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Supporting Information

Lewis Acid Accelerated Aryl Ether Bond Cleavage with Nickel: Orders of Magnitude Rate Enhancement Using AlMe₃

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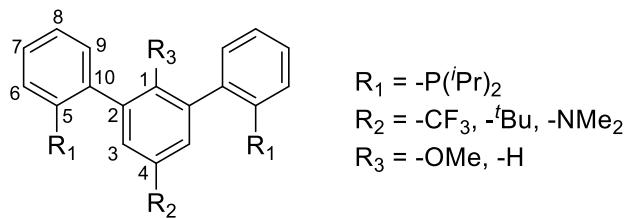
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Supporting Information

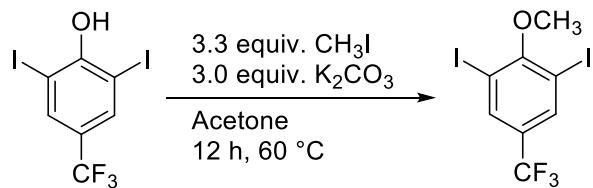
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I. Experimental Details

General considerations: Unless otherwise indicated, reactions performed under inert atmosphere were carried out in oven-dried glassware in a glovebox under a nitrogen atmosphere purified by circulation through RCI-DRI 13X-0408 Molecular Sieves 13X, 4x8 Mesh Beads and BASF PuriStar® Catalyst R3-11G, 5x3 mm (Research Catalysts, Inc.). Solvents for all reactions were dried by Grubbs' method.¹ Benzene-d₆ was vacuum distilled from sodium benzophenone ketyl. All other materials were used as received. [1,3-bis(2'-diisopropylphosphino)-4-tert-butyl-2-methoxybenzene]nickel(0)² (**1-tBu**), [1,3-bis(2'-diisopropylphosphino)-4-dimethylamino-2-methoxybenzene]nickel(0)² (**1-NMe₂**),² Mg(TMEDA)Me₂³, [1,3-bis(2'-diisopropylphosphino)-benzene]nickel(0)⁴, 1,3-diiodo-5-nitrobenzene, 1,3-bis(2'-diisopropylphosphinophenyl)-5-tert-butyl-2-(4'-dimethylaminophenoxy)benzene⁵ were synthesized following literature procedures. 2,6-diiodo-4-(trifluoromethyl)phenol was synthesized by a modification of the method of Pezzella and co-workers⁶ and matched previously reported spectra.⁷ In the following complexes, the carbons of the terphenyl backbone are assigned using the following schemes:

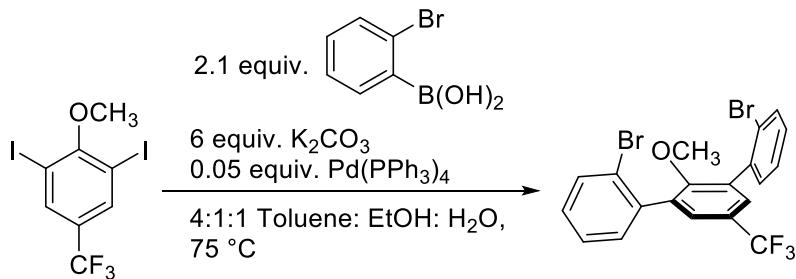


Synthesis of 1,3-diiodo-2-methoxy-5-trifluoromethyl-benzene.



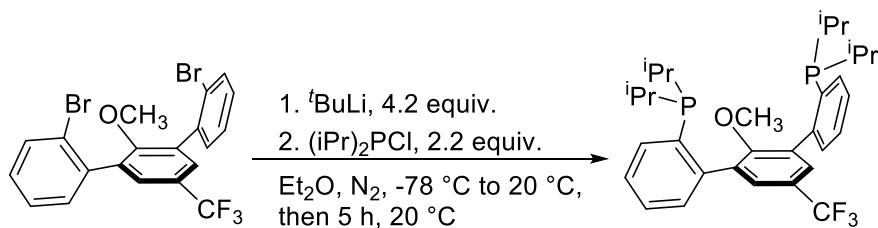
1,3-diido-2-methoxy-5-trifluoromethyl-benzene was synthesized using a modification of the procedure reported by Pandiarajan and co-workers for the methylation of phenols.⁸ In a 500 mL round bottom flask, K₂CO₃ (5.034 g, 36.4 mmol, 3.0 equiv.) was mixed with 2,6-diido-4-(trifluoromethyl)phenol⁶⁻⁷ (5.025 g, 12.1 mmol, 1.0 equiv.) in acetone (100 mL). CH₃I (5.687 g, 2.49 mL, 40.1 mmol, 3.3 equiv.) was added to this slurry via syringe. The round bottom was equipped with a reflux condenser and sealed with a septum and heated to 55 °C for 12 h. After 12 h, the solvent was removed from the slurry via rotovap. The solid residue was taken up in water and the organics were extracted three times with ethyl acetate (50 ml). The yellow organic fractions were combined and dried with magnesium sulfate. The ethyl acetate was removed by rotovap to afford a pale yellow oil. Yield: 4.52 g, 10.6 mmol, 87.0%. ¹H NMR (CDCl₃, 300 MHz) δ 8.01 (s, 2H, Ar-H₃) 3.90 (s, 3H, OCH₃).

Synthesis of 1,3-bis(2'-bromophenyl)-2-methoxy-5-trifluoromethyl-benzene.



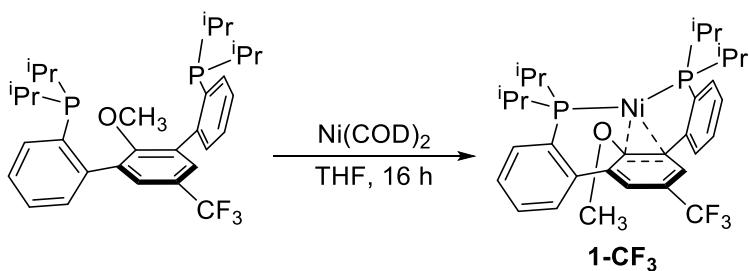
1,3-bis(2'-bromophenyl)-2-methoxy-5-trifluoromethyl-benzene was synthesized using the procedure reported for the synthesis of 1,3-bis(2'-bromophenyl)-2-methoxy-5-nitrobenzene.² Yield: 2.31 g, 53.9%. ¹H NMR (CDCl₃, 300 MHz) δ 7.49 (s, 2H, central Ar-H), 7.41 (d, 2H, Ar-H), 7.00 (d, 2H, Ar-H), 6.89 (t, 2H, Ar-H), 6.73 (t, 2H, Ar-H), 2.94 (s, 3H, OCH₃). ¹⁹F{¹H} NMR δ 61.31.

Synthesis of 1,3-bis(2'-diisopropylphosphino)-2-methoxy-5-trifluoromethylbenzene.



1,3-bis(2'-diisopropylphosphinophenyl)-2-methoxy-5-trifluoromethylbenzene was synthesized using the procedure reported for 1,3-bis(2'-diisopropylphosphinophenyl)-2-methoxy-5-nitrobenzene.² ¹H NMR (CDCl₃, 300 MHz) δ 7.60 (br m, 2H, Ar-H), 7.33 (br m, 4H, Ar-H), 7.12 (br m, 4H, Ar-H), 3.00 (m, 3H, OCH₃), 1.93 (septet, 2H, CH(CH₃)₂), 1.71 (septet, 2H, CH(CH₃)₂), 1.01 (m, 6H, CH(CH₃)₂), 0.87 (m, 18H, CH(CH₃)₂). ¹⁹F{¹H} NMR δ 61.31. ³¹P{¹H} NMR δ -2.55, -4.24.

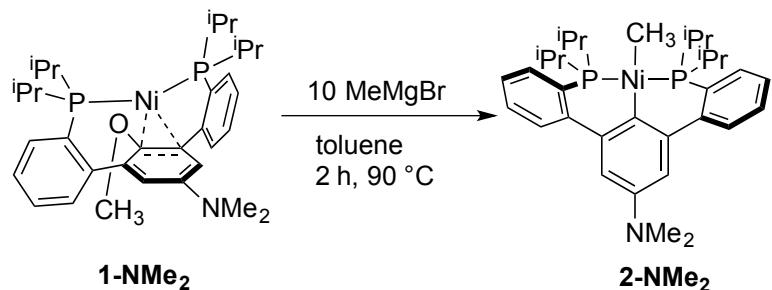
Synthesis of [1,3-bis(2'-diisopropylphosphino)-2-methoxy-4-trifluoromethylbenzene]nickel(0) (1-CF₃).



1-CF₃ was synthesized using the procedure reported for **1-NMe₂**.² Yield: 613.1 mg, 73.7%. ¹H NMR (C₆D₆, 499.85 MHz) δ 7.44 (m, 2H, Ar-H), 7.23 (m, 2H, Ar-H), 7.18 (m, 4H, Ar-H), 6.62 (s, 2H, Ar-H), 3.01 (s, 3H, OCH₃), 2.23 (m, 2H, CH(CH₃)₂), 1.94 (m, 2H, CH(CH₃)₂), 1.08 (mm, 18H, CH(CH₃)₂), 0.91 (mm, 6H, CH(CH₃)₂). ¹⁹F{¹H} NMR (C₆D₆, 282.33 MHz) δ -61.34 (s), ³¹P{¹H} NMR (C₆D₆, 121.48

MHz) δ 41.12 (s). $^{13}\text{C}\{\text{H}\}$ NMR (C_6D_6 , 125.70 MHz). δ 150.14 (t, Ar- C_{10}), 138.90 (t, Ar- C_5), 130.96 (s, Ar- C_9), 129.75 (t, Ar- C_6), 129.68 (s, Ar- C_{7-8}), 128.35 (s, Ar- C_2), 127.48 (s, Ar- C_{7-8}), 118.89 (s, Ar- C_3), 117.81 (q, Ar- CF_3), 111.29 (s, Ar- C_1), 99.40 (s, Ar- C_4), 58.98 (OCH_3), 27.38 ($\text{CH}-(\text{CH}_3)_2$), 21.71 ($\text{CH}-(\text{CH}_3)_2$), 19.77 ($\text{CH}-(\text{CH}_3)_2$), 19.60 ($\text{CH}-(\text{CH}_3)_2$), 19.06 ($\text{CH}-(\text{CH}_3)_2$). Anal. Calcd. for $\text{C}_{32}\text{H}_{41}\text{F}_3\text{NiOP}_2$ (%): C, 62.06; H, 6.67. Found: C, 61.77; H, 6.60.

Synthesis of [1,3-bis(2'-diisopropylphosphino)-4-dimethylaminophenyl]nickel(II)methyl (2-NMe₂)



A dark red toluene solution of [1,3-bis(2'-diisopropylphosphino)-4-dimethylamino-2-methoxybenzene]nickel(0) (**1-NMe₂**, 50.1 mg, 0.08 mmol) in toluene was treated with 10 equiv. of MeMgBr and heated to 90 °C in a sealed Schlenk tube for 2 hours. After cooling the volatile material was removed under vacuum giving an orange red solid. The residue was triturated with pentanes and hexanes to precipitate excess Grignard reagent. The resulting slurry was filtered through Celite. (**2**) was obtained from the elute as a yellow solid. Yield: 39.8 mg, 86.2%. ^1H NMR (C_6D_6 , 300 MHz) δ 7.74 (br d, 2H, Ar-H), 7.34 (br d, 2H, Ar-H), 7.24 (m, 2H, Ar-H), 7.10 (m, 2H, Ar-H), 6.92 (m, 2H, Ar-H), 2.61 (s, 6H, N(CH₃)₂), 2.46 (m, 2H, CH(CH₃)₂), 1.92 (m, 2H, CH(CH₃)₂), 1.05 (s, 24H, CH(CH₃)₂), 0.36 (t, 3H, CH₃), $^{13}\text{C}\{\text{H}\}$ NMR (CD_2Cl_2 , 100.54 MHz) δ 152.12 (t, Ar- C_{10}), 150.57 (s, Ar- C_4), 147.49 (t, Ar- C_5), 129.42 (s, Ar- C_7), 128.42 (s, Ar- C_9), 127.78 (s, Ar- C_2), 126.79 (s, Ar- C_6), 125.83 (s, Ar- C_8), 126.41 (s, Ar- C_1), 112.99 (s, Ar- C_3), 40.88 (s, N(CH₃)₂), 23.13 (s, CH(CH₃)₂), 19.97 (s, CH(CH₃)₂), 18.57 (s, CH(CH₃)₂), -18.20 (s, Ni-CH₃). $^{31}\text{P}\{\text{H}\}$ NMR (C_6D_6 , 121.48 MHz) δ 44.51 (s). Anal. Calcd. for $\text{C}_{33}\text{H}_{47}\text{NNiP}_2$ (%): C, 68.53; H, 8.19; N, 2.42. Found C, 68.33; H, 8.35; N, 2.15.

Example of a Kinetic Measurement.

In a glove box, a J. Young tube was charged with 11.3 mg (0.019 mmol) of **1-R** (**R** = - CF_3 , - $t\text{Bu}$, or -NMe₂) and 1.1 mg (0.006 mmol) of 1,3,5-trimethoxybenzene in C_6D_6 or d_8 -toluene. The J. Young tube was heated to the desired temperature in either an oil bath or in an NMR spectrometer. NMR spectra were collected at regular intervals.

Example of a Kinetic Measurement with Lewis Acid Additive.

In a glove box, a J. Young tube was charged with 7.3 mg (0.012 mmol) of **1-tBu** and 1.1 mg (0.004 mmol) of 1,3,5-trimethoxybenzene in 200 μL d_8 -toluene. This mixture in the J. Young tube was frozen in a liquid N₂ chilled cold well. After the solution was frozen, a 100 μL d_8 -toluene buffer layer was added to the tube and the frozen solution. On top of this layer was added a solution of AlMe₃ in d_8 -toluene. The J. Young tube was frozen and transferred to a dry ice acetone bath. The tube was transferred to the NMR instrument pre-adjusted at the desired temperature. NMR spectra were collected at regular intervals. With one equiv AlMe₃: ^1H NMR (500 MHz, $\text{C}_6\text{D}_5\text{CD}_3$) δ 8.00 (m, 2H, Ar-H), 7.26 (m, 2H, Ar-H), 7.11 (m, 2H, Ar-H), 6.87 (m, 2H, Ar-H), 6.15 (s, 2H, Ar-H), 3.39 (s, 3H, OCH₃), 1.97 (m, 2H, CH(CH₃)₂), 1.77 (m, 2H, CH(CH₃)₂), 1.24 (s, 9H, C(CH₃)₃), 1.00 (m, 6H, CH(CH₃)₂), 0.89 (m, 6H, CH(CH₃)₂), 0.82 (m, 6H,

$\text{CH}(\text{CH}_3)_2$, 0.76 (m, 6H, $\text{CH}(\text{CH}_3)_2$), -0.50 (br s, 9H, $\text{Al}(\text{CH}_3)_3$). $^{31}\text{P}\{\text{H}\}$ NMR ($\text{C}_6\text{D}_5\text{CD}_3$, 121.48 MHz) δ 35.86 (s).

II. Computational Details

Computational Details

All calculations were performed with DFT as implemented in Gaussian 09 Revision C.01.¹² Geometry optimizations and electronic structure calculations were performed with the TPSSh hybrid functional¹³ that, incorporating 10% exact exchange (c.f. BLYP 0% and B3LYP 20%), has been shown to be effective for calculating transition metal-containing compounds.¹⁴ The LANL2DZ basis set and effective core potential¹⁵ for Ni atoms and the 6-31++G(d,p) basis set¹⁶ for all other atoms was used. For all compounds isopropyl substituents on the synthesized phosphine ligands were truncated to methyl groups. Geometry optimizations performed without molecular symmetry constraints. Optimized structures were confirmed with subsequent frequency calculations that returned no (for intermediates) or one (for transition states) imaginary frequency vibrational modes.

Thermochemistry: The vibrational analyses (originally at 298 K) were re-tabulated with Gaussian's freqchk utility using 195 K, 1 atm, and the default scale factor (1/1.12). The resulting "Thermal correction to Gibbs Free Energy" was added to the SCF energy ("E(RTPSSH)") to yield *gas-phase Gibbs free energies*. Single-point calculations were performed on the gas-phase optimized structures using the integral equation formalism variant of the polarizable continuum model (IEFPCM)¹⁷ with $\epsilon=2.3741$ (representing toluene). *Solvation energies* were calculated as the difference in SCF energy between the gas-phase and IEFPCM single point calculations. Finally, the *solvated Gibbs free energies* were determined by adding the solvation energies to the gas-phase Gibbs free energies.

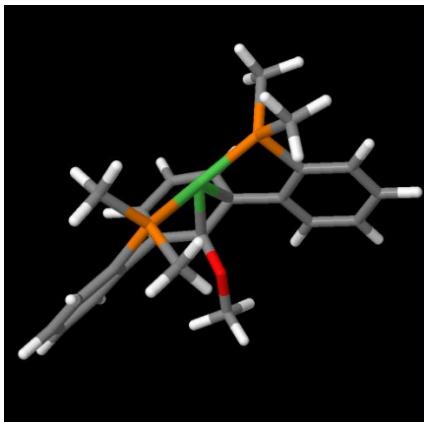
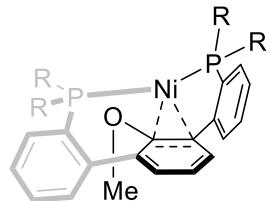
Not discussed in the main text, but also calculated: the dissociation of Al_2Me_6 to AlMe_3 was determined to be 1.88 kcal/mol uphill.

Atomic Cartesian Coordinates

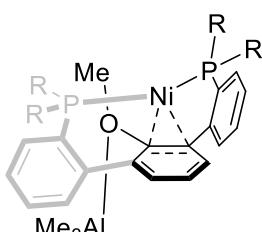
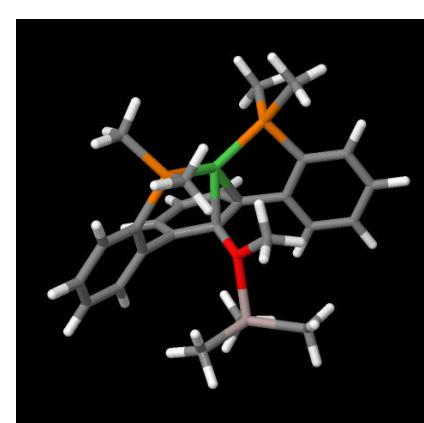
A

Ni	-0.25116	0.78497	0.52421
P	1.59511	1.64965	-0.27685
P	-2.31576	1.48325	0.54843
C	0.28492	-1.0247	0.01321
O	0.39953	-0.98845	-1.39063
C	-3.04757	0.02426	-0.31845
C	2.99138	0.425	-0.26845
C	-1.0266	-1.16894	0.62448
C	1.46624	-1.28749	0.80237
C	4.26964	0.77617	-0.73119
H	4.44032	1.76984	-1.1397
C	2.78877	-0.87538	0.26632
C	-2.29626	-1.16567	-0.18822
C	-4.24781	0.01867	-1.046
H	-4.8249	0.93339	-1.15471
C	5.34166	-0.11868	-0.67349
H	6.3195	0.17779	-1.04283
C	3.87974	-1.76289	0.32797
H	3.718	-2.75873	0.73271
C	-2.79055	-2.34651	-0.76477
H	-2.23267	-3.27092	-0.64074
C	-1.0759	-1.75685	1.93679
H	-2.05458	-1.9604	2.36592
C	5.14423	-1.39325	-0.13303
H	5.96833	-2.0993	-0.07869
C	1.34469	-1.80998	2.08423
H	2.23902	-1.949	2.6865
C	0.06914	-2.08006	2.63909
H	-0.00647	-2.5104	3.63359
C	-4.71203	-1.15845	-1.64093
H	-5.63786	-1.1519	-2.20973
C	-3.98415	-2.34391	-1.49326
H	-4.34477	-3.26425	-1.94464
C	-3.34482	1.58841	2.09475
C	-2.98698	2.93691	-0.39018
C	2.39389	3.14829	0.47421
C	1.52541	2.13996	-2.06272
H	1.6756	3.97354	0.43709
H	3.30976	3.45032	-0.04592
H	2.62971	2.9451	1.5225
H	0.82332	2.97188	-2.17427
H	1.15344	1.28622	-2.6336
H	2.50565	2.44336	-2.44735
H	-3.07595	2.49658	2.64384

H	-3.12603	0.72433	2.72737
H	-4.41617	1.60729	1.86616
H	-2.62324	3.85351	0.08476
H	-4.08269	2.96526	-0.40658
H	-2.6112	2.90981	-1.41683
C	0.74681	-2.25191	-1.97872
H	0.77764	-2.08199	-3.0568
H	-0.01018	-3.01067	-1.74737
H	1.72909	-2.5937	-1.63129

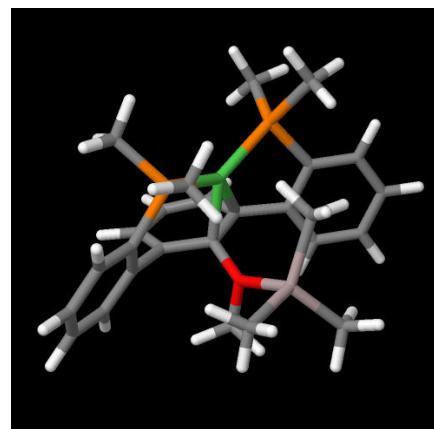
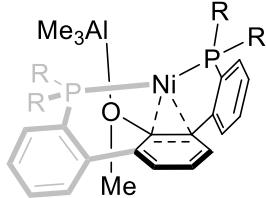


B_{trans}

Ni	-0.89023	1.09798	-0.35961	H	-5.30648	0.67323	-0.6152
P	0.81706	2.35983	-0.9572	H	-3.53332	2.05633	-3.13339
P	-2.89849	0.7301	-1.19538	H	-4.42625	0.51949	-3.15195
C	0.11654	-0.22371	0.66947	C	-2.70753	0.56834	-3.63229
O	0.95554	-1.09692	-0.11957	H	0.6373	-1.23103	-1.53364
C	-2.88372	-1.10623	-0.98608	H	1.59242	-1.26599	-2.06351
C	2.2696	2.05449	0.15243	H	0.05482	-0.35063	-1.82915
C	-1.28401	-0.54288	0.87956	H	0.07492	-2.14977	-1.70067
C	0.81317	0.59793	1.62932	Al	2.12944	-2.67468	0.63979
C	3.50129	2.69198	-0.0711	C	3.95366	-1.8636	0.59042
H	3.62334	3.34698	-0.93109	H	4.08693	-1.15753	-0.24208
C	2.12562	1.21535	1.28779	H	4.22657	-1.32565	1.50799
C	-2.0337	-1.55336	0.05155	H	4.70306	-2.65636	0.44669
C	-3.60831	-2.03899	-1.7445	C	1.78522	-4.06621	-0.76014
H	-4.25831	-1.70618	-2.54951	H	2.35086	-4.97183	-0.48696
C	4.57966	2.51796	0.79938	H	0.73067	-4.3751	-0.82185
H	5.5236	3.01839	0.60312	H	2.10725	-3.80203	-1.77644
C	3.21428	1.05954	2.16231	C	1.29913	-3.11647	2.40107
H	3.10003	0.4068	3.02303	H	0.64165	-3.99496	2.30544
C	-1.95324	-2.92239	0.3333	H	2.05773	-3.38575	3.15106
H	-1.33635	-3.24399	1.15881	H	0.68957	-2.31919	2.85144
C	-1.83953	-0.21272	2.16855				
H	-2.84479	-0.5644	2.38825				
C	4.43061	1.70075	1.92341				
H	5.26238	1.55334	2.60642				
C	0.18839	0.93887	2.82125				
H	0.70294	1.60372	3.50937				
C	-1.12275	0.48636	3.11586				
H	-1.57075	0.71642	4.07792				
C	-3.49325	-3.40817	-1.47561				
H	-4.04766	-4.12683	-2.07281				
C	-2.67062	-3.84786	-0.43229				
H	-2.58915	-4.90862	-0.21273				
C	-4.43195	1.24105	-0.28047				
C	-3.45356	0.98069	-2.94689				
C	0.61393	4.20059	-0.83405				
C	1.57434	2.2212	-2.64654				
H	-0.14097	4.52197	-1.55841				
H	1.55316	4.72882	-1.03084				
H	0.26393	4.45768	0.16918				
H	0.80882	2.4449	-3.39594				
H	1.93569	1.20326	-2.80825				
H	2.41107	2.91482	-2.77909				
H	-4.60822	2.30888	-0.44468				
H	-4.2793	1.07623	0.78888				

B_{cis}

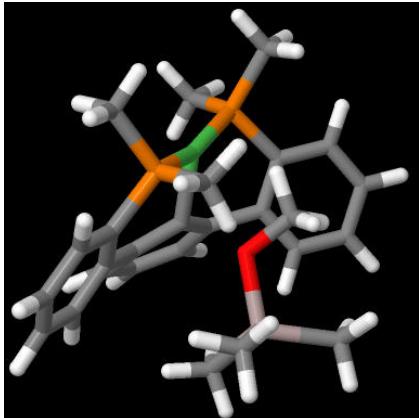
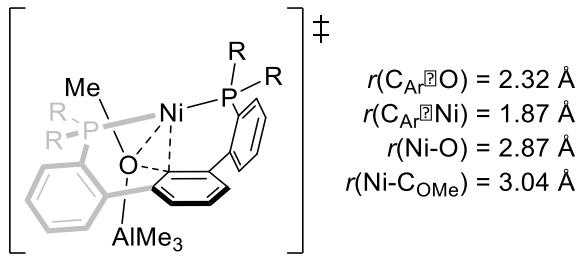
Ni	0.2584	-1.07022	-0.1488	H	4.17757	-3.07606	0.51107
P	-1.6987	-1.45322	-1.09207	H	2.66822	-3.09709	-2.55398
P	2.31892	-1.80917	-0.5245	H	4.18653	-2.29234	-2.09816
C	-0.23944	0.35943	1.02749	C	2.86405	-1.35927	-2.85891
O	-0.37922	1.66509	0.40707	H	-0.77695	2.68394	1.37256
C	3.15061	-0.26015	0.04758	H	-0.62612	3.64606	0.88429
C	-3.03079	-0.51963	-0.19725	H	-0.14148	2.59912	2.25703
C	1.08363	-0.07707	1.45986	H	-1.82727	2.54516	1.63509
C	-1.40976	-0.15559	1.71211	Al	-0.09409	2.4119	-1.48003
C	-4.32819	-0.39487	-0.71828	C	0.9319	1.03151	-2.49191
H	-4.55812	-0.8027	-1.69907	H	2.01354	1.16777	-2.35873
C	-2.75543	0.01281	1.08926	H	0.69917	-0.01223	-2.21855
C	2.38305	0.50258	0.95971	H	0.72144	1.12677	-3.56897
C	4.40583	0.20402	-0.37053	C	0.96261	4.07299	-1.11141
H	4.99368	-0.37199	-1.07999	H	1.40324	4.41445	-2.06159
C	-5.34504	0.24112	-0.00037	H	0.38163	4.92438	-0.72703
H	-6.33783	0.33327	-0.43154	H	1.80672	3.91151	-0.42644
C	-3.7926	0.62958	1.8101	C	-1.98405	2.76486	-2.02853
H	-3.57846	1.02136	2.8015	H	-2.42655	3.59508	-1.45779
C	2.90494	1.70985	1.44624	H	-2.02373	3.06857	-3.08639
H	2.33113	2.29161	2.16212	H	-2.66571	1.91157	-1.91638
C	1.15085	-0.80986	2.70455				
H	2.13812	-1.02668	3.10616				
C	-5.07683	0.74868	1.27327				
H	-5.86	1.23844	1.84499				
C	-1.26445	-0.9102	2.86452				
H	-2.15014	-1.33823	3.32701				
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H	0.11412	-1.73939	4.32935				
C	4.90368	1.42133	0.10564				
H	5.8702	1.78289	-0.23394				
C	4.1519	2.17298	1.01384				
H	4.53402	3.12044	1.38332				
C	3.08416	-3.1334	0.52683				
C	3.09962	-2.16973	-2.16421				
C	-2.32056	-3.19498	-0.91657				
C	-2.05655	-1.13171	-2.87817				
H	-1.68307	-3.86177	-1.50565				
H	-3.35797	-3.28602	-1.25727				
H	-2.25961	-3.49416	0.13312				
H	-1.35522	-1.72693	-3.47075				
H	-1.88543	-0.07632	-3.1007				
H	-3.07763	-1.40726	-3.16107				
H	2.76835	-4.11228	0.15182				
H	2.72967	-3.02608	1.55487				



C_{trans}

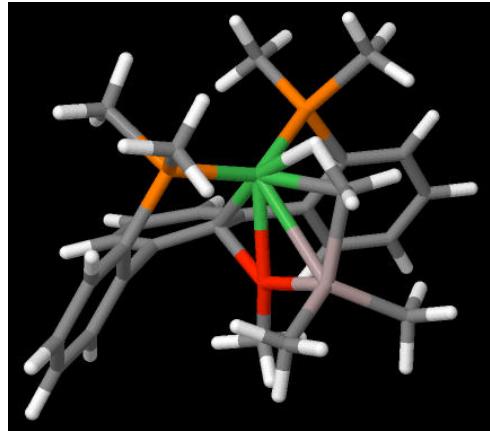
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P	1.27478	0.4411	-2.99949
C	0.5294	-0.74705	-0.05905
C	2.26239	1.47574	-1.87117
C	-2.43877	-1.75867	0.5669
C	1.89888	-0.37363	-0.14159
C	0.13654	-1.91263	0.64607
C	-3.68024	-2.13871	1.10408
H	-4.59688	-1.76537	0.65385
C	-1.23417	-2.23135	1.13692
C	2.4045	0.97286	-0.55807
C	2.81037	2.72136	-2.21222
H	2.69689	3.11248	-3.21942
C	-3.76602	-2.97818	2.21239
H	-4.73416	-3.25869	2.61579
C	-1.3489	-3.04289	2.28881
H	-0.45053	-3.34693	2.81355
C	3.11407	1.73463	0.38301
H	3.20497	1.36222	1.3986
C	2.87365	-1.30732	0.25213
H	3.92153	-1.03286	0.15902
C	-2.5832	-3.41822	2.81279
H	-2.61819	-4.03437	3.70644
C	1.16104	-2.8412	0.94874
H	0.88031	-3.81007	1.34936
C	2.50666	-2.55952	0.74452
C	3.5049	3.47271	-1.25943
H	3.91957	4.43956	-1.52921
C	3.65437	2.97677	0.03863
H	4.17703	3.56123	0.78979
C	0.92227	1.4999	-4.46948
C	2.46223	-0.80292	-3.67896
C	-3.4532	0.80592	-0.26472
C	-3.45813	-1.39365	-2.12304
H	-3.47522	1.58497	-1.03174
H	-3.02289	1.20436	0.65524
H	-4.4744	0.46091	-0.07364
H	-4.45467	-1.6261	-1.73246
H	-2.98654	-2.31811	-2.46618
H	-3.56428	-0.71342	-2.97424
H	1.84289	1.83697	-4.95757
H	0.33165	2.36856	-4.167
H	0.33949	0.9181	-5.18962
H	2.81937	-1.43192	-2.85998

H	3.31408	-0.30844	-4.15648
H	1.9493	-1.43614	-4.40928
H	3.26337	-3.29329	1.00408
O	-0.45618	1.08769	0.95898
C	-0.53774	2.25201	0.1636
H	0.39093	2.83659	0.17987
H	-1.35823	2.90513	0.50029
H	-0.75456	1.97357	-0.8891
Al	-0.35767	1.35723	2.83768
C	-2.28266	1.30895	3.44704
H	-2.34352	1.45688	4.53691
H	-2.90427	2.1013	2.99907
H	-2.77739	0.34869	3.23537
C	0.47899	3.17842	3.09491
H	1.4805	3.27543	2.64769
H	-0.12652	4.00849	2.69921
H	0.6022	3.37475	4.17196
C	0.77498	-0.10372	3.63127
H	0.26711	-1.07693	3.68555
H	1.72516	-0.26827	3.10053
H	1.04071	0.16477	4.66622



C_{cis}

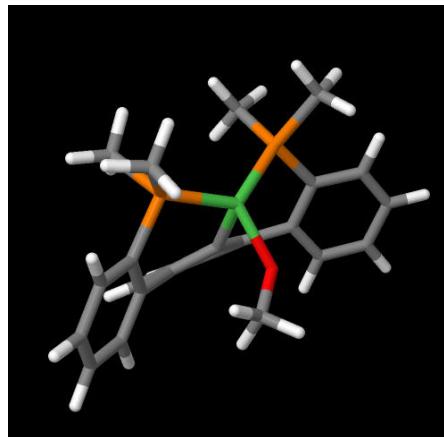
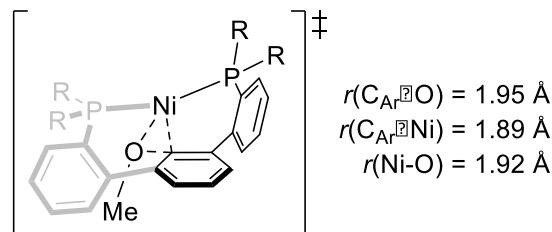
Ni	0.61608	0.91519	0.09175	H	2.22396	0.27229	4.18609
P	1.94286	0.62452	-1.63681	H	3.25431	0.58482	2.7578
P	0.93178	1.14807	2.27317	O	1.12275	-4.65515	1.28384
C	0.06228	-1.00348	0.20863	C	-1.3576	-0.24042	-0.46327
C	-0.57927	0.48901	3.05567	H	-2.44131	-1.19186	-0.54042
C	1.21473	-0.56907	-2.80746	H	-2.02173	-2.18764	-0.70903
C	-0.25614	-1.51879	1.52062	H	-3.06949	-0.91089	-1.3909
C	0.5459	-1.95724	-0.76278	H	-3.02769	-1.176	0.38231
C	1.23977	-0.41623	-4.20147	Al	-1.86074	1.57815	-0.91471
H	1.72116	0.45122	-4.6437	C	-0.44456	2.95594	-0.29874
C	0.58362	-1.69655	-2.22955	H	-0.53865	3.64499	-1.1544
C	-1.0219	-0.75751	2.55097	H	-0.84688	3.4786	0.5779
C	-1.31005	1.14041	4.05944	H	0.65655	2.8996	-0.14548
H	-0.97341	2.09952	4.44223	C	-3.5241	1.92899	0.13113
C	0.65286	-1.3682	-5.03999	H	-4.39563	1.35713	-0.21891
H	0.67387	-1.23039	-6.11717	H	-3.40521	1.71344	1.20274
C	0.00848	-2.64931	-3.0921	H	-3.80482	2.99103	0.05354
H	-0.48776	-3.5141	-2.65964	C	-2.06001	1.59421	-2.89983
C	-2.17698	-1.33144	3.11011	H	-2.34236	2.60043	-3.2472
H	-2.51619	-2.29475	2.73801	H	-1.14229	1.3151	-3.4346
C	0.15752	-2.81092	1.87991	H	-2.84887	0.91629	-3.25724
H	-0.02738	-3.13637	2.90123	‡	$r(C_{Ar}\ddot{O}) = 1.75 \text{ \AA}$ $r(C_{Ar}\ddot{P}Ni) = 2.00 \text{ \AA}$ $r(Ni\ddot{O}) = 2.35 \text{ \AA}$ $r(Ni-C_{AlMe}) = 2.33 \text{ \AA}$		
C	0.03912	-2.49114	-4.47956				
H	-0.42725	-3.23647	-5.11767				
C	0.95186	-3.23262	-0.33952				
H	1.39667	-3.8947	-1.07888				
C	0.79452	-3.66686	0.97871				
C	-2.47175	0.56545	4.58445				
H	-3.03266	1.08371	5.35692				
C	-2.89985	-0.6781	4.11287				
H	-3.7992	-1.13566	4.5151				
C	1.16388	2.82203	3.02015				
C	2.28983	0.19298	3.09564				
C	2.38694	2.0907	-2.66889				
C	3.60877	-0.11656	-1.29678				
H	2.85761	2.83797	-2.023				
H	1.4794	2.52759	-3.09395				
H	3.08521	1.83541	-3.47332				
H	4.15492	-0.30588	-2.22741				
H	3.47331	-1.05905	-0.75987				
H	4.18596	0.56644	-0.66581				
H	1.22995	2.77578	4.11283				
H	0.34209	3.48204	2.73154				
H	2.09458	3.24657	2.63181				
H	2.21639	-0.85721	2.80338				



C_{AlFree}

Ni	-0.07407	-0.83561	0.69181
P	1.91728	-1.58203	0.15099
P	-2.01676	-1.623	-0.08299
C	-0.07933	0.83834	-0.18938
C	-3.15309	-0.21438	0.20076
C	3.02686	-0.13023	0.30704
C	-1.3115	1.3256	-0.71598
C	1.15377	1.35042	-0.68625
C	4.32333	-0.20936	0.84333
H	4.72338	-1.17313	1.14425
C	2.50672	1.13068	-0.08365
C	-2.64773	1.07576	-0.09385
C	-4.43559	-0.34503	0.75645
H	-4.8281	-1.33107	0.98782
C	5.1197	0.92865	0.99567
H	6.11789	0.84234	1.41591
C	3.33093	2.26326	0.07027
H	2.93374	3.23684	-0.2033
C	-3.46482	2.19054	0.1627
H	-3.07491	3.18257	-0.04791
C	-1.28588	2.14581	-1.85555
H	-2.23193	2.45757	-2.29144
C	4.61789	2.1721	0.60344
H	5.21717	3.0702	0.72376
C	1.11719	2.17557	-1.8344
H	2.0621	2.49385	-2.26784
C	-0.08025	2.55496	-2.43239
C	-5.22888	0.77652	1.01705
H	-6.21755	0.65331	1.45062
C	-4.74031	2.04964	0.71526
H	-5.34106	2.93142	0.91989
C	-2.9022	-3.07987	0.63932
C	-2.22342	-1.94516	-1.89901
C	2.81332	-2.94086	1.03644
C	2.18838	-2.08321	-1.61656
H	2.21364	-3.85141	0.94445
H	2.90362	-2.69941	2.09919
H	3.80833	-3.13531	0.61983
H	3.25178	-2.23586	-1.83163
H	1.79775	-1.29779	-2.2688
H	1.637	-3.00728	-1.81679
H	-3.89413	-3.23086	0.19824
H	-3.0006	-2.95712	1.72157
H	-2.29656	-3.97143	0.45042
H	-1.85205	-1.07918	-2.45346

H	-3.27433	-2.11521	-2.15735
H	-1.63054	-2.82051	-2.18243
H	-0.07794	3.17229	-3.32573
O	-0.37618	0.74216	1.73802
C	0.61945	1.4283	2.47543
H	0.19447	1.61541	3.47144
H	0.86076	2.39764	2.0156
H	1.54714	0.85266	2.59342



Al₂Me₆

Al	1.30448	0.00555	0.00062
Al	-1.30454	0.00546	-0.00058
C	2.43789	-1.61272	-0.00017
H	3.09341	-1.64353	-0.88133
H	3.09494	-1.64406	0.87981
H	1.85337	-2.54191	0.00004
C	2.05479	1.83525	0.00016
H	1.28442	2.61718	-0.00227
H	2.68747	2.01218	0.88135
H	2.69079	2.0099	-0.8791
C	-0.00036	-0.23612	1.70304
H	-0.00063	-1.28942	2.00248
H	0.85002	0.2474	2.21118
H	-0.85165	0.24736	2.20973
C	0.00043	-0.23607	-1.70298
H	0.0003	-1.28934	-2.00252
H	-0.84989	0.24775	-2.21098
H	0.85177	0.24717	-2.20979
C	-2.4371	-1.61342	0.00009
H	-3.09221	-1.64503	0.88154
H	-3.09453	-1.6448	-0.87961
H	-1.85199	-2.54223	-0.00077
C	-2.05555	1.83484	-0.00017
H	-1.28548	2.61707	0.00294
H	-2.68768	2.01166	-0.88177
H	-2.69222	2.00904	0.87869

AlMe₃

Al	-0.00026	0.00021	-0.00018
C	1.2553	1.5286	0.0001
H	1.9202	1.496	0.87538
H	1.91576	1.49966	-0.87868
H	0.75552	2.50471	0.00335
C	-1.95191	0.32224	0.00035
H	-2.54623	-0.59923	0.01666
H	-2.25567	0.92615	0.86759
H	-2.25905	0.89584	-0.88627
C	0.69682	-1.851	-0.00033
H	0.36174	-2.40045	0.89148
H	0.31801	-2.41954	-0.8619
H	1.79186	-1.90498	-0.02597

III. Discussion, Kinetics and Tables

Scheme SI.1. Intramolecular Oxidative Addition of **1-R** in the Presence of Methylating Additives.

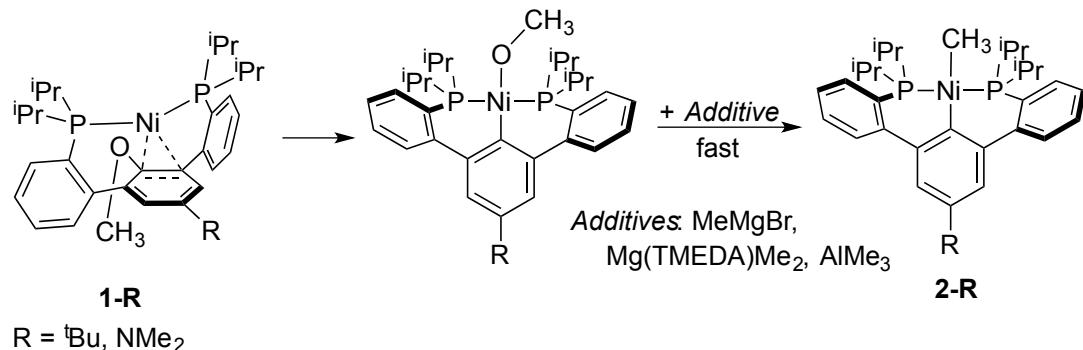


Table SI.1. Observed rate constants for **1-R**.

T (K)	1-NMe ₂ ^a k _{obs} (min ⁻¹ ·10 ⁻³)	1- ^t Bu ^a k _{obs} (min ⁻¹ ·10 ⁻³)	1-CF ₃ ^b k _{obs} (min ⁻¹ ·10 ⁻³)
318	2.19 ± 0.05	2.58 ± 0.05	-
333	10.2 ± 0.1	8.65 ± 0.09	2.94 ± 0.04
343	28.4 ± 0.1	-	8.05 ± 0.05
353	86 ± 3	70.0 ± 0.4	18.3 ± 0.2
363	-	-	-
373	-	-	105 ± 3

^a Rates obtained using 1.25 equivs of Mg(TMEDA)Me₂. ^b Rates obtained without added Mg(TMEDA)Me₂ as step subsequent to oxidative addition are slower for 1-CF₃ and do not interfere with the measurement.

Figure SI.1. Kinetics plots for **1-^tBu** with 1.25 equivs of Mg(TMEDA)Me₂ at different temperatures.

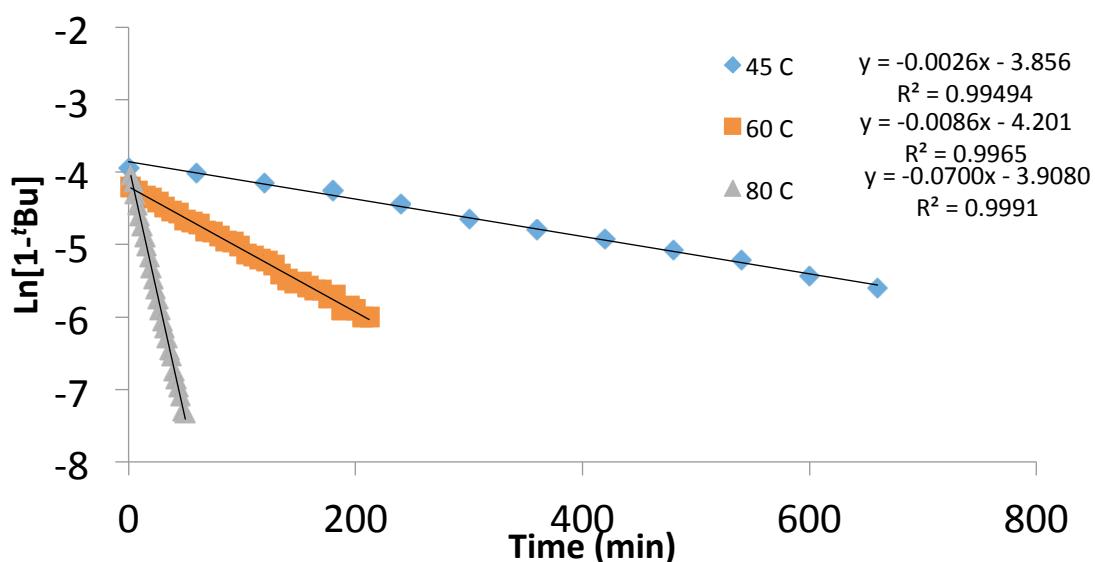


Figure SI.2. Kinetics plots for **1-CF₃** without additives at different temperatures.

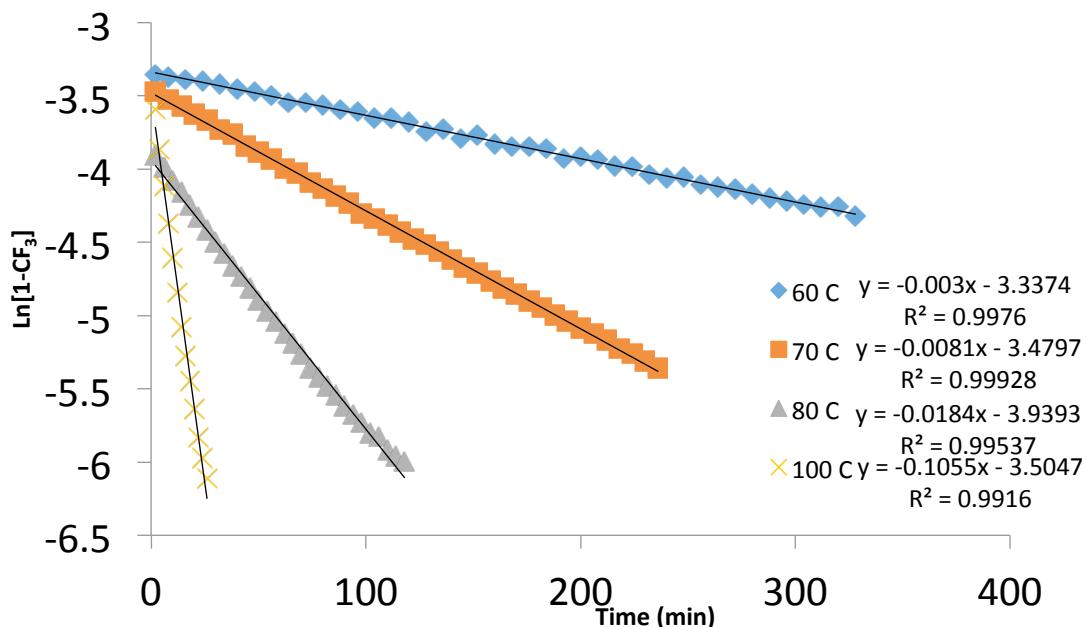


Figure SI.3. Kinetics plots for **1-NMe₂** with 1.25 equivs of Mg(TMEDA)Me₂ at different temperatures.

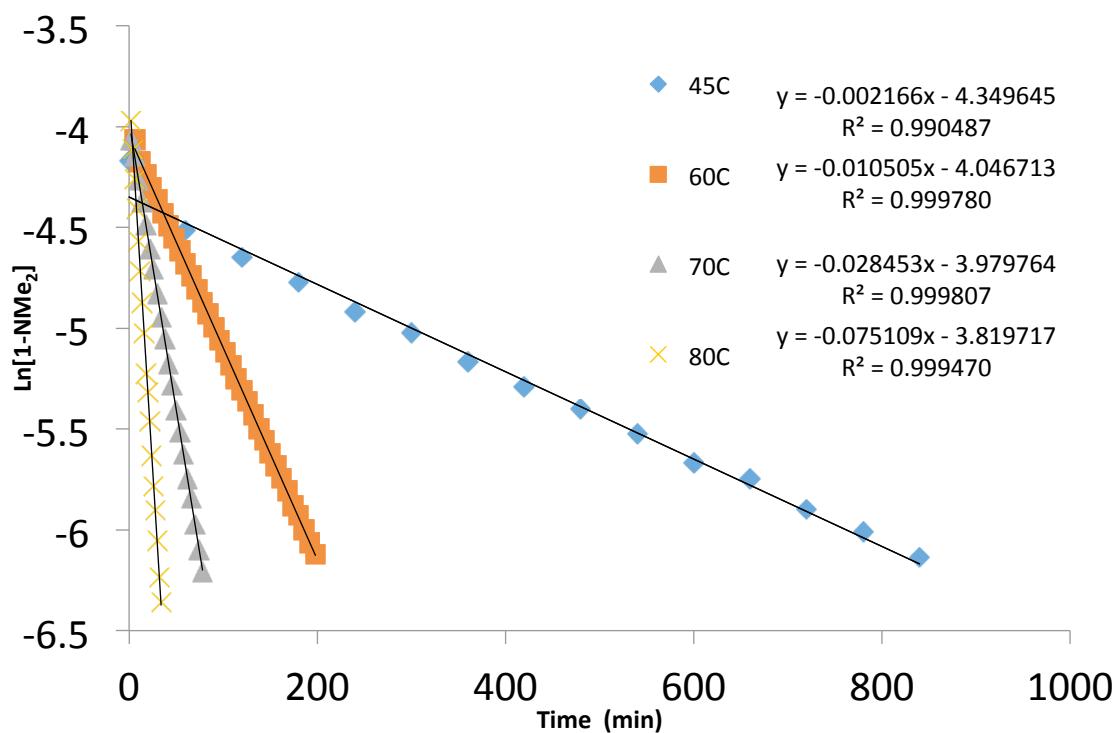
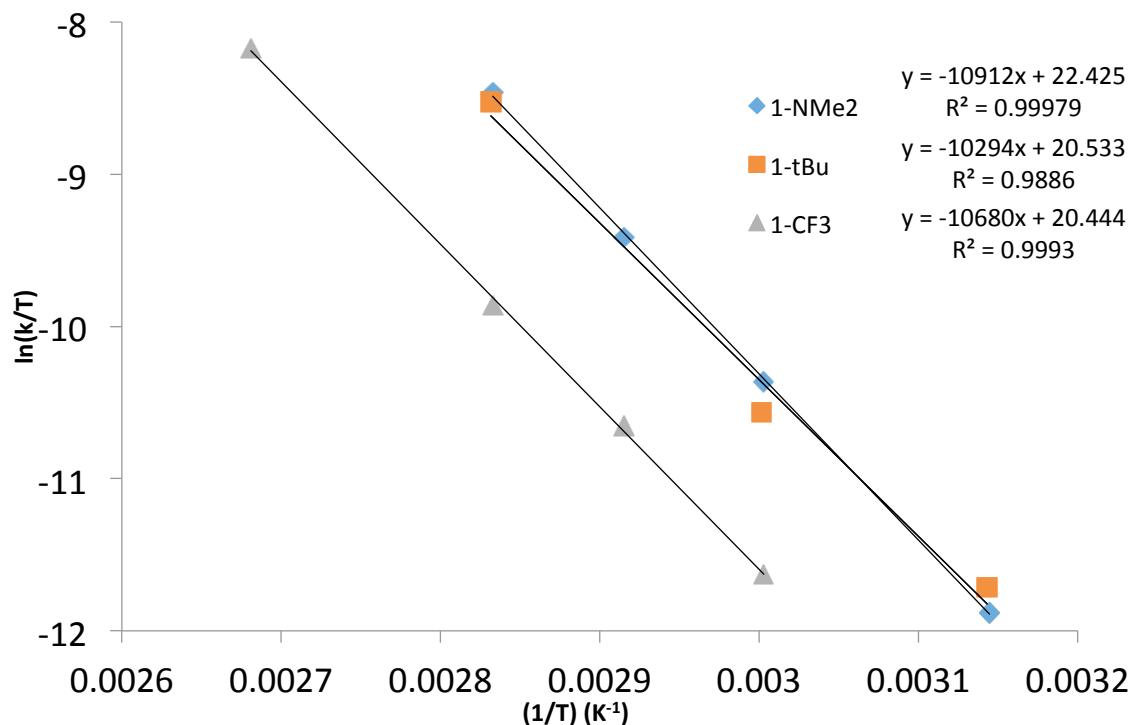


Figure SI.4. Eyring plots for **1-NMe₂**, **1-tBu**, and **1-CF₃**.



Discussion of substituent effects

Substituents were selected to cover a range of Hammett parameters. CO stretching frequency of corresponding Ni complexes was found to increase with increasing electron withdrawing character of the substituents (Table SI.2.). This effect is interpreted to be a consequence of a stronger metal backbonding interaction with the arene for electron withdrawing substituents, leading to lower backbonding to CO. With the carbonyl stretching frequencies used as a measure of the strength of the nickel arene interactions, the more electron withdrawing substituents leads to a stabilization of this interaction and a lowering of the ground state energy. The calculated activation parameters for different substituents are similar (Table 1, text) indicating that the ground state and transition state energies are affected in similar fashion (Figure SI.5.).

Table SI.2. Effect of arene substituents on CO stretching frequency in Ni(0) complexes.

	NMe ₂	t-Bu	CF ₃
σ_p	-0.83	-0.20	0.54
ν_{CO} (cm ⁻¹)	1912	1919	1943

Figure SI.5. Proposed reaction coordinate diagram for oxidative addition in **1-R**.

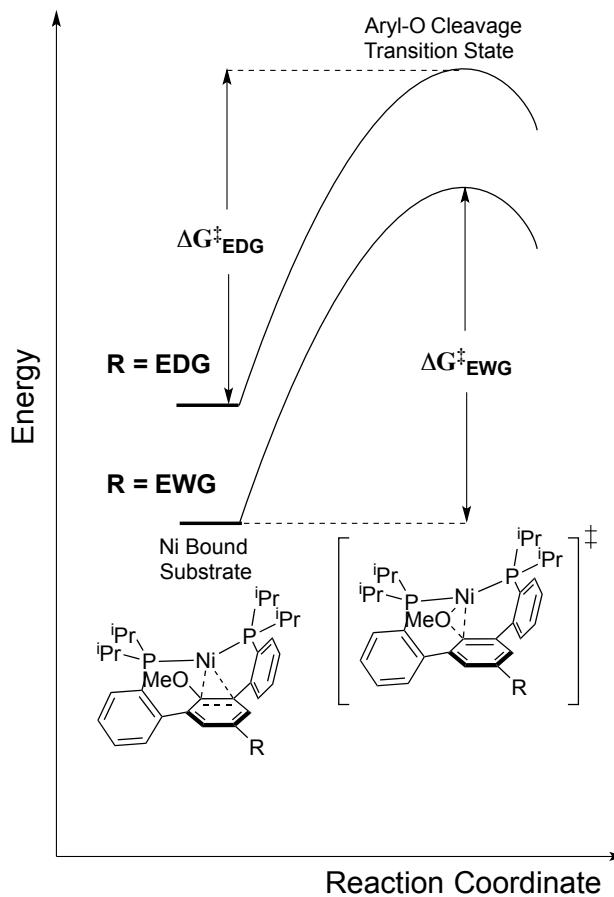


Table SI.3. Rate Acceleration of Aryl-Oxygen Bond Activation in **1-NMe₂**.

Additive	Equiv.	T(°C)	$k_{\text{obs}} (\text{min}^{-1}) \times 10^{-3}$
MeMgBr	1.00	80	78
Mg(TMEDA)Me ₂	1.25	80	70
MeMgBr	10.00	80	774

Figure SI.6. NMR spectra ($C_6D_5CD_3$) for the addition of $AlMe_3$ to $\mathbf{1-tBu}$ at $-80\text{ }^{\circ}C$.

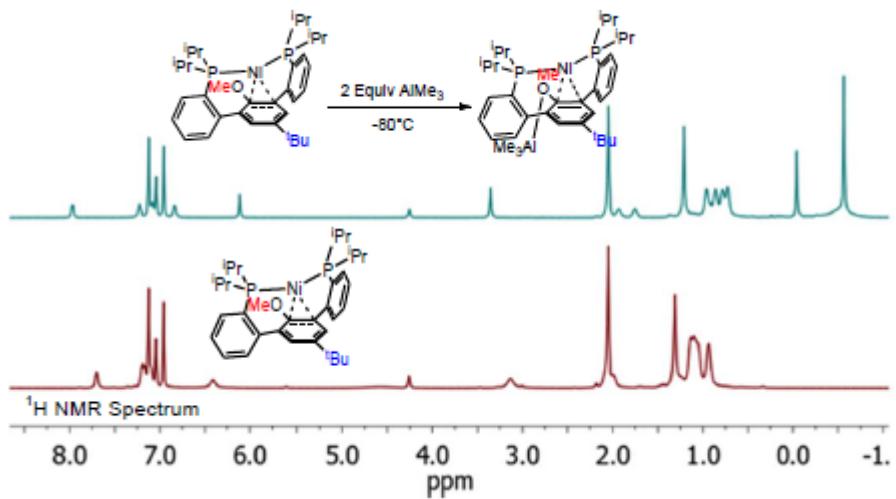


Figure SI.7. NOESY spectrum of $\mathbf{1-tBu}$ in the presence of $AlMe_3$ collected at $-80\text{ }^{\circ}C$.

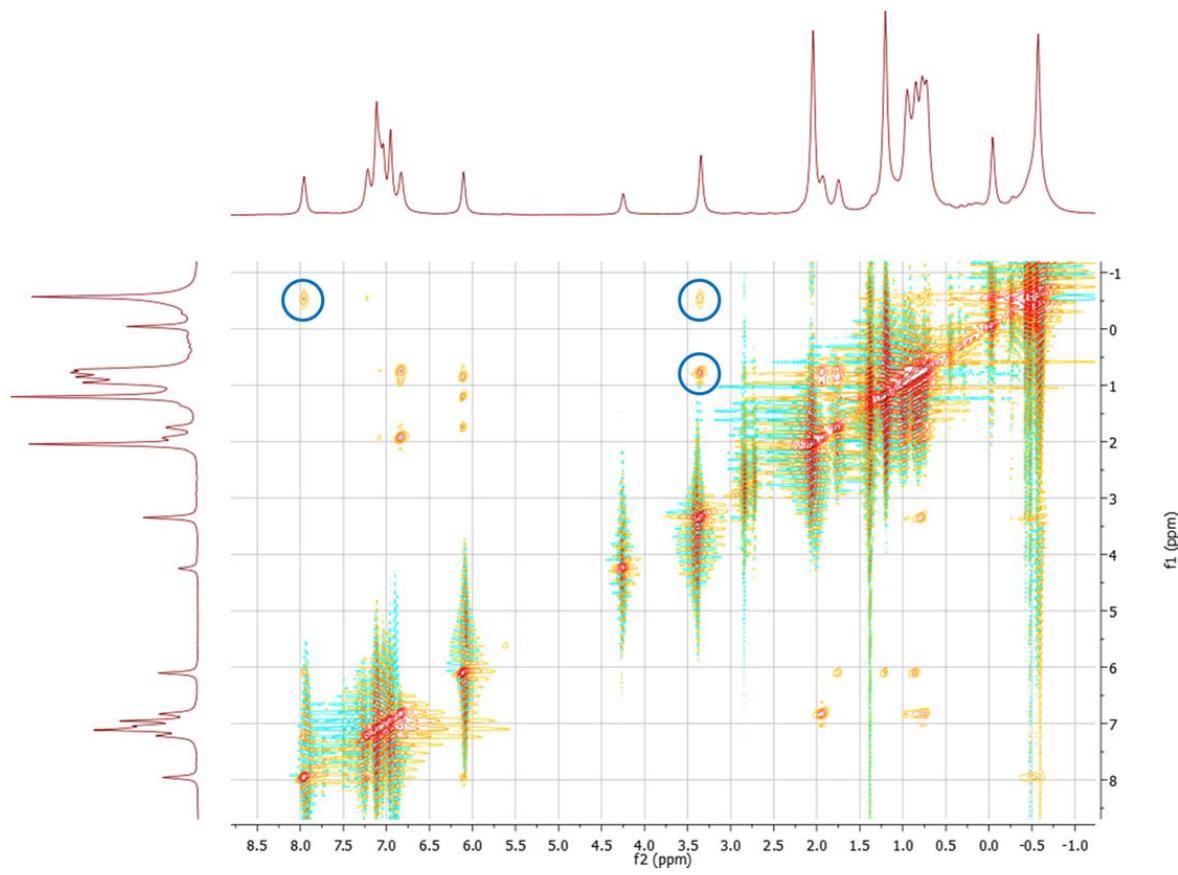


Figure SI.8. Kinetics plots for **1-tBu** with 10 equiv. AlMe₃ at different temperatures.

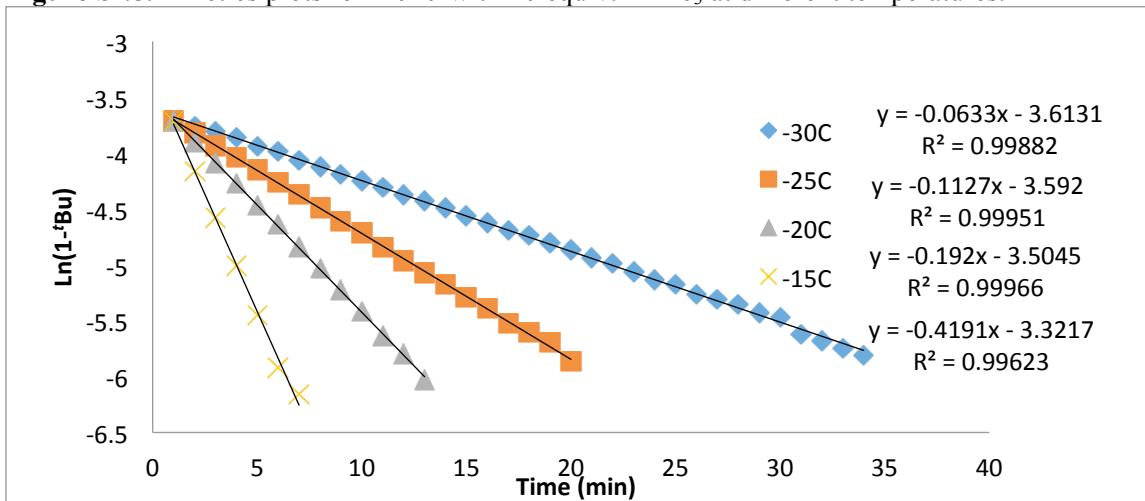


Figure SI.9. Kinetics plots for **1-tBu** with 2 equiv. AlMe₃ at different temperatures.

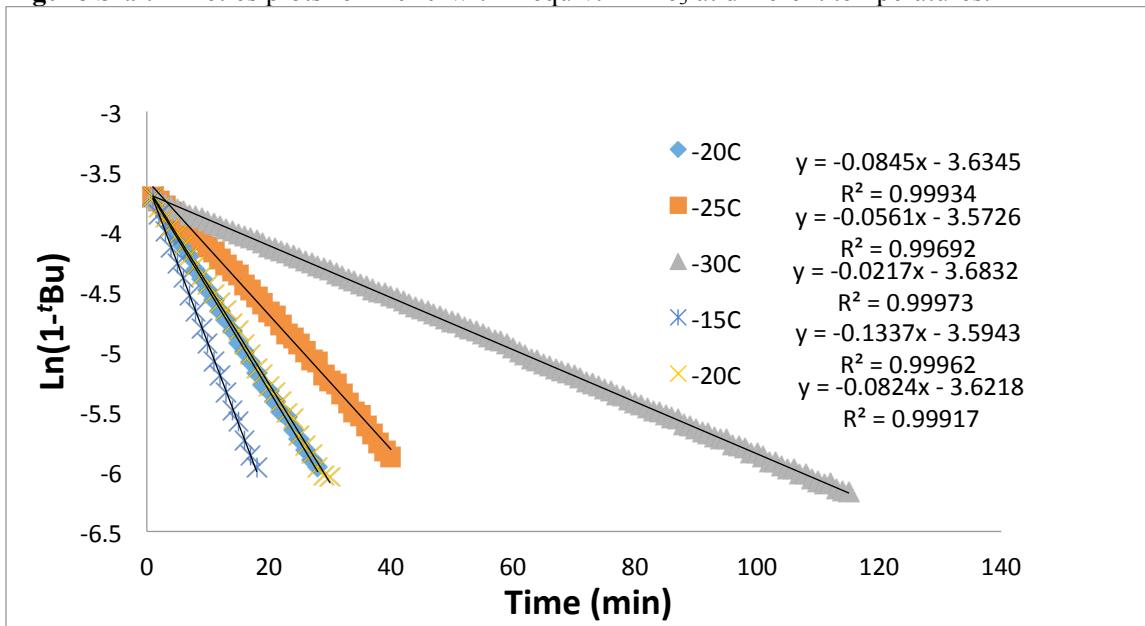


Figure SI.10. Eyring plots for **1-tBu** in the presence of 2 and 10 equiv. of AlMe₃.

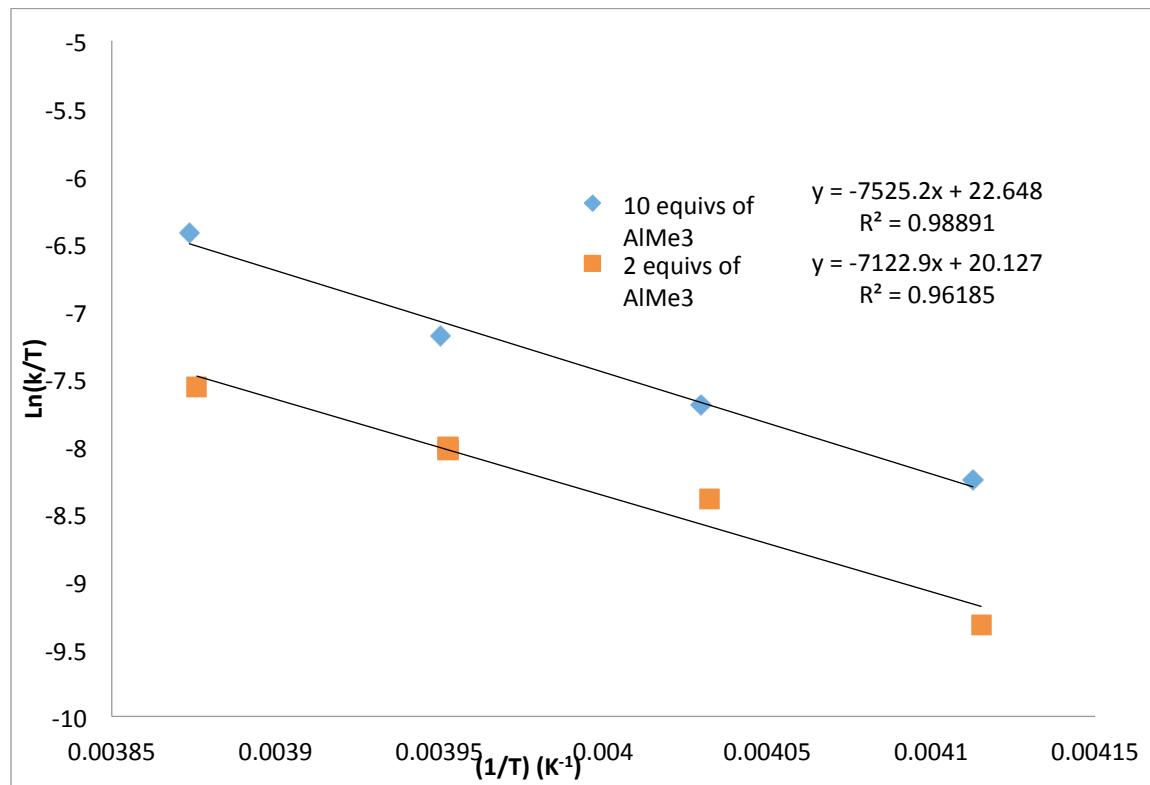


Figure SI.11. Rate constant dependence for the cleavage of the aryl oxygen bond of **1-tBu·AlMe₃** on the varying concentration of AlMe₃ at -40 °C.

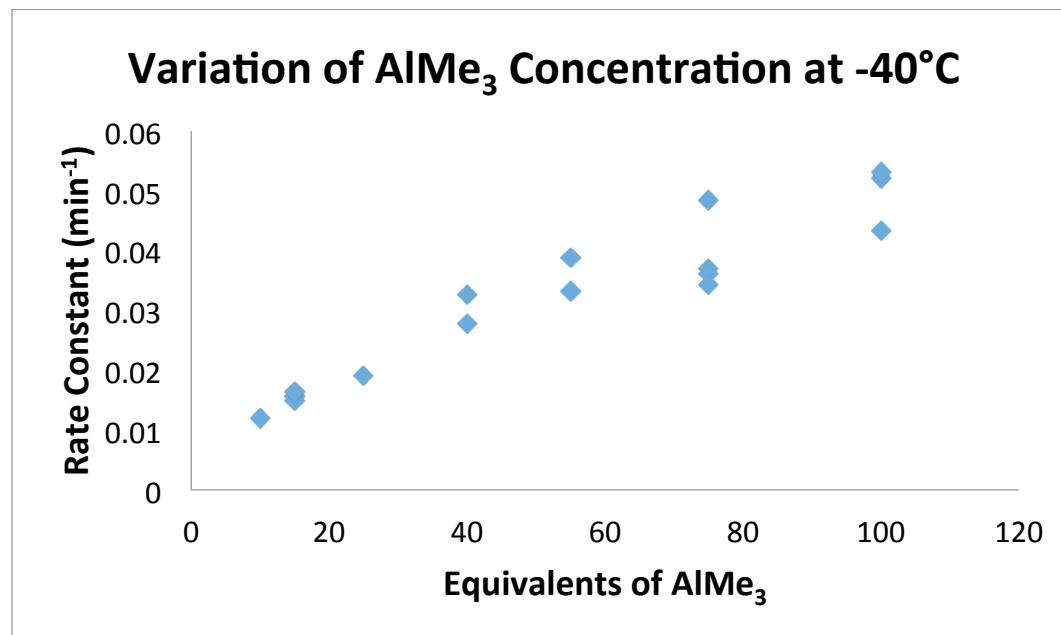
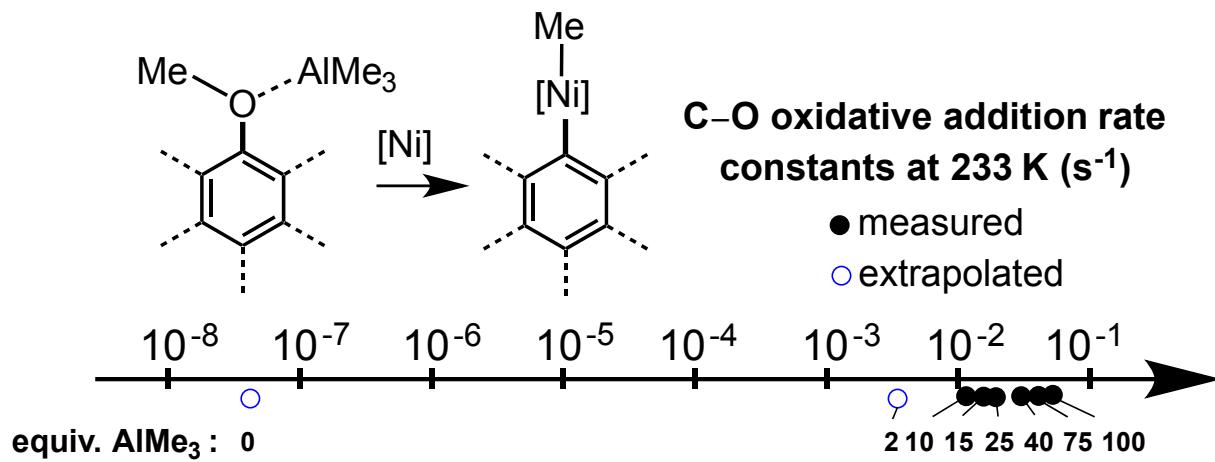
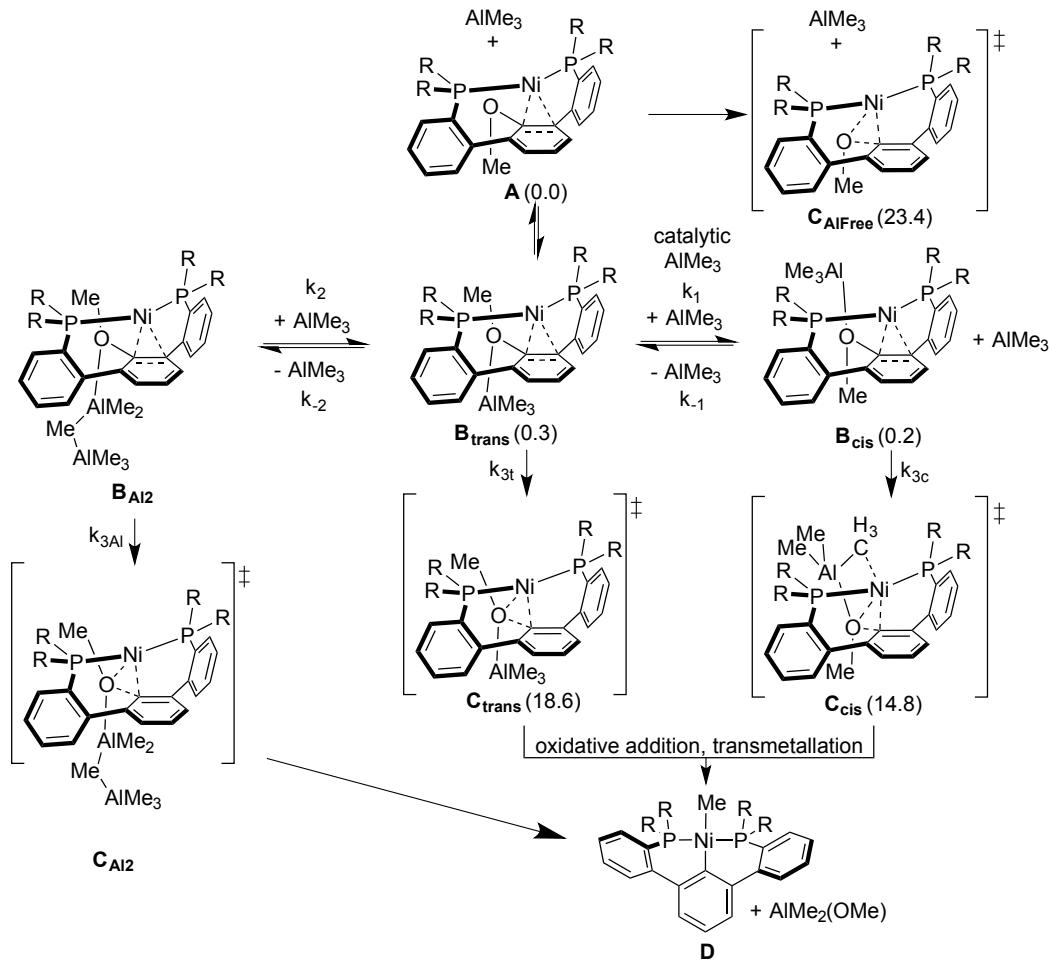


Figure SI.12. Rate constants for aryl ether C–O oxidative addition as a function of AlMe₃ addition.



Scheme SI.2. Potential mechanisms for aryl ether cleavage.



Kinetics analysis

Assuming only one Al center is involved in the oxidative addition transition state:

If $d[B_{cis}]/dt = 0$, then:

$$k_1[B_{trans}][Al] = k_{-1}[B_{cis}][Al] + k_{3c}[B_{cis}]$$

Solving for $[B_{cis}]$:

$$[B_{cis}] = \frac{k_1[B_{trans}][Al]}{k_{-1}[Al] + k_{3c}}$$

$$(1) \text{ rate(via } C_{trans} \text{ and } C_{cis}) = k_{3t}[B_{trans}] + k_{3c}[B_{cis}] = [B_{trans}] \left(k_{3t} + k_{3c} \frac{k_1[Al]}{k_{-1}[Al] + k_{3c}} \right)$$

Assuming that a second Al center is involved in the oxidative addition transition state (left route):

Assuming $d[B_{Al2}]/dt = 0$, then:

$$k_2[B_{trans}][Al] = k_{-2}[B_{Al2}] + k_{3Al}[B_{Al2}]$$

Solving for $[B_{Al2}]$:

$$[B_{Al2}] = \frac{k_2[B_{trans}][Al]}{k_{-2} + k_{3Al}}$$

Assuming only the pathway with two Al centers in the oxidative addition transition state is operative, then:

$$(2) \text{ rate(via } C_{Al2}) = k_{3Al}[B_{Al2}] = k_{3Al} \frac{k_2[B_{trans}][Al]}{k_{-2} + k_{3Al}}$$

Or, assuming only pathways through C_{Al2} and C_{trans} are operative:

$$(3) \text{ rate(via } C_{trans} + C_{Al2}) = k_{3t}[B_{trans}] + k_{3Al}[B_{Al2}] = [B_{trans}] \left(k_{3t} + k_{3Al} \frac{k_2[Al]}{k_{-2} + k_{3Al}} \right)$$

Or, assuming all three oxidative addition pathways are operative:

$$(4) \text{ rate} = \text{rate}(C_{trans}) + \text{rate}(C_{cis}) + \text{rate}(C_{Al2}) = \\ [B_{trans}] \left(k_{3t} + k_{3c} \frac{k_1[Al]}{k_{-1}[Al] + k_{3c}} + k_{3Al} \frac{k_2[Al]}{k_{-2} + k_{3Al}} \right)$$

The first equivalents of AlMe_3 bring the largest increase in rate ($\sim 10^5$ fold increase from no AlMe_3 , as extrapolated with the Eyring equation, to 10 equiv. of AlMe_3 at -40 °C), while large excess has a lower effect (~4 fold rate increase from 10 to 100 equiv. of AlMe_3 at -40 °C). Since the observed rate constants begin to level off at high concentrations of AlMe_3 (Figures SI.11 and SI.12), the C_{Al2} pathway alone or in combination with C_{trans} cannot explain the rate data. A mechanism involving the B_{cis} pathway is consistent with the rate constant dependence on AlMe_3 concentration. The B_{trans} pathway is major given the activation parameters which are inconsistent with a bimolecular rate determining step.

IV. References

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