Supporting Information

for

Tantallacyclopentadiene as a Unique Metal-containing Diene Ligand Coordinated to Nickel for Preparing Tantalum—Nickel Heterobimetallic Complexes

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1. NMR spectra of $TaCl_3(C_4H_2{}^tBu_2)Ni(COD)$ (4).

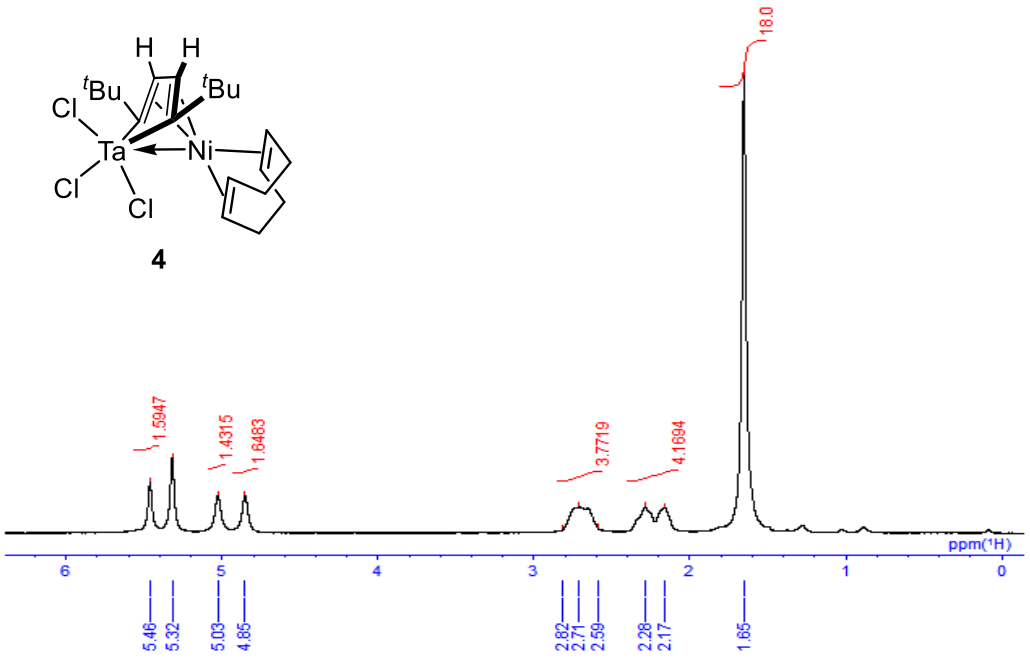

Figure S1. ^{1}H NMR spectrum of **4** in CD_2Cl_2 at 30 °C.

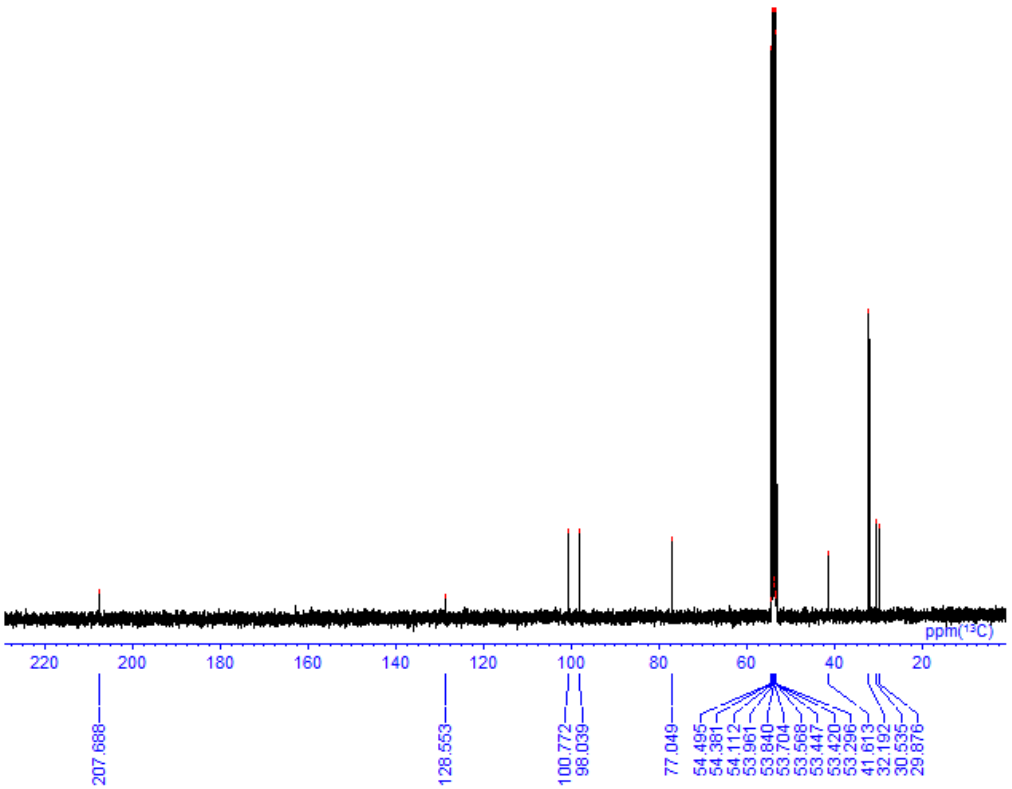

Figure S2. ^{13}C NMR spectrum of **4** in CD_2Cl_2 at 30 °C.

2. NMR spectra of $TaCl_3(C_4H_2{}^tBu_2)Ni(PMe_2Ph)_2$ (5).

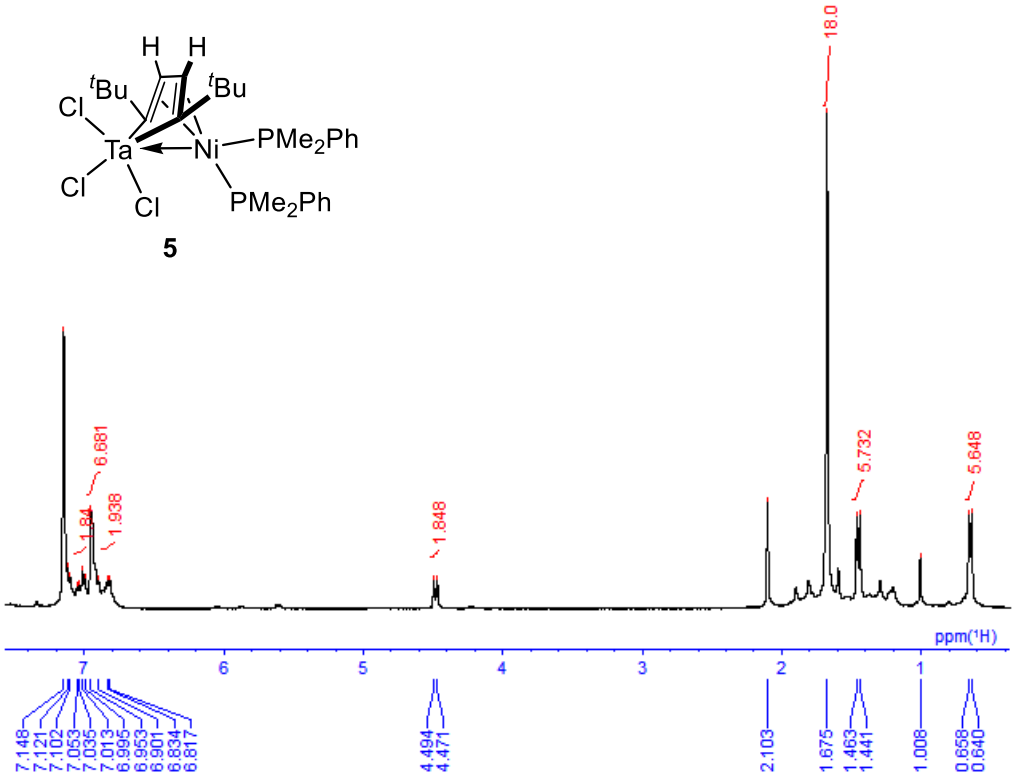

Figure S3. ^{1}H NMR spectrum of **5** in C_6D_6 at 30 °C.

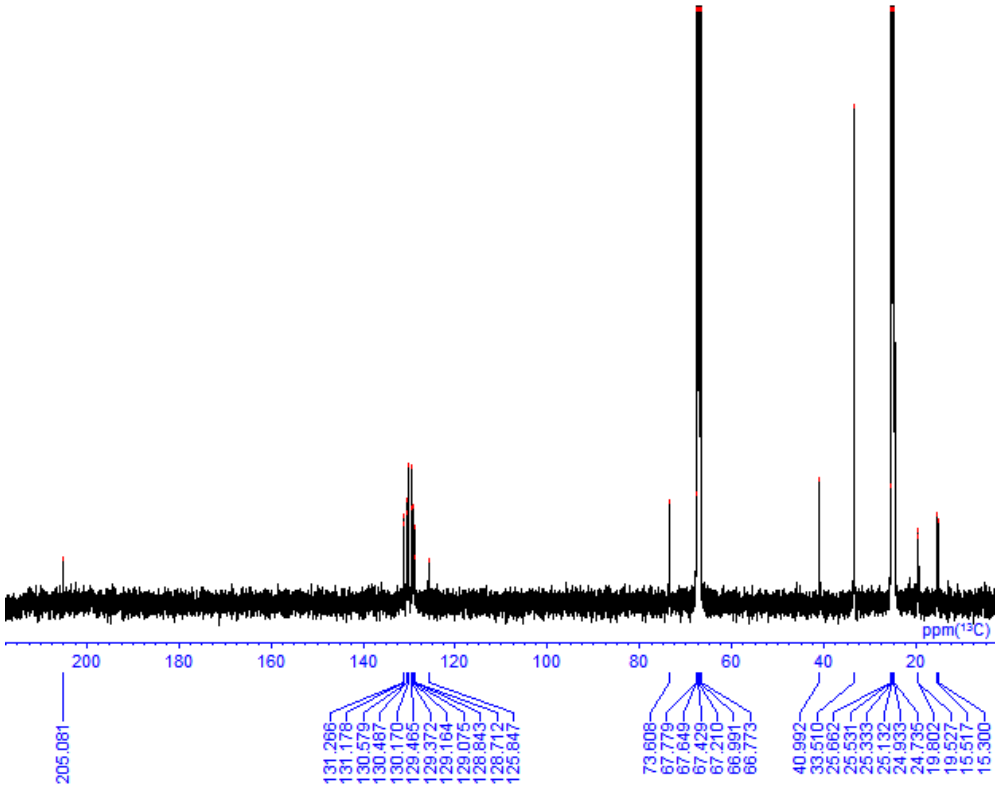

Figure S4. ^{13}C NMR spectrum of **5** in THF-d_8 at 30 °C.

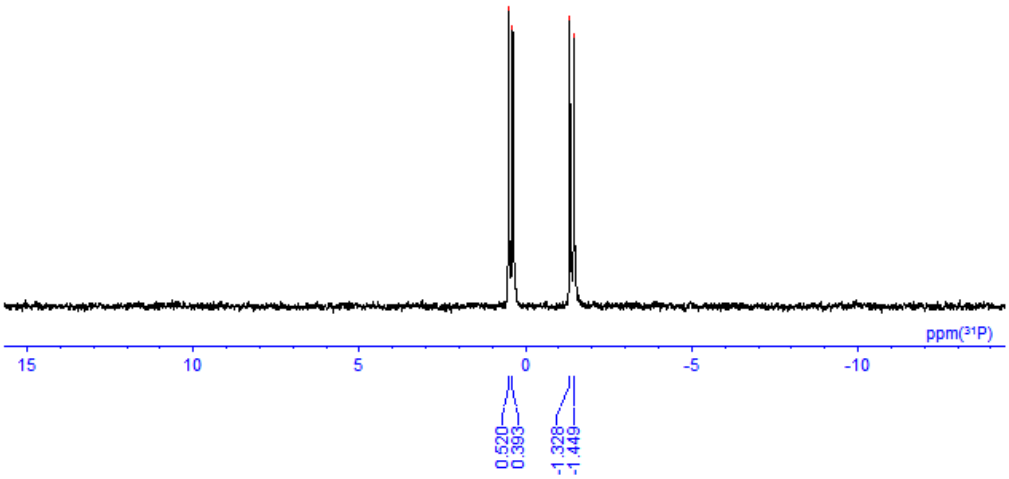

Figure S5. ^{31}P NMR Spectrum of **5** in THF-d_8 at 30 °C.

3. NMR spectra of $TaCl_3(C_4H_2{}^tBu_2)Ni(DPPE)$ (6a).

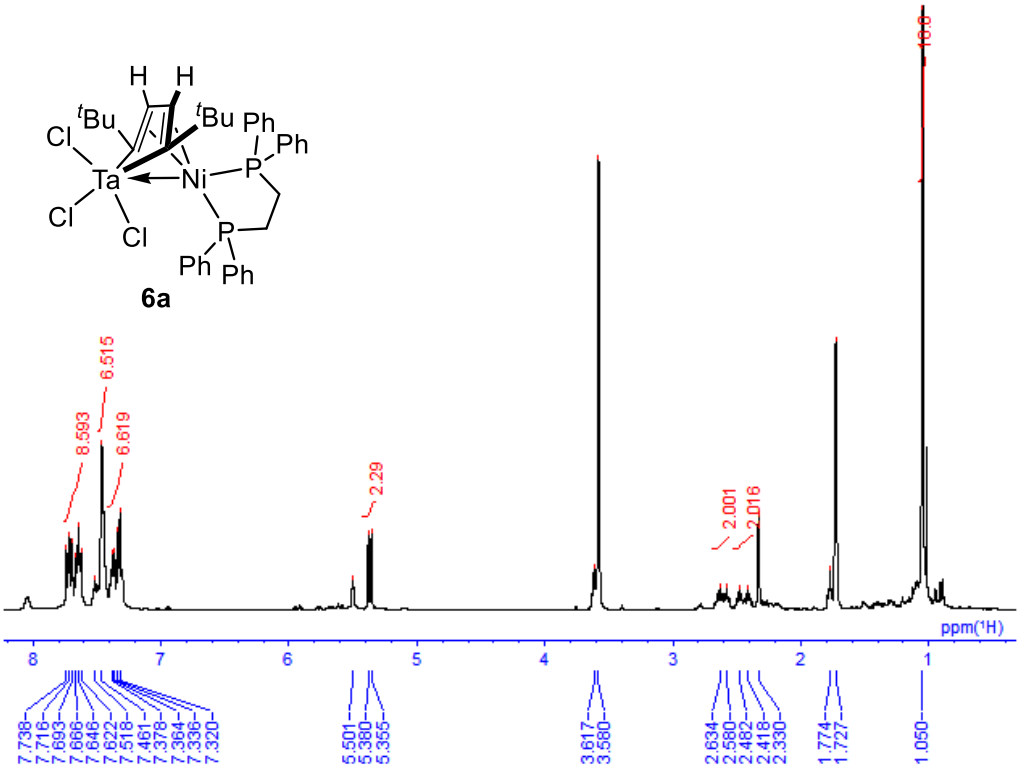

Figure S6. ^{1}H NMR Spectrum of **6a** in THF-d_8 at 30 °C.

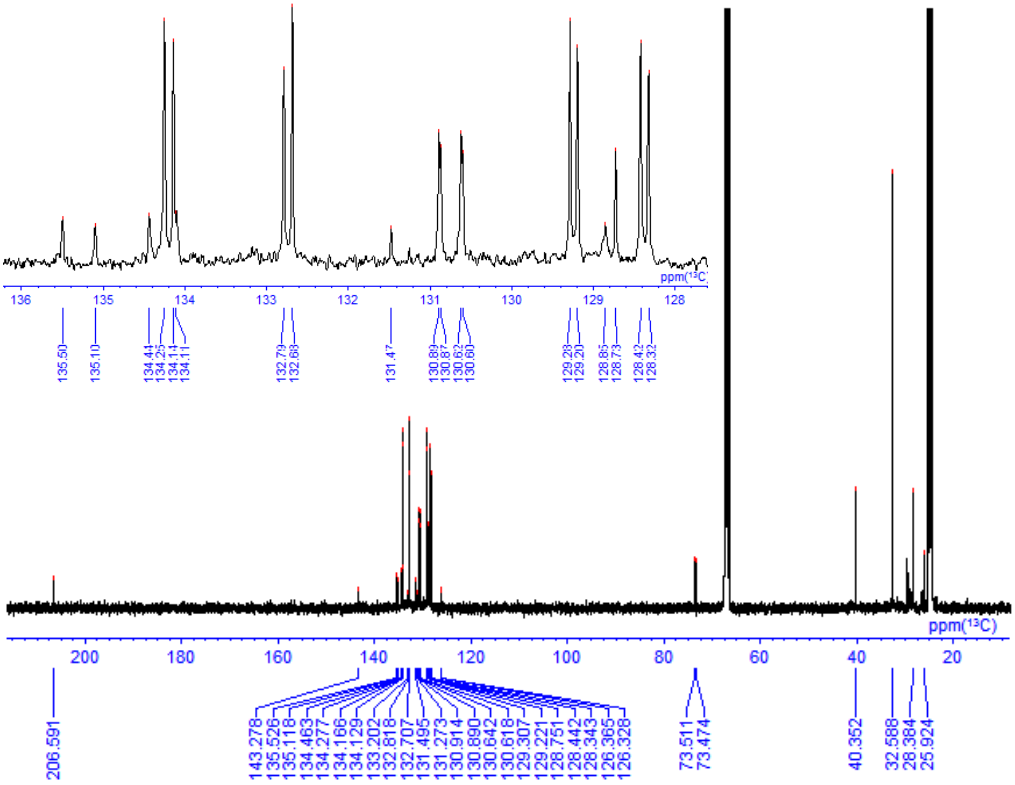

Figure S7. ^{13}C NMR Spectrum of **6a** in THF-d_8 at 30 °C.

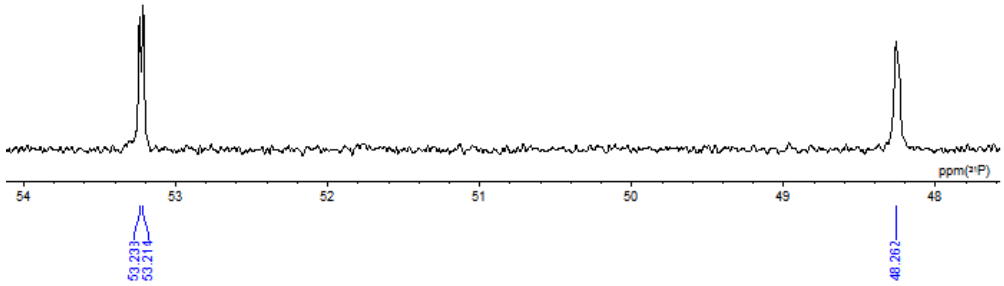

Figure S8. ^{31}P NMR Spectrum of **6a** in THF-d_8 at 30 °C.

4. NMR spectra of $TaCl_3(C_4H_2{}^tBu_2)Ni(DEPE)$ (6b).

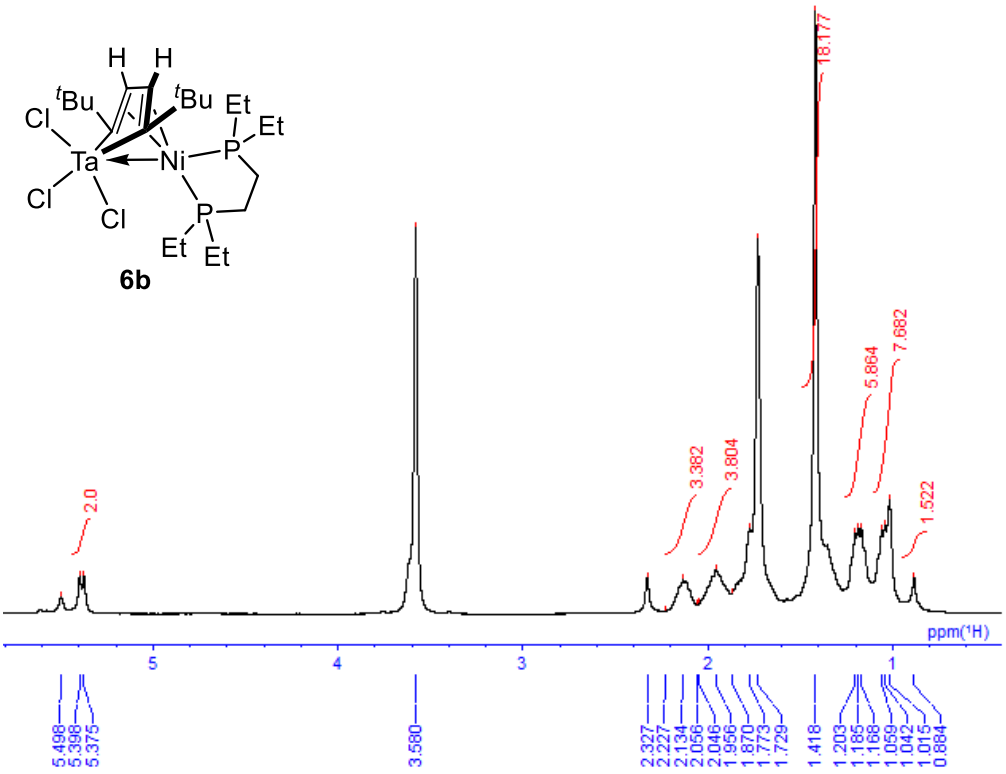

Figure S9. ^{1}H NMR Spectrum of **6b** in THF-d_8 at 30 °C.

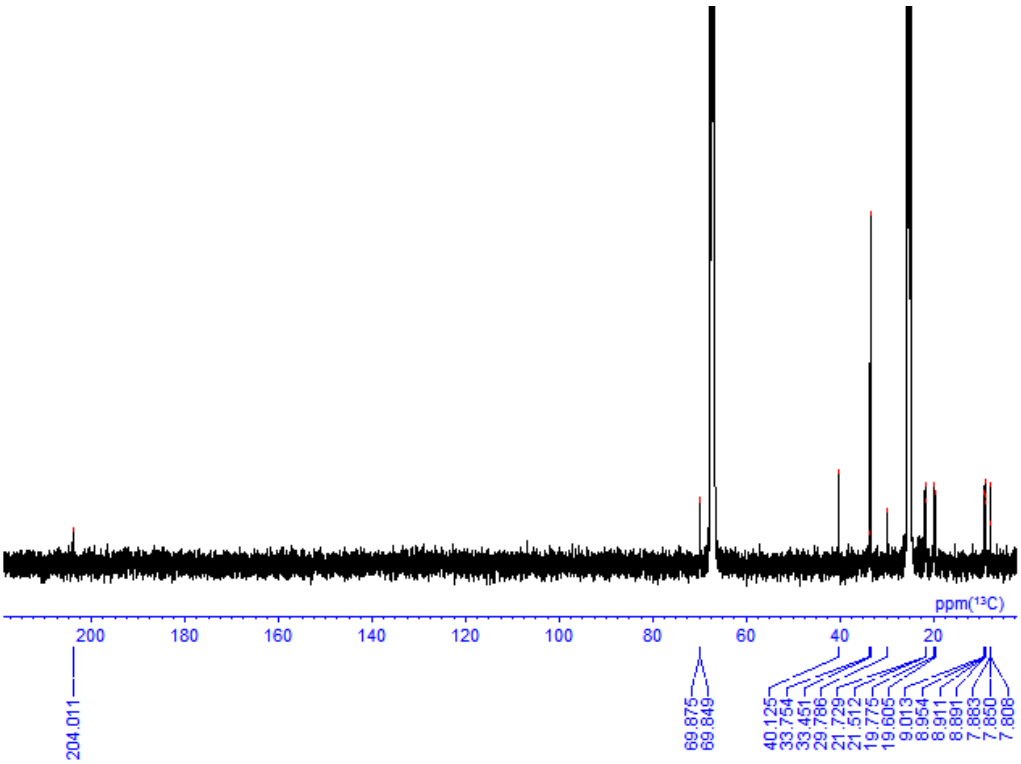

Figure S10. ^{13}C NMR Spectrum of **6b** in THF-d_8 at 30 °C.

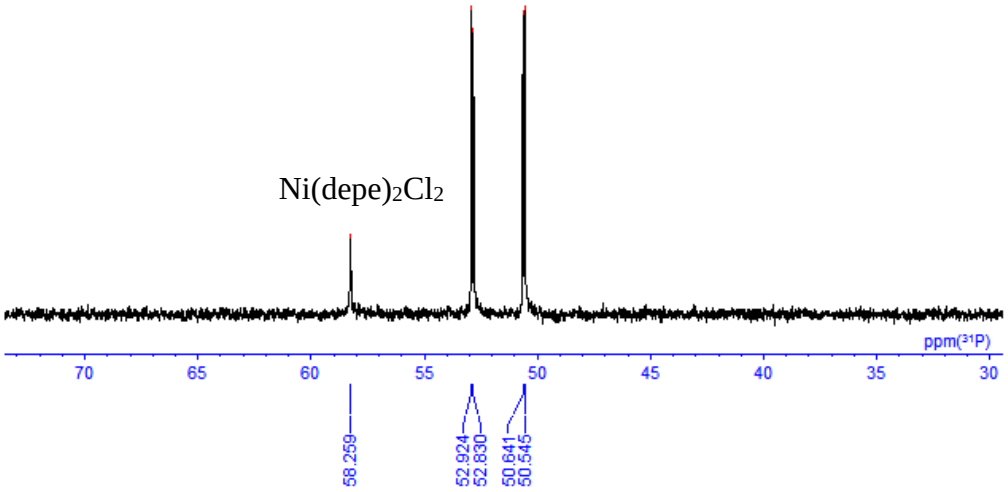

Figure S11. ^{31}P NMR Spectrum of **6b** in THF-d_8 at 30 °C.

5. NMR spectrum of $TaCl_3(C_4H_2{}^tBu_2)Ni(IPr)$ (7).

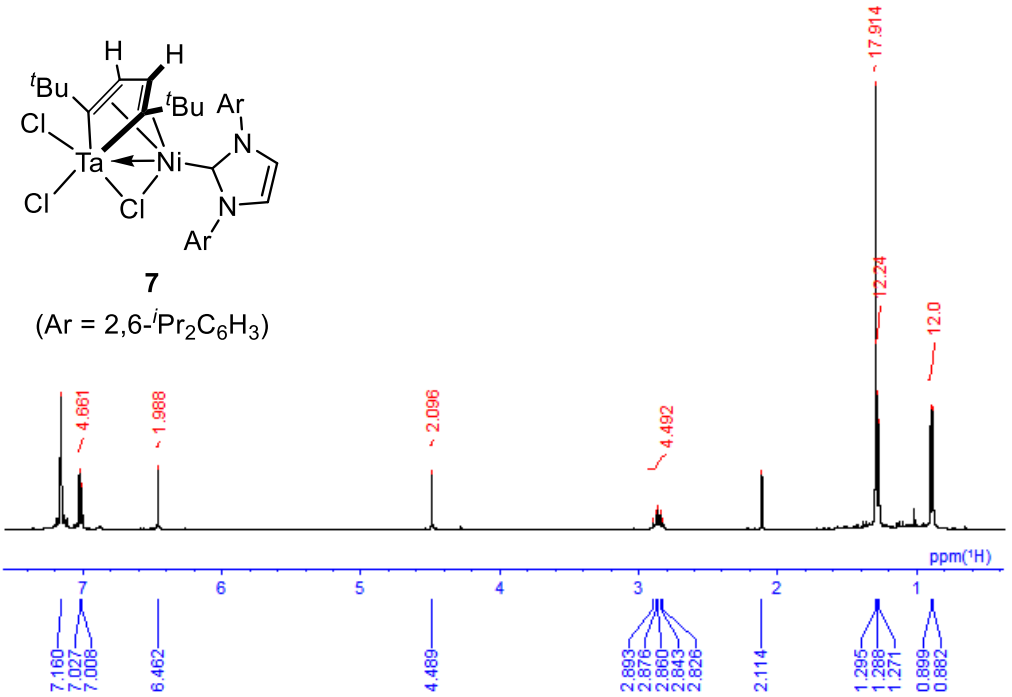

Figure S12. ^1H NMR Spectrum of **7** in C_6D_6 at 30 °C.

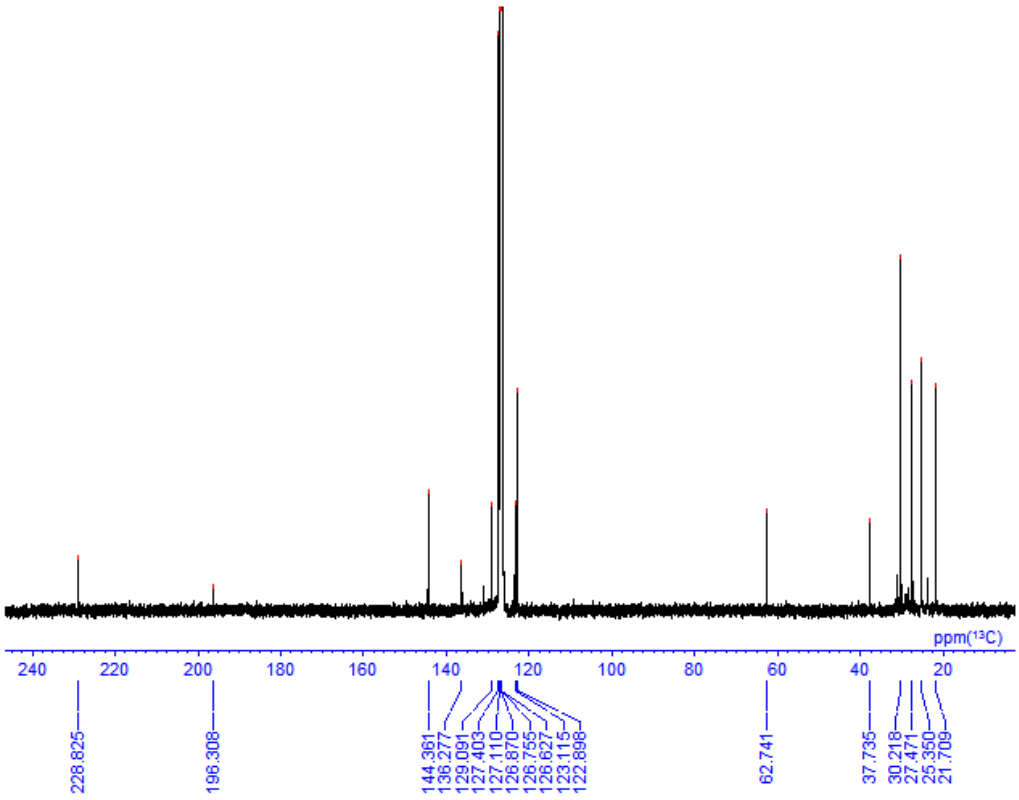

Figure S13. ^{13}C NMR Spectrum of **7** in C_6D_6 at 30 °C.

6. Crystal data and data collection parameters.

Table S1. Crystal data and data collection parameters of **4**, **6a**, and **7**.

	4	**6a**
empirical formula	$C_{20}H_{32}Cl_3NiTa$	$2(C_{38}H_{44}Cl_3NiP_2Ta)$, $1.5(C_6H_6)$
formula Weight	618.48	1934.61
crystal system	monoclinic	triclinic
space group	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)
a, Å	9.680(3)	13.970(12)
b, Å	16.427(5)	15.590(14)
c, Å	14.080(5)	19.400(17)
α, deg.	-	93.510(18)
β, deg.	104.420(3)	91.040(12)
γ, deg.	-	95.950(17)
V, Å^3	2168.3(12)	4193(6)
Z	4	2
D_{calcd}, g/cm^{-3}	1.894	1.532
μ [Mo-*K*α], mm^{-1}	6.275	3.348
T, K	113(2)	113(2)
crystal size, mm	0.31 × 0.25 × 0.23	0.34 × 0.18 × 0.15
θ range for data collection (deg.)	3.18 to 27.46	3.02 to 27.42
no. of reflections measured	19778	36920
unique data (R_{int})	0.0437	0.0502
data / restraints / parameters	4750 / 0 / 226	16664 / 0 / 892
*R*1 ($I > 2.0\sigma(I)$)	0.0430	0.0491
*wR*2 ($I > 2.0\sigma(I)$)	0.1063	0.1082
*R*1(all data)	0.0455	0.0638
*wR*2 (all data)	0.1085	0.1217
GOF on F^2	1.114	1.097
Δρ, e Å^{-3}	3.25, -1.74	1.89, -1.86

a) $R1 = (\Sigma||Fo| - |Fc||)/(\Sigma|Fo|)$ b) $wR2 = [\{\Sigma w(Fo^2-Fc^2)^2\}/\{\Sigma w(Fo^4)\}]^{1/2}$

Table S2. (continued)

	7
empirical formula	$C_{39}H_{56}Cl_3N_2NiTa$, 1.5(C_6H_6)
formula Weight	1016.01
crystal system	monoclinic
space group	*C*2/*c* (No. 15)
a, Å	44.286(13)
b, Å	11.294(3)
c, Å	19.288(5)
α, deg.	-
β, deg.	105.361(4)
γ, deg.	-
V, Å^3	9302(4)
Z	8
D_{calcd}, g/cm^{-3}	1.431
μ [Mo-*K*α], mm^{-1}	2.957
T, K	113(2)
crystal size, mm	0.31 × 0.13 × 0.13
θ range for data collection (deg.)	3.11 to 27.47
no. of reflections measured	42870
unique data (R_{int})	0.0429
data / restraints / parameters	10175 / 0 / 496
*R*1 ($I > 2.0\sigma(I)$)	0.0423
*wR*2 ($I > 2.0\sigma(I)$)	0.0941
*R*1(all data)	0.0458
*wR*2 (all data)	0.0969
GOF on F^2	1.156
Δρ, e Å^{-3}	2.87, -1.35

a) $R1 = (\Sigma||Fo| - |Fc||)/(\Sigma|Fo|)$ b) $wR2 = [\{\Sigma w(Fo^2-Fc^2)^2\}/\{\Sigma w(Fo^4)\}]^{1/2}$

7. Single-point DFT Calculation (B3LYP/LANL2DZ, 6-311G(d)) for IPr-coordinated Ta-Ni complex 7.

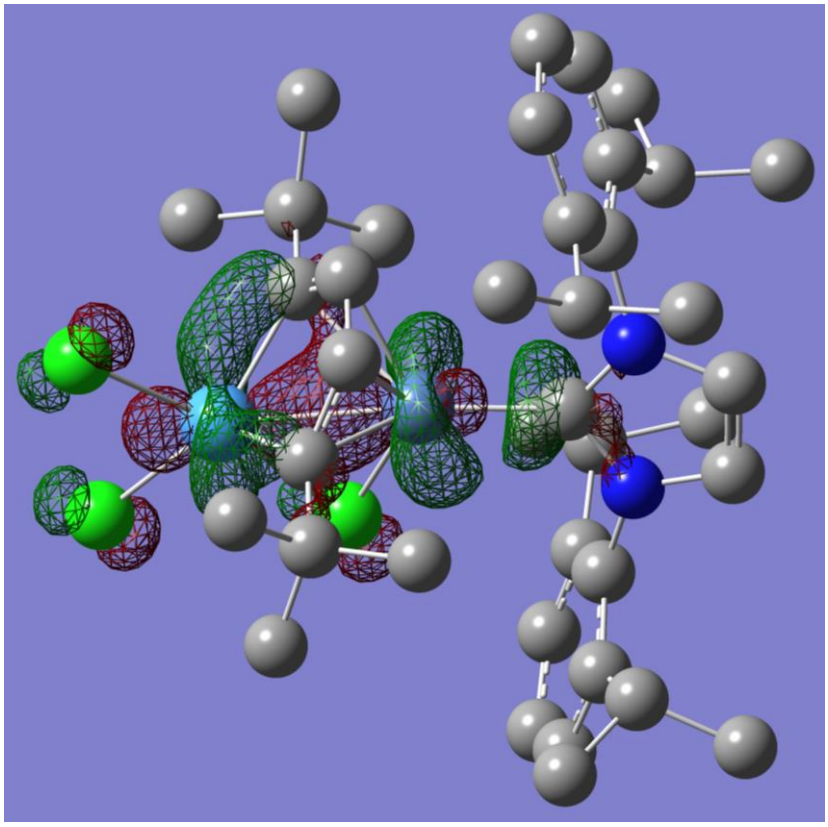

Figure S14. Molecular Orbital for HOMO-1 of complex **7**.

Table S3. Cartesian coordinates for the structural calculation of complex **7**.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	73	0	2.737869	-0.085703	-0.149792
2	28	0	0.157498	-0.004730	-0.039269
3	17	0	4.451535	-1.374406	0.863249
4	17	0	4.435363	1.186125	-1.220977
5	17	0	1.253241	1.591222	-1.240004
6	7	0	-2.719348	-0.659052	0.620528
7	7	0	-2.476224	1.379840	-0.022455
8	6	0	1.530144	-1.564753	-0.890824

9	6	0	0.872128	-1.914180	0.300785
10	6	0	0.953911	-1.083453	1.495828
11	6	0	1.646596	0.143190	1.560154
12	6	0	1.450015	-2.308083	-2.219107
13	6	0	2.813990	-2.183307	-2.914426
14	6	0	1.113233	-3.790613	-2.011243
15	6	0	0.386643	-1.626137	-3.090758
16	6	0	1.732065	1.011607	2.796380
17	6	0	0.350241	1.226120	3.432086
18	6	0	2.337640	2.356582	2.416277
19	6	0	2.646751	0.306366	3.813146
20	6	0	-1.770902	0.210010	0.130510
21	6	0	-3.949405	-0.024704	0.809042
22	6	0	-3.790118	1.242996	0.403996
23	6	0	-2.525228	-2.094485	0.730660
24	6	0	-2.160252	-2.650254	1.968411
25	6	0	-1.877090	-4.020784	1.991372
26	6	0	-2.009660	-4.794157	0.857353
27	6	0	-2.469871	-4.238133	-0.333075
28	6	0	-2.750441	-2.872303	-0.416626
29	6	0	-2.121950	-1.819765	3.239437
30	6	0	-1.184346	-2.387287	4.315348
31	6	0	-3.540415	-1.703851	3.848243
32	6	0	-3.338798	-2.290547	-1.696510
33	6	0	-2.982298	-3.070948	-2.965503
34	6	0	-4.877374	-2.206776	-1.592575
35	6	0	-1.955210	2.590128	-0.615991
36	6	0	-1.766858	3.719497	0.181946
37	6	0	-1.180302	4.837449	-0.429832
38	6	0	-0.856181	4.840367	-1.765995
39	6	0	-1.142541	3.736123	-2.545590
40	6	0	-1.703991	2.586107	-2.003111
41	6	0	-2.211085	3.805863	1.630326
42	6	0	-3.533735	4.593228	1.703791
43	6	0	-1.178413	4.481873	2.540659

44	6	0	-2.029296	1.384790	-2.886310
45	6	0	-1.304186	1.388760	-4.231169
46	6	0	-3.545850	1.284117	-3.113055
47	1	0	2.786176	-2.655778	-3.773054
48	1	0	3.017249	-1.237984	-3.067335
49	1	0	3.506961	-2.580008	-2.346125
50	1	0	1.068565	-4.239684	-2.881291
51	1	0	1.809579	-4.209257	-1.463066
52	1	0	0.248618	-3.868835	-1.557786
53	1	0	0.321017	-2.092962	-3.950362
54	1	0	-0.480091	-1.658902	-2.634729
55	1	0	0.640135	-0.692262	-3.244520
56	1	0	0.441603	1.791207	4.227712
57	1	0	-0.241343	1.664999	2.785841
58	1	0	-0.029321	0.360086	3.687709
59	1	0	2.396863	2.925249	3.212008
60	1	0	3.234937	2.217634	2.046533
61	1	0	1.771992	2.791631	1.744849
62	1	0	2.716188	0.852975	4.623844
63	1	0	2.268312	-0.568562	4.040588
64	1	0	3.537132	0.186000	3.422915
65	1	0	-4.743405	-0.415731	1.156635
66	1	0	-4.454769	1.921986	0.407874
67	1	0	-1.590193	-4.425952	2.801846
68	1	0	-1.782254	-5.716096	0.887603
69	1	0	-2.595038	-4.791686	-1.094335
70	1	0	-1.807422	-0.901298	3.003036
71	1	0	-1.205411	-1.807209	5.105101
72	1	0	-1.478174	-3.288140	4.563135
73	1	0	-0.270323	-2.426319	3.963517
74	1	0	-3.501709	-1.166520	4.666959
75	1	0	-4.138820	-1.273077	3.202480
76	1	0	-3.879530	-2.598749	4.060697
77	1	0	-2.987869	-1.360014	-1.799993
78	1	0	-3.395179	-2.638251	-3.741942

79	1	0	-2.008740	-3.083584	-3.078551
80	1	0	-3.314134	-3.989692	-2.888506
81	1	0	-5.239671	-1.831242	-2.422352
82	1	0	-5.243782	-3.104064	-1.452286
83	1	0	-5.122066	-1.630925	-0.838855
84	1	0	-1.005102	5.611943	0.091688
85	1	0	-0.436035	5.598894	-2.152162
86	1	0	-0.951237	3.763773	-3.475150
87	1	0	-2.373893	2.879260	1.967932
88	1	0	-3.827644	4.652736	2.637443
89	1	0	-3.398758	5.495369	1.346215
90	1	0	-4.218996	4.131733	1.175694
91	1	0	-1.520105	4.508570	3.458671
92	1	0	-0.340864	3.973138	2.518648
93	1	0	-1.013913	5.395366	2.226505
94	1	0	-1.743155	0.562778	-2.393976
95	1	0	-1.559956	0.592822	-4.742205
96	1	0	-1.552843	2.193170	-4.733251
97	1	0	-0.336282	1.383887	-4.080380
98	1	0	-3.740098	0.510120	-3.682064
99	1	0	-3.998255	1.178519	-2.250925
100	1	0	-3.864610	2.100410	-3.552170
101	1	0	0.359650	-2.714658	0.328207
102	1	0	0.512897	-1.387510	2.280482
