928	3.6927	-0.9242	H	0.1035	4.3969	3.3091
H	6.8126	2.8816	-2.3772	C	-2.7695	2.9092	0.2027
H	7.4215	1.9295	-1.015	C	-5.0872	2.2725	-0.019
H	1.3824	-0.0004	0.0002	H	-5.9202	1.6508	0.3007
N	1.5187	-2.6838	-0.9706	C	2.5392	4.2076	2.5992
N	-1.5205	-2.6835	-0.9701	H	2.9303	5.0129	1.9691
C	2.8539	-2.6961	-0.4237	H	2.2169	4.6472	3.5438
C	3.1643	-3.6373	0.5841	H	3.37	3.524	2.7894
C	-2.8557	-2.6953	-0.4231	C	-2.3064	4.4094	2.4948
C	-3.1661	-3.6349	0.5857	H	-3.1873	3.7988	2.7045
C	-2.4308	-4.2415	-2.6612	H	-1.9705	4.8777	3.4205
H	-3.2437	-3.5632	-2.931	H	-2.6289	5.2028	1.8122
H	-2.0936	-4.761	-3.5592	C	-2.9494	3.899	-0.7891
H	-2.8554	-4.9833	-1.9767	C	1.1978	1.9075	-3.0237
C	-3.8427	-1.8027	-0.8874	H	2.1676	1.5224	-2.6979
C	-5.1204	-1.8587	-0.3146	H	1.2769	2.188	-4.0794
H	-5.8797	-1.1708	-0.6789	H	0.9848	2.8138	-2.4515
C	1.2747	-3.5021	-2.0016	C	-4.2076	4.0321	-1.3817
C	-3.5633	-0.8122	-1.9902	H	-4.3456	4.7966	-2.1428
H	-3.1844	-1.3017	-2.8943	C	0.0846	0.8647	-2.8291
H	-4.4722	-0.2675	-2.2576	C	-5.2928	3.2275	-1.0167
H	-2.8101	-0.082	-1.6797	C	2.9412	2.7781	0.2433
C	3.8411	-1.804	-0.8876	C	3.1958	3.8246	-0.6697
C	-2.1422	-4.6418	1.0531	C	0.3706	-0.3597	-3.7162
H	-2.528	-5.2221	1.8959	H	-0.4006	-1.1272	-3.5935
H	-1.8735	-5.3487	0.2585	H	0.3792	-0.071	-4.7725
H	-1.2145	-4.1533	1.3636	H	1.3426	-0.8031	-3.4832
C	5.4466	-2.7666	0.6955	C	3.9526	1.8534	0.5686
C	2.14	-4.6443	1.0504	C	-1.2658	1.4758	-3.2473
H	2.5263	-5.227	1.8913	H	-1.5578	2.2879	-2.5782
H	1.2133	-4.1555	1.3632	H	-1.1989	1.8769	-4.2643
H	1.8694	-5.349	0.2545	H	-2.0593	0.7255	-3.2346
C	-4.4518	-3.6433	1.1326	C	2.1768	4.9005	-0.9619
H	-4.6825	-4.3664	1.9128	H	2.2222	5.7052	-0.2164
C	-5.4479	-2.7628	0.6974	H	2.3633	5.3582	-1.9369
C	5.1193	-1.8616	-0.3154	H	1.1551	4.5177	-0.9488

H	5.8792	-1.1747	-0.6801	C	4.4529	3.8913	-1.2784
C	-0.0012	-3.785	-2.5268	H	4.645	4.6951	-1.9855
H	-0.0014	-4.4344	-3.3928	C	5.4693	2.9744	-0.995
C	4.4502	-3.6475	1.1299	C	3.7364	0.7783	1.6034
H	4.6811	-4.3725	1.9082	H	2.9791	0.0516	1.2941
C	2.4283	-4.2415	-2.6623	H	4.6591	0.2233	1.7837
H	2.8528	-4.9839	-1.9783	H	3.4009	1.1955	2.5595
H	2.0909	-4.7605	-3.5605	C	5.1982	1.973	-0.0583
H	3.2414	-3.5633	-2.9317	H	5.9823	1.2685	0.2091
C	-1.2769	-3.502	-2.0011	C	-1.8283	4.8242	-1.1988
C	3.5624	-0.8131	-1.9902	H	-2.1716	5.5329	-1.9561
H	2.8077	-0.0841	-1.6805	H	-1.4392	5.4032	-0.3541
H	4.471	-0.2669	-2.2556	H	-0.9811	4.2724	-1.6188
H	3.1857	-1.3025	-2.8953	C	-6.6363	3.3866	-1.6873
C	6.8362	-2.8168	1.2878	H	-6.643	2.9133	-2.6767
H	7.3519	-3.7477	1.022	H	-7.4351	2.9286	-1.0978
H	7.4524	-1.9862	0.9316	H	-6.8866	4.4417	-1.8346
H	6.8085	-2.7688	2.3823	C	6.8106	3.0618	-1.6828
C	-6.8398	-2.8161	1.284	H	7.1006	4.1011	-1.8632
H	-7.3927	-3.6931	0.9244	H	7.5973	2.5887	-1.0884
H	-6.8127	-2.8814	2.3771	H	6.7889	2.559	-2.6576
H	-7.4217	-1.9299	1.0145				
H	-1.3824	0.0003	0.0001				

Atom Coordinates (PBE0)

5.4

Nb	0.096774	-1.36671	-0.14959
N	0.148532	-0.29864	1.505404
N	1.69622	-2.73516	-0.26568
N	-1.33196	-2.89113	-0.27557
C	-1.03713	-3.8447	-1.17411
C	3.883663	-1.67904	0.045145
C	1.519277	-3.74757	-1.12272
C	0.26184	-4.11116	-1.63401
H	0.303989	-4.86093	-2.41173
C	2.934835	-2.62029	0.429899
C	5.076731	-1.57375	0.747926
H	5.819854	-0.84805	0.436961
C	-2.14561	-4.68464	-1.73492
H	-2.58627	-5.31767	-0.96142
H	-1.77945	-5.32643	-2.53366
H	-2.95069	-4.05308	-2.11828

C	2.70638	-4.54365	-1.57669
H	3.497407	-3.88718	-1.9461
H	2.427042	-5.24745	-2.358
H	3.132495	-5.11035	-0.74509
C	3.19026	-3.45015	1.519854
C	0.06122	-2.02594	3.227994
H	-0.98624	-2.26276	3.023985
H	0.277865	-2.26038	4.273823
H	0.685361	-2.67583	2.609175
C	4.383125	-3.34075	2.216588
H	4.571001	-3.9901	3.063979
C	0.362074	-0.56035	2.927823
C	5.331821	-2.40224	1.831512
C	-2.59779	-2.92098	0.376287
C	-2.825	-3.85925	1.380437
C	-0.54929	0.353428	3.743189
H	-0.33651	1.404786	3.522119
H	-0.40508	0.202162	4.815464
H	-1.59765	0.156395	3.505069
C	-3.60402	-2.02966	0.021001
C	1.831886	-0.28027	3.244308
H	2.479006	-0.88829	2.609932
H	2.056793	-0.52272	4.286816
H	2.074539	0.772413	3.071032
C	-4.06034	-3.92475	2.003611
H	-4.234	-4.66153	2.779436
C	-5.0735	-3.04884	1.636048
C	-4.83872	-2.09921	0.651422
H	-5.62796	-1.41537	0.358294
Nb	-0.12305	1.272521	0.298396
N	-0.15577	0.226452	-1.35136
N	-1.70369	2.678943	0.338985
N	1.291897	2.824493	0.321656
C	1.024221	3.724889	1.274874
C	-3.9026	1.757729	-0.24501
C	-1.52445	3.635201	1.253525
C	-0.26313	3.933284	1.80174
H	-0.29298	4.617351	2.638626
C	-2.88731	2.683913	-0.45327
C	-5.02488	1.768411	-1.06349
H	-5.8202	1.051878	-0.89155
C	2.13655	4.565557	1.826821
H	2.442411	5.324625	1.102816
H	1.820974	5.074986	2.735384
H	3.01692	3.954272	2.035129

C	-2.69721	4.442066	1.723664
H	-3.55692	3.800631	1.925713
H	-2.44552	5.011634	2.616329
H	-3.0055	5.14963	0.94939
C	-3.00094	3.612432	-1.48693
C	-0.00051	1.950129	-3.07889
H	1.04394	2.175002	-2.85219
H	-0.19026	2.179983	-4.13083
H	-0.63079	2.611803	-2.48039
C	-4.12304	3.617401	-2.29984
H	-4.19904	4.340231	-3.10416
C	-0.32892	0.49079	-2.78008
C	-5.13843	2.693546	-2.09207
C	2.501662	2.926348	-0.41976
C	2.639065	3.944947	-1.36036
C	0.591909	-0.43784	-3.56701
H	0.362516	-1.48605	-3.34808
H	0.476397	-0.28844	-4.64297
H	1.636021	-0.25109	-3.30313
C	3.524744	2.00202	-0.24682
C	-1.79302	0.23006	-3.13541
H	-2.44852	0.853888	-2.52579
H	-1.98238	0.467707	-4.1858
H	-2.05614	-0.81759	-2.9619
C	3.800058	4.045841	-2.11005
H	3.900178	4.83958	-2.84136
C	4.82583	3.125956	-1.93583
C	4.684859	2.108803	-1.00213
H	5.486987	1.394126	-0.85448
H	-6.04288	-3.1095	2.116724
H	-2.02874	-4.53935	1.662564
H	-3.42226	-1.30479	-0.76539
H	-6.01507	2.697564	-2.72886
H	-2.19898	4.323027	-1.65675
H	-3.81668	1.039237	0.563312
H	1.827883	4.649885	-1.50608
H	5.73405	3.208576	-2.52096
H	3.415691	1.216536	0.493655
H	6.264168	-2.31576	2.376581
H	3.685963	-1.03961	-0.80852
H	2.443303	-4.17556	1.823717