Supporting Information

Rare [$(NHC)_2Ni–OH$] Type Terminal Nickel Hydroxo and [$(NHC)_2Ni$] Type Complexes of *N/O*-functionalized N-heterocyclic Carbenes (NHC) as Precatalysts for Highly Desirable Base-free Michael Reactions in Air at Ambient Temperature

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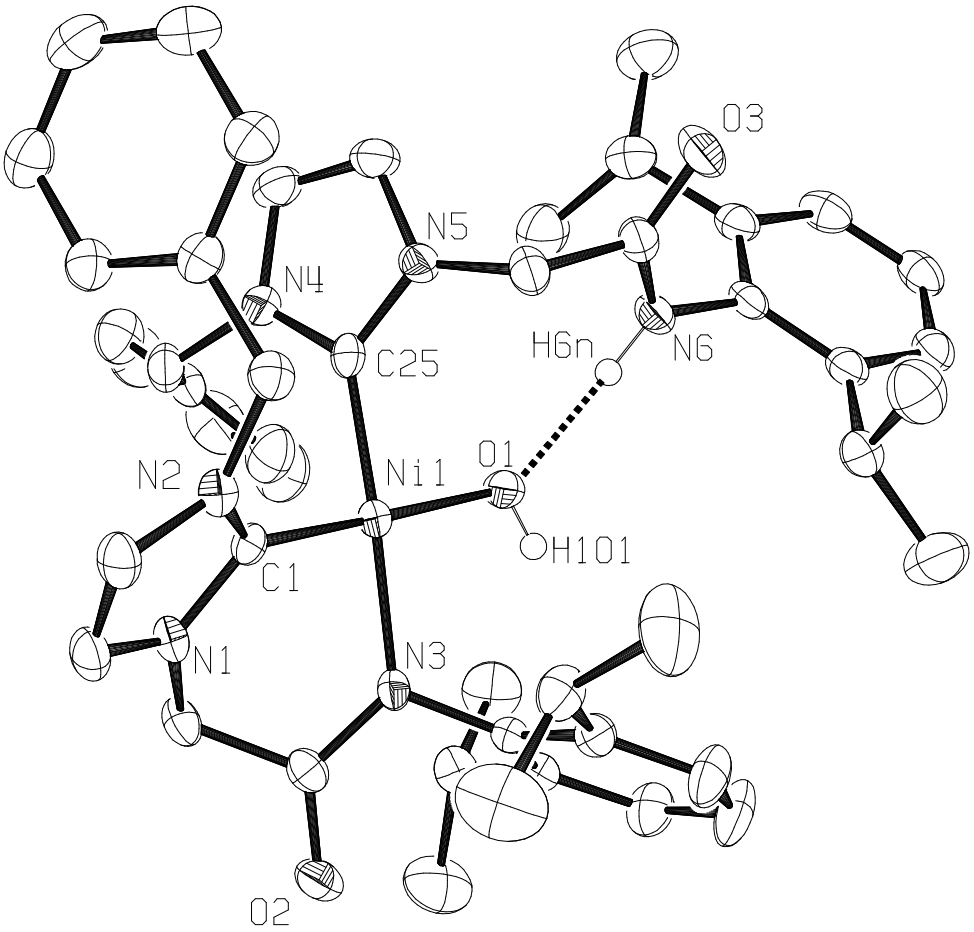


Figure S1. ORTEP of **2b**. Selected bond lengths (Å) and angles (°): N1-C1 1.350(3), N2-C1 1.360(3), Ni1-C1 1.871(2), Ni1-O1 1.8753(15), Ni1-N3 1.9481(17), N4-C25 1.351(3), N5-C25 1.355(3), Ni1-C25 1.873(2), C1-Ni1-C25 94.13(9), C1-Ni1-O1 173.66(8), C25-Ni1-N3 171.85(8).

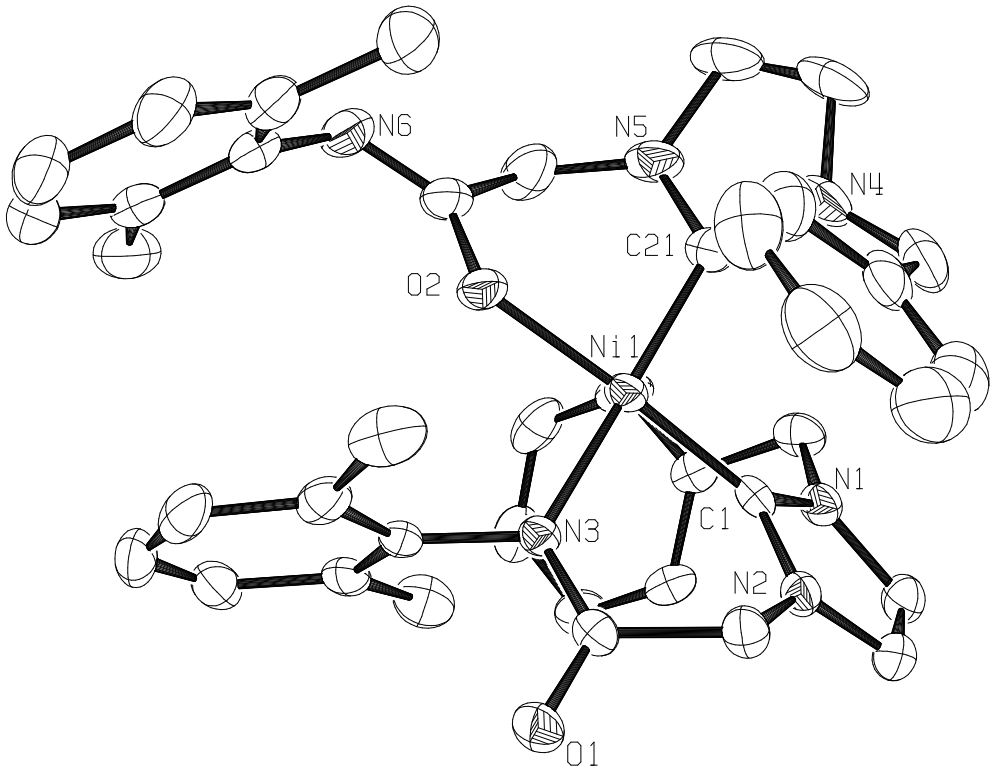


Figure S2. ORTEP of **4b**. Selected bond lengths (Å) and angles (^{o}): N1-C1 1.366(2), N2-C1 1.351(2), Ni1-C1 1.844(2), Ni1-O2 1.8987(13), Ni1-N3 1.9310(14), N4-C21 1.356(3), N5-C21 1.350(3), Ni1-C21 1.8650(18), C1-Ni1-C21 93.86(8), C1-Ni1-O2 174.95(7), C21-Ni1-N3 170.20(8).

Table S1. X-ray crystallographic data for **1b**, **2b**, **3b** and **4b**.

Compound	**1b**	**2b**	**3b**	**4b**
lattice	Monoclinic	Monoclinic	Triclinic	Monoclinic
formula	$C_{40}H_{61}N_6NiO_7$	$C_{50}H_{63}N_7NiO_4$	$C_{94}H_{107}N_{15}Ni_2O_7$	$C_{42}H_{43}N_7NiO_2$
formula weight	796.66	884.78	1676.37	736.54
Space group	P 2_1/c	P 2_1/n	P-1	P 2_1/n
a/Å	10.4293(3)	11.0293(10)	11.7448(4)	10.6399(2)
b/Å	21.3739(6)	23.097(3)	19.8621(4)	25.3622(8)
c/Å	19.8728(7)	18.6779(7)	20.7451(5)	13.8146(4)
α/°	90.00	90.00	85.025(2)	90.00
β/°	95.661(3)	95.022(4)	78.820(2)	92.123(2)
γ/°	90.00	90.00	81.708(2)	90.00
V/Å^3	4408.3(2)	4739.8(7)	4689.3(2)	3725.33(17)
Z	4	4	2	4
temperature (K)	120(2)	120(2)	150(2)	120(2)
radiation (λ, Å)	0.71073	0.71073	0.71073	0.71073
ρ(calcd.), g cm^{-3}	1.200	1.240	1.187	1.313
μ(Mo Kα), mm^{-1}	0.491	0.460	0.461	0.567
θ max, deg.	32.5097	32.6037	32.3965	32.6162
no. of data	7748	8317	16280	6558
no. of parameters	511	584	1085	474
R_1	0.0637	0.0368	0.0733	0.0314
wR_2	0.1826	0.0934	0.2293	0.0677
GOF	1.070	1.030	1.030	0.992

The density functional theory calculation was performed for the **1b** by using the GAUSSIAN 03[1] suite quantum chemical programs.

Table S2. B3LYP/LANL2DZ, 6-31G* optimized coordinates of **1b**.

Ground state electronic energy = -2282.7382925 hartree/particle

Ni	1.37241	-0.246681	0.257449
O	-0.405416	0.092835	0.708657
O	-3.085929	-1.933957	-2.603341
O	3.492573	2.985706	1.757665
N	0.95961	-3.137068	0.732555
N	-0.174796	-2.456588	-0.965616
N	-2.619123	-0.731778	-0.687283
H	-1.823613	-0.379921	-0.101651
N	3.797072	-1.283548	-1.279374
N	4.226112	-0.189495	0.52245
N	1.951601	1.573335	0.749475
C	0.733405	-2.04307	-0.042625
C	0.188793	-4.21493	0.306746
H	0.209148	-5.175471	0.796382
C	-0.524167	-3.786041	-0.764396
H	-1.246312	-4.286007	-1.391753
C	1.813339	-3.133819	1.937648
H	2.286546	-2.148808	1.925563
C	0.956364	-3.250359	3.202713
H	0.206197	-2.454884	3.230778
H	1.591007	-3.163935	4.09142
H	0.441782	-4.217366	3.250883
C	2.897932	-4.211926	1.846185
H	2.469131	-5.220793	1.83602
H	3.560066	-4.144556	2.715781
H	3.503723	-4.084722	0.942947
C	-0.780423	-1.613803	-1.998342
H	-0.63918	-2.080604	-2.976125
H	-0.270512	-0.649295	-1.963537
C	-2.303925	-1.441227	-1.794021
C	-3.967791	-0.435312	-0.298315
C	-4.539158	-1.155312	0.774851

C	-3.760592	-2.261011	1.482082
H	-3.05616	-2.676468	0.752541
C	-2.923481	-1.69114	2.647206
H	-2.172011	-0.980789	2.28671
H	-2.400176	-2.501293	3.17255
H	-3.566107	-1.18104	3.375531
C	-4.648238	-3.420785	1.965226
H	-4.020528	-4.242535	2.330592
H	-5.280771	-3.807354	1.158415
H	-5.301708	-3.124322	2.794427
C	-5.833228	-0.815993	1.185205
H	-6.292685	-1.351269	2.010369
C	-6.549999	0.191144	0.542809
H	-7.557276	0.435587	0.870894
C	-5.976862	0.879394	-0.521058
H	-6.544998	1.659336	-1.020796
C	-4.677386	0.59	-0.957864
C	-4.085976	1.370304	-2.127116
H	-3.033059	1.087208	-2.216523
C	-4.781681	0.989176	-3.449197
H	-4.701649	-0.087215	-3.626707
H	-4.319199	1.517278	-4.292675
H	-5.844949	1.259199	-3.429094
C	-4.120701	2.891951	-1.890072
H	-5.146676	3.270277	-1.808322
H	-3.643771	3.414605	-2.728079
H	-3.58486	3.16516	-0.974452
C	3.196103	-0.636274	-0.238817
C	5.181786	-1.233245	-1.156583
H	5.84638	-1.675071	-1.881554
C	5.449837	-0.540991	-0.020219
H	6.386199	-0.266327	0.440239
C	3.099686	-1.859787	-2.446182
H	2.043193	-1.683806	-2.246557
C	3.34429	-3.369741	-2.542748
H	4.402359	-3.597008	-2.71736
H	2.773204	-3.785443	-3.379502
H	3.027626	-3.877154	-1.626202
C	3.488001	-1.114817	-3.729195
H	3.299542	-0.041501	-3.628897
H	2.895658	-1.491892	-4.569551

H	4.546021	-1.258229	-3.97656
C	4.022108	0.672432	1.686211
H	4.989595	1.067328	1.995493
H	3.602741	0.08019	2.508431
C	3.103108	1.873007	1.376407
C	1.059036	2.671459	0.516889
C	0.947709	3.207663	-0.790569
C	1.865262	2.718823	-1.905761
H	2.162139	1.696728	-1.647743
C	3.150426	3.573512	-1.948495
H	2.916214	4.606715	-2.23408
H	3.862584	3.174984	-2.683644
H	3.635627	3.602316	-0.967937
C	1.194477	2.669689	-3.288918
H	0.263346	2.091004	-3.266134
H	1.868173	2.204456	-4.019996
H	0.95525	3.669352	-3.670079
C	0.034608	4.240316	-1.023146
H	-0.055174	4.663741	-2.019406
C	-0.759134	4.746877	0.00493
H	-1.462475	5.551608	-0.193707
C	-0.636784	4.223675	1.287138
H	-1.247161	4.630131	2.089343
C	0.265143	3.187912	1.571997
C	0.389725	2.686142	3.009575
H	1.039594	1.806641	2.994536
C	-0.959468	2.239209	3.60399
H	-1.67434	3.067792	3.670243
H	-0.813039	1.852697	4.620372
H	-1.414019	1.444673	3.003054
C	1.062648	3.750196	3.900125
H	2.036868	4.026779	3.489403
H	1.205536	3.363663	4.917688
H	0.443197	4.653172	3.971841
H	-0.465634	1.039063	0.912544

Table S3. B3LYP/LANL2DZ, 6-31G* optimized coordinates of **2b**.

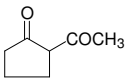
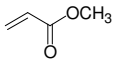
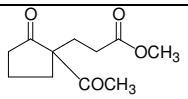
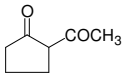
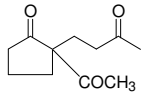
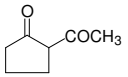
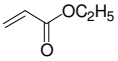
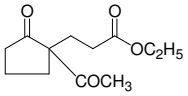
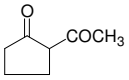
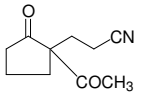
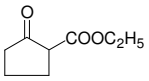
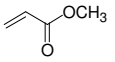
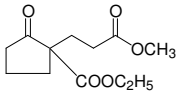
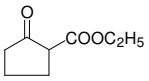
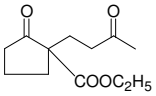
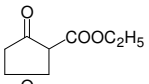
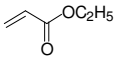
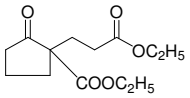
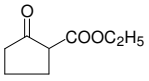
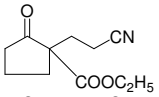
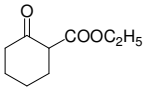
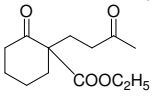
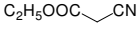
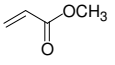
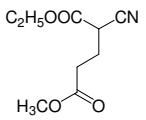
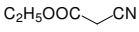
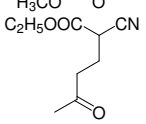
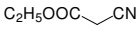
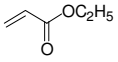
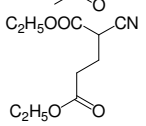
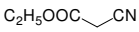
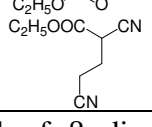
Ground state electronic energy = -2587.5712361 hartree/particle

Ni	-0.971359	0.526499	0.490663
O	0.848334	0.097021	0.567866
O	-1.277815	3.998823	2.738724
O	1.821773	-2.16947	-3.463522
N	-3.455301	1.644506	1.384601
N	-3.814391	0.820025	-0.566665
N	-0.664073	2.316328	1.263524
N	-1.589488	-2.357151	0.642025
N	-0.657285	-1.866865	-1.231705
N	2.260198	-0.981537	-1.532385
C	-2.843846	0.968679	0.381116
C	-4.774917	1.930572	1.075763
H	-5.421665	2.467615	1.752086
C	-5.004101	1.411025	-0.1567
H	-5.890929	1.397906	-0.76989
C	-3.610095	0.277653	-1.917443
H	-2.634359	-0.206653	-1.90266
H	-3.553032	1.116742	-2.620162
C	-4.696637	-0.686966	-2.344918
C	-4.852202	-1.92034	-1.695753
H	-4.189237	-2.180962	-0.874397
C	-5.844843	-2.811355	-2.0998
H	-5.953872	-3.76572	-1.591759
C	-6.694418	-2.482609	-3.160603
H	-7.465975	-3.179294	-3.476376
C	-6.545216	-1.259555	-3.814054
H	-7.199498	-0.998115	-4.641042
C	-5.550953	-0.366542	-3.40565
H	-5.434472	0.584505	-3.92065
C	-2.72658	2.123684	2.558491
H	-2.463804	1.272209	3.19712
H	-3.377734	2.79472	3.118216
C	-1.458656	2.913193	2.170606
C	0.536507	3.019507	0.916911
C	0.604263	3.699267	-0.32543
C	-0.628252	3.802357	-1.217483
H	-1.26102	2.93883	-0.98743
C	-1.435384	5.06999	-0.862813
H	-1.667559	5.102117	0.20621
H	-2.375127	5.107219	-1.429974
H	-0.86062	5.972619	-1.105405

C	-0.316233	3.754994	-2.722686
H	0.227167	4.644364	-3.062577
H	-1.248677	3.712341	-3.299801
H	0.287362	2.87703	-2.982319
C	1.797381	4.332286	-0.686259
H	1.860138	4.861162	-1.632913
C	2.910463	4.306241	0.152861
H	3.829595	4.805605	-0.143062
C	2.832958	3.648051	1.374876
H	3.698788	3.641082	2.031724
C	1.658889	2.998381	1.78322
C	1.618887	2.327827	3.155692
H	0.677847	1.774589	3.223385
C	2.756749	1.307449	3.354193
H	2.727121	0.5265	2.586264
H	2.659919	0.824948	4.335027
H	3.74515	1.780628	3.319653
C	1.619414	3.38496	4.278434
H	1.525593	2.901861	5.259696
H	0.783769	4.076995	4.147046
H	2.553756	3.960538	4.27906
C	-1.150881	-1.304118	-0.097418
C	-1.350482	-3.561938	-0.011327
H	-1.603969	-4.514055	0.428048
C	-0.768406	-3.251926	-1.196115
H	-0.41577	-3.870923	-2.006604
C	-2.134114	-2.249924	2.001299
H	-3.061029	-2.832503	2.044306
H	-2.396022	-1.196704	2.131506
C	-1.172201	-2.711033	3.079608
C	-1.569765	-3.68906	3.997232
H	-2.559155	-4.135378	3.915778
C	-0.709813	-4.093019	5.02165
H	-1.030052	-4.853764	5.72851
C	0.557136	-3.519937	5.130641
H	1.229317	-3.830848	5.925901
C	0.960235	-2.544698	4.212965
H	1.945545	-2.094601	4.294403
C	0.104205	-2.137639	3.188838
H	0.429554	-1.385238	2.471222
C	-0.027439	-1.13317	-2.330822

H	-0.155143	-0.070164	-2.11806
H	-0.525699	-1.391664	-3.268291
C	1.467687	-1.490347	-2.501357
C	3.68396	-1.160865	-1.507345
C	4.239011	-2.068872	-0.578386
C	3.337749	-2.915256	0.315843
H	2.408933	-2.357155	0.471593
C	3.931338	-3.19425	1.706412
H	4.805512	-3.854639	1.658854
H	3.18422	-3.689363	2.337157
H	4.235929	-2.266794	2.204805
C	2.977856	-4.236376	-0.397598
H	2.555865	-4.050217	-1.390585
H	2.250589	-4.810074	0.190993
H	3.872338	-4.857838	-0.529972
C	5.629992	-2.213179	-0.543066
H	6.080987	-2.904871	0.161901
C	6.448924	-1.487276	-1.405578
H	7.527798	-1.616315	-1.368242
C	5.884738	-0.595721	-2.311641
H	6.531195	-0.031632	-2.978577
C	4.49802	-0.404374	-2.37611
C	3.921217	0.590698	-3.377256
H	2.850995	0.685304	-3.170757
C	4.532237	1.996053	-3.219892
H	4.387934	2.381117	-2.204428
H	4.054892	2.694578	-3.918062
H	5.60732	2.001245	-3.435428
C	4.071659	0.068883	-4.820192
H	5.128952	-0.034066	-5.094832
H	3.608741	0.765007	-5.53114
H	3.590551	-0.90777	-4.925262
H	1.784838	-0.519129	-0.720542
H	1.302066	0.908523	0.844096

Table S4. Control and blank experiments of 1,4-Michael type activated C–H addition across α,β-activated substrates performed in presence and absence of $Ni(acac)_2$ and $NiCl_2•6H_2O$.

entry	reagent[a]	reagent[a]	product	$Ni(acac)_2$ yield[b] (%)	$NiCl_2•6H_2O$ yield[b] (%)	blank yield[b] (%)
1				0	0	0
2				8	0	0
3				0	0	0
4				0	0	0
5				0	0	0
6				12	0	0
7				0	0	0
8				0	0	0
9				0	0	0
10				0	0	0
11				5	0	0
12				0	0	0
13				0	0	0

[a] Reaction condition: 0.25 mmol of β–dicarbonyl or β–ketoester or α-cyano-ester compound, 0.38 mmol activated ethylene, 5 mol % of $Ni(acac)_2$, 3 mL of $CHCl_3$ at room temperature for 12 hours. [b] The yields were determined by GC using toluene as an internal standard.

References

[1]. (Complete reference 30) GAUSSIAN 03: Gaussian 03, Revision C.02, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A.; Gaussian, Inc., Wallingford CT, 2004.