Supporting Information:

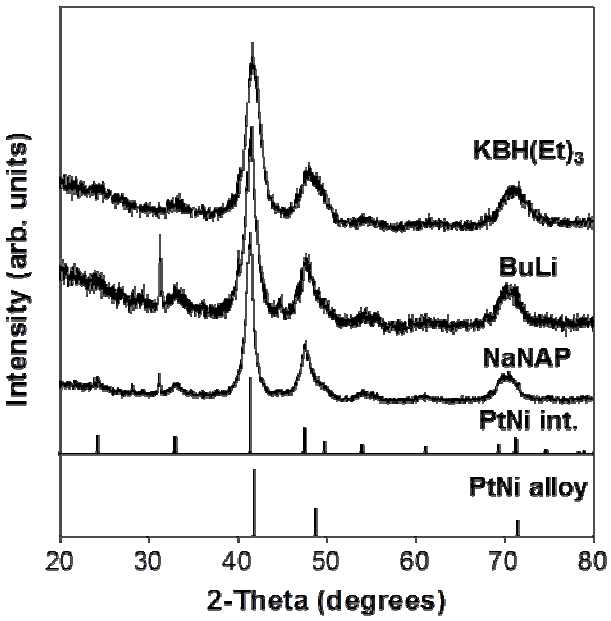

Figure S1. a) X-ray diffraction (XRD) patterns of PtNi nanoparticles made with $M(acac)_2$ precursors and annealed at 500°C using $KBH(Et)_3$ n-BuLi, and sodium naphthalide. The peak positions for the intermetallic phase of PtNi (PDF # 30652797) are shown as tick marks at the bottom. The peaks marked with an asterisk are due to ordering of the Pt-Ni to form a tetragonal structure. Pt-Ni alloys have an fcc structure lacking these peaks. The sharp line at 32 degrees is due to an unknown impurity.

There is a minor impurity phase present in the sample seen as a sharp peak at ~32°. This peak does not match any known oxide, carbide, or boride phases for either of the metals and remain unidentified. It is evident from the diffraction patterns that the domain size depends somewhat on the reducing agent used but are about 15-20 nm for the samples annealed at 500°C. The as-prepared samples all have a very broad diffraction pattern suggesting either amorphous particles or very small domain sizes making the Scherrer determination of particle sizes extremely difficult. Additionally, the ordering peaks are weak compared to the main peaks, and the broadening makes it difficult to observe them above background noise.

A great degree of aggregation and sintering can also be seen in the annealed sample as there was no effort to control aggregation up to this point. The main goal here was to synthesize the ordered intermetallic phase with a clean surface so its catalytic activity could be studied. Size control for these intermetallic phases has been demonstrated previously by simply attaching the particles to a support like carbon black, but that was not investigated here[1]. The products from each of the reducing agents looked quite similar by TEM with the as-made particles appearing nearly spherical and aggregated sintered particles after annealing to 500°C.

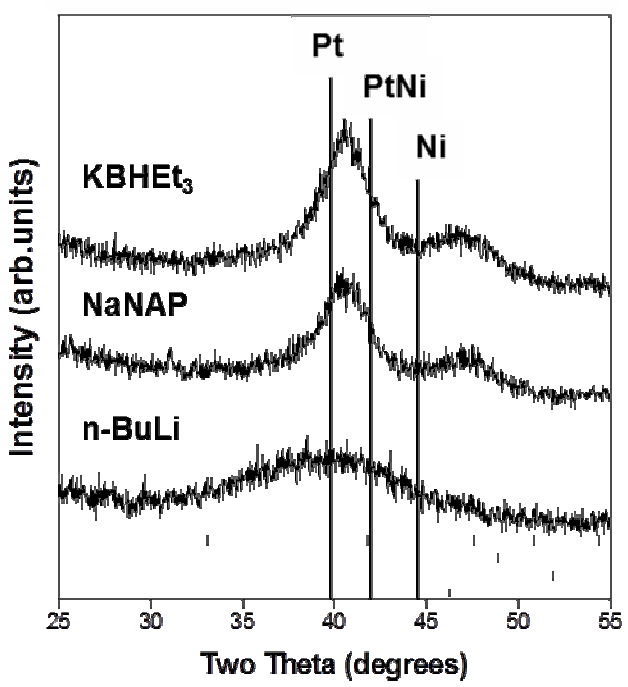

Figure S2. XRD of as made particles synthesized from Li_2NiCl_4 and $PtCODCl_2$ precursors using $KBH(Et)_3$, sodium naphthalide (NaNAP), and n-BuLi. The (111) peak position for Pt, Ni, and PtNi have been added in to emphasize the alloying that takes place between the Pt and Ni at room temperature.

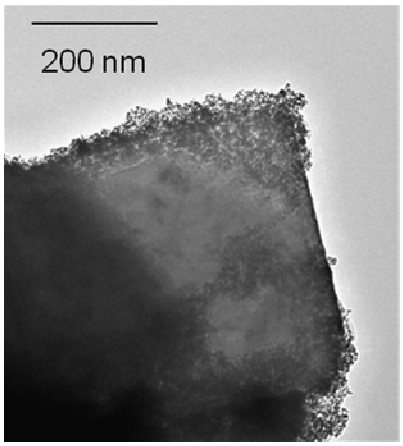

Figure S3. TEM image of the as made particles synthesized from Li_2NiCl_4 and $PtCODCl_2$ precursors using $KBH(Et)_3$. The sample is unwashed showing a large KCl crystal with small PtNi particles.

Table S1. Onset potentials and current densities at different voltages for PtNi nanoparticles synthesized with different reducing agents and precursors for formic acid oxidation (all potentials are vs. Ag/AgCl (NaCl sat.)).

catalyst	onset potential (mV)	current (mA)			
		-100 mV	0 mV	+100 mV	+200 mV
acac NaNAP as made	-30	-0.006	0.006	0.034	0.102
acac NaNAP 500°C	100	-0.003	-0.001	0.001	0.003
acac $KBHEt_3$ as made	-100	0.001	0.009	0.032	0.116
acac $KBHEt_3$ 500°C	100	-0.004	-0.002	0.001	0.008
acac BuLi as made	-30	-0.003	0.003	0.013	0.026
after cathodic treatment	-40	-0.004	0.006	0.026	0.058
acac BuLi 500°C	-175	0.018	0.075	0.204	0.419
Cl- NaNAP as made	-30	-0.001	0.003	0.017	0.069
Cl- NaNAP 500°C	-100	0.001	0.021	0.089	0.241
Cl- $KBHEt_3$ as made	-100	0.001	0.005	0.016	0.041
Cl- $KBHEt_3$ 500°C	-110	0.003	0.050	0.207	0.546
Cl- $KBHEt_3$ 600°C	-70	-0.004	0.034	0.154	0.420
Cl- $KBHEt_3$ 300°C	-60	-0.001	0.005	0.019	0.051
Cl- $LiBHEt_3$ as made	0	0	0.002	0.007	0.019
Cl- $LiBHEt_3$ 500°C	50	-0.008	-0.003	0.009	0.339

(1) Ghosh, T.; Leonard, B. M.; Zhou, Q.; DiSalvo, F. J. *Chemistry of Materials*, *22*, 2190-2202.