Electronic Supplementary Material (ESI) for ChemComm.

Electronic Supplementary Information

One Electron Reduction Transforms High-Valent Low-Spin Cobalt Alkylidene into High-Spin Cobalt(II) Carbene Radical

Amanda Grass,[a] James A. Bellow,[a] Gregory Morrison,[b] Hans-Conrad zur Loye,[b] Richard L. Lord,[c]* Stanislav Groysman[a]*

[a]Department of Chemistry, Wayne State University, 5101 Cass Ave, Detroit, MI, 48202, USA.

[b]Department of Chemistry and Biochemistry, University of South Carolina, Columbia, SC 29208, USA

[c]Department of Chemistry, Grand Valley State University, Allendale, MI, 49401, USA.

Table of Contents

1. Synthesis and Characterization of Complexes

General. All reactions involving air-sensitive materials were executed in a nitrogen-filled glovebox or by standard Schlenk line procedures. Cobalt chloride, bis(pentamethylcyclopentadienyl)cobalt(II), 2,6-dimethylphenyl isocyanide, and trimethoxybenzene were purchased from Sigma-Aldrich. Adamantyl isocyanide was purchased from Alfa Aesar. Potassium graphite and thallium hexafluorophosphate were purchased from Strem. The syntheses of complexes **1** and **2** were reported previously.[1,2] Diphenyldiazomethane were synthesized according to a reported literature procedure.[3] All solvents were purchased from Fisher Scientific and were of HPLC grade. The solvents were purified using an MBRAUN solvent purification system and stored over 3 Å molecular sieves. Deuterated benzene (C_6D_6) was purchased from Cambridge Laboratories and deuterated tetrahydrofuran (THF-d_8) was obtained from Sigma Aldrich. Both were degassed under argon, and stored over 3 Å molecular sieves. The complexes were characterized using NMR, IR, and UV/vis spectroscopy, X-ray crystallography, SQUID magnetometry, elemental analysis, and solution magnetometry by the Evans method. NMR and GC-MS spectra were recorded at the Lumigen Instrument Center (Wayne State University). NMR was performed on a Varian Mercury or Agilent 400 MHz Spectrometer in C_6D_6 or THF-d_8 at room temperature. Chemical shifts and coupling constants (J) were reported in parts per million (δ) and hertz (Hz), respectively. IR spectra of powdered samples were recorded on a Shimadzu IR Affinity-1 FT-IR Spectrometer outfitted with a MIRacle10 attenuated total reflectance accessory with a monolithic diamond crystal stage and pressure clamp. UV−visible spectra were obtained on a Shimadzu UV-1800 spectrometer. SQUID magnetometry was performed at the Magnetic Properties Measurement System Facility at University of South Carolina. Elemental analyses were performed by Midwest Microlab LLC. Formation of the ketenimine and organic byproducts was confirmed by GC-MS using Agilent 6890N spectrometer, Thermo TG5MS 30 m × 0.32 mm × 0.25 μm column, 7683 series injector, and Agilent 5973 detector.

Synthesis of [Co(OR$_2$)(CPh$_2$)][CoCp*$_2$] (3). A suspension of CoCp$_2$* (46 mg, 0.138 mmol) in diethyl ether was added to a stirring dark-brown ether solution of Co(OR)$_2$(CPh$_2$) (**2**, 85 mg, 0.128 mmol) at -35˚C. There was an immediate color change to lighter brown. The reaction was allowed to warm to room temperature and stirred for 1 hour. The solution was filtered, washed with diether ether, dissolved in THF, filtered, and dried in vacuo. Subsequent recrystallization of a THF solution layered with diethyl ether at -35˚C yields X-ray quality crystals of **3** (76 mg, 60% yield). ^{1}H NMR (400 MHz, THF-d$_8$) δ 108.4 (5H, Ph), δ 45.4 (1H, OR- Ph), δ 11.4 (2H, OR-Ph), δ 8.10 (5H, OR-Ph), δ 7.74 (4H, OR-Ph), δ 6.19 (18H, OR-^{t}Bu), -4.46 (30H, Cp*), -44.22 (5H, Ph). IR (cm^{-1}): 2974 (w), 2947 (w), 2885 (w), 1558 (m), 1474 (m), 1377 (m), 1280 (w), 1142 (w), 1061 (s), 1022 (w), 945 (m), 891 (m), 844 (w), 799 (w), 741 (m), 702 (s). λ_{max} ($\varepsilon_{M\,(L^{-1}cm^{-1}\,mol^{-1}}$) 500 nm (2040), 648 nm (760), 712 nm (590). μ_{eff} (Evans method) = 4.2 ± 0.2 μ_B (calcd 4.9). Anal. Calcd for $C_{63}H_{92}O_2Co_2$: C, 75.72; H, 9.28, Found: C, 76.08; H, 8.92.

Synthesis of [Co(OR$_2$)(CPh$_2$)][K(18-crown-6)] (4). A THF solution of 18-crown-6 (41 mg, 0.154 mmol) in was added to a stirring dark-brown THF solution of Co(OR)$_2$(CPh$_2$) (88 mg, 0.132 mmol), followed by a suspension of KC$_8$ (24 mg, 0.175 mmol) in THF. There was a color change to russet brown after 5 minutes and the reaction was stirred for 1 hour at room temperature. Solvent was removed in vacuo to afford a brown residue. The residue was dissolved in a solution of 15:1 diethyl ether:THF, filtered, and washed with additional diethyl ether. The filtrate was concentrated in vacuo. Subsequent recrystallization at -35 ˚C yields crystals of **4** (50 mg, 39% yield). IR (cm^{-1}): 2970 (w), 2940 (w), 2886 (w), 1473 (w), 1350 (w), 1103 (s), 1065 (s), 964 (m), 748 (m), 702 (s). λ_{max} ($\varepsilon_{M\ (L^{-1}cm^{-1}\ mol^{-1})}$) 503 nm (620), 651 nm (200), 712 nm (160). Anal. Calcd for $C_{55}H_{80}O_8Co$: C, 68.30; H, 8.34 Found: C, 67.97; H, 8.37.

Reaction of [Co(OR$_2$)(CPh$_2$)][CoCp*$_2$] with 2,6-dimethylphenyl isocyanide. A benzene solution of CN(2,6-$Me_2C_6H_3$) (40 mg, 0.303 mmol) in benzene was added to a stirring solution of [Co(OR$_2$)(CPh$_2$)][CoCp*$_2$] (93 mg, 0.0962 mmol) in benzene at room temperature. There was a color change to dark purple-black after 20 minutes and solution was stirred for an additional 2 hours. Solvent was removed in vacuo to afford a dark purple residue. The residue was dissolved in diethyl ether, filtered, and washed with additional diethyl ether. The filtrate was concentrated in vacuo and subsequent recrystallization at -35˚C yielded mixture of X-ray quality crystals of orange Co_2(CN(2,6-$Me_2C_6H_3$))$_8$ (**5**) and purple CoCp$_2$*($Me_2C_5Me_2$C(H)(η^2C(CN(2,6-Me_2C_6H-$_3$))(C(H)Ph$_2$) (**6**). The products display similar solubility in organic solvents and crystallize together. Orange and purple crystals were mechanically separated to give 22 mg (20% yield) of **5** and 22 mg (49%) of **6**, and further characterized. Synthesis, spectroscopic and structural characterization of orange Co_2(CN(2,6-$Me_2C_6H_3$))$_8$ was previously reported.[4] ^{1}H NMR spectrum of **5** matched literature spectrum and is reported below. ^{1}H NMR (400 MHz, C_6D_6) of **5**: δ 6.78 (br, 24H), 2.39 (s, 48H). **6** was characterized by X-ray crystallography, IR spectroscopy, ^{1}H NMR spectroscopy, and UV-vis spectroscopy. IR (cm^{-1}): 2917 (w), 2855 (w), 2381 (w), 2045 (s), 2014 (s), 1667 (s), 1582 (m), 1458 (m), 1373 (w), 1188 (m), 1126 (w), 1057 (w), 957 (m), 764 (m), 741 (m), 656 (s).^{1}H NMR (400 MHz, C_6D_6) δ 7.53 (d, 4H, o-Ph), δ 7.16 (t, 8H, m-Ph,), δ 7.08 (t, 3H, NC_6*H_3*), 6.98 (t, 2H, p-Ph,), δ 5.34(s, 1H, $Me_2C_5Me_2$C*H*), δ 3.82 (s, 6H, C*H*Ph$_2$), 2.22 (s, 6H, *Me_2*C_6H_3), δ 1.58 (bs, 6H, Me_2C_5*Me_2*CH), δ 1.33 (s, 15H, *Cp**), δ 1.27 (s, 6H, *Me_2*C_5Me_2CH). λ_{max} ($\varepsilon_{M\ (L^{-1}cm^{-1}\ mol^{-1})}$) 550 (12071).

Reaction of [Co(OR$_2$)(CPh$_2$)][K(18-crown-6)] with 2,6-dimethylphenyl isocyanide. A solution of CN(2,6-Me$_2$C$_6$H$_3$) (8.7 mg, 0.0663 mmol) in benzene/ether was added to a stirring solution of [Co(OR)$_2$(CPh$_2$)][K(18-crown-6)] (50 mg, 0.0519 mmol) in benzene/ether at -35˚C. There was a color change to dark green immediately and solution was stirred for 45 minutes, after which the solution transitions to a greenish brown. Solvent was removed in vacuo to afford a dark brown-green residue. The residue was washed repeatedly with hexanes. ^{1}H NMR of the residue shows formation of the previously reported ketenimine[5] and Co$_2$(CN(2,6-Me$_2$C$_6$H$_3$))$_8$ (**5**).[4] The hexane washings were concentrated at -35 ˚C to afford **5** in 18% yield.

Reaction of [Co(OR$_2$)(CPh$_2$)][CoCp*$_2$] with adamantyl isocyanide. A ether solution of CNAd (21 mg, 0.130 mmol) was added to a stirring brown-green suspension of [Co(OR$_2$)(CPh$_2$)][CoCp*$_2$] (29 mg, 0.029 mmol) in ether at room temperature. After 20 minutes, the reaction turned russet brown. The solution gradually darkened and was stirred for 3 hours total at room temperature. The solvent was removed in vacuo to afford a dark brown residue. The residue was dissolved in a 1:1 hexane:ether solution and filtered through a silica plug. The solvent was removed in vacuo and the faint yellow oil was shown by ^{1}H NMR to be the previously reported ketenimine (approximately 55% yield), in addition to free isocyanide and hydrolyzed ligand. GC-MS confirmed the presence of the ketenimine as the major product.

2. X-ray crystallographic details and structures of 3a and 5

The structures of **3**, **3a**, **5**, and **6** were confirmed by X-ray analysis. The structures of **2** and **5** was previously reported.[2,4b] Whereas the crystal data parameters for **5** matched those previously reported,[4b] its refinement parameters are slightly different and therefore are reported here. The crystals were mounted on a Bruker APEXII/Kappa three circle goniometer platform diffractometer equipped with an APEX-2 detector. A graphic monochromator was employed for wavelength selection of the Mo Kα radiation (λ = 0.71073 Å). The data were processed and the structure was solved using the APEX-2 software supplied by Bruker-AXS. The structure was refined by standard difference Fourier techniques with SHELXL (6.10 v., Sheldrick G. M., and Siemens Industrial Automation, 2000). Hydrogen atoms were placed in calculated positions using a standard riding model and refined isotropically; all other atoms were refined anisotropically. The structure of **3a** was of relatively low quality, due to weak diffraction and the disordered solvent. As we were not able to model the solvent satisfactorily, SQUEEZE was used.

Table S1. Crystal data and structure refinement for **3, 3a**, **5**, and **6**.

	3	**3a**	**5**	**6**
formula	$C_{63}H_{86}Co_2O_2$	$0.5C_{63}H_{86}Co_2O_2$	$C_{72}H_{72}Co_2N_8$	$C_{42}H_{48}CoN$
fw	993.18	496.59	1167.24	625.74
crystal system	Triclinic	Monoclinic	Triclinic	Orthorhombic
space group	*P*-1	*C*2/*c*	*P*-1	*Pbcn*
a (Å)	12.0917(7)	19.276(7)	12.0255(6)	14.6058(7)
b (Å)	13.2206(7)	15.481(6)	13.8796(7)	14.6784(7)
c (Å)	18.3083(10)	20.600(8)	21.0959(10)	30.7441(13)
α (deg)	83.843(3)	90.00	98.389(3)	90.00
β (deg)	74.551(3)	101.414(11)	99.020(3)	90.00
γ (deg)	73.230(3)	90.00	113.189(3)	90.00
V (Å^3)	2699.6(3)	6026(4)	3111.9(3)	6591.2(5)
D_c (g cm^{-3})	1.222	1.095	1.246	1.261
Z	2	8	2	8
μ (mm^{-1})	0.657	0.588	0.582	0.551
T (K)	100(2)	100(2)	100(2)	100(2)
R_1	0.0335	0.1046	0.0505	0.0474
GOF	1.023	0.976	1.000	0.962

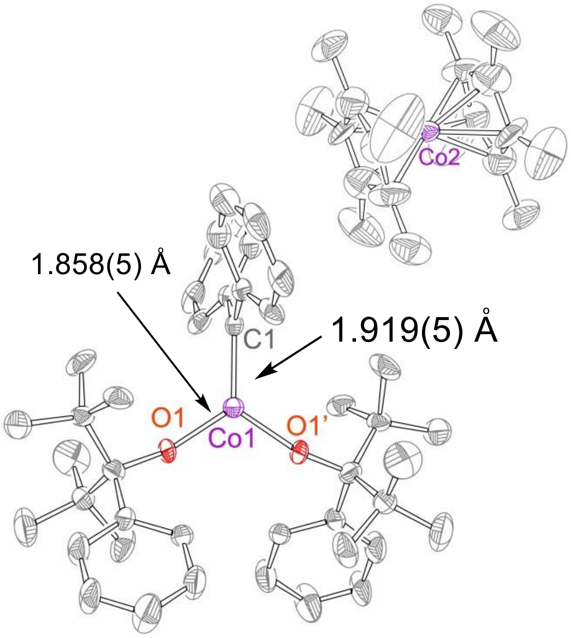

Figure S1. X-ray structure (50% probability ellipsoids) of **3a**, with selected bonds shown.

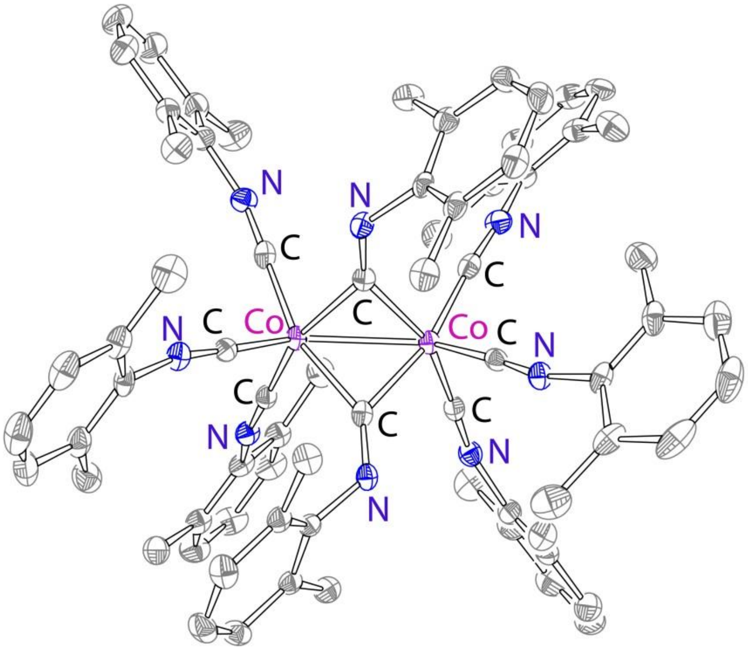

Figure S2. X-ray structure (50% probability ellipsoids) of **5**, with selected bonds shown.

3. Evans' method formula and procedure

The Evans method was performed on all complexes using a Wilmad coaxial insert (purchased from Aldrich) and a standard NMR tube. The sample was carefully weighed (10 – 20 mg) and dissolved in 1.00 mL C_6D_6 to afford solutions with known concentrations to perform the calculations. The solutions were added to the insert, and the insert was placed inside the outer NMR tube, which contained C_6D_6. NMR spectra were taken. The molar susceptibility χ_m of the compound was first calculated using Equation 1:[6]

$$\chi_m = \left[\frac{3\Delta\nu}{4\pi m\nu_0} + \chi_0\right]M \qquad (1)$$

where $\Delta\nu$ is the peak separation (Hz), m is the concentration of the solution (g/mL), ν_0 is the spectrometer operating frequency in Hertz, χ_0 is the molar susceptibility of the solvent (in cm^3/g), and M is the molar mass of the compound (g/mol). Diamagnetic corrections were calculated using Pascals constants. The solution state effective magnetic moment (μ_{eff}) was calculated using Equation 2:

$$\mu_{eff} = \sqrt{(2.383 \times 10^3)(\chi_m)} \qquad (2)$$

Three measurements were taken, the average of the three and the corresponding standard deviation were calculated. The uncertainty was estimated to be ~ 10%, based on weight measurement uncertainty.

Table S2. Observed magnetic moment for complex **3** using the Evans method (μ_{obs} (μ_B)).

	3
1	4.35
2	4.07
3	4.27
average	4.23
standard deviation	0.15
μ_{calc} (μB)	4.90

4. NMR and GC-MS Spectra

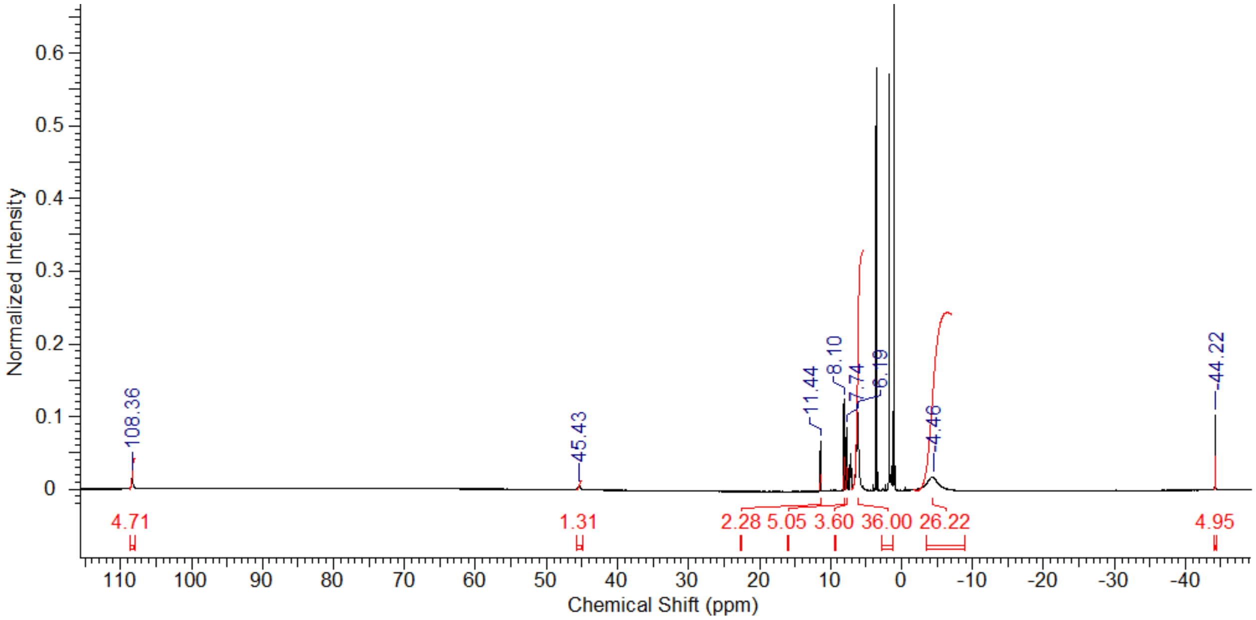

Figure S3. ^{1}H NMR spectrum of [Co(OR)$_2$(CPh$_2$)][CoCp*$_2$] (**3**).

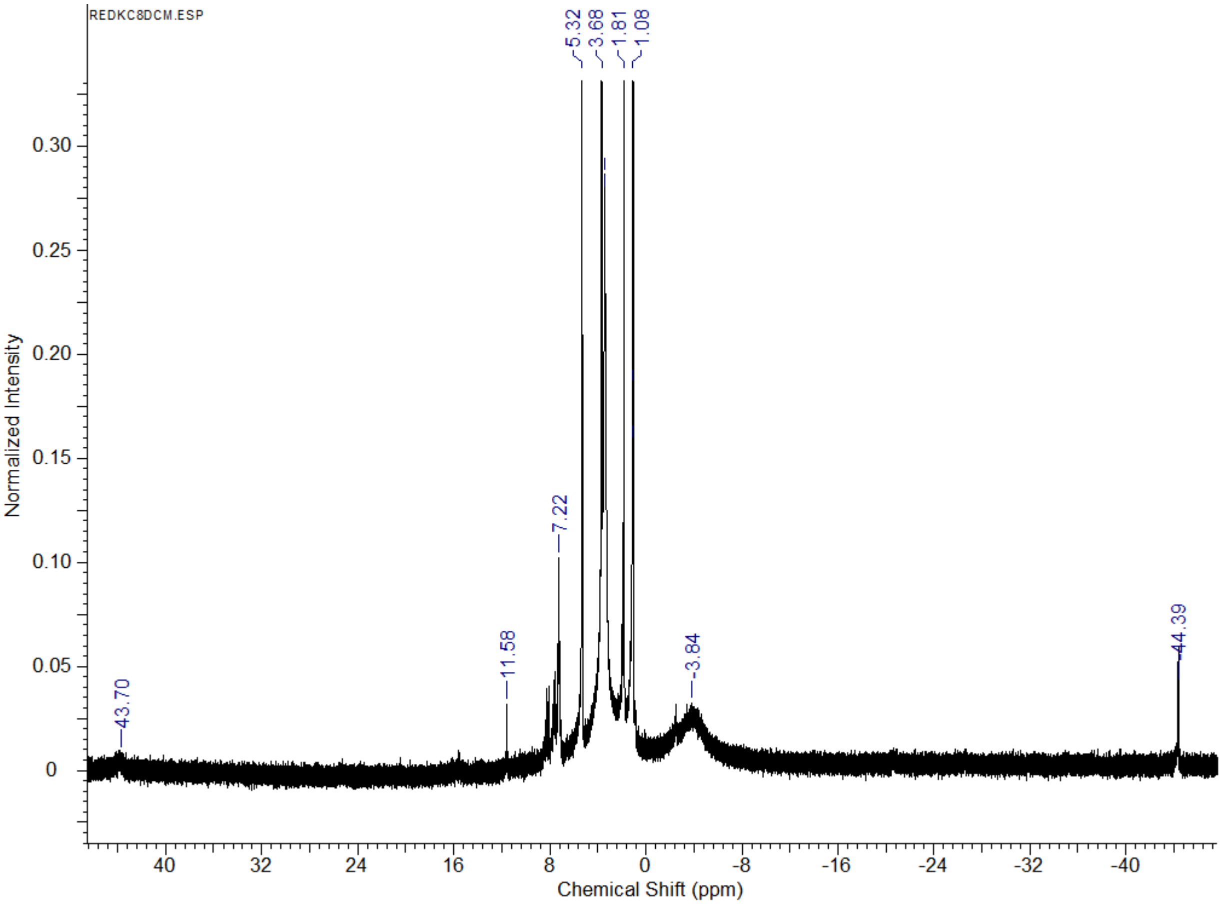

Figure S4. ^{1}H NMR spectrum (CD_2Cl_2) of [Co(OR)$_2$(CPh$_2$)][K(18-crown-6)].

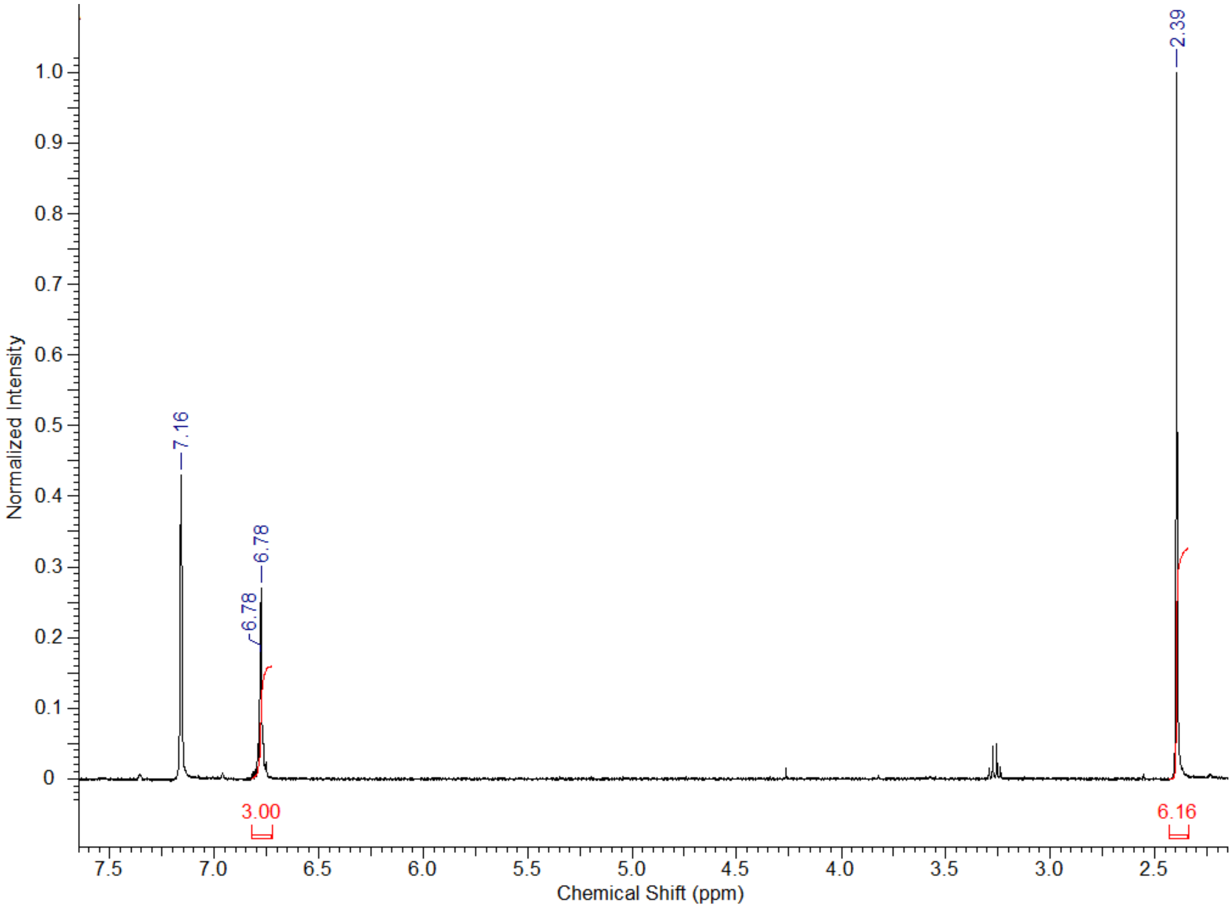

Figure S5. ^{1}H NMR spectrum of $Co_2(CN(2,6\text{-}Me_2C_6H_3))_8$ (**5**).

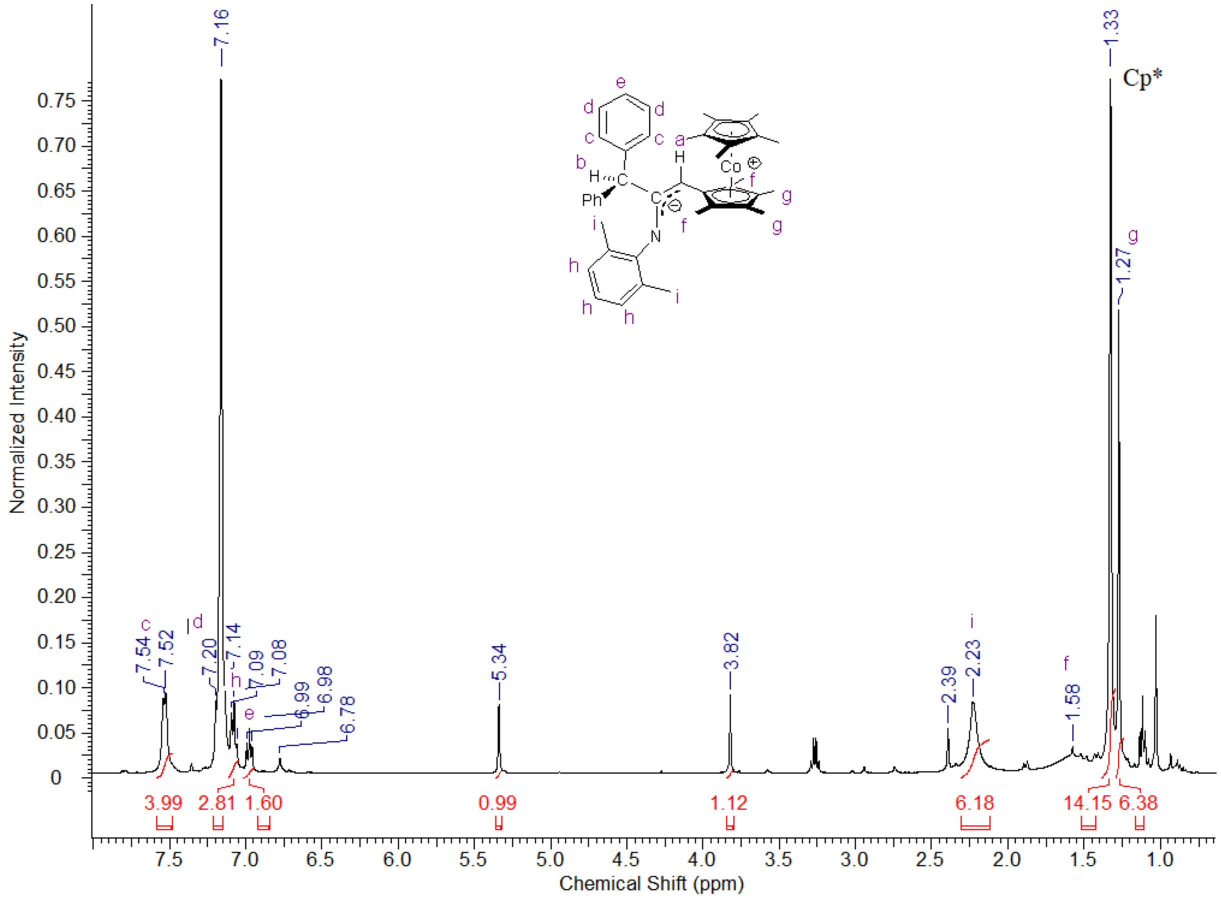

Figure S6. ^{1}H NMR spectrum of **6**.

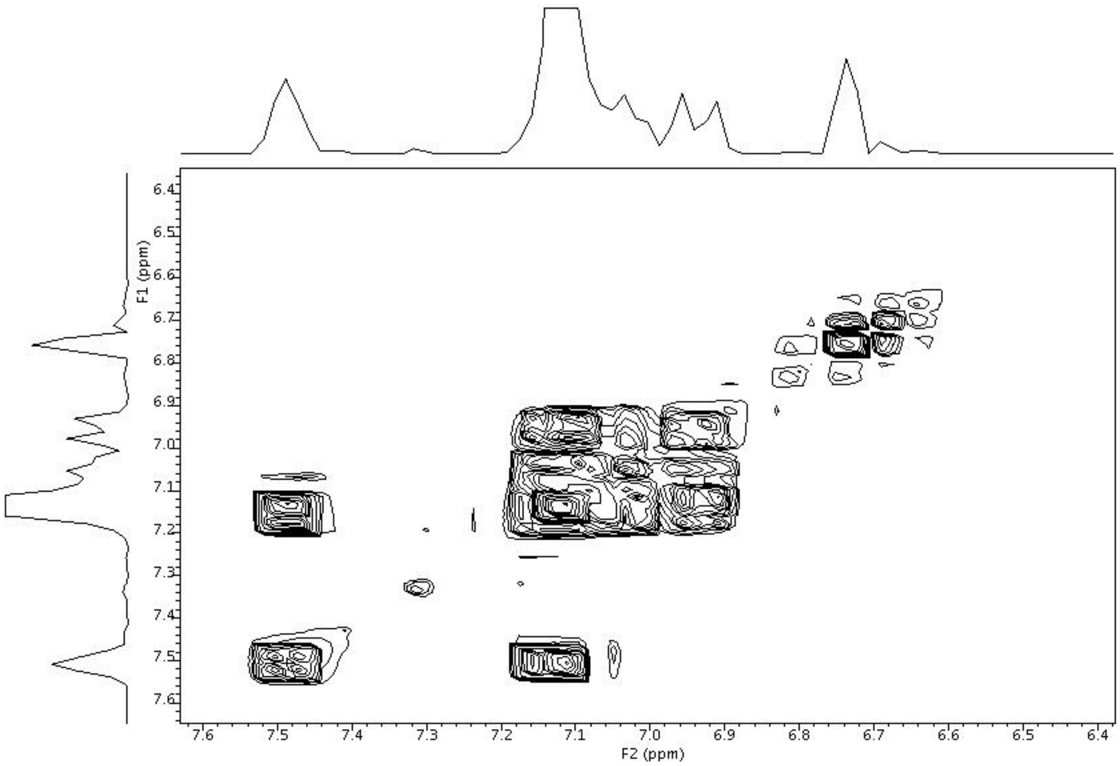

Figure S7. ^{1}H-^{1}H COSY NMR spectrum of **6**.

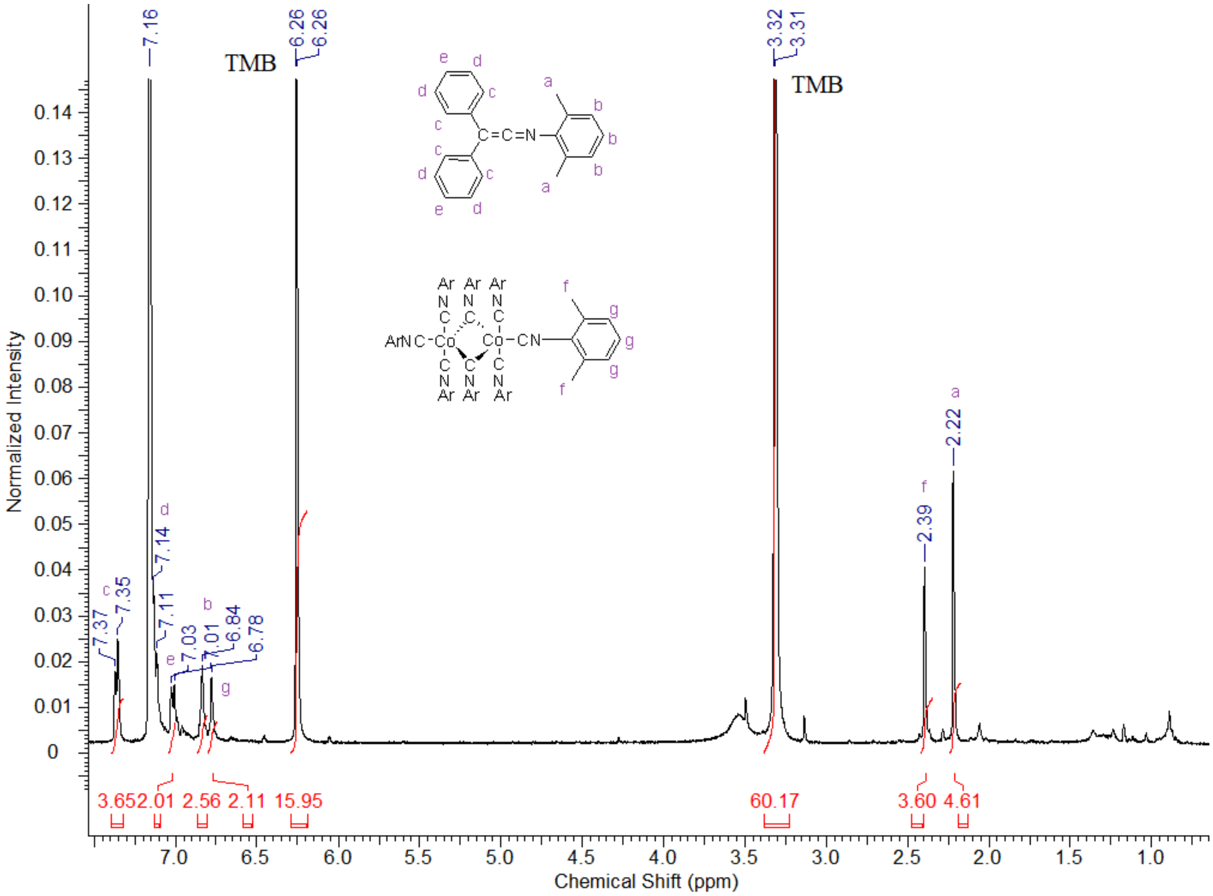

Figure S8. ^{1}H NMR spectrum of the reaction between [Co(OR)$_2$(CPh$_2$)][K(18-crown-6)] and CN-2,6-Me$_2$C$_6$H$_3$ to form Ph$_2$C=C=N-(2,6-Me$_2$C$_6$H$_3$) and Co$_2$(CN-2,6-Me$_2$C$_6$H$_3$)$_8$.

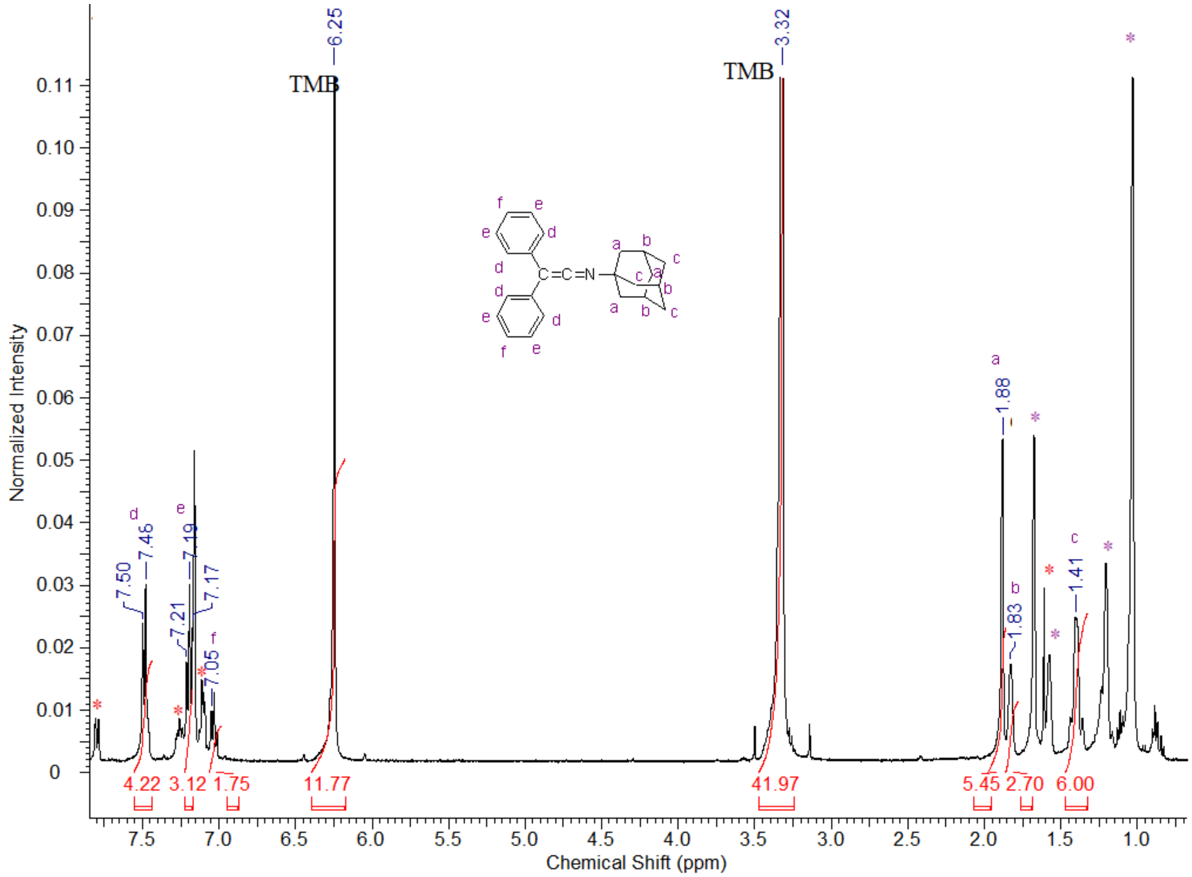

Figure S9. ^{1}H NMR spectrum of the reaction between [Co(OR)$_2$(CPh$_2$)][CoCp*$_2$] and CNAd to form ketenimine. Purple asterisks denote free isocyanide and red asterisks denote HOR.

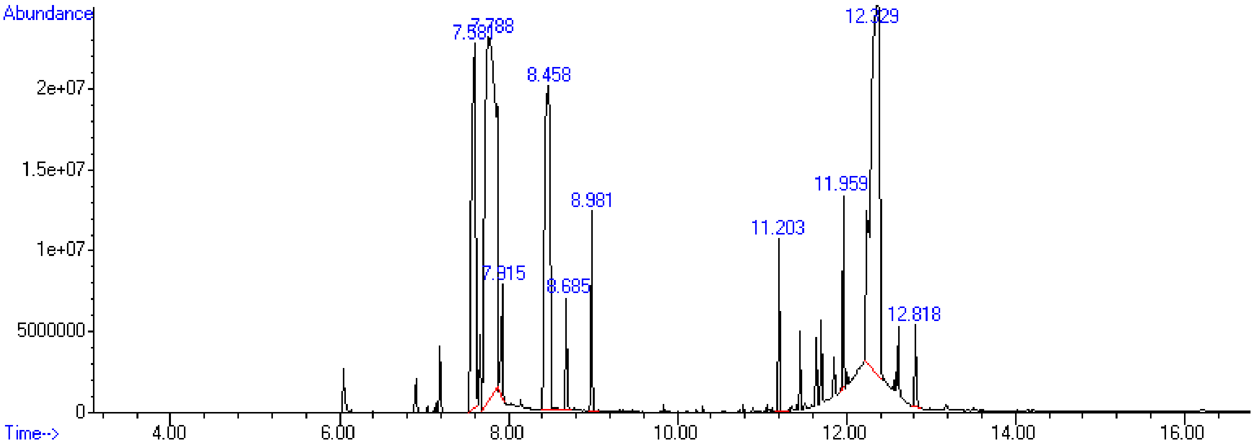

Figure S10. GC-MS of the filtered (silica plug) products mixture of the reaction between **3** and CNAd showing formation ketenimine (MS in **Figure S9** below).

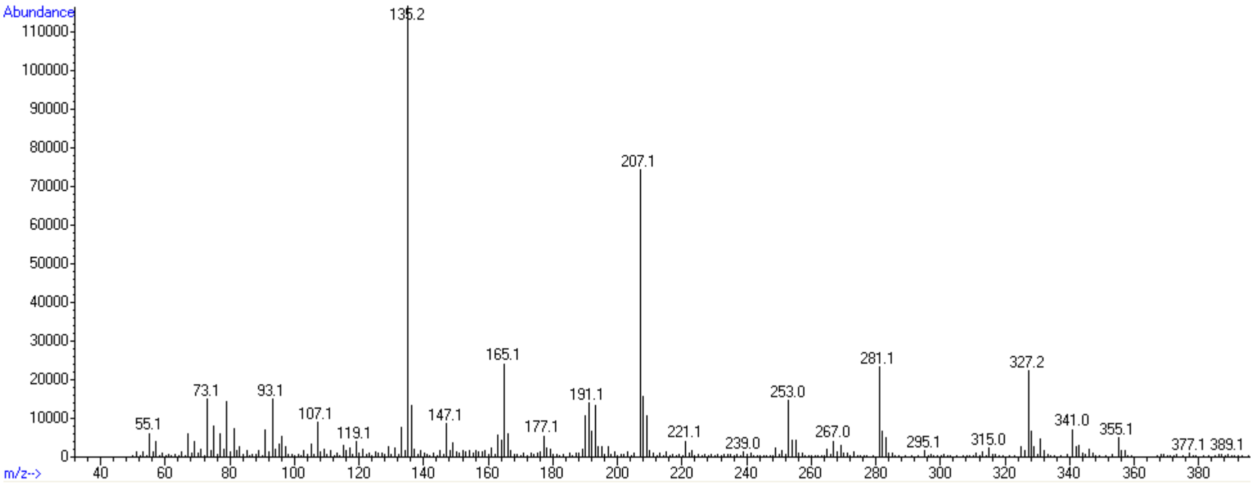

Figure S11. MS of the product eluting at 12.239 consistent with $Ph_2C{=}C{=}NAd$ (calculate mass 327).

5. IR spectra

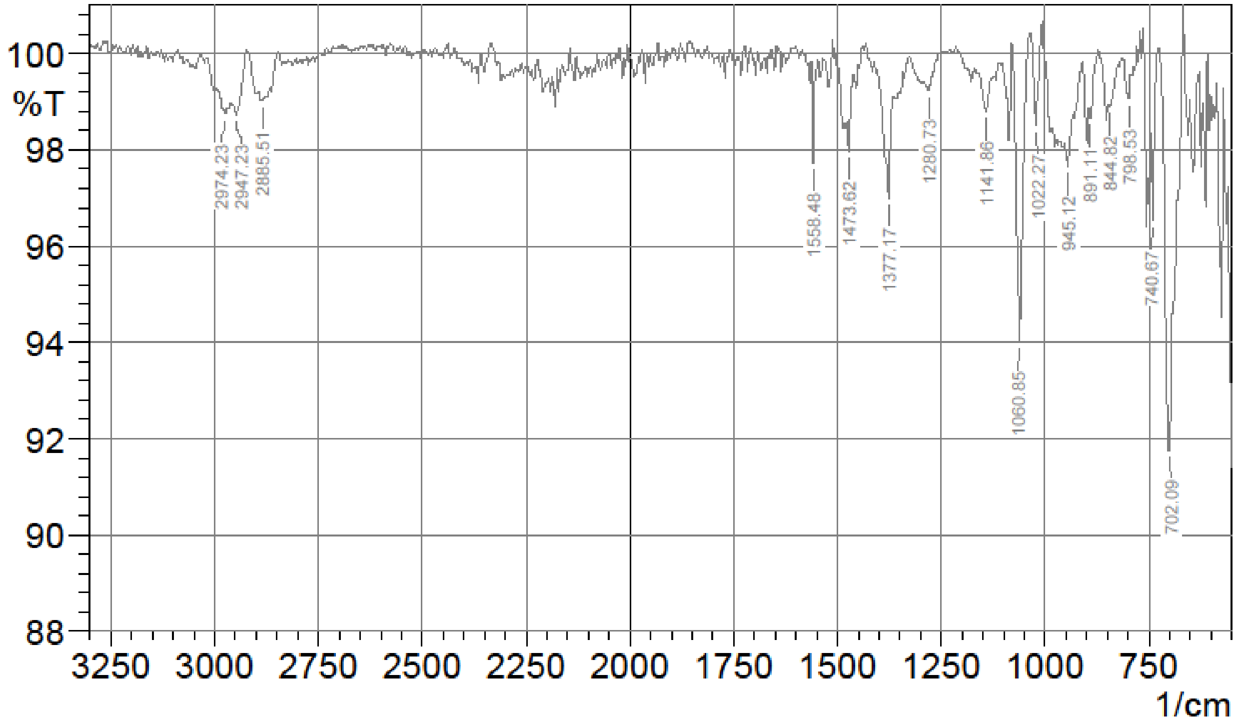

Figure S12. IR spectrum of $[Co(OR_2)(CPh_2)][CoCp^*_2]$ (**3**).

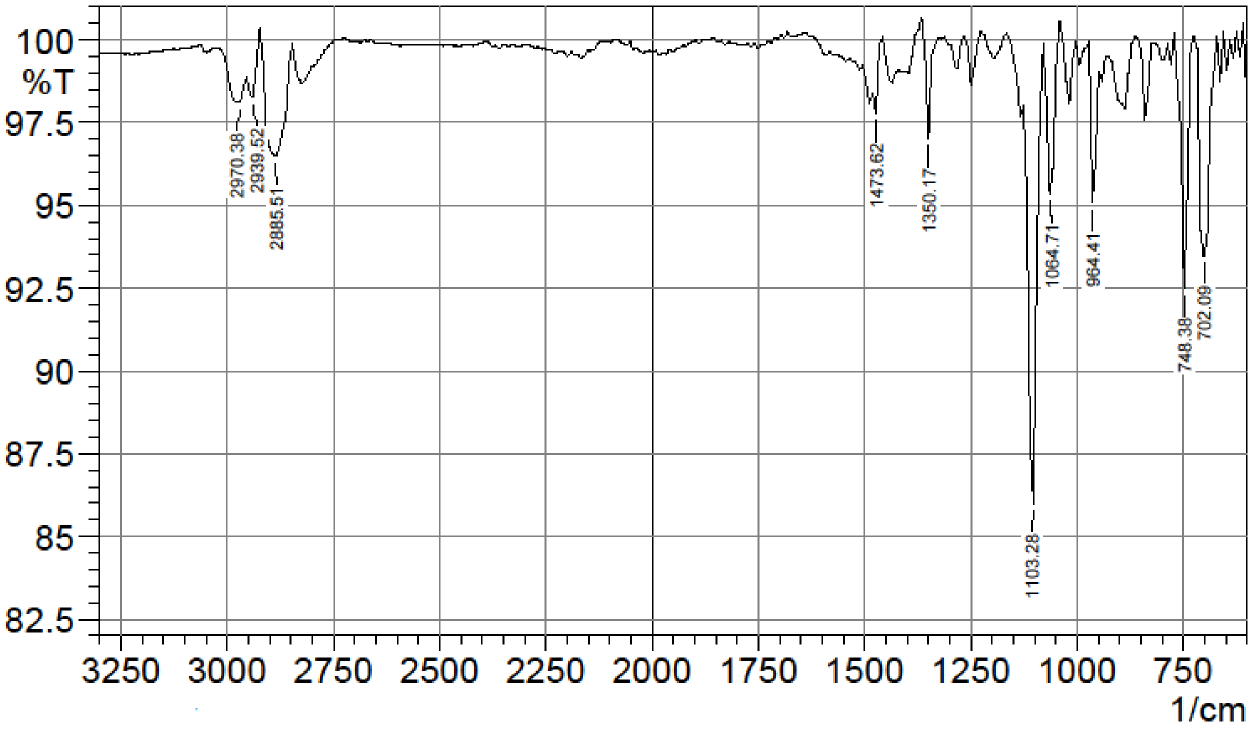

Figure S13. IR spectrum of [Co(OR)$_2$(CPh$_2$)][K(18-crown-6)] (**4**).

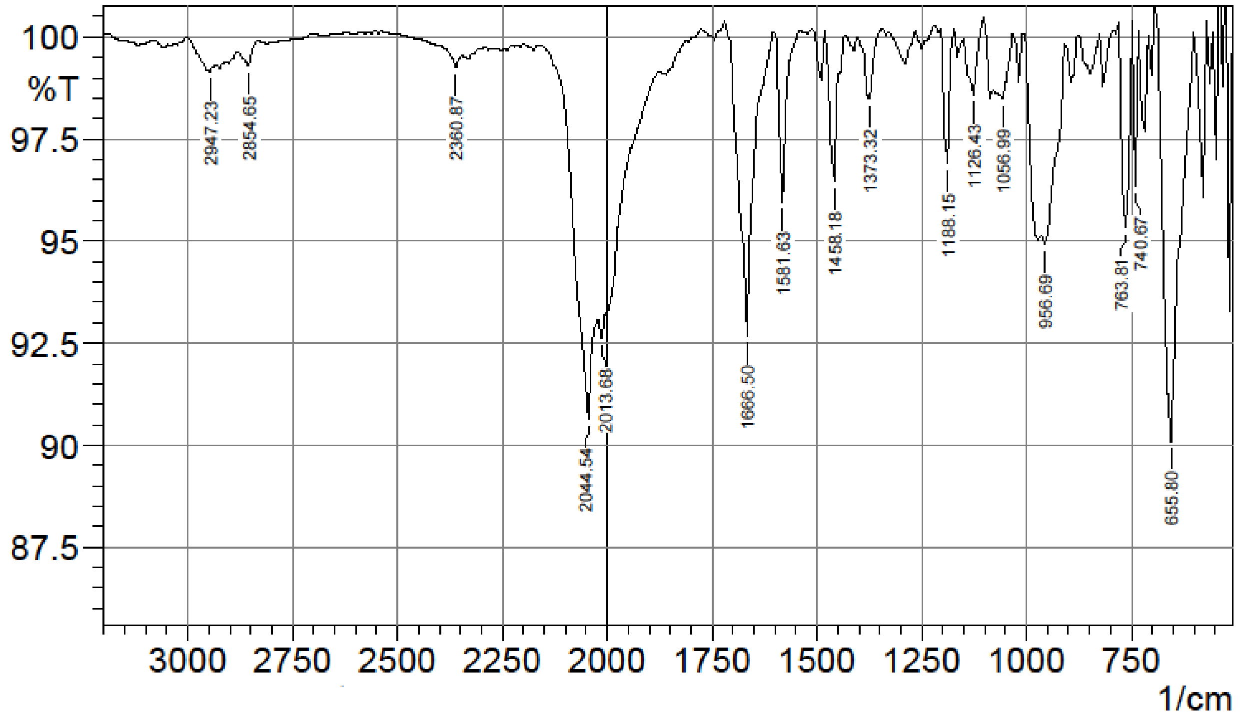

Figure S14. IR spectrum of **6**.

6. UV-vis spectra

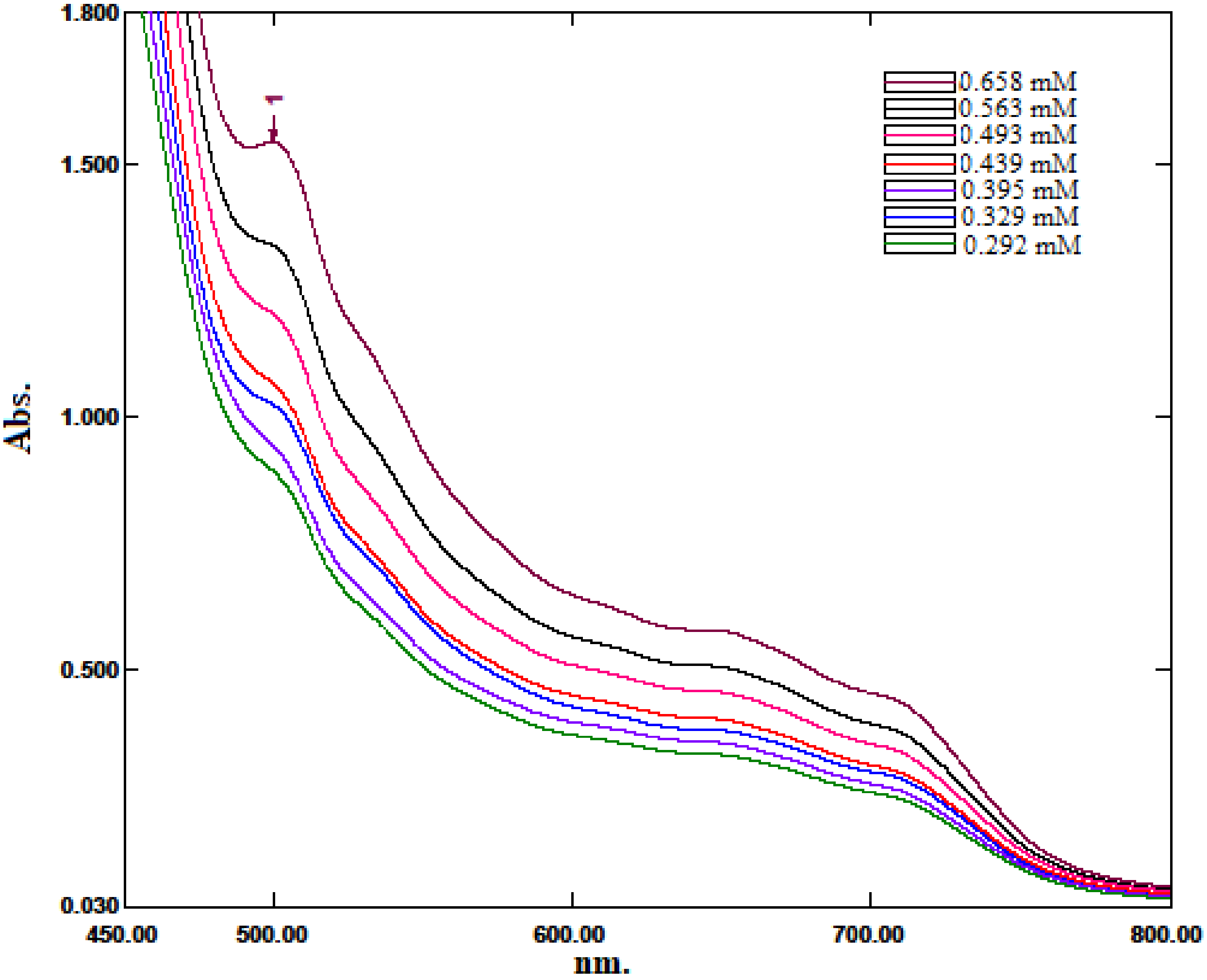

Figure S15. UV-Vis spectrum of $[Co(OR)_2(CPh_2)][CoCp^*_2]$ (**3**).

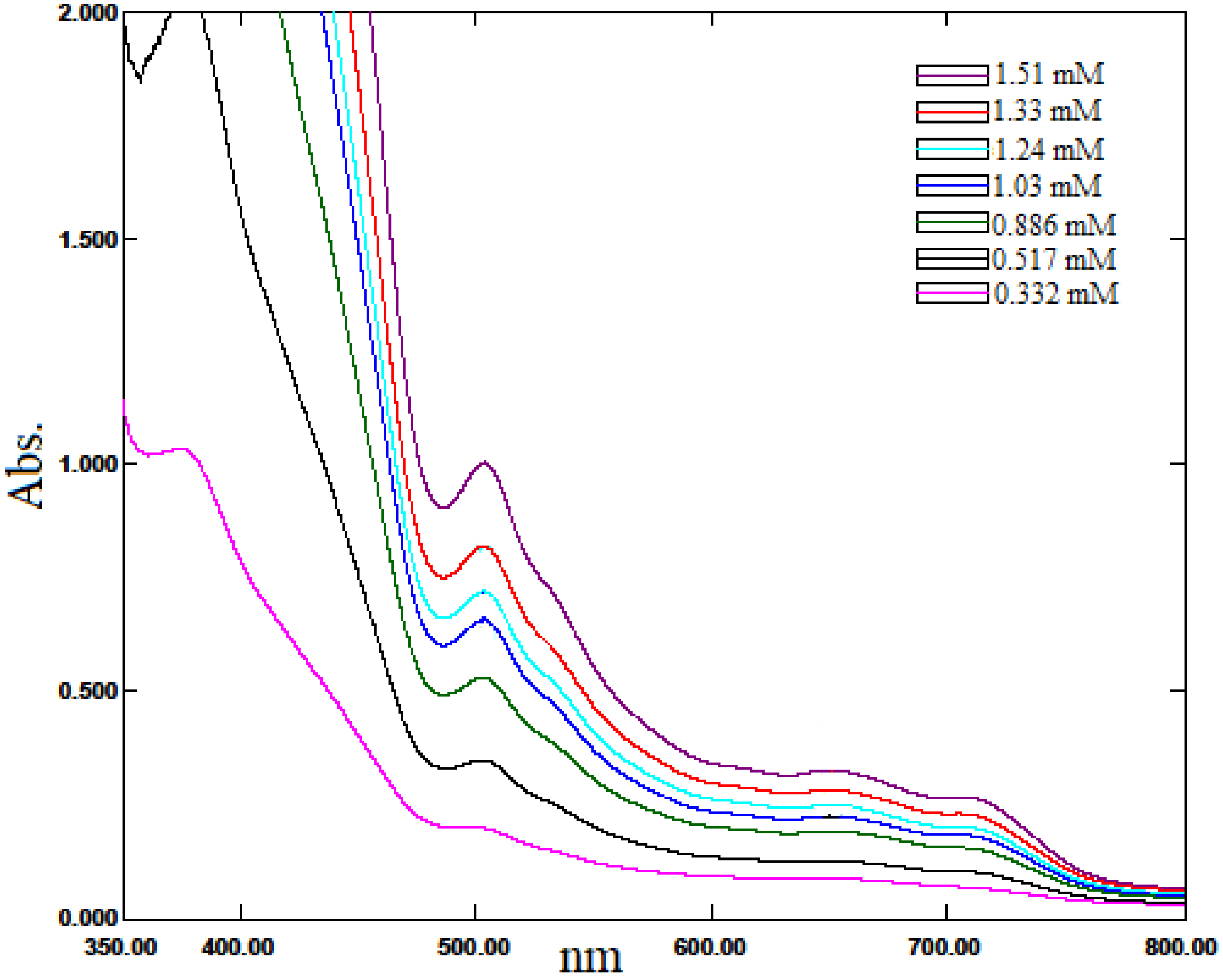

Figure S16. UV-Vis spectrum of [Co(OR)$_2$(CPh$_2$)][K(18-crown-6)] (**4**).

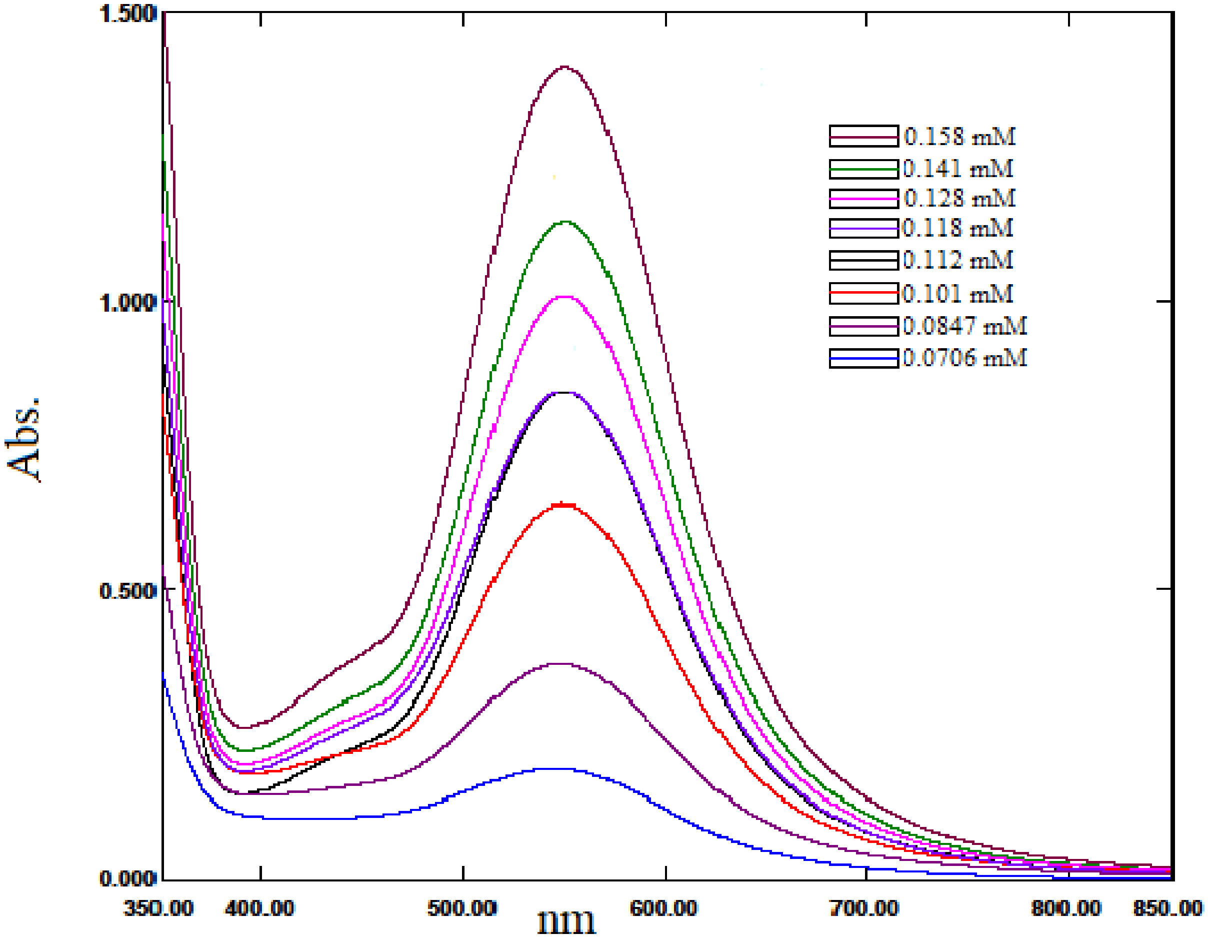

Figure S17. UV-Vis spectrum of **6.**

7. SQUID measurements

Solid state magnetic measurements were conducted on a Quantum Design Magnetic Properties Measurement System (QD-MPMS3). Data were collected under zero-field cooled (zfc) conditions from 2-300 K in an applied field of 1000 Oe. Observed magnetic moments were determined from Curie-Weiss fits. For the susceptibility of **2**, an appreciable temperature independent contribution was observed. For this reason, a modified Curie-Weiss law, $\chi = \chi_o + C/(T - \theta)$ where χ_o is the temperature independent term, was used. The raw data were corrected for sample shape and radial offset effects using the method reported by Morrison and zur Loye.[7]

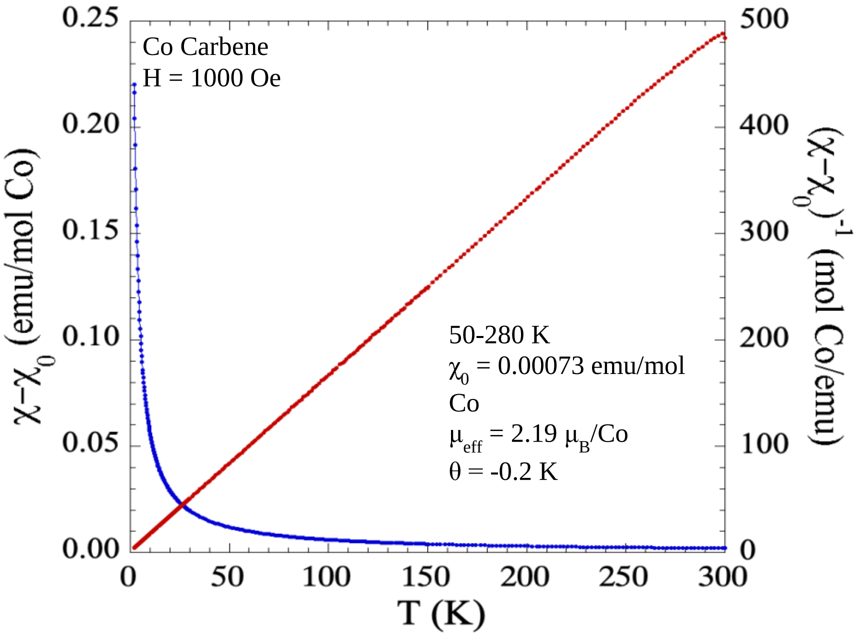

Figure S18. Magnetic susceptibility and inverse susceptibility for **2**.

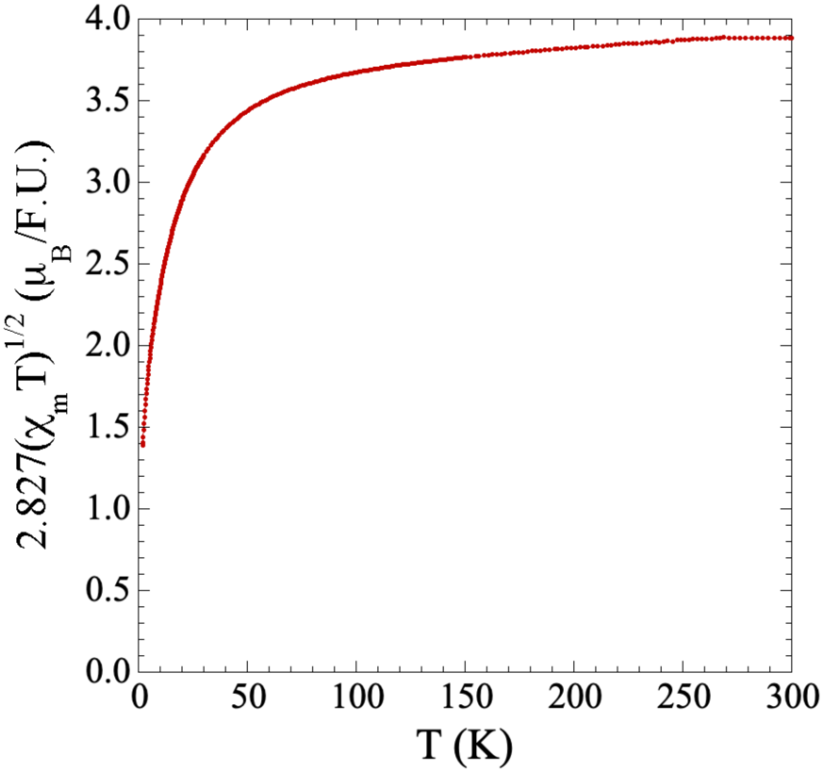

Figure S19. Magnetic moment of **3** estimated as $2.827(\chi_M T)^{1/2}$.

Fitting of ChiT for 3. The temperature dependent magnetic data for **3** were fit to Equation 3, which represents the magnetism of a "dimer" system with coupled S = 1/2 and S = 3/2 spins.

$$\mathcal{X}_M = \frac{Ng^2\mu_B^2}{3k_B(T-\theta)} \frac{6+30e^{\frac{4J}{k_BT}}}{3+5e^{\frac{4J}{k_BT}}} \tag{3}$$

In this equation, N stands for Avogadro's number, g for the Landé g-value, k_B for the Boltzmann's constant, and J for the exchange coupling between the Co(II) and radical spins. Shown in Figure S20, several combinations of g, J, and θ can be used to fit the experimental ChiT data. As expected based on the system following the Curie-Weiss law for T > 10 K, the data can be fit with g = 1.9, θ = -20.9 K, and J/k_B = 0, Figure S20 (left), which is equivalent to the Curie-Weiss fit. As DFT data indicates antiferromagnetic coupling between the Co(II) and radical spins, J/k_B = 0 K is not expected. The data can instead be fit with a small negative J/k_B ($J/k_B \leq -10$ K) and a less negative theta. A fit using g = 1.85, θ = -3 K, and J/k_B = -10 K is shown in Figure S20 (right). Fits with $J/k_B > -10$ K were not possible, indicating weak antiferromagnetic coupling between the spins within the dimer. Note that the Landé g-values less than 2 result from the observed moment, 4.03 μ_B/F.U., being less than the calculated moment for an uncoupled dimer, 4.24 μ_B/F.U. As the solution moment agrees well with the calculated moment, the slightly lower than expected SQUID moment is presumed to be due to the slight degradation of the sample during shipping.

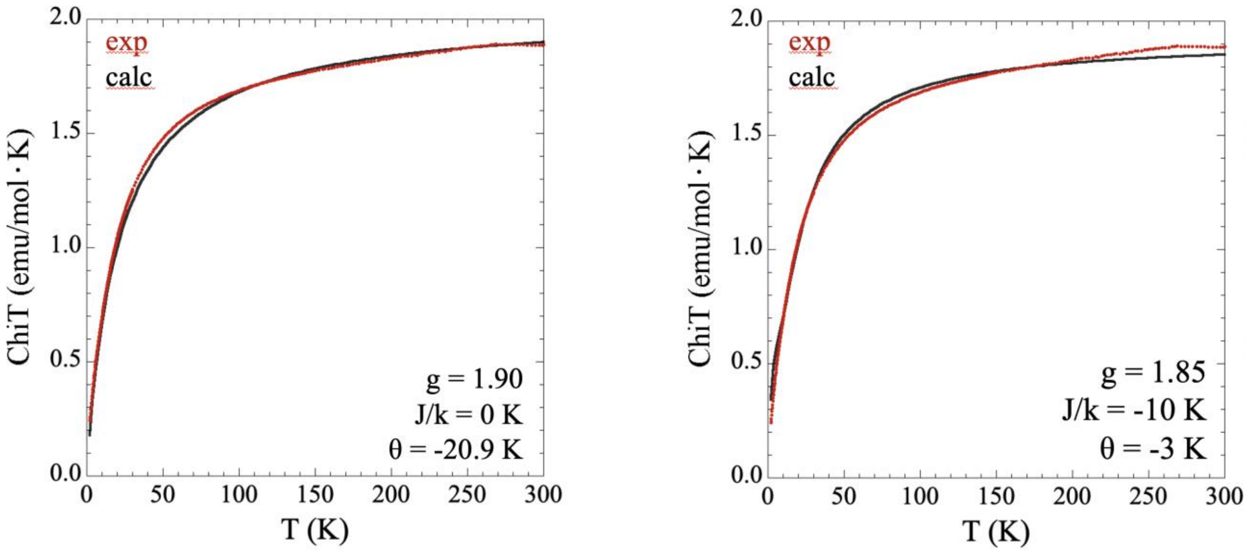

Figure S20. Two possible fits of the ChiT data for **3**.

8. Computational Data

Density functional theory calculations were carried out using Revision D01 of Gaussian 09.[8] Geometry optimizations were performed at the B3LYP/6-31G(d) level of theory.[9] All optimized structures were confirmed to have stable wavefunctions[10] and to be minima on the potential energy surface.[11] Cartesian coordinates may be found in the file titled "ReducedCarbene_OptimizedStructures.xyz", whereas frequencies and thermodynamics for each species may be found in Tables S4 and S5.

Two sets of states were optimized; a singlet and triplet whose initial guess wavefunctions correspond to low-spin Co(II) anti- or ferromagnetically coupled to carbene radical (**3' *S* = 0** and **3' *S* = 1**) and a triplet and quintet corresponding to high-spin Co(II) anti- or ferromagnetically coupled to carbene radical (**3' *S* = 1'** and **3' *S* = 2**). As evidenced by Table S3, the Mulliken spin analysis at the cobalt ion and carbene carbon for each of these states confirms these states though the higher energy triplet state has slightly more spin at Co and slightly less spin at C, suggesting more intermediate-spin Co(III) alkylidene character. The two lowest-energy states both demonstrate high-spin Co(II) character, consistent with the inferences from the crystallographic structures.

Table S3. Mulliken spins on the Co and $C_{carbene}$ atoms, as well as relative electronic and free energies (in kcal/mol).

	Co spin	**C spin**	**ΔE(SCF)**	**ΔG(gas)**
3' (*S* = 0)	1.06	–0.70	16.96	16.11
3' (*S* = 1)	1.40	0.26	15.23	14.55
3' (*S* = 1')	2.67	–0.63	0.00	0.00
3' (*S* = 2)	2.71	0.65	4.52	0.97

Because the quintet was so close in energy to the lowest energy state (**3' *S* = 1'**), a more detailed analysis of the electronic structure of **3' *S* = 2** (beyond Mulliken spins) was performed. As shown in Figure S20, the singly occupied molecular orbitals of this quintet state confirm the AF/F-coupled nature of these two lowest-energy states. We repeated the analysis of the Mulliken spins assuming this state is lowest in energy due to the nearly isoenergonic nature of these triplet/quintet states. Mulliken spin analysis of the $[Co(OR)_2]$ and $[CPh_2]$ fragments shows spins of 2.97 and 1.03, in contrast to 1.89 and –0.89 for **2**. Thus, consistent with the conclusions for the antiferromagnetic state presented in the paper, other than the spin flip from the AF- to F-coupled state, the magnitude of the spin at the carbene carbon only changes by ~0.1 whereas the spin at cobalt changes by ~1.1, consistent with metal-centered reduction.

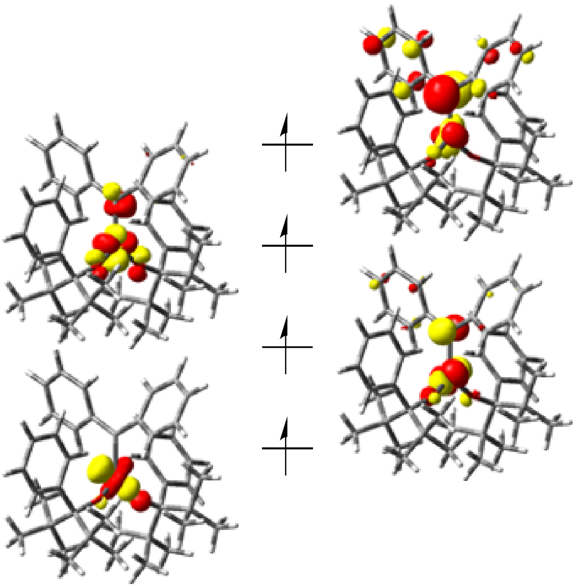

Figure S21. Corresponding orbitals (iso = 0.05 au) of **3’ S=2**.

Table S4. Harmonic frequencies (cm^{-1}) for the optimized species.

```
--------
3' (S=0)
--------
    6.5697     11.9039     20.9884
   27.5454     30.7284     35.0843
   43.9544     50.5611     53.9536
   55.3421     63.9911     68.1565
   68.6707     73.6773     84.9052
   88.1189     88.8255     92.0818
   99.8264    115.8513    120.1861
  125.0838    130.0122    164.3875
  179.4148    186.0601    207.5179
  211.7500    216.3747    223.2557
  233.3355    233.7602    237.2208
  248.6150    253.7240    256.8326
  259.9074    268.6625    275.3712
  278.3140    284.6316    288.8674
  290.3346    296.0609    298.5487
  303.5191    307.1848    310.9029
  320.4819    328.0916    331.5082
  333.0110    337.1695    339.8705
  340.9686    351.7724    357.3591
  362.2287    379.6447    391.1876
  397.0466    410.2970    417.8573
  419.9324    423.3925    426.2569
  429.0223    430.9896    431.2026
  432.2944    438.1942    441.2026
```

445.2463	446.8423	497.0755
511.1107	511.6736	561.3272
563.7855	564.1812	565.8127
570.3743	587.5436	629.5325
631.0884	635.7851	636.8137
657.0799	660.6971	669.3468
702.0359	707.0841	710.4635
720.0964	723.4811	724.1077
753.6944	755.9172	756.6541
766.8299	810.4468	813.2542
825.5560	828.7750	842.9947
855.3124	864.1477	867.7801
869.3129	889.6525	895.8661
896.2493	897.4381	903.2129
905.7423	918.9427	932.0025
935.7899	936.7404	937.4004
939.0630	940.1338	944.7782
948.9811	950.9326	953.3107
958.0411	963.5727	967.5323
968.9059	969.0208	972.2720
972.5977	973.6184	977.9677
987.5115	998.9376	1000.2936
1007.3366	1016.5391	1020.0333
1021.4914	1049.6543	1050.7766
1052.8624	1054.2438	1055.2993
1056.0735	1057.0181	1058.3921
1063.2716	1064.6643	1070.0026
1071.1461	1094.5090	1101.0624
1104.4219	1114.1549	1122.1055
1134.6022	1164.4869	1165.7438
1181.2539	1183.9597	1185.3392
1186.9110	1189.0528	1202.1371
1215.3626	1217.4486	1220.2018
1229.3444	1231.4109	1231.7136
1232.9894	1240.0887	1241.1085
1241.6423	1243.3328	1250.1024
1252.5645	1260.7558	1263.6188
1303.6719	1309.8511	1329.7408
1334.6355	1337.0582	1359.7980
1360.7479	1362.8362	1365.8094
1411.9019	1413.7517	1415.1669
1416.1247	1419.2469	1420.9205
1422.5429	1425.1106	1444.0401
1448.0287	1452.7943	1456.3267
1475.7910	1484.4963	1484.8403
1485.1451	1506.9612	1508.8888

```
 1510.2699   1511.1035   1517.0709
 1517.3172   1519.7633   1522.3496
 1523.7905   1524.2734   1525.9693
 1526.5848   1527.1750   1530.0755
 1532.0783   1534.0100   1534.3629
 1535.6358   1537.2761   1539.3296
 1540.9099   1544.7161   1549.3864
 1551.9547   1554.1912   1558.1820
 1559.9715   1565.4236   1591.7673
 1607.2974   1625.4735   1633.5036
 1634.2103   1637.6035   1655.2157
 1655.7241   3031.9438   3033.6041
 3033.6564   3034.8407   3035.7939
 3036.8785   3037.1229   3040.4297
 3045.0616   3046.2457   3048.3857
 3053.3285   3092.3021   3093.9527
 3096.8850   3101.5736   3108.1867
 3109.0567   3109.3036   3112.1440
 3113.2349   3116.1228   3133.2562
 3137.5825   3140.6803   3142.0463
 3144.6149   3145.4010   3146.7909
 3151.0916   3155.3659   3155.6192
 3156.2394   3157.6479   3158.3941
 3158.6864   3159.4166   3162.7301
 3166.2718   3169.2333   3174.2017
 3174.6747   3177.8345   3185.6384
 3187.0644   3188.4514   3190.0439
 3190.8305   3195.2746   3202.3514
 3204.0408   3207.2279   3239.2640
 3240.1289   3244.4010   3299.4078

--------
3' (S=1)
--------
    8.6942      11.7697      19.1899
   27.5271      33.5695      39.1850
   44.7979      48.9787      55.5682
   61.7143      63.0032      67.0528
   74.6835      77.2580      83.9659
   85.8882      90.2087      94.1944
  104.2587     116.1997     117.6148
  133.5922     137.9818     175.6680
  178.7928     190.0878     206.0897
  215.6375     221.7489     224.3895
  235.5830     237.3009     238.9565
  248.2701     251.8138     261.8029
```

```
 270.8075   273.6923   282.7623
 288.0306   290.8452   292.5833
 296.3302   299.1624   301.0961
 303.1252   305.5851   312.5185
 322.6984   328.8424   333.7003
 336.1623   337.4300   341.6563
 342.8219   355.6701   361.7981
 367.9036   385.8645   386.2914
 395.0881   407.5708   418.8809
 421.4640   425.2336   426.3672
 428.1482   431.0518   432.5442
 434.3158   438.9362   444.4275
 446.2491   448.4461   501.2806
 511.1586   513.0682   517.8124
 561.7402   563.7963   565.9897
 568.3566   588.0090   630.6356
 631.7201   635.8729   636.0727
 659.3226   662.3795   680.3741
 701.1594   707.8167   716.8177
 718.9807   722.6515   728.7050
 748.4641   750.7925   754.2934
 756.4435   810.4331   813.2102
 826.4434   828.9232   839.8769
 850.0018   861.0518   864.6195
 880.6086   883.8075   894.8383
 896.4039   897.5581   904.0453
 905.2509   929.8311   934.0538
 935.6150   936.4965   938.7655
 939.6107   940.7789   946.4809
 950.0075   951.5201   952.3596
 953.3195   962.2398   964.6274
 967.1058   968.4653   971.6770
 973.2804   975.0365   975.4284
 977.6126   991.8529   997.1298
1003.1697  1004.6354  1018.3479
1019.4926  1048.8739  1051.8215
1052.9863  1053.3566  1054.4056
1057.0604  1057.7374  1058.3235
1063.2417  1065.1918  1070.3174
1071.7094  1088.3534  1093.9417
1104.2358  1114.2048  1119.4249
1124.0147  1166.7808  1167.7884
1181.8415  1182.6985  1185.7404
1187.3662  1200.6867  1207.7865
1215.2598  1217.6423  1226.1957
1227.6150  1230.3247  1231.9492
```

```
 1232.8956   1238.8643   1240.9573
 1242.7482   1243.3673   1248.7510
 1250.4210   1260.1723   1262.8468
 1303.3607   1310.4551   1329.2003
 1335.3525   1335.6815   1360.1148
 1361.6214   1365.1544   1368.4932
 1413.8222   1415.9218   1416.4897
 1419.8226   1422.1407   1422.5369
 1423.1466   1426.3663   1446.4976
 1450.2636   1454.3285   1457.8910
 1476.3494   1484.1792   1485.0752
 1487.1029   1508.1047   1509.2651
 1510.2421   1511.9279   1519.2596
 1520.6327   1520.9813   1522.2321
 1523.4114   1524.7934   1525.2544
 1526.2057   1527.7447   1529.5439
 1532.5125   1533.8926   1535.2134
 1535.8311   1538.4666   1540.8585
 1544.4654   1545.6048   1547.5242
 1553.0937   1554.9042   1557.3750
 1559.9327   1564.8237   1593.3227
 1599.7349   1628.1224   1634.2768
 1634.4491   1643.9811   1656.0053
 1656.2114   3034.4771   3035.0858
 3035.5414   3036.5549   3037.7740
 3038.3559   3040.1216   3042.9944
 3047.0104   3047.1518   3051.1869
 3055.7926   3093.8854   3095.0186
 3099.3121   3100.6977   3111.4073
 3111.8066   3113.6668   3114.0103
 3117.0392   3119.1613   3137.4510
 3141.5352   3142.2822   3143.2680
 3147.2847   3147.9630   3149.6046
 3152.5654   3153.8028   3154.7668
 3156.0927   3157.4702   3158.1520
 3159.1830   3159.2828   3161.8854
 3162.8098   3163.1649   3175.4089
 3176.5344   3178.9079   3185.2940
 3186.0159   3186.8344   3191.2436
 3193.1116   3198.5868   3201.3169
 3203.6475   3205.1301   3242.5113
 3244.3965   3254.9773   3298.4195

--------
3' (S=1’)
--------
```

```
 15.6456     20.7322     22.9462
 29.0569     34.9960     38.4349
 45.1812     49.4937     52.9199
 54.1931     59.6791     65.5857
 69.3520     72.2032     82.4206
 88.8979     93.1001     94.7284
100.4087    112.0016    121.9399
125.7933    137.4377    164.8260
181.9786    190.7073    203.4208
215.4195    219.6091    227.2827
233.1934    245.9027    251.6680
253.2133    257.3327    261.4099
265.9029    272.4299    276.3203
281.1477    288.8475    292.0274
296.7241    297.9716    301.5315
303.2596    306.9360    312.8897
314.9398    328.6063    331.1361
335.7511    339.3895    345.5404
349.1714    362.1625    370.3802
376.8878    381.5961    389.0597
393.3528    404.8175    417.1508
420.5239    426.6316    427.5668
429.7367    433.2707    434.9844
437.2855    438.4486    444.0567
448.0996    454.6701    498.5997
514.4096    517.2284    562.9257
564.3372    568.4404    569.1926
573.1542    587.8377    630.3481
631.1516    635.7563    635.9561
650.4107    656.9431    669.5480
703.2139    704.7712    711.4393
712.5447    720.9827    724.2608
756.1819    756.4229    759.3957
771.5895    812.5183    813.5428
827.0893    828.5544    849.6233
857.8581    864.5911    865.0709
866.6114    890.5160    892.5281
894.2515    906.2111    908.7282
909.7433    920.1172    933.6279
933.8445    938.7861    939.2568
941.0069    941.3608    947.2200
950.6561    953.4622    954.1091
962.7352    966.0864    967.4360
968.4538    970.3233    974.5611
975.9196    984.7686    986.9122
994.5822    994.7129   1003.6532
```

1005.8976 1006.1027 1016.9032
1018.0651 1047.4470 1052.7837
1053.6175 1054.0618 1055.0679
1055.9574 1057.4425 1057.7325
1061.7951 1065.2451 1069.7735
1072.0235 1091.1411 1098.3941
1104.8264 1114.2489 1119.8330
1131.4896 1159.2550 1160.8584
1180.1483 1183.1851 1183.9570
1184.4652 1186.6509 1202.9444
1212.0921 1216.6966 1219.0175
1227.7868 1229.3852 1231.0873
1233.2137 1239.6925 1241.0891
1242.5551 1243.4739 1249.5697
1252.0142 1260.4112 1260.9557
1295.3276 1309.6728 1330.0320
1332.0529 1335.2548 1356.5268
1359.8184 1362.9017 1365.7930
1412.7444 1414.6925 1417.1470
1418.2973 1419.6503 1421.5939
1425.1748 1427.5431 1447.8151
1447.9657 1455.3131 1456.5891
1477.1113 1483.4924 1484.1537
1485.6805 1506.9290 1508.5182
1514.1557 1516.4563 1519.2965
1520.5386 1521.7353 1523.2947
1523.5935 1524.8654 1525.7570
1528.0353 1529.6724 1530.8048
1534.0230 1534.8766 1536.3103
1536.8962 1539.9434 1541.6233
1545.7054 1546.7579 1550.1410
1553.4276 1555.9428 1556.7405
1561.2193 1567.4434 1601.2728
1606.5785 1628.8538 1632.4838
1633.3608 1638.4499 1654.3486
1654.9597 3030.5415 3033.3354
3033.7359 3036.7898 3038.1753
3038.4939 3039.8680 3040.4500
3045.0354 3048.1669 3050.2218
3051.5427 3094.4953 3096.7968
3098.3475 3098.8475 3106.4832
3109.1585 3109.3795 3109.6518
3111.9889 3114.8223 3123.3067
3137.0089 3140.3982 3142.7543
3145.4489 3148.1398 3148.8957
3150.6000 3152.6690 3156.6255

```
 3156.8532   3157.6052   3157.7733
 3157.8963   3168.5310   3168.7269
 3169.3055   3170.1630   3172.5057
 3174.8899   3185.2045   3185.9182
 3186.6479   3186.9964   3188.9842
 3190.9867   3195.3001   3196.5482
 3199.3488   3204.8164   3243.3621
 3247.1433   3250.1460   3266.8278

--------
3' (S=2)
--------
    6.5817     10.9882     18.7119
   23.2972     25.3922     32.8414
   36.1832     40.9317     44.2074
   48.3081     55.7590     60.8221
   62.9446     69.0819     72.3750
   81.0692     81.2822     86.4431
   97.1651    111.3832    112.5719
  116.1996    139.8326    150.8969
  160.5557    175.4653    192.3937
  204.7132    211.1588    213.9551
  223.4442    234.2554    235.1169
  249.2785    252.7100    255.1627
  258.7670    264.8469    273.3819
  276.7447    287.4404    288.3782
  292.6223    295.7838    300.2089
  301.6544    307.9462    313.1233
  315.2007    330.1412    333.5095
  335.7556    338.4434    342.2309
  344.0409    356.9228    364.4678
  368.4510    371.5383    384.4631
  398.3162    409.0608    411.8630
  413.3935    420.7896    426.9416
  429.2048    430.2412    432.4169
  434.0624    438.8457    439.5310
  446.4468    446.7650    494.5758
  511.1633    513.2628    562.2589
  562.9720    563.8933    565.5636
  568.6243    586.7140    629.4261
  630.1958    635.7977    636.1364
  657.0370    659.6580    665.7977
  701.4255    708.9216    710.6410
  721.4873    723.1186    724.4490
  755.0807    755.8999    756.7865
  767.3168    810.5147    813.9117
```

824.6110 827.0459 841.0847
852.5403 863.8894 865.5288
867.2260 888.8593 894.5280
895.1875 897.7570 904.9014
908.4760 912.7432 934.3144
935.8453 936.9701 937.2471
939.5229 941.5277 948.6985
951.2004 954.3224 955.4213
957.8568 964.6560 965.6162
967.3151 971.3217 975.5129
976.0056 976.7207 980.5892
983.0118 999.1169 1002.7029
1003.3061 1008.3872 1018.3837
1019.6355 1050.5985 1051.9184
1053.0727 1054.1569 1055.6727
1057.1158 1057.5299 1058.0842
1063.3589 1065.7816 1069.7800
1071.2281 1098.7195 1103.5824
1105.6187 1115.0470 1126.0253
1142.9508 1160.4406 1163.4022
1181.2176 1182.7425 1185.6068
1186.5635 1193.7805 1200.1871
1215.2866 1216.3925 1222.6097
1229.5606 1230.9012 1232.4194
1233.0065 1240.3064 1241.2594
1241.9042 1243.0560 1250.7909
1251.0362 1260.5856 1261.6169
1303.3402 1307.4665 1327.0261
1334.4791 1334.7066 1359.1210
1360.2207 1361.6480 1365.4292
1410.8492 1414.0100 1415.3231
1417.4673 1419.8879 1420.7095
1422.2771 1424.6009 1445.4383
1448.2776 1453.0116 1456.4790
1474.9100 1483.5109 1484.1462
1484.3870 1507.1241 1508.0659
1510.2790 1511.3087 1514.2069
1518.1077 1520.5472 1520.5755
1521.6919 1522.5060 1523.7503
1526.1350 1527.4985 1529.7161
1533.3279 1534.2326 1535.1959
1535.9876 1538.6631 1540.1986
1543.0918 1543.3001 1549.5379
1552.1274 1555.1269 1557.4066
1562.2873 1564.8822 1592.3324
1599.6691 1621.9443 1633.2197

1633.3211 1634.8925 1655.0254
1655.4126 3032.2889 3033.5631
3034.4021 3034.5420 3035.1512
3037.0349 3039.5845 3041.6220
3045.7559 3046.5822 3050.8102
3053.7663 3093.1736 3094.8825
3097.2724 3098.2615 3105.5798
3108.4979 3112.5879 3113.7449
3113.9900 3118.0136 3136.0033
3138.5643 3138.9585 3140.6659
3143.1404 3146.9959 3150.6277
3152.4173 3154.3690 3155.8691
3156.6969 3158.3359 3158.8530
3160.0606 3160.5390 3164.5298
3165.9843 3166.6554 3174.6940
3174.7661 3175.9498 3180.7843
3185.0085 3190.5307 3190.5474
3190.9013 3191.0318 3194.6354
3200.7540 3206.7321 3242.6177
3243.6089 3248.3363 3270.8542

Table S5. Energies (E_h) for the optimized species.

Species	E(SCF)	H(gas)	G(gas)
3’ (*S* = 0)	-3205.394009	-3204.460570	-3204.593084
3’ (*S* = 1)	-3205.396773	-3204.463075	-3204.595569
3’ (*S* = 1’)	-3205.421043	-3204.487265	-3204.618762
3’ (*S* = 2)	-3205.413833	-3204.480576	-3204.617222

9. Scheme Demonstrating Quinoidial Distortion in the Structures of 2 and 3.

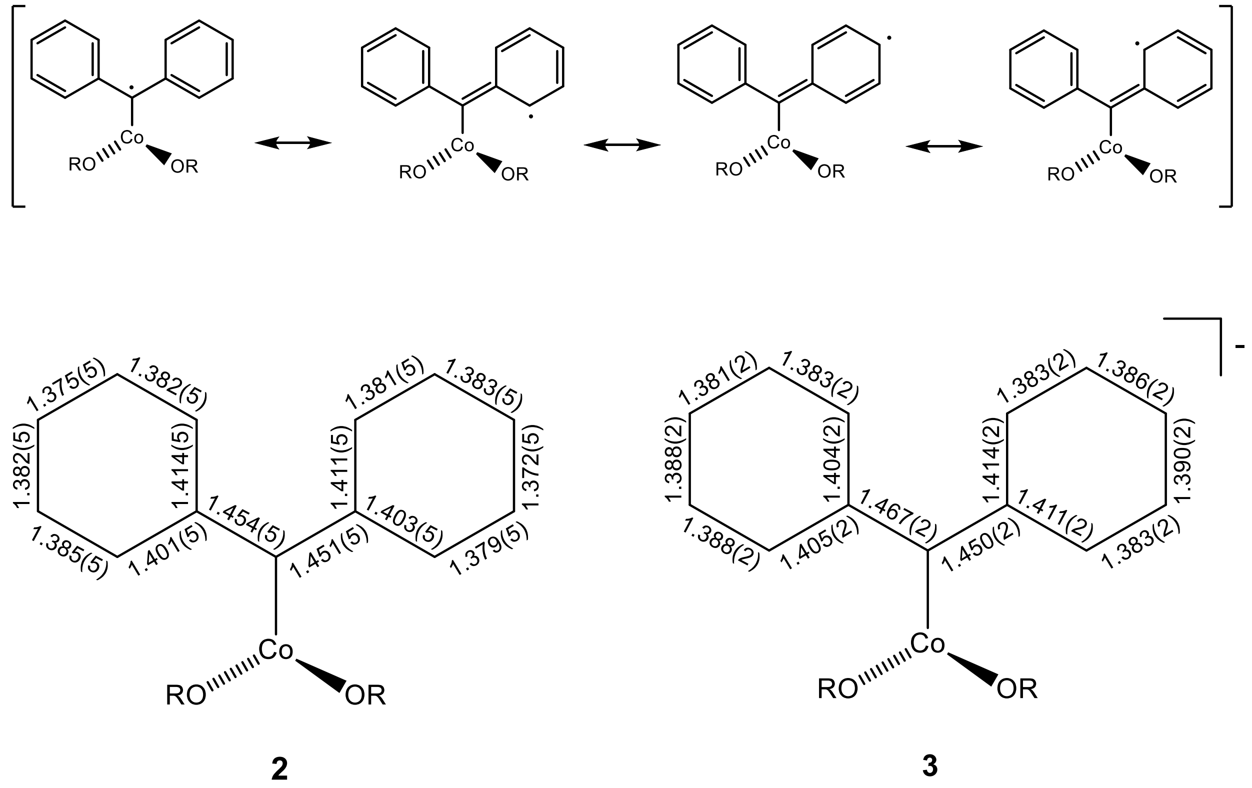

Figure S22. Top: Resonances structures (shown for only one of the two rings) demonstrating radical delocalization into the aryl rings of the carbene. Bottom: Carbene aryl bond distances in the structures of **2** and **3** consistent with quinoidal distortion.

10. References

---

1. J. A. Bellow, M. Yousif, D. Fang, E. G. Kratz, G. A. Cisneros and S. Groysman, *Inorg. Chem.* 2015, **54**, 5624- 5633.

2. J. A. Bellow, S. A. Stoian, J. Van Tol, A. Ozarowski, R. L. Lord and S. Groysman, *J. Am. Chem. Soc.* 2016, **138**, 5531-5534.

3. M. Hu, J. Rong, W. Miao, C. Ni, Y. Han and J. Hu, *Org. Lett.* 2014, **16**, 2030-2033.

4. (a) Y. Yamamoto and H. Yamazaki, *Inorg. Chem*. 1978, **17**, 3111-3114. (b) P. A. Leach, S. J. Geib, S. J. Corella, G. F. Garnock and N. J. Cooper, *J. Am. Chem. Soc*. 1994, **116**, 8566-8574.

5. A. Grass, N. S. Dewey, R. L. Lord and S. Groysman, *Organometallics* 2019, **38**, 962−972.

6. D. F. Evans, *J. Chem. Soc.*, 1959, 2003-2005.

7. G. Morrison and H.-C. zur Loye, *J. Solid State Chem*. 2015, **221**, 334-337.

8. Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

9. (a) S. H. Vosko, L. Wilk and M. Nusair, *Can. J. Phys.* 1980, **58**, 1200. (b) C. Lee, W. Yang and R.G. Parr, *Phys. Rev. B* 1988, **37**, 785. (c) A. D. Becke, *J. Chem. Phys.* 1993, **98**, 5648. (d) P.J. Stephens, F. J. Devlin, C. F. Chabalowski and M. J. Frisch, *J. Phys. Chem.* 1994, **98**, 11623.

10. (a) H. B. Schlegel and J. J. McDouall, in *Computational Advances in Organic Chemistry*; Oeretir, C; Csizmadia, I. G., Eds.; Kluwer Academic: Amsterdam, The Netherlands, 1991. (b) R. Bauernschmitt and R. Ahlrichs, *J. Chem. Phys.* 1996, **104**, 9047.

11. H. B. Schlegel, *WIREs Comput. Mol. Sci.* 2011, **1**, 790.