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SUPPORTING INFORMATION

Title: [Co(MeTAA)] Metalloradical Catalytic Route to Ketenes via Carbonylation of Carbene Radicals
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Contents

1. Experimental Procedures

General Procedures. All manipulations, except the carbonylation reactions, were performed under a nitrogen atmosphere using standard Schlenk techniques. All solvents used for catalysis were dried over and distilled from sodium (toluene, tetrahydrofuran, diethyl ether) or CaH_2 (dichloromethane, hexane, ethyl acetate, methanol, acetonitrile). Unless specified, all chemicals were purchased from commercial suppliers (Sigma Aldrich, Acros or Strem) and used without further purification. NMR spectra (^1H, and $^{13}C\{1H\}$) were measured on a Bruker AV400, AV300, DRX 500 or DRX 300 spectrometer or on a Varian Mercury 300 spectrometer, referenced internally to residual solvent resonance of $CHCl_3$ (δ = 7.26 ppm for ^1H, δ = 77.2 ppm for ^{13}C) or DMSO (δ = 2.50 ppm for ^1H, δ = 39.5 ppm for ^{13}C). Unless noted otherwise, the NMR spectra were measured in $CDCl_3$. Individual peaks are reported as: multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), integration, coupling constant in Hz. Mass spectra of the synthesized compounds were recorded on an Agilent-5973 GC-MS spectrometer, and the corresponding HRMS data were recorded on a JEOL AccuTOF 4G via direct injection probe using either EI or ESI. Chirality was determined using a Shimadzu HPLC setup equipped with an UV-Vis detector (SPD-10Avp).

Catalyst preparation. [Co(MeTAA)] has been synthesized according to reported procedures.[1] [Co(TPP)] and [Co(salens)] have been purchased from Sigma-Aldrich or Strem and used without further purification.

General Procedure for Synthesis of the *N*-tosylhydrazone salts.[2] An equimolar mixture of corresponding aldehyde and N-tosylhydrazide was placed in a round bottom flask and dissolved in methanol (2 mL/mmol). The reaction mixture was stirred overnight at room temperature. The white precipitate was collected by filtration, and washed with cold methanol and hexane to obtain the pure product. The formed N-tosylhydrazone was then deprotonated in methanol using 1 equivalent of sodium methoxide. After evaporation of methanol, the pure product was obtained as a white powder.

Typical Carbene Carbonylation Procedures. In a typical carbonylation experiment a stainless steel autoclave (150 mL) equipped with inserts suitable for five glass vials (4 mL) was

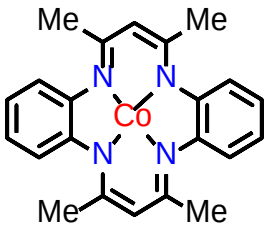
employed. The vials were charged with appropriate amounts of solvent, substrates (N-tosylhydrazone sodium salts and nucleophiles or imines) and catalyst, together with Teflon stirring bars. Before starting the catalytic reactions, the charged autoclave was purged three times with CO and then pressurized to the desired pressure. After catalysis, the autoclave was cooled to room temperature, and purged with nitrogen so that any excess CO was removed. The reaction mixture is then analysed and purified using typical organic work-up, preparative TLC or flash column chromatography.

Co^{II}-catalysed β-lactam synthesis using different N-tosylhydrazone sodium salts and imines. Under a nitrogen atmosphere, [Co(MeTAA)] (3 mol%), and the desired *N*-tosylhydrazone sodium salt (1.0 eq, 0.34 mmol) were added to a flame-dried 4 ml glass vial. Then the vial was sealed with a stopper and evacuated. The desired imine (1.2 eq., 0.408 mmol) in 3.0 ml of toluene were added via syringe. A small needle was inserted at the top of the vial. The vials were then inserted into an autoclave (150 mL) equipped with inserts suitable for five such glass vials and pressurized to 20 bar of CO. The pressurized autoclave was then stirred at 60^{o} C for 16h. The autoclave was subsequently cooled to room temperature, and purged with nitrogen so that any excess CO is removed. The resulting mixture was concentrated and the residue was purified by preparative TLC or flash silica gel chromatography.

Co^{II}-Catalysed amide/ester synthesis using N-tosylhydrazone sodium salt and different nucleophiles. Under a nitrogen atmosphere, [Co(MeTAA)] (4 mol%), DABCO (2.0 eq., 0.8 mmol), and the desired *N*-tosylhydrazone sodium salt (1.0 eq., 0.4 mmol) were added to a 4 ml flame-dried glass vial. Then the vial was sealed with a stopper and evacuated. Anhydrous toluene (3.0 mL) and the desired nucleophile (alcohol or amine) (2.2 eq., 0.88 mmol) were added *via* syringe. A small needle was inserted at the top of the vial. The vials were then inserted into an autoclave (150 mL) equipped with inserts suitable for five such glass vials and pressurized with 20 bar of CO. The pressurized autoclave was then stirred at 60 ^{o}C for 16h. The autoclave was subsequently cooled to room temperature, and purged with nitrogen so that any excess CO is removed. The resulting mixture was concentrated and the residue was purified by preparative TLC or flash silica gel chromatography.

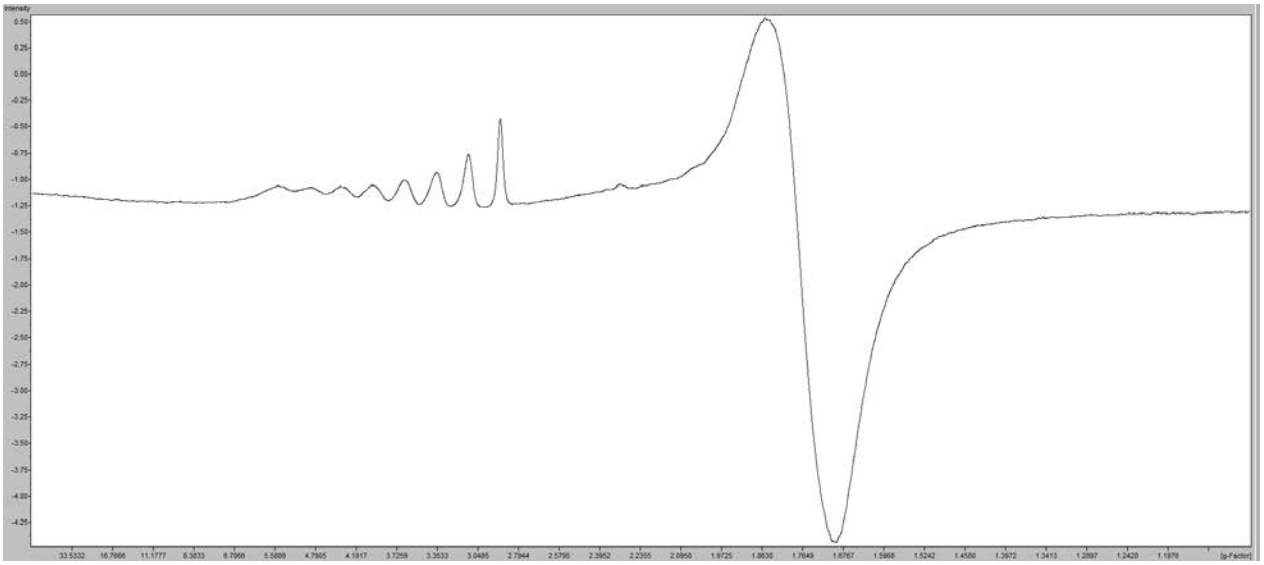
2. Catalyst characterization

[Co(MeTAA)]: (as reported in reference [3])



Elemental analysis calcd. for $C_{22}H_{22}CoN_4$: C, 65.83; H, 5.52; N, 13.96; calcd. for $C_{22}H_{22}CoN_4 \cdot 1.5H_2O$: C, 61.68; H, 5.88; N, 13.08; Found: C, 61.46; H, 5.67; N, 12.58.

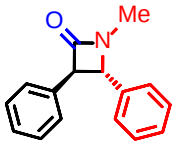
EPR:



HRMS (EI): Calcd. for $C_{22}H_{22}CoN_4$ m/z 401.1176, Found m/z 401.1156

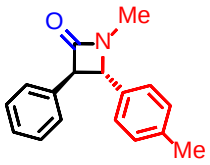
3. Compound Characterization

***trans*-1-Methyl-3,4-diphenylazetidin-2-one**[4, 5]



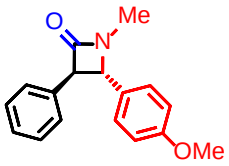
^{1}H NMR (500 MHz, $CDCl_3$): δ 2.87 (s, 3H), 4.17 (s, 1H), 4.45 (d, *J* = 2.5 Hz, 1H), 7.26-7.45 (m, 10 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 26.95, 65.25, 65.61, 126.18, 127.26, 127.53, 128.58, 128.78, 129.08, 134.96, 137.27, 168.35.

***trans*-1-Methyl-3-phenyl-4-*para*-tolylazetidin-2-one**[5]



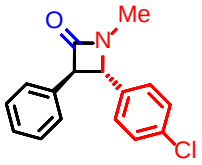
^{1}H-NMR (400 MHz, $CDCl_3$): δ= 2.39 (s, 3H), 2.86 (s, 3H), 4.16 (s, 1H), 4.43 (d, *J*= 2.1 Hz, 1H), 7.27-7.39 (m, 9h). ^{13}C NMR (75 MHz, $CDCl_3$): 168.32, 138.51, 135.04, 134.12, 129.72, 128.71, 127.52, 127.24, 126.12, 65.76, 65.24, 27.04, 21.38 ppm

***trans*-4-(4-Methoxyphenyl)-1-methyl-3-phenylazetidin-2-one**[4]



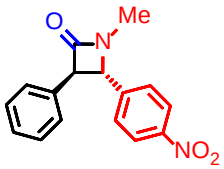
^{1}H NMR (300 MHz, $CDCl_3$): δ 2.84, (s, 3H), 3.85 (s, 3H), 4.14 (s, 1H), 4.41 (d, *J* = 2.0 Hz, 1H), 6.95 (d, *J* = 7.5 Hz), 7.22-7.36 (m, 7H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 27.02, 55.34, 65.07, 65.73, 114.62, 127.16, 127.35, 127.65, 128.92, 129.12, 135.17, 159.99, 168.85.

***trans*-4-(4-Chlorophenyl)-1-methyl-3-phenylazetidin-2-one**[4]



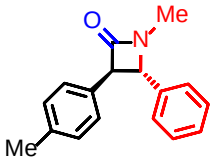
^{1}H NMR (300 MHz, $CDCl_3$): δ 2.89 (s, 3H), 4.16 (s, 1H), 4.46 (d, *J* = 2 Hz, 1H), 7.29-7.45 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 27.15, 64.79, 65.90, 127.35, 127.66, 127.67, 127.82, 128.97, 128.99, 128.43, 129.47, 129.68, 134.59, 134.72, 135.91, 168.30.

trans-4-(4-Nitrophenyl)-1-methyl-3-phenylazetidin-2-one[4]



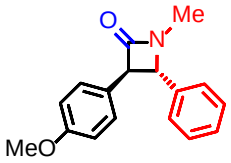
^{1}H NMR (400 MHz, $CDCl_3$): δ= 2.92 (s, 3H), 4.17 (s, 1H), 4.58 (d, *J*= 2.1 Hz, 1H), 7.25-7.40 (m, 5H), 7.51 (d, *J*= 8.6 Hz, 2H), 8.27 (d, *J*= 8.6 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 27.23, 64.32, 65.91, 124.25, 126.93, 127.18, 127.87, 128.82, 134.08, 144.82, 147.85, 167.66.

***trans*-1-Methyl-4-phenyl-3-*p*-tolylazetidin-2-one**[4]



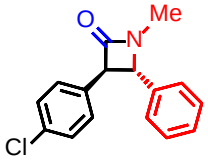
^{1}H NMR (300 MHz, $CDCl_3$): δ 2.34 (s, 3H), 2.85 (s, 3H), 4.11 (s, 1H), 4.41 (d, *J* = 2 Hz, 1H), 7.10-7.19 (m, 4H), 7.29-7.46 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.12, 27.07, 65.22, 65.77, 126.27, 127.16, 128.53, 129.18, 129.76, 131.85, 137.33, 137.47, 168.89.

***trans*-3-(4-Methoxyphenyl)-1-methyl-4-phenylazetidin-2-one**[4]



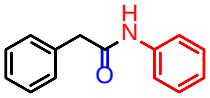
^{1}H NMR (300 MHz, $CDCl_3$): δ 2.87 (s, 3H), 3.80 (s, 3H), 4.41 (s, 1H), 4.40 (d, *J* = 2 Hz, 1H), 6.89 (d, *J* = 9 Hz, 2H), 7.21-7.45 (m, 7H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 27.07, 55.35, 65.22, 65.77, 114.31, 126.27, 127.26, 128.53, 128.65, 129.18, 137.47, 159.10, 168.89.

***trans*-3-(4-Chlorophenyl)-1-methyl-4-phenylazetidin-2-one**[4]



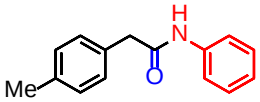
^{1}H NMR (300 MHz, $CDCl_3$): δ 2.86 (s, 2H), 4.14 (s, 1H), 4.41 (d, *J* = 2 Hz, 1H), 7.20-7.45 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 27.14, 64.97, 65.32, 126.27, 128.75, 128.88, 129.08, 129.29, 133.48, 133.54, 137.04, 167.95.

N, 2-diphenylacetamide[4,6]



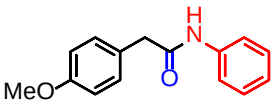
^{1}H NMR (500 MHz, $CDCl_3$): δ 3.73 (s, 2H), 7.05 (t, *J* = 7.2 Hz, 1H), 7.24-7.40 (m, 9H) 7.54 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 44.91, 119.81, 124.50, 127.74, 128.96, 129.30, 129.57, 134.40, 137.58, 169.05.

2-(4-Methylphenyl)-*N*-phenylacetamide[4]



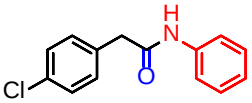
^{1}H NMR (500 MHz, $CDCl_3$): δ 2.39 (s, 3H), 3.72 (s, 2H7.08 (t, *J* = 7.5 Hz), 7.16-7.31 (m, 6H), 7.39-7.43 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.21, 44.49, 119.80, 124.37, 128.94, 129.56, 129.99, 131.29, 137.49, 137.64, 169.37.

2-(4-Metoxyphenyl)-*N*-phenylacetamide[4]



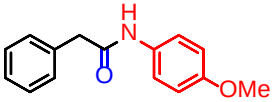
^{1}H NMR (500 MHz, $CDCl_3$): δ 3.62 (s, 2H), 3.78 (s, 3H), 6.88 (d, *J* = 8.5 Hz, 2H), 7.08 (t, *J* = 7.5 Hz, 1H), 7.19-7.28 (m, 4H), 7.42 (d, *J* = 8.5, 2H), 7.53 (br, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 43.73, 55.21, 114.51, 119.83, 124.30, 126.41, 128.85, 130.51, 137.74, 158.97, 169.73.

2-(4-Chlorophenyl)-*N*-phenylacetamide[4]



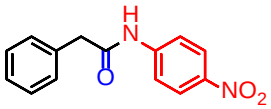
^{1}H NMR (500 MHz, $CDCl_3$): δ 3.70 (s, 2H), 7.10 (t, *J* = 7.5 Hz), 7.22-7.40 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 44.05, 104.63, 119.85, 124.64, 129.02, 129.32, 130.85, 132.85, 133.65, 137.7, 168.50.

N-(4-methoxyphenyl)-2-phenylacetamide[7]



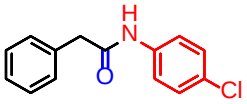
^{1}H NMR (500 MHz, $CDCl_3$): δ 3.66 (s, 2H), 3.70 (s, 3H), 6.74 (d, *J* = 8.5 Hz, 2H), 6.89 (s, 1H), 7.19-7.35 (m, 7H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 44.59, 55.36, 113.96, 121.67, 127.56, 129.14, 129.46, 130.52, 134.42, 156.44, 168.80.

N-(4-nitrophenyl)-2-phenylacetamide[7]



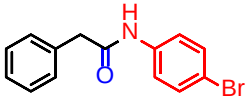
^{1}H NMR (500 MHz, $CDCl_3$): δ 3.75 (s, 2H), 7.28-7.39 (m, 5H), 7.54 (d, *J* = 11.5 Hz, 2H), 8.04 (br, 1H), 8.09 (d, *J* = 11 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 44.76, 119.29, 125.06, 127.98, 129.35, 129.48, 133.73, 143.53, 143.77, 170.06.

***N*-(4-chlorobenzyl)-2-phenylacetamide**[8]



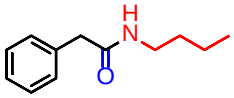
^{1}H NMR (400 MHz, d^6-DMSO): δ= 3.94 (s, 2H), 7.50-7.67 (m, 5H), 7.77 (d, *J*= 8.6 Hz, 2H), 7.92 (d, *J*= 8.6 Hz, 2H), 10.61 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): *δ*= 169.15, 136.14, 134.12, 129.55, 129.47, 129.38, 128.91, 127.85, 121.02, 44.77.

***N*-(4-bromobenzyl)-2-phenylacetamide**[8]



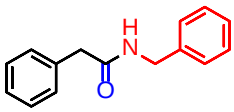
^{1}H NMR (400 MHz, d^6-DMSO): δ= 3.66 (s, 2H), 7.21-7.37 (m, 5H), 7.47 (d, *J*= 8.8 Hz, 2H), 7.61 (d, *J*= 8.8 Hz, 2H), 10.36 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): *δ*= 169.04, 136.67, 134.13, 131.93, 129.56, 129.32, 127.88, 121.34, 117.05, 44.81.

N-butyl-2-phenylacetamide[4,9]



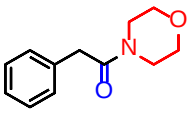
^{1}H NMR (500 MHz, $CDCl_3$): δ 0.85 (t, 7.5 *J* = Hz, 3H), 1.2 (m, 2H), 1.36 (m, 2H), 3.17 (q, *J* = 6.7 Hz, 2H), 5.56 (s, 2H), 5.34 (s, 1H), 7.24-7.37 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.73, 19.99, 31.55, 39.42, 43.96, 127.35, 129.05, 129.49, 135.05, 170.88.

N-benzyl-2-phenylacetamide[10]



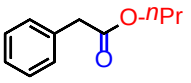
^{1}H NMR (500 MHz, $CDCl_3$): δ 3.61 (s, 2H), 4.39 (s, 2H), 5.74 (s, 1H), 7.16-7.34 (m, 10H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 43.59, 43.86, 127.44, 127.50, 128.68, 129.10, 129.49, 134.78, 138.14, 170.93.

1-morpholino-2-phenylethanone[4,11]



^{1}H NMR (500 MHz, $CDCl_3$): δ 3.41-3.44 (m, 2H), 3.46-3.48 (m, 2H), 3.63 (s, 4H), 3.75 (s, 2H), 7.23-7.32 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 41.04, 42.04, 46.88, 66.32, 66.93, 126.68, 128.10, 128.96, 134.78, 169.58.

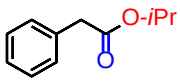
***O*-(*n*-propyl)-2-phenylacetamide**[12]



^{1}H NMR (400 MHz, $CDCl_3$): δ= 0.95 (t, *J*= 7.4 Hz, 3H), 1.68 (tq, *J*= 7.1 Hz, 7.4 Hz, 2H), 3.66 (s, 2H), 4.09 (t, *J*=6.7 Hz, 2H), 7.24-7.40 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 10.32, 21.93, 41.52, 66.55, 127.06, 128.52, 129.37, 134.22, 171.78;

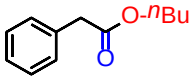
***O*-(*iso*-propyl)-2-phenylacetamide**[12]

^{1}H NMR (400 MHz, $CDCl_3$): δ= 1.26 (d, *J*= 6.3 Hz, 6H), 3.61 (s, 2H), 5.05 (septet, *J*= 6.3 Hz, 1H), 7.24-7.38 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.84, 41.72, 68.23, 126.91, 128.54, 129.22, 134.44, 171.17.



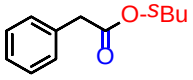
***O*-(*n*-butyl)-2-phenylacetamide**[12]

^{1}H NMR (400 MHz, $CDCl_3$): δ= 0.95 (t, *J*= 7.4 Hz, 3H), 1.38 (tq, *J*= 7.5 Hz, 7.4 Hz, 2H), 1.64 (tt, *J*= 7.5 Hz, 6.9 Hz, 2H), 3.65 (s, 2H), 4.13 (t, *J*= 6.7 Hz, 2H), 7.27-7.39 (m, 5H). ^{13}C NMR (100 MHz, CDCl3) δ 13.72, 19.15, 30.63, 41.57, 64.82, 127.01, 128.53, 129.32, 134.21, 171.76.



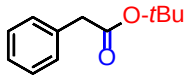
***O*-(*sec*-butyl)-2-phenylacetamide**[12]

^{1}H NMR (400 MHz, $CDCl_3$): δ= 0.88 (t, *J*= 7.4 Hz, 3H), 1.23 (d, *J*= 6.3 Hz, 3H), 1.49-1.68 (m, 2H), 3.63 (s, 2H), 4.84-4.93 (m, 1H), 7.24-7.39 (m, 5H). ^{13}C NMR (100 MHz, CDCl3) δ 19.05, 27.73, 41.57, 70.96, 127.02, 128.53, 129.32, 134.25, 171.71.



***O*-(*tert*-butyl)-2-phenylacetamide**[12]

^{1}H NMR (400 MHz, $CDCl_3$): δ= 1.47 (s, 9H), 3.56 (s, 2H), 7.23-7.40 (m, 5H). ^{13}C NMR (100 MHz, CDCl3) δ 28.12, 42.79, 80.86, 126.93, 128.56, 129.27, 134.84, 170.95.



4. Computational Data

Geometry optimizations were carried out with the Turbomole program package[13] coupled to the PQS Baker optimizer[14] via the BOpt package.[15] We used unrestricted ri-DFT-D3 calculations at the BP86 level,[16] in combination with the def2-TZVP basis set,[17] and a small (m4) grid size. All minima (no imaginary frequencies) and transition states (one imaginary frequency) were characterized by calculating the Hessian matrix. ZPE and gas-phase thermal corrections (entropy and enthalpy, 298 K, 1 bar) from these analyses were calculated. The nature of the transition states was confirmed by following the intrinsic reaction coordinate.

DFT calculations without using dispersion corrections strongly underestimate the metal-ligand interactions, as was clear from a series of test calculations. We therefore employed Grimme's version 3 (disp3) dispersion corrections. Used as such, the computed dispersion corrected metal-ligand association/dissociation energies to/from the non-solvated [Co(MeTAA)] catalyst are overestimated though. This is due to neglected dispersion interactions between the metal binding site of the catalyst and a solvent molecule in solution. We therefore used the Van der

Waals complex between [Co(MeTAA)] and a discrete toluene solvent molecule (interacting with catalyst at the metal binding site) as the energetic reference point in our calculations to prevent overestimation of the metal-ligand interactions as a result of such uncompensated dispersion forces. However, this approach also leads to an erroneous cancelation of translational entropy contributions to the computed free energies. This is because the translational entropy contributions to substrate/product association/dissociation are fully counterbalanced by the translational entropy contributions resulting from dissociation/association of the involved solvent molecule in the DFT calculated thermodynamics ([Co(MeTAA)(toluene)] + L ↔ [Co(MeTAA)(L)] + toluene). This is not realistic in comparison to actual solution phase chemistry, for which the translational entropy contributions associated with substrate/product association/dissociation steps can of course not be neglected. In solution the catalyst is completely surrounded by solvent molecules, leading to small translational entropy contributions to the toluene molecule association/dissociation steps. These are of little influence on the translational entropy contributions associated with substrate/product association/dissociation. Hence, the latter are not canceled by the former in toluene solution. Therefore we applied a translational entropy contribution of –26 cal mol^{-1} K^{-1} to the computed free energies of all substrate/product binding/dissociation steps in the catalytic cycle. A similar approach was used in a recently published paper from our group.[18]

Cartesian coordinates of the optimized geometries in xyz format and the enthalpies, free energies and SCF and ZPE-corrected energies are provided in a separate zip file.

Table S1 – Energies of the optimized geometries

SPECIES	$<S^2>$	SCF (au)	ZPE (au)	SCF+ZPE (au)	ENTHALPY (au)	FREE ENERGY (298) (au)	FREE ENERGY (298) (kcal)
N_2	0	-109.58042	0.00535	-109.5751	-109.57176	-109.5935	-68770.95899
EDA	0	-416.16004	0.10149	-416.0586	-416.04893	-416.09267	-261102.0904
Toluene	0	-271.67806	0.12397	-271.5541	-271.54672	-271.58553	-170422.4917
BzN2	0	-379.98073	0.11099	0.11949	0.07868	-379.8697	-379.86124
CO	0	-113.36534	0.00484	0.00815	-0.01428	-113.3605	-113.35719
Ketene from EDA (**F'**)	0	-420.01198	0.10135	0.11098	0.06713	-419.9106	-419.901
Ketene from BzN2 (**F**)	0	-383.83199	0.11083	0.11937	0.07814	-383.7212	-383.71262
CoMeTAA	0.7628	-2454.2354	0.38508	-2453.85	-2453.82584	-2453.89959	-1539845.229
CoMeTAA toluene adduct (**A**)	0.7637	-2725.9389	0.5109	-2725.428	-2725.3965	-2725.48625	-1710268.43
CoMeTAA CO adduct (**A'**)	0.7571	-2567.6345	0.39196	-2567.243	-2567.21588	-2567.29583	-1611002.443
CoMeTAA carbon bound EDA adduct (**B'**)	0.7604	-2870.4229	0.48783	-2869.935	-2869.9004	-2869.99786	-1800950.833
TS1-EDA	0.7714	-2870.4059	0.48518	-2869.921	-2869.88633	-2869.98265	-1800941.289
CoMeTAA carbene radical from EDA (**C'**)	0.7558	-2760.8477	0.4782	-2760.369	-2760.33714	-2760.4306	-1732196.34
TS2-EDA	0.7614	-2760.8185	0.47796	-2760.341	-2760.30903	-2760.39931	-1732176.705
CoMeTAA bridging carbene from EDA (**D'**)	0.765	-2760.8389	0.4796	-2760.359	-2760.32739	-2760.41827	-1732188.603
TS3-EDA	0.7581	-2874.211	0.48519	-2873.726	-2873.69117	-2873.78982	-1803330.324
CoMeTAA ketene adduct from EDA (**E'**)	0.7587	-2874.273	0.48782	0.52255	0.42472	-2873.785	-2873.75048
CoMeTAA_carbon_bound_BzN2_adduct (**B**)	0.761	-2834.2491	0.49781	0.53134	0.43633	-2833.751	-2833.71774
TS1-BzN_2	0.7685	-2834.2353	0.49556	-2833.74	-2833.70657	-2833.80045	-1778236.616
CoMeTAA carbene radical from BzN_2 (**C**)	0.7644	-2724.6744	0.48784	0.51902	0.42919	-2724.187	-2724.15534
TS2- BzN_2	0.7603	-2724.6486	0.48771	-2724.161	-2724.1305	-2724.21818	-1709472.704
CoMeTAA bridging carbene from BzN_2 (**D**)	0.7652	-2724.6629	0.48922	-2724.174	-2724.1429	-2724.23145	-1709481.031
TS3-BzN_2	0.7626	-2838.0377	0.49347	-2837.544	-2837.51013	-2837.60606	-1780624.672
CoMeTAA ketene adduct from BzN2 (**E**)	0.7588	-2838.0982	0.49753	0.53118	0.43574	-2837.601	-2837.56697

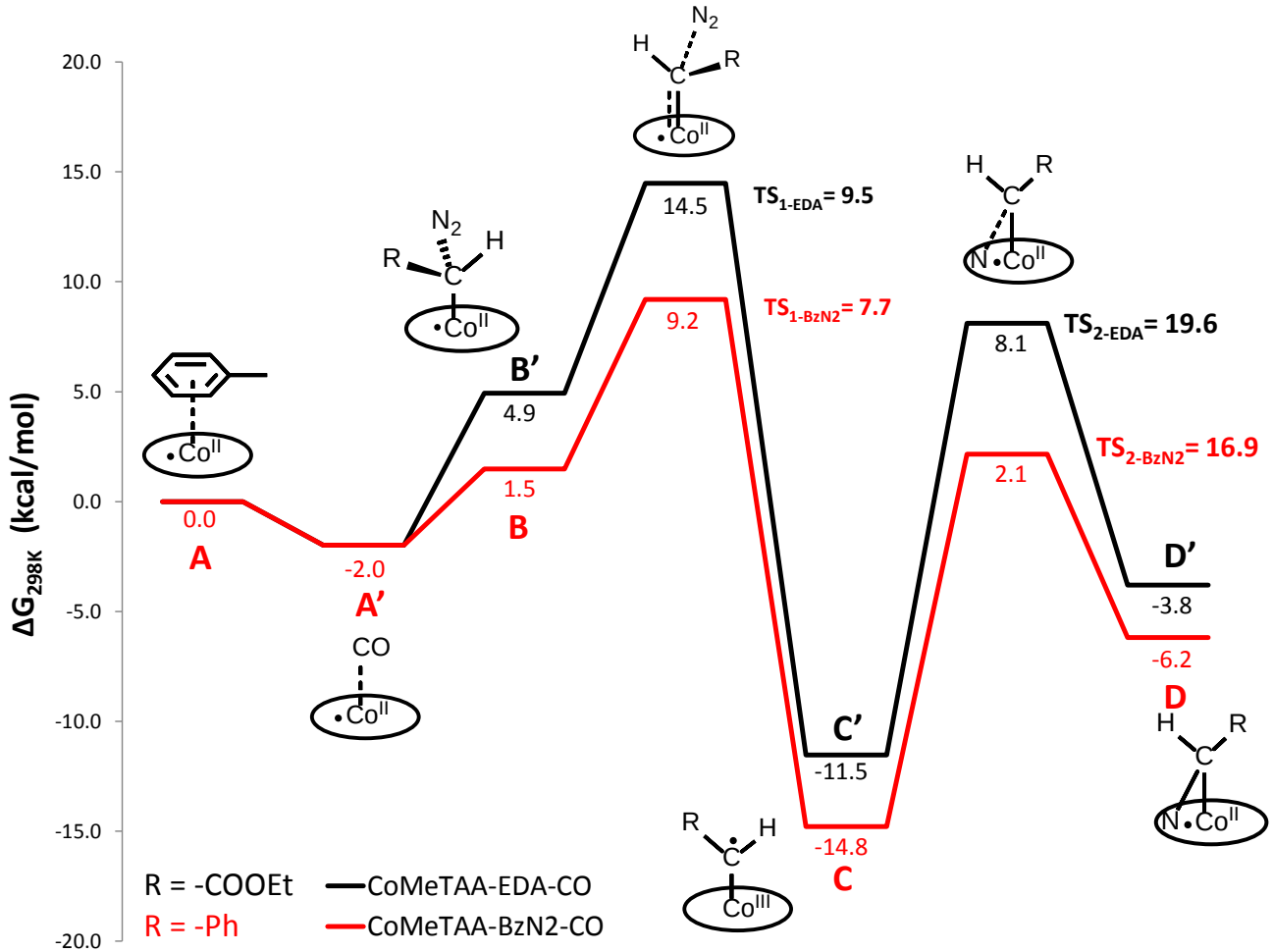


Figure S1 - Energy diagram of the activation of EDA and BzN_2 by [Co(MeTAA)] and generation of carbene radicals **C**/**C'** and bridging carbene **D**/**D'**. All energies relative to **A** (transition state barriers relative to the preceding intermediate also reported).

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