

Supporting Information

for

**Cyclometallation Reactions of a Three-Coordinate Cobalt(I) Complex Bearing a
Nonsymmetric N-Heterocyclic Carbene Ligand**

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Table S1. Crystal data and summary of data collection and refinement.

	1	2•1.5 <i>n</i>-hexane	4	5
formula	C ₄₂ H ₄₇ ClCoPN ₂	C ₅₁ H ₆₇ CoPN ₂	C ₄₆ H ₅₇ CoPN ₂ Si	C ₂₉ H ₃₆ CoN ₂
Crystalsize (mm ³)	0.12 x 0.1 x 0.06	0.2 x 0.16 x 0.08	0.35 x 0.15 x 0.06	0.25 x 0.2 x 0.15
Fw	705.16	797.96	755.92	471.53
crystal system	Triclinic	Monoclinic	Triclinic	Orthorhombic
space group	P -1	P 21/c	P -1	P b a c
<i>a</i> , Å	12.053(4)	18.139(5)	11.7137(14)	20.7929(17)
<i>b</i> , Å	12.394(4)	14.698(4)	11.7791(13)	10.5688(8)
<i>c</i> , Å	12.694(4)	17.703(5)	17.1943(19)	22.0184(18)
<i>α</i> , deg	89.115(6)	90	73.315(2)	90
<i>β</i> , deg	87.656(7)	113.541(4)	81.611(2)	90
<i>γ</i> , deg	75.046(6)	90	62.113(2)	90
<i>V</i> , Å ³	1830.4(11)	4327(2)	2008.4(4)	4838.7(7)
<i>Z</i>	2	4	2	8
<i>D</i> _{calcd} , Mg/m ³	1.279	1.225	1.250	1.295
radiation (<i>λ</i>), Å	Mo K α (0.71073)	Mo K α (0.71073)	Mo K α (0.71073)	Mo K α (0.71073)
2 θ range, deg	3.212 to 54.694	2.450 to 55.324	2.472 to 61.398	3.700 to 51.998
μ , mm ⁻¹	0.617	0.470	0.531	0.728
<i>F</i> (000)	744	1716	806	2008
no. of obsd reflns	8144	10007	12275	4651
no. of params refnd	429	505	467	385
goodness of fit	0.929	1.031	0.897	1.192
R1	0.0637	0.0712	0.0569	0.0964
wR2	0.1194	0.1733	0.1338	0.1663

NMR spectra:

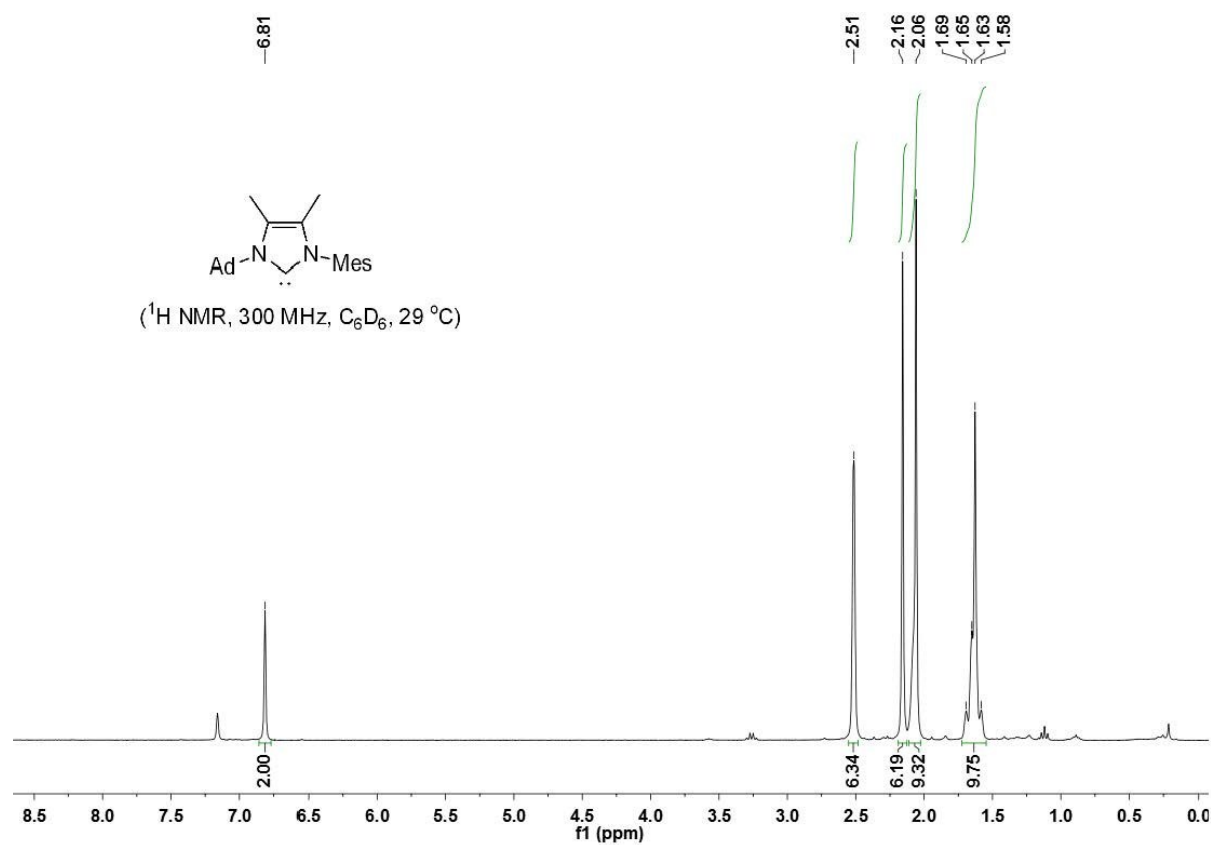


Figure S1. ^1H NMR spectrum of IAdMes in C_6D_6 .

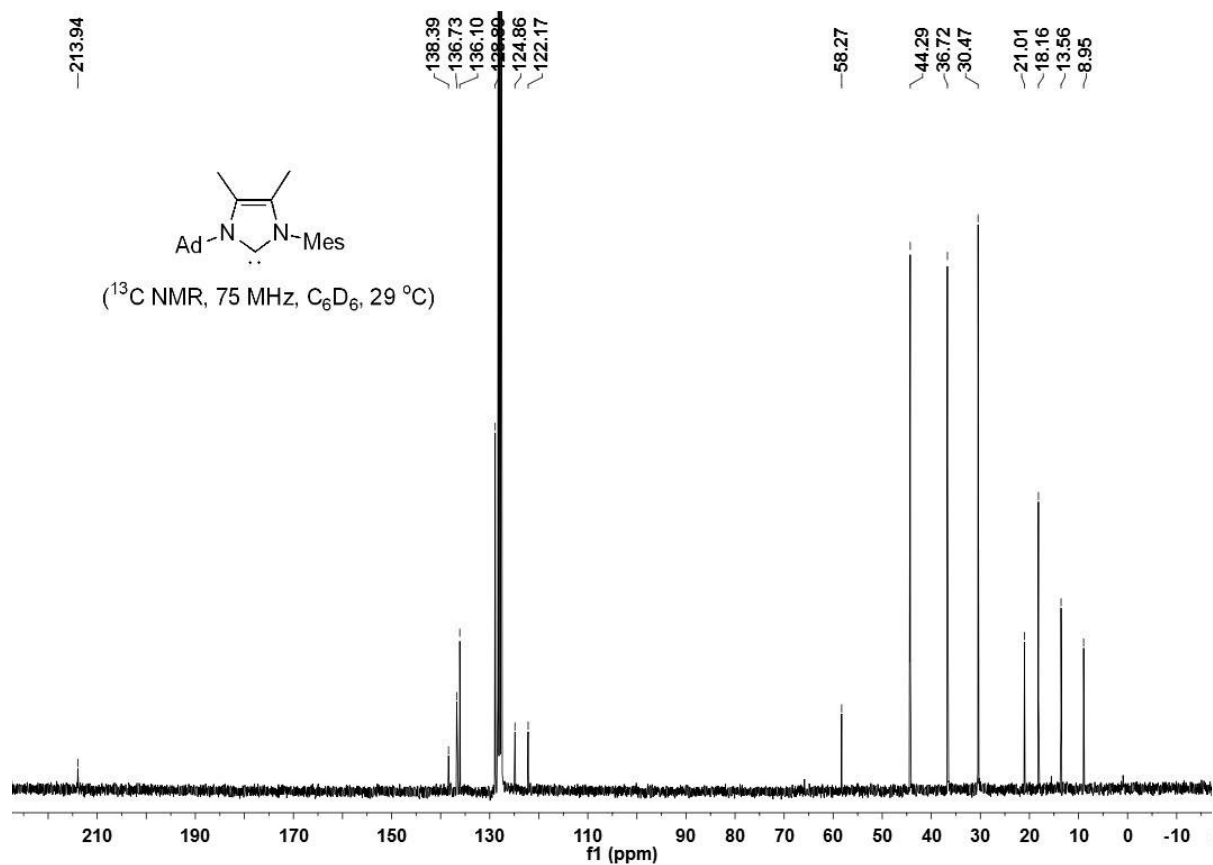


Figure S2. ^{13}C NMR spectrum of IAdMes in C_6D_6 .

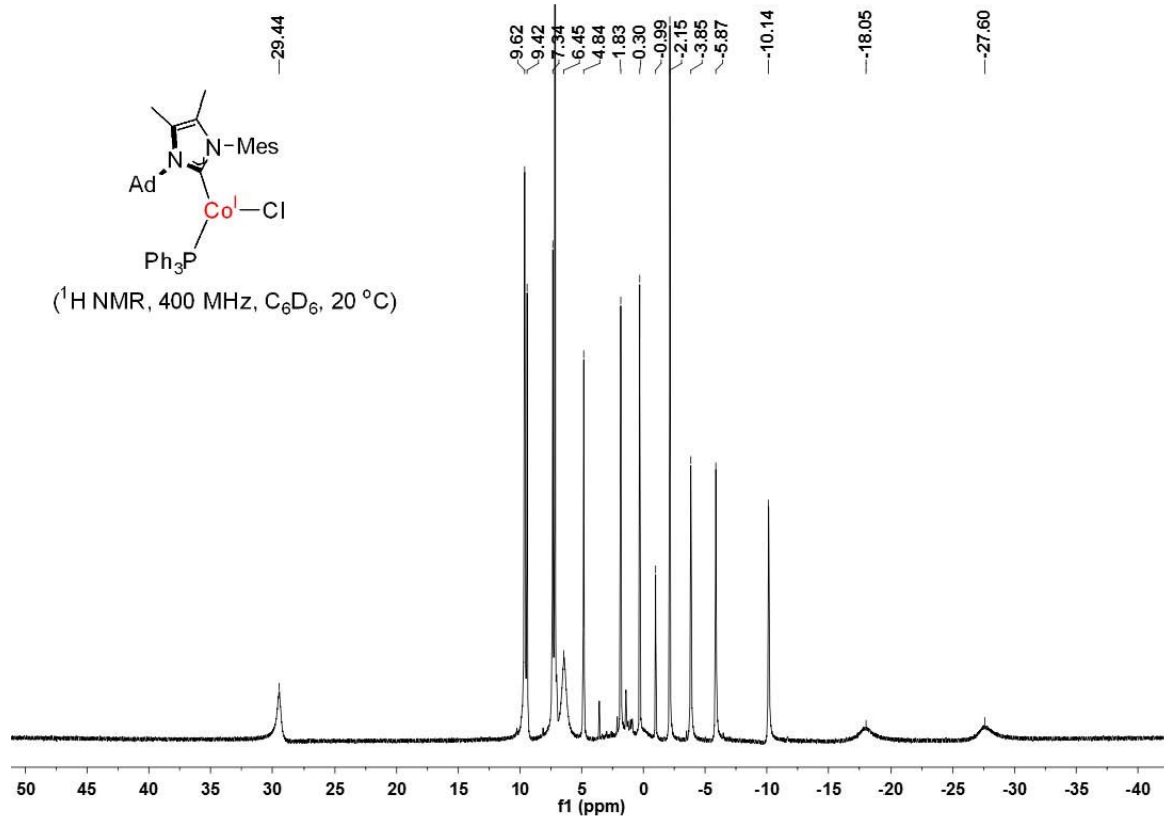


Figure S3. ^1H NMR spectrum of $[(\text{IAdMes})(\text{PPh}_3)\text{CoCl}]$ (1) in C_6D_6 .

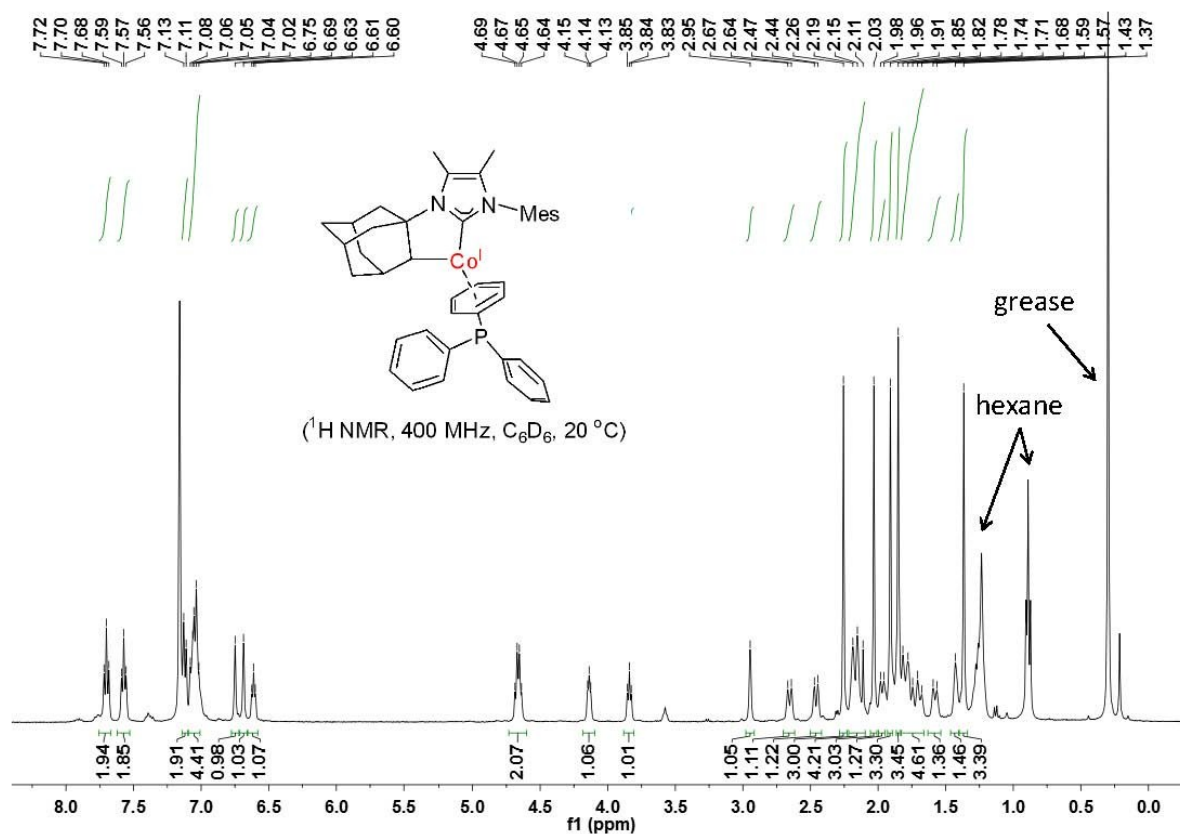
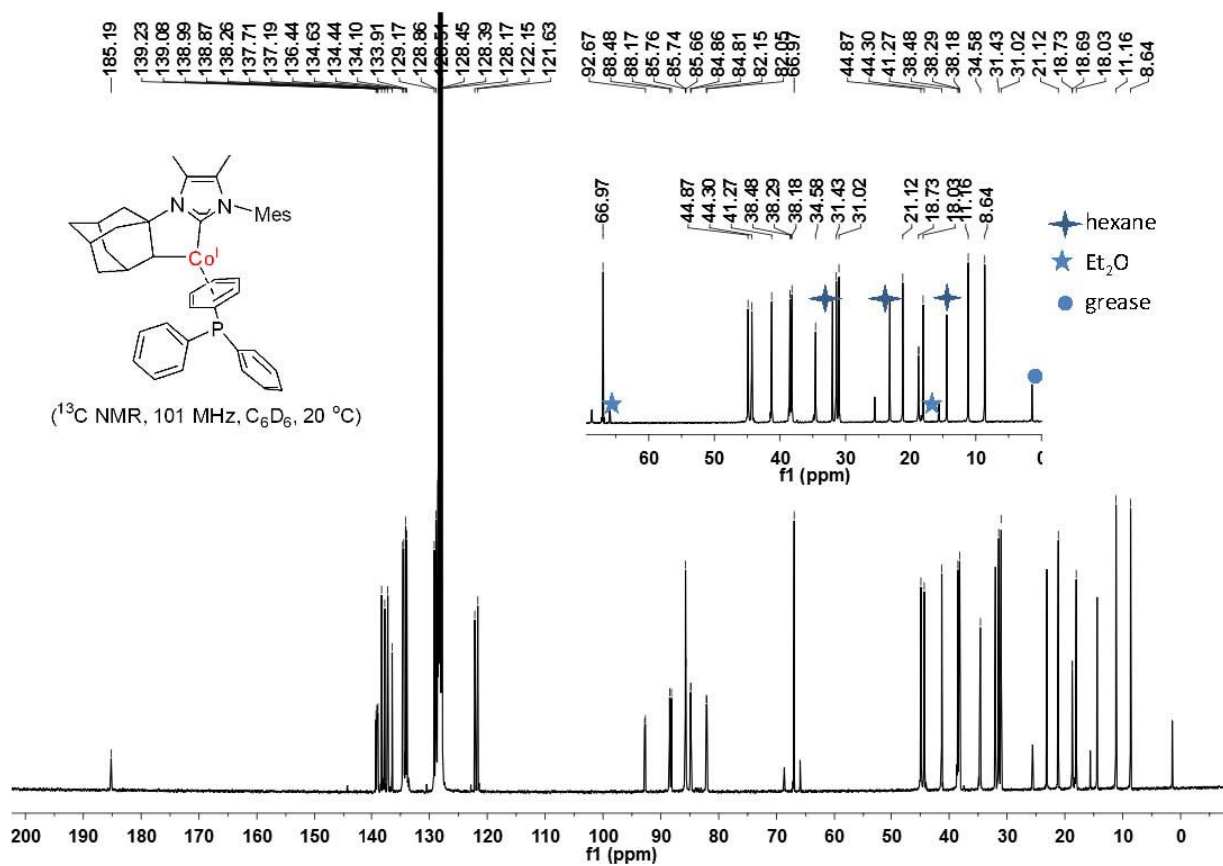


Figure S4. ^1H NMR spectrum of $[(\text{IAd}'\text{Mes})\text{Co}(\eta^6\text{-PhPPh}_2)]$ (2) in C_6D_6 .



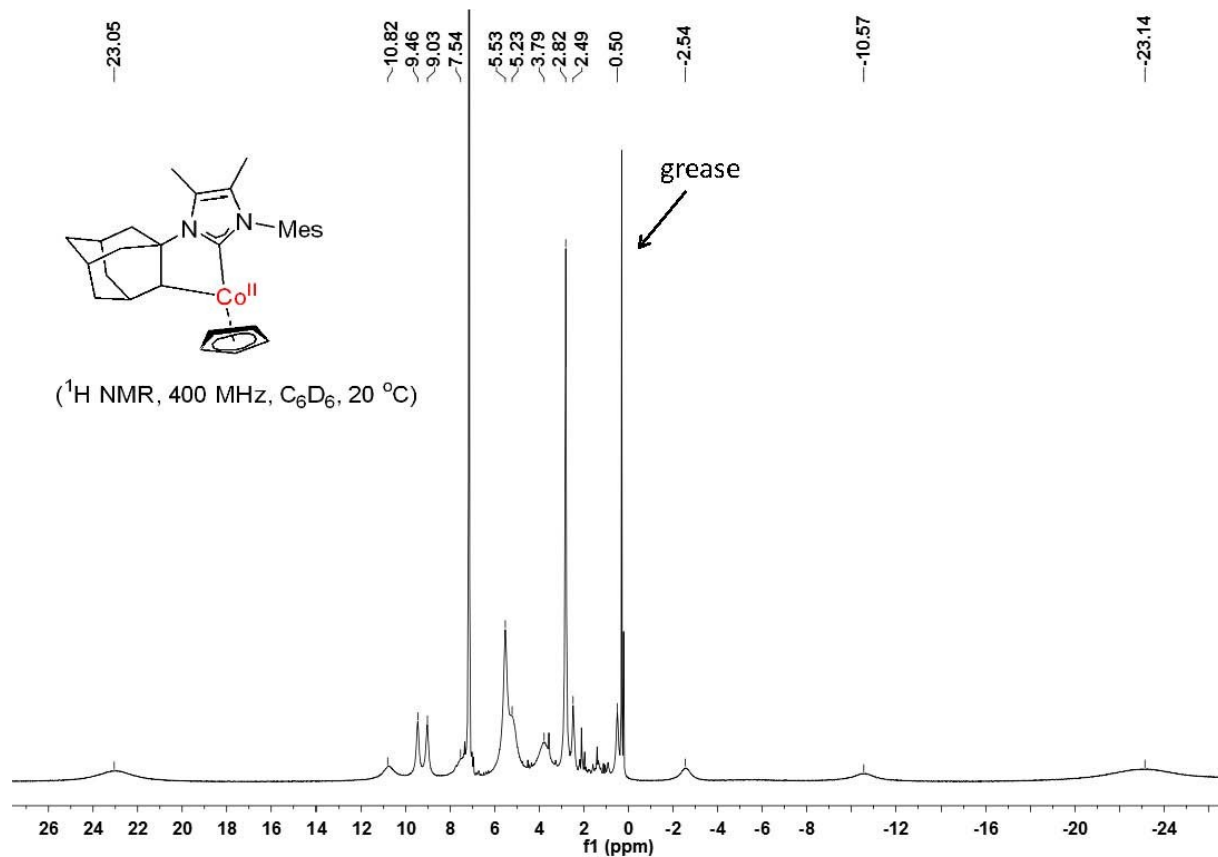


Figure S9. ^1H NMR spectrum of $[(\text{IAd}'\text{Mes})\text{Co}(\eta^5\text{-Cp})]$ (5) in C_6D_6 .

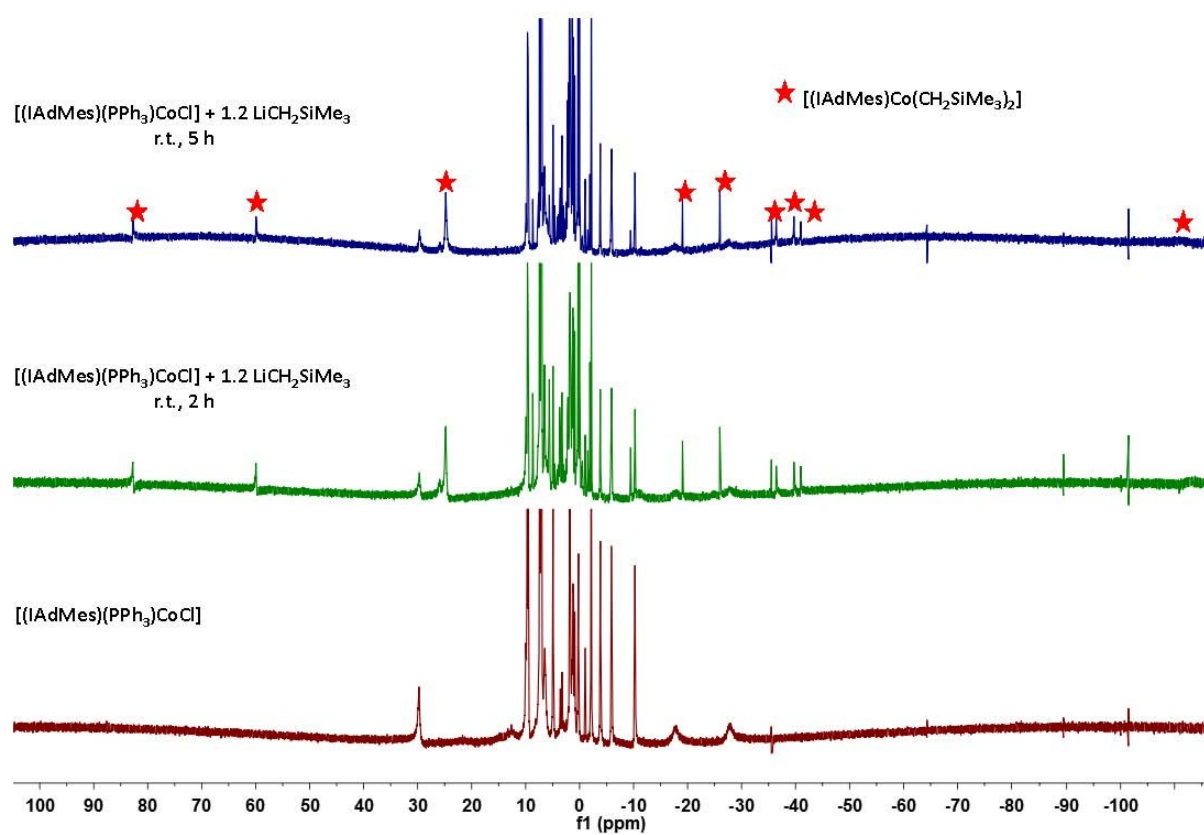


Figure S10.

^1H NMR spectra of the reaction of $[(\text{IAdMes})(\text{PPh}_3)\text{CoCl}]$ (1) with 1.2 equiv of $\text{LiCH}_2\text{SiMe}_3$ in C_6D_6 at room temperature.

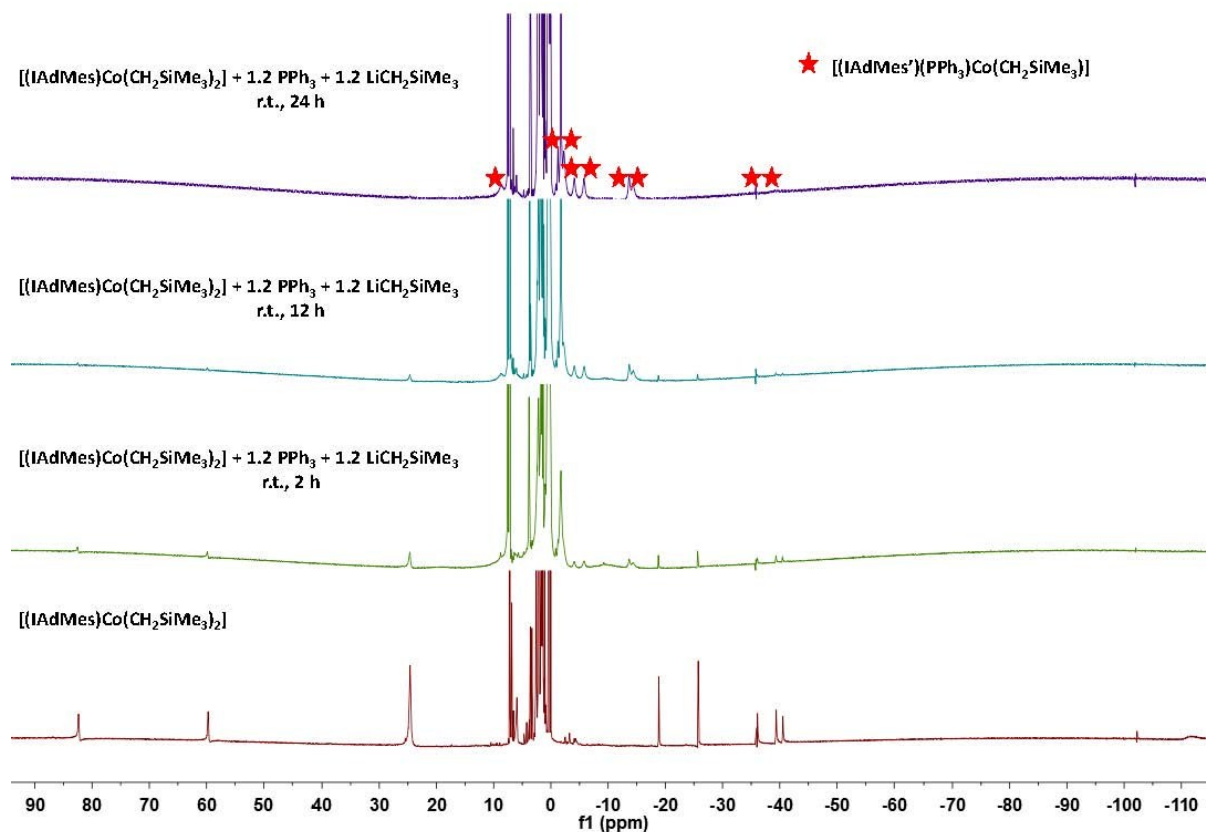


Figure S11. ^1H NMR spectrum of the reaction of $[(\text{IAdMes})\text{Co}(\text{CH}_2\text{SiMe}_3)]$ (**3**) with 1.2 equiv of PPh_3 and $\text{LiCH}_2\text{SiMe}_3$ in C_6D_6 at room temperature.

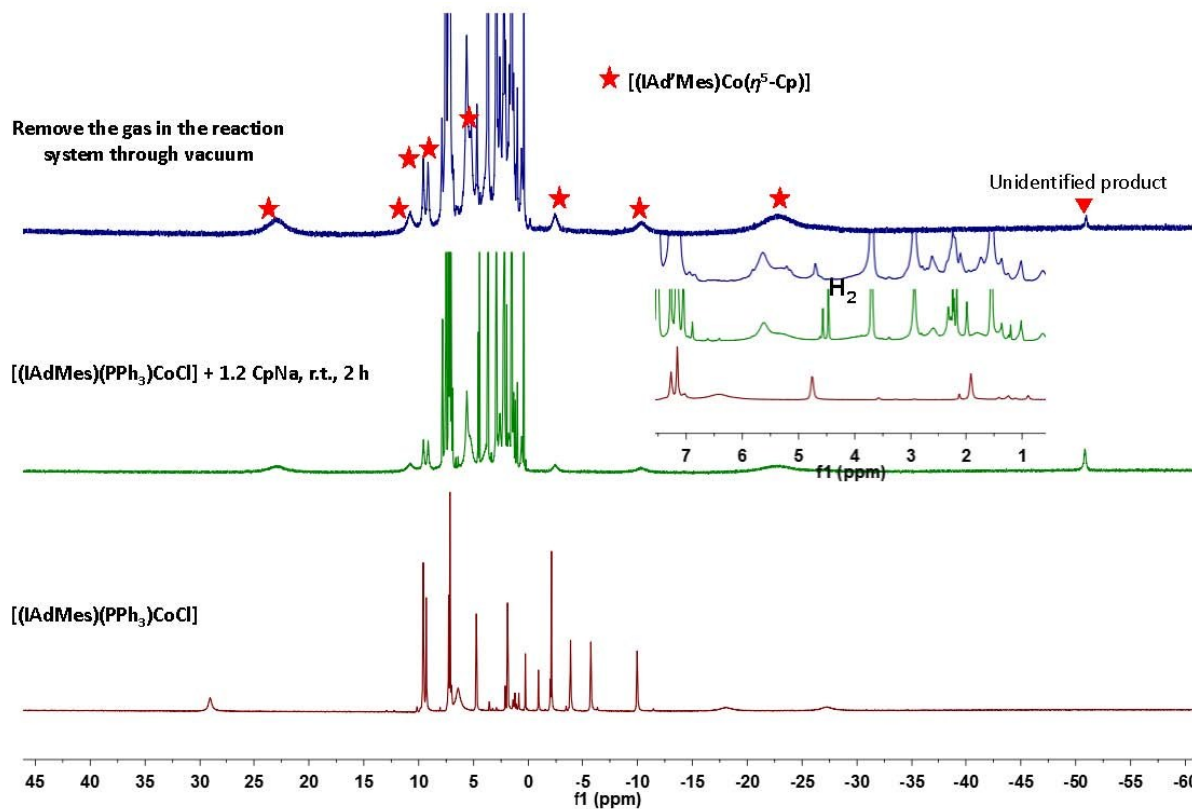


Figure S12. ^1H NMR spectrum of the reaction of $[(\text{IAdMes})(\text{PPh}_3)\text{CoCl}]$ (**1**) with 1.2 equiv of CpNa in C_6D_6 at room temperature.

Absorption spectra:

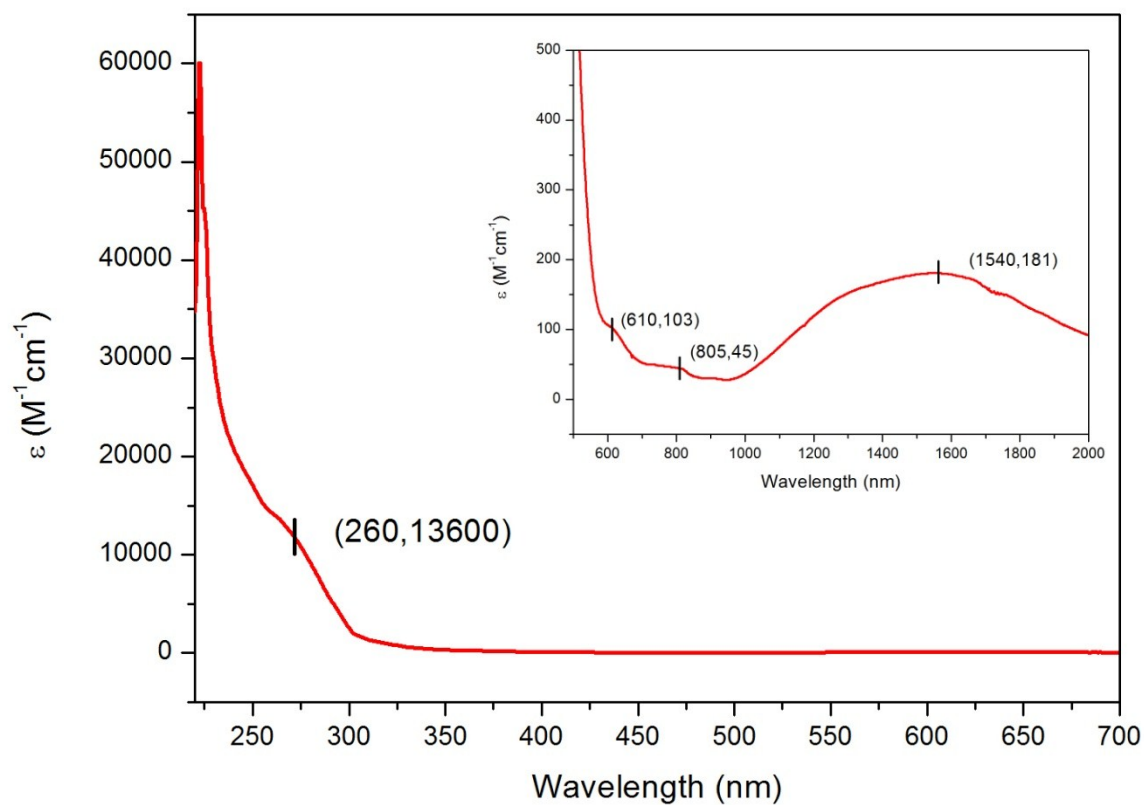


Figure S13. Absorption spectra of $[(\text{IAdMes})(\text{PPh}_3)\text{CoCl}]$ (**1**) measured at room temperature in THF.

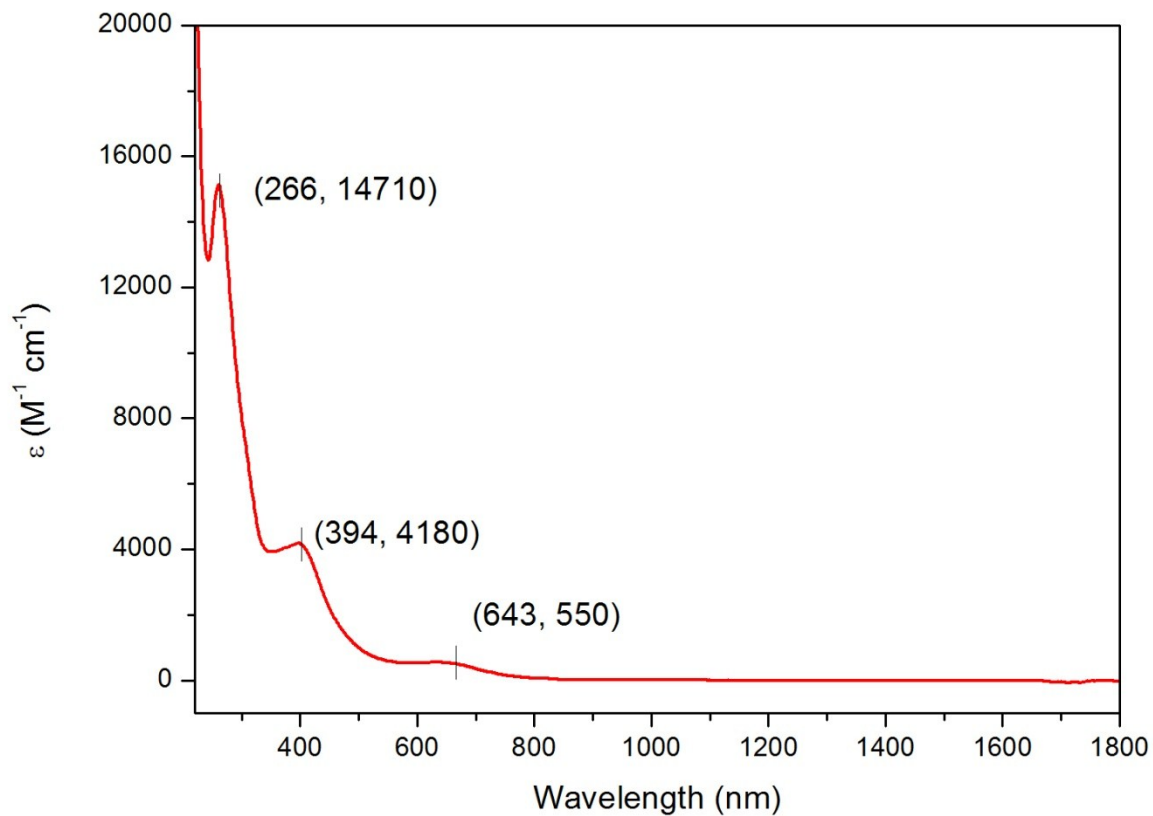


Figure S14. Absorption spectra of $[(\text{IAd}'\text{Mes})\text{Co}(\eta^6\text{-PhPPh}_2)]$ (**2**) measured at room temperature in THF.

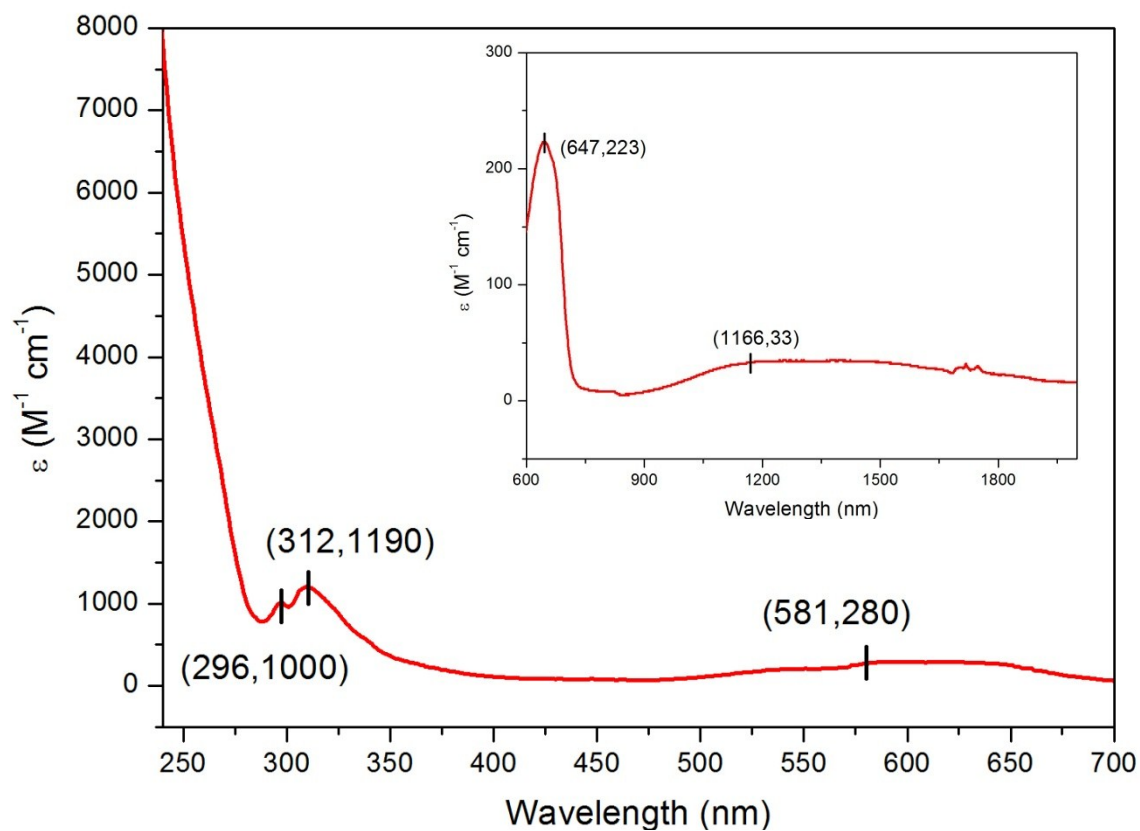


Figure S15. Absorption spectra of $[(\text{IAdMes})\text{Co}(\text{CH}_2\text{SiMe}_3)_2]$ (**3**) measured at room temperature in THF.

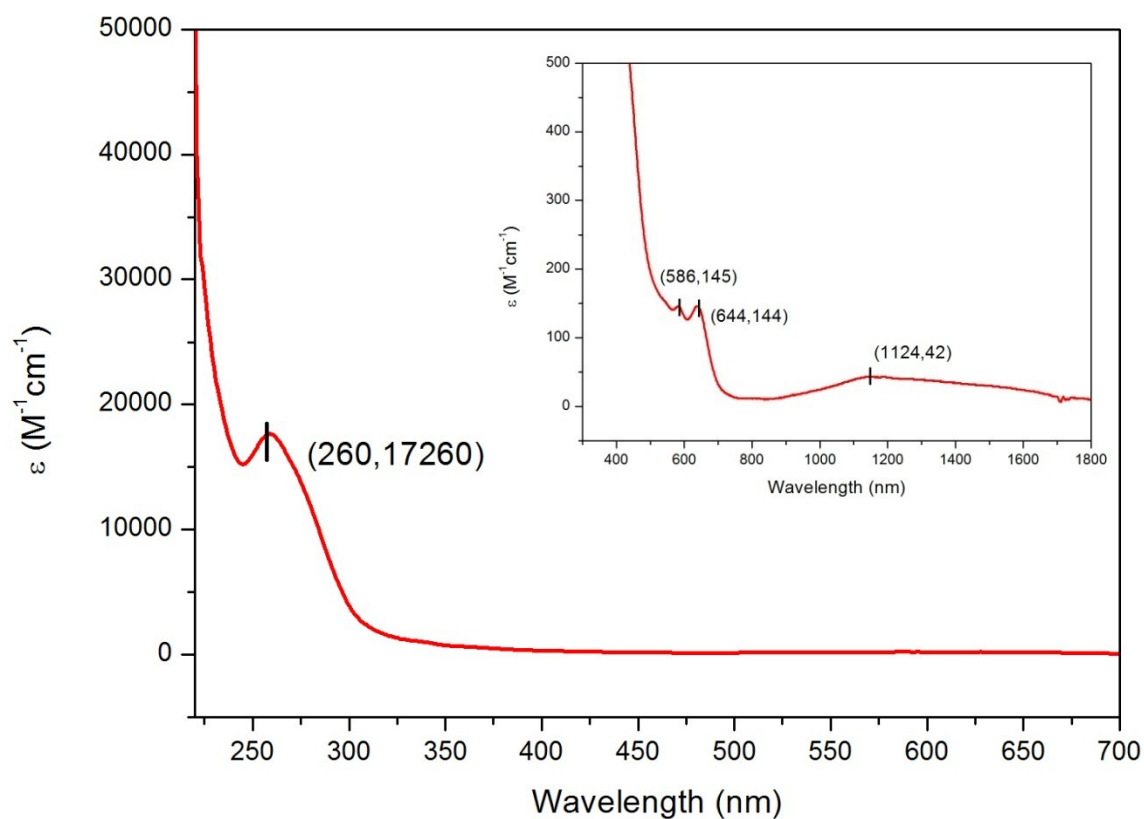


Figure S16. Absorption spectra of $[(\text{IAdMes}')(\text{PPh}_3)\text{Co}(\text{CH}_2\text{SiMe}_3)]$ (**4**) measured at room temperature in THF.

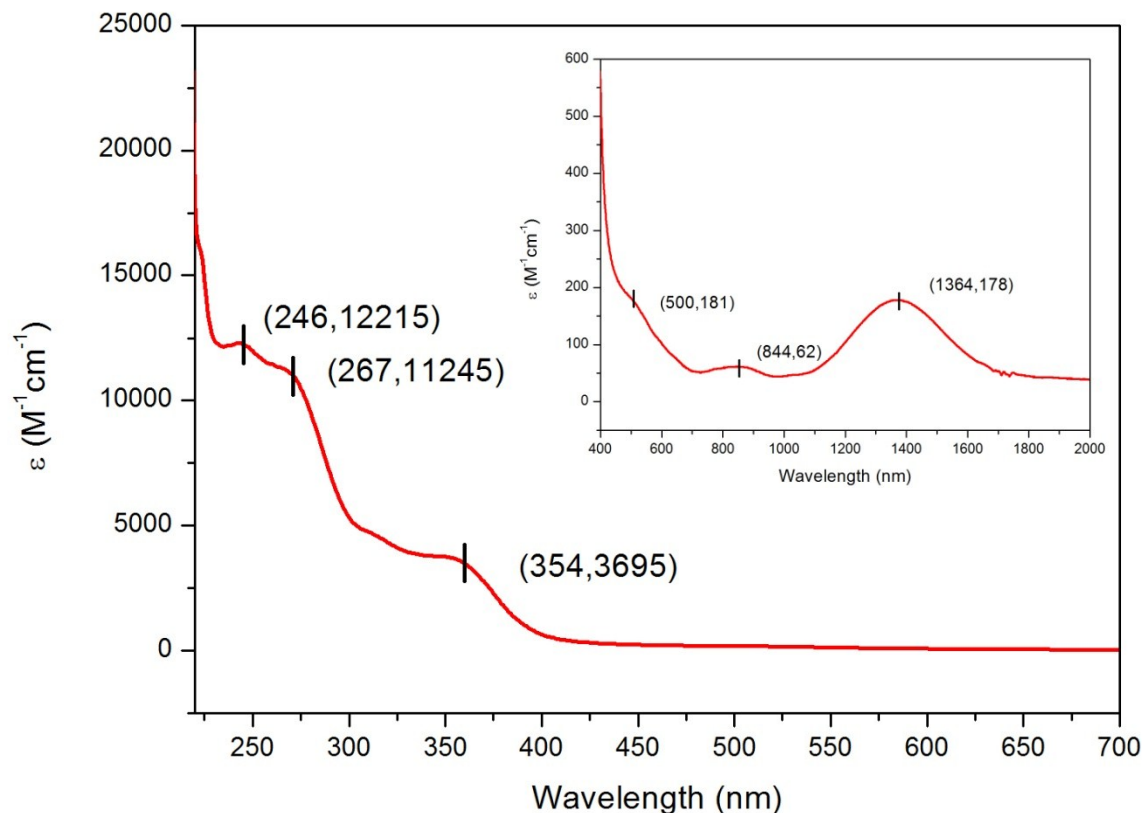


Figure S17. Absorption spectra of [(IAd'Mes)Co(η^5 -Cp)] (**5**) measured at room temperature in THF.

Cartesian coordinates for the calculated structure:

Coordinates for the optimized structure of (IAdMesMe₂)Co(η^5 -Cp) (**F**) ($S = 0$)

Co	0.07976448102988	-1.96073877380413	-0.37937672725033
N	0.63418871965454	0.39249607061695	-1.82830940903295
N	0.25125648322418	0.94210874485903	0.24823497651748
C	0.31583872130068	-0.16542204870200	-0.58172912415035
C	-1.55673411285485	-3.04487767713117	0.44255790225728
C	-0.59735337772105	-3.93528273621107	-0.13489007566397
C	0.67125248565819	-3.78725818718953	0.54934723351573
C	0.52358252934172	-2.74552019374584	1.50527172846135
C	-0.84503764513411	-2.26115409554106	1.41505395686819
C	0.53472793751161	2.13624767030071	-0.43857546502154
C	0.78976456905607	1.78963985215890	-1.74601273801841
C	0.54967082625645	3.45865173867273	0.25211497923345
C	1.12319494702228	2.69603711344945	-2.88376640144008
C	-0.26801249166020	0.90707771456716	1.57709805318277
C	0.60640017609948	0.71647315801167	2.66260471863495
C	0.04847637810158	0.67726461060867	3.95613366780912
C	-1.33551534433925	0.82619565960681	4.17470851947974
C	-2.17861082725093	1.00269457336768	3.05601750788807
C	-1.66638260858594	1.03519169920843	1.74916042600530
C	-2.54703564921250	1.10951379648005	0.52707729711279
C	-1.92498551025904	0.77737665238518	5.56511529399329

C	2.08136941067752	0.52435773330267	2.41262342611655
C	0.89921868152567	-0.51620392325638	-2.95276725892978
C	0.30434977778849	-1.88145938273762	-2.52871238466984
C	0.24168482296166	-0.07072961607657	-4.28130792322987
C	2.42107595579118	-0.69669288148994	-3.18924532490191
C	0.57044600331985	-2.95292920795349	-3.59678693965854
C	-0.11319966768525	-2.48895641349252	-4.90188382066527
C	0.48990838145545	-1.14658308145274	-5.36187948061867
C	2.00550746387564	-1.32681999924249	-5.59451539062666
C	2.67668662521176	-1.76315156396422	-4.27487218495555
C	2.08657386377555	-3.11719889684939	-3.82735894291505
H	-2.62184388246282	-2.96442652871159	0.20075500015222
H	-0.77561368832824	-4.63569899867250	-0.96242836960669
H	1.57395088125576	-4.37830805918470	0.35451373842789
H	1.28086401048005	-2.39305712141017	2.21439386750144
H	-1.28440825713799	-1.49152405419735	2.05605541320297
H	-0.40303662646791	3.66562039899688	0.78518015232246
H	0.70984673500828	4.27719320357897	-0.47458873847167
H	1.35226753417405	3.50869656077904	1.01897503261462
H	2.04426669109111	2.39056693386799	-3.42374269319333
H	1.28084827337528	3.72550670907304	-2.51096186661992
H	0.30736638139152	2.74825906761271	-3.63368703125696
H	0.72025812970243	0.52343494291480	4.81602344723091
H	-3.26691543759752	1.09585826834829	3.19878380138178
H	-2.21325244481793	1.90697379729601	-0.16659832129107
H	-3.61007840340057	1.27460574736546	0.78486120738535
H	-2.45589048537190	0.15780088547509	-0.04132784920103
H	-1.14400233357085	0.80308419067841	6.34863813738810
H	-2.52580309368367	-0.14536998296838	5.71198618725274
H	-2.61869923430789	1.62628746985251	5.73064827108680
H	2.22849393139501	-0.17555485704210	1.56668593668591
H	2.59423268594449	0.11781606022345	3.30537810283175
H	2.58867021303040	1.47585504636984	2.14393804896697
H	-0.78872166486805	-1.78265122520567	-2.34990454885540
H	1.02713580620311	-2.22376774566365	-1.61531620944101
H	-0.84632151856713	0.07860205088684	-4.11662213043521
H	0.67539052143224	0.89092664486613	-4.61357581817844
H	2.91718630817997	-0.97719885922054	-2.23476053681709
H	2.87522098052190	0.27083094832013	-3.49787027241436
H	0.12678062491370	-3.91290852093873	-3.26377162144029
H	-1.20131741616319	-2.36596711604088	-4.72302573524177
H	-0.00794514247178	-3.25973316673491	-5.69780150933818
H	-0.00854440325300	-0.83092049181768	-6.30335144828563
H	2.15902272942776	-2.10940888917452	-6.36781760915843
H	2.46506225261586	-0.38867841311299	-5.97191566175736
H	3.77247962449952	-1.86547381332173	-4.42459337984947
H	2.59151065578974	-3.46385002440875	-2.90092161162668
H	2.25926705610194	-3.88006916743467	-4.61596347727918

Coordinates for the optimized structure of (IAdMesMe₂)Co(η^5 -Cp) (F) (S = 1)

Co	-0.37812789542923	-2.00599036117040	-0.22476281176653
N	0.57360305968844	0.28717141242951	-1.85411863788941
N	0.12813948475578	0.88629120039827	0.18427638160970
C	0.14056757198130	-0.22324099595829	-0.63354035507912
C	-1.88031636391892	-3.22993954391223	0.65763899606814
C	-0.78789953896575	-4.03504008585247	0.18142716234522
C	0.38566829141595	-3.63876884505360	0.91929551497822
C	-0.00089767161313	-2.63365946148167	1.87097302615344
C	-1.39912521739491	-2.38478890119491	1.71487566916900
C	0.52786537528126	2.04857892794976	-0.48019498918118
C	0.81555942733926	1.67736881353117	-1.77647667354814
C	0.57125422698783	3.37552989551486	0.20224099819950
C	1.19785087162348	2.59036158725084	-2.89861378258089
C	-0.30847880625398	0.86280767813488	1.54648670912564
C	0.64760873049794	0.69891488981984	2.56855737985055
C	0.19622900461865	0.72074989256777	3.90258516165348
C	-1.16459099769356	0.89741116215942	4.22266727290260
C	-2.08830080368843	1.03843469159838	3.16746708496778
C	-1.68522914628573	1.01305364212994	1.82201934829935
C	-2.67561270497584	1.06497952161983	0.68994363886194
C	-1.64202446097406	0.91634819169775	5.65620462275733
C	2.09404140206816	0.46252161659290	2.21510325677854
C	0.90076511285389	-0.59677854747386	-3.00279539946351
C	0.42996529163358	-2.03856364081940	-2.70345372074554
C	0.21926396023183	-0.11612031064674	-4.30738973194019
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C	0.10570088837948	-2.49702241180681	-5.15139737530399
C	0.58262656916001	-1.06445969673160	-5.46971143163767
C	2.11342128733150	-1.06635216598982	-5.66338689294103
C	2.79394673442818	-1.58378631995442	-4.37751317920228
C	2.31087797731601	-3.01435046501545	-4.05832430514695
H	-2.92311894952613	-3.27031502920934	0.31667546237813
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H	0.93113523123518	0.59467464627309	4.71346614132468
H	-3.16036916680871	1.16525403220015	3.38758189695430
H	-2.32836257977132	1.72883969412200	-0.12632875944181
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H	-2.77053433759074	0.04675901918953	0.25117753785134
H	-0.81631218747393	1.11398243208972	6.36650237369455
H	-2.09581481852394	-0.05750780573893	5.94380556917825
H	-2.42120705891776	1.69064789720580	5.80111007616029
H	2.16430560112613	-0.29832487111756	1.41284919700211
H	2.66910717312326	0.10313108687381	3.08955335371038
H	2.59967565020044	1.37877893355958	1.84366070858072
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H	0.93680962675160	-2.37432336382376	-1.76131386490662
H	-0.88038256031595	-0.08201366108843	-4.14709304912189
H	0.55313869148170	0.90904441524533	-4.54833861260567
H	2.92782349560174	-0.97368887280517	-2.26747181407121
H	2.82144901190932	0.37536998506400	-3.41920816121173
H	0.41658683851586	-4.00851245277179	-3.60556451705844
H	-0.99841931136281	-2.51646668330655	-5.02863167948914
H	0.35758726708803	-3.17577911375195	-5.99388773956810
H	0.07682916749333	-0.70522202257220	-6.39101861264872
H	2.39450326065861	-1.70411751716702	-6.52988688771901
H	2.46986098343813	-0.03696175312862	-5.88516030004839
H	3.89679047190558	-1.58056610187996	-4.50997207525338
H	2.82408627376818	-3.39160622068667	-3.14932984578763
H	2.57075162363029	-3.69613516161168	-4.89606429236240