# Supporting Information

## Spontaneous Generation of H Radical by an Organometallic Cobalt Complex via Metal-Ligand Cooperation

Eugene Khaskin,[†] Yael Diskin-Posner,[‡] Lev Weiner,[‡] Gregory Leitus,[‡] David Milstein[*†]
*[†]Department of Organic Chemistry, [‡]Department of Chemical Research Support,*
*Weizmann Institute of Science, Rehovot, 76100, Israel.*

### Table of Contents

**General Procedures:** All experiments with metal complexes and the phosphine ligand were carried out under an atmosphere of purified nitrogen in a Vacuum Atmospheres glovebox equipped with a MO 40-2 inert gas purifier, in J. Young NMR tubes, or using standard Schlenk techniques. Deuterated benzene and toluene were dried over lithium aluminum hydride (LAH) and filtered. Deuterated THF and dioxane were degassed via three freeze – pump - thaw cycles, dried over LAH, and distilled under vacuum. The ligands 2,6-bis(di-tButyl-phosphinomethyl)pyridine (tBu-PNP)[1] and 6-bis(di-tButyl-phosphinomethyl)pyridine (tBu-PNP)[2] were prepared according to literature procedures.

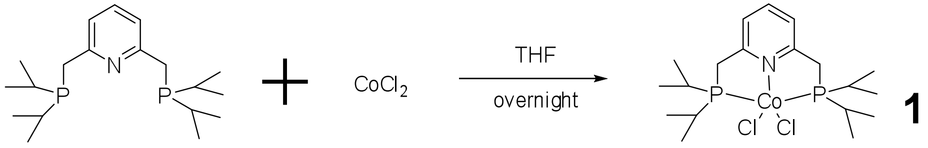
$^1$H, $^{13}$C and $^{31}$P NMR spectra were recorded at 250 or 400, 100 and 162 MHz respectively, using a Bruker AMX-250 and AMX-400 NMR spectrometers. $^1$H and $^{13}$C NMR chemical shifts are reported in ppm downfield from tetramethylsilane. $^{31}$P NMR chemical shifts are reported in parts per million downfield from $H_3PO_4$ and referenced to an external 85% solution of phosphoric acid in $D_2O$. Abbreviations used in the NMR follow-up experiments: b, broad; s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; v, virtual; vb, very broad. Elemental analyses were performed by the Weizmann Institute Chemical Research Support Unit. Evans Method measurements[3] were recorded at three different concentrations, with the average being given. The residual solvent peak ($C_6D_6$) was used as the reference.[4]

ESR measurements: All measurements were performed on a Bruker ELEXSYS 500 spectrometer in hermetically close capyllary at 295K and 120K temperature.

**Note on Elemental Analyses:** Except for the dichloride complexes **1** and **4**, which were mildly air-sensitive, complexes were highly air-sensitive and reliable elemental analyses for these complexes were not obtained.

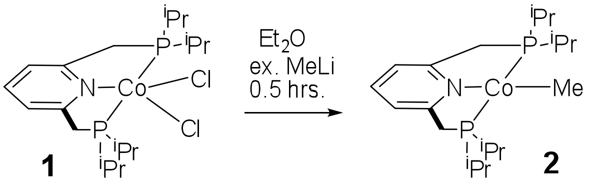
## Description of Reactivity:

### Synthesis of [Co($^{i}$Pr-PNP)(Cl)$_2$] 1.



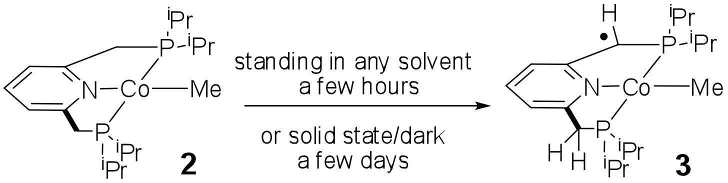
100 mg of $^{i}$Pr-PNP ligand (0.295 mmol) and 37.5 mg of $CoCl_2$ (0.295 mmol) were mixed together in a vial in 4ml of THF and left to stir overnight. If large crystals of the product are desired, the mixture can be stirred intermittently for a few minutes every half an hour for two hours and then left to stand overnight. A vial of $CoCl_2$ that gave a blue solution was left in 4 ml of THF beside the reaction mixture. The product was a darker blue/purple color in comparison. After leaving the reaction overnight, stirring was stopped and the solids were allowed to settle. The purple THF solution was carefully decanted. The solids were washed three times with 2 ml portions of THF to give **1** as a dark purple, crystalline solid (120 mg, 0.256 mmol, 86.8%). As **1** is strongly paramagnetic, its identity can be confirmed by X-Ray crystallography (not reported; file was not finalized since structure presents no special interest). Anal. Calcd. for $C_{19}H_{35}Cl_2CoNP_2$: C, 48.63; H, 7.52; N, 2.67 Found: C, 46.72; H, 7.33; N, 2.59.

### Synthesis of [Co($^{i}$Pr-PNP)(Me)] 2.



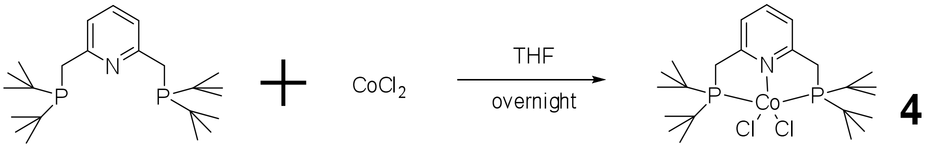
30 mg. of complex **1** (0.064 mmol) was put in a vial in 4 ml. of diethyl ether, to which 20 mg of dry MeLi (0.91 mmol; large excess) were added. The mixture was stirred for half an hour, during which time the purple crystals disappeared and the solution turned a strong dark black/brown color. The solution was evaporated to dryness under high vacuum, redissolved in 3 ml of benzene and quickly filtered through a celite plug in a glass pipette. The solids leftover were washed with another portion of benzene and filtered. The benzene washings were combined and evaporated to dryness. The complex was not allowed to remain standing in benzene for longer than a few minutes during the entire process. After evaporation of the solvent, complex **2** was obtained as a dark brown solid powder (18 mg, 0.046 mmol, 72 % yield). Complex **2** is not stable in solution and decays to complex **3**. $^{1}$HNMR obtained in $C_6D_6$ shows a symmetrical diamagnetic complex with unusual pyridine H shifts, in line with Budzelaar's formulation of such mono-alkyl complexes as a Co(II) center anti-ferromagnetically coupled to a ligand centered radical.[5] As $^{13}$CNMR cannot be obtained due to significant decomposition to paramagnetic complex **3** after an hour of standing, the structure of **2** is further confirmed by analogous complexes **4**, **5**, and **10** (see below). NMR broadening depends on the amount of **3** present by the time a spectrum is obtained . $^{31}$P{$^{1}$H}NMR ($C_6D_6$): 60.0 (bs) . $^{1}$HNMR($C_6D_6$): -1.19 (t, 3H, $J_{PH}$ = 10.9 Hz, Co-$CH_3$), 1.24 (q, 12H, $J_{PH}$ = 12.0 Hz, $J_{HH}$ = 5.9 Hz, P(CH(C$H_3$)$_2$)$_2$), 1.38 (q, 12H $J_{PH}$ = 12.0 Hz, $J_{HH}$ = 5.9 Hz, P(CH(C$H_3$)$_2$) + P(CH(C$H_3$)), 1.60 (bt, 4H, $J_{PH}$ = 5.1 Hz, arm-$CH_2$), 2.36 (bm, 4H, P(C$H$($CH_3$)$_2$-Co), 2.28 (bm, 3H, P(C$H$($CH_3$)$_2$), 5.64 (d, 2H, $J_{HH}$ = 7.3 Hz, pyridine-metaH), 8.64 (bt, 1H, $J_{HH}$ = 7.3 Hz, pyridine-paraH).

## Synthesis of [Co($^i$Pr-PNP)$^*$(Me)] 3.



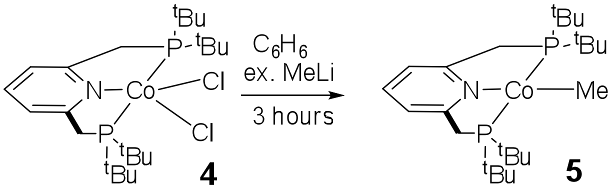
Any amount of complex **2** will decay to complex **3** if left in solution or in the solid state. The transformation is more rapid in solution. For a full transformation to **3**, 30 mg of **1** were taken and reacted with excess MeLi as in the reaction to make **2** above, and after evaporating the benzene washings under high vacuum, were dissolved in 4 ml. of pentane and allowed to stand for 16 hrs. After this time, the pentane was allowed to slowly evaporate. The solids were re-dissolved in pentane (2x 3 ml) and filtered through a celite plug. The combined dark red pentane washings were allowed to slowly evaporate to give a red, crystalline solid that was characterized by X-ray spectroscopy as complex **3**. $^1$HNMR ($C_6D_6$): -39.3 (bs), -27.63 (bs), - 16.714 (bs), -8.59 (bs), 0.87 (bt, 3H, $J_{PH}$ = 7.0 Hz, Co-C$H_3$), 1.23 (2H, bm, P-C$H_2$), 0-2 (bs), 6.5-8 (bs, $^i$Pr-CH$_3$), 10-13.5 (bs, $^i$Pr-CH$_3$), 14.5-17 (bs, $^i$Pr-CH$_3$), 40-43 (bs), 49-52 (bs).

## Synthesis of [Co($^t$Bu-PNP)(Cl)$_2$] 4.



Complex **4** was prepared in the same way as detailed above for the synthesis of **1**. 100 mg of $^t$Bu-PNP ligand (0.253 mmol) and 32.8 mg of $CoCl_2$ (0.295 mmol) were dissolved together in a vial in THF (5 ml). It is important to prepare a vial of $CoCl_2$ for comparison in THF for this reaction, as a $CoCl_2$ solution is light blue and small amounts of **4** dissolved in THF give a darker blue solution. When the solution stops turning a darker blue after an interval of several hours, it is safe to stop the reaction. Usually reaction times of 1 day are more than sufficient to ensure conversion to a blue, crystalline solid (95 mg, 0.18 mmol, 69%). Washings with THF will remove non-reacted starting materials, but as **4** is slightly more soluble than **1** in THF, yield is compromised. Identity of **4** can be confirmed by X-ray analysis (not reported; file was not finalized since structure presents no special interest). Anal. Calcd. for $C_{23}H_{43}Cl_2CoNP_2$: C, 52.58; H, 8.25; N, 2.67. Found: C, 50.30; H, 7.97; N, 1.97.

## Synthesis of [Co($^t$Bu-PNP)(Me)] 5.

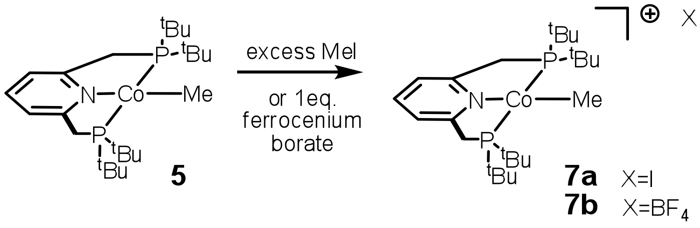


50 mg. of complex **4** (0.0917 mmol) were suspended in 4 mL of benzene and a large excess of solid MeLi was added (25 mg, 1.13 mmol). The two solids were stirred rapidly for 3 hrs. During the first ten minutes a gradual, and increasingly rapid color change was observed from a colorless solution to very dark black. The solution was left to react for the full amount of time. Afterwards, the solution was filtered through a celite plug and the benzene evaporated under high vacuum to give complex **5** as a dark, black solid (containing a small amount of **6**). Unlike complex **4**, no $^{31}$PNMR peak was observed, due to residual paramagnetism. Recorded yield of a good sample of **5** with less than 5% impurity of complex **6** is 32 mg (6.82e-5 mmol, 74.4%). This particular reaction was repeated at least thirty times in order to find the best conditions for the synthesis of pure **5**. There was no discernible factor that affected the amount of **6** present with regard to **5**. Sometimes the mixture is 50/50 by NMR. In order not to lose large amounts of complex **4** if only **5** and not **6** is desired, the best protocol may be to set three parallel reactions of 30 mg each of complex **4** under the conditions described here. It is very likely that at least one of the vials will turn out to contain complex **5** of >95% purity after filtration. Complex **5** is stable in the solid state and in benzene solution. $^{1}$HNMR ($C_6D_6$): -1.07 (t, 3H, $J_{PH}$ = 10.2 Hz, Co-$CH_3$), 1.49 (bt, 40H, $J_{PH}$ = 12.0 Hz, $J_{HH}$ = 5.6 Hz, $P(C(CH_3)_3)$ and $PCCH_2$ at 1.52 ppm), 5.58 (d, 2H, $J_{HH}$ = 7.2Hz, pyridine-metaH), 8.64 (vt, 1H, pyridine-paraH). $^{1}$HNMR ($C_6D_6$): 29.5, 33.5 (t, $J_{PC}$=4.7Hz), 37.7 (t, $J_{PC}$=6.6Hz), 64.6, 106.8, 123.8 (t, $J_{PC}$=7.4Hz), 153.8 (t, $J_{PC}$=6.6Hz).

**Synthesis of [Co($^{t}$Bu-PNP)*(Me)] 6 and its reactivity with $H_2$.**

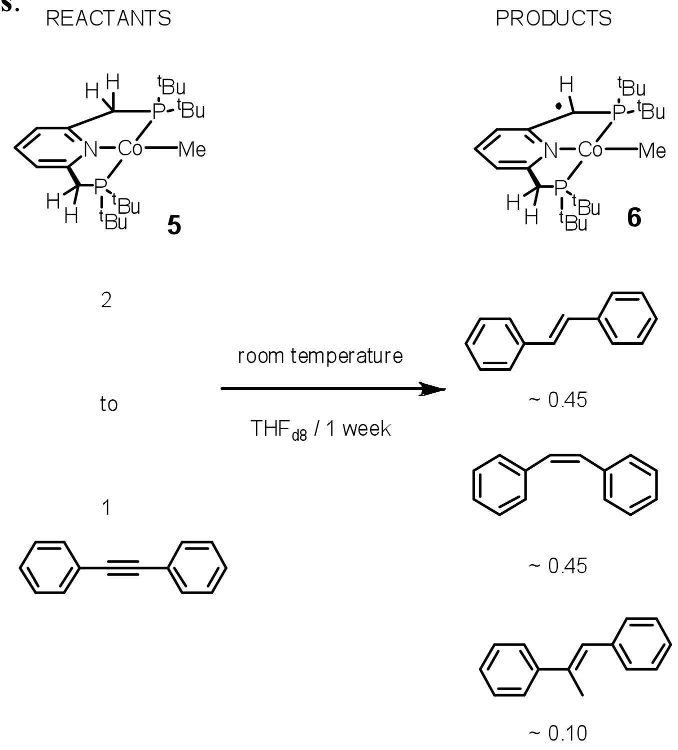
A sample of complex **5** (10 mg), was dissolved in 2 mL of pentane and allowed to stand for one day. Afterwards, the pentane was allowed to slowly evaporate to give a red, crystalline solid. A good structure could not, however, be obtained. The solid was re-dissolved in 4 ml of pentane and filtered through a celite plug, then the solvents were evaporated under high vacuum to give **6** as a dark reddish solid/powder (8.3 mg, 83%). A minor amount of **5** is still present at the end of the reaction (see NMR Figure S10). Unlike for complex **3**, even after longer reaction times, it is difficult to eliminate the trace amount of starting material. Complex **6** (5mg) decomposes upon the addition of $H_2$ (~3ml at 1atm, 4x excess) (Figure S17) to give an undetermined paramagnetic species. The peak of excess hydrogen is unaffected by paramagnetism. $^{1}$HNMR ($C_6D_6$): -30.23 (bs), -26.72 (bs), - 15.96 (bs), -7.49 (bs), 1.10 (bs, 3H, Co-$CH_3$), 1.48 (2H, bm, P-$CH_2$), 9-13 (bs, $^{t}$Bu-$CH_3$), 11-15 (bs, $^{t}$Bu-$CH_3$), 14.5-17 (bs, $^{i}$Pr-$CH_3$), 40-43 (bs), 61-63 (bs).

### Synthesis of [Co($^t$Bu-PNP)(Me)]$^+$[I]$^-$ 7a and [Co($^t$Bu-PNP)(Me)]$^+$[BF$_4$]$^-$ 7b .



16.5 mg of complex **6** (0.0351 mmol) were added to a vial and suspended in 2 ml of benzene. A large excess of MeI was added via microsyringe (5 μL.) and the solution was stirred for a few min. During this time the color of the solution changed from dark black to green. The stirring was stopped and the solution was set aside. After one week, X-Ray quality crystals of **7a** were obtained as a green solid (~21 mg, quantitative yield). It is also possible to add ferrocenium borate in a stoichiometric amount to obtain the same complex, but with borate as the counterion. The yield was not accurately measured for the latter reaction, however, the regular green crystalline material was characterized by X-ray crystallography to give **7b**. As this structure is redundant, it is only included as a CIF file attachment with the manuscript.

**GC Experiments**:



Two experiments were performed with complex **5** inside a Young NMR tube. The first experiment consisted of a 1:1 mixture of complex **5** (5 mg, 0.0106 mmol) and diphenylacetylene (1.9 mg, 0.0106e mmol) dissolved in 0.4 ml of THF$_{d8}$. The reaction and the subsequent transformation of **5** to **6** was followed by NMR. After one day of reaction time most of complex **5** was transformed to **6**. Concurrently, a reaction with diphenylacetylene was also observed.

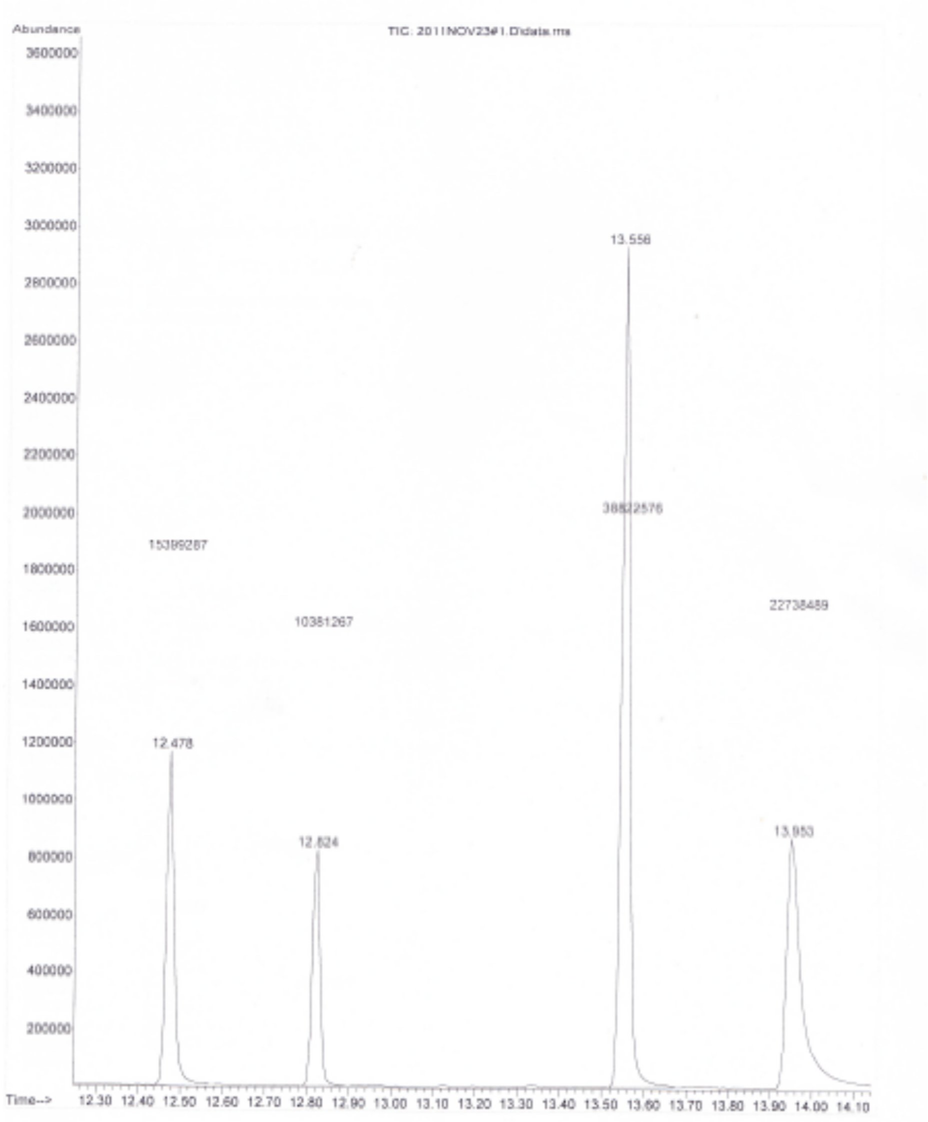
However, the paramagnetic complex **5** broadened the peaks of all other species in solution and it was difficult to assign particular frequencies. A sample was taken from the NMR tube for GC/MS analysis. The program used had a 3 min hold time at 50 $^{o}$C, then a 15$^{o}$ C/min ramp until 280 degrees; this gave sufficient separation of isomers, but a lower ramp should increase the separation between α-methylstilbene and E-stilbene. Subsequently, run times of standard samples of diphenylacetylene, Z-stilbene, E-stilbene and α-methylstilbene were obtained and compared with the run times of the peaks to determine the distribution of products. The m/z pattern of the products matched that of the standard samples as well. All the peaks contained natural isotope patterns, confirming that hydrogenation of the triple bond occurred as a result of hydrogen transfer from the complex and not from the deuterated solvent. The spectrum (the region of interest is introduced below) and the run-times of the standards are also given (Figure S3). In the first run with the 1:1 mixture of 8 and diphenylacetylene the peak at 12.82 min did not match any of the standards and based on run-time and isotope pattern, it was assigned as Z-methyl-stilbene. The products make up ~50% of the total with the unreacted starting material making up the other half. A longer reaction time did not lead to any substantitive change. Despite the presence of methyl-stilbene as one of the products of the reaction, we were only able to detect complex **6** by NMR as one of the products. Presumably, methyl transfer occurs by hemolytic rupture of the Co-$CH_3$ bond, however the product is either insoluble or it falls out of solution, or is very paramagnetic and impossible to observe via NMR. Regardless, it is a minor product.

The second reaction was performed in dioxane-d8 (as we ran out of THF-d8) and consisted of a 2:1 mixture of complex **5** (10.5 mg, 0.0224 mmol) and diphenylacetylene (2.0 mg, 0.0112 mmol). Unlike in THF, the reaction in dioxane was much slower and showed only partial (~20%) transformation to complex **6** after 40 hrs. We already saw with benzene and pentane that certain solvents can dramatically retard or accelerate the reaction **5→6**. However, in order to see if diphenylacetylene could be fully consumed by this ratio of reactants, which was the primary purpose of the experiment, the reaction was heated at 70$^{o}$C for 24 hrs, after which time complete transformation was observed by NMR. While this means that the conditions between the two reactions described here were not exactly the same (70 $^{o}$C vs. room temperature and THF vs. dioxane solvent), we believe that they are close enough to make credible conclusions) The heating procedure however, would also isomerizes any Z-stilbenes present in solution to E-stilbenes; so even if the former are primary products of the reaction, they would not be detected. As in the previous experiment, paramagnetic broadening resulted in us not being able to assign compounds via NMR except to say in general that olefinic peaks appeared along with the appearance of complex **6**. The resulting GC/MS spectrum, ran with the same program described earlier, is reproduced in Figure S4. There is no diphenyl-acetylene present and Z-stilbenes are minor traces. There is a large peak for E-methylstilbene and a major peak for E-stilbene (~80%). As the peaks are overlapping, integration was not reliable in this case. The last peak was identified conclusively as E-stilbene by sampling the decomposition pattern in the large shoulder region where the 194 m/z peak from the E-methylstilbene peak is missing. All of the products did not show any deuterium incorporation.

Controls were performed by leaving **5** in THF-d8 and heating it at 70 $^{o}$C in dioxane-d8 in a Young tube without any substrate to capture H radicals. In both cases a transformation to complex **6** as the only NMR visible product was observed.

***Figure S3***: GC/MS trace of a 1:1 reaction of complex **5** and diphenylacetylene.

| Compound | Run time |
|---|---|
| Diphenylacetylene | 13.6-13.7 min |
| Z-stilbene | 12.4-12.5 min |
| Z-methylstilbene (?) | 12.8 min (no standard present, but 194 m/z peak is seen) |
| α-methylstilbene | 13.9 min (not present here; no 194 m/z peak) |
| E-stilbene | 13.94-14.00 min |



```
peak  R.T. first  max last  PK    peak      corr.    corr.    % of
  #   min   scan scan scan  TY   height     area    % max.   total
---  ----- ----- ---- ---- ---  -------   -------  ------  -------
  1  12.478  1182 1187 1200 BB   1067359  15399287  39.67%  17.631%
  2  12.824  1226 1231 1241 BB    801219  10381267  26.74%  11.886%
  3  13.556  1319 1324 1340 BB   2781886  38822576 100.00%  44.449%
  4  13.953  1367 1374 1406 BB    867837  22738489  58.57%  26.034%
```

***Figure S4***: GC/MS trace of a 2:1 reaction of complex **5** and diphenylacetylene.

| Compound | Run time |
|---|---|
| Diphenylacetylene | 13.6-13.7min |
| Z-stilbene | 12.4-12.5min |
| α-methylstilbene | 13.9min |
| E-stilbene | 13.94-14.00 min |

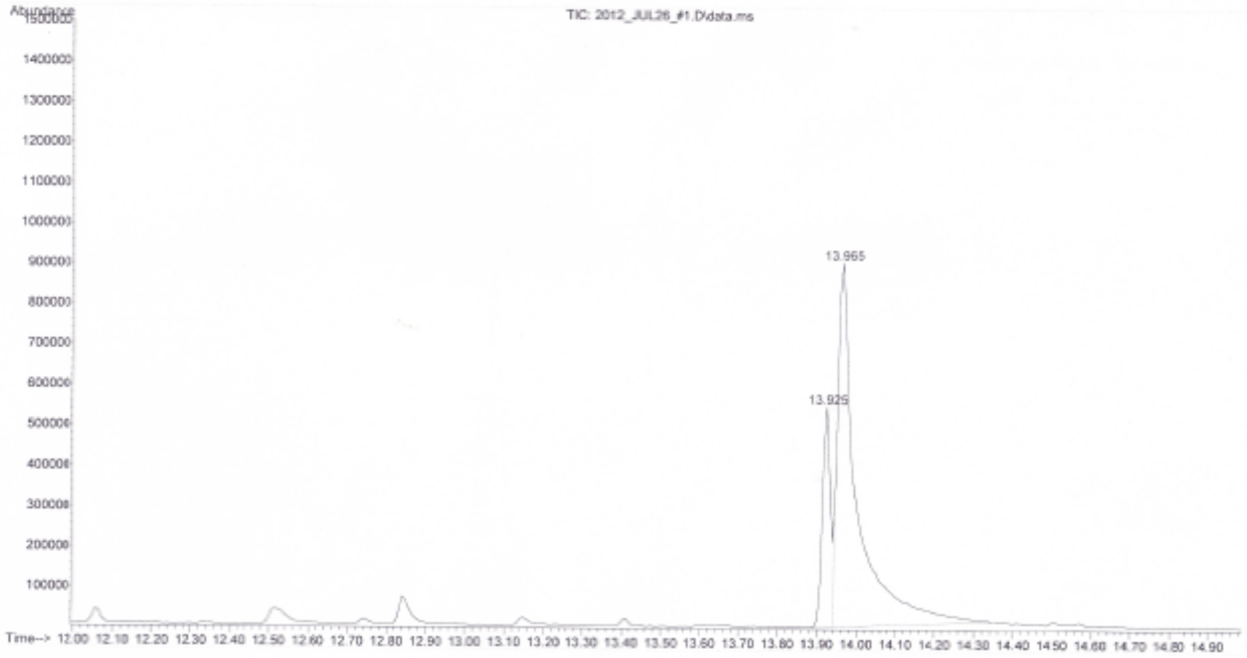


***Figure S5***: $^1$HNMR reaction of synthesis of **2**. Only complex peaks integrated. Paramagnetic **3** is present (i.e. peak at 0.8 ppm and broad region under 1.22 $^i$Pr peak). Impurities at 0.5 and 1 ppm.

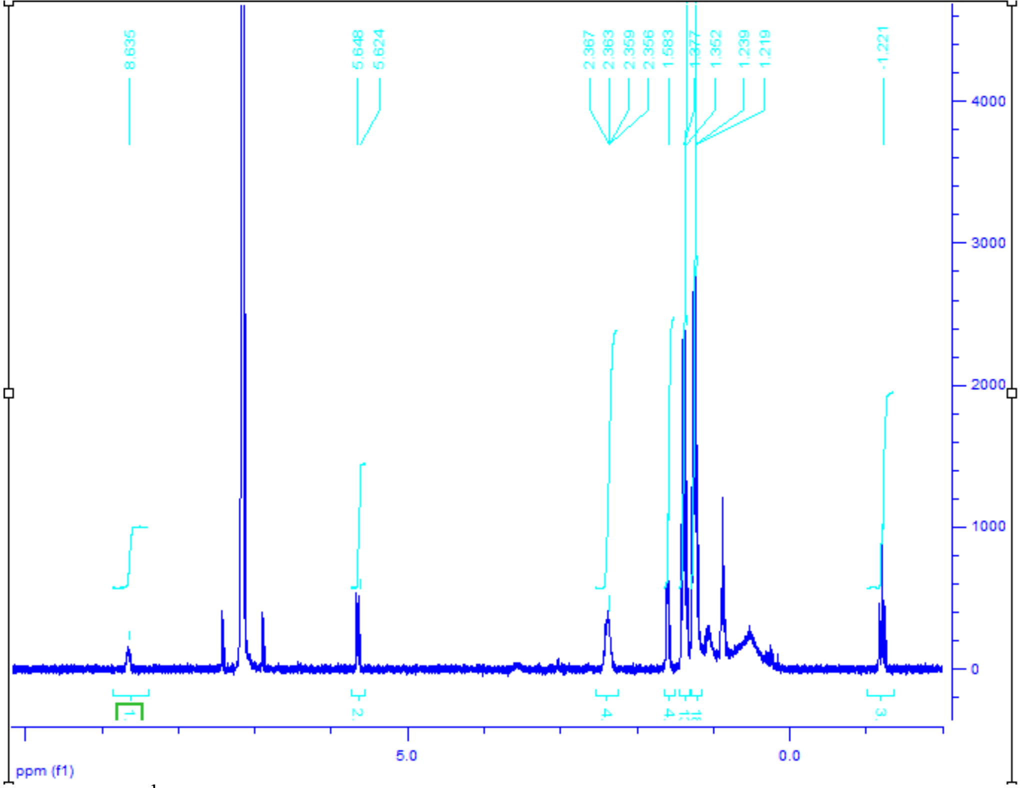


***Figure S6***: $^1$HNMR expansion of aliphatic region of **2**. (lb exp=0.1)

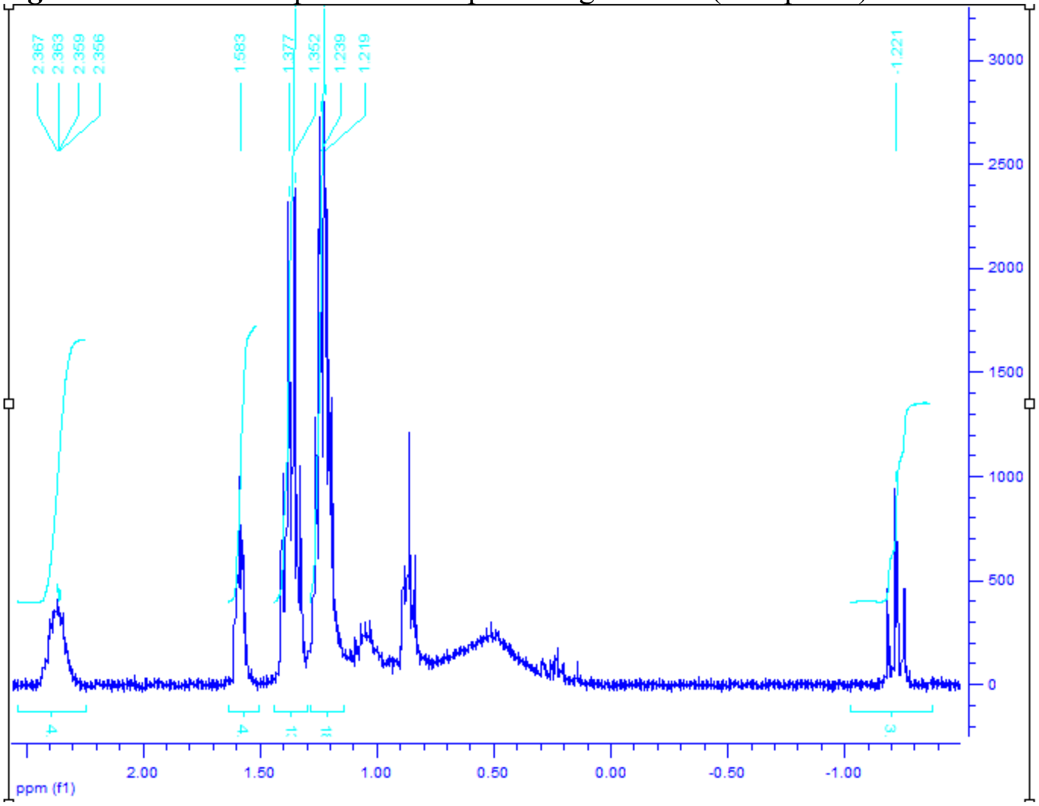


***Figure S7***: $^{1}$HNMR expansion of aromatic region of **2**. (lb exp=0.1)

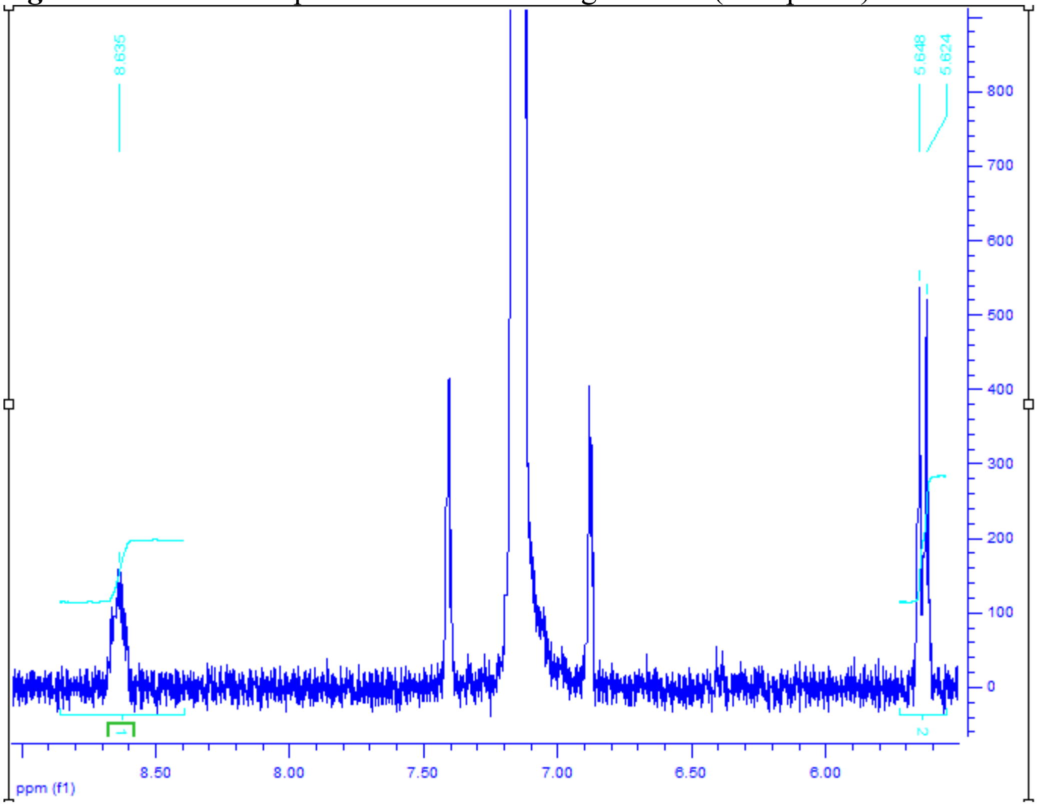


***Figure S8***: $^{1}$HNMR of **3**.

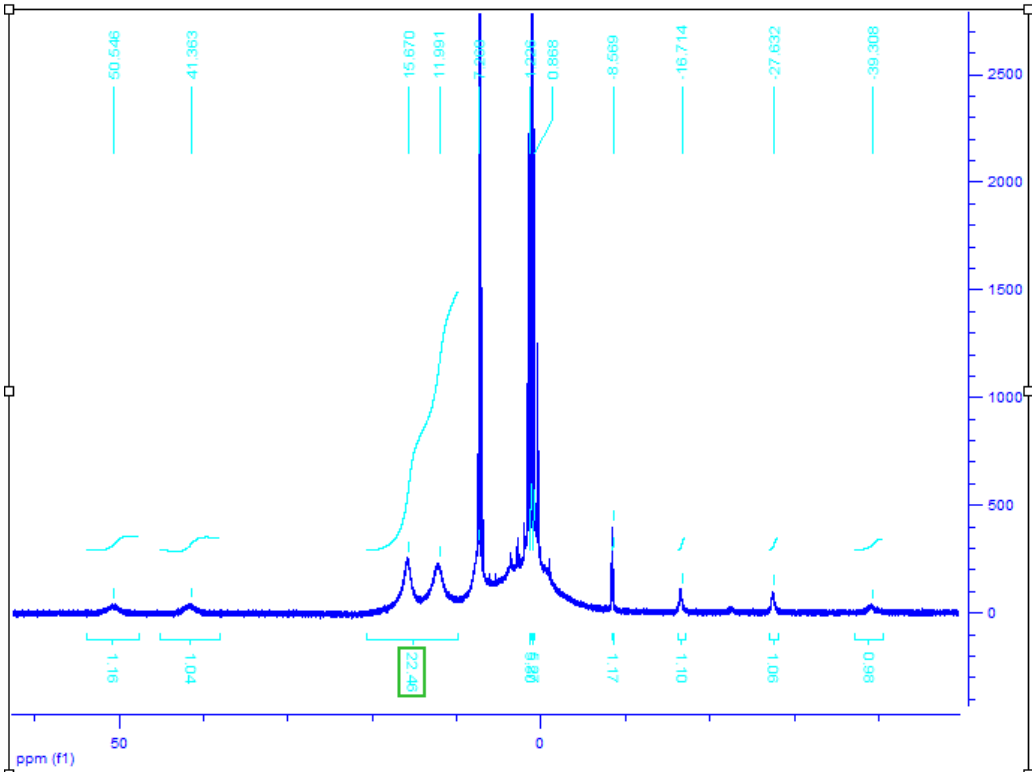


***Figure S9***: expansion $^{1}$HNMR of **3**.

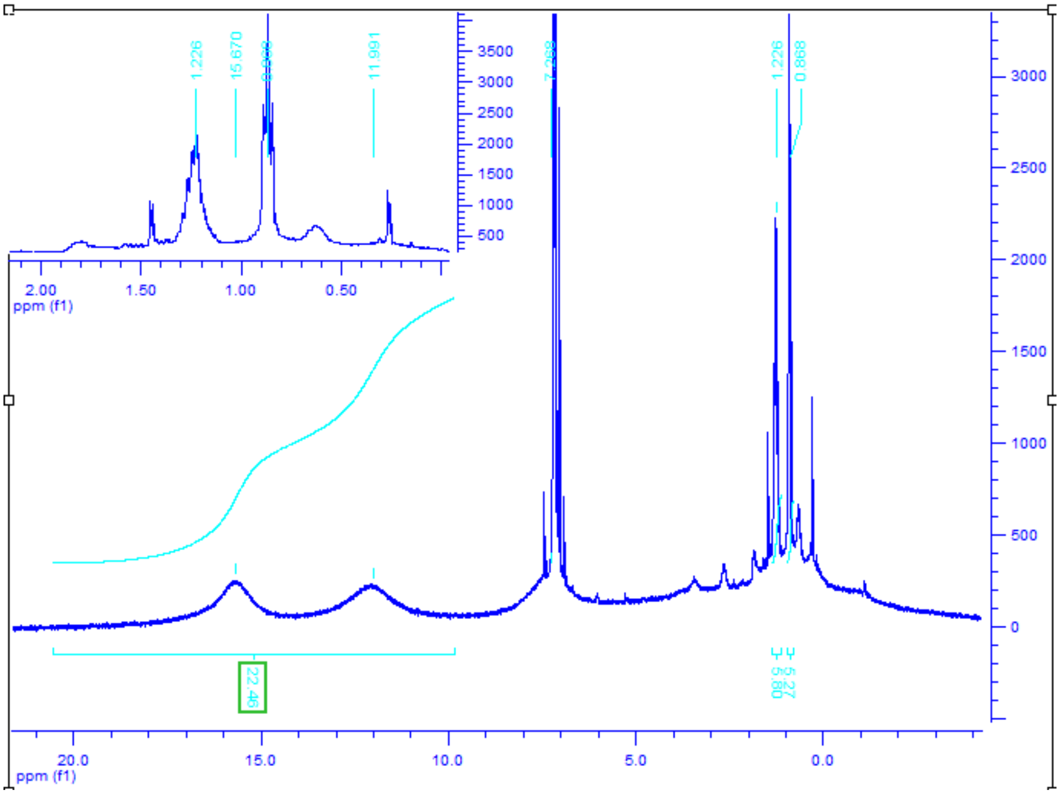


***Figure S10***: expansion $^{1}$HNMR of **3**.

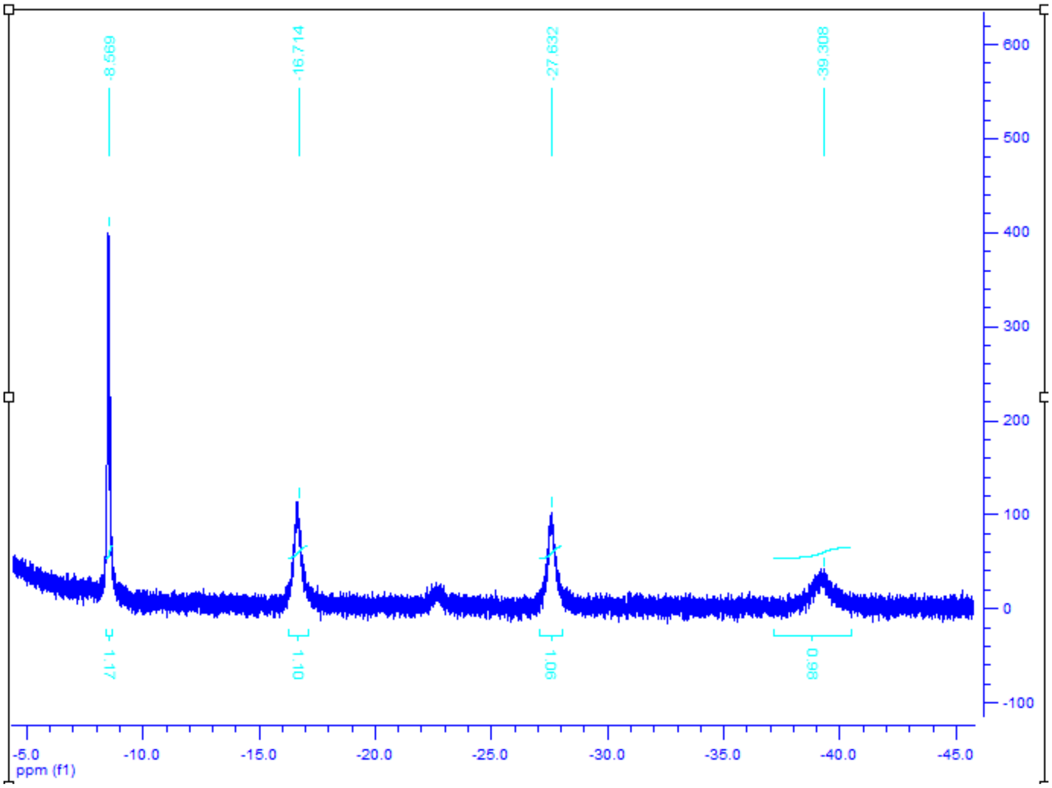


***Figure S11***: $^{1}$HNMR of **5**. Peak at 1 ppm is complex **6**.

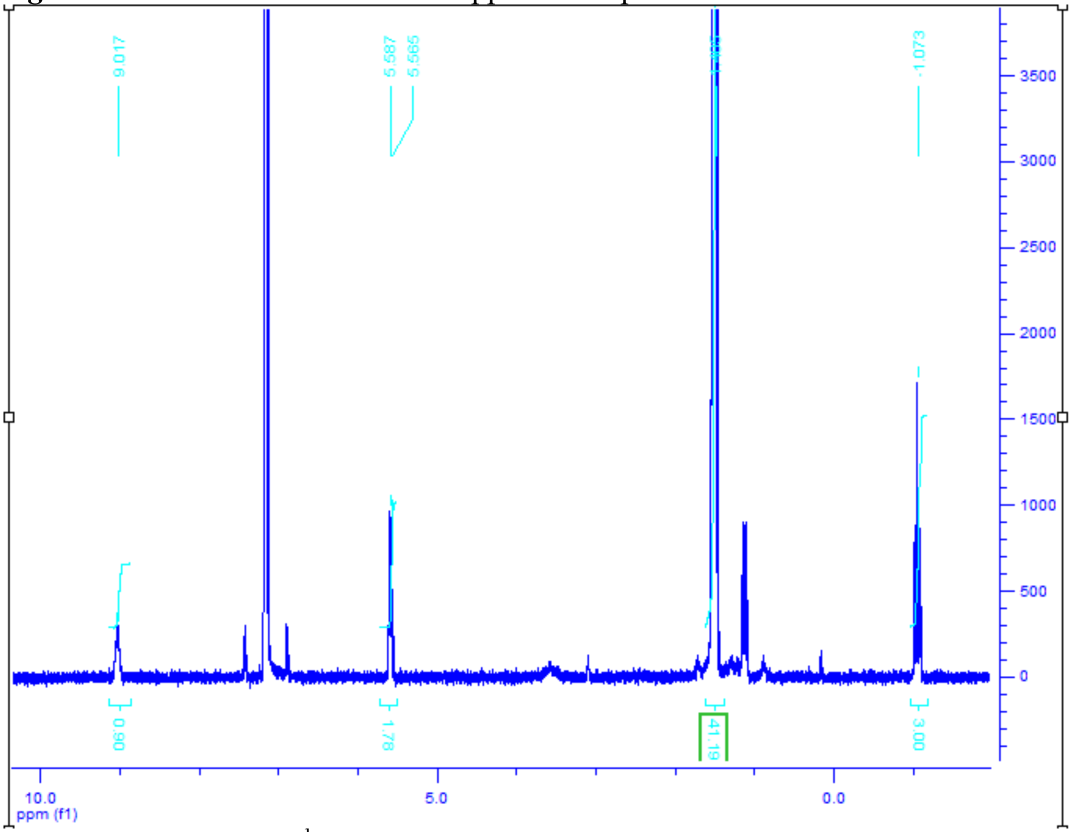


***Figure S12***: expansion $^{1}$HNMR of **5**.

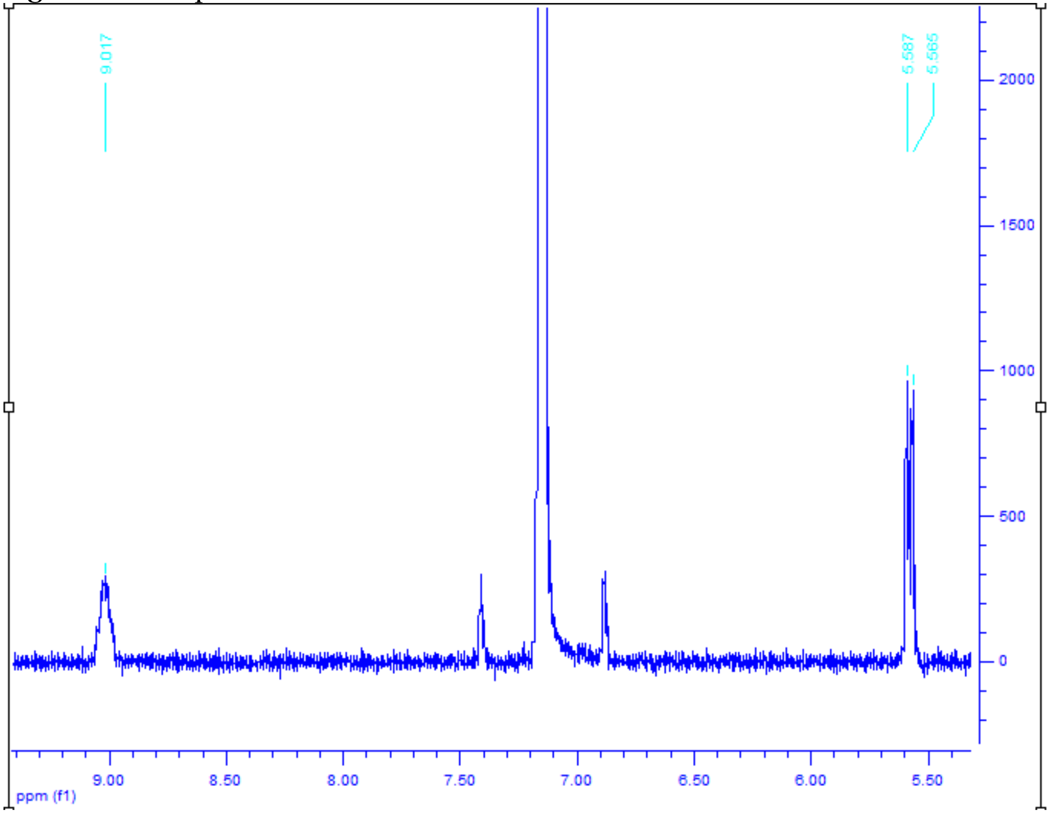


***Figure S13***: $^{13}$CNMR of **5**. Impurity at 15 ppm (from paramagnetic **6**?)

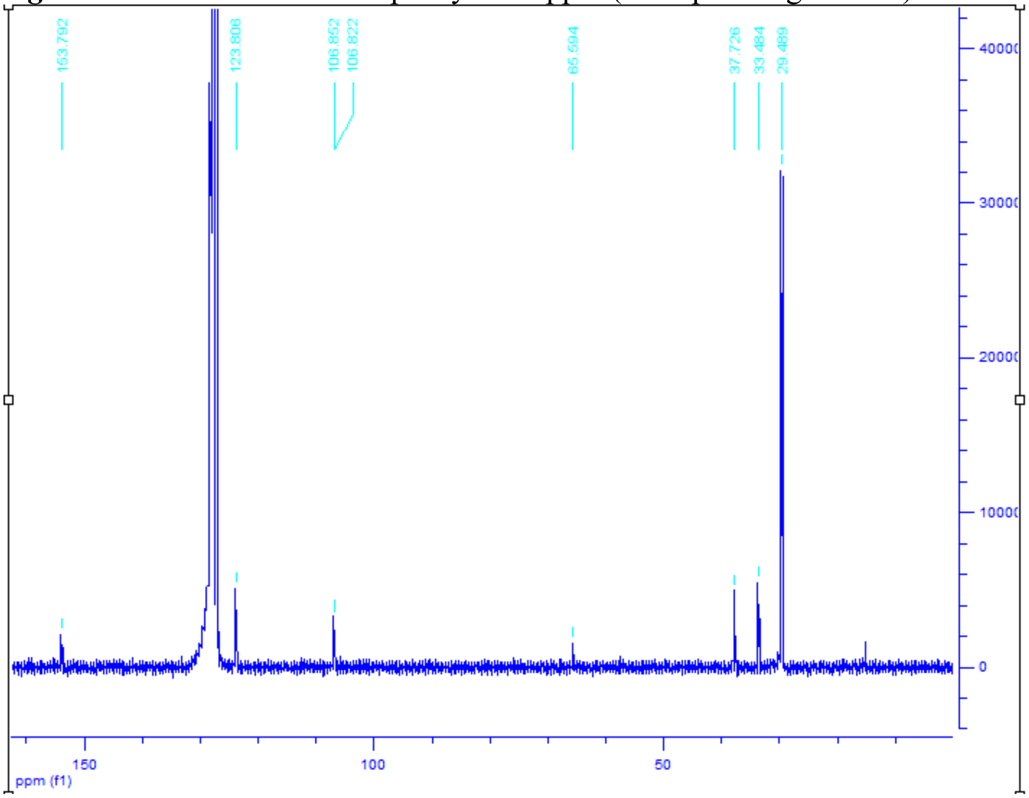


***Figure S14***: $^{1}$HNMR of **6**. Small amount of complex **5** is still present.

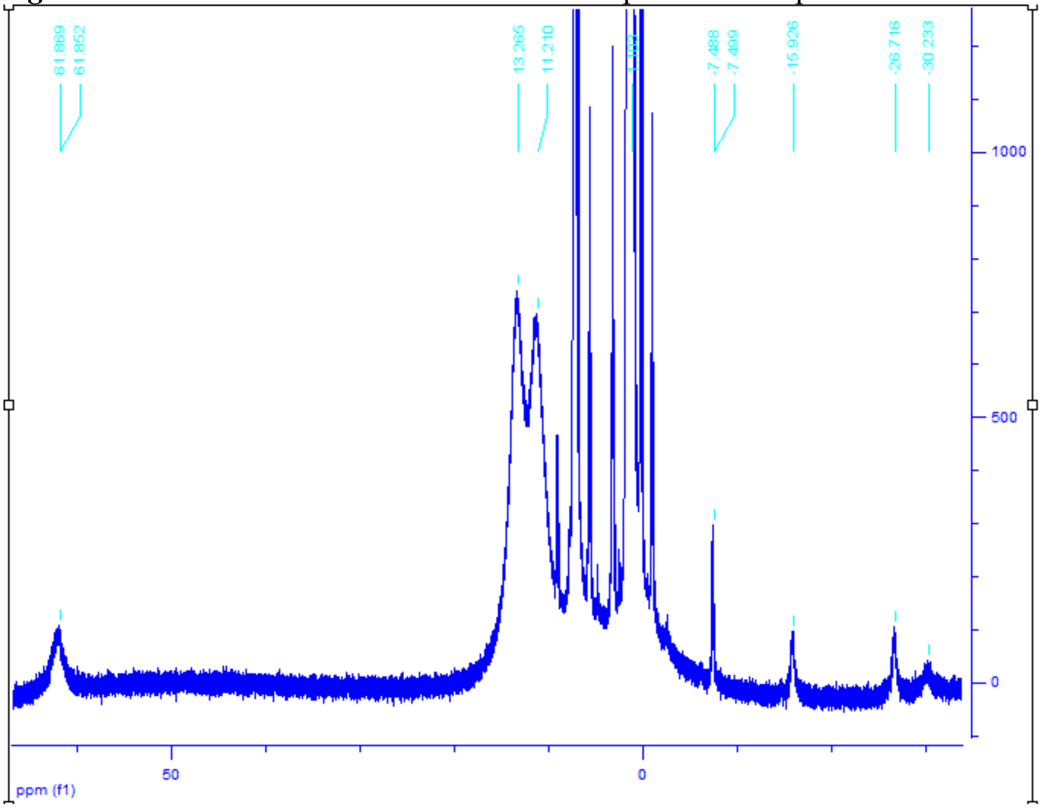


***Figure S15***: expansion of $^{1}$HNMR of **6**.

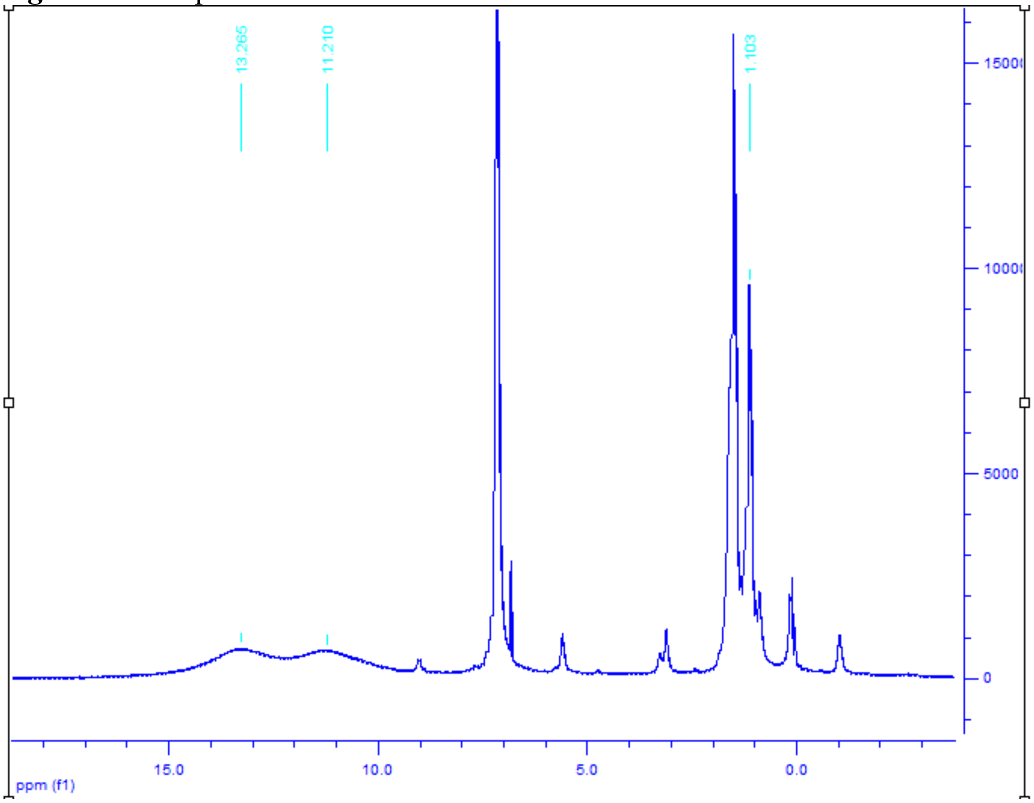


***Figure S16***: $^{1}$HNMR of **6** without any **5** present, but missing peak at 62 ppm.

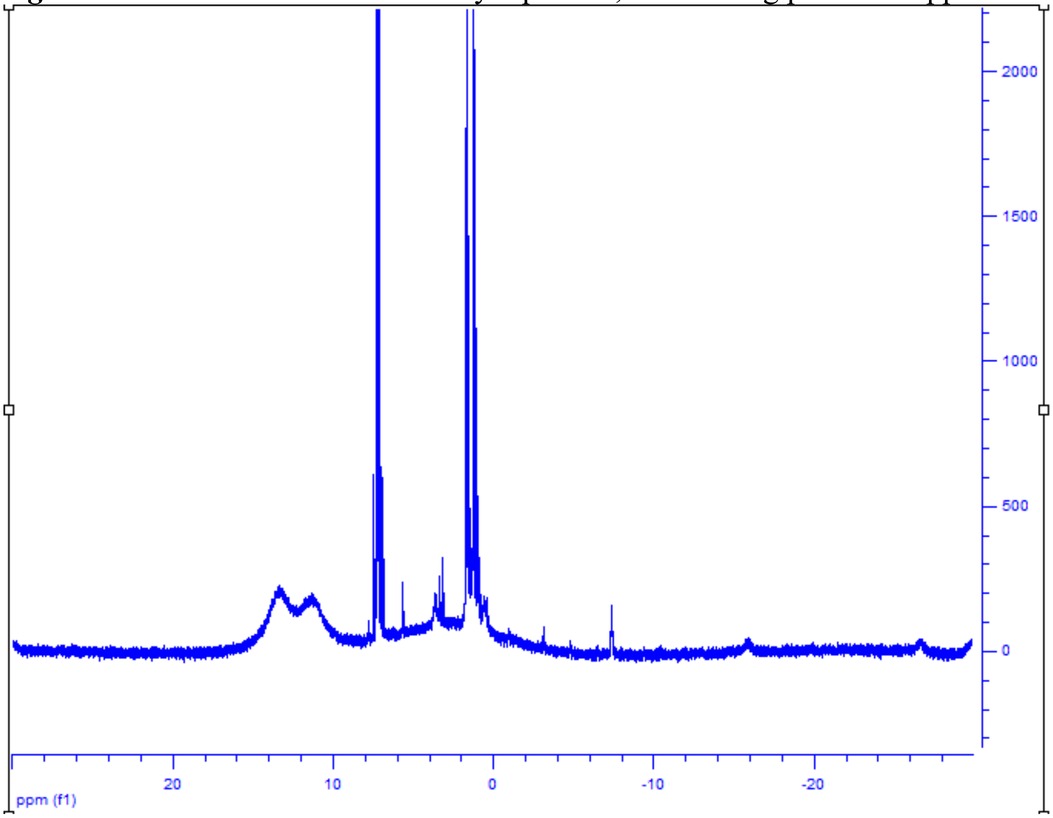


***Figure S17***: $^1$HNMR of the decomposition product of **6** upon addition of $H_2$ (4.5 ppm).

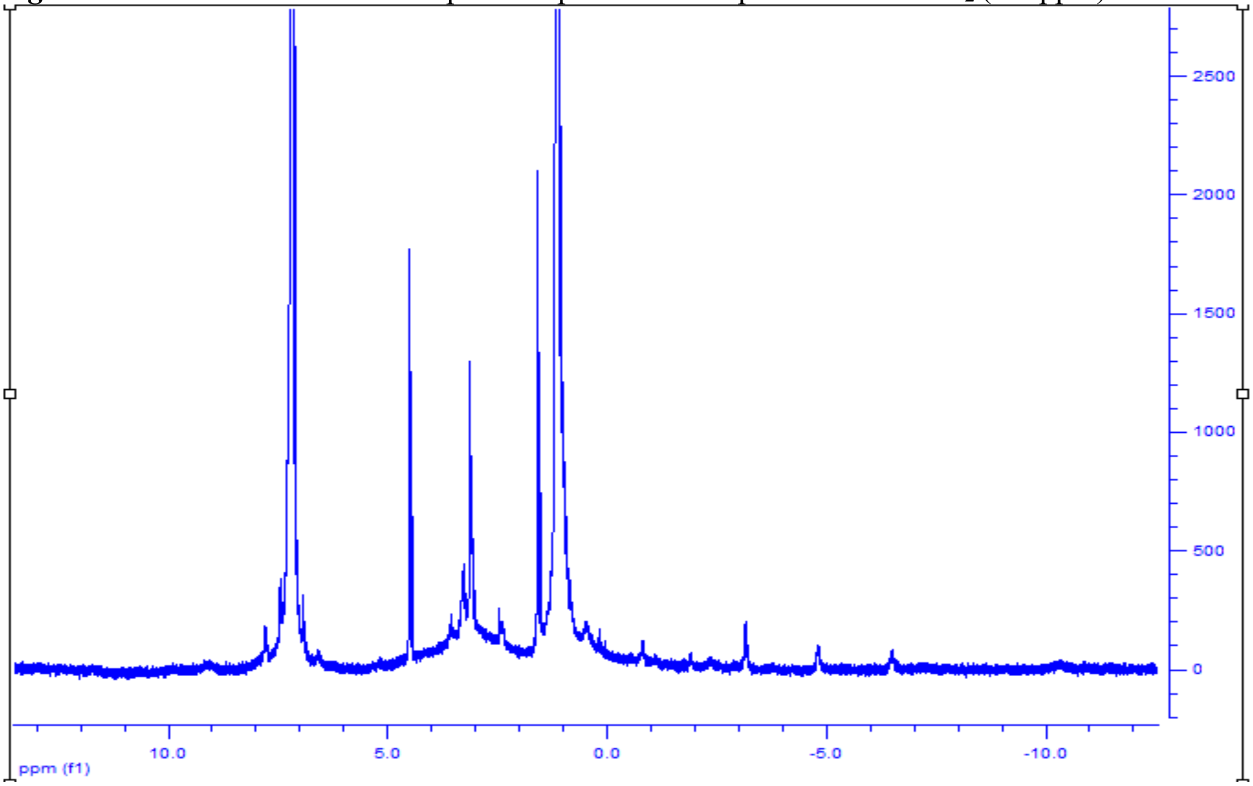


***Table S1***. X-ray diffraction experimental data[a]

| Complex | 3 | 7b | 7a |
|---|---|---|---|
| Formula | $C_{20}H_{37}CoNP_2$ | $C_{24}H_{46}BCoF_4P_2$ | $C_{24}H_{46}CoNP_2I$ |
| Mw | 412.38 | 556.30 | 596.39 |
| Description | *Black plate* | *Yellow prism* | *Yellow plate* |
| Space group | *P2₁/n* | *P-1* | *P-1* |
| Crystal system | Monoclinic | Triclinic | Triclinic |
| a[Å] | 11.0860(1) | 8.3331(3) | 8.2349(3) |
| b[Å] | 13.6610(3) | 12.3139(5) | 12.3743(4) |
| c[Å] | 28.9400(6) | 14.4758(5) | 14.5566(5) |
| α[°] |  | 73.052(2) | 73.304(2) |
| β[°] | 95.6100(12) | 76.271(2) | 76.195(2) |
| γ[°] |  | 88.469(3) | 88.421(8) |
| Volume [$Å^3$] | 4361.9(1) | 1378.86(9) | 1378.42(8) |
| Z | 8 | 2 | 2 |
| $\rho_{calcd}$ mg $m^{-3}$ | 1.256 | 1.340 | 1.437 |
| μ [$mm^{-1}$] | 0.936 | 0.778 | 1.869 |
| $R_1$ [I> 2σ(I)] [%] | 5.62 | 3.44 | 3.41 |
| $R_1$ (all data) | 8.73 | 5.04 | 4.96 |

| | | | |
|---|---|---|---|
| **[%]** | | | |
| **No. of Reflections (unique)** | **61089(7977)** | **22984(8406)** | **24085(6937)** |
| **$R_{int}$** | **0.067** | **0.0331** | **0.0348** |
| **Parameters** | **451** | **339** | **275** |
| **2θ[°]** | **54.96** | **61.10** | **54.96** |
| **Goodness of fit** | **1.057** | **1.009** | **1.055** |

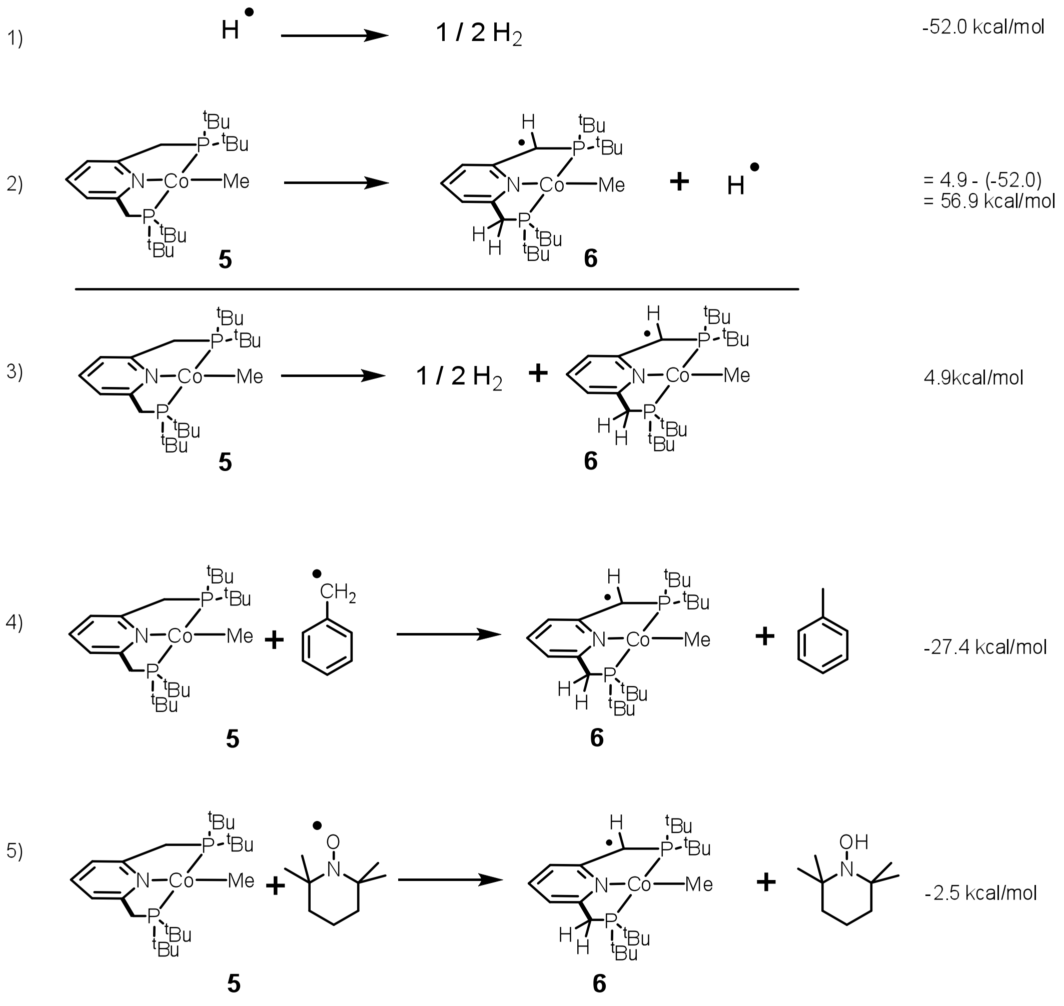
[a] Crystals were coated in Hampton Paratone oil mounted in a fiber.

Crystal data were measured either at 100 $^{0}$K on a Bruker Kappa Apex-II CCD diffractometer or at 120 $^{0}$K on a Nonius KappaCCD diffractometer equipped with ($\lambda$(Mo-K$\alpha$) = 0.71073 Å) radiation, graphite monochromator and MiraCol optics. The data were processed with APEX-II or Nonius collect package programs. Structures were solved by either the AUTOSTRUCTURE module or SIR-97 and refined with full-matrix least-squares refinement based on $F^2$ with SHELXL-97. Full details can be found in the CIF files and Table S1.

## DFT Calculations:

**Computational details.** Theoretical calculations in this work have been performed using density functional theory (DFT) method, (6) specifically functional PBE, (7) implemented in an original program package “Priroda”. (8,9) In PBE calculations relativistic Stevens-Basch-Krauss (SBK) effective core potentials (ECP) (10) optimized for DFT-calculations have been used. Basis set was 311-split for main group elements with one additional polarization p-function for hydrogen, additional two polarization d-functions for elements of higher periods. (11) Full geometry optimization has been performed without constraints on symmetry. For all species under investigation frequency analysis has been carried out. All minima have been checked for the absence of imaginary frequencies. The transition state possessed just one imaginary frequency. Using the Intrinsic Reaction Coordinate Method, L*Ru(H)(OEt); LRu($H_2$)(OEt) and the corresponding transition state were proven to be connected by a single minimal energy reaction path.

***Figure S18*:** Species considered in the current study (all species calculated except H atom). Values are given as $\Delta G_{298}$, with all species calculated in the gas phase.



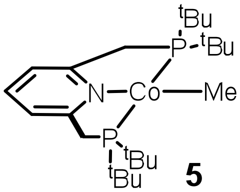
## Computational discussion.

The reaction was calculated for complexes with the tBu substituent (**5** and **6**) so as not to deal with iPr conformational isomers although a crystal structure of **2** was available. Another reason is that **5** appears to be more stable than **2** in that it does not decompose towards **6** in the solid state or in benzene solution. Values are given as $\Delta G_{298}$, with all species calculated in the gas phase. In the discussion below, 'reaction' refers to reactions numbered 1-5 in Figure S17.

Reaction 1 one was obtained from the value of 104 kcal/mol (1st year chemistry books, Wikipedia, common knowledge) for the homolytic splitting of hydrogen. Reaction 3 had all the species calculated, with complex **6** having the lowest energy in the doublet configuration. Based on the values for reactions 1 and 3, we arrive at a value of 56.9 kcal/mol for reaction 2, or spontaneous homolytic bond cleavage, much more than energy available at room temperature, however much lower than the ~90 kcal/mol bond strength of a typical benzylic CH bond. . It is much more likely that the reaction occurs by hydrogen abstraction, as suggested by the experiment with diphenylacetylene where the fate of the hydrogen atom is determined. Equation 4 is a reaction between complex **5** and a benzylic radical, to make **6** and toluene. The reaction is very exergonic and suggests that trace reactive species can cause this reaction to occur. It is indeed very difficult to trap/obtain species **2** and **5** and not their reaction products, as is suggested by the calculation. Diphenylacetylene can be considered as a stand-in for a reactive species in equation 4. It is possible to envision that in a natural system, a pendant amino acid might react in such a way to neutralize a radical with both in proximity, but not coordinating to, a cobalt center.

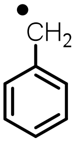
In addition to the diphenylacetylene experiment, a reaction with TEMPO was carried out with complex **2** (excess) and monitored via EPR as described in the main text of the document and above in the SI, with an EPR signal characteristic of complex **3** appearing as the signal of TEMPO diminished. Due to TEMPO being regenerated after the admittance of oxygen, there is every indication that a hydrogen atom from the complex is captured by TEMPO. This was modeled in reaction 5. Since TEMPO is a stable radical that can be handled under air in an organic laboratory setting, the reaction is accordingly much less favorable than in the case of the benzyl radical, but is still exergonic (-2.5kcal/mol).

***Figure S19***: Optimized Geometries.

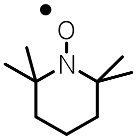


**5**

4HPNP-Co-Me

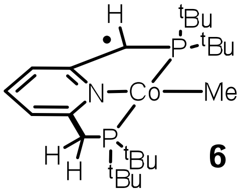


benzyl radical



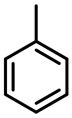
TEMPO

$H_2$
hydrogen

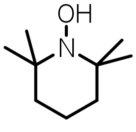


**6**

3HPNP-Co-Me-doublet



toluene



TEMPOH

4HPNP-Co-Me

| | | | |
|---|---|---|---|
| Co | 18.67625286 | 0.97490261 | 7.31308384 |
| P | 16.74557000 | 1.66413067 | 8.05561202 |
| P | 20.72398902 | 0.39024657 | 6.80000301 |
| C | 18.68998839 | 2.41402751 | 9.85746165 |
| C | 19.22500596 | 3.13194874 | 10.92614598 |
| H | 18.55001266 | 3.49226267 | 11.70406482 |
| C | 20.60197173 | 3.36549484 | 11.00926356 |
| H | 21.03591747 | 3.91944313 | 11.84153771 |
| C | 21.39766281 | 2.85197722 | 9.97991225 |
| H | 22.47870174 | 3.00075025 | 9.98371503 |
| C | 20.82378588 | 2.15507642 | 8.91695605 |
| C | 17.22206552 | 2.09970712 | 9.81734242 |
| H | 16.62371139 | 2.89881413 | 10.28141569 |
| C | 21.68636991 | 1.66031810 | 7.78948835 |
| H | 22.66458675 | 1.31269254 | 8.15687700 |
| C | 21.48687532 | 0.64532032 | 5.03615061 |
| C | 21.09377354 | -0.51921692 | 4.10632655 |
| H | 21.40366242 | -0.27858222 | 3.07507416 |
| H | 20.00927551 | -0.69143908 | 4.09927929 |
| H | 21.59464416 | -1.45751775 | 4.38350840 |
| C | 23.01921868 | 0.81754901 | 5.01978547 |
| H | 23.33885113 | 1.04037406 | 3.98701892 |
| H | 23.35348786 | 1.65653510 | 5.64663905 |
| C | 20.85139174 | 1.94673313 | 4.49829819 |
| H | 21.12313562 | 2.82340265 | 5.10546483 |
| H | 19.75646217 | 1.88541862 | 4.47361183 |
| H | 21.21793661 | 2.12921358 | 3.47371255 |
| C | 21.29926726 | -1.30431543 | 7.54622878 |
| C | 20.37082544 | -2.41566282 | 7.01720258 |

| | | | |
|---|---|---|---|
| H | 20.63537948 | -3.37012340 | 7.50366309 |
| H | 20.45412325 | -2.56127040 | 5.93191704 |
| H | 19.32140154 | -2.18929386 | 7.25127253 |
| C | 21.06708356 | -1.18464075 | 9.06808940 |
| H | 20.03560096 | -0.86897854 | 9.28584482 |
| H | 21.75588355 | -0.47273858 | 9.54539036 |
| H | 21.23484784 | -2.17051365 | 9.53365904 |
| C | 22.76766759 | -1.68246373 | 7.29220722 |
| H | 23.46587653 | -0.89299893 | 7.60766464 |
| H | 22.96259840 | -1.91863043 | 6.23718989 |
| H | 23.01224136 | -2.58646560 | 7.87656887 |
| N | 19.46051350 | 1.91646041 | 8.81606964 |
| C | 16.11445304 | 3.33375809 | 7.31022479 |
| C | 14.83837416 | 3.90444189 | 7.95078227 |
| H | 14.63848735 | 4.90452385 | 7.52835782 |
| H | 14.93663838 | 4.02703732 | 9.03981201 |
| H | 13.95265141 | 3.28665081 | 7.74992420 |
| C | 15.91214383 | 3.14287539 | 5.79332805 |
| H | 15.08413679 | 2.46215400 | 5.55676439 |
| H | 16.82361471 | 2.74446946 | 5.32608807 |
| H | 15.68449492 | 4.11888890 | 5.33170302 |
| C | 15.24850035 | 0.46493782 | 8.36396858 |
| C | 14.36775424 | 0.87108040 | 9.56396218 |
| H | 13.56434814 | 0.12347742 | 9.68148253 |
| H | 13.88742014 | 1.84822721 | 9.42815525 |
| H | 14.92619826 | 0.89174270 | 10.50987142 |
| C | 15.89415147 | -0.90553788 | 8.66144117 |
| H | 16.54864839 | -0.87020159 | 9.54565196 |
| H | 16.49977530 | -1.25451427 | 7.81483027 |
| H | 15.10144931 | -1.64685788 | 8.86179571 |
| C | 14.34576569 | 0.32665602 | 7.12230027 |
| H | 13.60593375 | -0.47030796 | 7.30943095 |
| H | 14.90936940 | 0.04933183 | 6.22212658 |
| H | 13.78296069 | 1.24604147 | 6.91021810 |
| C | 17.87679287 | 0.04533929 | 5.73254002 |
| H | 16.78002465 | -0.04973528 | 5.70794570 |
| H | 18.27560086 | -0.97473668 | 5.59201772 |
| H | 18.14478692 | 0.61407554 | 4.82099853 |
| C | 17.27038675 | 4.33733022 | 7.51119170 |
| H | 18.21188704 | 3.94148545 | 7.10125186 |
| H | 17.43216070 | 4.58530611 | 8.57023107 |
| H | 17.02667399 | 5.27509397 | 6.98389988 |
| H | 21.88323361 | 2.49389661 | 7.09471376 |
| H | 17.04270229 | 1.18087558 | 10.40104436 |
| H | 23.55494453 | -0.08358913 | 5.33970666 |

## 3HPNP-Co-Me-doublet

| | | | |
|---|---|---|---|
| Co | 18.65363171 | 0.83933651 | 7.43974956 |
| P | 16.72204931 | 1.69742590 | 8.13876092 |
| P | 20.76945367 | 0.29524374 | 6.87372235 |
| C | 18.73923994 | 2.62165197 | 9.80195408 |
| C | 19.28620956 | 3.48714057 | 10.73627512 |
| H | 18.64152456 | 3.99545803 | 11.45206072 |
| C | 20.69409452 | 3.67062314 | 10.75105167 |
| H | 21.14916295 | 4.35023281 | 11.47478098 |
| C | 21.47646147 | 2.98240517 | 9.85958475 |

| | | | |
|---|---|---|---|
| H | 22.56077509 | 3.09816677 | 9.85453279 |
| C | 20.88872551 | 2.08753240 | 8.89401019 |
| C | 17.25695010 | 2.34422872 | 9.81208199 |
| H | 16.68626216 | 3.21931778 | 10.15642028 |
| C | 21.66004998 | 1.36664496 | 7.99187628 |
| H | 22.74537569 | 1.45641849 | 8.02201720 |
| C | 21.37486430 | 0.79352114 | 5.10628102 |
| C | 20.64769459 | 0.02862611 | 3.98473805 |
| H | 20.97321859 | 0.43249393 | 3.01063893 |
| H | 19.55924027 | 0.14894641 | 4.04938310 |
| H | 20.87335585 | -1.04489049 | 3.98478059 |
| C | 22.89642064 | 0.62246187 | 4.94793443 |
| H | 23.21277889 | 1.06621097 | 3.98815327 |
| H | 23.45449992 | 1.13150435 | 5.74669737 |
| C | 21.01945921 | 2.29034819 | 4.98321513 |
| H | 21.53014690 | 2.89176038 | 5.74776072 |
| H | 19.93587417 | 2.45299339 | 5.09241924 |
| H | 21.32138715 | 2.65519113 | 3.98696105 |
| C | 21.33515030 | -1.50208530 | 7.34016598 |
| C | 21.05801969 | -2.54471754 | 6.24390013 |
| H | 21.24584965 | -3.55262430 | 6.65256484 |
| H | 21.72095417 | -2.42051156 | 5.37624709 |
| H | 20.01715515 | -2.52033836 | 5.89357455 |
| C | 20.48823406 | -1.83441896 | 8.58771681 |
| H | 19.41505282 | -1.86466523 | 8.34785449 |
| H | 20.64148746 | -1.08867548 | 9.38223131 |
| H | 20.78643856 | -2.82001252 | 8.98492702 |
| C | 22.82322326 | -1.55433875 | 7.73336145 |
| H | 23.04386991 | -0.85624854 | 8.55235540 |
| H | 23.49302751 | -1.32556713 | 6.89357803 |
| H | 23.06664679 | -2.57271900 | 8.08262776 |
| N | 19.48237631 | 1.94582674 | 8.86708756 |
| C | 16.17106778 | 3.27654039 | 7.17669269 |
| C | 14.91085534 | 3.96213922 | 7.73149787 |
| H | 14.75487949 | 4.91185270 | 7.19193043 |
| H | 15.00271539 | 4.20776286 | 8.79965029 |
| H | 14.00520995 | 3.35727269 | 7.58889675 |
| C | 15.96015201 | 2.90786681 | 5.69436531 |
| H | 15.13438332 | 2.20062583 | 5.54305269 |
| H | 16.86948001 | 2.46691589 | 5.26368122 |
| H | 15.72481229 | 3.82310665 | 5.12582357 |
| C | 15.20153890 | 0.60053670 | 8.61100662 |
| C | 14.30379514 | 1.21528649 | 9.70412468 |
| H | 13.50367011 | 0.49580313 | 9.94867266 |
| H | 13.82019527 | 2.14637487 | 9.38512076 |
| H | 14.85250731 | 1.41393542 | 10.63509690 |
| C | 15.80726850 | -0.71205564 | 9.15661641 |
| H | 16.41947838 | -0.54278640 | 10.05518035 |
| H | 16.43831645 | -1.21207419 | 8.41074144 |
| H | 14.98993779 | -1.39644965 | 9.43938941 |
| C | 14.34005833 | 0.28134125 | 7.37314991 |
| H | 13.58526197 | -0.47463098 | 7.64758855 |
| H | 14.93286853 | -0.12656821 | 6.54367976 |
| H | 13.79633224 | 1.16367851 | 7.00822699 |
| C | 17.84422631 | -0.33912152 | 6.05560808 |
| H | 16.86839813 | -0.76250194 | 6.33644589 |
| H | 18.47061086 | -1.17184825 | 5.70626479 |

| | | | |
|---|---|---|---|
| H | 17.66422212 | 0.31437678 | 5.17949511 |
| C | 17.35749115 | 4.26164550 | 7.26181558 |
| H | 18.29343468 | 3.79974672 | 6.91553944 |
| H | 17.52165583 | 4.63715491 | 8.28164717 |
| H | 17.14302073 | 5.13042424 | 6.61738508 |
| H | 23.19545665 | -0.43494500 | 4.93031316 |
| H | 17.05797970 | 1.52803379 | 10.52653526 |

## Benzyl radical

| | | | |
|---|---|---|---|
| C | -0.71847953 | -0.12130398 | 0.00493911 |
| C | 0.39829656 | 0.69989268 | 0.04820104 |
| C | 1.68887121 | 0.14711690 | 0.07782808 |
| C | 1.84577954 | -1.24830456 | 0.06177754 |
| C | 0.73761093 | -2.08101868 | 0.01796734 |
| C | -0.58693141 | -1.54451660 | -0.01025180 |
| C | -1.71501273 | -2.38277831 | -0.05680636 |
| H | -2.72134766 | -1.96769029 | -0.07924645 |
| H | -1.60910973 | -3.46619616 | -0.07019309 |
| H | 0.86508698 | -3.16489666 | 0.00637377 |
| H | 2.84702092 | -1.68092045 | 0.08444405 |
| H | 2.56342214 | 0.79690878 | 0.11121310 |
| H | 0.27274378 | 1.78352777 | 0.05918601 |
| H | -1.71931900 | 0.31335955 | -0.01856733 |

## Toluene

| | | | |
|---|---|---|---|
| C | -0.68812657 | -0.20325814 | -0.07545895 |
| C | 0.39318429 | 0.65804605 | 0.12495797 |
| C | 1.69604696 | 0.15356009 | 0.16415143 |
| C | 1.90606658 | -1.21802452 | -0.00043658 |
| C | 0.82149934 | -2.07604494 | -0.20016682 |
| C | -0.49172440 | -1.58339070 | -0.23811011 |
| C | -1.66497407 | -2.51541287 | -0.42240556 |
| H | -2.48179746 | -2.02871106 | -0.97243855 |
| H | -2.07110510 | -2.83389476 | 0.55066721 |
| H | 0.99543358 | -3.14623390 | -0.33100522 |
| H | 2.91904212 | -1.62238003 | 0.02371412 |
| H | 2.54135082 | 0.82482015 | 0.31899038 |
| H | 0.21775254 | 1.72774771 | 0.24818984 |
| H | -1.70245477 | 0.20037288 | -0.10722314 |
| H | -1.37430487 | -3.42302496 | -0.96820502 |

## Hydrogen

| | | | |
|---|---|---|---|
| H | -0.767682 | -0.059709 | 0.000000 |
| H | 0.152283 | 0.026572 | 0.000000 |

## TEMPO

| | | | |
|---|---|---|---|
| C | -0.93019754 | -0.37463915 | -0.51914271 |
| C | -0.10180932 | 0.90745938 | -0.31337536 |
| N | 1.36681707 | 0.62064404 | -0.51411748 |
| C | 2.02948039 | -0.68426486 | -0.14355443 |
| C | 1.05703306 | -1.85883754 | -0.36069013 |
| C | -0.34647623 | -1.59913894 | 0.18230718 |
| C | -0.31406681 | 1.49941983 | 1.09535476 |
| C | -0.50395502 | 1.95253169 | -1.36481053 |

| | | | |
|---|---|---|---|
| O | 2.13939441 | 1.65041798 | -0.55730196 |
| C | 3.24674134 | -0.84849342 | -1.06591048 |
| C | 2.51010091 | -0.61003712 | 1.32054264 |
| H | 1.50288861 | -2.75445273 | 0.09856995 |
| H | 0.98349611 | -2.06105231 | -1.44241005 |
| H | -0.99254560 | -0.58521002 | -1.59997255 |
| H | -1.95661596 | -0.17087381 | -0.17738551 |
| H | -0.98636233 | -2.47545496 | -0.00099625 |
| H | -0.32624498 | -1.45540101 | 1.27418627 |
| H | 1.67702053 | -0.61128695 | 2.03532343 |
| H | 3.09732140 | 0.30547494 | 1.46757505 |
| H | 3.14953786 | -1.47614841 | 1.54330277 |
| H | 3.96300083 | -0.03394414 | -0.91187004 |
| H | 2.93720069 | -0.84355923 | -2.12015318 |
| H | 3.73900641 | -1.80729918 | -0.85080676 |
| H | -0.15583223 | 0.75814844 | 1.88931751 |
| H | -1.34200967 | 1.87880334 | 1.18509875 |
| H | 0.38154676 | 2.33406122 | 1.25069657 |
| H | 0.05847266 | 2.88196869 | -1.22317430 |
| H | -1.57870228 | 2.16409750 | -1.27467767 |
| H | -0.30563207 | 1.57803472 | -2.37855849 |

## TEMPOH

| | | | |
|---|---|---|---|
| C | -0.95619964 | -0.45921360 | -1.53943950 |
| C | -0.07249240 | 0.77773364 | -1.81126466 |
| N | 1.20844025 | 0.27293070 | -2.39653491 |
| C | 1.99814377 | -0.76454460 | -1.66276657 |
| C | 1.04118814 | -1.94678736 | -1.39579840 |
| C | -0.25537168 | -1.52911102 | -0.70342481 |
| C | 0.07128243 | 1.65269136 | -0.54583377 |
| C | -0.74942533 | 1.62446264 | -2.90522106 |
| O | 2.08524660 | 1.43125415 | -2.59355732 |
| C | 3.09847209 | -1.24123433 | -2.62914888 |
| C | 2.67696957 | -0.28782957 | -0.35888460 |
| H | 1.58443118 | -2.69856901 | -0.80260658 |
| H | 0.79295028 | -2.41664379 | -2.36191931 |
| H | -1.24518716 | -0.89814407 | -2.50875332 |
| H | -1.88236945 | -0.11712237 | -1.05229289 |
| H | -0.91437786 | -2.40233243 | -0.58148865 |
| H | -0.05064760 | -1.15608602 | 0.31252000 |
| H | 1.97329702 | -0.16583822 | 0.47243857 |
| H | 3.18885827 | 0.66839914 | -0.52455852 |
| H | 3.42982113 | -1.02664867 | -0.04837555 |
| H | 3.85112970 | -0.45813127 | -2.78835148 |
| H | 2.66115496 | -1.51465808 | -3.59960679 |
| H | 3.60709047 | -2.12288940 | -2.21364161 |
| H | 0.32197750 | 1.07443370 | 0.35069150 |
| H | -0.87922149 | 2.16975036 | -0.35018666 |
| H | 0.84670324 | 2.41420693 | -0.69648173 |
| H | -0.19768333 | 2.55701634 | -3.08133195 |
| H | -1.77199393 | 1.88671967 | -2.59827872 |
| H | -0.80085014 | 1.06024878 | -3.84693764 |
| H | 2.16891341 | 1.45002141 | -3.56207321 |

## EPR Data

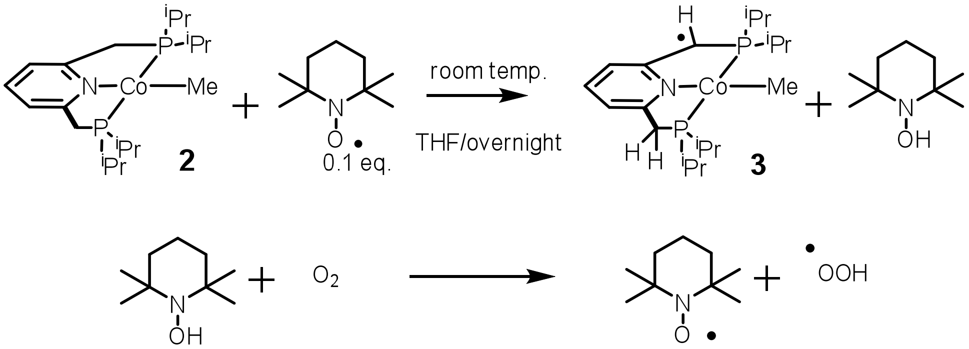
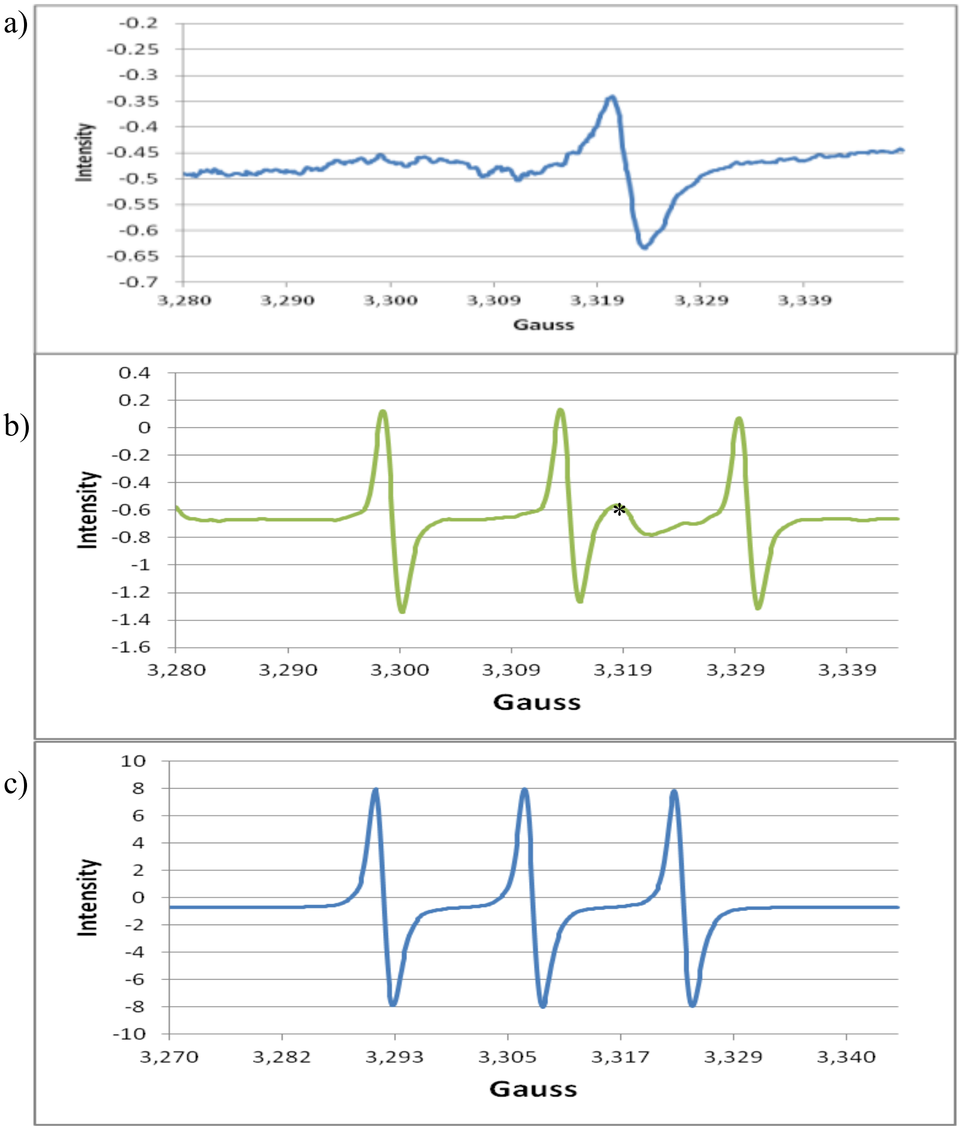


***Figure S20*****:** a) Signal of **3** by itself b) EPR of **2** → **3** reaction and TEMPO three hours after mixing (complex **3** signal marked by *) before complete disappearance of TEMPO triplet c) same mixture after TEMPO signal disappears overnight and oxygen admitted; note: y-axis scaled differently for better graphical representation.



**References:**

1. A. Jansen, S. Pitter, *Monatsch. Chem.* 1999, **130**, 783.

2. N. Ahmad, J.J. Levison, S.D. Robinson, M.F. Uttley, *Inorg. Synth*. 1974, **15**, 45.

3. D.F. Evans, *J. Chem. Soc.*, 1959, 2003.

4. K. De Buysser, G.G. Herman, E. Bruneel, S. Hoste, I. Van Driessche, *Chem. Phys.* 2005, **315**, 286.

5. (a) Q. Knijnenburg, D. Hetterscheid, T.M. Kooistra, P.H.M. Budzelaar, *Eur.J.Inorg.Chem.*, 2004, 1204-11. (b) Q. Knijnenburg, S. Gambarotta, P.H.M. Budzelaar, *Dalton. Trans.*, 2006, 5442-8. (c) D. Zhu, P.H.M. Budzelaar, *Organometallics*, 2008, **27**, 2699-705. (d) D. Zhu, I. Thapa, I. Korobkov, S. Gambarotta, P.H.M. Budzelaar, *Inorg. Chem.*, 2011, **50**, 9879-87. (e) D. Zhu, I. Korobkov, P.H.M. Budzelaar, *Organometallics*, 2012, **31**, 3958-71.

6. R. G. Parr, W. Yang, *Density-functional theory of atoms and molecules* (Oxford University Press: Oxford, 1989)

7. J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.*, 1996, 77, 3865.

8. D. N. Laikov, *Chem. Phys. Lett.*, 1997, **281**, 151.

9. D. N. Laikov, Yu. A. Ustynyuk, *PRIRODA-04: a quantum-chemical program suite. New possibilities in the study of molecular systems with the application of parallel computing. Russian Chemical Bulletin*, 2005, **54**, 820.

10. (a) W. J. Stevens, H. Basch, M. Krauss, *J. Chem. Phys.*, 1984, **81**, 6026. (b) W. J. Stevens, H. Basch, M. Krauss, P. Jaisen, *Can. J. Chem.*, 1992, **70**, 612. (c) T. R. Cundari, W. J. Stevens, *J. Chem. Phys.*, 1993, **98**, 5555.

11. For some examples of these parameters being used on other transition metal systems see: (a) A. Yahav-Levi, I. Goldberg, A. Vigalok, A. N. Vedernikov, *J. Am. Chem. Soc.*, 2008, **130**, 724. (b) A. A. Popov, L. Dunsch, *J. Am. Chem. Soc.*, 2007, **46**, 6309. (c) A. A. Koridze, A. V. Polezhaev, S. V. Safronov, A. M. Sheloumov, F. M. Dolgushin, M. G. Ezernitskaya, B. V. Lokshin, P. V. Petrovskii, A. S. Peregudov, *Organometallics*, 2010, **29**, 4360.