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Which one is faster?A kinetic investigation of Pd and Ni catalyzed Negishi-type oxidative coupling reactions

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Supporting Information

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Analytical methods and reagents

All reactions and manipulations were performed in a nitrogen-filled self-prepared three-necked micro reactor. IR spectra were recorded on a Bruker TENSOR 27 spectrometer using a diamond probe. Gas chromatographic analyses were performed on Varian GC 2000 gas chromatography instrument with a FID detector. Yields of Ar-Ar were obtained from GC and biphenyl was added as internal standard. The glassware was oven dried at 120 ^{o}C for more than 1 hour prior to use. THF were dried and distilled from sodium/benzophenone ketyl under nitrogen. $ZnCl_2$ was from commercial source and reflux with $SOCl_2$ for 5 h. $SOCl_2$ was removed and $ZnCl_2$ as a white fine powder was obtained. $Ni(acac)_2$ was commercial available and reflux with toluene using an oil-water separator to make it dried and stored in glovebox. $Pd(OAc)_2$ was commercial available. Tetrabutylammonium bromide was commercial available. Arylzinc reagent was prepared from the corresponding aryl Grignard reagent with $ZnCl_2$ and the concentration was based on the titration by I_2/LiCl.[1] 2-Chloro-1,2-diphenyl-ethanone (Desyl-Cl) was prepared from $SOCl_2$ and benzoin.[2] All of other substrates were obtained from commercial source (Acros and Aldrich) and used without further purification.

Preparation of arylzinc reagent

Arylzinc reagent was prepared from aryl bromide and magnesium chips. To a 100 mL three-neck tube was added magnesium chips (22 mmol) and THF (10 mL). The mixture of aryl bromide (20 mmol) and THF (20 mL) was allowed to drop in slowly via a dropping funnel. Then the mixture was heated to 70 ^{o}C, 3 h later, the mixture was injected to the tube filled with the solution of $ZnCl_2$ (30 mmol in 30 mL THF). The mixture was allowed to cool down to room temperature. After stirring for 2h, the concentration of the arylzinc reagent was identified based on the titration by I_2/LiCl.[1]

General procedures of Negishi-type oxidative coupling reactions

In an oven dried self-prepared three-necked micro reactor with a magnetic stirrer, 2-Chloro-1,2-diphenyl-ethanone (115.3 mg, 0.5 mmol), biphenyl (73.5 mg) as the internal standard were added. The reactor was allowed to be vacuumed and purged with nitrogen for three times. The arylzinc reagent (0.39 M, 5 mL, 1.95 mmol) was added in via a syringe. The mixture was allowed to stir at 0 ^{o}C or 60 ^{o}C and recorded by IR spectrometer. At the same time, solution of $Ni(acac)_2$ or $Pd(OAc)_2$ in THF (0.1 mL) was added in by a micro syringe. The concentration of catalyst precursor was set from $1x10^{-3}$ M to $1x10^{-7}$ M. The progress of the reaction can be observed from the characteristic IR spectra of arylzinc reagent and Ar-Ar. After about 3 h, the reaction was stopped and quenched by saturated NH_4Cl and the yield was determined by GC. For experiments which the catalyst precursor concentration was in the range between $1x10^{-6}$ M to $1x10^{-7}$ M, TetraButylAmmonium Bromide (160 mg) was added.

Sample preparation for TEM

In an oven dried self-prepared three-necked micro reactor with a magnetic stirrer, 2-Chloro-1,2-diphenyl-ethanone (115.3 mg, 0.5 mmol), was added. The reactor was allowed to be vacuumed and purged with nitrogen for three times. The arylzinc reagent (0.39 $molL^{-1}$, 5 mL, 1.95 mmol) was added in via a syringe. The mixture was allowed to stir at 60 ^oC, then solution of $Ni(acac)_2$ or $Pd(OAc)_2$ in THF (0.1 mL, 0.001 mol%) was added in by a micro syringe. After 15 min, the mixture was drawn via a syringe and dropped on a copper net for TEM examination. The copper net was washed with water and alcohol for three times. Then copper net was dried via an aurilave.

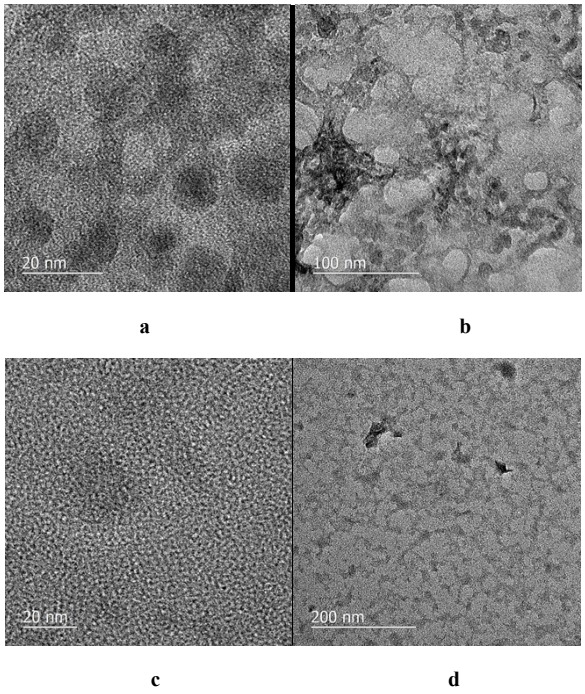

Figure S1 TEM sample from model reaction. **a. b.** $1x10^{-6}$ M $Pd(OAc)_2$ as catalyst; **c. d.** $1x10^{-6}$ M $Ni(acac)_2$ as catalyst.

Pd nanoparticle of the size in the range of 5-10 nm was observed via TEM, whereas no discernable nanoparticle was observed for Ni at the same condition.

XANES Data Collection and Analysis

Data of Ni

General Information

X-ray absorption measurements were acquired on the insertion device beam line of the Materials Research Collaborative Access Team (MRCAT) at the Advanced Photon Source, Argonne National Laboratory. The data were collected in transmission quick scan mode. Insertion device experiments utilized a cryogenically cooled double-crystal Si (111) monochromator in conjunction with an uncoated glass mirror to minimize the presence of harmonics. The monochromator was scanned continuously during the measurements with data points integrated over 0.5 eV for 0.03 s per data point. The ionization chambers were optimized for the maximum current with linear response (~10^{10} photons detected/sec) with 10% absorption (30% He and 70% N_2) in the incident ion chamber and 70% absorption (70% N_2 and 30% Ar) in the transmission detector. A Ni foil spectrum (edge energy 8333 eV) was acquired simultaneously with each measurement for energy calibration and multiple scans were taken to ensure spectrum reproducibility.

All the solution samples were prepared in a glove box and placed in a sample holder made of PEEK (polyether ether ketone) equipped with a screw top and O-ring fitting to prevent exposure to air and water. For solution samples, the Ni concentration was adjusted to be 0.05 - 0.1 M with a path length of 3.5 mm. Each solid sample was mixed with boron nitride to a weight ratio of about 2% (Ni) in the glove box. The mixture was grinded well with mortar and pestle, and then 20 mg of the mixture was pressed into a cylindrical sample holder consisting of six wells with a radius of 2.0 mm, forming a self-supporting wafer. The sample holder was placed in a quartz tube (1–in. OD, 10–in. length) sealed with Kapton windows by two Ultra-Torr fittings and then used for transmission mode measurement.

The edge energy of the X-Ray absorption near edge structure (XANES) spectrum was determined from the inflection point in the edge, i.e., the maximum in the first derivative of the XANES spectrum. The pre-edge energy was determined from the maximum of the pre-edge peak. Background removal and normalization procedures were carried out using the Athena software package using standard methods.

Solution Sample Preparation

Ni(acac)$_2$/THF solution: 0.3 mmol Ni(acac)$_2$ was added into a 20 mL vial in a glove box. After the vial was sealed, it was taken out of the glove box and 3 mL of dry THF was added through syringe. Then the solution was transferred into the XAFS solution cell through syringe and used for XANES measurement.

Ni(acac)$_2$ + 5 PhZnCl THF solution: 0.3 mmol Ni(acac)$_2$ was added into a 20 mL vial in a glovebox. After the vial was sealed, it was taken out of the glove box and 3 mL of PhZnCl (0.5 M) was added through syringe. Then the solution was transferred into the XAFS solution cell through syringe and used for XANES measurement.

Ni(acac)$_2$ + 5 PhZnCl + desyl-Cl THF solution: 0.3 mmol Ni(acac)$_2$ and 0.3 mmol 2-Chloro-1,2-diphenyl-ethanone (Desyl-Cl) were added into a 20 mL vial in a glove box. After the vial was sealed, it was taken out of the glove box and 0.3 mL of dry THF was added through syringe. Then 3 mL of PhZnCl (0.5 M) was added through syringe and then the solution was transferred into the XAFS solution cell through syringe and used for XANES measurement.

Table S1 Edge Energy and Oxidation States

Sample	Pre-edge Energy (eV)	Edge Energy (eV)	Oxidation State
Ni foil	N.A.	8333.0	0
$Ni(PPh_3)_4$	N.A.	8333.2	0
$Ni(acac)_2$ (solid)	8333.5	8346.2	II
$NiCl_2$	8333.4	8341.4	II
K_2NiF_6	8335.4	8344.4	IV
$Ni(acac)_2$ (THF solution)	8333.5	8345.9	II
Ni(acac)2 + 5 PhZnCl in THF	8333.7	8346.1	0 and II
Ni(acac)2 + 5 PhZnCl + desyl-Cl in THF	8333.6	8346.1	II

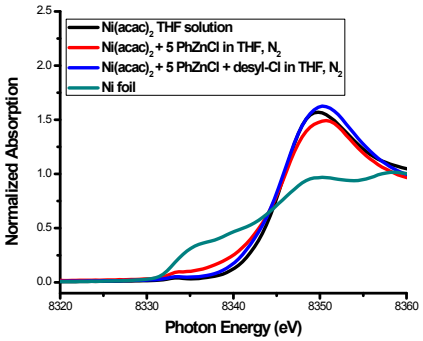

Figure S2 EXAFS results of Ni sample.

Sample $Ni(acac)_2$ + 5 PhZnCl THF solution: $Ni(acac)_2$ can be reductive to Ni(0) by PhZnCl slowly, mixture of Ni(0) and Ni(II) could be observed via EXAFS.

$Ni(acac)_2$ + 5 PhZnCl + desyl-Cl THF solution: in the similar condition of reaction, Ni(II) was obtained.

Data of Pd

General Information

X-ray absorption measurements were acquired on the insertion device beam line of the Materials Research Collaborative Access Team (MRCAT) at the Advanced Photon Source, Argonne National Laboratory. The data were collected in transmission quick scan mode. Insertion device experiments utilized a cryogenically cooled double-crystal Si (111) monochromator in conjunction with an uncoated glass mirror to minimize the presence of harmonics. The monochromator was scanned continuously during the measurements with data points integrated over 0.5 eV for 0.03 s per data point. The ionization chambers were optimized for the maximum current with linear response (~10^{10} photons detected/sec) with 10% absorption (65% Ar and 35% N_2) in the incident ion chamber and 15% absorption (100% Ar) in the transmission detector. A Pd foil spectrum (edge energy 24350 eV) was acquired simultaneously with each measurement for energy calibration.

All the solution samples were prepared in a glove box and placed in a sample holder made of PEEK (polyether ether ketone) equipped with a screw top and O-ring fitting to prevent exposure to air and water. For solution samples, the Pd concentration was adjusted to be 0.05 - 0.1 M with a path length of 10.0 mm. Each solid sample was mixed with boron nitride to a weight ratio of about

5% (Pd) in the glove box. The mixture was grinded well with mortar and pestle, and then 20 mg of the mixture was pressed into a cylindrical sample holder consisting of six wells with a radius of 2.0 mm, forming a self-supporting wafer. The sample holder was placed in a quartz tube (1–in. OD, 10–in. length) sealed with Kapton windows by two Ultra-Torr fittings and then used for transmission mode measurement.

The edge energy of the X-Ray absorption near edge structure (XANES) spectrum was determined from the inflection point in the edge, i.e., the maximum in the first derivative of the XANES spectrum. The pre-edge energy was determined from the maximum of the pre-edge peak. Background removal and normalization procedures were carried out using the Athena software package using standard methods.

Solution Sample Preparation

$Pd(OAc)_2$ + 10 PhZnBr + 10 desyl-Cl THF solution: 0.1 mmol $Pd(OAc)_2$ and 1 mmol 2-Chloro-1,2-diphenyl-ethanone (Desyl-Cl) were added into a 20 mL vial in a glove box. After the vial was sealed, it was taken out of the glove box and 5 mL of dry DMF was added through syringe. Then 2 mL of PhZnCl (0.5 M) was added through syringe and then the solution was transferred into the XAFS solution cell through syringe and used for XANES measurement.

Table S2 Summary of the XANES results

Sample	Conditions	Edge Energy (eV)	Oxidation State
Pd foil	Air, RT	24350.0	0
Pd(PPh3)4	Solid, N2, RT	24350.0	0
Pd(DBA)2	Solid, N2, RT	24350.1	0
PdO	Solid, air, RT	24353.3	II
Na2PdCl4	Solid, N2, RT	24352.5	II
Pd(OAc)2	Solid, air, RT	24353.1	II
Pd(OAc)2 + 10 desyl-Cl + 10 PhZnBr		24350.0	80% Pd(0) + 20% Pd(II)

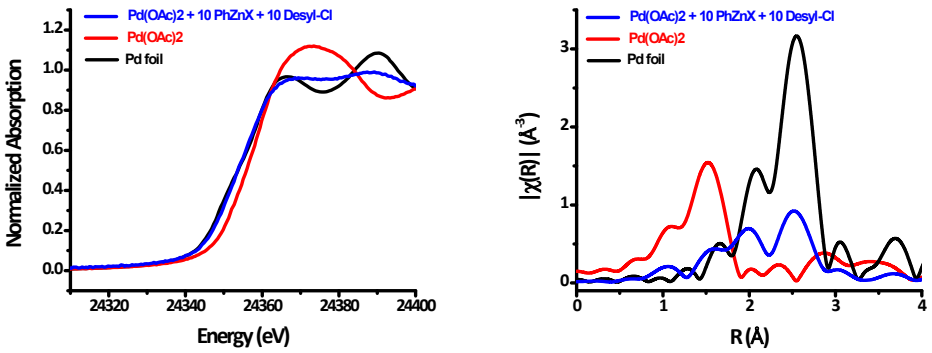

Figure S3 EXAFS results of Pd sample.

Sample $Pd(OAc)_2$ + 10PhZnCl + 10 Desyl-Cl solution: mixture of Pd(0) and Pd(II) could be observed via EXAFS. R space can show that the particle size of Nano Pd is about 2 nm.

Details of DFT calculations

DFT calculations were performed using the B3LYP method[3-4] with the Gaussian09 program[5]. The 6-31+G(d) basis set was used for the C, H, O and Cl, and the SDD basis set was used for the Pd and Zn. Frequency calculations at the same level of theory have been performed to identify all of the stationary points as minima (zero imaginary frequencies) or transition states (one imaginary frequency) and to provide free energies at 298.15 K. The solvation energies were calculated by performing single-point self-consistent reaction field (SCRF) calculations based on the polarizable continuum model (PCM).[6-7] THF was used as the solvent, which was agreed with experimental conditions, and the UAHF was used as atomic radii keyword for the PCM calculations.

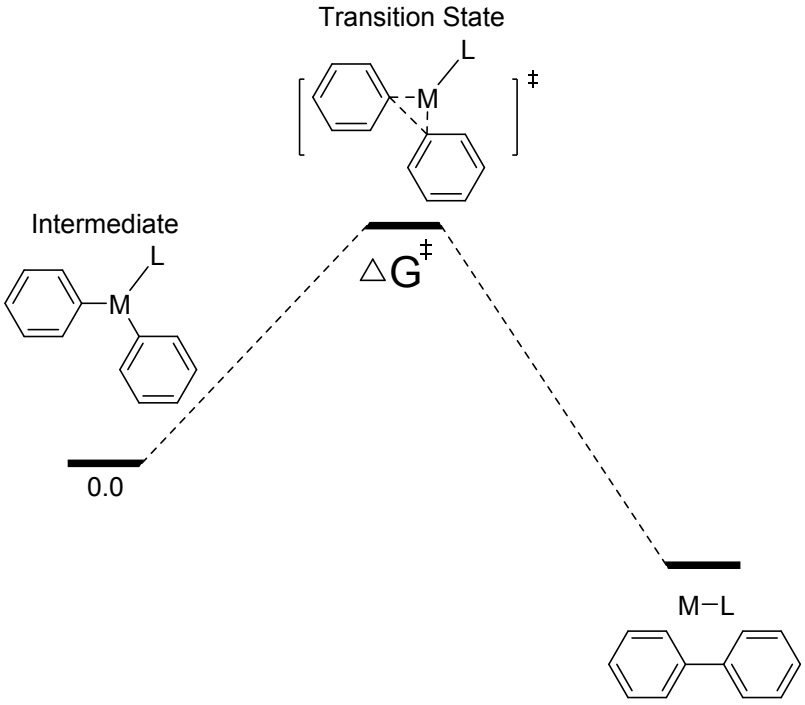

Figure S4 Energy profile for the reductive elimination

Pd(Ligand=THF)

Intermediate

Pd	0.07214900	-0.76896300	-0.00163800
C	-0.07297900	1.21375800	0.01000600
C	-0.17732000	1.91535200	1.22149200
C	-0.20489000	1.92016300	-1.19606600
C	-0.44786800	3.29052400	1.22489000

H	-0.03811900	1.40039900	2.16863400
C	-0.47506200	3.29533100	-1.18855400
H	-0.08986700	1.40804300	-2.14817900
C	-0.60156900	3.98471400	0.02113100
H	-0.52679400	3.81858000	2.17319100
H	-0.57598000	3.82674700	-2.13290300
H	-0.80495500	5.05282600	0.02553800
C	2.04557000	-0.60182500	-0.00225100
C	2.76828200	-0.73377900	1.19879700
C	2.77013300	-0.52548100	-1.20648000
C	4.16540200	-0.83111800	1.19196900
H	2.24328900	-0.76209900	2.15120600
C	4.16688400	-0.62308400	-1.21412500
H	2.24614600	-0.38821200	-2.14974400
C	4.86950500	-0.77830300	-0.01494100
H	4.70264200	-0.94070200	2.13211000
H	4.70576000	-0.56977000	-2.15819900
H	5.95484200	-0.84723800	-0.02024100
O	-2.11112700	-1.32912600	-0.00849900
C	-2.92469100	-1.18602900	1.19249800
C	-2.91908300	-1.08982100	-1.19023800
C	-4.32878100	-0.80394000	0.70578800
H	-2.90744600	-2.15213600	1.70931100
H	-2.46464400	-0.42721200	1.83076200
C	-4.35344400	-1.34456400	-0.73460100
H	-2.76950000	-0.05306000	-1.51592400
H	-2.56182900	-1.76916600	-1.96828200
H	-4.44980300	0.28534500	0.70449300
H	-5.11313300	-1.23122200	1.33825800
H	-5.08765800	-0.83825300	-1.36912900

H	-4.57335100	-2.41894000	-0.74346400

Transition State

Pd	0.42917800	-0.03664100	-0.00021900
C	-1.30450500	1.02522300	0.00852600
C	-1.69009600	1.65104200	-1.19414800
C	-1.68868800	1.63171700	1.22152000
C	-2.40192700	2.85386100	-1.18294900
H	-1.43833400	1.19589500	-2.14806200
C	-2.40064200	2.83446700	1.23034900
H	-1.43558200	1.16147600	2.16773000
C	-2.76109700	3.45345000	0.02878300
H	-2.68038800	3.32039100	-2.12569600
H	-2.67798100	3.28589300	2.18074900
H	-3.32320900	4.38398400	0.03656900
C	-1.36309900	-0.99364800	-0.00805900
C	-1.78288700	-1.57668400	-1.22090500
C	-1.78381100	-1.59639500	1.19478700
C	-2.56407600	-2.73555500	-1.22949800
H	-1.50308200	-1.12209200	-2.16727900
C	-2.56491400	-2.75533000	1.18388600
H	-1.50490100	-1.15723900	2.14867800
C	-2.95970800	-3.33230800	-0.02774600
H	-2.86768600	-3.17011100	-2.17972900
H	-2.86926900	-3.20530300	2.12667500
H	-3.57531000	-4.22836400	-0.03529700
O	2.64449000	-0.05517000	-0.00055300
C	3.46908700	-0.05454700	-1.19608300
C	3.46892500	-0.02260400	1.19395700
C	4.88424000	0.26575100	-0.70948600
H	3.40267500	-1.04919900	-1.65340600

H	3.05556100	0.68532700	-1.88607600
C	4.88738900	-0.32834100	0.70982800
H	3.38890000	0.97804900	1.63618100
H	3.06625400	-0.75762200	1.89536400
H	5.04116500	1.35036400	-0.67120500
H	5.65226900	-0.16678000	-1.35817600
H	5.65037800	0.11292900	1.35860700
H	5.05527300	-1.41134400	0.67230400

Pd(Ligand=Cl^-)

Intermediate

Pd	0.13104900	1.04044500	-0.00343300
Cl	1.56500700	2.99485900	-0.00204800
C	1.20425400	-0.61885400	0.08507700
C	2.32333800	-0.69769200	-0.76734700
C	0.99151500	-1.67235600	0.99341500
C	3.19484800	-1.79297800	-0.71368900
H	2.52694300	0.11258700	-1.46181200
C	1.87310800	-2.75993000	1.05567300
H	0.13228500	-1.64865500	1.65651300
C	2.97664100	-2.83101800	0.19933000
H	4.05359400	-1.82728300	-1.38345600
H	1.68866300	-3.55776400	1.77470500
H	3.65717900	-3.67970000	0.24419100
C	-1.55597400	-0.03354200	-0.06641600
C	-1.82489700	-1.17012400	-0.85772300
C	-2.64308100	0.50414400	0.65900300
C	-3.10812800	-1.72555400	-0.93681800
H	-1.01824400	-1.62916900	-1.42337700
C	-3.92864600	-0.04992800	0.58946700

H	-2.48770200	1.37676900	1.29369600
C	-4.16969800	-1.17067500	-0.21245000
H	-3.27884700	-2.59803800	-1.56751400
H	-4.74044100	0.39409900	1.16550200
H	-5.16650600	-1.60488200	-0.27086000

Transition State

Pd	0.00094100	1.18787100	-0.00000200
C	-0.96544200	-0.60843300	0.00000200
C	-1.58807900	-1.01409100	-1.20464900
C	-1.58806700	-1.01410600	1.20465400
C	-2.77780900	-1.74537400	-1.20519100
H	-1.13793100	-0.74316000	-2.15591100
C	-2.77779600	-1.74539000	1.20519800
H	-1.13790900	-0.74318800	2.15591400
C	-3.38495200	-2.11919800	0.00000400
H	-3.23624900	-2.02147900	-2.15408700
H	-3.23622600	-2.02150700	2.15409500
H	-4.30950200	-2.69307600	0.00000500
C	0.96448700	-0.60994000	-0.00000300
C	1.58639800	-1.01672100	-1.20465400
C	1.58640600	-1.01670500	1.20464900
C	2.77476700	-1.75021600	-1.20519500
H	1.13675200	-0.74496000	-2.15591500
C	2.77477500	-1.75019900	1.20519200
H	1.13676600	-0.74493000	2.15590900
C	3.38121400	-2.12517100	-0.00000100
H	3.23265900	-2.02722700	-2.15409200
H	3.23267400	-2.02719700	2.15409000
H	4.30463800	-2.70086000	0.00000000
Cl	0.00327300	3.58345800	0.00000300

Pd(Ligand=OAc^-)

Intermediate

C	-4.74501300	-0.17448600	0.04239700
H	-5.10903800	-1.10419700	-0.40543800
H	-5.18102800	0.69108300	-0.46630800
H	-5.07047600	-0.14970600	1.09077600
C	-3.22418500	-0.11353600	-0.00581100
O	-2.65322100	1.02125900	0.00261300
O	-2.56319100	-1.19846500	-0.02507000
Pd	-0.61812600	-0.01693200	-0.00672800
C	0.70458200	1.47256900	-0.06641700
C	1.94815400	1.49190400	-0.73141600
C	0.28773800	2.68092300	0.53576400
C	2.73335600	2.65145700	-0.79095100
H	2.31317200	0.58828900	-1.21162500
C	1.07448700	3.83885000	0.49140900
H	-0.67916600	2.72012600	1.03377900
C	2.30613000	3.83223100	-0.17409200
H	3.68501500	2.62924500	-1.32252900
H	0.72031200	4.75045000	0.97313700
H	2.91864500	4.73187100	-0.21527000
C	0.79127300	-1.42109500	0.06272100
C	1.97605600	-1.39530400	0.82718500
C	0.51059700	-2.61676500	-0.63498000
C	2.83395900	-2.50172300	0.89254500
H	2.23647300	-0.49699000	1.38038800
C	1.37184300	-3.72012600	-0.58563300
H	-0.40740500	-2.69117900	-1.21460800
C	2.54225200	-3.67046600	0.18084300

H	3.73605500	-2.44716000	1.50238100
H	1.12351200	-4.62352300	-1.14304900
H	3.21164000	-4.52838000	0.22612800

Transition State

C	4.99660500	-0.00033600	0.02673300
H	5.32491800	-0.00489200	1.07491800
H	5.39877800	0.90020100	-0.44869000
H	5.39842900	-0.89717200	-0.45598500
C	3.46672400	-0.00005000	-0.01468300
O	2.86338900	1.11384300	-0.01638100
O	2.86322800	-1.11388100	-0.01667100
Pd	0.77509500	-0.00004600	-0.00809800
C	-1.04238000	0.93243700	0.00103000
C	-1.42716400	1.57536200	1.20740500
C	-1.43943900	1.57511800	-1.20149600
C	-2.12629900	2.78271900	1.21143600
H	-1.16593300	1.11985800	2.15933700
C	-2.13859800	2.78245000	-1.19869200
H	-1.18787300	1.11943200	-2.15594000
C	-2.49176400	3.40067300	0.00814100
H	-2.38378400	3.24927000	2.16195700
H	-2.40576800	3.24877400	-2.14664400
H	-3.04115300	4.34000400	0.01084900
C	-1.04241800	-0.93242500	0.00102500
C	-1.43960100	-1.57507800	-1.20148000
C	-1.42733000	-1.57524700	1.20741600
C	-2.13902200	-2.78226300	-1.19863700
H	-1.18793500	-1.11948200	-2.15594300
C	-2.12672800	-2.78245700	1.21148200
H	-1.16601300	-1.11977100	2.15933900

C	-2.49233100	-3.40036700	0.00821100
H	-2.40628200	-3.24855200	-2.14658200
H	-2.38431200	-3.24891300	2.16202400
H	-3.04193000	-4.33957100	0.01094800

Pd(Ligand=$ZnCl_2$)

Intermediate

C	-0.31353100	0.98877000	-0.38906300
C	-0.03833400	1.83318200	0.71158900
C	-1.05911900	1.51453700	-1.47270600
C	-0.50029200	3.15127200	0.72665700
H	0.53401000	1.45956900	1.55332900
C	-1.50973800	2.83922900	-1.45059800
H	-1.28794200	0.88845700	-2.33000000
C	-1.22999600	3.65797700	-0.35348700
H	-0.28732000	3.78200200	1.58584900
H	-2.08129800	3.22430100	-2.29124500
H	-1.58472400	4.68515700	-0.33660400
C	2.22180100	-0.26482300	0.04660900
C	2.68499100	-0.87735400	1.22340400
C	3.07836500	0.57683100	-0.68002700
C	4.01060600	-0.69095600	1.63641800
H	2.02622300	-1.50429500	1.82051500
C	4.40239100	0.75736900	-0.26140000
H	2.72394400	1.08794900	-1.57084000
C	4.87018900	0.12489700	0.89476400
H	4.36448700	-1.17888600	2.54169200
H	5.06428900	1.39992100	-0.83757800
H	5.89612500	0.27466700	1.22129900
Pd	0.48357000	-0.86827400	-0.67297200

Zn	-1.85225100	-0.55833500	0.42428000
Cl	-3.10585100	-0.33066700	2.14693900
Cl	-1.70288500	-1.96896600	-1.37758900

Transition State

C	-1.31162000	-1.06943000	0.02423500
C	-1.02278800	-1.63983300	1.27364700
C	-2.30567300	-1.64630300	-0.78241400
C	-1.69330800	-2.79449700	1.68944100
H	-0.28464000	-1.19163600	1.93189800
C	-2.97126100	-2.80182200	-0.36097100
H	-2.57053400	-1.20188900	-1.73834200
C	-2.66777000	-3.37951600	0.87543900
H	-1.45254700	-3.23193600	2.65525600
H	-3.73272300	-3.24330100	-0.99934500
H	-3.19192900	-4.27247100	1.20529100
C	-1.31134200	1.06961900	0.02424200
C	-1.02221400	1.63999500	1.27359700
C	-2.30534800	1.64670700	-0.78230500
C	-1.69240400	2.79483400	1.68943600
H	-0.28408800	1.19163700	1.93176200
C	-2.97060100	2.80240500	-0.36082100
H	-2.57043100	1.20232600	-1.73818500
C	-2.66682200	3.38006400	0.87553400
H	-1.45141700	3.23224700	2.65520600
H	-3.73203500	3.24404600	-0.99911700
H	-3.19072600	4.27315500	1.20542500
Zn	2.24791300	-0.00020000	0.21320800
Cl	2.32156100	0.00004800	-2.06533900
Cl	3.22253300	-0.00034100	2.10811000
Pd	0.09610900	-0.00009800	-0.99712100

Pd(Ligand=PhZnCl)

Intermediate

C	2.22141200	-0.99908600	-0.20426100
C	2.79223500	-1.03888200	-1.48789600
C	2.99003100	-1.41990200	0.89350400
C	4.08741100	-1.53808000	-1.67485600
H	2.23281800	-0.68644300	-2.35219700
C	4.28472500	-1.91938000	0.70402700
H	2.58693600	-1.36033900	1.90153100
C	4.83560600	-1.98072600	-0.57958900
H	4.51167400	-1.57342400	-2.67609900
H	4.86491800	-2.24987900	1.56296900
H	5.84413600	-2.36028500	-0.72432300
C	0.80449800	1.20998900	0.57358600
C	1.42298500	2.15249900	-0.26464600
C	0.50002700	1.57363700	1.89901400
C	1.69960200	3.44167200	0.20425600
H	1.69284900	1.88807500	-1.28201000
C	0.78755200	2.86286600	2.36430500
H	0.04700300	0.85578700	2.57848200
C	1.38482100	3.80067500	1.51758200
H	2.16689900	4.16266600	-0.46219500
H	0.54372400	3.12854100	3.39050200
H	1.60552200	4.80157800	1.87930700
Pd	0.25879300	-0.64133900	-0.01812400
Zn	-1.65913600	0.90316200	-0.67395000
Cl	-2.30180800	2.66655800	-1.69488700
C	-2.02347700	-0.93605400	0.10306400
C	-2.37736900	-1.96743500	-0.80056000

C	-2.47738600	-1.05034300	1.43729100
C	-3.11832400	-3.07614100	-0.38017400
H	-2.06939300	-1.90891200	-1.84275700
C	-3.22675500	-2.15294400	1.85632900
H	-2.23728700	-0.27383500	2.16014500
C	-3.54370500	-3.16862800	0.94855700
H	-3.36858500	-3.86132000	-1.08926500
H	-3.56032800	-2.22141000	2.88889700
H	-4.12391600	-4.02796500	1.27508600

Transition State

C	1.49792600	0.94486000	0.47278400
C	1.80607300	1.14486500	1.82920800
C	1.82282900	1.95041700	-0.45168900
C	2.38917300	2.34286700	2.25464400
H	1.59392200	0.37019100	2.56141700
C	2.40423800	3.14795300	-0.02127300
H	1.62455400	1.81021500	-1.51032200
C	2.68935100	3.35001400	1.33197500
H	2.61256400	2.48406100	3.30978700
H	2.63356100	3.92174500	-0.75004700
H	3.14595600	4.27893400	1.66338800
C	1.96563300	-1.06404400	-0.26484400
C	2.54384700	-1.90176300	0.70252000
C	2.44193300	-1.11223500	-1.58505500
C	3.54713100	-2.80822900	0.34237000
H	2.21976900	-1.85248800	1.73877900
C	3.44636900	-2.01841700	-1.94006700
H	2.03484900	-0.44620400	-2.34103700
C	4.00124600	-2.86936200	-0.97853800
H	3.97908400	-3.45911200	1.09915200

H	3.79885700	-2.05327100	-2.96843100
H	4.78860600	-3.56618400	-1.25431400
Zn	-1.75646800	1.19688400	-0.50198200
Cl	-2.28507400	3.11542300	-1.28363700
C	-2.13028100	-0.69704200	0.18288000
C	-2.60108100	-0.86266100	1.50928000
C	-2.52387900	-1.66030400	-0.77950200
C	-3.39968100	-1.95257100	1.86122400
H	-2.33260300	-0.13709100	2.27336600
C	-3.31558800	-2.75704200	-0.42245200
H	-2.20676200	-1.55752200	-1.81456000
C	-3.75431100	-2.90225500	0.89611400
H	-3.74428900	-2.06340800	2.88646700
H	-3.59360400	-3.49133900	-1.17440500
H	-4.37590100	-3.75051700	1.17171600
Pd	0.05165600	-0.45667400	0.05114900

Ni(Ligand=THF)

Intermediate

Ni	-0.14394500	-0.66866600	0.01697500
C	0.23706500	1.14230200	0.05861000
C	0.66339800	1.80029900	-1.10982700
C	0.22833700	1.86987800	1.26269000
C	1.09595400	3.13309000	-1.07077300
H	0.65078900	1.28186800	-2.06743700
C	0.66478200	3.20065700	1.30316800
H	-0.13576300	1.40596000	2.17664800
C	1.10297300	3.83707500	0.13727100
H	1.42018700	3.62157200	-1.98801500
H	0.64903300	3.74360500	2.24642800

H	1.43372600	4.87257600	0.16748900
C	-1.97708200	-0.47816400	-0.00970500
C	-2.75740300	0.31749400	-0.87052000
C	-2.65405000	-1.40272600	0.81587000
C	-4.14741200	0.17489200	-0.92923900
H	-2.27466500	1.05978800	-1.50154800
C	-4.04725100	-1.55051700	0.75928100
H	-2.09836100	-2.02059500	1.52291200
C	-4.79775600	-0.76097700	-0.11581300
H	-4.72671100	0.79762000	-1.60856100
H	-4.54286200	-2.27281000	1.40543700
H	-5.87944200	-0.86679100	-0.15851000
O	1.69635100	-1.49061400	0.04332800
C	2.43635600	-1.67651100	-1.19872000
C	2.62127500	-1.24539200	1.15129200
C	3.85807000	-2.01278900	-0.75690400
H	1.93493300	-2.46914300	-1.75931000
H	2.39492800	-0.74121300	-1.76853900
C	4.00975200	-1.15750400	0.51268700
H	2.30638100	-0.32686700	1.65037700
H	2.52809100	-2.09238800	1.83977100
H	4.59656100	-1.77080700	-1.52751200
H	3.94576100	-3.07997900	-0.52022200
H	4.24182700	-0.11972600	0.24807100
H	4.79318400	-1.52175100	1.18439300

Transition State

Ni	0.41091600	-0.00064700	-0.00002000
C	-1.22142500	-0.91357100	0.00381600
C	-1.55671700	-1.56760400	1.21755500
C	-1.58534500	-1.57053600	-1.19968800

C	-2.17757900	-2.81729800	1.22461500
H	-1.32983500	-1.09210700	2.16782300
C	-2.20644100	-2.82004700	-1.18895500
H	-1.38280300	-1.09636200	-2.15602300
C	-2.50716000	-3.45453000	0.02234100
H	-2.40851400	-3.29572200	2.17441600
H	-2.46097000	-3.30017700	-2.13182500
H	-2.99986600	-4.42351100	0.02935900
C	-1.22026400	0.91429400	-0.00380600
C	-1.58332000	1.57173300	1.19970200
C	-1.55484600	1.56870400	-1.21754600
C	-2.20289300	2.82199800	1.18896800
H	-1.38130800	1.09733600	2.15603900
C	-2.17419500	2.81914700	-1.22460200
H	-1.32860000	1.09290500	-2.16781500
C	-2.50291700	3.45681800	-0.02232400
H	-2.45678500	3.30246100	2.13184000
H	-2.40461100	3.29782000	-2.17440300
H	-2.99442600	4.42640600	-0.02933700
O	2.36636800	-0.00133100	0.00000200
C	3.19193700	-0.02510700	1.19808800
C	3.19193000	0.02281000	-1.19807400
C	4.60709300	0.29141600	0.71143600
H	2.78238000	0.70839900	1.89640400
H	3.11627100	-1.02607600	1.63873800
C	4.60713300	-0.29351300	-0.71145200
H	2.78250300	-0.71066600	-1.89649700
H	3.11608800	1.02383100	-1.63857800
H	5.37269700	-0.14992800	1.35689700
H	4.76919700	1.37542400	0.68084900

H	4.76939500	-1.37749800	-0.68087600
H	5.37266500	0.14795100	-1.35691600

Ni(Ligand=Cl^-)

Intermediate

Ni	0.01272400	1.05370200	0.00327900
C	1.32009400	-0.26181600	0.07153200
C	1.35476300	-1.37018400	0.94154300
C	2.44905000	-0.05709400	-0.75174800
C	2.46457500	-2.22335700	0.99959500
H	0.50064300	-1.57291400	1.58290800
C	3.55491200	-0.91641700	-0.70908200
H	2.47133100	0.79634400	-1.42675100
C	3.57084000	-2.00520700	0.17050300
H	2.46187800	-3.06525400	1.69210300
H	4.40884200	-0.72997300	-1.36036800
H	4.43108600	-2.67186100	0.20961500
C	-1.41389400	-0.14308800	-0.06293000
C	-2.57583600	0.33254300	0.58793300
C	-1.54067400	-1.35417300	-0.77439000
C	-3.79464100	-0.35727800	0.53062900
H	-2.53316800	1.26619600	1.14968500
C	-2.75661300	-2.04573000	-0.84399200
H	-0.67211700	-1.76547700	-1.28318000
C	-3.89208800	-1.55329000	-0.18921200
H	-4.66747700	0.04036300	1.04856600
H	-2.81810600	-2.97446000	-1.41160800
H	-4.83649500	-2.09332500	-0.23856100
Cl	0.49731700	3.23513200	0.00726300

Transition State

Ni	0.00000000	1.21424300	0.00000000
C	0.87393200	-0.45199400	-0.03244900
C	1.61058300	-0.66901200	1.17029000
C	1.47817100	-0.93568200	-1.22797000
C	2.87362800	-1.25929600	1.16412900
H	1.18977500	-0.34513200	2.11851200
C	2.73774100	-1.53164100	-1.22959600
H	0.94823300	-0.83214000	-2.17103600
C	3.45281000	-1.69956500	-0.03453100
H	3.41706400	-1.37099400	2.10203100
H	3.17049900	-1.86616300	-2.17206300
H	4.43538200	-2.16699100	-0.03710200
C	-0.87393200	-0.45199300	0.03244900
C	-1.47817200	-0.93568100	1.22797100
C	-1.61058400	-0.66901200	-1.17029000
C	-2.73774200	-1.53163900	1.22959700
H	-0.94823400	-0.83213800	2.17103700
C	-2.87362800	-1.25929500	-1.16412900
H	-1.18977500	-0.34513200	-2.11851200
C	-3.45281100	-1.69956200	0.03453100
H	-3.17050100	-1.86616000	2.17206400
H	-3.41706500	-1.37099300	-2.10203100
H	-4.43538300	-2.16698900	0.03710200
Cl	0.00000100	3.39589800	0.00000000

Ni(Ligand=acac$^-$)

Intermediate

C	-3.76372200	-2.52484300	-0.04413700
H	-3.50380900	-3.13940900	0.82660800
H	-4.84351800	-2.33960600	-0.04302000

H	-3.49946200	-3.10535900	-0.93662300
C	-2.94745700	-1.23942500	-0.01853500
C	-3.62075900	-0.00004800	0.00009400
H	-4.70650500	-0.00005900	0.00017000
C	-2.94748400	1.23934900	0.01856100
C	-3.76378000	2.52474700	0.04427700
H	-4.84357100	2.33948800	0.04289400
H	-3.49972800	3.10507500	0.93695000
H	-3.50368000	3.13950700	-0.82627200
O	-1.68953900	-1.39479500	-0.01405400
O	-1.68957500	1.39475100	0.01388400
Ni	-0.29344100	-0.00000900	-0.00011300
C	1.03851800	-1.35438700	-0.08139000
C	2.07838500	-1.39316600	-1.03560100
C	0.98078200	-2.44978400	0.80912500
C	2.98853400	-2.45618400	-1.11196900
H	2.18871800	-0.56527100	-1.73360900
C	1.89879500	-3.50779700	0.76040100
H	0.18690100	-2.48671800	1.55353600
C	2.90983200	-3.52167400	-0.20769100
H	3.76974200	-2.44579200	-1.87304800
H	1.81937200	-4.32827300	1.47507300
H	3.62252400	-4.34442700	-0.25491500
C	1.03847700	1.35440300	0.08129900
C	0.98078500	2.44983300	-0.80917900
C	2.07825000	1.39318500	1.03561300
C	1.89874800	3.50788300	-0.76031700
H	0.18697900	2.48676400	-1.55366900
C	2.98834600	2.45623900	1.11211800
H	2.18855100	0.56526300	1.73359400

C	2.90968000	3.52177000	0.20788500
H	1.81936500	4.32838500	-1.47496500
H	3.76947800	2.44584800	1.87327400
H	3.62232300	4.34455900	0.25522300

Transition State

C	3.79392200	-2.43342300	0.65804100
H	4.86968700	-2.23141200	0.59910500
H	3.55132500	-2.78187800	1.67016800
H	3.54500700	-3.25068300	-0.03073600
C	2.94206700	-1.21143900	0.32419700
C	3.59701700	-0.00014400	0.00001900
H	4.68366500	-0.00017700	0.00003500
C	2.94216300	1.21120500	-0.32417100
C	3.79415200	2.43308700	-0.65804500
H	4.86989300	2.23107900	-0.59864000
H	3.55195900	2.78123400	-1.67037700
H	3.54496900	3.25055300	0.03038600
O	1.68805200	-1.39250000	0.36662600
O	1.68816700	1.39236500	-0.36666100
Ni	0.31576800	-0.00005500	-0.00001800
C	-1.39871000	-0.84072100	-0.02948300
C	-1.98339200	-1.55705500	1.06194600
C	-1.49788000	-1.48246500	-1.30831400
C	-2.54508800	-2.81853400	0.90475900
H	-1.98865900	-1.09939200	2.04903800
C	-2.04604100	-2.75436400	-1.45700000
H	-1.11539800	-0.97095000	-2.18884600
C	-2.57965600	-3.44145000	-0.35580000
H	-2.95986400	-3.33184100	1.77273700
H	-2.05852400	-3.21979400	-2.44286200

H	-3.02098700	-4.42879500	-0.47599100
C	-1.39860600	0.84082800	0.02949200
C	-1.49767800	1.48258400	1.30832400
C	-1.98319400	1.55724900	-1.06193100
C	-2.04565200	2.75456400	1.45701500
H	-1.11526900	0.97101200	2.18885500
C	-2.54470400	2.81881000	-0.90474000
H	-1.98853700	1.09958700	-2.04902400
C	-2.57917200	3.44173000	0.35581900
H	-2.05806200	3.21999300	2.44287800
H	-2.95941200	3.33217800	-1.77271400
H	-3.02035900	4.42913900	0.47601400

Ni(Ligand=$ZnCl_2$)

Intermediate

C	2.14934800	-0.22621400	-0.02454700
C	2.97046600	0.84650100	-0.41151300
C	2.68570500	-1.23793300	0.79511000
C	4.31508000	0.88039900	-0.02713800
H	2.56750300	1.65173800	-1.02051200
C	4.03347200	-1.20049900	1.17852500
H	2.06389700	-2.06295500	1.14148400
C	4.84771600	-0.14177100	0.76730700
H	4.94706900	1.70642600	-0.34576800
H	4.43896500	-1.99171500	1.80501800
H	5.89099200	-0.10775500	1.07119500
C	-0.34150500	0.94861900	-0.28959700
C	-1.07225400	1.57667400	-1.33509800
C	-0.12929300	1.69126000	0.90116900
C	-1.54787800	2.88486900	-1.19885800

H	-1.26194300	1.03811300	-2.25973600
C	-0.62148900	2.99014000	1.03672200
H	0.42789000	1.24616200	1.71891900
C	-1.32321800	3.59158600	-0.01410200
H	-2.09731100	3.34590600	-2.01568800
H	-0.45304400	3.53502400	1.96201600
H	-1.69975700	4.60549600	0.09389400
Ni	0.53324000	-0.67583300	-0.77239300
Zn	-1.71055300	-0.69399900	0.27880800
Cl	-1.19849800	-1.91076700	-1.65518100
Cl	-3.16828400	-0.96246300	1.82247800

Transition State

C	1.21042800	-1.02299500	-0.02827600
C	0.87917100	-1.61977300	-1.25862500
C	2.19173900	-1.63229600	0.77803500
C	1.48106800	-2.81968300	-1.64797900
H	0.15784900	-1.15494600	-1.92436700
C	2.78856700	-2.83305800	0.38392900
H	2.49863200	-1.17673800	1.71656400
C	2.43575600	-3.43144100	-0.82977100
H	1.20351600	-3.27297000	-2.59641800
H	3.53602800	-3.29507400	1.02432900
H	2.90724500	-4.36035100	-1.13903200
C	1.20965600	1.02355600	-0.02807200
C	0.87812600	1.62020500	-1.25840400
C	2.19034800	1.63355300	0.77846900
C	1.47911000	2.82065300	-1.64751900
H	0.15730100	1.15486600	-1.92432700
C	2.78628500	2.83483100	0.38459200
H	2.49742800	1.17815200	1.71701400

C	2.43318000	3.43307900	-0.82909200
H	1.20134200	3.27382700	-2.59594900
H	3.53326800	3.29737500	1.02516900
H	2.90396700	4.36240900	-1.13816100
Zn	-2.08757800	-0.00049500	-0.04345700
Cl	-3.50700000	-0.00033300	-1.63998000
Cl	-1.77324600	-0.00104500	2.28908100
Ni	0.00051300	-0.00028800	0.97573000

Ni(Ligand=PhZnCl)

Intermediate

C	0.45071200	1.32000500	0.34018200
C	0.01874300	1.76152000	1.61492200
C	0.92410300	2.29793800	-0.56466700
C	0.05094900	3.11743200	1.96373000
H	-0.33259400	1.04129900	2.35176300
C	0.94366800	3.65092000	-0.21787600
H	1.28575300	1.99608500	-1.54326800
C	0.51076500	4.06511000	1.04650600
H	-0.28550900	3.42796300	2.95015800
H	1.30409400	4.38355300	-0.93596700
H	0.53107800	5.11859400	1.31299200
C	2.26313100	-0.59642100	-0.14638200
C	3.17152300	-0.42163300	0.91314200
C	2.75231800	-1.09682400	-1.36961200
C	4.51584600	-0.78278200	0.77194800
H	2.83114200	-0.00239800	1.85740400
C	4.09885700	-1.45720100	-1.51321900
H	2.08673800	-1.21432500	-2.22464300
C	4.98238100	-1.30195400	-0.44111700

H	5.20156400	-0.65295500	1.60678300
H	4.45624900	-1.84919400	-2.46329000
H	6.02911100	-1.57482300	-0.55221200
Zn	-1.65895800	0.61375700	-0.48138900
Cl	-3.04507000	1.96979000	-1.39717600
C	-1.48100300	-1.34486300	0.15702900
C	-1.85604100	-1.66338500	1.48461300
C	-1.62437800	-2.36045800	-0.82141800
C	-2.31253600	-2.93880300	1.82618100
H	-1.78076600	-0.90907300	2.26533800
C	-2.07095200	-3.64059600	-0.47974700
H	-1.38051600	-2.15302500	-1.86163900
C	-2.41551500	-3.92967500	0.84403600
H	-2.58553000	-3.16090400	2.85491100
H	-2.15944200	-4.40673100	-1.24604000
H	-2.76830900	-4.92309800	1.10933200
Ni	0.41308700	-0.53893200	0.00937600

Transition State

C	1.42936600	0.79335800	0.65299100
C	1.65081500	0.79686100	2.04616800
C	1.82628600	1.92444000	-0.08681300
C	2.20040700	1.91442500	2.68068600
H	1.39052400	-0.07227900	2.64611000
C	2.37385400	3.04089900	0.55231900
H	1.71196300	1.94089500	-1.16694500
C	2.56277800	3.04306700	1.93767900
H	2.35036100	1.89908700	3.75800000
H	2.65681900	3.90879100	-0.03868900
H	2.99580400	3.90906200	2.43130500
C	1.79535400	-0.99303900	-0.32713400

C	2.34602200	-1.99975100	0.48858900
C	2.20093900	-0.91491800	-1.67344400
C	3.23312200	-2.93963300	-0.04524000
H	2.08741200	-2.05545500	1.54295600
C	3.09022700	-1.85491600	-2.20196400
H	1.82308400	-0.12364400	-2.31561700
C	3.60783800	-2.87087900	-1.39089500
H	3.63972600	-3.71918300	0.59498200
H	3.38315600	-1.78946600	-3.24736900
H	4.30673600	-3.59515800	-1.80132300
Zn	-1.49691700	1.06807000	-0.79300900
Cl	-2.15434600	2.76881300	-1.92026800
C	-1.86870700	-0.68766800	0.29726900
C	-2.37462500	-0.53302700	1.61290300
C	-2.35386100	-1.77896900	-0.46738300
C	-3.28201600	-1.44801100	2.15129800
H	-2.04355700	0.30410300	2.22361400
C	-3.25538700	-2.69904000	0.07649200
H	-2.01429100	-1.92003400	-1.49099500
C	-3.71982400	-2.53409500	1.38468000
H	-3.64929900	-1.31452800	3.16600600
H	-3.59947100	-3.53859100	-0.52259300
H	-4.42774000	-3.24484600	1.80371800
Ni	0.07659400	-0.40197500	0.09723000

Catalyst inhibition reactions

Ligand inhibition reactions

In an oven dried self-prepared three-necked micro reactor with a magnetic stirrer, 2-Chloro-1,2-diphenyl-ethanone (115.3 mg, 0.5 mmol), biphenyl (73.5 mg) as the internal standard were added. TetraButylAmmonium Bromide (160 mg) was added. The reactor was allowed to be vacuumed and purged with nitrogen for three times. The arylzinc reagent (0.4 M, 5 mL, 2 mmol) was added in via a syringe. The mixture was allowed to stir at 60 ^{o}C and recorded by IR spectrometer. At the same time, solution of $Pd(OAc)_2$ in THF (0.1 mL) was added in by a micro syringe. The concentration of catalyst precursor was set at $1x10^{-6}$ M. The progress of the reaction can be observed from the characteristic IR spectra of arylzinc reagent and Ar-Ar. After about 1 h, solution of PPh_3 in THF (0.05 mL) was added in by a micro syringe. The concentration of catalyst precursor was set at $2.5x10^{-5}$ M. After about 2 h, the reaction was stopped and quenched by saturated NH_4Cl and the yield was determined by GC.

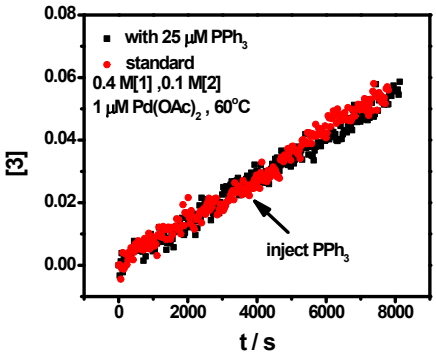

Figure S5 ligand inhibition experiments

There is no discernable difference can be observed in the presence of 25 equiv. of PPh_3.

Mecury inhibition reaction

In an oven dried vial with a magnetic stirrer, 2-Chloro-1,2-diphenyl-ethanone (92.1 mg, 0.4 mmol), biphenyl (73.5 mg) as the internal standard were added. TetraButylAmmonium Bromide (160 mg) was added. The reactor was allowed to be vacuumed and purged with nitrogen for three times. The arylzinc reagent (0.4 M, 4 mL, 1.6 mmol) was added in via a syringe. The mixture was allowed to stir at 60 ^{o}C. At the same time, solution of $Ni(acac)_2$ or $Pd(OAc)_2$ in THF (0.1 mL) was added in by a micro syringe. The concentration of catalyst precursor was set at $1x10^{-6}$ M. Then 0.1 mL(6.7 mmol) Hg was added in by a syringe. After about 2 h, the reaction was stopped and quenched by saturated NH_4Cl and the yield was determined by GC.

Table S3 Mercury poisoning reactions results

entry	Catalyst	Hg	Yield%
1	Pd(OAc)2	none	70
2	Pd(OAc)2	6.7 mmol	70
3	Ni(acac)2	none	77
4	Ni(acac)2	6.7 mmol	77

Kinetics Results related

In an oven dried self-prepared three-necked micro reactor with a magnetic stirrer, 2-Chloro-1,2-diphenyl-ethanone (115.3 mg, 0.5 mmol), biphenyl (73.5 mg) as the internal standard were added. TetraButylAmmonium Bromide (160 mg) was added. The reactor was allowed to be vacuumed and purged with nitrogen for three times. The arylzinc reagent (0.4 M, 5 mL, 2 mmol) was added in via a syringe. The mixture was allowed to stir at 60 °C and recorded by IR spectrometer. At the same time, solution of $Ni(acac)_2$, $Pd(OAc)_2$ or $Pd(acac)_2$ in THF (0.1 mL) was added in by a micro syringe. The concentration of catalyst precursor was set at $1x10^{-6}$ M. The progress of the reaction can be observed from the characteristic IR spectra of arylzinc reagent and Ar-Ar. After about 2 h, the reaction was stopped and quenched by saturated NH_4Cl and the yield was determined by GC.

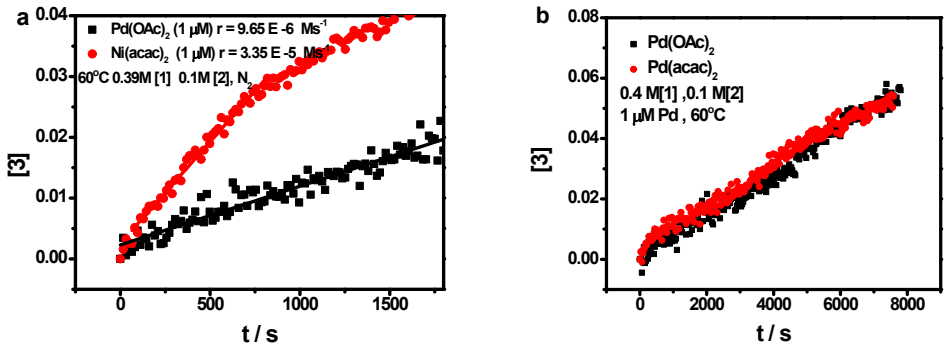

Figure S6 Reaction progress profiles at 60 °C with the catalyst precursor concentration at $1x10^{-6}$ M. a) comparison between $Pd(OAc)_2$ and $Ni(acac)_2$; b) comparison between $Pd(OAc)_2$ and $Pd(acac)_2$;

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