Reduction of Imines by Hydroxycyclopentadienyl Ruthenium Hydride: Intramolecular Trapping Evidence for Hydride and Proton Transfer Outside the Coordination Sphere of the Metal

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Supporting Information

General Experimental Information. All air-sensitive materials were manipulated under dry nitrogen in a glovebox or by standard high vacuum and Schlenk line techniques. Solvents were dried and distilled under nitrogen prior to use. *N*-benzylidenemethylamine, *N*-benzylideneaniline, *N*-methylbenzylamine, *N*-phenylbenzylamine, isopropylamine, aniline and *p*-isopropylaniline were used as obtained (Aldrich). 4-Amino-*N*-(benzylidene)aniline[1] and 4-(*N*-benzylamino)aniline[2] were prepared as described previously. {[2,5-Ph_2-3,4-Tol_2(η^5-C_4CO)]$_2$H}$Ru_2(CO)_4$(μ-H) (**1**),[3] [2,5-Ph_2-3,4-Tol_2(η^5-C_4COH)]$Ru(CO)_2H$ (**2**),[3] [2,5-Ph_2-3,4-Tol_2(η^4-C_4CO)$Ru(CO)_2$]$_2$ (**3**),[3] and [2,5-Ph_2-3,4-Tol_2(η^4-C_4CO)]$(CO)_2RuNH_2(CHMe_2)$ (**5**)[4] were synthesized according to literature procedures.

^{1}H and ^{13}C {H} NMR spectra were obtained on a Varian Unity 500 spectrometer. Solution IR spectra were measured on a Mattson Polaris FT-IR spectrometer using a 0.1 mm CaF_2 cell.

[2,5-Ph_2-3,4-Tol_2(η^5-C_4COH)]$Ru(CO)_2H$ (2).[3] A solution of **1** (11.4 mg, 0.01 mmol) in THF (0.45 mL) in a resealable NMR tube was degassed by three successive freeze-pump-thaw cycles and placed under 1 atm H_2 at –78 °C. The tube was sealed at –78 °C and heated at 90 °C in a constant temperature bath for 8 h to form **2**. The THF solvent was evaporated under vacuum and toluene-d_8 (0.5 mL) was added.

[2,5-Ph_2-3,4-Tol_2(η^4-C_4CO)]$(CO)_2RuNH_2Ph$ (7). Aniline (7.3 μL, 0.08 mmol) was added via syringe to a CD_2Cl_2 suspension of ruthenium cyclopentadienone dimer **3** (45.6 mg, 0.04 mmol) and the mixture was stirred for 30 min, until all the material dissolved. Solvent was evaporated under vacuum to afford **7** (45.4 mg, 85 %), mp 166–169 °C (dec). IR (CD_2Cl_2) 2017 (s), 1958 (s) cm^{-1}. ^{1}H NMR (CD_2Cl_2, 500 MHz) δ

2.22 (s, tolyl CH_3), 4.46 (s, NH_2), 6.55 (d, ^3J = 8.0 Hz, 2 H, aromatic), 6.92 (m, 5 H, aromatic), 6.99 (t, ^3J = 8.0 Hz, 2 H, aromatic), 7.03 (d, ^3J = 8.0 Hz, 4 H, aromatic), 7.19 (m, 6 H, aromatic), 7.53 (m, 4 H, aromatic). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 125 MHz) δ 21.17 (tolyl CH_3); 84.47 (C 3, 4 of Cp); 103.61 (C 2, 5 of Cp); 118.97, 124.86, 126.81, 128.06, 128.62, 128.87, 129.43, 131.01, 132.20, 133.09, 138.00, 146.97 (aromatic); 163.84 (C1 of Cp); 200.06 (CO). HRMS (ESI) $(M+H)^+$ Calcd for $C_{39}H_{31}NO_3{}^{102}Ru$, 664.1425; Found, 664.1401.

[2,5-Ph_2-3,4-Tol_2(η^4-C_4CO)](CO)$_2$Ru$NH_2C_6H_4$-p-$CHMe_2$ (10). *p*–Isopropylaniline (12 μL, 0.08 mmol) was added via syringe to a CD_2Cl_2 suspension of ruthenium cyclopentadienone dimer **3** (50 mg, 0.04 mmol) and the mixture was stirred for 30 min, until all the material dissolved. Solvent was evaporated under vacuum to afford **10** (48 mg, 77 %), mp 183–186 °C (dec). IR (CD_2Cl_2) 2016 (s), 1957 (s) cm^{-1}. ^1H NMR (C_6D_6, 500 MHz) δ 1.78 (s, 6 H, tolyl CH_3), 3.06 (t, ^3J = 5.8 Hz, NH), 3.69 (d, ^3J = 5.5 Hz, CH_2), 3.75 (br s, NH_2), 5.91 (d, ^3J = 8.5 Hz, 2 H, aromatic), 6.18 (d, ^3J = 8.5 Hz, 2 H, aromatic), 6.65 (d, ^3J = 8.0 Hz, 4 H, aromatic), 6.97-7.12 (m, 11 H, aromatic), 7.21 (d, ^3J = 8.5 Hz, 4 H, aromatic), 8.14 (d, ^3J = 8.5 Hz, 4 H, aromatic). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 125 MHz) δ 21.16 (tolyl CH_3); 24.01, 33.73, 84.44 (C 3, 4 of Cp); 103.45 (C 2, 5 of Cp); 118.90, 126.75, 127.18, 128.02, 128.59, 128.94, 131.05, 132.21, 133.13, 137.93, 144.56, 145.61 (aromatic); 163.88 (C1 of Cp); 200.14 (CO). MS (ESI) $(M+H)^+$ Calcd for $C_{42}H_{37}NO_3Ru$, 706.1895; Found, 706.1910.

Kinetics of Amine Exchange Reaction will be illustrated for the reaction of aniline with **6** which leads to displacement of *N*-phenylbenzylamine. A solution of aniline (12 mL, 132 mmol) in 30 mL CD_2Cl_2 was added via a gas-tight syringe to a

resealable NMR tube containing **6** (5.0 mg, 6.6 mmol, 0.02 M) in CD_2Cl_2 at – 40 °C. The tube was evacuated and nitrogen was readded. The tube was inserted into a NMR spectrometer having a probe temperature of 25 ° C. The disappearance of **6** was measured by integrating its tolyl methyl resonances at δ 2.18 and 2.24. The formation of free *N*-phenylbenzylamine and **7** was observed. Reactions were followed through three half-lives. All the kinetic runs were done with at least a 10-fold excess of aniline and followed pseudo-first order kinetics.

***T_1* Measurement of 2-H_2NCHMe_2.** At – 60 ºC, an inversion-recovery NMR experiment was carried out. An inversion-recovery experiment is a two pulse sequence that involves first a 180 º pulse then a relaxation time (varied) then a 90 º pulse and acquisition of a FID. The proton resonances height versus relaxation time were fit to an exponential fitting program provided by Varian software to determine the T_1 times.

DFT Computational methods. The model reactions of $(C_5H_4OH)Ru(CO)_2H$ (**2–H**) with both $H_2C{=}O$ and $H_2C{=}NCH_3$ were calculated. The geometries for all critical species (reactants, intermediates, transition states and products) were optimized using the hybrid density functional theory, B3LYP.[5] The effective core potential (ECP) of Hay and Wadt[6] and the corresponding basis set (augmented by an *f* function) were used for Ru; the 6-31++G(d,p) basis[7] was used for all other main group elements. Vibrational frequency calculations were subsequently carried out to verify the character of the optimized structures, and to obtain the zero-point vibrational energies. To estimate the effect of solvation, single point calculations with an implicit solvation model (IEF-PCM[8]) were carried out at the gas phase optimized structures; a dielectric constant of 7.58 was used for tetrahydrofuran (THF) as the solvent. Moreover, a complex between THF and **2-H** was computed to estimate the binding energy between THF and the Cp-OH group of **2-H**; this was motivated by the consideration that the aldehyde or imine has to replace a THF molecule in the first solvation shell of **2-H** during the reaction. Finally, a set of single point energy calculations at the MP2 level were carried out in the gas phase to obtain better estimates of energetics; a larger basis set, 6-311++G(d,p),[9] was used for the main group elements in these MP2 calculations. All calculations were performed with the Gaussian98 program.[10] The optimized structures for $H_2C{=}O$ and $H_2C{=}NCH_3$ reduction are shown in Figures S1-S4, and the energetics at various levels are summarized in Tables S1-S2 and in reaction energy diagrams shown in Figures S5 and S6.

The mechanism of $H_2C{=}O$ reduction and estimation of its activation enthalpy. As shown in Table S1 and Figure S5, the activation enthalpy for reduction of formaldehyde, calculated from the enthalpy difference between **C-O** (formaldehyde

hydrogen bonded to CpOH) and **TS-O** (transition state for formaldehyde reduction), is 9.1 kcal mol^{-1} at the MP2 level (including zero-point correction and solvation correction at the B3LYP level). However, we note that the formaldehyde has to replace a THF molecule bound to **2-H** to form **C-O**. Calculations show that the binding energy of THF in **2–H•THF** is 4.7 kcal mol^{-1} (including solvation correction) larger than that of formaldehyde in **C–O**. Therefore, the apparent activation enthalpy for formaldehyde reduction can be estimated to be 4.7 + 9.1 = 13.8 kcal mol^{-1}, which is close to the experimental value of 12 kcal mol^{-1}. **TS-O** can be classified as an early transition state since the CpO–H and the Ru–H distances are lengthened by only 0.1 Å in going from **C-O to TS-O**.

Different binding modes of the formaldehyde reduction products to $(C_5H_4OH)Ru(CO)_2$. Following the mechanism for reduction of formaldehyde in Figure 4, the direct product of reduction is **D-O** (-10.7 kcal mol^{-1}), which has a hydrogen bond between the O-H of methanol and the cyclopentadienone carbonyl and an agostic interaction between a C-H bond of methanol and Ru. Breaking the agostic interaction gives intermediate **E-O** (-2.7 kcal mol^{-1}), which retains the hydrogen bond between the O–H of methanol and the cyclopentadienone carbonyl; this implies a strong agostic interaction in **D–O** of about 8.0 kcal mol^{-1}. Breaking the hydrogen bond gives intermediate **A-H** (+0.2 kcal mol^{-1}), the unsaturated cyclpentadienone ruthenium dicarbonyl intermediate, which has no interaction with methanol; this implies a hydrogen bond strength in **E–O** (and **D-O**) of about 2.9 kcal mol^{-1}. Coordination of the alcohol to ruthenium gives an alcohol complex **F–O** (-19.9 kcal mol^{-1}), which has an internal hydrogen bond from the O–H of coordinated methanol to the cyclopentadienone

carbonyl. Combination of ruthenium hydride **2–H** with unsaturated intermediate **A-H** produces the diruthenium bridging hydride **1–H** (-24.8 kcal mol^{-1}). In agreement with the great stability calculated for **1–H**, the products of the reduction of aldehydes by **2** are alcohol and diruthenium bridging hydride **1**.

How facile is the conversion of the direct product of reduction **D-O**, which has both a hydrogen bond and an agostic interaction linking methanol to the Ru complex, to the alcohol complex **F–O** or to the thermodynamic product **1–H**? Considering the significant structural changes, we only estimated the energy cost associated the isomerization to alcohol complex **F–O** with breaking the agostic interaction between Ru and the CH to give **D–O**. In other words, we assume that the isomerization occurs through breaking the agostic interaction followed by a rapid coordination of the oxygen lone pair to the metal; thus the strength of the agostic interaction (energy difference between **D–O** and **E–O** = 7.0 kcal mol^{-1}) gives an estimate for the energy bottleneck of the isomerization. For conversion of **D–O** to the thermodynamic product **1–H**, the reaction might involve trapping of **E–O** by metal hydride **2–H** (energy bottleneck = energy difference between **D–O** and **E–O** = 7.0 kcal mol^{-1}). Alternatively, formation of **1–H** might involve breaking both the agositic and hydrogen bonding interactions in **D–O** to form unsaturated intermediate **A–H,** which is then trapped by **2–H** (energy bottleneck = energy difference between **D–O** and **A–H** = 10.9 kcal mol^{-1}).

The mechanism for reduction of $H_2C{=}NCH_3$ (Figures 4S and 6S and Table S2) is similar to that for reduction of $H_2C{=}O$, but there are significant differences. In contrast to the early transition state seen for $H_2C{=}O$ reduction, the transition state for $H_2C{=}NCH_3$ reduction **TS-N** shows that the CpO–H hydrogen has been substantially transferred to N

(1.364 Å O---H, 1.134 Å H---N) while the Ru–H distance lengthened by only 0.1 Å in going from **C-N** to **TS-N**. The activation enthalpy for reduction of $H_2C{=}NCH_3$ calculated from the enthalpy difference between **C-N** ($H_2C{=}NCH_3$ hydrogen bonded to CpOH) and **TS-N** (transition state for $H_2C{=}NCH_3$ reduction) is 4.8 kcal mol^{-1} at the MP2 level (including zero-point correction and solvation correction at the B3LYP level). We noted that $H_2C{=}NCH_3$ has to replace a THF molecule bound to **2-H** to form **C-N**. This is a small difference since calculations show that the binding energy of THF in **2-H•THF** is 0.3 kcal mol^{-1} (including solvation correction) smaller than that of $H_2C{=}NCH_3$ in **C–N**. The calculated activation enthalpy for $H_2C{=}NCH_3$ reduction starting from **2-H•THF** (4.8 - 0.2 = 4.5 kcal mol^{-1}) is 9.3 kcal mol^{-1} lower than that for formaldehyde reduction. This is consistent with the faster rates observed for reaction of **2** with imines compared to aldehydes.

Different binding modes of the $H_2C{=}NCH_3$ reduction products to $(C_5H_4OH)Ru(CO)_2$. Following the mechanism for reduction of $H_2C{=}NCH_3$ in Figure 5, the direct product of reduction is **D–N** (-17.3 kcal mol^{-1}), which has a hydrogen bond between the N–H of dimethylamine and the cyclopentadienone carbonyl and an agostic interaction between a C-H bond of dimethylamine and Ru. Breaking the agostic interaction gives intermediate **E-N** (-4.0 kcal mol^{-1}), which retains the hydrogen bond between the N–H of dimethylamine and the cyclopentadienone carbonyl; this implies a strong agostic interaction in **D–N** of about 9.3 kcal mol^{-1}. Breaking the hydrogen bond gives intermediate **A-H** (–2.2 kcal mol^{-1}), which has no interaction with methanol; this implies a hydrogen bond strength in **E–N** (and **D–N**) of about 2.9 kcal mol^{-1}. Coordination of dimethylamine to ruthenium gives amine complex **F-N** (-41.5 kcal

mol^{-1}), which has an internal hydrogen bond from the N–H of coordinated dimethylamine to the cyclopentadienone carbonyl. Combination of ruthenium hydride **2–H** with unsaturated intermediate **A-H** produces the diruthenium bridging hydride **1–H** (-27.0 kcal mol^{-1}). In contrast to aldehyde reduction by **2** whish leads to diruthenium bridging hydride **1**, imine reduction leads to the formation of more stable amine complexes.

The barrier for conversion of the direct reduction product **D-N**, which has both a hydrogen bond and an agostic interaction linking dimethylamine to the Ru complex, to the amine complex **F–N** can be estimated from the energy cost associated with breaking the agostic interaction between Ru and the CH to give **D–N**, which then rapidly coordinates nitrogen to the metal to give **F–N**. The strength of the agostic interaction is estimated from the energy difference between **D–N** and **E–N** = 13.3 kcal mol^{-1}.

Figure S1. Optimized structures of **2–H** and **2–H•THF**, and **1** at the B3LYP level (see footnote of Table S1). The distances are given in Angstroms, and the angles are in degrees.

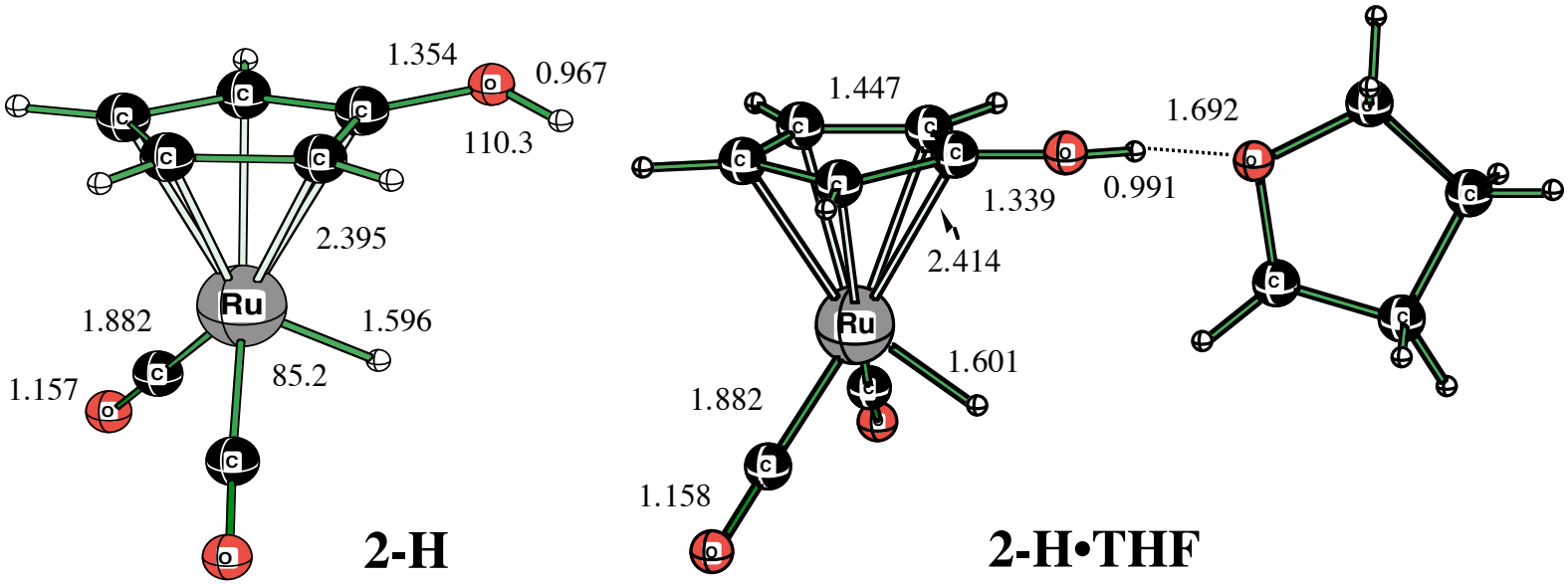
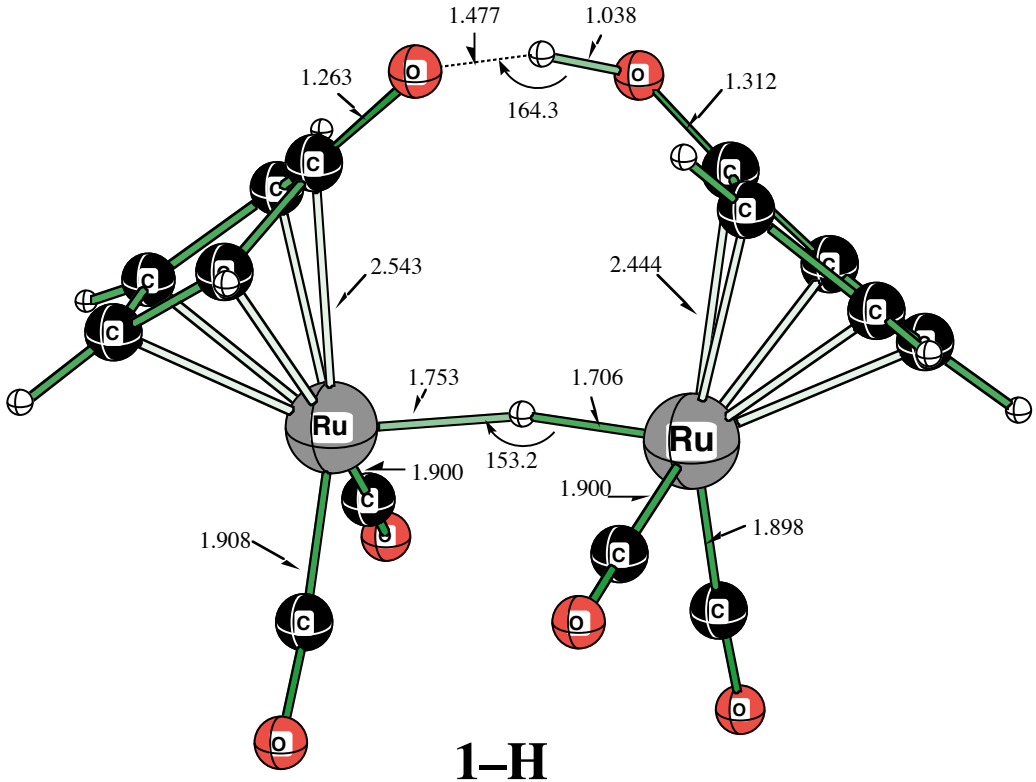


Figure S2. Optimized structure of **1–H** at the B3LYP/BSII+PCM level. The binding energy of **1–H** relative to **2–H** + **A–H** without ZPE is -25.0 kcal mol^{-1}. The distances are given in Angstroms, and the angles are in degrees.



1–H

Figure S3. Optimized geometries for critical structures involved in the reduction of formaldehyde by the model compound **2–H** (all substituents on the Cp ring (Ph, Tol) were replaced by hydrogens). The structures were optimized at the B3LYP level with double-zeta plus polarization quality basis set (see footnote of Table S1). The distances are given in Angstroms, and the angles are in degrees.

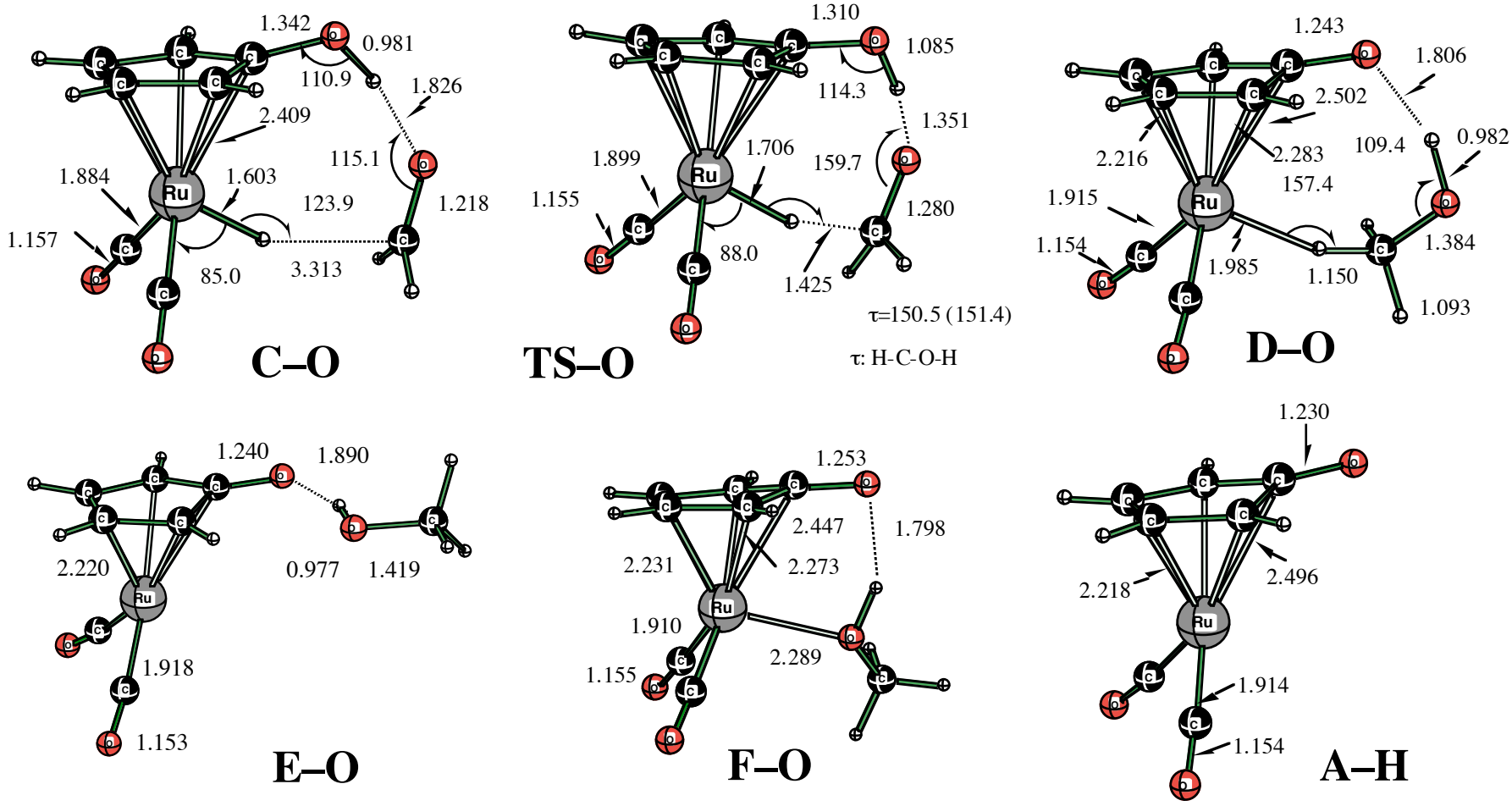


Table S1. Energetics of critical structures (reactant, intermediates, transition states and product) for the reduction of formaldehyde by model Ru compound **2–H**.

	B3LYP/BSII[b]	B3LYP/BSII[b] + PCM[c]	MP2/BSIII[b] + PCM[c]
2–H	*-589.98578*	*-589.98579*	*-588.44754*
H_2C=O	*-114.50977*	*-114.51028*	*-114.24226*
C–O	-6.7	-2.4	-5.3
TS–O	0.7	2.7	3.8
D–O	-7.6	-6.3	-10.7
A–H + CH_3OH	1.3	-2.0	0.2
E–O	-4.9	-3.7	-2.7
F–O	-16.5	-14.9	-19.9
2–H•THF + H_2C=O	-11.5	-7.1	-10.0

a. For reactant molecules (**2–H**, formaldehyde), the total energies are given in hartree in italics. For all other species, relative energies are given in kcal/mol. Zero-point energy corrections were included for all relative energies. For the Ru compound **2–H**, all substituents on the Cp ring (Ph, Tol) were replaced by hydrogens. For structures, refer to Figures S1-S3.

b. BSII: Hay-Wadt Lanl2dz basis + f polarization function on Ru, 6-31++G(d,p) on all other main group elements. BSIII: Hay-Wadt Lanl2dz basis + f polarization function on Ru, 6-311++G(d,p) on all other main group elements. In the MP2 calculations, geometries optimized at the B3LYP/BSII calculations were used.

c. In PCM calculations, the Pauling set of radii was used; the solvent was THF. PCM calculations were only carried out at the B3LYP/II level at gas phase optimized structures.

Table S2. Energetics of critical structures (reactant, intermediates, transition states and product) for the reduction of $H_2C{=}NCH_3$ by Ru compound **2–H**.[a]

	B3LYP/BSII[b]	B3LYP/BSII[b] + PCM[c]	MP2/BSIII[b] + PCM[c]
2-H	*-589.98578*	*-589.98579*	*-588.44754*
$H_2C{=}NCH_3$	*-133.95333*	*-133.95507*	*-133.57246*
C–N	-10.3	-5.6	-10.3
TS–N	-1.6	1.5	-5.5
D–N	-10.8	-7.5	-17.3
A-H + $(CH_3)_2NH$	-0.2	-2.8	-2.2
E–N	-3.8	-0.8	-4.0
F–N	-29.9	-24.5	-41.5
2–H•THF + $H_2C{=}NCH_3$	-11.5	-7.1	-10.0

a. For notations, see footnotes of Table S1. For structures, refer to Figure S1, S-2, and S4.

Figure S4. Optimized geometries for critical structures involved in the reduction of CH_2=NCH_3 by the model compound **2–H** (all substituents on the Cp ring (Ph, Tol) were replaced by hydrogens). The structures were optimized at the B3LYP level with double-zeta plus polarization quality basis set (see footnote of Table S1). The distances are given in Angstroms, and the angles are in degrees.

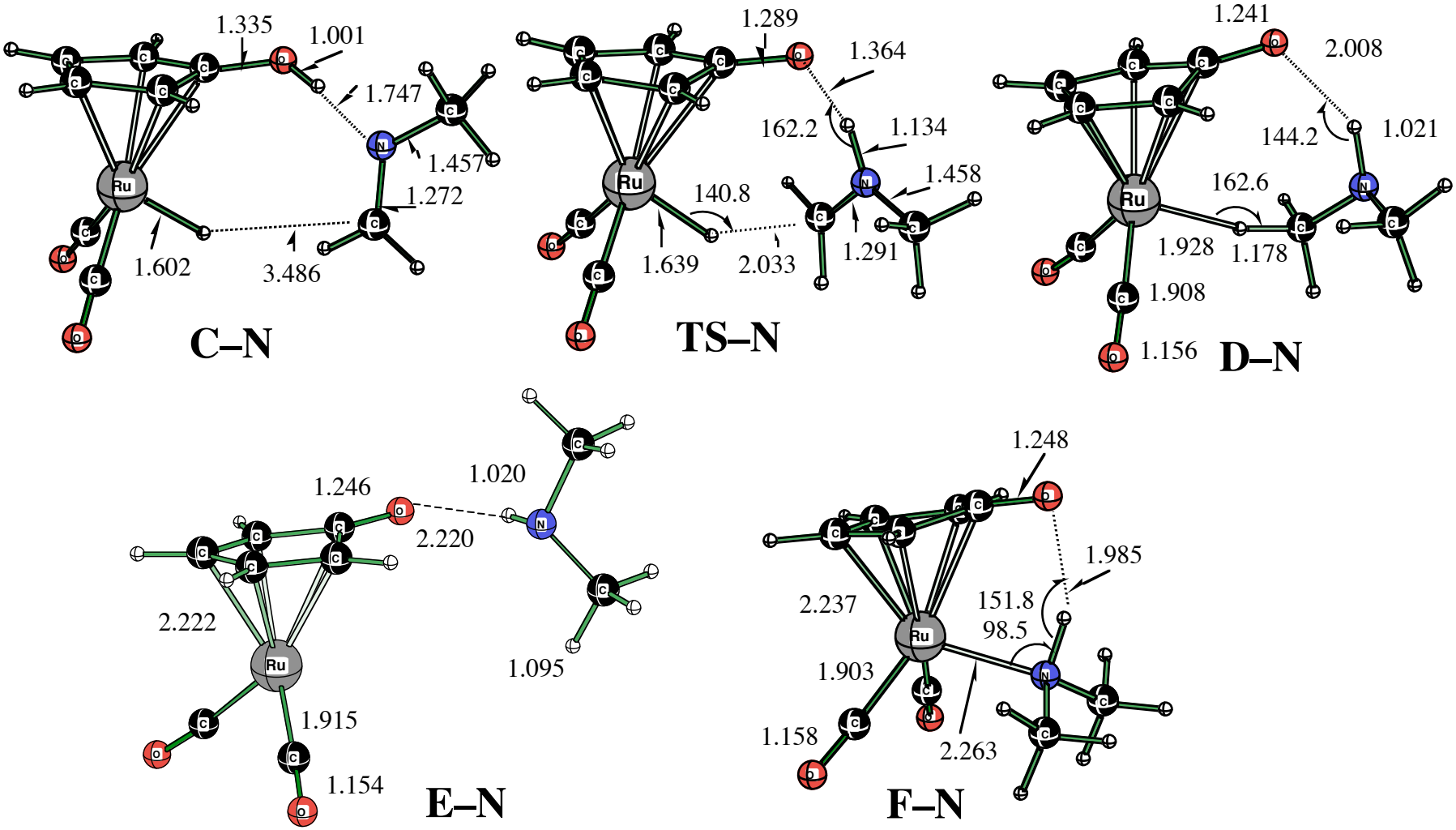


Figure S5. Schematic potential energy surface (based on the MP2 results shown in Table S1) for the reduction of formaldehyde by the model compound **2–H**. To be consistent during the entire process, the energy of a THF molecule infinitely apart from the calculated structure is included for all species after isolated reactant and **2–H** (positive horizontal axis). The energy level shown for **1–H** of -24.8 kcal mol^{-1} is actually for **1-H** + CH_3OH relative to **2-H** + **2-H** + H_2C=O.

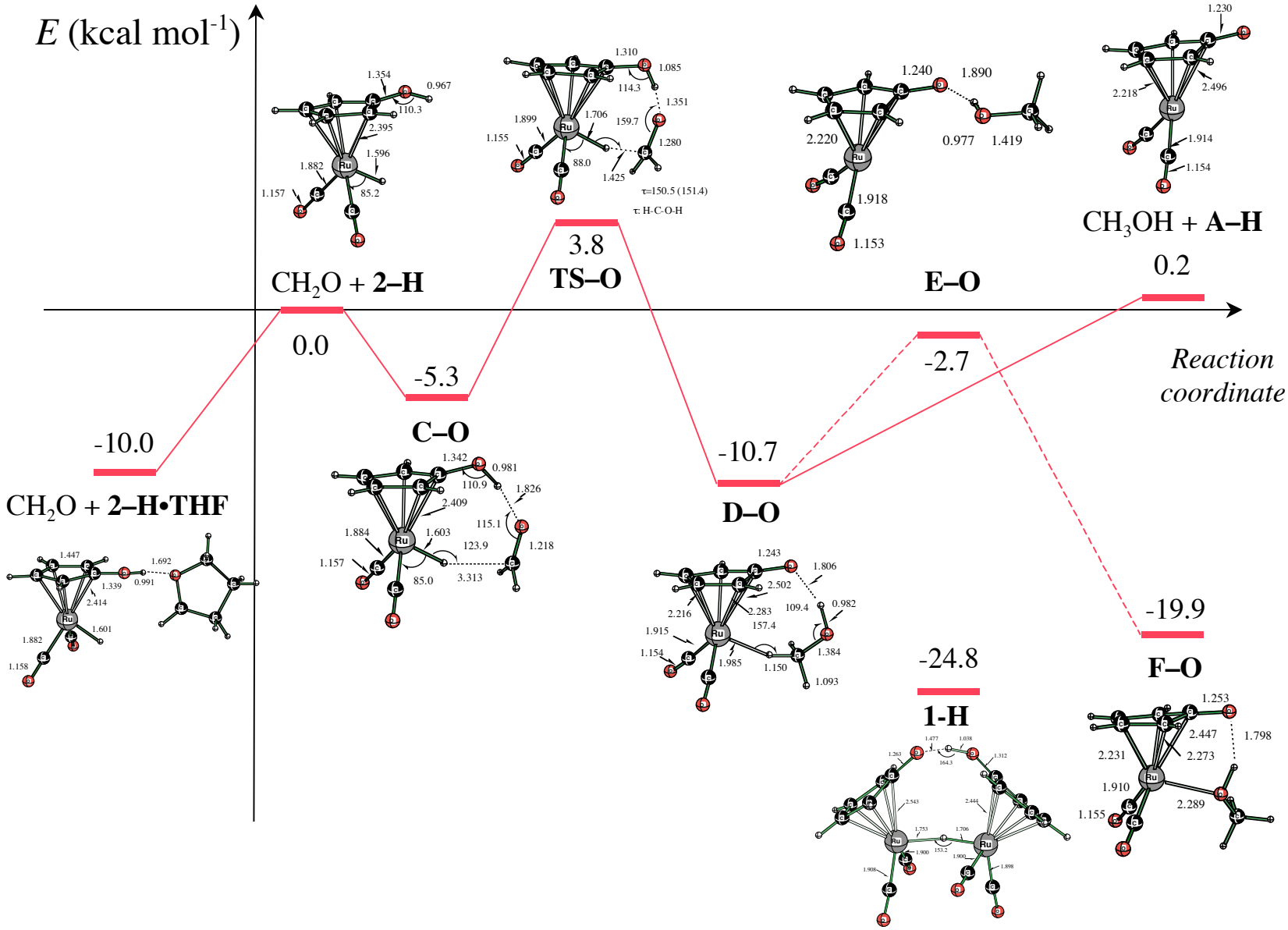


Figure S6. Schematic potential energy surface (based on the MP2 results shown in Table S1) for the reduction of formaldehyde by the model compound **2–H**. To be consistent during the entire process, the energy of a THF molecule infinitely apart from the calculated structure is included for all species after isolated reactant and **2–H** (positive horizontal axis). The energy level shown for **1–H** of -27.2 kcal mol^{-1} is actually for **1-H** + $NH(CH_3)_2$ vs. **2-H** + **2-H** + $H_2C{=}NCH_3$.

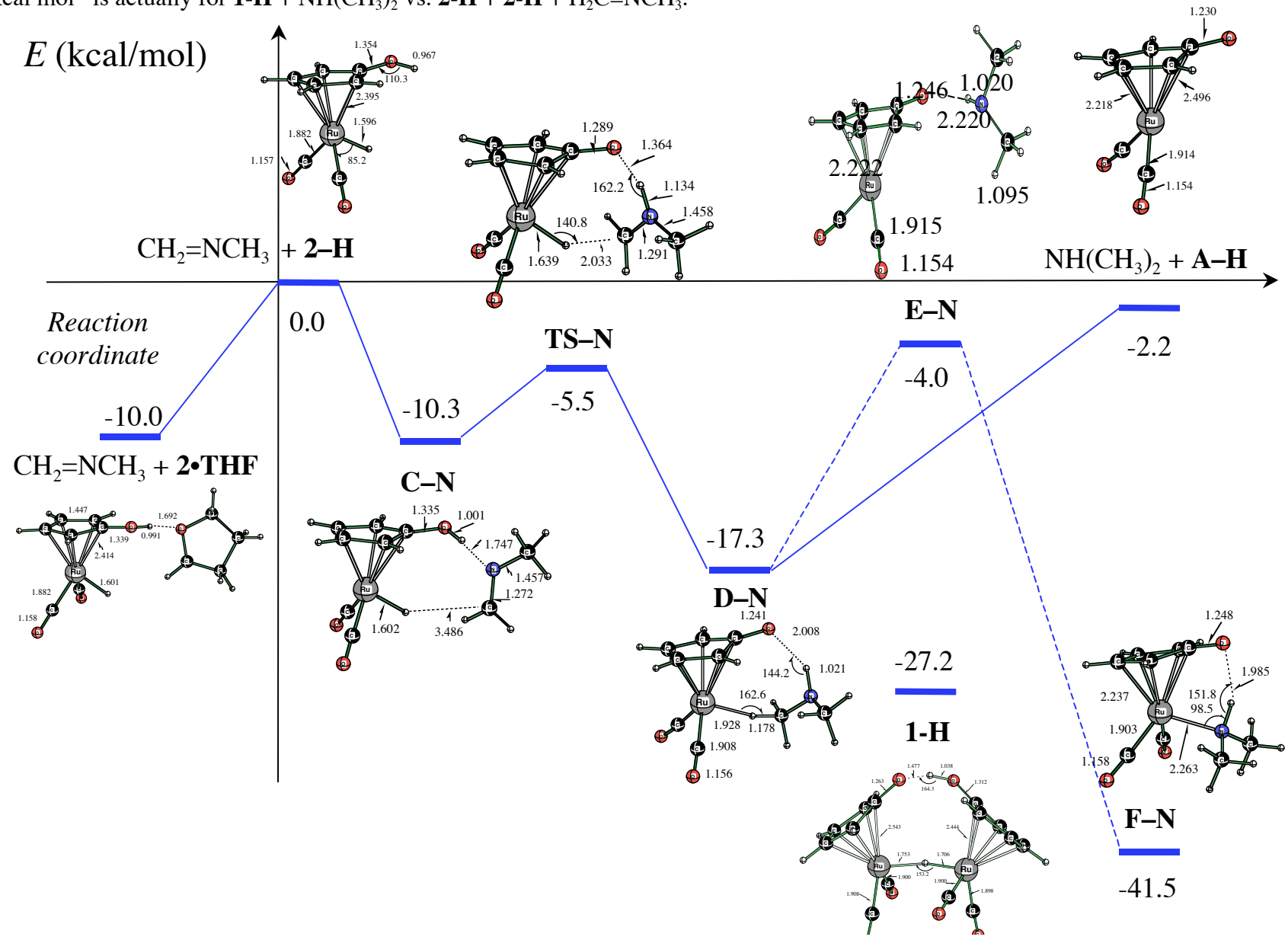


Table S3. xyz Coordinates for Species Optimized at B3LYP/BSII level

2-H

Ru -0.34278 -0.00097 -0.10222
C 2.03436 0.02153 -0.38910
C 1.62823 1.13952 0.39057
C 1.62521 -1.17252 0.27637
C 1.07986 -0.78203 1.55821
C 1.08558 0.62825 1.62902
O 2.71722 0.14635 -1.55136
H 2.70864 -0.68897 -2.03761
H -0.47997 0.02905 -1.69237
C -1.67036 -1.33251 -0.17116
C -1.62837 1.37337 -0.14274
O -2.46627 -2.17116 -0.21885
O -2.39791 2.23640 -0.17300
H 1.81406 -2.18417 -0.05727
H 1.81517 2.17392 0.13986
H 0.73166 -1.46165 2.32367
H 0.74138 1.22813 2.45987

$H_2C=O$

C 0.00000 0.00000 -0.53175
O 0.00000 0.00000 0.67794
H 0.00000 0.94137 -1.11652
H 0.00000 -0.94137 -1.11652

CH_3OH

C -0.04655 0.66698 0.00000
O -0.04655 -0.75809 0.00000
H -1.09352 0.97743 0.00000
H 0.44017 1.07936 0.89446
H 0.44017 1.07936 -0.89446
H 0.86489 -1.07331 0.00000

A-H

Ru 0.30470 0.00001 -0.18862
C -2.18423 0.00002 -0.38036
C -1.58653 -1.17164 0.32094
C -1.58659 1.17151 0.32128
C -0.94250 0.72502 1.49564
C -0.94246 -0.72545 1.49543
O -2.85967 0.00015 -1.40865
C 1.62171 1.38879 -0.20861
C 1.62182 -1.38866 -0.20869
O 2.37982 2.25592 -0.13128
O 2.38002 -2.25572 -0.13138
H -1.77323 2.19996 0.04226
H -1.77310 -2.20001 0.04160
H -0.53467 1.34167 2.28626
H -0.53458 -1.34232 2.28586

C–O

Ru -0.67008 0.09840 -0.02216
C 1.18992 -1.43168 -0.05633
C 0.99967 -0.88174 1.25121
C -0.01278 -2.09326 -0.44042
C -0.89816 -2.09198 0.70221
C -0.28081 -1.34983 1.73411
O 2.28130 -1.37649 -0.83452
H 2.89994 -0.68158 -0.52237
H 0.13060 1.00857 -1.07033
C -2.12747 0.32098 -1.19538
C -1.05303 1.70847 0.87282
O -3.01167 0.43668 -1.93260
O -1.26127 2.69869 1.43645
H -0.16178 -2.61291 -1.37625
H 1.74360 -0.34657 1.82507
H -1.86312 -2.57670 0.75277
H -0.68603 -1.16246 2.71898
O 3.80199 0.87587 -0.21143
C 3.31130 1.86751 -0.71971
H 3.80951 2.84960 -0.63623
H 2.35637 1.82337 -1.27113

D–O

Ru 0.47601 -0.01169 0.00261
C -1.77594 -1.10075 -0.02067
C -0.81707 -1.57718 -1.04350
C -1.02220 -1.19798 1.25103
C 0.16153 -1.95083 1.02739
C 0.28902 -2.18491 -0.39035
O -2.88298 -0.56852 -0.21105
C 1.53334 0.82081 1.36442
C 1.76120 0.38697 -1.35885
O 2.17422 1.24528 2.22462
O 2.54186 0.54051 -2.19497
H -1.41354 -0.88876 2.21095
H -1.03120 -1.61046 -2.10341
H 0.84490 -2.31830 1.78194
H 1.08127 -2.75536 -0.85745
O -2.61056 2.13341 0.15332
C -1.46093 2.30525 -0.59706
H -2.95049 1.22062 0.02556
H -0.59743 1.64221 -0.22572
H -1.58404 2.08873 -1.66519
H -1.08798 3.32194 -0.45140

TS–O

Ru 0.46720 -0.06875 0.00458
C -1.78796 -0.87722 -0.04458
C -0.94998 -1.60973 -0.95879
C -1.19688 -1.00487 1.26906
C -0.10226 -1.92782 1.17235
C 0.05183 -2.30030 -0.19540
O -2.83183 -0.16415 -0.38600
H -2.72795 0.89338 -0.16658
H -0.22008 1.46145 -0.30362
C 1.58203 0.76642 1.29565
C 1.74552 0.18516 -1.37843
O 2.24488 1.24623 2.11016
O 2.50767 0.30076 -2.23820
H -1.59268 -0.56207 2.17253
H -1.13265 -1.69920 -2.02062
H 0.49390 -2.29320 1.99784
H 0.77937 -3.00091 -0.58177
O -2.32232 2.16245 0.05841
C -1.21157 2.46631 -0.49975

H -1.13464 2.43962 -1.59884
H -0.59388 3.23571 -0.01580

F–O

Ru -0.27886 -0.21079 0.00638
C 2.15713 0.01629 -0.00816
C 1.57996 -0.28657 1.31580
C 1.63538 -1.05183 -0.88428
C 0.99307 -2.04197 -0.08321
C 0.95708 -1.56968 1.27201
O 2.71798 1.07906 -0.36464
C -1.56146 -0.72374 -1.31206
C -1.63620 0.15551 1.29419
O -2.30088 -1.10185 -2.11476
O -2.42107 0.32267 2.12675
H 1.84373 -1.12065 -1.94358
H 1.74441 0.31453 2.20005
H 0.62052 -3.00066 -0.41968
H 0.55518 -2.11917 2.11323
O 0.17399 1.88614 -0.79097
C -0.36869 3.10049 -0.25339
H 0.00630 3.95656 -0.82371
H -1.45281 3.04520 -0.36087
H -0.11019 3.21857 0.80512
H 1.16522 1.90117 -0.74789

E–O

Ru 0.87747 0.11618 -0.15606
C -1.14629 -1.30255 0.09298
C 0.14916 -2.01981 0.15376
C -1.01083 -0.20977 1.09099
C 0.14686 -0.44625 1.86332
C 0.87065 -1.56004 1.28128
O -2.05707 -1.46296 -0.73237
C 1.24741 1.96686 0.18471
C 2.59056 -0.18766 -0.95561
O 1.46439 3.05810 0.48816
O 3.64112 -0.43932 -1.36159
H -1.77687 0.53487 1.26778
H 0.40404 -2.86246 -0.47464
H 0.45265 0.09300 2.75062
H 1.78554 -1.97991 1.67882

H -3.38122 -0.14427 -0.44987
O -3.82800 0.64266 -0.08178
C -5.09966 0.80361 -0.69036
H -5.56051 1.69423 -0.25366
H -5.02233 0.95337 -1.77725
H -5.76065 -0.05489 -0.50113

2-H-THF

Ru -1.52453 0.18685 -0.03261
C 0.02855 -1.65905 -0.12098
C -0.19601 -1.23308 1.22736
C -1.22956 -2.02687 -0.68408
C -2.21332 -1.98757 0.37457
C -1.58241 -1.50138 1.54189
O 1.18647 -1.72617 -0.78911
H 1.90293 -1.23235 -0.31425
H -0.47065 1.02215 -0.90115
C -2.80040 0.82611 -1.26011
C -1.66171 1.73450 1.02634
O -3.57706 1.19970 -2.03338
O -1.71917 2.67995 1.69386
H -1.37326 -2.39795 -1.68893
H 0.57031 -0.91334 1.91979
H -3.25016 -2.27974 0.28255
H -2.04709 -1.35448 2.50720
O 3.13277 -0.28462 0.35912
C 3.02965 1.12839 0.03934
C 4.49105 -0.74843 0.14156
C 4.26157 1.43873 -0.80897
C 5.31491 0.50072 -0.19441
H 4.82611 -1.26256 1.04744
H 4.47828 -1.46521 -0.68873
H 3.02922 1.69736 0.97809
H 2.07613 1.28721 -0.47057
H 5.73261 0.94244 0.71738
H 4.54513 2.49401 -0.76271
H 4.07793 1.17907 -1.85766
H 6.14377 0.27880 -0.87242

1-H
Ru 1.67603 -0.37047 0.08889
C 1.96619 2.00051 -0.61069
C 2.35381 1.75289 0.76994

C 2.71111 1.07706 -1.44440
C 3.69953 0.42366 -0.60909
C 3.48096 0.84109 0.75333
O 1.06080 2.86626 -1.05276
H 0.31182 3.11635 -0.31154
H 0.02542 -0.16298 -0.33016
C 1.71068 -2.03263 -0.82119
C 1.32178 -1.17127 1.76783
O 1.77260 -3.05303 -1.40938
O 1.16291 -1.62955 2.84335
H 2.64340 1.03286 -2.52134
H 1.96309 2.28631 1.62406
H 4.48383 -0.23671 -0.95155
H 4.07305 0.54948 1.60954
O -0.62186 3.02061 0.69324
C -1.61915 2.21260 0.52009
Ru -1.71055 -0.25835 -0.12310
C -2.22287 1.33125 1.53141
C -2.31104 1.89881 -0.73958
C -3.42065 0.75271 0.97336
C -3.47613 1.09913 -0.43047
C -1.77957 -1.90623 0.82275
C -1.79712 -1.12209 -1.80715
O -1.88623 -2.91167 1.43187
O -1.89058 -1.61421 -2.87555
H -1.92872 1.31023 2.57111
H -2.09946 2.37515 -1.68654
H -4.16430 0.18058 1.51101
H -4.27549 0.84431 -1.11239

$H_2C{=}NCH_3$

N 0.13921 -0.53587 -0.00007
C 1.18526 0.18234 -0.00012
H 1.16507 1.28389 0.00017
H 2.16403 -0.29920 0.00051
C -1.15013 0.13522 0.00006
H -1.71811 -0.18751 -0.87961
H -1.71740 -0.18694 0.88029
H -1.07885 1.23552 -0.00050

$NH(CH_3)_2$

H 0.00000 1.34374 0.50154
N 0.00000 0.56145 -0.14636
C -1.21849 -0.22274 0.02035
H -1.28208 -0.96854 -0.78076
H -1.27808 -0.76259 0.98438
H -2.09238 0.43062 -0.06425
C 1.21849 -0.22274 0.02035
H 1.28208 -0.96854 -0.78076
H 2.09238 0.43062 -0.06425
H 1.27808 -0.76259 0.98438

C–N

Ru 1.01130 0.12476 -0.03040
C -0.77999 -1.49978 -0.03154
C 0.46627 -2.11295 -0.36122
C -0.63562 -0.87485 1.25068
C 0.65518 -1.25800 1.77974
C 1.32817 -2.01623 0.79527
O -1.85484 -1.54020 -0.82258
H 0.17615 0.94045 -1.12780
C 1.29543 1.78926 0.79646
C 2.47158 0.37031 -1.19450
O 1.44150 2.81326 1.31938
O 3.35918 0.49963 -1.92636
H -1.41319 -0.34751 1.78519
H 0.65997 -2.66685 -1.26889
H 1.03134 -1.00575 2.76173
H 2.31386 -2.45089 0.88611
N -3.63416 0.49336 -0.35838
C -3.19447 1.66076 -0.60522
H -2.13594 1.79317 -0.82925
H -3.83975 2.54897 -0.60128
C -5.04848 0.30791 -0.06236
H -5.47513 -0.38534 -0.79468
H -5.14823 -0.15874 0.92321
H -5.61680 1.24846 -0.07826
H -2.52562 -0.83881 -0.57729

TS–N

Ru -0.74423 -0.10290 0.03154
C 0.98243 1.69249 -0.02842
C -0.02300 1.79639 -1.07470
C 0.23786 1.62939 1.21672
C -1.14152 1.93969 0.94675
C -1.30073 2.04498 -0.46145
O 2.26032 1.61078 -0.17613
H 2.84868 0.40785 -0.43589
H 0.45210 -1.19859 -0.20427
C -1.35055 -1.24122 1.40945
C -1.73205 -1.02868 -1.28340
O -1.70583 -1.92223 2.27701
O -2.32942 -1.57636 -2.11244
H 0.69094 1.54906 2.19568
H 0.19855 1.87288 -2.13110
H -1.91773 2.08959 1.68509
H -2.21888 2.28857 -0.97913
N 3.06795 -0.70403 -0.45893
C 2.23650 -1.40303 -1.15753
H 1.74973 -0.94046 -2.00718
H 2.13452 -2.47559 -1.00706
C 3.73060 -1.24831 0.72045
H 4.76516 -0.89749 0.74763
H 3.21720 -0.88612 1.61764
H 3.71247 -2.34152 0.70875

D–N

Ru -0.64700 -0.10143 0.01887
C 0.95470 1.84850 0.00490
C -0.22305 1.95319 -0.89091
C 0.36451 1.48931 1.31611
C -1.04303 1.69348 1.26312
C -1.40467 1.98397 -0.09986
O 2.15564 1.88683 -0.30619
H 3.10744 0.18299 -0.78128
H 0.91823 -1.03304 -0.61129
C -1.07331 -1.43475 1.31567
C -1.80454 -0.88057 -1.28480
O -1.35323 -2.18480 2.14933
O -2.54260 -1.28374 -2.07760
H 0.94550 1.30131 2.20918
H -0.16041 2.17320 -1.94852

H -1.72987 1.67317 2.09917
H -2.40521 2.21224 -0.44363
N 3.06673 -0.83516 -0.71302
C 1.86296 -1.34251 -1.24329
H 1.67607 -0.97775 -2.25356
H 1.82617 -2.43522 -1.21405
C 3.40572 -1.29146 0.62632
H 4.34526 -0.83115 0.94104
H 2.62767 -1.03830 1.36889
H 3.53603 -2.37932 0.62711

F–N

Ru 0.11699 -0.40995 0.00135
C -2.12594 0.68404 -0.00726
C -1.82995 -0.18978 -1.16267
C -1.83100 -0.17341 1.16086
C -1.68069 -1.52819 0.72374
C -1.67981 -1.53834 -0.70626
O -2.32619 1.91595 -0.01616
C 1.31369 -0.96481 1.37237
C 1.31228 -0.97948 -1.36470
O 1.99091 -1.34065 2.23292
O 1.98788 -1.36430 -2.22255
H -1.92274 0.15318 2.18859
H -1.92094 0.12216 -2.19501
H -1.61102 -2.40406 1.35556
H -1.61008 -2.42320 -1.32540
N 0.60546 1.80015 -0.00883
H -0.35776 2.16837 -0.02260
C 1.25784 2.31434 1.21621
C 1.28935 2.29984 -1.22257
H 1.32496 3.41058 1.19562
H 0.67981 2.00843 2.08924
H 2.26673 1.90173 1.29584
H 1.36120 3.39592 -1.21073
H 2.29789 1.88202 -1.27440
H 0.73081 1.98836 -2.10632

E–N

Ru 1.17048 0.13020 -0.13351
C -0.74313 -1.45939 -0.15962
C 0.60390 -2.07563 -0.04216
C -0.77331 -0.43945 0.92475

C 0.33515 -0.64911 1.77218
C 1.19306 -1.65374 1.17217
O -1.57225 -1.62432 -1.06116
C 1.35120 1.97032 0.36497
C 2.95735 0.03228 -0.81246
O 1.44770 3.04953 0.76250
O 4.05399 -0.09679 -1.14948
H -1.61815 0.22095 1.08719
H 0.97904 -2.84178 -0.70734
H 0.52664 -0.16128 2.71940
H 2.10682 -2.03044 1.61342
H -3.31049 -0.30902 -0.63637
N -3.85620 0.38101 -0.12057
C -5.04359 -0.25296 0.44317
H -5.54855 0.44484 1.12250
H -5.78119 -0.57094 -0.31735
H -4.75122 -1.13393 1.02340
C -4.17668 1.50881 -0.98933
H -4.63444 2.31220 -0.39909
H -3.25874 1.90353 -1.43658
H -4.87679 1.25595 -1.80755

X-ray Crystal Structure Determination of [2,5-Ph_2-3,4-Tol_2(η^4-C_4CO)]$(CO)_2RuNH_2C_6H_4$-*p*-$NHCH_2Ph$ (9). X-ray quality crystals were grown by cooling a CH_2Cl_2/hexane solution of **9** to –20 ºC for one week. A colorless crystal with approximate dimensions 0.20 x 0.02 x 0.02 mm^3 was selected under oil under ambient conditions and attached to the tip of a nylon loop. The crystal was mounted in a stream of cold nitrogen at 100(2) K and centered in the X-ray beam by using a video camera.

The crystal evaluation and data collection were performed on a Bruker CCD-1000 diffractometer with Mo K_α (λ = 0.71073 Å) radiation and the diffractometer to crystal distance of 4.9 cm.

The initial cell constants were obtained from three series of ω scans at different starting angles. Each series consisted of 20 frames collected at intervals of 0.3º in a 6º range about ω with the exposure time of 10 seconds per frame. A total of 67 reflections were obtained. The reflections were successfully indexed by an automated indexing routine built into the SMART program. The final cell constants were calculated from a set of 3249 strong reflections from the actual data collection.

The data were collected by using the hemisphere data collection routine. The reciprocal space was surveyed to the extent of a full sphere to a resolution of 0.80 Å. A total of 14798 data were harvested by collecting three sets of frames with 0.30º scans in ω with an exposure time 90 sec per frame. These highly redundant datasets were corrected for Lorentz and polarization effects. The absorption correction was based on fitting a function to the empirical transmission surface as sampled by multiple equivalent measurements.[11]

The systematic absences in the diffraction data were consistent with the space groups $P2_1$ and $P2_1/m$. The E-statistics strongly suggested the non-centrosymmetric space group $P2_1$ that yielded chemically reasonable and computationally stable results of refinement.

A successful solution by the direct methods provided most non-hydrogen atoms from the *E*-map. The remaining non-hydrogen atoms were located in an alternating series of least-squares cycles and difference Fourier maps. All non-hydrogen atoms were refined with anisotropic displacement coefficients. All hydrogen atoms were included in the structure factor calculation at idealized positions and were allowed to ride on the neighboring atoms with relative isotropic displacement coefficients.

The final least-squares refinement of 471 parameters against 5737 data resulted in residuals R (based on F^2 for $I \geq 2\sigma$) and wR (based on F^2 for all data) of 0.0466 and 0.0924, respectively. The final difference Fourier map was featureless.

Figure S7. Molecular drawings of **9** shown with 30% probability ellipsoids.

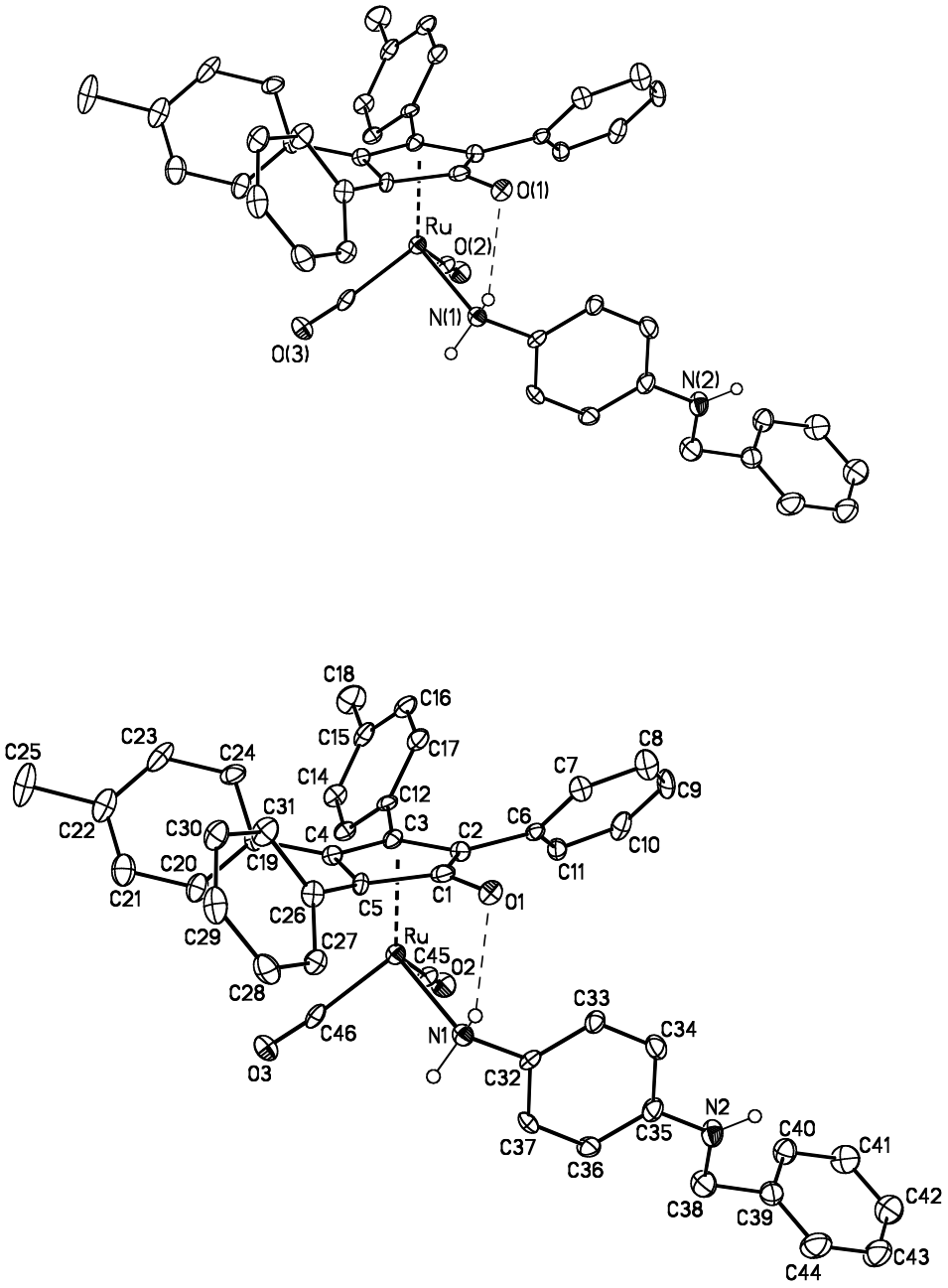


Table S4. Crystal data and structure refinement for [2,5-Ph_2-3,4-Tol_2(η^4-C_4CO)]$(CO)_2RuNH_2C_6H_4$-*p*-$NHCH_2Ph$ (**9**).

Empirical formula	$C_{46}H_{38}N_2O_3Ru$	
Formula weight	767.85	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1$	
Unit cell dimensions	a = 11.719(3) Å	α= 90°.
	b = 9.906(2) Å	β= 97.938(10)°.
	c = 17.403(5) Å	γ = 90°.
Volume	2000.9(10) $Å^3$	
Z	2	
Density (calculated)	1.274 Mg/m^3	
Absorption coefficient	0.433 mm^{-1}	
F(000)	792	
Crystal size	0.40 x 0.31 x 0.17 mm^3	
Theta range for data collection	2.25 to 24.88°.	
Index ranges	-13<=h<=13, -11<=k<=11, -20<=l<=20	
Reflections collected	14798	
Independent reflections	5737 [R(int) = 0.0696]	
Completeness to theta = 24.88°	99.3 %	
Absorption correction	Multi-scan with SADABS	
Max. and min. transmission	0.9301 and 0.8459	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5737 / 1 / 471	
Goodness-of-fit on F^2	0.964	
Final R indices [I>2sigma(I)]	R1 = 0.0466, wR2 = 0.0833	
R indices (all data)	R1 = 0.0779, wR2 = 0.0924	

Absolute structure parameter	0.01(4)
Largest diff. peak and hole	0.810 and -0.568 e.Å^{-3}

Table S5. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for [2,5-Ph_2-3,4-Tol_2(η^4-C_4CO)](CO)$_2$Ru$NH_2C_6H_4$-*p*-$NHCH_2Ph$ (**9**). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ru	8790(1)	8004(1)	1025(1)	21(1)
O(1)	9936(3)	10927(4)	639(2)	24(1)
O(2)	6331(4)	6990(4)	737(2)	37(1)
O(3)	9550(4)	5088(4)	1152(3)	33(1)
N(1)	9068(4)	8374(4)	-165(2)	24(1)
N(2)	5295(5)	9315(5)	-2477(3)	39(1)
C(1)	9636(7)	10219(8)	1182(4)	26(2)
C(2)	8480(5)	10126(6)	1411(3)	20(1)
C(3)	8512(5)	9158(5)	2037(3)	21(1)
C(4)	9644(5)	8602(5)	2178(3)	20(1)
C(5)	10306(5)	9149(5)	1608(3)	22(1)
C(6)	7523(5)	11088(5)	1139(3)	20(1)
C(7)	7781(6)	12441(6)	1102(3)	28(2)
C(8)	6913(6)	13376(6)	919(4)	40(2)
C(9)	5775(5)	12984(10)	767(3)	34(1)
C(10)	5507(6)	11624(7)	800(3)	36(2)
C(11)	6387(6)	10687(6)	987(3)	26(2)
C(12)	7606(5)	8985(6)	2550(3)	23(2)
C(13)	7262(5)	7688(6)	2736(3)	26(2)
C(14)	6512(6)	7516(6)	3278(3)	31(2)
C(15)	6097(6)	8596(7)	3648(4)	33(2)
C(16)	6427(5)	9863(7)	3454(3)	32(2)
C(17)	7189(5)	10067(7)	2910(3)	31(2)
C(18)	5307(6)	8386(7)	4253(4)	54(3)
C(19)	10128(5)	7736(6)	2841(3)	20(2)
C(20)	10895(6)	6706(6)	2746(4)	33(2)
C(21)	11416(6)	5977(7)	3372(4)	40(2)
C(22)	11202(7)	6238(7)	4105(4)	44(2)
C(23)	10457(7)	7293(7)	4213(4)	45(2)
C(24)	9914(4)	8014(10)	3585(3)	33(1)
C(25)	11793(7)	5467(8)	4802(4)	70(3)

C(26)	11577(5)	9042(6)	1660(3)	26(2)
C(27)	12116(5)	8687(5)	1033(3)	27(2)
C(28)	13329(6)	8658(6)	1117(4)	34(2)
C(29)	13969(6)	8958(6)	1814(4)	34(2)
C(30)	13433(5)	9342(6)	2427(4)	32(2)
C(31)	12253(5)	9386(6)	2350(4)	32(2)
C(32)	8101(5)	8643(6)	-754(3)	22(2)
C(33)	7632(6)	9900(6)	-866(3)	28(2)
C(34)	6721(6)	10135(6)	-1435(4)	33(2)
C(35)	6225(6)	9076(7)	-1901(4)	32(2)
C(36)	6710(5)	7803(8)	-1785(3)	31(2)
C(37)	7630(6)	7592(5)	-1213(4)	26(2)
C(38)	4637(6)	8200(9)	-2831(4)	44(2)
C(39)	3586(6)	8724(6)	-3377(4)	39(2)
C(40)	2587(6)	8999(6)	-3086(4)	41(2)
C(41)	1626(7)	9510(7)	-3585(5)	51(2)
C(42)	1727(7)	9682(7)	-4353(5)	55(2)
C(43)	2734(8)	9397(8)	-4643(5)	63(2)
C(44)	3650(7)	8877(8)	-4142(4)	57(2)
C(45)	7275(6)	7374(6)	808(3)	21(2)
C(46)	9298(7)	6188(7)	1066(4)	26(2)

Table S6. Bond lengths [Å] and angles [°] for [2,5-Ph_2-3,4-Tol_2(η^4-C_4CO)](CO)$_2$Ru$NH_2C_6H_4$-*p*-$NHCH_2Ph$ (**9**).

Ru-C(45)	1.871(7)	C(13)-C(14)	1.387(8)
Ru-C(46)	1.893(7)	C(14)-C(15)	1.372(8)
Ru-C(3)	2.161(5)	C(15)-C(16)	1.369(8)
Ru-N(1)	2.172(4)	C(15)-C(18)	1.510(8)
Ru-C(4)	2.196(6)	C(16)-C(17)	1.404(8)
Ru-C(5)	2.230(6)	C(19)-C(24)	1.380(7)
Ru-C(2)	2.250(5)	C(19)-C(20)	1.385(8)
Ru-C(1)	2.407(8)	C(20)-C(21)	1.378(8)
O(1)-C(1)	1.264(8)	C(21)-C(22)	1.359(9)
O(2)-C(45)	1.160(6)	C(22)-C(23)	1.391(10)
O(3)-C(46)	1.134(7)	C(22)-C(25)	1.518(9)
N(1)-C(32)	1.444(7)	C(23)-C(24)	1.384(9)
N(2)-C(35)	1.395(8)	C(26)-C(27)	1.379(8)
N(2)-C(38)	1.436(9)	C(26)-C(31)	1.386(8)
C(1)-C(5)	1.459(9)	C(27)-C(28)	1.409(8)
C(1)-C(2)	1.467(9)	C(28)-C(29)	1.368(8)
C(2)-C(3)	1.449(8)	C(29)-C(30)	1.365(8)
C(2)-C(6)	1.499(8)	C(30)-C(31)	1.372(8)
C(3)-C(4)	1.426(8)	C(32)-C(33)	1.364(8)
C(3)-C(12)	1.488(8)	C(32)-C(37)	1.381(7)
C(4)-C(5)	1.447(7)	C(33)-C(34)	1.372(9)
C(4)-C(19)	1.486(7)	C(34)-C(35)	1.403(8)
C(5)-C(26)	1.483(8)	C(35)-C(36)	1.386(9)
C(6)-C(7)	1.378(7)	C(36)-C(37)	1.379(8)
C(6)-C(11)	1.379(8)	C(38)-C(39)	1.538(9)
C(7)-C(8)	1.380(8)	C(39)-C(44)	1.352(9)
C(8)-C(9)	1.379(8)	C(39)-C(40)	1.366(9)
C(9)-C(10)	1.386(11)	C(40)-C(41)	1.417(9)
C(10)-C(11)	1.392(8)	C(41)-C(42)	1.369(9)
C(12)-C(17)	1.366(8)	C(42)-C(43)	1.375(10)
C(12)-C(13)	1.398(8)	C(43)-C(44)	1.385(10)
C(45)-Ru-C(46)	88.6(3)	N(1)-Ru-C(4)	135.76(19)
C(45)-Ru-C(3)	95.5(2)	C(45)-Ru-C(5)	159.4(2)
C(46)-Ru-C(3)	123.6(2)	C(46)-Ru-C(5)	103.8(3)
C(45)-Ru-N(1)	97.3(2)	C(3)-Ru-C(5)	64.0(2)
C(46)-Ru-N(1)	96.2(2)	N(1)-Ru-C(5)	97.64(18)
C(3)-Ru-N(1)	138.37(18)	C(4)-Ru-C(5)	38.14(19)
C(45)-Ru-C(4)	125.1(2)	C(45)-Ru-C(2)	100.6(2)
C(46)-Ru-C(4)	97.0(3)	C(46)-Ru-C(2)	159.9(3)
C(3)-Ru-C(4)	38.18(19)	C(3)-Ru-C(2)	38.3(2)

N(1)-Ru-C(2)	100.29(18)	C(9)-C(8)-C(7)	121.2(6)
C(4)-Ru-C(2)	63.1(2)	C(8)-C(9)-C(10)	118.9(7)
C(5)-Ru-C(2)	62.7(2)	C(9)-C(10)-C(11)	119.6(6)
C(45)-Ru-C(1)	133.8(3)	C(6)-C(11)-C(10)	121.1(6)
C(46)-Ru-C(1)	137.7(3)	C(17)-C(12)-C(13)	118.9(5)
C(3)-Ru-C(1)	62.1(2)	C(17)-C(12)-C(3)	121.0(6)
N(1)-Ru-C(1)	80.8(2)	C(13)-C(12)-C(3)	119.8(5)
C(4)-Ru-C(1)	61.5(2)	C(14)-C(13)-C(12)	120.0(5)
C(5)-Ru-C(1)	36.4(2)	C(15)-C(14)-C(13)	121.6(5)
C(2)-Ru-C(1)	36.5(2)	C(16)-C(15)-C(14)	117.9(5)
C(32)-N(1)-Ru	120.1(3)	C(16)-C(15)-C(18)	121.3(6)
C(35)-N(2)-C(38)	119.8(5)	C(14)-C(15)-C(18)	120.7(6)
O(1)-C(1)-C(5)	126.7(6)	C(15)-C(16)-C(17)	121.8(6)
O(1)-C(1)-C(2)	126.9(7)	C(12)-C(17)-C(16)	119.8(6)
C(5)-C(1)-C(2)	105.5(6)	C(24)-C(19)-C(20)	117.7(6)
O(1)-C(1)-Ru	125.0(5)	C(24)-C(19)-C(4)	120.9(6)
C(5)-C(1)-Ru	65.1(4)	C(20)-C(19)-C(4)	121.1(5)
C(2)-C(1)-Ru	65.9(3)	C(21)-C(20)-C(19)	121.0(6)
C(3)-C(2)-C(1)	108.5(5)	C(22)-C(21)-C(20)	121.6(7)
C(3)-C(2)-C(6)	126.8(5)	C(21)-C(22)-C(23)	118.1(6)
C(1)-C(2)-C(6)	123.6(5)	C(21)-C(22)-C(25)	122.1(7)
C(3)-C(2)-Ru	67.5(3)	C(23)-C(22)-C(25)	119.7(7)
C(1)-C(2)-Ru	77.6(4)	C(24)-C(23)-C(22)	120.6(7)
C(6)-C(2)-Ru	130.1(4)	C(19)-C(24)-C(23)	121.0(7)
C(4)-C(3)-C(2)	108.1(5)	C(27)-C(26)-C(31)	118.5(6)
C(4)-C(3)-C(12)	125.2(5)	C(27)-C(26)-C(5)	122.4(6)
C(2)-C(3)-C(12)	125.6(5)	C(31)-C(26)-C(5)	118.9(5)
C(4)-C(3)-Ru	72.2(3)	C(26)-C(27)-C(28)	119.4(6)
C(2)-C(3)-Ru	74.2(3)	C(29)-C(28)-C(27)	120.5(6)
C(12)-C(3)-Ru	128.9(4)	C(30)-C(29)-C(28)	119.9(6)
C(3)-C(4)-C(5)	108.2(5)	C(29)-C(30)-C(31)	119.9(6)
C(3)-C(4)-C(19)	127.1(5)	C(30)-C(31)-C(26)	121.7(6)
C(5)-C(4)-C(19)	124.4(5)	C(33)-C(32)-C(37)	119.0(5)
C(3)-C(4)-Ru	69.6(3)	C(33)-C(32)-N(1)	122.1(5)
C(5)-C(4)-Ru	72.2(3)	C(37)-C(32)-N(1)	118.9(5)
C(19)-C(4)-Ru	129.1(4)	C(32)-C(33)-C(34)	121.1(6)
C(4)-C(5)-C(1)	108.6(5)	C(33)-C(34)-C(35)	120.6(6)
C(4)-C(5)-C(26)	124.1(5)	C(36)-C(35)-N(2)	121.6(6)
C(1)-C(5)-C(26)	123.2(5)	C(36)-C(35)-C(34)	117.8(6)
C(4)-C(5)-Ru	69.7(3)	N(2)-C(35)-C(34)	120.6(6)
C(1)-C(5)-Ru	78.4(4)	C(37)-C(36)-C(35)	120.5(6)
C(26)-C(5)-Ru	136.2(4)	C(36)-C(37)-C(32)	120.9(6)
C(7)-C(6)-C(11)	118.9(6)	N(2)-C(38)-C(39)	110.0(6)
C(7)-C(6)-C(2)	118.3(6)	C(44)-C(39)-C(40)	120.6(7)
C(11)-C(6)-C(2)	122.5(5)	C(44)-C(39)-C(38)	119.9(7)
C(6)-C(7)-C(8)	120.3(6)	C(40)-C(39)-C(38)	119.5(7)

C(39)-C(40)-C(41)	119.6(7)	C(39)-C(44)-C(43)	121.2(7)
C(42)-C(41)-C(40)	118.3(7)	O(2)-C(45)-Ru	174.5(5)
C(41)-C(42)-C(43)	121.8(8)	O(3)-C(46)-Ru	173.4(6)
C(42)-C(43)-C(44)	118.4(8)		

Symmetry transformations used to generate equivalent atoms:

Table S7. Anisotropic displacement parameters ($Å^2$ x 10^3) for [2,5-Ph_2-3,4-Tol_2(η^4-C_4CO)]$(CO)_2RuNH_2C_6H_4$-*p*-$NHCH_2Ph$ (**9**). The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ru	17(1)	25(1)	21(1)	1(1)	2(1)	-1(1)
O(1)	18(3)	31(2)	24(2)	2(2)	5(2)	-5(2)
O(2)	30(3)	35(3)	43(3)	-2(2)	3(2)	-3(2)
O(3)	28(3)	27(3)	45(3)	1(2)	9(2)	3(3)
N(1)	18(3)	24(3)	28(3)	-2(2)	0(2)	0(2)
N(2)	41(4)	29(3)	40(4)	1(3)	-16(3)	-3(3)
C(1)	24(5)	32(4)	21(4)	-9(4)	0(4)	0(4)
C(2)	11(4)	26(3)	24(3)	-3(3)	0(3)	1(3)
C(3)	21(4)	23(3)	19(3)	0(3)	-1(3)	-5(3)
C(4)	12(4)	27(3)	22(3)	-3(3)	2(3)	0(3)
C(5)	19(4)	24(3)	20(3)	3(3)	-3(3)	4(3)
C(6)	15(4)	28(3)	16(3)	-4(3)	0(3)	4(3)
C(7)	24(4)	27(3)	33(4)	4(3)	7(3)	-1(3)
C(8)	38(5)	37(5)	47(4)	11(3)	11(4)	6(4)
C(9)	23(4)	39(3)	40(3)	13(6)	6(3)	17(6)
C(10)	25(5)	57(5)	27(4)	13(3)	6(3)	10(4)
C(11)	28(4)	25(3)	26(4)	4(3)	3(3)	2(3)
C(12)	19(4)	31(4)	17(4)	-9(3)	-2(3)	2(3)
C(13)	25(4)	29(5)	22(3)	-2(3)	1(3)	-6(3)
C(14)	30(4)	35(4)	28(4)	2(3)	6(3)	-7(3)
C(15)	23(4)	58(4)	17(4)	6(3)	3(3)	5(3)
C(16)	25(4)	51(4)	19(4)	-3(3)	3(3)	6(3)
C(17)	28(4)	39(4)	23(4)	-1(3)	-3(3)	1(3)
C(18)	49(5)	78(7)	38(4)	4(4)	22(3)	3(4)
C(19)	15(3)	20(4)	27(3)	4(3)	2(2)	-1(3)
C(20)	32(5)	37(4)	29(4)	12(3)	2(3)	-3(3)
C(21)	30(5)	41(4)	47(5)	11(4)	1(4)	-2(4)
C(22)	33(5)	60(5)	38(5)	14(4)	-6(4)	-6(4)
C(23)	48(5)	60(5)	23(4)	6(3)	-11(4)	-12(4)
C(24)	23(3)	47(3)	28(3)	-14(6)	-4(3)	3(6)
C(25)	49(6)	94(7)	58(6)	33(5)	-17(4)	9(5)
C(26)	21(4)	28(3)	29(4)	6(3)	5(3)	-3(3)
C(27)	25(4)	31(3)	26(4)	1(3)	0(3)	-1(3)
C(28)	25(4)	36(4)	45(5)	3(3)	13(4)	7(3)
C(29)	13(4)	34(4)	54(5)	14(3)	-2(4)	-6(3)
C(30)	18(4)	44(4)	32(4)	2(3)	-4(3)	-2(3)

C(31)	15(4)	46(4)	34(4)	0(3)	-1(3)	-5(3)
C(32)	19(4)	33(3)	13(3)	0(3)	2(3)	-2(3)
C(33)	32(5)	24(3)	24(4)	1(3)	-6(3)	-5(3)
C(34)	39(5)	21(3)	38(4)	2(3)	1(4)	2(3)
C(35)	30(5)	36(4)	27(4)	1(3)	-8(3)	1(4)
C(36)	28(4)	33(5)	29(3)	-10(4)	-6(3)	1(4)
C(37)	31(4)	13(4)	35(4)	0(3)	6(3)	3(3)
C(38)	36(4)	44(5)	48(4)	-4(4)	-7(3)	2(5)
C(39)	42(5)	34(4)	38(5)	-2(3)	-2(4)	1(3)
C(40)	34(5)	46(4)	41(5)	4(3)	4(4)	2(4)
C(41)	30(5)	66(5)	56(5)	-5(4)	-1(4)	2(4)
C(42)	42(6)	63(5)	53(6)	-7(4)	-15(4)	2(4)
C(43)	61(7)	87(6)	38(5)	-3(4)	-3(5)	31(5)
C(44)	52(6)	78(6)	42(6)	-6(4)	14(5)	14(5)
C(45)	14(4)	27(3)	22(3)	-2(3)	0(3)	-5(3)
C(46)	23(5)	42(5)	14(4)	8(3)	2(3)	-2(4)

Table S8. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for [2,5-Ph_2-3,4-Tol_2(η^4-C_4CO)](CO)$_2$Ru$NH_2C_6H_4$-*p*-$NHCH_2Ph$ (**9**).

	x	y	z	U(eq)
H(1A)	9564	9095	-159	29
H(1B)	9448	7634	-325	29
H(2)	5113	10147	-2624	47
H(7)	8560	12732	1203	33
H(8)	7103	14307	898	48
H(9)	5184	13636	641	41
H(10)	4729	11334	696	43
H(11)	6202	9755	1010	31
H(13)	7542	6923	2490	31
H(14)	6280	6630	3397	37
H(16)	6132	10624	3695	38
H(17)	7415	10956	2792	37
H(18A)	5149	9257	4484	81
H(18B)	5677	7780	4659	81
H(18C)	4582	7984	4010	81
H(20)	11064	6498	2240	40
H(21)	11938	5275	3289	48
H(23)	10319	7521	4722	54
H(24)	9387	8710	3668	40
H(25A)	12043	6100	5225	104
H(25B)	12465	4990	4659	104
H(25C)	11254	4813	4973	104
H(27)	11675	8465	551	33
H(28)	13706	8428	685	41
H(29)	14785	8899	1871	41
H(30)	13876	9578	2907	39
H(31)	11889	9659	2779	38
H(33)	7941	10624	-545	33
H(34)	6423	11024	-1513	39
H(36)	6406	7071	-2102	37
H(37)	7943	6710	-1133	31
H(38A)	4376	7625	-2424	52
H(38B)	5126	7644	-3128	52
H(40)	2537	8848	-2553	49
H(41)	930	9728	-3391	61
H(42)	1084	10006	-4695	66
H(43)	2799	9553	-5174	76
H(44)	4335	8623	-4340	68

Table S9. Torsion angles [°] for [2,5-Ph_2-3,4-Tol_2(η^4-C_4CO)]$(CO)_2RuNH_2C_6H_4$-*p*-$NHCH_2Ph$ (**9**).

C(45)-Ru-N(1)-C(32)	25.4(4)	N(1)-Ru-C(2)-C(1)	-58.8(4)
C(46)-Ru-N(1)-C(32)	114.8(4)	C(4)-Ru-C(2)-C(1)	77.6(4)
C(3)-Ru-N(1)-C(32)	-81.4(5)	C(5)-Ru-C(2)-C(1)	34.5(4)
C(4)-Ru-N(1)-C(32)	-138.6(4)	C(45)-Ru-C(2)-C(6)	-34.6(5)
C(5)-Ru-N(1)-C(32)	-140.3(4)	C(46)-Ru-C(2)-C(6)	-150.6(8)
C(2)-Ru-N(1)-C(32)	-76.8(4)	C(3)-Ru-C(2)-C(6)	-120.0(6)
C(1)-Ru-N(1)-C(32)	-107.9(4)	N(1)-Ru-C(2)-C(6)	64.9(5)
C(45)-Ru-C(1)-O(1)	-89.1(6)	C(4)-Ru-C(2)-C(6)	-158.7(5)
C(46)-Ru-C(1)-O(1)	91.3(7)	C(5)-Ru-C(2)-C(6)	158.2(6)
C(3)-Ru-C(1)-O(1)	-158.2(7)	C(1)-Ru-C(2)-C(6)	123.7(7)
N(1)-Ru-C(1)-O(1)	2.2(6)	C(1)-C(2)-C(3)-C(4)	-2.7(6)
C(4)-Ru-C(1)-O(1)	158.2(7)	C(6)-C(2)-C(3)-C(4)	-171.1(5)
C(5)-Ru-C(1)-O(1)	118.6(8)	Ru-C(2)-C(3)-C(4)	64.7(4)
C(2)-Ru-C(1)-O(1)	-119.3(8)	C(1)-C(2)-C(3)-C(12)	165.7(6)
C(45)-Ru-C(1)-C(5)	152.2(3)	C(6)-C(2)-C(3)-C(12)	-2.7(9)
C(46)-Ru-C(1)-C(5)	-27.4(5)	Ru-C(2)-C(3)-C(12)	-126.9(6)
C(3)-Ru-C(1)-C(5)	83.1(4)	C(1)-C(2)-C(3)-Ru	-67.4(4)
N(1)-Ru-C(1)-C(5)	-116.5(4)	C(6)-C(2)-C(3)-Ru	124.1(6)
C(4)-Ru-C(1)-C(5)	39.6(3)	C(45)-Ru-C(3)-C(4)	144.3(3)
C(2)-Ru-C(1)-C(5)	122.0(5)	C(46)-Ru-C(3)-C(4)	52.3(4)
C(45)-Ru-C(1)-C(2)	30.2(5)	N(1)-Ru-C(3)-C(4)	-108.3(4)
C(46)-Ru-C(1)-C(2)	-149.4(4)	C(5)-Ru-C(3)-C(4)	-37.4(3)
C(3)-Ru-C(1)-C(2)	-38.9(3)	C(2)-Ru-C(3)-C(4)	-115.5(4)
N(1)-Ru-C(1)-C(2)	121.5(4)	C(1)-Ru-C(3)-C(4)	-78.4(3)
C(4)-Ru-C(1)-C(2)	-82.5(4)	C(45)-Ru-C(3)-C(2)	-100.2(4)
C(5)-Ru-C(1)-C(2)	-122.0(5)	C(46)-Ru-C(3)-C(2)	167.8(4)
O(1)-C(1)-C(2)-C(3)	177.6(6)	N(1)-Ru-C(3)-C(2)	7.2(5)
C(5)-C(1)-C(2)-C(3)	7.9(7)	C(4)-Ru-C(3)-C(2)	115.5(4)
Ru-C(1)-C(2)-C(3)	60.9(4)	C(5)-Ru-C(3)-C(2)	78.1(3)
O(1)-C(1)-C(2)-C(6)	-13.5(10)	C(1)-Ru-C(3)-C(2)	37.1(3)
C(5)-C(1)-C(2)-C(6)	176.8(5)	C(45)-Ru-C(3)-C(12)	23.0(6)
Ru-C(1)-C(2)-C(6)	-130.2(6)	C(46)-Ru-C(3)-C(12)	-68.9(6)
O(1)-C(1)-C(2)-Ru	116.7(7)	N(1)-Ru-C(3)-C(12)	130.5(5)
C(5)-C(1)-C(2)-Ru	-53.0(4)	C(4)-Ru-C(3)-C(12)	-121.3(6)
C(45)-Ru-C(2)-C(3)	85.4(4)	C(5)-Ru-C(3)-C(12)	-158.6(6)
C(46)-Ru-C(2)-C(3)	-30.7(9)	C(2)-Ru-C(3)-C(12)	123.2(7)
N(1)-Ru-C(2)-C(3)	-175.1(3)	C(1)-Ru-C(3)-C(12)	160.4(6)
C(4)-Ru-C(2)-C(3)	-38.7(3)	C(2)-C(3)-C(4)-C(5)	-3.8(6)
C(5)-Ru-C(2)-C(3)	-81.8(4)	C(12)-C(3)-C(4)-C(5)	-172.2(5)
C(1)-Ru-C(2)-C(3)	-116.3(5)	Ru-C(3)-C(4)-C(5)	62.2(4)
C(45)-Ru-C(2)-C(1)	-158.3(4)	C(2)-C(3)-C(4)-C(19)	169.7(5)
C(46)-Ru-C(2)-C(1)	85.6(9)	C(12)-C(3)-C(4)-C(19)	1.3(9)
C(3)-Ru-C(2)-C(1)	116.3(5)	Ru-C(3)-C(4)-C(19)	-124.2(5)

C(2)-C(3)-C(4)-Ru	-66.0(4)	N(1)-Ru-C(5)-C(1)	63.1(4)
C(12)-C(3)-C(4)-Ru	125.5(6)	C(4)-Ru-C(5)-C(1)	-115.0(5)
C(45)-Ru-C(4)-C(3)	-45.3(4)	C(2)-Ru-C(5)-C(1)	-34.6(3)
C(46)-Ru-C(4)-C(3)	-138.4(4)	C(45)-Ru-C(5)-C(26)	160.6(6)
N(1)-Ru-C(4)-C(3)	115.3(3)	C(46)-Ru-C(5)-C(26)	35.0(6)
C(5)-Ru-C(4)-C(3)	118.0(4)	C(3)-Ru-C(5)-C(26)	155.9(6)
C(2)-Ru-C(4)-C(3)	38.8(3)	N(1)-Ru-C(5)-C(26)	-63.4(6)
C(1)-Ru-C(4)-C(3)	80.2(3)	C(4)-Ru-C(5)-C(26)	118.5(7)
C(45)-Ru-C(4)-C(5)	-163.3(3)	C(2)-Ru-C(5)-C(26)	-161.0(6)
C(46)-Ru-C(4)-C(5)	103.6(4)	C(1)-Ru-C(5)-C(26)	-126.4(7)
C(3)-Ru-C(4)-C(5)	-118.0(4)	C(3)-C(2)-C(6)-C(7)	125.8(6)
N(1)-Ru-C(4)-C(5)	-2.7(4)	C(1)-C(2)-C(6)-C(7)	-41.1(8)
C(2)-Ru-C(4)-C(5)	-79.2(3)	Ru-C(2)-C(6)-C(7)	-143.9(5)
C(1)-Ru-C(4)-C(5)	-37.8(3)	C(3)-C(2)-C(6)-C(11)	-48.7(8)
C(45)-Ru-C(4)-C(19)	76.5(5)	C(1)-C(2)-C(6)-C(11)	144.5(6)
C(46)-Ru-C(4)-C(19)	-16.6(5)	Ru-C(2)-C(6)-C(11)	41.7(7)
C(3)-Ru-C(4)-C(19)	121.7(6)	C(11)-C(6)-C(7)-C(8)	0.3(9)
N(1)-Ru-C(4)-C(19)	-122.9(4)	C(2)-C(6)-C(7)-C(8)	-174.4(5)
C(5)-Ru-C(4)-C(19)	-120.2(6)	C(6)-C(7)-C(8)-C(9)	-0.3(9)
C(2)-Ru-C(4)-C(19)	160.6(5)	C(7)-C(8)-C(9)-C(10)	0.0(8)
C(1)-Ru-C(4)-C(19)	-158.0(6)	C(8)-C(9)-C(10)-C(11)	0.2(8)
C(3)-C(4)-C(5)-C(1)	8.9(7)	C(7)-C(6)-C(11)-C(10)	-0.1(8)
C(19)-C(4)-C(5)-C(1)	-164.9(5)	C(2)-C(6)-C(11)-C(10)	174.4(5)
Ru-C(4)-C(5)-C(1)	69.5(4)	C(9)-C(10)-C(11)-C(6)	-0.1(8)
C(3)-C(4)-C(5)-C(26)	166.7(5)	C(4)-C(3)-C(12)-C(17)	116.3(7)
C(19)-C(4)-C(5)-C(26)	-7.1(9)	C(2)-C(3)-C(12)-C(17)	-50.1(9)
Ru-C(4)-C(5)-C(26)	-132.7(5)	Ru-C(3)-C(12)-C(17)	-148.5(5)
C(3)-C(4)-C(5)-Ru	-60.6(4)	C(4)-C(3)-C(12)-C(13)	-56.7(9)
C(19)-C(4)-C(5)-Ru	125.7(5)	C(2)-C(3)-C(12)-C(13)	136.8(6)
O(1)-C(1)-C(5)-C(4)	-180.0(6)	Ru-C(3)-C(12)-C(13)	38.4(9)
C(2)-C(1)-C(5)-C(4)	-10.2(7)	C(17)-C(12)-C(13)-C(14)	-0.2(10)
Ru-C(1)-C(5)-C(4)	-63.7(4)	C(3)-C(12)-C(13)-C(14)	173.0(5)
O(1)-C(1)-C(5)-C(26)	22.0(10)	C(12)-C(13)-C(14)-C(15)	-0.5(10)
C(2)-C(1)-C(5)-C(26)	-168.3(5)	C(13)-C(14)-C(15)-C(16)	1.3(10)
Ru-C(1)-C(5)-C(26)	138.3(6)	C(13)-C(14)-C(15)-C(18)	-178.3(6)
O(1)-C(1)-C(5)-Ru	-116.3(7)	C(14)-C(15)-C(16)-C(17)	-1.6(10)
C(2)-C(1)-C(5)-Ru	53.4(4)	C(18)-C(15)-C(16)-C(17)	178.0(6)
C(45)-Ru-C(5)-C(4)	42.1(8)	C(13)-C(12)-C(17)-C(16)	-0.1(10)
C(46)-Ru-C(5)-C(4)	-83.6(4)	C(3)-C(12)-C(17)-C(16)	-173.2(6)
C(3)-Ru-C(5)-C(4)	37.4(3)	C(15)-C(16)-C(17)-C(12)	1.1(10)
N(1)-Ru-C(5)-C(4)	178.1(3)	C(3)-C(4)-C(19)-C(24)	-41.7(9)
C(2)-Ru-C(5)-C(4)	80.4(3)	C(5)-C(4)-C(19)-C(24)	130.8(6)
C(1)-Ru-C(5)-C(4)	115.0(5)	Ru-C(4)-C(19)-C(24)	-134.6(5)
C(45)-Ru-C(5)-C(1)	-73.0(7)	C(3)-C(4)-C(19)-C(20)	144.5(6)
C(46)-Ru-C(5)-C(1)	161.4(3)	C(5)-C(4)-C(19)-C(20)	-43.0(8)
C(3)-Ru-C(5)-C(1)	-77.6(4)	Ru-C(4)-C(19)-C(20)	51.6(8)

C(24)-C(19)-C(20)-C(21)	0.6(9)
C(4)-C(19)-C(20)-C(21)	174.6(6)
C(19)-C(20)-C(21)-C(22)	-0.1(10)
C(20)-C(21)-C(22)-C(23)	-1.6(10)
C(20)-C(21)-C(22)-C(25)	-178.4(7)
C(21)-C(22)-C(23)-C(24)	2.7(11)
C(25)-C(22)-C(23)-C(24)	179.6(7)
C(20)-C(19)-C(24)-C(23)	0.6(10)
C(4)-C(19)-C(24)-C(23)	-173.4(6)
C(22)-C(23)-C(24)-C(19)	-2.2(11)
C(4)-C(5)-C(26)-C(27)	135.0(6)
C(1)-C(5)-C(26)-C(27)	-70.4(8)
Ru-C(5)-C(26)-C(27)	39.3(8)
C(4)-C(5)-C(26)-C(31)	-48.8(8)
C(1)-C(5)-C(26)-C(31)	105.8(7)
Ru-C(5)-C(26)-C(31)	-144.6(5)
C(31)-C(26)-C(27)-C(28)	1.3(8)
C(5)-C(26)-C(27)-C(28)	177.5(5)
C(26)-C(27)-C(28)-C(29)	1.0(8)
C(27)-C(28)-C(29)-C(30)	-2.6(9)
C(28)-C(29)-C(30)-C(31)	2.0(9)
C(29)-C(30)-C(31)-C(26)	0.3(9)
C(27)-C(26)-C(31)-C(30)	-2.0(9)
C(5)-C(26)-C(31)-C(30)	-178.3(5)
Ru-N(1)-C(32)-C(33)	83.2(6)
Ru-N(1)-C(32)-C(37)	-96.2(6)
C(37)-C(32)-C(33)-C(34)	-1.4(9)
N(1)-C(32)-C(33)-C(34)	179.3(5)
C(32)-C(33)-C(34)-C(35)	2.0(10)
C(38)-N(2)-C(35)-C(36)	15.7(9)
C(38)-N(2)-C(35)-C(34)	-166.2(6)
C(33)-C(34)-C(35)-C(36)	-2.1(10)
C(33)-C(34)-C(35)-N(2)	179.7(6)
N(2)-C(35)-C(36)-C(37)	179.9(6)
C(34)-C(35)-C(36)-C(37)	1.8(9)
C(35)-C(36)-C(37)-C(32)	-1.2(9)
C(33)-C(32)-C(37)-C(36)	1.0(9)
N(1)-C(32)-C(37)-C(36)	-179.6(5)
C(35)-N(2)-C(38)-C(39)	173.7(6)
N(2)-C(38)-C(39)-C(44)	94.6(7)
N(2)-C(38)-C(39)-C(40)	-87.0(7)
C(44)-C(39)-C(40)-C(41)	-3.0(10)
C(38)-C(39)-C(40)-C(41)	178.6(6)
C(39)-C(40)-C(41)-C(42)	1.5(10)
C(40)-C(41)-C(42)-C(43)	-1.3(11)
C(41)-C(42)-C(43)-C(44)	2.4(12)
C(40)-C(39)-C(44)-C(43)	4.2(11)
C(38)-C(39)-C(44)-C(43)	-177.4(7)
C(42)-C(43)-C(44)-C(39)	-3.8(12)
C(46)-Ru-C(45)-O(2)	95(5)
C(3)-Ru-C(45)-O(2)	-29(5)
N(1)-Ru-C(45)-O(2)	-169(5)
C(4)-Ru-C(45)-O(2)	-3(5)
C(5)-Ru-C(45)-O(2)	-33(6)
C(2)-Ru-C(45)-O(2)	-67(5)
C(1)-Ru-C(45)-O(2)	-85(5)
C(45)-Ru-C(46)-O(3)	-66(7)
C(3)-Ru-C(46)-O(3)	29(7)
N(1)-Ru-C(46)-O(3)	-163(6)
C(4)-Ru-C(46)-O(3)	59(7)
C(5)-Ru-C(46)-O(3)	97(7)
C(2)-Ru-C(46)-O(3)	52(7)
C(1)-Ru-C(46)-O(3)	114(6)

Table S10. Hydrogen bonds for [2,5-Ph_2-3,4-Tol_2(η^4-C_4CO)]$(CO)_2RuNH_2C_6H_4$-*p*-$NHCH_2Ph$ (**9**) [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1A)...O(1)	0.92	2.29	2.999(6)	133.6
N(1)-H(1B)...O(1)#1	0.92	1.95	2.861(5)	172.1

Symmetry transformations used to generate equivalent atoms:
#1 -x+2,y-1/2,-z

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