Electronic Supplementary Information for:

Rapid and ordered carbonylation and oxygenation of a cobalt(II) methyl complex

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Experimental

General experimental methods

All reactions were performed using standard Schlenk techniques under an atmosphere of dry argon. Benzene and diethyl ether were dried and deoxygenated using an IT PureSolv system. Benzene-d_6 was degased with freeze-pump-thaw cycles, heated to reflux over a Na/K alloy, and then vacuum transferred. To^{M}CoCl and To^{M}CoOAc (**3**) were synthesized following the reported procedures.[1] ^{1}H and ^{11}B NMR spectra were collected on a Bruker Avance III 600 spectrometer. ^{11}B NMR spectra were referenced to an external sample of $BF_3{\cdot}Et_2O$. Infrared spectra were measured on a Bruker Vertex 80 FTIR spectrometer. EPR were obtained on an X-band Elexsys 580 FT- EPR spectrometer in continuous wave mode, and the spectra simulated using XSophe. UV-Vis spectra were recorded on an Agilent 8453 UV-vis spectrophotometer. The electronic spectrum of To^{M}CoOAc was not previously disclosed and is reported here. Elemental analyses were performed using a Perkin-Elmer 2400 Series II CHN/S. Single crystal X-ray diffraction data was collected on an APEX II.

To^{M}CoMe (1). Methyllithium (1.6 M in diethyl ether, 1.00 mL, 1.6 mmol) was added to a solution of To^{M}CoCl (0.510 g, 1.07 mmol) in benzene (50 mL). The green reaction mixture was stirred for 1.5 h, the salt byproduct was removed by filtration, and the solvent was evaporated to afford To^{M}CoMe as a dark aquamarine solid (0.353 g, 0.773 mmol, 72%). X-ray quality crystals were obtained from pentane at –40 °C. ^{1}H NMR (benzene-d_6, 600 MHz): δ 15.44 (s, 6 H, CNCMe$_2$*CH*$_2$O), 14.18 (s, 2 H, C_6H_5), 10.61 (s, 2 H, C_6H_5), 8.88 (s, 1 H, *p*-C_6H_5), –12.05 (s, 18 H, CNC*Me*$_2$CH$_2$O). ^{11}B NMR (benzene-d_6, 128 MHz): δ 100.3. IR (KBr, cm^{-1}): ν 2967 (m), 2925 (m), 2897 (m), 2861 (m), 1594 (s, ν_{CN}), 1462 (m), 1386 (m), 1352 (m), 1269 (m), 1194 (m), 1160 (m), 960 (m). UV-vis (Et_2O) λ_{max} = 346 (ε: 1412 M^{-1}cm^{-1}), 581 (ε: 388 M^{-1}cm^{-1}), 617 (ε: 424 M^{-1}cm^{-1}), 697 (ε: 1078 M^{-1}cm^{-1}). μ_{eff} (C_6D_6) = 4.2(2) μ_B as determined by the Evans method. Anal. Calcd. for $C_{22}H_{32}BCoN_3O_3$: C, 57.91; H, 7.07; N, 9.21 Found: C, 57.93; H, 7.18; N, 9.20. Mp. 235-237 °C, dec.

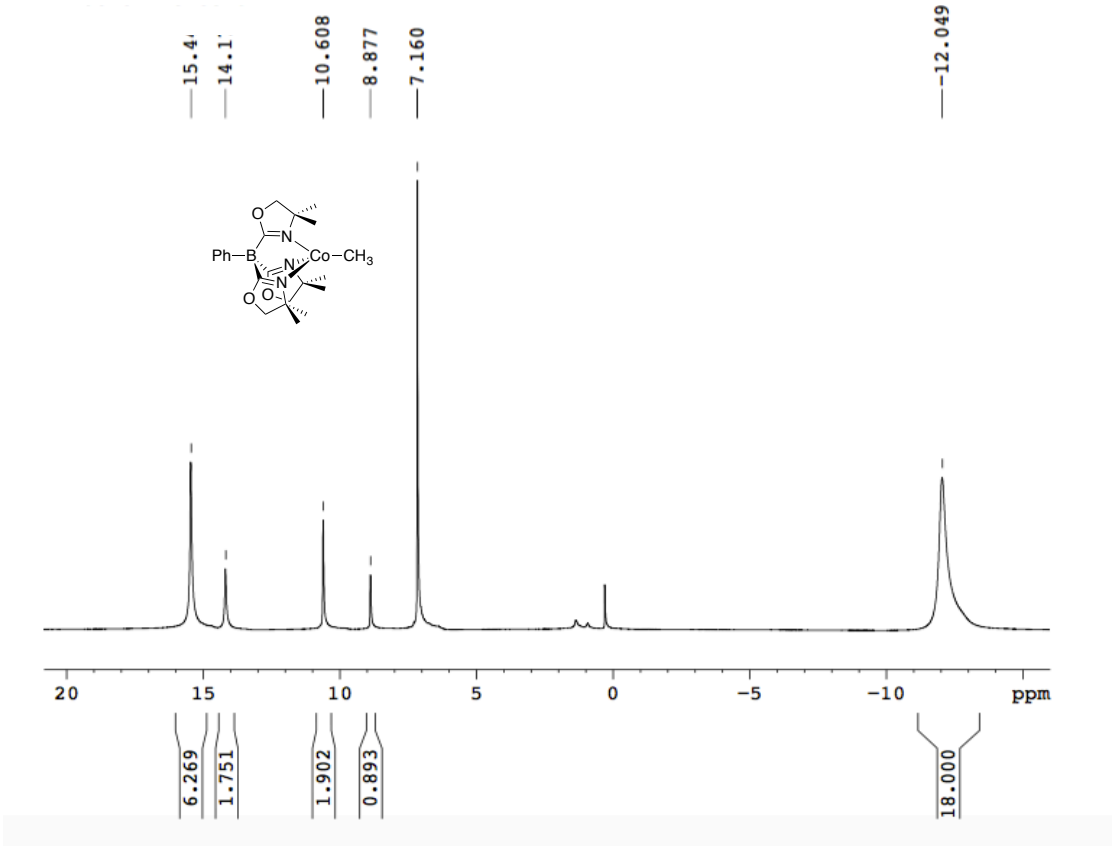

Figure S1. ^{1}H NMR spectrum of To^{M}CoMe (**1**) acquired in benzene-d_6 at room temperature.

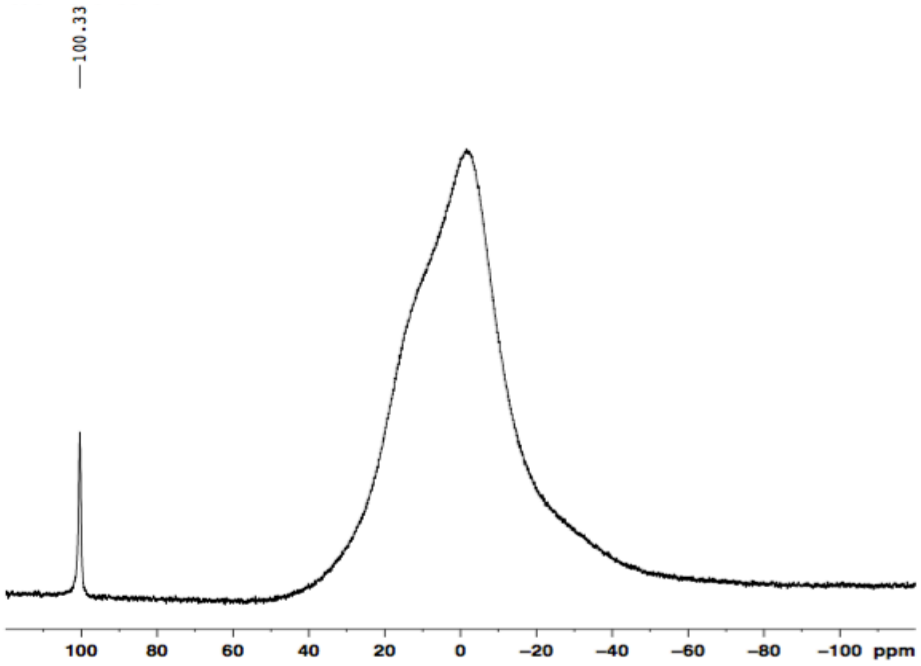

Figure S2. ^{11}B NMR spectrum of To^{M}CoMe (**1**) acquired in benzene-d_6 at room temperature.

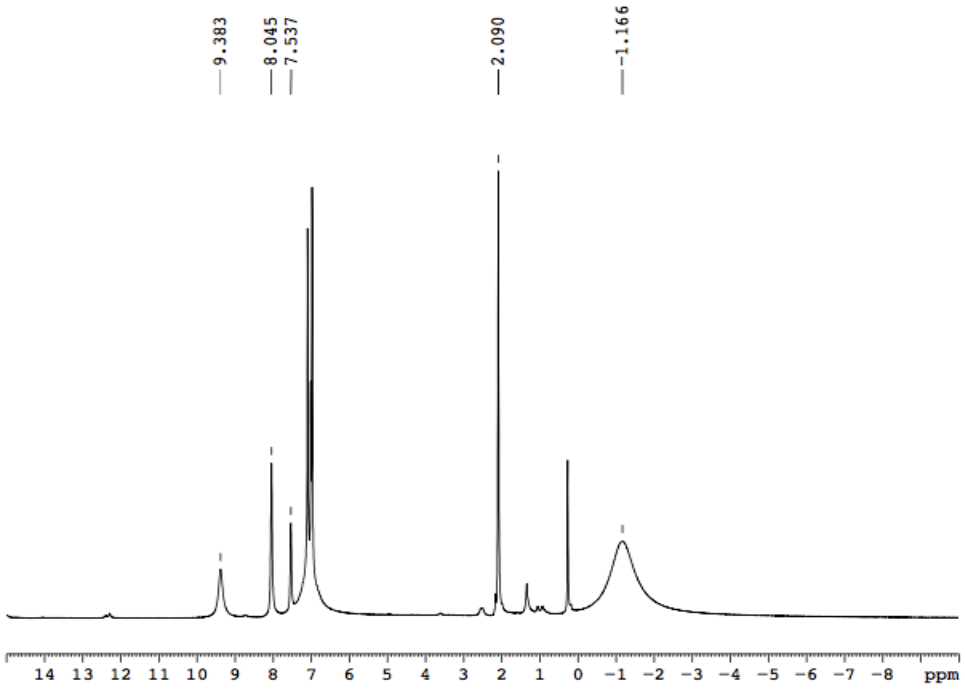

Figure S3. ^{1}H NMR spectrum of To^{M}Co(CMe=O)CO (**2**) acquired in toluene-d_8 at room temperature.

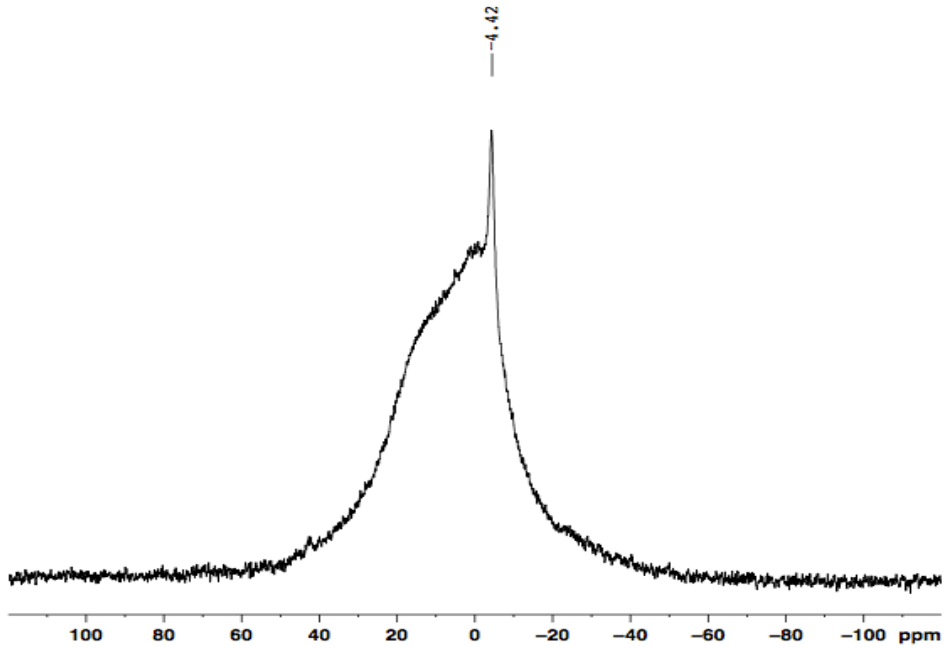

Figure S4. ^{11}B NMR spectrum of To^{M}Co(CMe=O)CO (**2**) acquired in toluene-d_8 at room temperature.

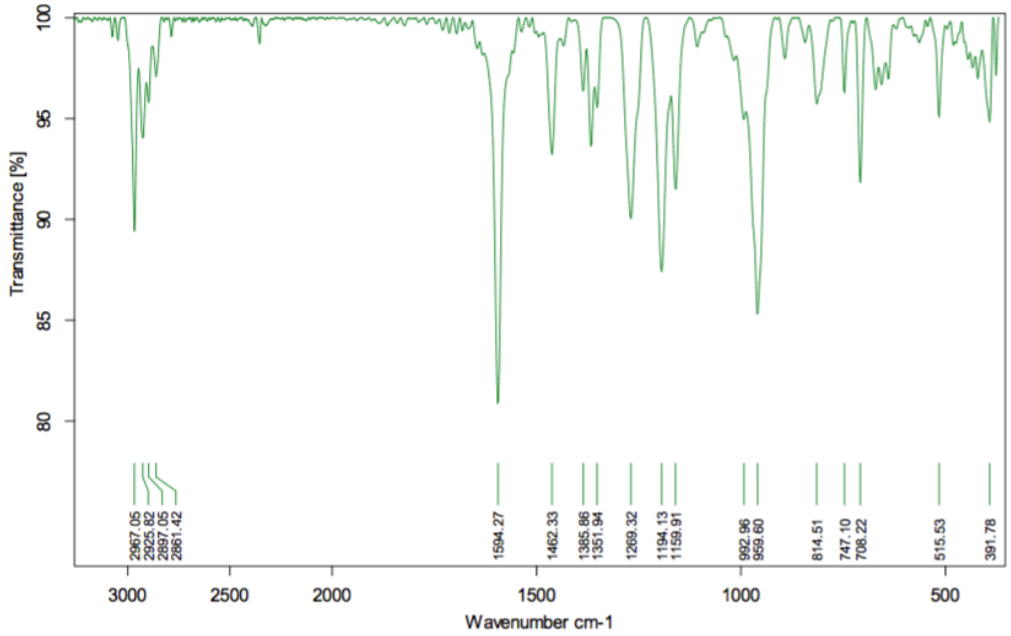

Figure S5. Infrared spectrum (KBr) of To^{M}CoMe (**1**).

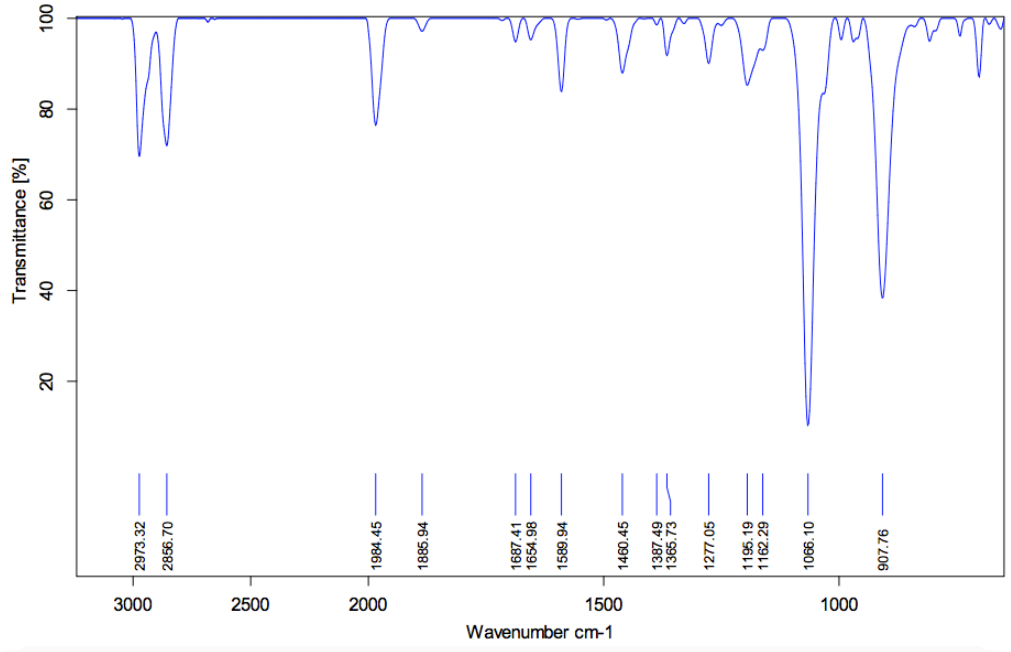

Figure S6. Infrared spectrum (ATR, ZnSe crystal) of To^{M}Co(CMe=O)CO (**2**) in tetrahydrofuran.

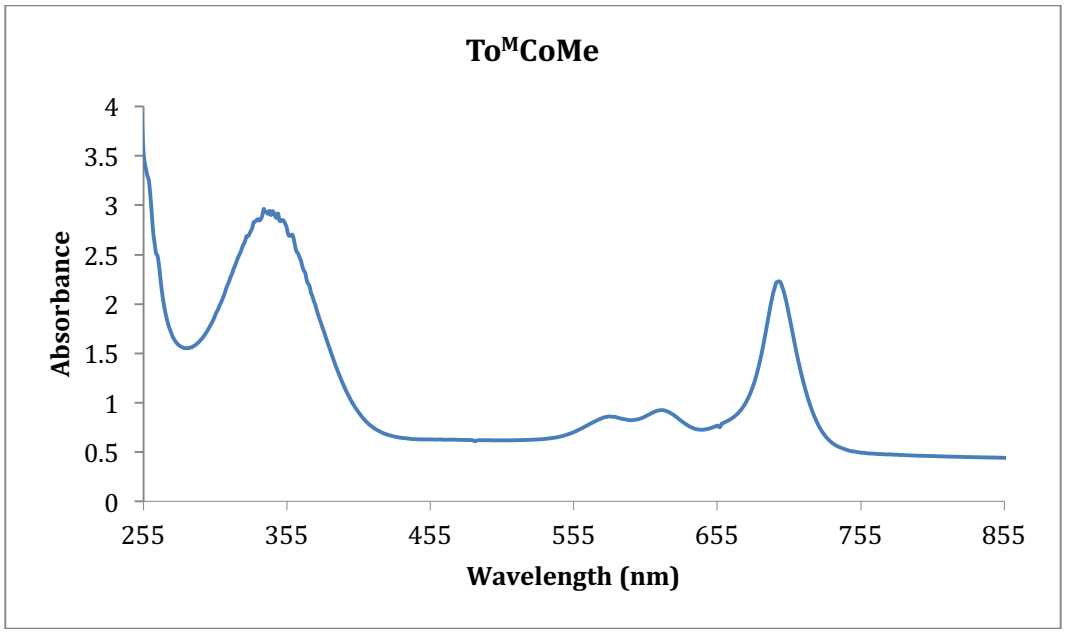

Figure S7. UV-Vis spectrum of To^{M}CoMe (**1**) in Et_2O.

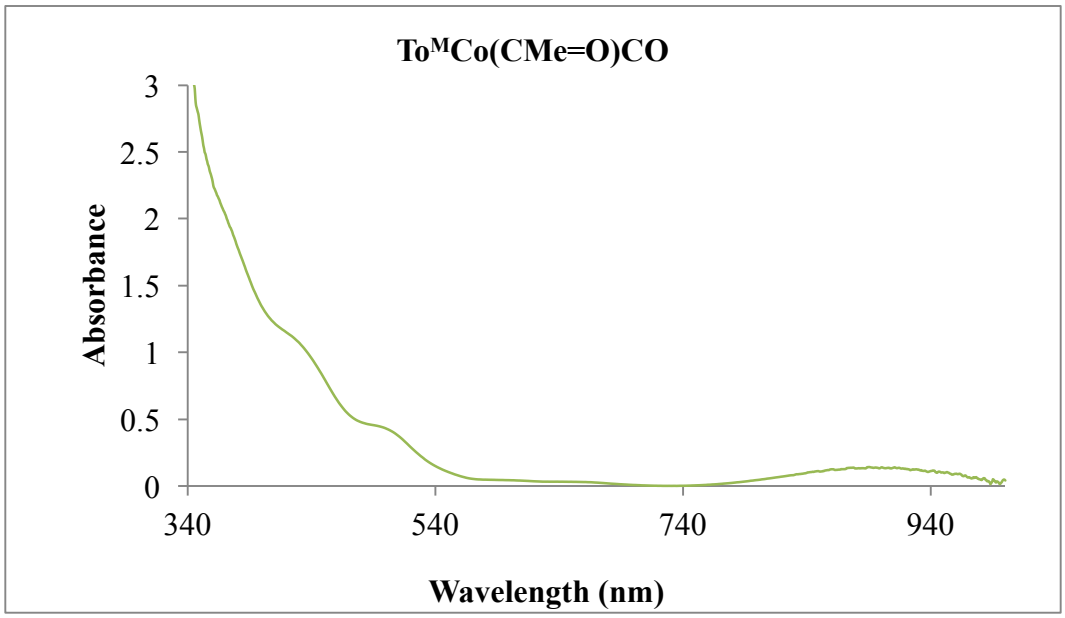

Figure S8. UV-Vis spectrum of To^{M}Co(CMe=O)CO (**2**) in tetrahydrofuran at –100 °C.

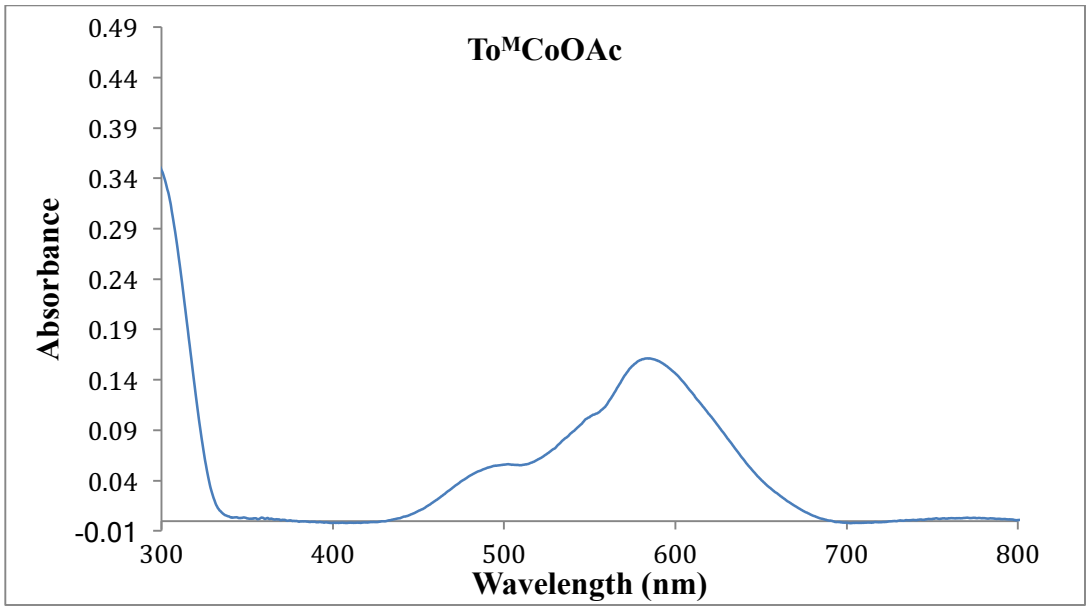

Figure S9. UV-Vis spectrum of crystals of To^{M}CoOAc (**3**) in tetrahydrofuran at room temperature.

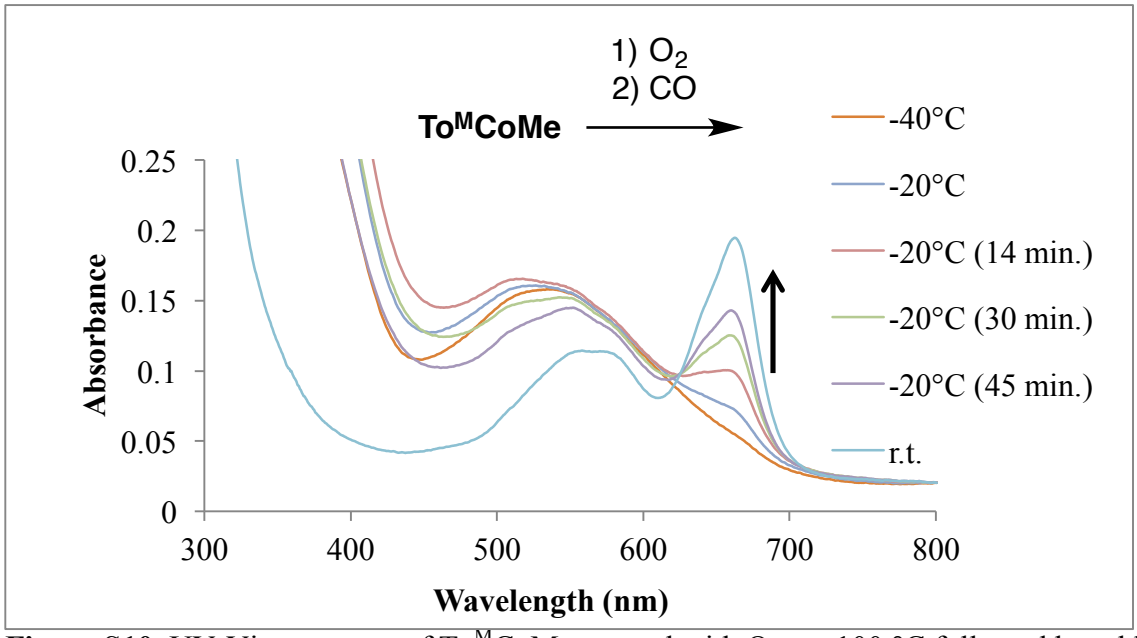

Figure S10. UV-Vis spectrum of To^{M}CoMe reacted with O_2 at –100 °C followed by addition of CO at –100 °C in tetrahydrofuran. The reaction was monitored as the reaction warmed up to room temperature.

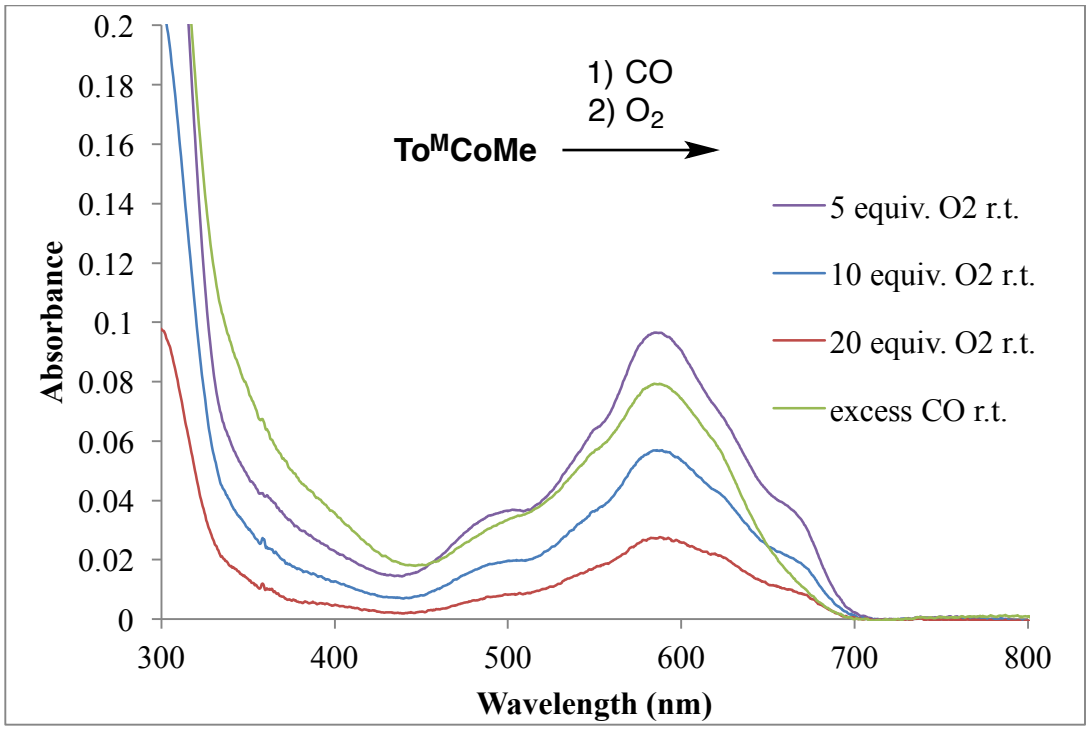

Figure S11. UV-Vis spectrum of To^{M}CoMe reacted with CO at room temperature followed by addition of O_2 at room temperature in tetrahydrofuran.

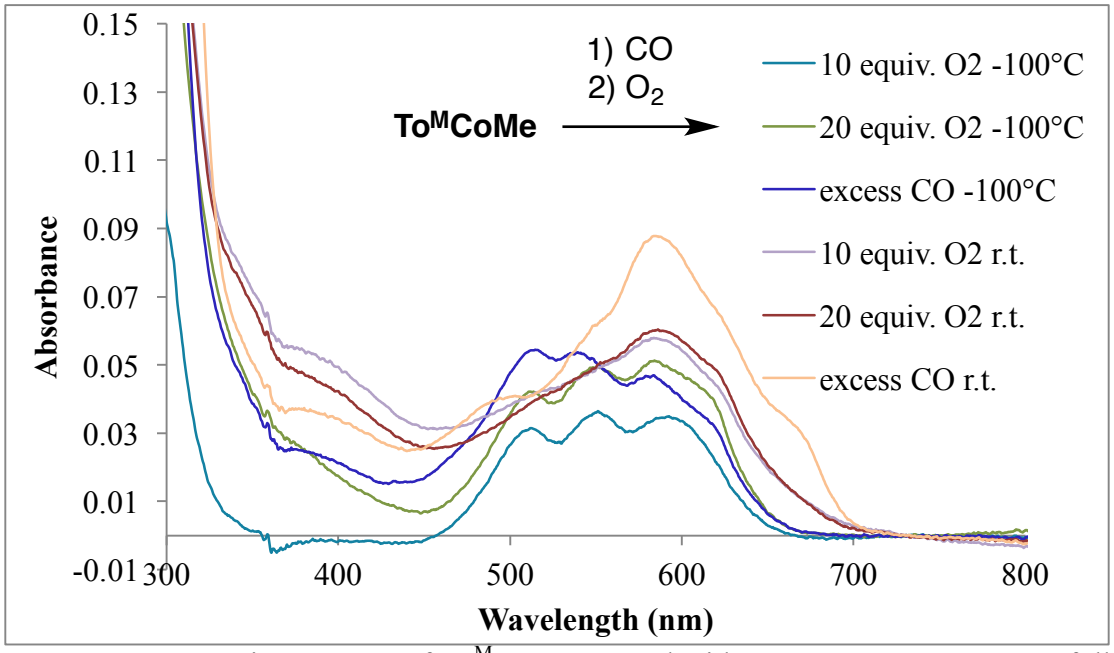

Figure S12. UV-Vis spectrum of To^{M}CoMe reacted with CO at room temperature followed by addition of O_2 at –100 °C in tetrahydrofuran (λ_{max} = c.a. 510, 550, and 585 nm). The reaction was monitored again after allowing the solution to warm to room temperature (λ_{max} = c.a. 585 nm).

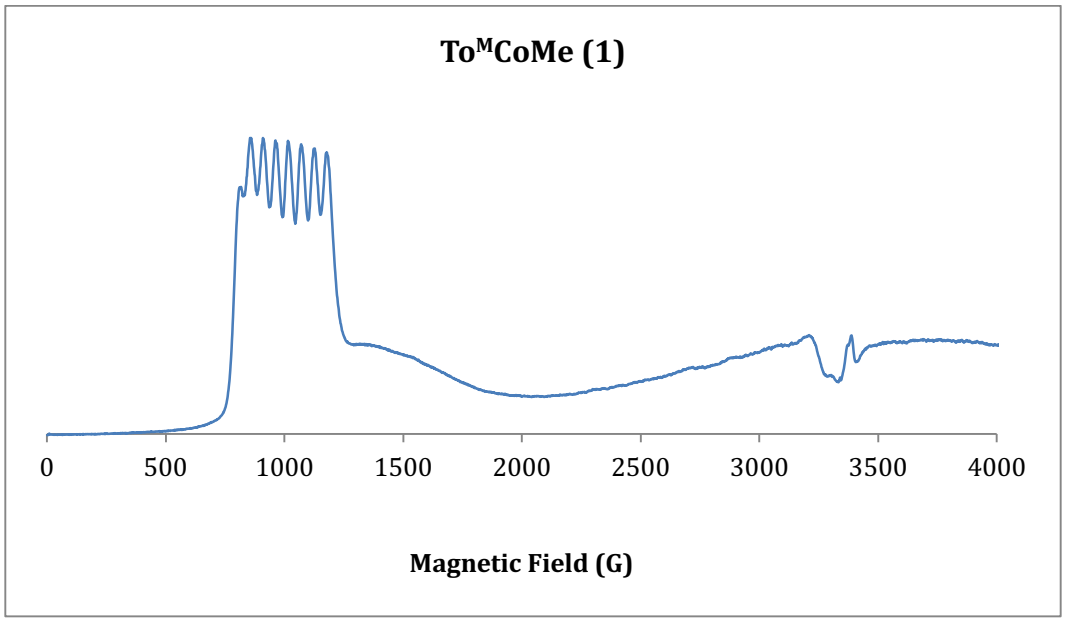

Figure S13. X-Band EPR spectrum of To^{M}CoMe (**1**) in toluene at 5 K.

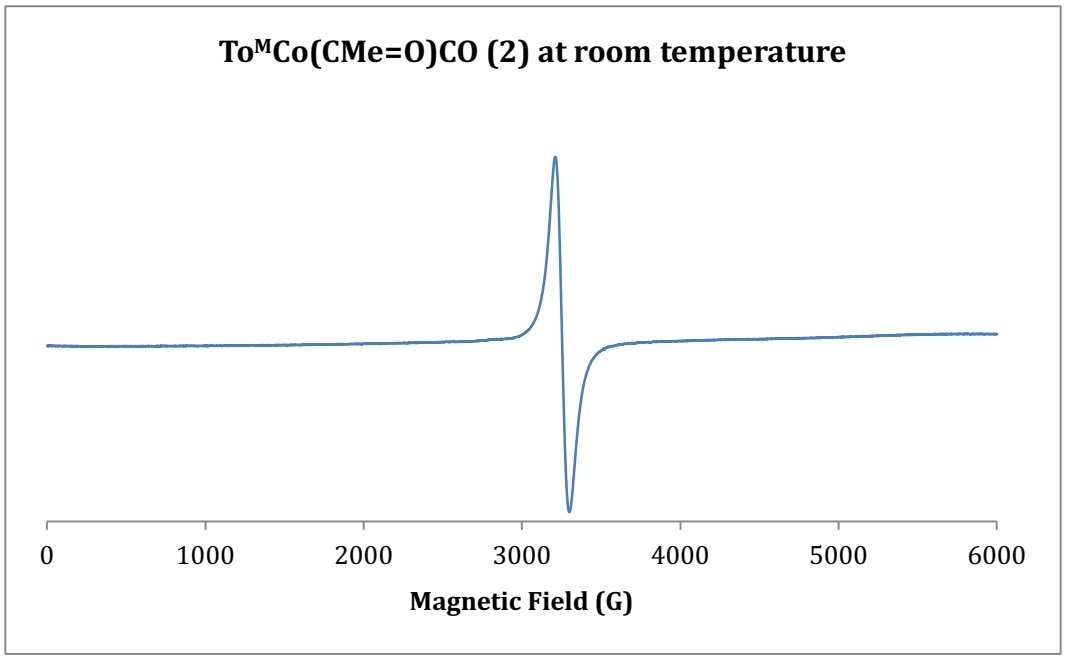

Figure S14. X-Band EPR spectrum of To^{M}Co(CMe=O)CO (**2**) in tetrahydrofuran at room temperature.

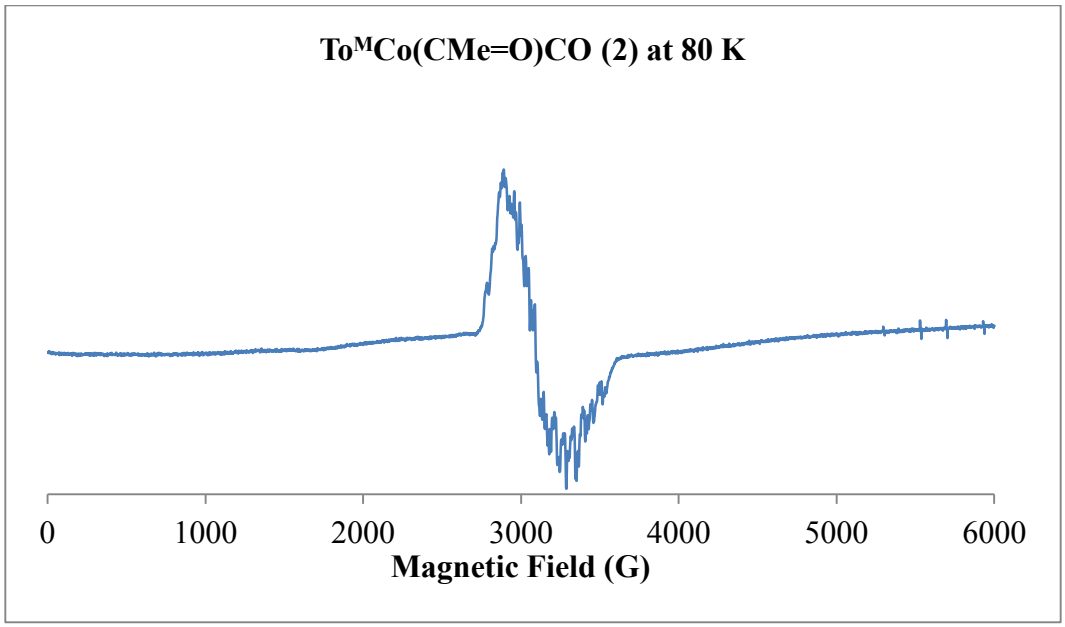

Figure S15. X-Band EPR spectrum of To^{M}Co(CMe=O)CO (**2**) in tetrahydrofuran at 80 K.

DFT Calculations: Cartesian Coordinates For All Structures

Cartesian coordinates, chemical formulas, and single point energy values are provided for high spin and low spin calculations.

All optimization, Hessian, and energy calculations were performed using the 6-311+g* basis set[2-5] and the PBE[6] functional using the NWChem[7] Computational Chemistry suite. Cartesian coordinates are in units of angstroms. All TDDFT calculations were performed using the same functional and basis set, both with and without a COSMO solvation model for THF.[8] The results both with and without the solvation were essentially identical.

Table S1. To^{M}CoMe starting material: $C_{22}H_{32}BCoN_3O_3$.

Element	X	Y	Z
Co	0.15651852	1.94540046	-0.24177561
B	-0.08445358	-1.14746571	0.1672626
C	-1.94585137	1.64555321	-3.37999209
H	-1.51255827	2.62858554	-3.17696209
H	-2.79524755	1.78264459	-4.05707929
H	-1.19262645	1.04092551	-3.89236591
C	-2.38701175	0.97861342	-2.0838946
C	-3.39949046	1.84918339	-1.34523053
H	-3.7249667	1.36818558	-0.41836705

H	-4.28302424	2.03062372	-1.96586077
H	-2.9585922	2.81689809	-1.09072603
C	-2.90575037	-0.4580846	-2.30505599
H	-3.96100075	-0.58686534	-2.05582981
H	-2.73160877	-0.82047118	-3.32252276
C	-1.17761811	-0.50598811	-0.87723162
C	-1.90755514	2.29084949	2.84088158
H	-1.79200617	3.15549687	2.1817113
H	-2.20120544	2.65472525	3.83086781
H	-2.71823072	1.66959471	2.4495833
C	-0.60445937	1.50061836	2.91796817
C	0.51989748	2.36691325	3.47076398
H	1.46261182	1.81345801	3.49486408
H	0.29117119	2.7001312	4.48826316
H	0.66132848	3.25397638	2.84758853
C	-0.76879985	0.18015372	3.6976593
H	0.03053946	0.01305959	4.42532645
H	-1.73469053	0.08297365	4.19757934
C	-0.33787379	-0.27780455	1.53891183
C	3.2709706	1.39959246	-2.32023793
H	2.7128933	0.87813844	-3.10260244
H	4.32471987	1.43475003	-2.61531232
H	2.90045772	2.42673092	-2.26477759
C	3.10616189	0.69982722	-0.97795948
C	3.84272754	1.45864468	0.1223799
H	3.44279624	2.47141285	0.2224168
H	4.91094521	1.53546276	-0.1052048
H	3.73283738	0.95228099	1.08566807
C	3.51244551	-0.78795369	-1.03205844
H	3.69006655	-1.14220872	-2.05183146
H	4.37951189	-1.02913662	-0.41388293
C	1.38032276	-0.62705359	-0.36057544
N	-1.22639638	0.73568063	-1.21337476
N	-0.25430833	1.00630952	1.57794734
N	1.68184764	0.59591162	-0.62526237

O	-2.1358354	-1.27753823	-1.40987246
O	-0.67936619	-0.85482838	2.70309952
O	2.38195578	-1.50514468	-0.50982969
C	0.298957	3.93037902	-0.48450566
C	-0.14805185	-2.75618438	0.22818691
C	-0.24286154	-3.52060294	1.39631093
C	-0.25071449	-4.91394012	1.36386075
C	-0.16125121	-5.59011811	0.15501154
C	-0.06170287	-4.85611937	-1.02287716
C	-0.0555931	-3.4686073	-0.97722153
H	-0.31630314	-3.02586425	2.35741011
H	-0.32761662	-5.47176824	2.29389097
H	-0.16781907	-6.67643962	0.12807535
H	0.01108102	-5.36768158	-1.97936813
H	0.0241079	-2.92330744	-1.91551612
H	1.09116343	4.38056125	0.13203464
H	-0.62672407	4.4636784	-0.22115361
H	0.5260448	4.21506298	-1.52243717

Density Functional Theory Single Point Energies
Doublet (low) = –1417.005732 hartree
Quartet (high) = –1417.084129 hartree
Delta E = 49 kcal/mol between two spin configurations (favoring the quartet)

Table S2. $To^{M}Co(Me)CO$: $C_{23}H_{32}BCoN_3O_4$

Element	X	Y	Z
Co	0.18895951	1.80355962	0.20859267
B	-0.00031418	-1.35522619	-0.12569667
C	-3.6577186	1.36572856	0.66204991
H	-3.32589883	2.34803735	0.31806156
H	-4.63862174	1.48919393	1.13307444
H	-3.77746995	0.72094877	-0.21345698
C	-2.65908943	0.76263196	1.64836538
C	-2.52127098	1.64268236	2.88069384
H	-1.76221096	1.24840182	3.56097389
H	-3.47224963	1.69386715	3.42143611
H	-2.23549915	2.66060266	2.60862157
C	-3.04098315	-0.68265194	2.01716623
H	-2.8492312	-0.90950519	3.07147812
H	-4.07363849	-0.94276253	1.77691571
C	-1.21481646	-0.698856	0.73353062
C	3.04540154	0.90224625	2.75681712
H	2.63092017	1.88211944	2.99030916
H	4.08126838	0.87977618	3.1119579
H	2.48021024	0.1496752	3.31426915
C	3.00437946	0.60756285	1.25823266
C	3.74622578	1.67613225	0.4674928
H	3.70214136	1.46793183	-0.60515182
H	4.79970047	1.71285336	0.76357443
H	3.31755478	2.66552591	0.64142288
C	3.56841724	-0.79797423	0.97691435
H	4.21395222	-0.82831106	0.09279739
H	4.10184455	-1.23197646	1.82428855
C	1.38131339	-0.7837984	0.52042556
C	-1.39846662	1.78393423	-3.25134948
H	-2.16022595	1.0252742	-3.05079592
H	-1.47237059	2.07356921	-4.30469993
H	-1.62980586	2.6635324	-2.6486031
C	-0.00295596	1.24281286	-2.94581659

C	1.06606842	2.28402566	-3.23817092
H	0.88805342	3.20046308	-2.6693617
H	1.0683067	2.54955298	-4.30017164
H	2.05951566	1.90889746	-2.97790739
C	0.24839262	-0.07318289	-3.69803991
H	-0.42069571	-0.23418776	-4.54457365
H	1.2865404	-0.17563073	-4.03191216
C	0.00506855	-0.50900092	-1.51925414
N	-1.3660746	0.5553729	0.96332616
N	1.60961843	0.45951339	0.7742402
N	0.06313519	0.77720136	-1.54370834
O	-2.17465799	-1.50364882	1.22490737
O	2.41973705	-1.6097274	0.70530824
O	-0.00089198	-1.09915522	-2.72556777
C	0.51659335	2.94588732	1.80726631
C	-0.10645999	-2.95847548	-0.19504041
C	0.27741808	-3.72844402	0.91221374
C	0.12828431	-5.10963842	0.9417095
C	-0.419718	-5.77501932	-0.14971626
C	-0.81652162	-5.03843893	-1.25824485
C	-0.6625675	-3.65445409	-1.27512877
H	0.70808069	-3.23833213	1.7818744
H	0.44073458	-5.66930551	1.81982529
H	-0.53773607	-6.85517535	-0.13396108
H	-1.2505914	-5.54219013	-2.11842258
H	-0.98191774	-3.11100208	-2.15774876
C	-0.69614839	3.23655439	-0.24266953
O	-1.26133102	4.20651674	-0.45859404
H	0.50856316	2.24577846	2.64444104
H	1.50897232	3.40489848	1.73044498
H	-0.18246654	3.75343505	2.0438029

Density Functional Theory Single Point Energies

Doublet (low spin) = –1530.305323 hartree

Quartet (high spin) = –1530.257968 hartree

Delta E = 30 kcal/mol between two spin configurations (favoring the doublet)

Table S3. $To^{M}Co(CMe{=}O)CO$ (**2**): $C_{24}H_{32}BCoN_3O_5$

Element	X	Y	Z
Co	0.00457031	1.66928008	-0.07021966
B	0.07960781	-1.51000167	-0.07942578
C	-3.72333231	1.57353909	0.64370148
H	-3.31861383	2.54852565	0.92590027
H	-4.76713782	1.54545447	0.97298879
H	-3.71095356	1.4997161	-0.44683659
C	-2.93582807	0.44107389	1.27918959
C	-2.90062478	0.58807133	2.79967738
H	-2.34460908	-0.23626304	3.2555426
H	-3.91730317	0.5785838	3.20672639
H	-2.42927147	1.52410137	3.099527
C	-3.49844807	-0.93408091	0.89436855
H	-4.09556651	-1.40405508	1.67752914
H	-4.07959005	-0.90498582	-0.0349543
C	-1.30674376	-0.88917521	0.49424341
C	2.78766589	1.60805434	2.6456827
H	2.50522254	2.64929256	2.49875016
H	3.7939657	1.60112791	3.07836297
H	2.11092611	1.15023579	3.37246954
C	2.79621211	0.82064342	1.33995169
C	3.59808017	1.55356637	0.26846241
H	3.65373351	0.95891354	-0.64846575
H	4.62020345	1.73856023	0.61532692
H	3.13919131	2.51693492	0.03558332
C	3.34251625	-0.59821092	1.59589868
H	4.2953813	-0.79461421	1.09945729
H	3.44179127	-0.82451318	2.66139173
C	1.31299133	-0.75466615	0.66522419
C	-1.12596692	1.10214812	-3.72360634
H	-1.83137576	0.28327721	-3.55546972
H	-1.06061682	1.28108394	-4.801727
H	-1.5350889	2.00317441	-3.26342508
C	0.25002967	0.75578034	-3.15749756

C	1.24477308	1.87956926	-3.40486746
H	0.89128229	2.82101913	-2.97578714
H	1.38923002	2.03997996	-4.47808667
H	2.21632437	1.65045052	-2.9596281
C	0.74319665	-0.59144881	-3.7097863
H	0.23324705	-0.91086415	-4.61975346
H	1.82558271	-0.60842964	-3.87520017
C	0.20669876	-0.83494	-1.55459188
N	-1.5507402	0.34836018	0.74893743
N	1.43553212	0.52154704	0.81738787
N	0.13620594	0.4397907	-1.71683597
O	-2.3385953	-1.73838083	0.66490395
O	2.36342175	-1.4863555	1.04882609
O	0.44644762	-1.53904986	-2.67152457
C	0.35085187	3.0727064	1.17985062
C	0.11106508	-3.11226631	0.0591664
C	0.29064213	-3.68205993	1.32772045
C	0.25378026	-5.05503366	1.53571453
C	0.03076316	-5.91500003	0.46526493
C	-0.15611866	-5.37948779	-0.80213621
C	-0.11766888	-4.00075822	-0.99730903
H	0.46552882	-3.03499271	2.18459802
H	0.39957937	-5.45601021	2.53557116
H	0.00101622	-6.99026767	0.61926148
H	-0.33418242	-6.0378963	-1.64869787
H	-0.26774385	-3.61625849	-2.00011566
C	-0.31675617	3.19504359	2.52490579
O	1.20807385	3.85736695	0.8323658
H	-0.29963034	2.23519746	3.04444193
H	-1.36793843	3.4629666	2.3753822
H	0.16665092	3.96806782	3.12861428
C	-1.04662936	2.89557525	-0.78893716
O	-1.71208025	3.71951773	-1.21080679

Density Functional Theory Single Point Energies
Doublet (low spin) = –1643.554558 hartree
Quartet (high spin) = –1643.501237 hartree
Delta E = 33 kcal/mol between two spin configurations (favoring the doublet)

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