Enzyme-like Catalysis via Ternary-Complex Mechanism: Alkoxy-bridged Dinuclear Cobalt Complex Mediates Chemoselective *O*-Esterification over *N*-Amidation

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1. General Information

Materials and Methods

All catalytic reactions were carried out by the standard Schlenk techniques under an argon atmosphere. Toluene, diisopropyl ether, methyl benzoate, benzyl alcohol, *n*-hexanol, *n*-hexylamine and ligands in Table S1 (excluding solid compounds) were purchased from commercial source and distilled over calcium hydride. Commercial available solid materials, such as DMAP, 1,4,7-triazacyclononane, 1,2-phenylenediamine and derivatives of 2,2'-bipyridine, were used after drying under reduced pressure (<0.02 mmHg) at ambient temperature for 2 h. Methyl 3-phenylpropanoate was synthesized from the corresponding carboxylic acid with methanol by the acid-catalyzed standard esterification and purified by distillation. Metal salts in Figure 1 were purchased from commercial source and used without removal of crystal water.

Nuclear magnetic resonance (^{1}H NMR) spectra were measured on a Bruker Avance 400 Spectrometer operating at 400 MHz in 5ϕ mm NMR tubes. All ^{1}H NMR chemical shifts were reported in ppm relative to internal references of TMS at δ 0.00. Low and high resolution mass spectra were recorded by JEOL JMS-700. IR spectra were recorded on Jasco FT/IR-410 spectrometer. Elemental analyses were conducted by Perkin-Elmer 2400II at the Faculty of Engineering Science, Osaka University. GC analyses were recorded on a Shimadzu GC-2014 gas chromatograph with J&W Scientific DB-5 column. UV-vis spectra were recorded on Agilent 8453 and Hitachi U-3500 spectrometer.

General Procedure for Chemoselective Acylation (Figure 1)

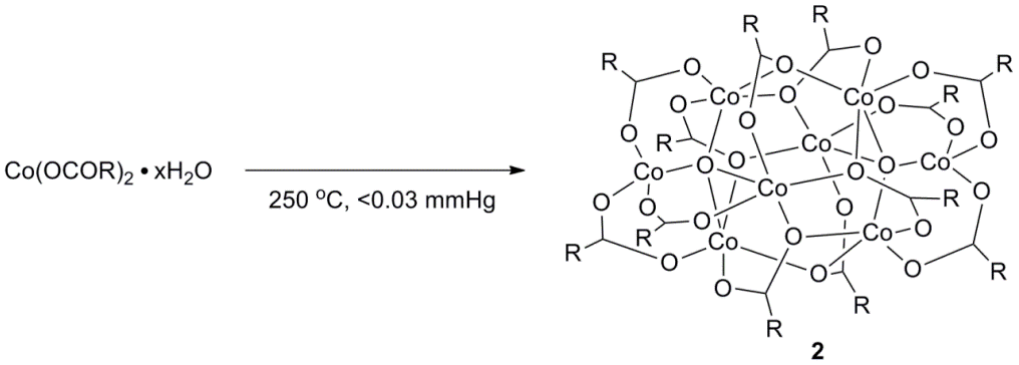
Methyl 3-phenylpropionate **3a** (1.0 mmol), *n*-hexanol **4a** (1.2 mmol), *n*-hexylamine **5a** (1.2 mmol), and catalyst (5.0 mol% on metal), in diisopropyl ether (1.7 mL, 0.6 M) were refluxed for 15 h under an argon atmosphere. Yields of product **6aa** and **7aa** were determined by GC analysis using DB-5 column.

General Procedure for Transesterification (Tables 1, 2, and S1)

Ester **3** (2.0 mmol), alcohol **4** (2.4 mmol), catalyst (5.0 mol% on metal) with or without nitrogen-containing ligand (5.0-20 mol%) in toluene (3.4 mL, 0.6 M) were refluxed for periodic time under an argon atmosphere. For Table 1 and Table S1, yields of products **6** were determined by GC analysis using DB-5 column. For Table 2, isolated yields of products **6** were determined after purification by flash column chromatography. Spectral data of products **6** were described in previous reports.[S1]

2. Preparation of Cobalt Clusters 2a—2c

The pivalate-bridged μ-oxo cobalt cluster, $Co_8(OCO^tBu)_{12}O_2$ (**2c**) was originally prepared by Blake who determined its chemical formula to be $Co_4(OCO^tBu)_6O$, and suggested that its structure was analogous to that of beryllium and zinc oxoacetates, $M_4(OCOCH_3)_6O$, in non-coordinating solvents such as carbon tetrachloride and benzene.[S2] In the last decade, Eremenko *et al.* determined the structure of **2c** to be the dimmer of **2c** in solid state by X-ray analysis.[S3-S5] According to their synthetic procedure as well as the sublimation method, we prepared and characterized **2c** by X-ray analysis for the sample prepared by the sublimation method, Mass spectrum, and elemental analysis as well as molecular weight measurement using an cryoscopic method. $Co_8(OCOCF_3)_{12}O_2$ (**2a**) and $Co_8(OCOCH_3)_{12}O_2$ (**2b**) were prepared by the same synthetic method as **2c**; however, we could not determine their structure since **2a** and **2b** could not be crystallized and cryoscopic and ebullioscopic methods could not be available due to their low solubility in any non-coordinating solvents. On the basis of UV-vis spectral data of **2a** and **2b** in toluene compared with that found for **2c**, even low solubility of **2a** and **2b** hampered to estimate their e values rigorously, it was likely assumed that **2a** and **2b** also adopt the dimer structure of tetranuclear, that is Co_8 cluster formula, $Co_8(OCOCF_3)_{12}O_2$ (**2a**) and $Co_8(OCOCH_3)_{12}O_2$ (**2b**). Molecular weight in benzene solution of **2c** was estimated to be ca. 1270 by cryoscopic method. The obtained value suggests that octanuclear cluster **2c** exists in equilibrium with its half segment, $Co_4(OCO^tBu)_6O$ in solution. Melting points of cobalt clusters **2a**—**2c** were not determined because of their sublimation property.



Spectral Data of Cobalt Clusters 2a—2c

2a: purple solid, 23% yield. IR (NaCl film) 1719, 1624, 1453, 1207, 1147, 843, 795, 723 cm^{-1}; UV (THF) λ_{max} (log ε) 525 (2.11), 475 (sh, 1.93); MS (ESI+) *m*/*z* (relative intensity) 817 ($[Co_4(OCOCF_3)_5O]^+$, 40), 1461 ($[Co_7(OCOCF_3)_9O_2]^+$, 15); HRMS (ESI+) *m*/*z* ($[Co_4(OCOCF_3)_5O]^+$) calcd. for 816.6524 found 816.6523; Anal. Calcd for $C_{24}F_{36}O_{26}Co_8$: C, 15.50. Found: C, 15.42.

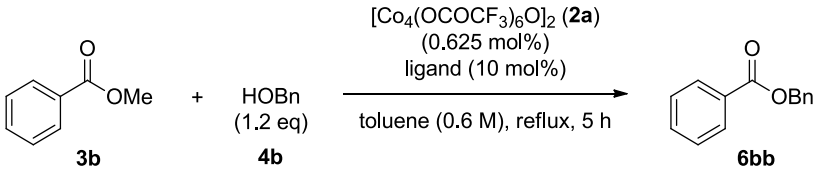
2b: purple solid, 21% yield. IR (nujol) 1536, 1456, 1377, 1346, 1261, 1026, 942, 799, 722, 670 cm^{-1}; UV (MeOH) λ_{max} (log ε) 280 (sh, 4.56), 383 (4.13); MS (ESI+) *m*/*z* (relative intensity) 294 ($[Co_2(OCOCH_3)_3]^+$, 100), 549 ($[Co_4(OCOCH_3)_5O]^+$, 11) ; HRMS (ESI+) *m*/*z* ($[Co_4(OCOCH_3)_5O]^+$) calcd. for 546.7937 found 546.7933; Anal. Calcd for $C_{24}H_{36}O_{26}Co_4$: C, 23.78; H, 2.99. Found: C, 23.66; H, 3.19.

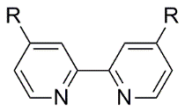
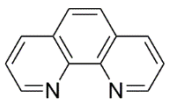
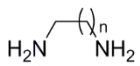
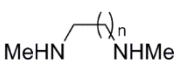
2c: dark blue solid, 42% yield. IR (nujol) 1608, 1540, 1485, 1457, 1398, 1377, 1340, 1214, 799, 615 cm^{-1}; UV (toluene) λ_{max} (log ε) 546 (2.91), 588 (3.05), 617(3.04); MS (ESI+) *m*/*z* (relative intensity) 421 ($[Co_2(OCO^tBu)_3]^+$, 100), 495 ($[Co_3(OCO^tBu)_3O]^+$, 66), 757 ($[Co_4(OCO^tBu)_5O]^+$, 18), 881 ($[Co_4(OCO^tBu)_6ONa]^+$, 50); HRMS (ESI+) *m*/*z* ($[Co_4(OCO^tBu)_6ONa]^+$) calcd. for 881.0790 found 881.0795; Anal. Calcd for $C_{60}H_{108}O_{26}Co_8$: C, 41.97; H, 6.34. Found: C, 41.57; H, 6.69.

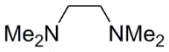
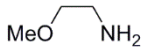
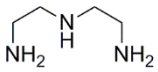
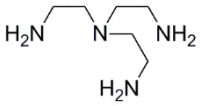
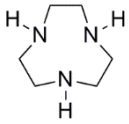
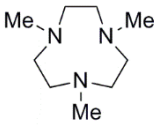
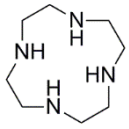
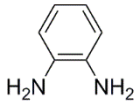
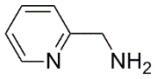
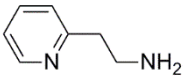
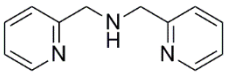
3. Additive Effects of Nitrogen-containing Ligands to Cobalt Cluster 2a

The presence of amine additive was already found to be essentially important for improving catalytic activity of zinc clusters for the transesterification reaction: in fact, monodentate nitrogen ligands such as primary and secondary amines as well as *N*-heteroaromatic compounds effectively accelerated catalytic activity of the zinc cluster **1** for transesterification.[S1c] We examined the transesterification catalyzed by the cobalt cluster **2a** in the presence of monodentate or multidentate-chelating nitrogen ligands as additives, and results are summarized in Table S1.

Table S1. Chelating Ligand Screening for Transesterification Catalyzed by Octanuclear Cobalt Cluster **2a**[a]



entry	Ligand		yield of **6bb** (%)[b]
1[c]	None		20
2[c]	*n*-hexylamine		**87**
3[c]	Cyclohexylamine		**85**
4[c]	Piperidine		**93**
5[c]	Triethylamine		26
6[c]	Aniline		22
7[c]	Pyridine		57
8[c]	DMAP		**86**
9		R = H (**8a**)	67
10		R = Me (**8b**)	68
11		R = *t*-Bu (**8c**)	34
12		R = OMe (**8d**)	77
13		R = OH (**8e**)	trace [d]
14		(**8f**)	71
15		n = 1 (**17a**)	70
16		n = 2 (**17b**)	**89**
17		n = 3 (**17c**)	**88**
18		n = 4 (**17d**)	**86**
19		n = 1 (**17e**)	**87**
20		n = 2 (**17f**)	**86**

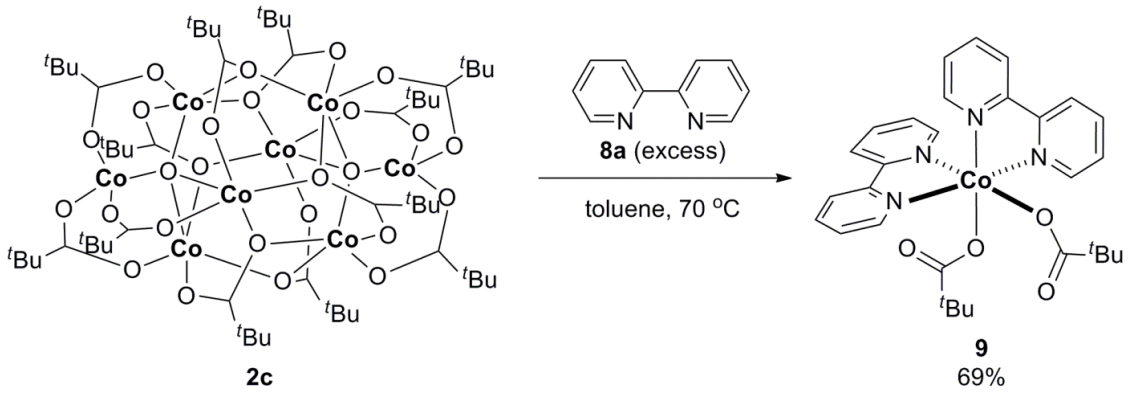
21		(**17g**)	70
22		(**17h**)	39
23[e]		(**17i**)	**83**
24[f]		(**17j**)	**80**
25[e]		(**17k**)	38
26[e]		(**17l**)	trace
27[f]		(**17m**)	50
28		(**17n**)	10
29		(**18a**)	**91**
30		(**18b**)	**87**
31[e]		(**18c**)	57

[a] 2.0 mmol scale. Nuclearity of cobalt cluster **2a** was assigned as eight on the basis of structure analyses of pivalate derivative **2c**. [b] Determined by GC analysis. Average of two runs, and bold letter indicates the results with more than 80% yields. [c] 20 mol% of ligand was used. [d] Insoluble compounds precipitated. [e] 6.7 mol% of ligand was used. [f] 5 mol% of ligand was used.

4. Reactions of $Co_8(OCO^tBu)_{12}O_2$ (2c) and 2,2'-Bipyridine (8a) with or without 4-Methylbenzyl alcohol (4c)

A mixture of $[Co_4(OCO^tBu)_6O]_2$ (**2c**, 68.7 mg, 0.040 mmol) and 2,2'-bipyridine (**8a**, 50.0 mg, 0.32 mmol, 8.0 equiv.) in toluene (5.0 mL) was stirred at 70 °C for 1 h. After cooling to room temperature, a dark purple compound was obtained from reaction mixture. We could not determine the crystal structure of the dark purple compound, because a suitable crystal for X-ray analysis was not obtained. When using large excess amount of 2,2'-bipyridine (**8a**, 500 equiv), orange crystals of *cis*-$Co(\eta^1\text{-}OCO^tBu)_2$(2,2'-bipyridine)$_2$ (**9**) were obtained from reaction mixture in 69%. The crystals were washed with hexane and dried under reduced pressure. The complex **9** was previously reported in literature S6.

4-Methylbenzyl alcohol (**4c**, 39.1 mg, 0.32 mmol, 8.0 equiv.) was added to a mixture of $[Co_4(OCO^tBu)_6O]_2$ (**2c**, 68.0 mg, 0.0396 mmol) and 2,2'-bipyridine (**8a**, 50.0 mg, 0.32 mmol, 8.0 equiv.) in toluene (5.0 mL), and the reaction mixture was stirred at 70 °C for 1 h, and then the solution was concentrated and cooled to room temperature. A red crystal of $Co_2(\mu_2\text{-}OCH_2C_6H_4\text{-}4\text{-}CH_3)_2(\eta^2\text{-}OCO^tBu)_2$(2,2'-bipyridine)$_2$ (**10**) was obtained from reaction mixture, and the crystal was filtrated and washed with hexane and dried under reduced pressure (31% yield). From the filtrate dark purple crystal of $Co_3(\mu_2\text{-}OH)(\mu_2\text{-}OCO^tBu)_4(\eta^1\text{-}OCO^tBu)_2$(2,2'-bipyridine)$_2$ (**11**) was obtained in 24% yield. The complex **11** was previously reported in literature S7.



Spectral Data of Complexes 9—11

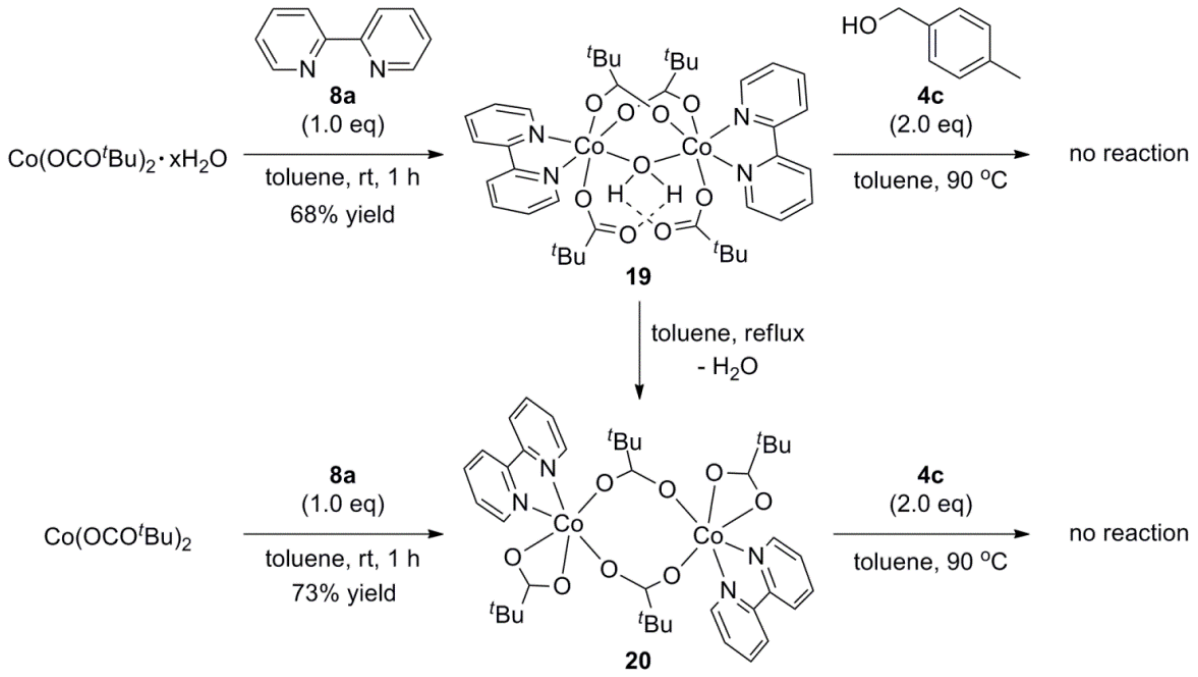
9: orange crystal, 69% yield, mp; 89-90 °C (dec); IR (nujol) 1592, 1456, 1376, 1339, 1225, 1157, 1056, 1015, 768, 754, 728 cm^{-1}; UV (toluene) λ_{max} (log ε) 379 (2.98), 555 (sh, 1.84). 604 (sh, 1.64); MS (ESI+): *m*/*z* (relative intensity) 316 ($[Co(OCO^tBu)(bpy)]^+$, 39), 472 ($[Co(OCO^tBu)(bpy)_2]^+$, 4), 577 ($[Co_2(OCO^tBu)_3(bpy)]^+$, 23), 733 ($[Co_2(OCO^tBu)_3(bpy)_2]^+$, 100); HRMS (ESI+) *m*/*z* ($[Co(OCO^tBu)(bpy)_2]^+$) calcd. for $C_{25}H_{25}N_4O_2Co$ 472.1310 found 472.1289; Anal. calcd for $C_{30}H_{34}N_4O_4Co$: C62.82 H5.98 N9.77; found C62.67 H6.08 N10.01.

10: red crystals, 31% yield, mp 109–112 °C (dec); IR (nujol) 1586, 1414, 1375, 1225, 1154, 1072, 1019, 890, 804, 764, 735 cm^{-1}; UV (toluene) λ_{max} (log ε) 395 (2.89), 452 (sh, 2.58), 535 (2.49), 579 (2.48), 617 (sh, 2.40); MS (ESI+): *m*/*z* (relative intensity) 472 ($[Co(OCO^tBu)(bpy)_2]^+$, 100), 733 ($[Co_2(OCO^tBu)_3(bpy)_2]^+$, 39), 753 ($[Co_2(OCH_2\text{-}C_6H_4\text{-}4\text{-}CH_3)(OCO^tBu)_2(bpy)_2]^+$, 19); HRMS (ESI+) *m*/*z* ($[Co_2(OCH_2\text{-}C_6H_4\text{-}4\text{-}CH_3)(OCO^tBu)_2(bpy)_2]^+$) calcd. for $C_{38}H_{43}N_4O_5Co_2$ 753.1897 found 753.1876; Anal. calcd for $C_{46}H_{52}N_4O_6Co_2$: C63.16 H5.99 N6.40; found C63.28 H5.98 N6.00.

11: dark purple crystals, 24% yield, mp 208–210 °C (dec); IR (nujol) 1585, 1414, 1375, 1225, 1174, 1154, 1056, 1019, 893, 789, 766, 739 cm^{-1}; UV (toluene) λ_{max} (log ε) 398 (2.02), 538 (1.76), 583 (1.79), 625 (sh, 1.71); MS (ESI+): *m*/*z* (relative intensity) 316 ($[Co(OCO^tBu)(bpy)]^+$, 47), 472 ($[Co(OCO^tBu)(bpy)_2]^+$, 5), 577 ($[Co_2(OCO^tBu)_3(bpy)]^+$, 28), 733 ($[Co_2(OCO^tBu)_3(bpy)_2]^+$, 100), 994 ($[Co_3(OCO^tBu)_5(bpy)_2]^+$, 0.1); HRMS (ESI+) *m*/*z* ($[Co_3(OCO^tBu)_5(bpy)_2]^+$) calcd. for $C_{45}H_{61}N_4O_{10}Co_3$ 994.2384 found 994.2341; Anal. calcd for $C_{45}H_{62}N_4O_{11}Co_3$: C53.42 H6.18 N5.54; found C53.31 H5.87 N5.63.

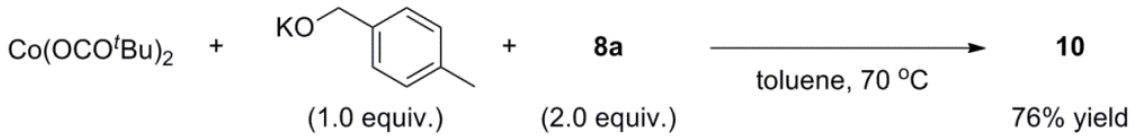
5. Complexation of $Co(OCO^tBu)_2$ with 2,2'-bipyridine (8a)

We carried out the reaction of a hydrated salt, $Co(OCO^tBu)_2(H_2O)_x$ with 1 equiv of **8a** to give a dinuclear complex, $Co_2(\mu_2\text{-}OCO^tBu)_2(OCO^tBu)_2(\mu_2\text{-}H_2O)(bpy)_2$ (**19**), as originally reported by Eremenko *et al.*[S4] The reaction of **19** with the alcohol **4c** did not proceed. Azeotropic removal of water from the solution of **19** in toluene afforded the corresponding dinuclear complex, $Co_2(\mu_2\text{-}OCO^tBu)_2(OCO^tBu)_2(bpy)_2$ (**20**), which was alternatively derived by treating anhydrous $Co(OCO^tBu)_2$ with **8a**. The complex **20** also did not reacted with the alcohol **4c** in toluene at 90 °C. The complexes **19** and **20** showed only moderate catalytic activities for the transesterification under the same condition as Table 1, even though complex **19** with the dinuclear skeleton mediated better catalytic activity than the cobalt pivalate salt and octanuclear cluster **2c** without any additives (49% yield for **19** and 48% yield for **20**).



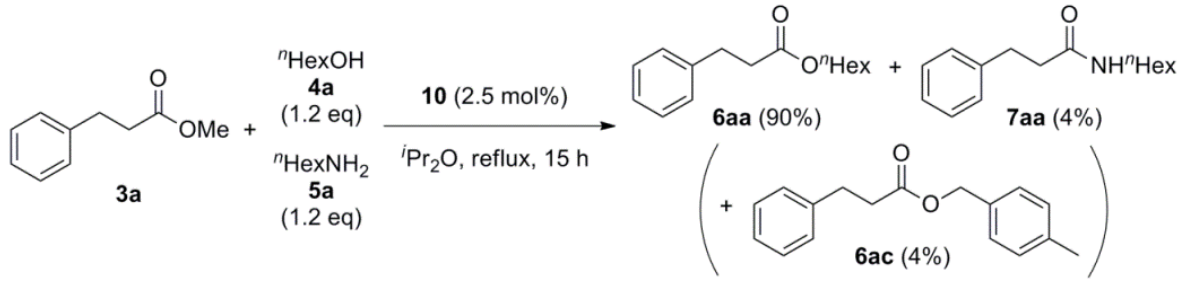
6. Preparation of Complex 10 by Reaction of $Co(OCO^tBu)_2$ and 2,2'-Bipyridine (8a) with Potassium Salt of 4c

A mixture of $Co(OCO^tBu)_2$ (52.2 mg, 0.20 mmol), 2,2'-bipyridine (**8a**, 62.5 mg, 0.40 mmol, 1.0 equiv.), and the potassium salt of **4c** (32.1 mg, 0.20mmol, 1.0 equiv.) in toluene (2.5 mL) was stirred at 70 °C for 15 h. After filtration, the red crystals of complex **10** were obtained from the resulting filtrate in 76% yield. The crystals were washed with hexane and dried under reduced pressure. When the sodium salt of **4c** was used as an alkoxide source, a mixed metal cluster compound **21** was obtained (Figure S9.)



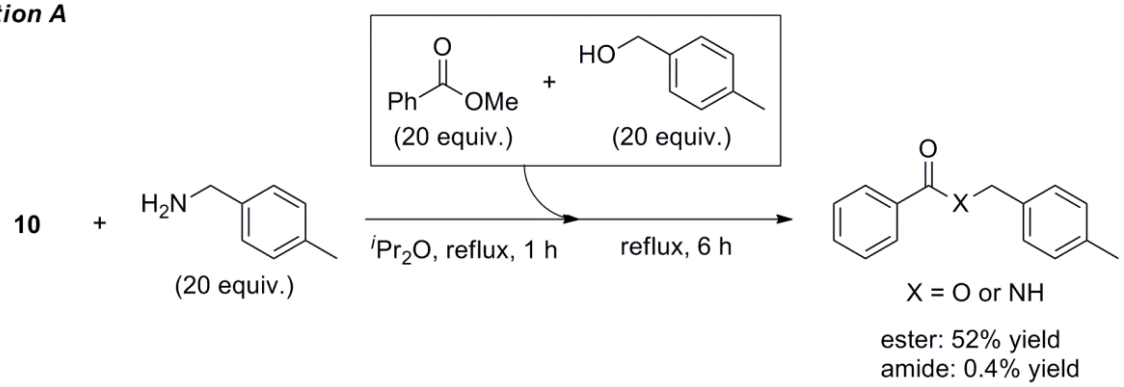
7. Selective O-Acylation Catalyzed by Complex 10

We investigated chemoselectivity of the complex **10** for the acylation in the presence of both alcohol and amine. The reaction proceeded with highly *O*-selective manner, giving the corresponding ester product in 90% yield.

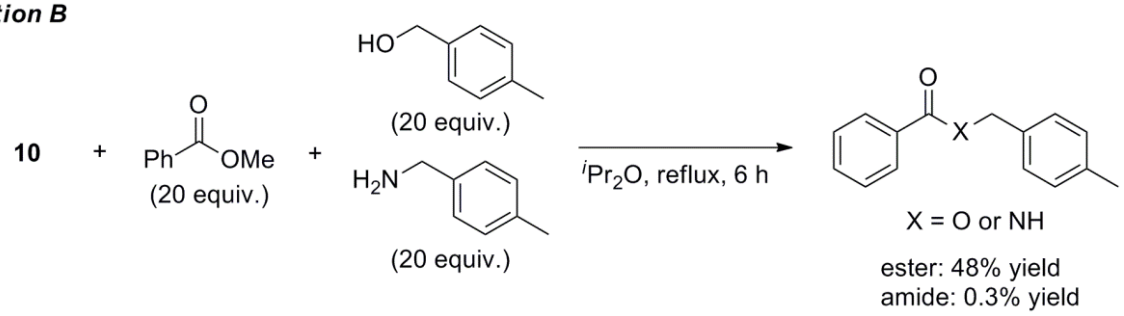


In addition, we conducted control experiments under two conditions; condition A: the complex **10** and 4-methylbenzyl amine were first reacted for 1 h in refluxed diisopropyl ether, and then methyl benzoate and 4-methylbenzyl alcohol were added to the reaction mixture and reacted for an additional 6 h; and condition B: all components were added at the same time and reacted in refluxed diisopropyl ether for 6 h. There was not much difference in chemoselectivity between conditions A and B, and we therefore suggest that the formation of a Co-amidate complex is unlikely.

Condition A



Condition B



8. UV-vis and ESI-MS Measurements

All samples were prepared in a glove box under an argon atmosphere and measured in a sealed cell which was filled with argon. Curve 1 in Figure 2 shows the absorption spectrum of **2c** in toluene without any additives and substrates, displaying three bands centered at 546 (ε = 813 $M^{-1}cm^{-1}$), 588 (ε = 1116 $M^{-1}cm^{-1}$), and 617 (ε = 1096 $M^{-1}cm^{-1}$) nm assignable to $^4A_2(F) \rightarrow {}^4T_1(P)$, $^4A_2(F) \rightarrow {}^4T_1(P)$ and $^4A_2(F) \rightarrow {}^4T_2(F)$ transitions, respectively, typical of tetrahedral Co(II) species.[S1,S8] Cryoscopic measurement of **2c** in benzene allocated the molecular weight of 1270, indicating that there was an equilibrium between octanuclear cluster **2c** (Mw = 1716) and its half segment, $Co_4(OCO^tBu)_6O$ (Mw = 858), in solution, as 34% of **2c** was estimated to dissociate into the tetranuclear cluster. When UV spectra of the toluene solutions of **2c** were measured in the presence of 20 equiv. of the alcohol **4c**, 20 equiv. of the ester **3b**, and both of them, all of these spectra were superimposed with that of **2c**, indicating that that neither alcohol nor ester were able to coordinate to the cobalt atoms of **2c**. Such the inertness of the pivalate cluster **2c** toward alcohol and ester explained the low catalytic activity of **2c** upon conducted without any amine additives.

The reaction mixture of complex **10** with the phenyl ester **12** and the alcohol **4c** afforded a UV-vis spectrum exhibited in Figure S1, curve b. An absorption band around 395 nm was shifted to around 375 nm, and intensity of a band at 500-700 nm was decreased compared to spectrum (curve a). The UV-vis absorbance of the reaction mixture of **10** with 12 equiv. of phenol (curve c) had exactly similar shape with curve b. They suggested that these two reaction mixtures contained almost the same components, which were the complex **10**, $Co_2(OCO^tBu)_2(bpy)_2(OCH_2\text{-}C_6H_4\text{-}4\text{-}CH_3)(OPh)$ (**13-A**), and $Co_2(OCO^tBu)_2(bpy)_2(OPh)_2$ (**13-B**). Figure S2 showed ESI-MS spectrum of reaction mixture of complex **10** with 2.0 eq of phenyl ester **12** at 60 ^oC after 2 h. The peak at *m/z* 725 is assigned to $[Co_2(OCO^tBu)_2(bpy)_2(OPh)]^+$, indicating the generation of phenoxy-bridged complex **13** during reaction.

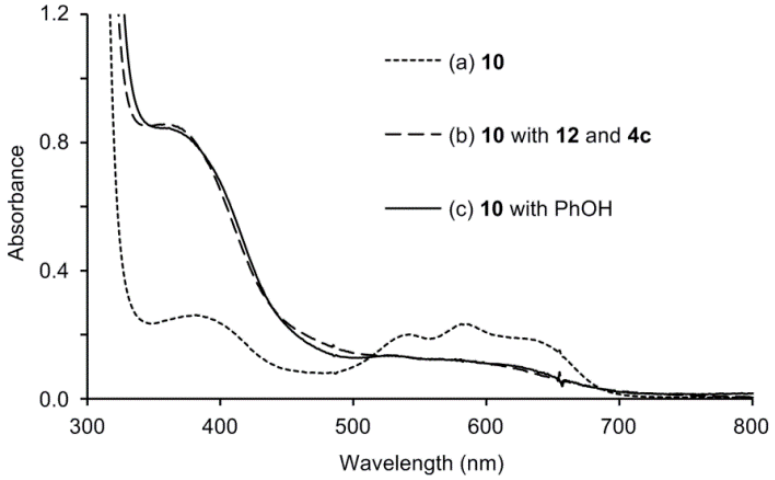


Figure S1. UV spectra of (a) the toluene solution of complex **10** (fine dashed line), (b) the reaction mixture of complex **10** with the phenyl ester **12** (20 equiv.) and the alcohol **4c** (20 equiv.) in toluene (coarse dashed line), and (c) the reaction mixture of complex **10** with 24 equiv. of phenol in toluene (solid line). All measurements were carried out at 60 ^{o}C. Concentrations: for all measurements [**10**] = 8.37 x10^{-4} M, for (a) [**12**] = 8.37 x 10^{-3} M, [**4c**] = 8.37 x 10^{-3} M, for (c) [phenol] = 2.00 x 10^{-2} M.

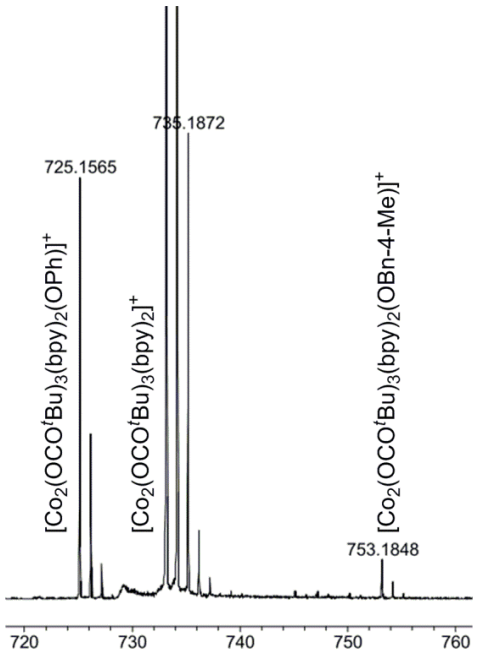


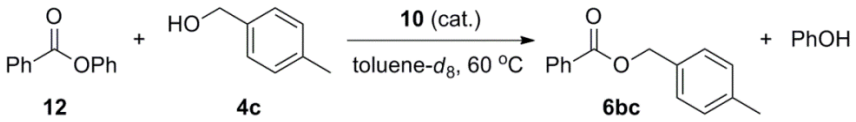
Figure S2. Poditive mode ESI-MS analysis of the reaction mixture of the complex **10** with 2.0 equiv. of the phenyl ester **12** (60 ^{o}C, 2 h). Cone voltage = 70 V. Four peaks at m/z 472 (assigned to $[Co(OCO^{t}Bu)(bpy)_2]^+$), 725 (assigned to $[Co_2(OCO^{t}Bu)_2(bpy)_2(OPh)]^+$), 733 (assigned to $[Co_2(OCO^{t}Bu)_3(bpy)_2]^+$), and 753 (assigned to $[Co_2(OCO^{t}Bu)_2(bpy)_2(OCH_2\text{-}4\text{-}Me\text{-}C_6H_4)]^+$) were detected.

9. Kinetic Experiments

Initial Rate Determination for Kinetic Studies

Initial velocity (v) was defined as time change in concentration of the produced benzyl ester **6bc** in the initial stage of reaction, experimentally determining from gradient of linear plot of the concentration against time. The concentration of **6bc** in reaction mixture was measured by monitoring the signals assigned to benzyl groups of **4c** and the product by ^{1}H NMR. The reaction initiated by heating the reaction mixture to 60 °C. A toluene solution of complex **10** was placed in a NMR tube and the solvent was removed under reduced pressure. Solutions of **12**, **4c** or phenol in toluene-d_8 were added to the NMR tube containing complex **10**. The mixture was diluted with toluene-d_8 to desired concentration, and then heated at 60 °C in oil bath. The reaction mixture was cooled with ice bath to stop the reaction before ^{1}H NMR measurements, which carried out at the reaction times in early stage (yields of the product < 5%). Experimental details and collected data were shown in supporting information.

Determination of Reaction Order on Catalyst 10



Under pseudo first-order conditions with large excess of substrates **12** and **4c**, changes in the concentrations of these two were thought to be negligible, and reaction order on catalyst **10** was defined as x in following rate equation, in which k is an experimental kinetic constant containing terms for substrate concentrations:

$$v = k_{obs}[\mathbf{10}]^x$$

By taking logarithms, above equation was rewritten as follows:

$$\ln v = \ln(k_{obs}) + x\ln([\mathbf{10}])$$

Hence, the reaction order on the catalyst **10** could be calculated from gradient of the linear plot of ln(v) against ln([**10**]). Collected initial velocity data and double logarithm plot were exhibited in Table S2 and Figure S3. The reaction order on catalyst **10** and pseudo-first order rate constant k_{obs} were determined to be 0.88 and 5.21 x 10^{-3} ($M^{-1}s^{-1}$), respectively. The reaction order on catalyst **10** was significantly affected time range for initial velocity measuring. Slight increase of time range for measuring initial velocity decreased the value of reaction order on catalyst **10**. Such the increase of phenol that inhibit the catalytic activity resulted in the estimation of the reaction order on catalyst **10** to 0.88, just a slightly less than 1-order.

[Experimental Detail]

A toluene solution of complex **10** (1.39 mM, 40 to 240 μL) was placed in a NMR tube and the solvent was removed under reduced pressure. 30 μL of solution containing **12** (1.64 M), 50 μL of solution containing **4c** (1.31 M) and 420 μL of toluene-d_8 were added to the NMR tube containing complex **10**, and then the mixture was heated at 60 ^{o}C in oil bath. The reaction mixture was cooled with ice bath to stop the reaction before ^{1}H NMR measurements, which carried out at reaction times 5, 10, 15, 20 and 25 min.

Table S2. Conditions and Initial Velocity Data to Determine Reaction Order on Catalyst **10** in Transesterification of **12** with **4c**.

Entry	[**10**] (10^{-4} M)	v (10^{-6} M s^{-1})
1	1.12	0.756
2	2.23	1.27
3	3.35	2.07
4	4.46	2.35
5	6.69	3.69

For each run, [**12**] = 9.87 x 10^{-2} M and [**4c**] = 1.31 x 10^{-1} M.

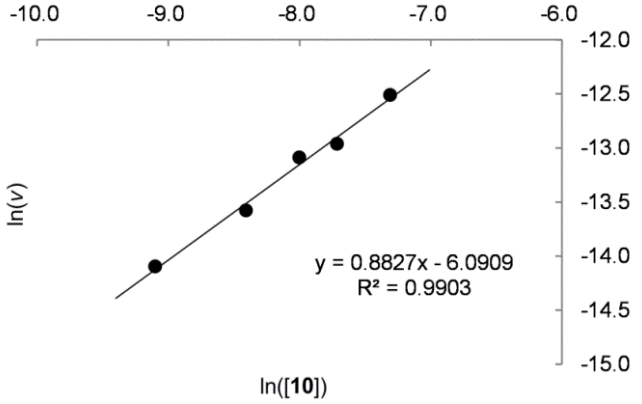


Figure S3. Double Logarithm Plot of Reaction Rate against Initial Concentration of Complex **10**.

Plot of Inverse Rate v^{-1} versus Inverse Substrate Concentration [S] $^{-1}$

The Michaelis-Menten constants $K_{m,\mathbf{12}}$, $K_{m,\mathbf{4c}}$ and catalytic constant k_{cat} were estimated by Lineweaver-Burk plot (1/[S] vs 1/v plot). When two substrate conentrations were varied, Lineweaver-Burk plots gave the series of straight lines intersecting at a single point to the left of the ordinate, being consistent with a ternary complex mechanism. The rate equation for the ordered ternary complex mechanism is as follows:

$$v = \frac{V_{\max}[\mathrm{A}][\mathrm{B}]}{K_{ia}K_b + K_{ma}[B] + K_b[A] + [A][B]}$$

[Experimental Detail]

A toluene solution of complex **10** (3.52 mM, 120 μL) was placed in a NMR tube and the solvent was removed under reduced pressure. 60 to 300 μL of solution containing **12** (0.721 M), 60 to 300 μL of solution containing **4c** (0.729 M) and toluene-d_8 were added to the NMR tube containing complex **10** with one substrate concentration being kept constant while the other was varied (total amount was 700 μL), and then the mixture was heated at 60 ^{o}C in oil bath. The operation for collecting initial velocity data was similar to the method illustrated in above. Collected data were summarized in Table S3 and plots of inverse rate versus inverse substrate concentration were shown in Figure 4 (a) and (b).

Table S3. Conditions and Initial Velocity Data to Plot Inverse Rate v^{-1} against Inverse Substrate Concentration [**12**] $^{-1}$ or [**4c**] $^{-1}$.

entry	[**12**] (10^{-1} M)	[**4c**] (10^{-1} M)	v (10^{-6} M s^{-1})
1	1.24	0.625	2.26
2	1.24	1.25	3.30
3	1.24	1.87	4.33
4	1.24	2.50	5.25
5	1.24	3.12	6.16
6	1.25	7.57	12.1
7	1.85	0.625	2.79
8	1.85	1.25	4.07
9	1.85	1.87	5.41
10	1.85	2.50	6.45
11	1.85	3.12	7.43
12	1.87	7.57	16.3
13	2.47	0.625	3.53
14	2.47	1.25	5.42
15	2.47	1.87	7.16
16	2.47	2.50	8.68
17	2.47	3.12	9.44
18	2.49	7.57	18.8
19	3.09	0.625	3.96
20	3.09	1.25	5.95
21	3.09	1.87	7.67
22	3.09	2.50	9.37

23	3.09	3.12	10.9
24	3.11	7.57	22.2
25	9.40	0.625	7.48
26	9.40	1.25	12.0
27	9.40	1.87	14.8
28	9.40	2.08	16.3
29	9.40	2.50	18.0

For each run, [**10**] = 6.03 x 10^{-4} M.

Inhibition Experiments with Phenol

The typical pattern for competitive inhibition was observed in Figure 4 (c). The rate equation for Michaelis-Menten mechanism with competitive inhibition is as follows:

$$v = \frac{V_{\max}[\mathrm{S}]}{K_m\left(1 + \frac{[\mathrm{I}]}{K_i}\right) + [\mathrm{S}]}$$

(I: inhibitor, K_i: inhibition constant)

Collected data were summarized in Table S4 and Dixon plot was generated to yield an inhibition constant K_i, and shown in Figure S4.

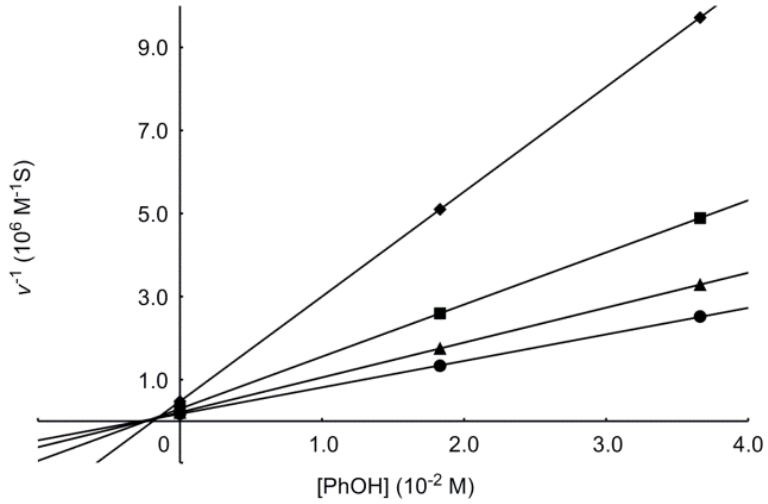


Figure S4. Dixon Plot for Inhibition on **10**-catalyzed Transesterification of **12** with **4c** by Phenol.

[Experimental Detail]

A toluene solution of complex **10** (1.39 mM, 200 μL) was placed in a NMR tube and the solvent was removed under reduced pressure. 500 μL of solution containing **12** (1.04 M), 20 to 80 μL of solution containing **4c** (0.280 M), 0 to 20 μL of solution containing phenol (1.10

M) and toluene-d_8 were added to the NMR tube containing complex **10** with phenol concentration being kept constant while concentration of **4c** was varied (total amount was 600 mL), and then the mixture was heated at 60 ^{o}C in oil bath. The operation for collecting initial velocity data was similar to the method illustrated in above.

Table S4. Conditions and Initial Velocity Data for Inhibition Experiments of PhOH on Transesterification of **12** with **4c** catalyzed by **10**.

entry	[PhOH] (10^{-2} M)	[**4c**] (10^{-2} M)	v (10^{-7} M s^{-1})
1	0	0.934	21.1
2	0	1.87	33.9
3	0	2.80	47.3
4	0	3.73	55.4
5	0	4.67	64.4
6	1.83	0.93	1.96
7	1.83	1.87	3.86
8	1.83	2.8	5.71
9	1.83	3.73	7.51
10	3.66	0.93	1.03
11	3.66	1.87	2.05
12	3.66	2.8	3.04
13	3.66	3.73	3.97

For each run, [**10**] = 4.65 x 10^{-4} M and [**12**] = 8.63 x 10^{-1} M.

10. Computational Methods

All calculations reported in the present study were carried out using density functional theory with the B3LYP-D functional,[S9] as implemented in the Gaussian09 program package.[S10] For geometry optimizations, the 6-31G(*d*,*p*) basis set was used for the C, N, O, H elements, and the LANL2DZ[S11] pseudopotential for Co. Based on these optimized geometries, single-point calculations were carried out with the 6-311+G(*2d*,*2p*) basis set for all elements. The stationary points were confirmed as minima (no imaginary frequencies) or transition states (only one imaginary frequency) by analytical frequency calculations at the same theory level as the geometry optimizations. The reported energies are Gibbs free energies which include zero-point vibrational corrections, thermal corrections at 298 K, and solvation free energies. The latter are calculated as single-point corrections on the optimized structures using the conductor-like polarizable continuum model (CPCM)[S12] method with the UFF radii and with the parameters for toluene. All possible spin states were considered. In general, we found that high-spin ferromagnetic (septet) and high-spin antiferromagnetic (open-shell singlet) species have very similar energies, while the other possible spin combinations have considerably higher energies (by more than 20 kcal/mol). Thus, all species reported in the present study were located on the septet surface. Full models of all the reaction components were used with the exception of pivalate groups which were modeled as acetates.

It should be pointed out that methods it was impossible to locate ternary complex **14-A** using the standard B3LYP functional. It is well known that standard DFT methods lack a description of London dispersion forces. In recent years different approaches have been proposed to correct this.[S13] Here we used the empirical correction proposed by Grimme[S9c] already in the geometry optimizations.

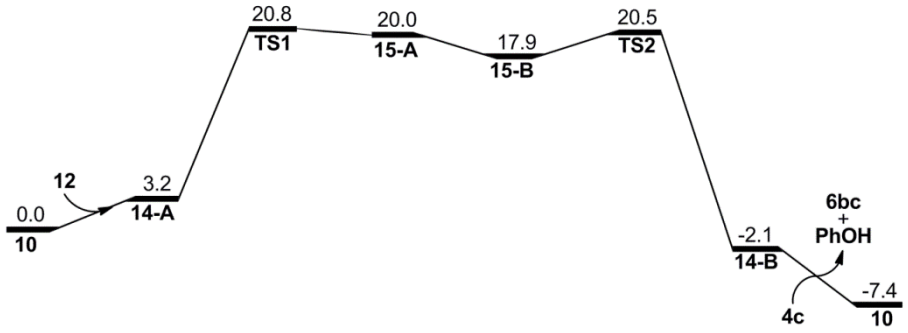
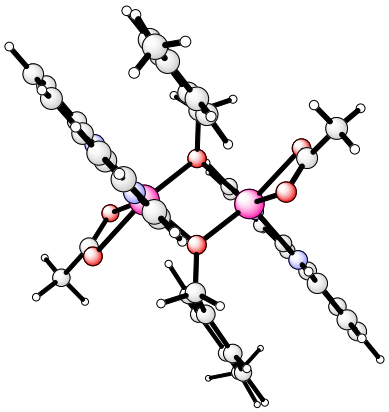


Figure S5. Energy diagram for the catalytic cycle of **10**.

Optimized structures and Cartesian coordinates of stationary points

- Complex **10**



B3LYP-D/6-311+g(2d,2p) energy: -4985.3484058070 a.u.

ZPE: 0.725379 a.u.

Thermal correction to Gibbs Free Energy: 0.634423 a.u.

Solvation energy: -10.22 kcal/mol

Co	-0.88145500	1.23389200	0.40954600
Co	0.89071700	-1.20347300	-0.33112900
O	0.66711500	0.14412300	1.15513400
O	-0.61918500	-0.08267300	-1.09558400
O	-0.12138100	3.09438000	-0.30235900
O	0.03868600	-3.02244100	0.39914900
O	-0.52264500	2.89710800	1.86293400
O	0.48555100	-2.87304200	-1.76150700
N	-2.83596100	1.95709500	-0.29439300
N	2.80062300	-1.98999200	0.41515900
N	-2.35793200	0.29861200	1.68445600
N	2.41436700	-0.37748100	-1.61865900
C	1.59009800	0.50003300	2.14540100
C	-1.48277200	-0.38291600	-2.15420700
C	2.89482100	1.01961300	1.56688200
C	-2.83110400	-0.89988900	-1.68529400
C	4.13034700	0.62963500	2.08599700
C	-4.01701800	-0.50517800	-2.30773200
C	5.32419800	1.08337600	1.51560000
C	-5.25523800	-0.96223600	-1.84721500
C	5.30997100	1.94823000	0.41733700
C	-5.33742400	-1.83385600	-0.75659500

C	4.06514900	2.35918200	-0.08428900
C	-4.14140900	-2.24745700	-0.15032900
C	2.87661700	1.89779000	0.47245900
C	-2.90799300	-1.78286400	-0.59834700
C	6.58827500	2.39620000	-0.24869500
C	-6.67006700	-2.29017000	-0.21293000
C	-0.08089500	3.56421100	0.88859400
C	-0.00204400	-3.50613300	-0.78609900
C	0.58319400	4.90705800	1.11387900
C	-0.72341500	-4.81967600	-1.00820300
C	-2.97265400	2.77804300	-1.33801300
C	2.88968800	-2.79060700	1.47994200
C	-4.22196600	3.19218100	-1.80180800
C	4.11325900	-3.25929300	1.95974300
C	-3.92731600	1.51177000	0.35570100
C	-3.65728200	0.57551600	1.47327700
C	3.69881800	-0.69968700	-1.38222400
C	-4.65934600	-0.03209900	2.23611200
C	4.73333800	-0.15654600	-2.14985700
C	-4.29443500	-0.96216700	3.20691200
C	4.41737300	0.74530600	-3.16335200
C	-2.94526700	-1.26814000	3.38867900
C	3.08319300	1.09213700	-3.37845600
C	-2.00311000	-0.60494600	2.60185400
C	2.10706200	0.50076200	-2.57618400
H	1.82366500	-0.36597000	2.79225800
H	-1.65874500	0.51169400	-2.78053600
H	1.14704900	1.28202800	2.78243100
H	-1.01394600	-1.14923400	-2.79256300
H	4.16079900	-0.06715800	2.92091000
H	-3.97424800	0.19362200	-3.14022300
H	6.27847100	0.74792900	1.91679800
H	-6.17089500	-0.62437700	-2.32825000
H	4.03106800	3.02403900	-0.94434000
H	-4.18169200	-2.91630800	0.70653900
H	1.92532100	2.18418600	0.03952300
H	-1.99834600	-2.06867900	-0.08412900
H	6.61692000	3.48586900	-0.37096500

H	-6.71098800	-3.38201600	-0.11539100
H	6.67951900	1.95949300	-1.25363800
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H	-2.04094600	3.11021200	-1.78454200
H	1.93995200	-3.06230400	1.92940000
H	-4.29482200	3.85367400	-2.65872400
H	4.14823100	-3.90099100	2.83386800
H	-5.05775800	-1.45288600	3.80369000
H	5.20709100	1.18366400	-3.76641300
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H	2.80018900	1.80439100	-4.14607700
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H	1.04898300	0.72853500	-2.66037100
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C	5.17894700	-2.06500200	0.16378800
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C	5.27568100	-2.89003000	1.28121600
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C	-5.35976000	2.74114100	-1.13247300
C	-5.21403400	1.89254800	-0.03795500
H	-6.08576000	1.52284900	0.48762900
H	-6.35042000	3.04233600	-1.46003000
H	-7.49479400	-1.97533400	-0.86144900
H	7.46797100	2.09525400	0.33060900
H	5.76631200	-0.41225300	-1.94851800
H	-5.70399700	0.19527500	2.06186000
H	0.35739700	5.59044100	0.28992700
H	1.66840100	4.74421400	1.13016000
H	0.27643200	5.33726000	2.07024400
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H	-0.40077700	-5.28712100	-1.94168000
H	-0.56670600	-5.49376100	-0.16100100

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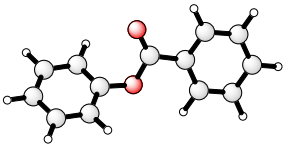


B3LYP-D/6-311+g(2d,2p) energy: -652.0848477910 a.u.

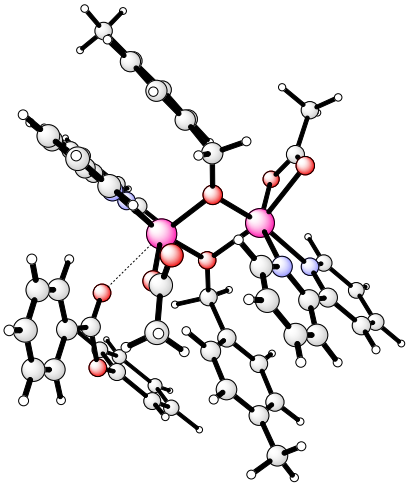
ZPE: 0.195518 a.u.

Thermal correction to Gibbs Free Energy: 0.155579 a.u.

Solvation energy: -2.31 kcal/mol

O	0.08539300	-1.73758700	-0.47240200
C	0.43369200	-0.61852000	-0.16697100
C	1.84995600	-0.17525300	-0.04989000
C	2.20834500	1.12869000	0.32371100
C	2.84747300	-1.12129400	-0.32851600
C	3.55481600	1.47794700	0.41698000
H	1.43389800	1.85573400	0.53773800
C	4.19108800	-0.76700800	-0.23531600
H	2.54565600	-2.12312800	-0.61466700
C	4.54613600	0.53289800	0.13793600
H	3.83140200	2.48719700	0.70694600
H	4.96121100	-1.50116500	-0.45214900
H	5.59416100	0.80914100	0.21111200
O	-0.43098000	0.40589800	0.11273000
C	-1.81253600	0.22301500	0.06573600
C	-2.44941800	-0.87802500	0.63994700
C	-2.53884600	1.25776900	-0.52122400
C	-3.84397500	-0.93381500	0.61133600
H	-1.86495200	-1.67401100	1.08168100
C	-3.93247900	1.18966900	-0.53822000
H	-2.00536700	2.09876600	-0.95185800
C	-4.58871700	0.09329500	0.02612600
H	-4.34886300	-1.78842700	1.05187300
H	-4.50267300	1.99390400	-0.99360200
H	-5.67299200	0.03930000	0.01049100

- 14-A



B3LYP-D/6-311+g(2d,2p) energy: -5637.4579685120 a.u.

ZPE: 0.923253 a.u.

Thermal correction to Gibbs Free Energy: 0.8158690000 a.u.

Solvation energy: -10.03 kcal/mol

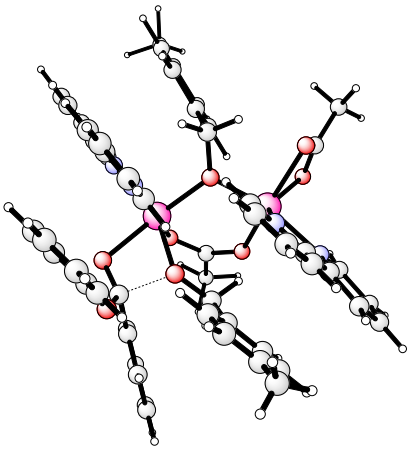
Co	-0.94364500	0.32837700	-0.25149700
Co	0.45674300	-2.40963500	-0.48970100
O	0.58264800	-0.70058300	0.59223600
O	-1.13393200	-1.39503600	-1.24078900
O	-0.54061200	1.48754100	-3.53737200
O	-0.32730900	-3.88691700	0.82134600
O	-0.01229700	1.72523900	-1.35309800
O	-0.27702100	-4.33661200	-1.34257500
N	-2.93816900	1.08536300	-0.86806600
N	2.46608900	-3.15721900	0.04178700
N	-2.21834100	0.13830100	1.47187400
N	1.78223800	-1.73192800	-2.07276800
C	1.60787300	-0.38665400	1.49115600
C	-2.24939100	-1.87998900	-1.93488400
C	2.88570200	0.05149300	0.80393600
C	-3.46405100	-2.02386100	-1.03544100
C	4.12252900	-0.47577100	1.17694000
C	-4.73490700	-1.62823500	-1.45587300
C	5.30234300	-0.04149500	0.56690600
C	-5.83456800	-1.71560300	-0.59643000
C	5.27118200	0.93692500	-0.43243300

C	-5.69077000	-2.21036500	0.70356200
C	4.02479500	1.47042800	-0.79615400
C	-4.41661400	-2.63349600	1.11265000
C	2.84663000	1.03245400	-0.19694400
C	-3.31825100	-2.53511700	0.26355800
C	6.53039900	1.37070400	-1.14329500
C	-6.85675200	-2.25698500	1.66143000
C	0.10940800	1.99596000	-2.60882400
C	-0.61962600	-4.64572300	-0.17015800
C	1.19828100	3.02142500	-2.91288700
C	-1.45581900	-5.88155700	0.08916500
C	-3.22204400	1.49036700	-2.11193900
C	2.70944900	-3.92943900	1.10531900
C	-4.48548200	1.97421500	-2.45980800
C	3.98350600	-4.41654600	1.39860500
C	-3.89237000	1.11960900	0.08209500
C	-3.49159400	0.56493200	1.39590500
C	3.10515800	-1.92695500	-1.90748100
C	-4.36575000	0.43203900	2.47948600
C	4.04174000	-1.27173800	-2.70965500
C	-3.90496900	-0.17027600	3.64726700
C	3.58553200	-0.39114700	-3.69198700
C	-2.58968200	-0.63154600	3.70310200
C	2.21634200	-0.18318900	-3.84079500
C	-1.77577900	-0.45270700	2.58531600
C	1.34324100	-0.88022900	-3.00185500
H	1.83999900	-1.26277200	2.12219400
H	-2.50792300	-1.20651600	-2.77029700
H	1.28103400	0.42266300	2.16334700
H	-1.99727000	-2.86262400	-2.36278000
H	4.16025000	-1.24825600	1.94159200
H	-4.85847400	-1.20986900	-2.45209400
H	6.25676500	-0.47463800	0.85978500
H	-6.81286000	-1.37732300	-0.93202300
H	3.98281200	2.23381900	-1.57014100
H	-4.28094300	-3.01484600	2.12243100
H	1.88704000	1.43422400	-0.50629300
H	-2.33155000	-2.82037100	0.61093300

H	6.53568300	2.45217800	-1.32289700
H	-6.98345100	-3.25816500	2.09174000
H	6.61751200	0.88265400	-2.12495500
H	-6.70219100	-1.56567100	2.50199800
H	-2.39842100	1.41963500	-2.82152600
H	1.83816700	-4.15829200	1.71143000
H	-4.68110400	2.28783900	-3.48000300
H	4.14353300	-5.03338100	2.27669700
H	-4.57128600	-0.29183200	4.49622900
H	4.29845800	0.14256100	-4.31408800
H	-2.19822300	-1.12266500	4.58745800
H	1.80402300	0.51828700	-4.55658400
H	-0.74935000	-0.79776300	2.54201900
H	0.27122300	-0.72711100	-3.03607800
C	3.47241600	-2.83175600	-0.79223700
C	4.77205000	-3.30691400	-0.58418400
H	5.56512900	-3.05323600	-1.27720000
C	5.02914400	-4.10333600	0.52803000
H	6.03243800	-4.47684700	0.71144100
C	-5.47060800	2.04574400	-1.47541800
C	-5.17377500	1.61023700	-0.18617400
H	-5.92951600	1.63905400	0.58900200
H	-6.46153800	2.42546300	-1.70732300
H	-7.79294600	-1.97996300	1.16464500
H	7.42517200	1.11320900	-0.56603600
H	5.10327900	-1.40598400	-2.54130600
H	-5.39294800	0.76696200	2.40651300
H	1.15558000	3.33130800	-3.96009300
H	2.17099300	2.55735700	-2.71180700
H	1.09724700	3.88819400	-2.25306100
H	-2.50331300	-5.56387100	0.16802900
H	-1.36366900	-6.59434200	-0.73378400
H	-1.17228100	-6.34449600	1.03900000
C	0.61401200	5.50082900	-0.11607000
C	0.16596800	6.37952800	-1.10305500
C	-1.03178500	6.12478400	-1.77777400
C	-1.79170400	4.99455300	-1.45743600
C	-1.35099100	4.11943300	-0.47005000

C	-0.14249000	4.36231300	0.19748100
H	1.54802500	5.68429900	0.40240200
H	0.75439500	7.25805900	-1.35094400
H	-1.37105900	6.80537300	-2.55383800
H	-2.71696200	4.78539600	-1.98614900
H	-1.90474400	3.22338600	-0.22838600
C	0.29495100	3.36588200	1.20440500
O	-0.33133600	2.37143200	1.51942000
O	1.49366700	3.70301400	1.76263300
C	2.02701000	2.93480100	2.79912900
C	3.35380400	2.53782600	2.66927200
C	1.28173500	2.63856500	3.94161300
C	3.94611100	1.81310200	3.70514200
H	3.89109000	2.75692700	1.75431900
C	1.88576100	1.91101800	4.96720200
H	0.24866900	2.95674300	4.01021200
C	3.21624600	1.49472900	4.85193100
H	4.97317200	1.48005700	3.59586200
H	1.31341200	1.66892000	5.85816800
H	3.67879400	0.92439200	5.65221200

- TS1



B3LYP-D/6-311+g(2d,2p) energy: -5637.4320626200 a.u.

ZPE: 0.922515 a.u.

Thermal correction to Gibbs Free Energy: 0.81817 a.u.

Solvation energy: -10.11 kcal/mol

C	0.13203600	3.35481700	-2.90433100

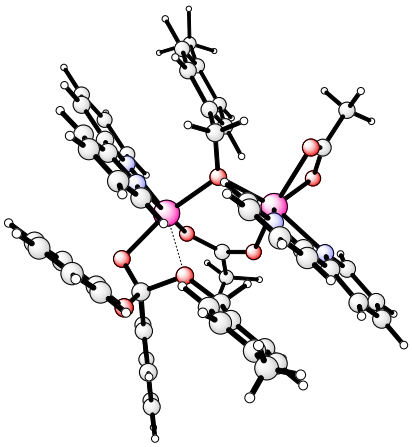
C	0.14783600	2.45013700	-1.84489700
C	-2.07421000	2.88028500	-1.32147800
C	-2.16794900	3.81296300	-2.36158100
C	-1.05228600	4.04331200	-3.16307700
H	1.03161700	3.53705700	-3.47983400
H	1.03063300	1.88777600	-1.56454300
H	-3.09047700	4.35110300	-2.54288300
H	-1.10447000	4.76632600	-3.97139100
C	-3.19937200	2.54188200	-0.41199900
C	-4.47986700	3.09380800	-0.52422600
C	-5.47228000	2.68033300	0.36207500
H	-4.70462500	3.82188900	-1.29411100
C	-3.86810000	1.23144200	1.38981500
C	-5.16939300	1.73012800	1.33585300
H	-6.47539300	3.08828800	0.28244200
H	-3.55468100	0.48269900	2.10952900
H	-5.92066000	1.36894300	2.02903700
N	-0.92942100	2.21096100	-1.09474000
N	-2.91806400	1.63275100	0.54067900
Co	-0.38797800	-2.42439100	-0.49603700
Co	-0.94178100	0.78167300	0.55261500
C	-1.90052100	-4.14448200	-1.51725000
O	-1.31685900	-3.36363600	-2.32056400
O	-1.64368000	-4.10438900	-0.26673300
C	-2.96334200	-5.10318400	-2.01328400
C	-0.83088200	-1.53597800	2.42815200
O	-0.23645100	-2.26303200	1.58466400
O	-1.31021000	-0.38233800	2.21437000
C	-0.94827700	-2.07703200	3.84531100
O	-1.39823200	-0.71350600	-0.72962800
C	-2.45234400	-0.60008900	-1.65358100
H	-2.29156000	-1.31479300	-2.47316100
H	-2.47317500	0.40980900	-2.09447000
C	-3.80674700	-0.86820300	-1.02540200
C	-3.93399800	-1.72987200	0.07140500
C	-4.95660300	-0.25321100	-1.52985800
C	-5.18400200	-1.95398700	0.65025100
H	-3.05107300	-2.21968700	0.46519100

C	-6.20451800	-0.47981800	-0.94902700
H	-4.86931200	0.42631100	-2.37530400
C	-6.33679700	-1.32650800	0.15894100
H	-5.26719400	-2.62676700	1.50144400
H	-7.08649100	0.01668600	-1.34885500
C	-7.67762900	-1.52811800	0.82433900
H	-7.72992500	-2.50127100	1.32479000
H	-7.86488400	-0.75878900	1.58740400
H	-8.49622900	-1.47008500	0.09789600
O	1.19690900	0.79938000	0.67309800
H	-2.86523800	-5.26942900	-3.08881400
H	-3.94355000	-4.65402700	-1.81040700
H	-2.90893900	-6.04974000	-1.46756400
H	-1.83497700	-1.67148300	4.34075700
H	-0.97158700	-3.16980600	3.84134300
H	-0.06525700	-1.74437200	4.40377000
O	-0.20791400	2.42365200	1.75046800
C	1.02970900	2.22178800	1.87040300
C	2.03182400	-0.16191300	-3.43171800
C	1.03525400	-0.62723000	-2.57610400
C	2.38356500	-2.35435400	-1.81377200
C	3.43165600	-1.95324400	-2.64669900
C	3.25092300	-0.83956700	-3.46227700
H	1.85467900	0.71689200	-4.04269600
H	0.07168200	-0.14405800	-2.47244800
H	4.37739500	-2.47905100	-2.63713500
H	4.05921700	-0.49887400	-4.10132300
C	2.46185300	-3.49794000	-0.87429000
C	3.62913100	-4.22995000	-0.63167200
C	3.58518000	-5.27031900	0.29446000
H	4.55301600	-3.97669100	-1.13697800
C	1.26907800	-4.76746400	0.66431500
C	2.38737000	-5.55019900	0.95535400
H	4.47886400	-5.85152800	0.50220600
H	0.30312200	-4.90998600	1.13661200
H	2.31916100	-6.35094400	1.68427200
N	1.21143600	-1.69406900	-1.79488500
N	1.31543100	-3.77487100	-0.22709100

C	1.61315200	1.65142500	3.13072400
C	0.73986700	1.06888700	4.05574600
C	2.99252100	1.65090900	3.38090900
C	1.24256000	0.50175300	5.22817800
H	-0.31807700	1.04513300	3.82476200
C	3.49104000	1.07974800	4.55229500
H	3.66557300	2.08295800	2.64946600
C	2.61752700	0.50579100	5.48048700
H	0.55877600	0.05543500	5.94524000
H	4.56154800	1.08002000	4.73874900
H	3.00641000	0.06239600	6.39334600
O	1.96167500	3.12616900	1.33115700
C	1.65895200	4.06660800	0.38150000
C	0.46688300	4.80616400	0.34431400
C	2.68904200	4.34860300	-0.52619600
C	0.32177300	5.80949900	-0.61405000
H	-0.32028900	4.58035400	1.04838900
C	2.52847700	5.35873600	-1.47515400
H	3.61000800	3.77928100	-0.45575900
C	1.34078800	6.09271500	-1.52803700
H	-0.60387900	6.37774800	-0.64286200
H	3.33739000	5.57541700	-2.16834000
H	1.21395700	6.88101900	-2.26464800
C	2.07027100	-0.26284500	0.93360500
H	2.21755900	-0.40754300	2.01493100
H	1.61819200	-1.19598000	0.58827800
C	3.42565600	-0.12029900	0.27248900
C	4.40903100	-1.09666900	0.48199300
C	3.71547000	0.93512900	-0.59384300
C	5.63565800	-1.03023900	-0.17756600
H	4.19960200	-1.92645900	1.15303700
C	4.94739800	1.00676300	-1.24699300
H	2.96183800	1.69681900	-0.74214600
C	5.92592500	0.02385100	-1.05615100
H	6.38401900	-1.80208200	-0.00791800
H	5.15181900	1.83577900	-1.92283300
C	7.26616300	0.11423200	-1.74694500
H	7.70538700	-0.87854400	-1.89712400

H	7.17811800	0.60310200	-2.72410200
H	7.98156100	0.70034500	-1.15394800

- 15-A



B3LYP-D/6-311+g(2d,2p) energy: -5637.4352206500 a.u.

ZPE: 0.924191 a.u.

Thermal correction to Gibbs Free Energy: 0.820521 a.u.

Solvation energy: -10.45 kcal/mol

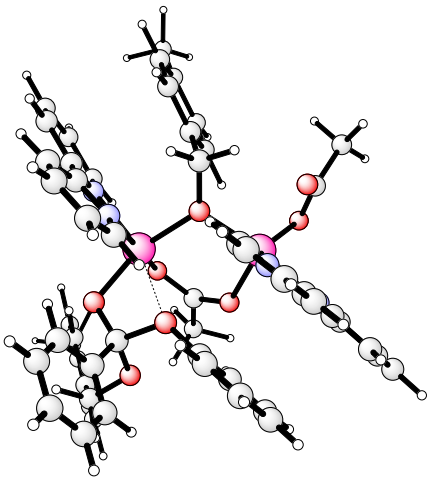
C	0.20828200	3.47680600	-2.82591800
C	0.15469100	2.48456300	-1.84946700
C	-2.05046400	2.97791800	-1.32994800
C	-2.07281300	4.00880500	-2.27758400
C	-0.93022000	4.25262300	-3.03641800
H	1.13077800	3.66561300	-3.36048100
H	1.01121400	1.86615100	-1.61125200
H	-2.95868900	4.61886200	-2.41002700
H	-0.92390700	5.05400600	-3.76886400
C	-3.21240300	2.62780300	-0.47375400
C	-4.49115100	3.16667500	-0.65151600
C	-5.52095100	2.75224600	0.19028100
H	-4.68494400	3.87989200	-1.44404400
C	-3.95684100	1.32096200	1.30047800
C	-5.25600300	1.81311500	1.18549200
H	-6.52313300	3.14912200	0.05867700
H	-3.67424600	0.57614300	2.03607600
H	-6.03539500	1.45103500	1.84594400
N	-0.94723200	2.23103600	-1.14071100

N	-2.96915900	1.72281000	0.49420700
Co	-0.43696700	-2.38193900	-0.41151100
Co	-1.02796400	0.82047000	0.55822400
C	-1.99268100	-4.09844300	-1.36116800
O	-1.37759900	-3.37911400	-2.19755200
O	-1.73321200	-4.01231100	-0.11266600
C	-3.09828200	-5.02983900	-1.81163600
C	-0.88740700	-1.43675600	2.47473400
O	-0.23227900	-2.14389400	1.65807200
O	-1.44737500	-0.32957800	2.21324200
C	-0.97173700	-1.92877100	3.91023800
O	-1.43212900	-0.67344400	-0.72463600
C	-2.46120100	-0.56528600	-1.67800200
H	-2.28737200	-1.29435000	-2.48194200
H	-2.45706000	0.43919100	-2.13104600
C	-3.83584000	-0.80970600	-1.08422200
C	-4.00289800	-1.62827000	0.03935600
C	-4.96687500	-0.21537000	-1.65231500
C	-5.27332100	-1.83485800	0.57910300
H	-3.13413200	-2.09518300	0.48694900
C	-6.23522900	-0.42372700	-1.10999100
H	-4.84917500	0.43183900	-2.51928000
C	-6.40778300	-1.23040000	0.02191700
H	-5.38659500	-2.47419100	1.45227700
H	-7.10244700	0.05541500	-1.56013300
C	-7.77187100	-1.41083700	0.64475200
H	-7.84251800	-2.36670200	1.17531100
H	-7.98631100	-0.61667900	1.37456200
H	-8.56380900	-1.37764600	-0.11210900
O	1.28271800	0.65967300	0.78658200
H	-3.03139000	-5.22273300	-2.88494000
H	-4.05685300	-4.54266200	-1.59395700
H	-3.06270800	-5.96576400	-1.24607600
H	-1.90982100	-1.60641700	4.37069700
H	-0.87124900	-3.01604800	3.95417800
H	-0.14614300	-1.47156900	4.46904800
O	-0.03350500	2.27790000	1.55941600
C	1.20262000	1.88700500	1.67307400

C	1.98214400	-0.32132500	-3.48436200
C	1.01111600	-0.68850400	-2.55488200
C	2.31392700	-2.43800500	-1.76453800
C	3.33449200	-2.13588200	-2.66966800
C	3.16352000	-1.06135600	-3.53802200
H	1.81464100	0.52941400	-4.13636500
H	0.07499200	-0.15715900	-2.43411600
H	4.24913600	-2.71445700	-2.68330500
H	3.95005600	-0.79988700	-4.23859900
C	2.38012500	-3.54414000	-0.78097700
C	3.53521900	-4.28994700	-0.52274000
C	3.47872100	-5.29557400	0.44083400
H	4.45953400	-4.06903500	-1.04254300
C	1.17738800	-4.73022900	0.81480400
C	2.28164700	-5.52681600	1.12159400
H	4.36224800	-5.88713400	0.66241000
H	0.21417400	-4.83486800	1.30228600
H	2.20411800	-6.29985800	1.87875500
N	1.17717200	-1.71890600	-1.72304000
N	1.23538600	-3.77110800	-0.11185300
C	1.68169900	1.56165800	3.08745900
C	0.72463400	1.16593500	4.02778600
C	3.03141000	1.61785500	3.46000700
C	1.11321700	0.83044600	5.32685900
H	-0.31263100	1.11575900	3.71910300
C	3.41769800	1.28161500	4.75925200
H	3.77103200	1.92433600	2.72897500
C	2.45986700	0.88650400	5.69700100
H	0.36130600	0.52898900	6.05176800
H	4.46684500	1.33011200	5.03899700
H	2.76041100	0.62741200	6.70886300
O	2.22591400	2.78900200	1.12465000
C	1.95138700	3.84462200	0.31075200
C	0.83353000	4.68981100	0.43568300
C	2.93149300	4.13746800	-0.65370200
C	0.70505100	5.78567800	-0.41711800
H	0.08761900	4.46532500	1.18345900
C	2.79220300	5.24507500	-1.49038000

H	3.80648700	3.49861200	-0.70995600
C	1.67155700	6.07294600	-1.38614000
H	-0.16513900	6.42923400	-0.31472300
H	3.56677100	5.46232000	-2.22205600
H	1.56033300	6.93568700	-2.03699300
C	2.22340900	-0.38015300	1.01755900
H	2.44519400	-0.47027400	2.08611800
H	1.71859400	-1.30385600	0.73383000
C	3.50964600	-0.25050400	0.23542300
C	4.51957100	-1.20268900	0.43108700
C	3.71151300	0.74377200	-0.72101000
C	5.69186400	-1.16548200	-0.32241200
H	4.37647700	-1.98820900	1.16947400
C	4.89096500	0.78786700	-1.46532800
H	2.94144500	1.48732000	-0.86429900
C	5.89888200	-0.16579400	-1.28411400
H	6.46327400	-1.91568200	-0.15949800
H	5.02737100	1.57306000	-2.20646700
C	7.18367000	-0.10276100	-2.07547800
H	7.60672000	-1.10197100	-2.23013400
H	7.02435600	0.35975200	-3.05614800
H	7.94309900	0.49460200	-1.55303300

- 15-B



B3LYP-D/6-311+g(2d,2p) energy: -5637.4339935100 a.u.

ZPE: 0.923234 a.u.

Thermal correction to Gibbs Free Energy: 0.815987 a.u.

Solvation energy: -10.43 kcal/mol

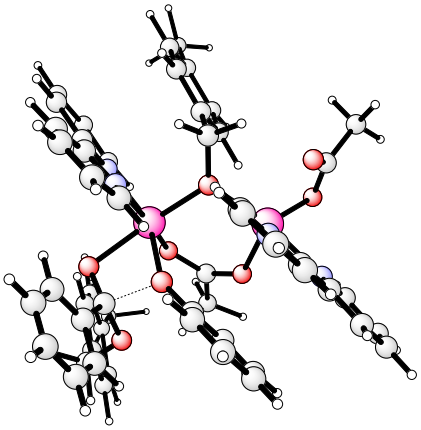
C	0.39047100	-1.90027900	4.55354800
C	0.35245200	-1.37327600	3.26189500
C	-1.93664900	-1.71341900	3.09507600
C	-1.98260200	-2.26637000	4.38110500
C	-0.80330900	-2.34969900	5.11987800
H	1.33349000	-1.97525100	5.08454600
H	1.24497400	-1.04703000	2.73766200
H	-2.91444600	-2.64230400	4.78772700
H	-0.81545200	-2.77787400	6.11786300
C	-3.12354500	-1.59974400	2.21037300
C	-4.43678900	-1.76831100	2.65949900
C	-5.48373400	-1.62039900	1.75196600
H	-4.63847100	-1.98488900	3.70224700
C	-3.86448700	-1.15151000	0.05151700
C	-5.19899500	-1.30583600	0.42445500
H	-6.51143700	-1.73181200	2.08439500
H	-3.56066100	-0.88670400	-0.95552200
H	-5.98726100	-1.15796400	-0.30455500
N	-0.78227400	-1.26761200	2.56749800
N	-2.86035500	-1.30190000	0.92243000
Co	0.25997700	2.28002500	-0.30636700
Co	-0.86153800	-0.77738300	0.38132800
C	-1.08213200	4.40689100	-0.39451600
O	-0.47870300	4.18148500	0.69133800
O	-0.91108300	3.64789400	-1.40856000
C	-2.08039500	5.54139000	-0.49866600
C	-0.50926200	0.16023700	-2.34089100
O	0.35369800	0.99840100	-1.95061300
O	-1.29771900	-0.47885200	-1.57661100
C	-0.58954100	-0.13128200	-3.82475600
O	-0.93986500	1.15113000	0.84290800
C	-1.85541600	1.67355300	1.77270900
H	-1.51372200	2.66776900	2.09317800
H	-1.90050800	1.02859100	2.66643100
C	-3.25718900	1.79806900	1.20388200
C	-3.46279200	2.00881600	-0.16561600
C	-4.37315200	1.71001100	2.04134600

C	-4.75694200	2.12651000	-0.67449700
H	-2.60576800	2.07291000	-0.82494300
C	-5.66585700	1.82669500	1.52849300
H	-4.22755300	1.53508800	3.10570500
C	-5.87890100	2.02902400	0.15944200
H	-4.89943200	2.29190400	-1.74052900
H	-6.52234300	1.74718300	2.19520700
C	-7.27754900	2.09707700	-0.40629400
H	-7.30948900	2.70977400	-1.31393700
H	-7.64844000	1.09741600	-0.67596400
H	-7.98183700	2.51939800	0.31940700
O	1.75215200	-0.93159800	0.37669700
H	-1.91426400	6.28006700	0.28922300
H	-3.08396000	5.11348800	-0.38132400
H	-2.02716000	6.00838600	-1.48658500
H	-1.61142300	-0.39060900	-4.10891900
H	-0.22200200	0.71939200	-4.40430200
H	0.03441500	-1.00801700	-4.03053500
O	0.13560400	-2.50829800	0.28697000
C	1.39856500	-2.34615300	-0.03233300
C	2.60764000	1.79325500	3.39534800
C	1.64190700	1.72402300	2.39225400
C	2.99622200	2.86852600	0.89266600
C	4.01135600	2.98373200	1.84677100
C	3.80983100	2.44169200	3.11375000
H	2.41493900	1.35189600	4.36775400
H	0.68421000	1.23448400	2.52493600
H	4.94248000	3.48042500	1.60379900
H	4.58731900	2.51830100	3.86806500
C	3.09819000	3.38807200	-0.49152000
C	4.24713700	3.98602500	-1.01840500
C	4.24005600	4.38713500	-2.35269500
H	5.13375200	4.11379500	-0.40943100
C	1.98420400	3.59075700	-2.51881400
C	3.09441500	4.18195400	-3.12394100
H	5.12264600	4.84748500	-2.78722000
H	1.05178100	3.40469000	-3.04063100
H	3.05695300	4.47443300	-4.16800700

N	1.83725200	2.24927600	1.18116900
N	1.99591900	3.21376100	-1.23927200
C	2.99404000	-0.42639300	0.06456500
C	3.98993900	-0.43440800	1.04559300
C	3.24861800	0.12061300	-1.19744300
C	5.24350800	0.11350200	0.76852300
H	3.77090600	-0.88026500	2.00951800
C	4.50697100	0.65819500	-1.46746000
H	2.44784000	0.13726100	-1.92360900
C	5.50774500	0.66013000	-0.48989000
H	6.01391400	0.10848500	1.53516200
H	4.69916700	1.09779900	-2.44239700
H	6.48451600	1.08410900	-0.70745800
C	2.35924000	-3.28007300	0.70992300
C	1.93759200	-3.91394300	1.88315300
C	3.67208100	-3.47006800	0.26131800
C	2.82231500	-4.71069700	2.61279300
H	0.90801700	-3.77999200	2.19414200
C	4.55724000	-4.26886100	0.98785100
H	3.98547100	-2.98388100	-0.65583200
C	4.13662000	-4.88649400	2.16891200
H	2.48446200	-5.20318000	3.52152700
H	5.57483100	-4.40839900	0.63270100
H	4.82528200	-5.50927200	2.73402000
O	1.67808700	-2.34297700	-1.43714500
C	1.43335400	-3.59638000	-2.08808400
H	1.22844300	-4.37084900	-1.33938400
H	2.35227500	-3.87995300	-2.61792300
C	0.28367300	-3.51158900	-3.06247300
C	-1.02212700	-3.29862000	-2.59933600
C	0.49909700	-3.63550200	-4.43728400
C	-2.08005000	-3.21553600	-3.49910200
H	-1.17638000	-3.15930600	-1.53590000
C	-0.56694800	-3.55065300	-5.33819400
H	1.51068200	-3.79135300	-4.80611700
C	-1.87176400	-3.34105500	-4.88129000
H	-3.08602200	-3.02982200	-3.12797100
H	-0.38387000	-3.64045300	-6.40653300

C	-3.03151000	-3.25392500	-5.84508700
H	-2.68306800	-3.10338800	-6.87252000
H	-3.63305200	-4.17298000	-5.82863400
H	-3.70085200	-2.42490000	-5.58522300

- **TS2**



B3LYP-D/6-311+g(2d,2p) energy: -5637.4303129900 a.u.

ZPE: 0.921880 a.u.

Thermal correction to Gibbs Free Energy: 0.816129 a.u.

Solvation energy: -10.28 kcal/mol

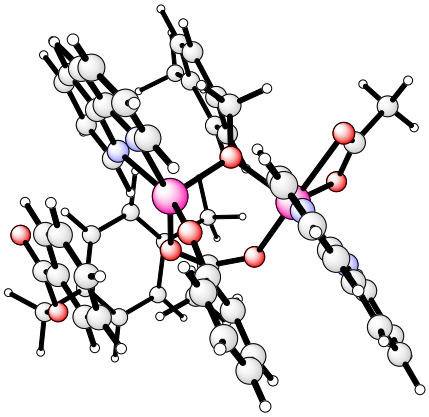
C	-0.61645700	-2.33395400	-4.33559700
C	-0.56357200	-1.68751500	-3.09994000
C	1.75499900	-1.81754400	-3.02984300
C	1.78487600	-2.48033600	-4.26268700
C	0.58314500	-2.73379600	-4.92332500
H	-1.57319500	-2.53543300	-4.80534100
H	-1.45214100	-1.38479600	-2.55767500
H	2.72481000	-2.80650500	-4.69223700
H	0.58686800	-3.24984300	-5.87896900
C	2.97271300	-1.51438600	-2.23479300
C	4.27421200	-1.69144300	-2.71659700
C	5.34748100	-1.36439000	-1.89032300
H	4.44851000	-2.05841100	-3.72137800
C	3.77668700	-0.72433900	-0.20017900
C	5.10120100	-0.87167300	-0.60986500
H	6.36525300	-1.48086800	-2.25052500
H	3.49840500	-0.33886300	0.77445400
H	5.91083600	-0.58923700	0.05321400

N	0.58866500	-1.42687300	-2.47918200
N	2.75007800	-1.03788700	-0.99588200
Co	-0.61637200	2.35920000	0.09337500
Co	0.72012700	-0.67328700	-0.40963000
C	0.36520400	4.64748100	-0.29043400
O	-0.27599900	4.14975500	-1.25804000
O	0.41365700	4.05274700	0.83847200
C	1.15121000	5.93055300	-0.47206300
C	0.61640000	0.58759300	2.26199100
O	-0.29574600	1.38672300	1.90667300
O	1.25844200	-0.18395100	1.48839300
C	0.96354900	0.51794500	3.73768100
O	0.61565700	1.22114700	-1.01105400
C	1.41529400	1.71265300	-2.05869300
H	0.96350100	2.63421200	-2.45175500
H	1.45765100	0.98031000	-2.88331300
C	2.83407400	2.00787700	-1.61033300
C	3.09394800	2.45031000	-0.30532200
C	3.90910200	1.84312900	-2.48690500
C	4.40205600	2.70725200	0.10339000
H	2.26648900	2.58643400	0.38163100
C	5.21746900	2.10392000	-2.07445100
H	3.72137900	1.48936100	-3.49882100
C	5.48594300	2.53005200	-0.76905200
H	4.58783600	3.04950400	1.11956000
H	6.04355400	1.95949800	-2.76787300
C	6.90362800	2.75876500	-0.30092600
H	6.97432700	3.64702100	0.33739700
H	7.27152900	1.90781700	0.29028800
H	7.58573700	2.88967400	-1.14823600
O	-1.42279600	-1.21597900	-0.17682100
H	0.76048900	6.50908500	-1.31285700
H	2.19317900	5.65906500	-0.68367200
H	1.13742900	6.52275900	0.44742500
H	2.04838200	0.57905800	3.86548400
H	0.46802700	1.31831600	4.29172400
H	0.65475900	-0.45821400	4.12499400
O	0.44787100	-2.74572800	0.03472900

C	-0.74733600	-2.83302300	0.43520800
C	-3.16821300	1.09996500	-3.27590100
C	-2.11758200	1.30540300	-2.38361700
C	-3.51628100	2.32860100	-0.83944800
C	-4.62150500	2.15929100	-1.67877400
C	-4.44078400	1.54054800	-2.91336900
H	-2.98722700	0.60959100	-4.22677400
H	-1.10193900	0.98392600	-2.58007500
H	-5.60248200	2.50247100	-1.37407100
H	-5.28671100	1.39890700	-3.57950100
C	-3.57800600	2.98048700	0.49013400
C	-4.76551300	3.39288300	1.10237400
C	-4.70012900	3.96368000	2.37163800
H	-5.71993300	3.24849800	0.61076700
C	-2.32019900	3.67426300	2.31507400
C	-3.45938400	4.10619600	2.99613500
H	-5.60937100	4.28613700	2.87070800
H	-1.31870700	3.74690200	2.72505000
H	-3.37252600	4.54033100	3.98660500
N	-2.29463100	1.90225400	-1.20384000
N	-2.38922900	3.13388500	1.09731000
C	-2.66425800	-0.85418100	0.18885900
C	-3.74660200	-1.14859100	-0.66254900
C	-2.92251900	-0.21877900	1.41733300
C	-5.04823600	-0.79742200	-0.30576100
H	-3.54529900	-1.66608500	-1.59492100
C	-4.22705400	0.12370700	1.76740100
H	-2.08699600	0.02256200	2.05812800
C	-5.29834800	-0.15754900	0.91153400
H	-5.87015800	-1.02665300	-0.97998100
H	-4.40756600	0.63116900	2.71178300
H	-6.31268600	0.11451000	1.19177800
C	-1.69461300	-3.76711700	-0.25582500
C	-1.31071700	-4.35788600	-1.46681400
C	-2.96934400	-4.02015700	0.26586200
C	-2.19556900	-5.18695800	-2.15403600
H	-0.31514800	-4.15578900	-1.84479000
C	-3.85440400	-4.85224000	-0.42284700

H	-3.25452400	-3.54911300	1.19907900
C	-3.47173400	-5.43410200	-1.63389800
H	-1.89107000	-5.64684000	-3.09082300
H	-4.84448400	-5.04037000	-0.01684400
H	-4.16141100	-6.08224100	-2.16837800
O	-1.03410800	-2.63897000	1.78521100
C	-0.46344900	-3.64283500	2.64930600
H	-0.15736500	-4.50977400	2.05023200
H	-1.26833500	-3.96512900	3.32020700
C	0.70202000	-3.12906500	3.46124700
C	1.89857400	-2.74354600	2.84373100
C	0.60693000	-3.04656300	4.85457500
C	2.96745100	-2.28707400	3.61049600
H	1.96126200	-2.77176900	1.76319200
C	1.68186400	-2.58785900	5.61966200
H	-0.31844300	-3.34314000	5.34386000
C	2.87722800	-2.19573500	5.00601300
H	3.88662700	-1.97780300	3.11728200
H	1.59012800	-2.52646100	6.70172400
C	4.02071700	-1.64320500	5.82276600
H	4.12775700	-2.17630800	6.77447700
H	4.96846500	-1.71546600	5.27808000
H	3.85612900	-0.58300700	6.05976300

- 14-B



B3LYP-D/6-311+g(2d,2p) energy: -5637.4689358100 a.u.

ZPE: 0.923889 a.u.

Thermal correction to Gibbs Free Energy: 0.818181 a.u.

Solvation energy: -10.09 kcal/mol

C	1.74333500	4.77429400	-2.55220400
C	1.64664400	3.63324200	-1.75616100
C	-0.65019300	3.48903400	-2.09436300
C	-0.63517000	4.63744700	-2.89658200
C	0.57765200	5.28249300	-3.12880800
H	2.70445900	5.25349800	-2.70653200
H	2.48972200	3.18498600	-1.23876300
H	-1.55302800	5.02762100	-3.32012800
H	0.60941700	6.17482600	-3.74710100
C	-1.88231100	2.72879900	-1.77406200
C	-3.11504200	2.97478900	-2.38400400
C	-4.21192600	2.19384100	-2.02347300
H	-3.21485400	3.74428200	-3.14036500
C	-2.79092300	1.01644400	-0.49890400
C	-4.05152100	1.19810600	-1.06619300
H	-5.17558000	2.35757100	-2.49589700
H	-2.60052400	0.26378000	0.25456000
H	-4.87569200	0.56371700	-0.76701300
N	0.48171500	3.01170900	-1.54181000
N	-1.73729300	1.76077400	-0.84671800
Co	1.60938400	-1.70864100	-0.94538700
Co	0.29492600	1.26539400	-0.22745000
C	1.28224400	-3.36317700	-2.80533900
O	1.99748200	-2.35630100	-3.06827300
O	0.80986900	-3.54034600	-1.63256000
C	0.92478700	-4.35847200	-3.89143600
C	-0.34608100	-1.14964500	1.41699200
O	0.49274400	-1.88532200	0.82450000
O	-0.48285700	0.09969600	1.25083600
C	-1.29785700	-1.80967800	2.39590600
O	0.53162900	-0.12123900	-1.62054500
C	-0.09674400	-0.07568100	-2.87378900
H	0.51832500	-0.62264200	-3.60317700
H	-0.17500200	0.96829000	-3.22358000
C	-1.49284900	-0.67501100	-2.84950500
C	-1.83697800	-1.66775600	-1.92203200
C	-2.46505100	-0.24568500	-3.75770200

C	-3.12278800	-2.20682600	-1.91010700
H	-1.09618500	-2.02084300	-1.21571700
C	-3.75351100	-0.78300400	-3.73832600
H	-2.21472400	0.53138000	-4.47725600
C	-4.10560800	-1.76790300	-2.80764400
H	-3.36760800	-2.98255900	-1.19060100
H	-4.49957500	-0.42917700	-4.44718300
C	-5.50917100	-2.32379800	-2.75201700
H	-5.50389400	-3.38708100	-2.48661400
H	-6.12005600	-1.80728900	-1.99701300
H	-6.02061700	-2.21284200	-3.71449400
O	2.11152300	1.72201200	0.37958200
H	1.58269600	-4.24269300	-4.75595000
H	-0.11132800	-4.17369600	-4.20070100
H	0.97708000	-5.37926900	-3.50057100
H	-2.19601300	-2.12270300	1.85112100
H	-0.84134900	-2.69896500	2.83821500
H	-1.61201800	-1.10004800	3.16345400
O	-3.88594500	2.36757700	2.14027500
C	-2.92992300	2.04143700	2.82767100
C	4.75424400	1.26450600	-1.70096200
C	3.57688300	0.51668500	-1.69608800
C	4.49972700	-1.06526700	-0.26854100
C	5.71244200	-0.37438800	-0.21991600
C	5.83167000	0.81163700	-0.94168900
H	4.81398500	2.18300500	-2.27536100
H	2.68311200	0.81424800	-2.23166000
H	6.53559600	-0.74082900	0.38014400
H	6.75876200	1.37596600	-0.90766100
C	4.24184600	-2.33222400	0.45596400
C	5.13613500	-2.90888700	1.36403100
C	4.77537500	-4.09855800	1.99322400
H	6.07858600	-2.42605900	1.59197700
C	2.70063100	-4.03847600	0.79297700
C	3.53914900	-4.68062700	1.70469500
H	5.45059200	-4.56280100	2.70627400
H	1.72141400	-4.41543100	0.51754300
H	3.22664400	-5.60556900	2.17790000

N	3.46298400	-0.61490200	-0.99962900
N	3.05200900	-2.89974600	0.19144000
C	2.95744000	1.39007000	1.33003100
C	4.04652500	2.24886200	1.62685600
C	2.86498600	0.17975900	2.05937900
C	5.00328500	1.90087300	2.57746200
H	4.12393700	3.18117500	1.07259000
C	3.82828700	-0.15726900	3.00813200
H	2.05757500	-0.50161800	1.82928900
C	4.91102300	0.68936500	3.27403500
H	5.83157700	2.57830500	2.77596700
H	3.73880300	-1.10427100	3.53597700
H	5.65684500	0.42033900	4.01697100
C	-1.57293400	2.61943700	2.68533200
C	-1.38001900	3.57588900	1.67807100
C	-0.49160100	2.21479300	3.48067300
C	-0.11429900	4.11509700	1.46170900
H	-2.22835700	3.86525400	1.06852000
C	0.77264900	2.75476400	3.26086100
H	-0.64417300	1.46048300	4.24316000
C	0.96358900	3.69710900	2.24720500
H	0.03865600	4.83799700	0.66617700
H	1.62285500	2.40939300	3.83880300
H	1.96295700	4.07030400	2.05253000
O	-3.00702200	1.10997000	3.80891500
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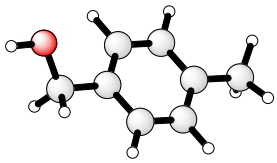
H	-5.07957300	1.24996600	3.84027400
H	-4.30160900	0.24767600	5.10351100
C	-4.50329000	-0.72876700	3.19615200
C	-4.77114000	-0.61214400	1.82615400
C	-4.39033500	-2.00623300	3.75224200
C	-4.88943200	-1.74810900	1.02851900
H	-4.87285900	0.37891600	1.40176400
C	-4.52641200	-3.14344500	2.95448700
H	-4.18606800	-2.11110800	4.81513900
C	-4.76353500	-3.03239300	1.57860200
H	-5.06962100	-1.64400900	-0.03712600
H	-4.43475900	-4.13075100	3.40054900

C	-4.84889100	-4.26119200	0.70616300
H	-5.28530200	-5.10567500	1.25065200
H	-5.45300400	-4.07251400	-0.18715400
H	-3.85039300	-4.57015700	0.36808100

- 4c



B3LYP-D/6-311+g(2d,2p) energy: -386.2337289994 a.u.

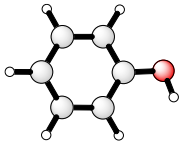
ZPE: 0.160046 a.u.

Thermal correction to Gibbs Free Energy: 0.124647 a.u.

Solvation energy: -2.29 kcal/mol

C	-0.09774400	1.36621500	-0.01735700
C	1.28550800	1.19233400	-0.07134100
C	1.85147600	-0.08807800	-0.02425300
C	0.98909600	-1.18816600	0.07315100
C	-0.39400100	-1.01818300	0.13690100
C	-0.95207000	0.26429300	0.09418700
H	-0.51927400	2.36784000	-0.07136800
H	1.93578500	2.05917100	-0.16413800
H	1.40930600	-2.19118900	0.09602900
H	-1.05486100	-1.87629200	0.20001000
C	3.34964400	-0.27616800	-0.05915900
H	3.77117300	-0.28391100	0.95533600
H	3.61934600	-1.22680000	-0.53226300
H	3.83869600	0.53440300	-0.61058900
C	-2.44393200	0.47018500	0.20984100
H	-2.71020100	0.58998800	1.27486700
H	-2.71968500	1.41056000	-0.29615500
O	-3.13012700	-0.64332600	-0.35105100
H	-4.05712700	-0.57175300	-0.09513400

- **PhOH**



B3LYP-D/6-311+g(2d,2p) energy: -307.5792988804 a.u.

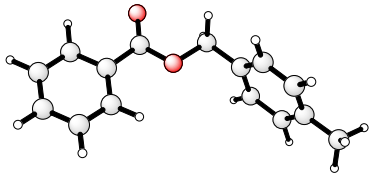
ZPE: 0.104580 a.u.

Thermal correction to Gibbs Free Energy: 0.075609 a.u.

Solvation energy: -2.18 kcal/mol

C	-1.17234900	-1.19136900	-0.00003500
C	0.22127900	-1.22548500	-0.00001200
C	0.94212800	-0.02488200	0.00001100
C	0.26477900	1.20019900	0.00000600
C	-1.13204800	1.22071000	-0.00001300
C	-1.85856400	0.02828300	-0.00002100
H	-1.72647900	-2.12603100	-0.00003500
H	0.76685300	-2.16365300	0.00001600
H	0.82987500	2.13054100	0.00000100
H	-1.64970200	2.17600200	0.00000300
H	-2.94400900	0.04755200	-0.00001600
O	2.30678300	-0.11121900	-0.00000800
H	2.67785100	0.78061000	0.00047000

- **6bc**



B3LYP-D/6-311+g(2d,2p) energy: -730.7517238130 a.u.

ZPE: 0.251772 a.u.

Thermal correction to Gibbs Free Energy: 0.205709 a.u.

Solvation energy: -2.66 kcal/mol

O	-1.85299000	-2.37193200	0.10867800
C	-1.64665100	-1.17395600	0.04658600
C	-2.71547900	-0.13554900	-0.00249200
C	-4.04858700	-0.56957600	0.01880000

C	-2.42644700	1.23566500	-0.06702400
C	-5.08590000	0.35988100	-0.02435500
H	-4.24379000	-1.63568600	0.06937900
C	-3.46795800	2.16242500	-0.10969600
H	-1.39287200	1.56266600	-0.08296100
C	-4.79640600	1.72682800	-0.08853800
H	-6.11803300	0.02194200	-0.00801600
H	-3.24435000	3.22417900	-0.15954700
H	-5.60515300	2.45167300	-0.12199300
O	-0.40671200	-0.63735800	0.01440900
C	0.68414600	-1.59367100	0.06659900
H	0.57843600	-2.18609500	0.98138700
H	0.59505400	-2.27326200	-0.78685600
C	1.97050900	-0.82167300	0.03860900
C	2.66676100	-0.63579900	-1.15982500
C	2.47890500	-0.24705600	1.20994100
C	3.84889500	0.10506100	-1.18645600
H	2.27687500	-1.07245600	-2.07603900
C	3.65812300	0.49512000	1.18116800
H	1.94159600	-0.38066300	2.14564400
C	4.36333200	0.67897600	-0.01694900
H	4.38061300	0.24245300	-2.12487200
H	4.04150700	0.93809200	2.09724000
C	5.66000700	1.45225700	-0.03839000
H	6.51212900	0.79701500	0.18744400
H	5.83978800	1.89788800	-1.02259800
H	5.65631300	2.25297500	0.70921800

11. X-ray Diffraction Study for Complexes 9, 10, 11 and 21

Suitable crystals were grown by slow evaporation of the saturated toluene solution for **9**, **10** and **21**, by the diffusion of hexane into the toluene solution for **11**. The crystals were mounted on the CryoLoop (Hampton Research Corp.) with a layer of light mineral oil and placed in a nitrogen stream at 113(1) K. Measurements were made on Rigaku R-AXIS RAPID imaging plate area detector or Rigaku AFC7R/Mercury CCD detector with graphite-monochromated Mo Kα (0.71075 Å) radiation. Crystal data and structure refinement parameters were listed below. The structures were solved by direct methods (SIR92)[S14], and refined on F^2 by full-matrix least-squares method, using SHELXL-97.[S15] Non-hydrogen atoms were anisotropically refined. Hydrogen atoms were included in the refinement on calculated positions riding on their carrier atoms. The function minimized was $[\Sigma w(F_o^2-F_c^2)^2]$ ($w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$), where $P = (\mathrm{Max}(F_o^2, 0) + 2F_c^2)/3$ with $\sigma^2(F_o^2)$ from counting statistics. The function $R1$ and $wR2$ were $(\Sigma||F_o|-|F_c||)/\Sigma|F_o|$ and $[\Sigma w(F_o^2- F_c^2)^2/\Sigma(wF_o^4)]^{1/2}$, respectively. The ORTEP-3 program was used to draw the molecule.[S16]

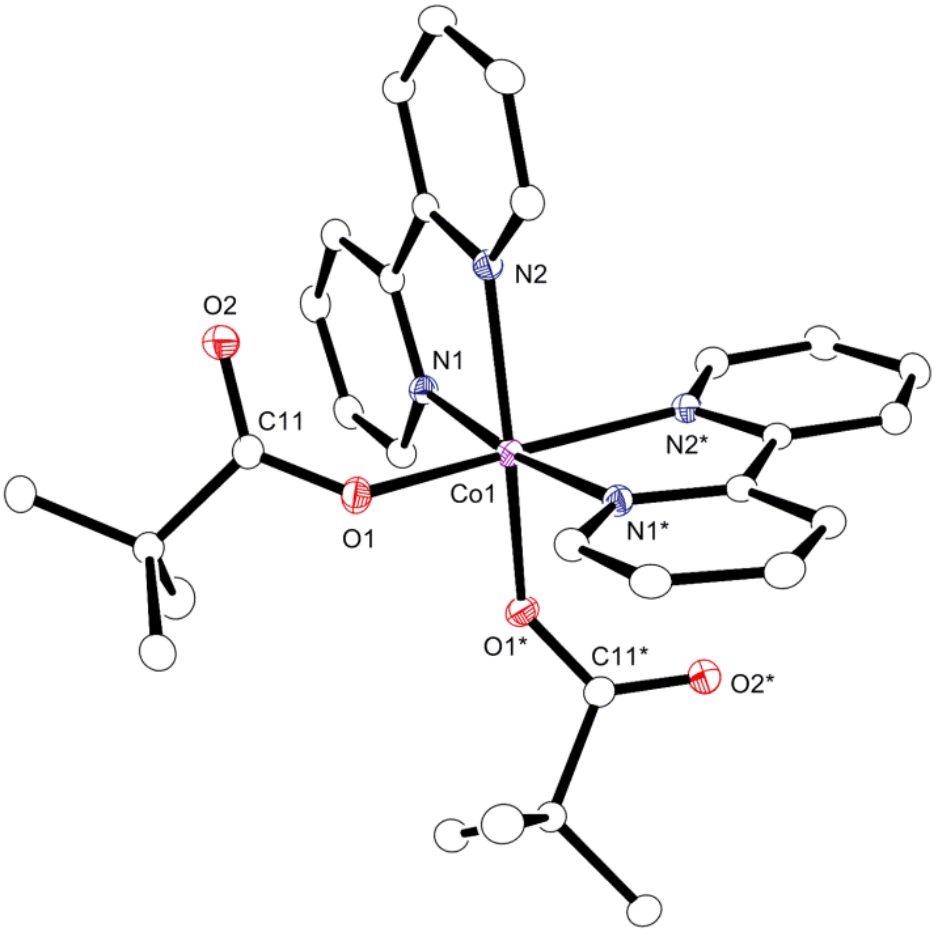


Figure S6. Molecular structure of complex **9** with thermal ellipsoids at 30% probability. All H-atoms and the solvent molecule (toluene) were omitted for clarity. Selected bond distances (Å) and angles (degree): Co1—O1, 2.0282(16); Co1—N1, 2.1521(16); Co1—N2, 2.1442(17); O1—Co1—N1, 89.13(6); N1—Co1—N2, 75.51(6); N1—Co1—N2, 75.86(18).

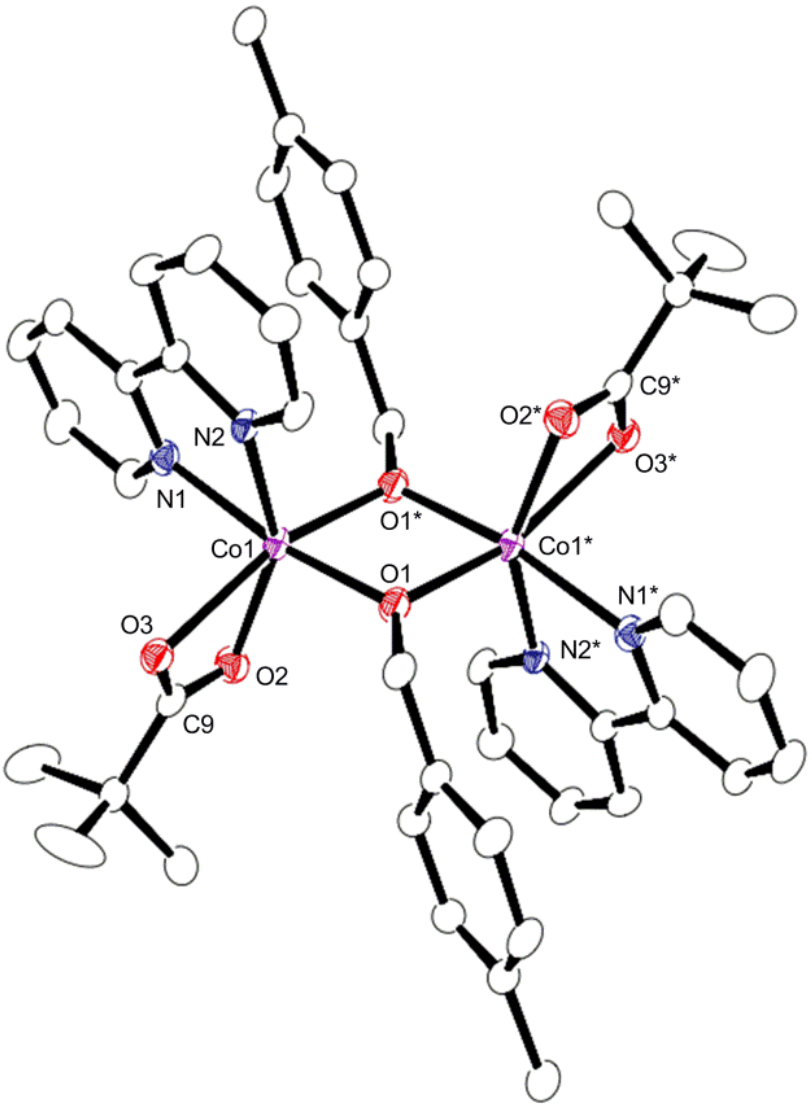


Figure S7. Molecular structure of complex **10** with thermal ellipsoids at 30% probability. All H-atoms and the solvent molecule (toluene) were omitted for clarity. Selected bond distances (Å) and angles (degree): Co1—O1, 2.016(4); Co1—O1*, 2.014(4); Co1—O2, 2.108(5); Co1—O3, 2.315(5); Co1—N1, 2.154(5); Co1—N2, 2.107(5); C9—O2, 1.281(8); C9—O3, 1.270(7); Co1—O1—Co1*, 101.17(17); O1—Co1—O1*, 78.83(16); O2—Co1—O3, 59.8(2); O2—Co1—N2, 151.01(17); N1—Co1—N2, 75.86(18).

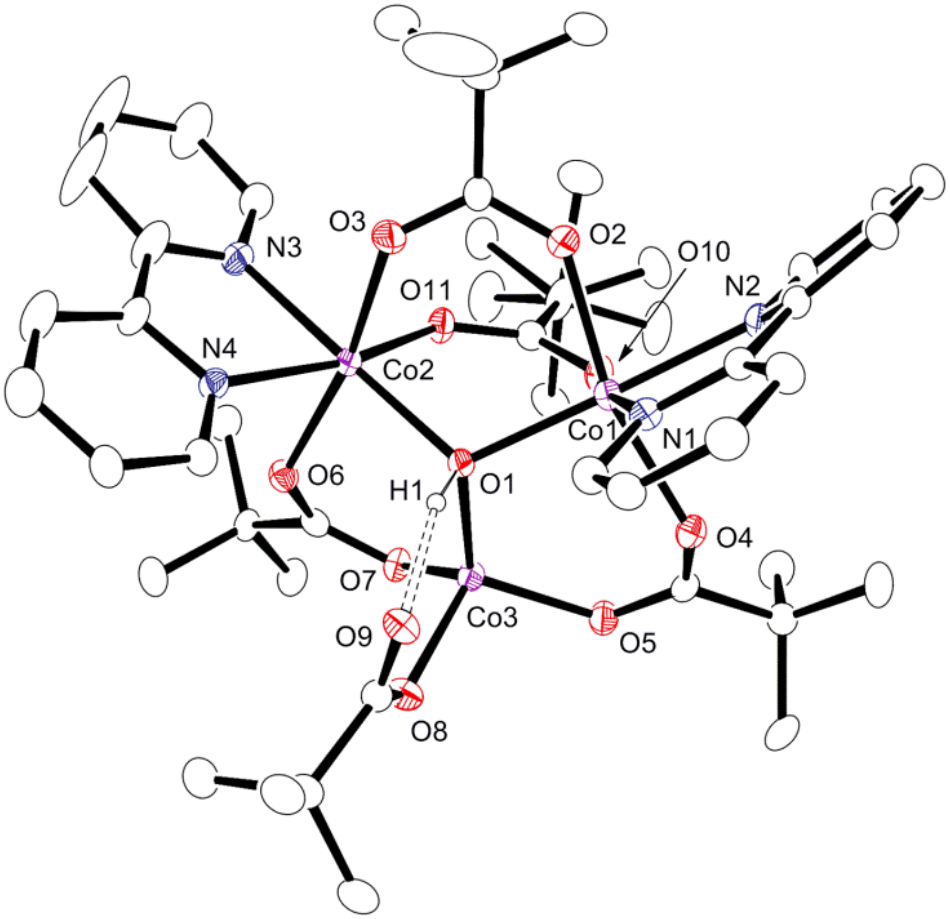


Figure S8. Molecular structure of complex **11** with thermal ellipsoids at 30% probability. All H-atoms except H1 were omitted for clarity. Selected bond distances (Å) and angles (degree): Co1—O1, 2.082(3); Co1—O2, 2.057(4); Co1—O4, 2.132(3); Co1—O10, 2.092(3); Co1—N1, 2.160(4); Co1—N2, 2.140(4); Co2—O1, 2.094(3); Co2—O3, 2.038(4); Co2—O6, 2.112(3); Co2—O11, 2.090(3); Co2—N3, 2.153(4); Co2—N4, 2.148(4); Co3—O1, 1.976(3); Co3—O5, 1.959(3); Co3—O7, 1.985(3); Co3—O8, 1.985(3); Co1—O1—Co2, 112.87(14); Co1—O1—Co3, 107.72(15); Co2—O1—Co3, 1107.95(14).

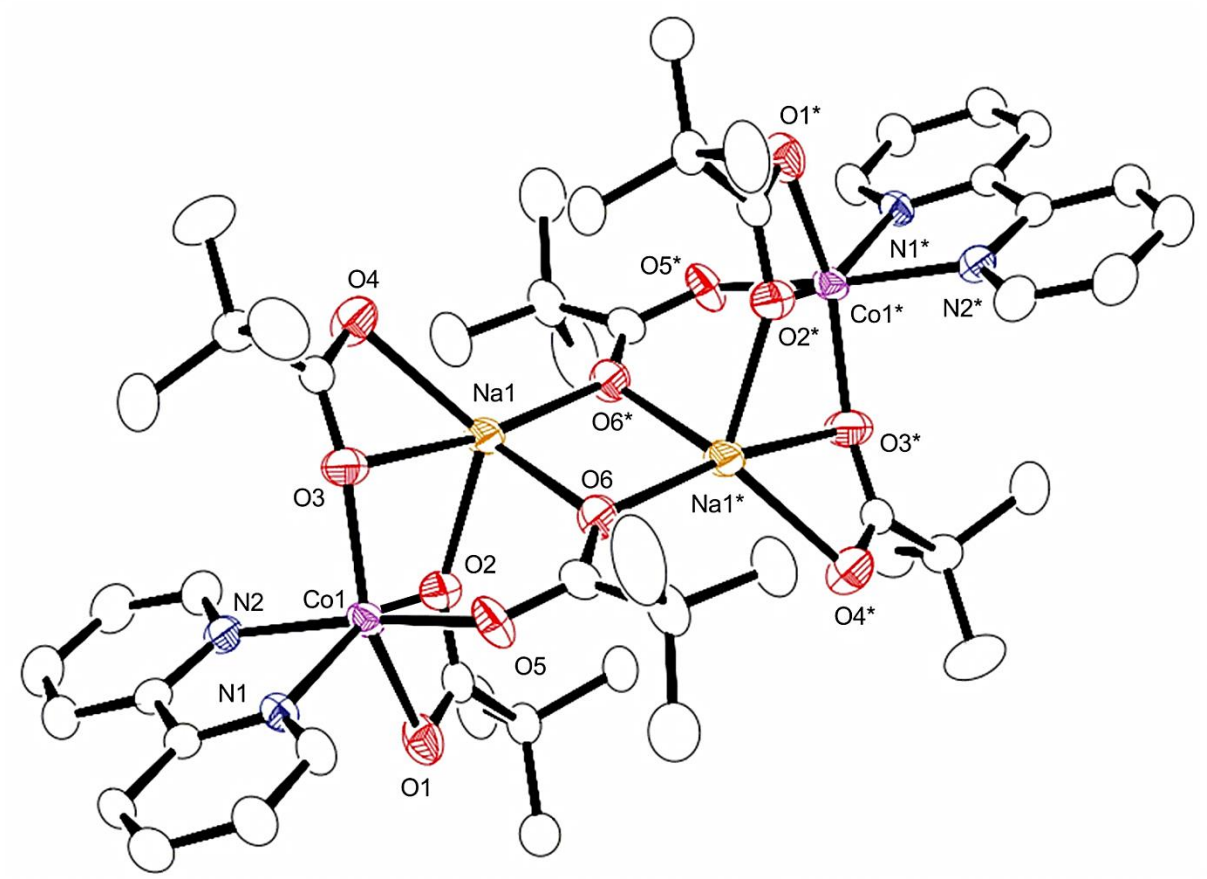


Figure S9. Molecular structure of complex **21** with thermal ellipsoids at 30% probability. All H-atoms were omitted for clarity. Selected bond distances (Å) and angles (degree): Co1—O1, 2.132(3); Co1—O3, 1.992(3); Co1—O5, 2.029(2); Co1—N1, 2.099(3); Co1—N2, 2.127(3); Na1—O2, 2.256(3); Na1—O3, 2.487(3); Na1—O4, 2.363(3); Na1—O6, 2.253(3); Na1—O6—Na1*, 89.86(9); Co1—O3—Na1, 90.04(10); O2—Na1—O3, 81.76(10); O2—Na1—O4, 117.33(10); O2—Na1—O6, 110.46(10); O2—Na1—O6*, 86.77(10); O1—Co1—O3, 148.26(10); O1—Co1—O5, 91.81(9); O1—Co1—N1, 98.26(9).

Table S5. Crystal Data and Data Collection Parameters.

	9	**10**
empirical formula	$C_{30}H_{34}CoN_4O_4$, C_7H_8	$C_{60}H_{68}Co_2N_4O_6$
formula weight	665.70	1059.09
crystal system	Monoclinic	Monoclinic
space group	*C*2/*c* (No. 15)	$P2_1/n$ (No. 14)
a, Å	12.0528(13)	10.416(8)
b, Å	15.1077(15)	15.759(11)
c, Å	18.2869(16)	16.874(12)
α, deg.	-	-
β, deg.	94.605(5)	94.919(6)
γ, deg.	-	-
V, Å^3	3319.1(6)	2760(4)
Z	4	2
*D*calcd, g/cm^{-3}	1.332	1.274
μ [Mo-*K*α], mm^{-1}	0.563	0.654
T, K	113(2)	113(2)
crystal size, mm	0.26 x 0.26 x 0.24	0.29 x 0.06 x 0.06
θ range for data collection (deg.)	3.01 to 27.49	3.25 to 27.47
no. of reflections measured	15683	25853
unique data (*R*int)	3816 (0.0487)	6084 (0.1412)
data / restraints / parameters	3816 / 0 / 247	6083 / 0 / 325
*R*1 ($I > 2.0\sigma(I)$)	0.0425	0.0937
*wR*2 ($I > 2.0\sigma(I)$)	0.1052	0.2022
*R*1 (all data)	0.0556	0.1712
*wR*2 (all data)	0.1116	0.2485
GOF on F^2	1.093	1.027
$\Delta\rho$, e Å^{-3}	0.633, -0.423	0.859, -0.626

a) $R1 = (\Sigma||Fo| - |Fc||)/(\Sigma|Fo|)$ b) $wR2 = [\{\Sigma w(Fo^2\text{-}Fc^2)^2\}/\{\Sigma w(Fo^4)\}]^{1/2}$

Table S5 (Continued)

	11	**21**
empirical formula	$C_{45}H_{62}Co_3N_4O_{11}$	$C_{50}H_{70}Co_2N_4Na_2O_{12}$
formula weight	1011.80	1082.97
crystal system	Monoclinic	Monoclinic
space group	*C*2/*c* (No. 15)	$P2_1/n$ (No. 14)
a, Å	44.804(17)	13.924(5)
b, Å	10.788(4)	13.144(5)
c, Å	22.008(8)	15.140(6)
α, deg.	-	-
β, deg.	110.260(4)	97.499(4)
γ, deg.	-	-
V, Å^3	9980(6)	2747(2)
Z	8	2
*D*calcd, g/cm^{-3}	1.347	1.309
μ [Mo-*K*α], mm^{-1}	1.044	0.680
T, K	113(2)	113(2)
crystal size, mm	0.20 x 0.20 x 0.20	0.43 x 0.30 x 0.25
θ range for data collection (deg.)	3.07 to 27.47	3.10 to 27.48
no. of reflections measured	42376	21459
unique data (*R*int)	9794 (0.0892)	6084(0.0386)
data / restraints / parameters	9790 / 0 / 607	4836 / 0 / 316
*R*1 ($I > 2.0\sigma(I)$)	0.0652	0.0519
*wR*2 ($I > 2.0\sigma(I)$)	0.1386	0.1197
*R*1 (all data)	0.1134	0.0560
*wR*2 (all data)	0.1712	0.1165
GOF on F^2	1.046	1.117
$\Delta\rho$, e Å^{-3}	0.835, -0.557	0.829, -0.626

a) $R1 = (\Sigma||Fo| - |Fc||)/(\Sigma|Fo|)$ b) $wR2 = [\{\Sigma w(Fo^2\text{-}Fc^2)^2\}/\{\Sigma w(Fo^4)\}]^{1/2}$

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