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VIP

A Cobalt(II) Complex Bearing the Amine(imine)diphosphine PN(H)NP Ligand for Asymmetric Transfer Hydrogenation of Ketones

Shangfei Huo,[a] Hong Chen,[a] and Weiwei Zuo*[a]

Abstract: Novel chiral cobalt complex **a** containing amine(imine)diphosphine PN(H)NP ligand and complex **b** containing bis(amine)diphosphine PN(H)N(H)P ligand were synthesized. The structures of two complexes were characterized by X-ray crystallography and high resolution mass spectrometry. The catalytic performances of cobalt complexes **a** and **b** for asymmetric transfer hydrogenation (ATH) of ketones under mild conditions were evaluated using 2-propanolisopropanol as solvent and hydrogen source after being activated by 8 equivalents of base. Complex **a** showed a good reactivity for reduction of ketones, with a turnover number (TON) of up to 555, and a maximum enantiomeric excess (*ee*) value of up to 91 %. Complex **b** exhibited inertness for hydrogenation of ketones. Electronic structure studies on **a** and **b** were conducted to account for the function of ligands on the catalytic performances.

Introduction

Chiral alcohols are important to pharmaceutical, fragrance, and agrochemical industries,[1] and they are conventionally produced by asymmetric hydrogenation of prochiral ketones via catalysts based on precious metals.[2] But applications are limited for these precious metal complexes due to their high cost and toxicity. Hence it is important to seek some earth abundant and low or non-toxic metals as substitutions to these precious metals. As an earth abundant metal, cobalt has its potential to achieve this goal, and some examples of hydrogenation of ketones with cobalt complexes have been reported.

A cobalt(II) complex of $[(PNHP^{Cy})Co(CH_2SiMe_3)]BAr^F{}_4$ $\{BAr^F{}_4 = B(3,5\text{-}(CF_3)_2C_6H_3)_4\}$ and its analogs were applied in hydrogenating some ketones to obtain alcohols at 25–60 °C with high yields.[3] Potassium bis(anthracene) cobaltate was used as catalyst to reduce aromatic and aliphatic ketones under H_2 atmosphere, and good yields were obtained, but with no enantioselectivity.[4] Sina et al. designed their triazine-based $PN_{3-5}P$ cobalt complexes to hydrogenate ketones under H_2 atmosphere, and good to high yields were obtained, yet with no enantioselectivity.[5]

Liu et al. developed a cobalt catalytic system that was generated by combining pincer NHC ligand with $CoCl_2$ in situ for hydrogenation of ketones, and maximum TON of up to 2160 was obtained.[6] Cobalt complex bearing $P^{2C-PPh2}{}_2N^{Ph}{}_2$ ligand was applied for hydrogenation of ketones, and 93–99 % yields were obtained under 30 bar H_2 pressure at 50–100 °C.[7] Yang et al. synthesized a cobalt–NHC pincer complex for transfer hydrogenation of a broad range of ketones, using 2-propanolisopropanol as solvent and hydrogen source in the presence of sodium *tert*-butoxide, and moderate to excellent yields were obtained.[8]

Robter et al. developed cobalt complexes with chiral nitrogen containing ligands for asymmetric hydrogenation of acetophenone using 2-propanol isopropanolas hydrogen source, and *ee* value of up to 58 % was achieved, but with low conversion of 8 %.[9] Zhang[10] et al. obtained chiral alcohols by combining tetradentate aminophosphine ligand with $CoCl_2{\cdot}6H_2O$ as catalyst for hydrogenation of ketones. Alcohols were obtained with moderate to high yields and *ee* values at 2 mol-% catalyst loading and 60 bar H_2 pressure. However, the catalytic system required 400 mol-% of KOH to initiate the hydrogenation reaction.

The development of cobalt-catalyzed hydrogenation of ketones was slow relative to that with precious metals and iron, and the examples of cobalt complexes for hydrogenation of ketones, especially for asymmetric hydrogenation of ketones are limited. Herein, we report a new type of cobalt complex that contains an amine(imine)diphosphine PN(H)NP ligand[11] for asymmetric transfer hydrogenation of ketones. The structure of novel cobalt pre-catalyst **a** bearing amine(imine)diphosphine PN(H)NP ligand is showed in Figure 1. For comparison, complex **b** containing bis(amine)diphosphine PN(H)N(H)P ligand is also synthesized and showed in Figure 1. We postulated that amidoene(imido) structure in the real catalyst derived from deprotonation of complex **a** by base could activate the cobalt metal center for catalysis, which has been demonstrated in the related

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iron catalysts.[12] In this work, the catalytic performance of two catalysts were tested. Results indicated that cobalt complex **a** could hydrogenate a large broad of ketones to obtain corresponding chiral alcohols with moderate TON and moderate to good *ee* values.

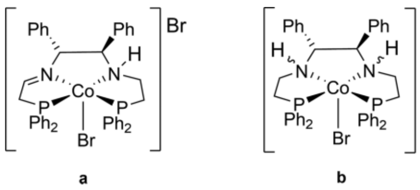
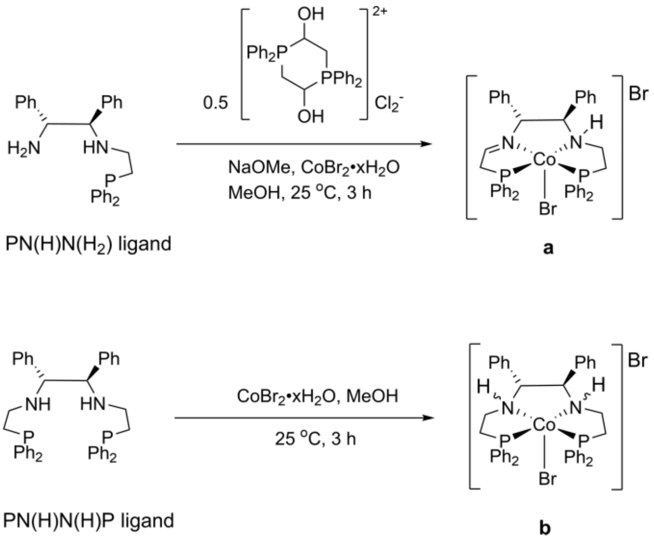


Figure 1. Structures of cobalt pre-catalysts of **a** and **b**.

Results and Discussion

Complex **a** was synthesized via a template reaction between PN(H)N(H$_2$)[11] ligand and diphenylphosphino-acetaldehyde in the presence of cobalt(II) bromide hydrate, where diphenylphosphino-acetaldehyde was released by diphenylphosphino-acetaldehyde hydrochloride dimer upon it treatment with NaOMe. Complex **b** was synthesized via reaction between PN(H)N(H)P[13] ligand and cobalt(II) bromide hydrate in MeOH (Scheme 1). Complexes **a** and **b** were purified by crystallization and characterized by FT-IR and high resolution mass spectrometry. The structures of the complexes **a** and **b** were further determined by X-ray single crystal diffraction and the molecular structures are shown in Figure 2 and Figure 3, respectively. It could be seen that one bromine atom connects to Co center, while the other bromine atom is dissociative, in both **a** and **b**. Four atoms of PNNP form a plane, and occupy four points in the equatorial plane, composing a pentahedron forming a square-pyramidal geometry with cobalt atom. There is a difference between two complexes where complex **a** contains unsaturated C=N bond but **b** does not. In the case of **a**, the bond lengths are as follow: N1–C2 (1.267 Å), N2–C5 (1.476 Å). The length of two carbon–nitrogen bonds is significantly different, indicating there is a C=N double bond. For **b**, the bond lengths are as follow: N1–C2 (1.488 Å), N2–C5 (1.483 Å). The length of two



Scheme 1. Synthesis of complexes **a** and **b**.

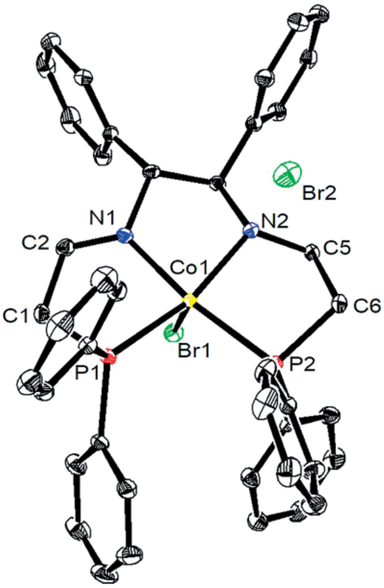


Figure 2. The molecular structure of complex **a** with the thermal ellipsoids set at 50 % probability. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°] are as follows: Co(1)–N(1) 1.934(3), Co(1)–N(2) 1.981(3), Co(1)–P(1) 2.1910(11), Co(1)–P(2) 2.2116(11), Co(1)–Br(1) 2.5619(6), P(1)–C(1) 1.846(4), P(2)–C(6) 1.837(4), N(1)–C(2) 1.267(5), N(2)–C(5) 1.476(5), C(1)–C(2) 1.487(6), C(5)–C(6) 1.539(6), N(1)–Co(1)–N(2) 84.59(13), N(1)–Co(1)–P(1) 83.74(10), N(2)–Co(1)–P(1) 161.54(11), N(1)–Co(1)–P(2) 171.47(10), N(2)–Co(1)–P(2) 86.92(10), P(1)–Co(1)–P(2) 104.28(4), N(1)–Co(1)–Br(1) 88.23(10), N(2)–Co(1)–Br(1) 96.80(11), P(1)–Co(1)–Br(1) 97.07(3), P(2)–Co(1)–Br(1) 93.58(3).

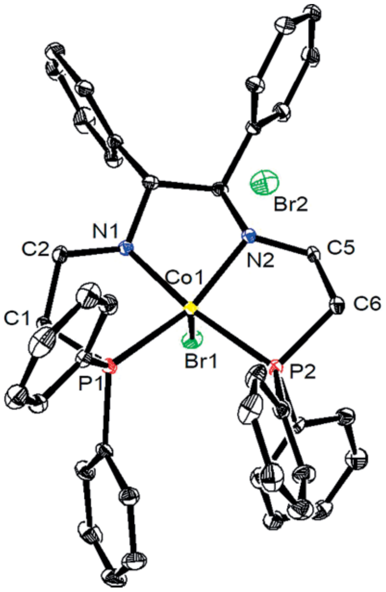
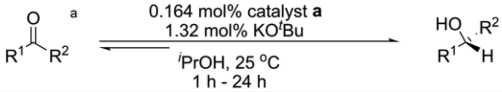


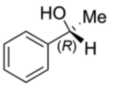
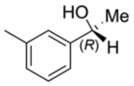
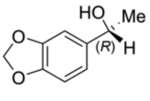
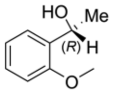
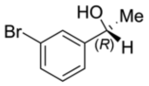
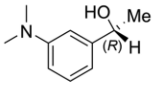
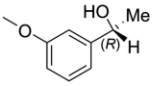
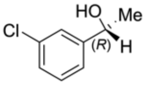
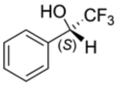
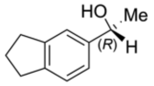
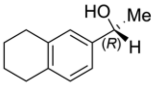
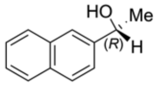
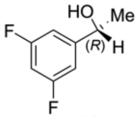
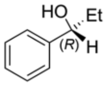
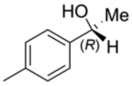
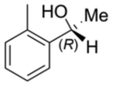
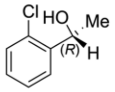
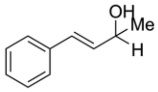
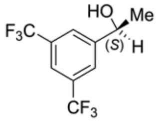
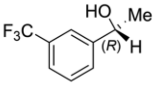
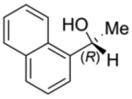
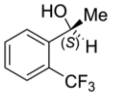
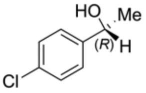
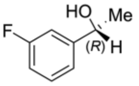
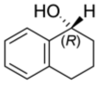
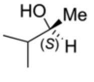
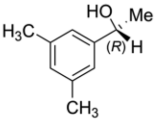
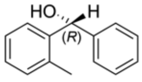
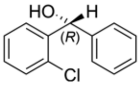
Figure 3. The molecular structure of complex **b** with the thermal ellipsoids set at 50 % probability. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°] are as follows: Co(1)–N(1) 1.986(3), Co(1)–N(2) 1.985(2), Co(1)–P(1) 2.2022(9), Co(1)–P(2) 2.2107(9), Co(1)–Br(1) 2.5853(5), P(1)–C(1) 1.833(3), P(2)–C(6) 1.836(3), N(1)–C(2) 1.488(4), N(2)–C(5) 1.483(4), C(1)–C(2) 1.529(4), C(5)–C(6) 1.531(5), N(1)–Co(1)–N(2) 84.43(10), N(1)–Co(1)–P(1) 85.66(8), N(2)–Co(1)–P(1) 158.49(8), N(1)–Co(1)–P(2) 170.41(8), N(2)–Co(1)–P(2) 87.10(8), P(1)–Co(1)–P(2) 103.80(4), N(1)–Co(1)–Br(1) 83.54(8), N(2)–Co(1)–Br(1) 96.80(8), P(1)–Co(1)–Br(1) 101.00(3), P(2)–Co(1)–Br(1) 93.03(3).

carbon–nitrogen bonds is almost same, indicating there are two C–N single bonds.

Asymmetric transfer hydrogenation of ketones with complexes **a** and **b** were performed using 2-propanolisopraponal as solvent and hydrogen source after activated with 8 equivalent of potassium *tert*-butoxide. Asymmetric transfer hydrogenation of acetophenone with complex **a** afforded (*R*)-1-phenylethanol with 74 % conversion of acetophenone (Table 1). Interestingly, *ee* value was 70 % at 10 min. When the reaction was in equilibrium at 12 h, *ee* value was 72 %, a little better higher than the

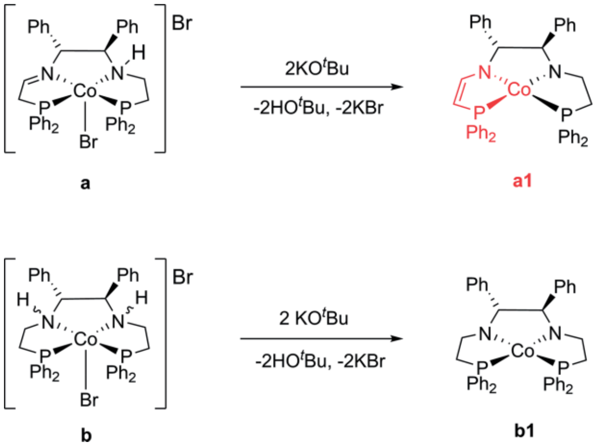
Table 1. Asymmetric transfer hydrogenation of ketones catalyzed by complexes **a** and **b**.[a]



Alcohol product						
TON	450 (0[b])	464	396	390	43 (22[c])	476
ee	72% (0[b])	55%	31%	55%	53% (68%[c])	51%
Conv.	74% (0[b])	76%	65%	64%	7% (36%[c])	78%
Time	12 h (12 h[b])	12 h	12 h	24 h	12 h (3 h[c])	12 h
Alcohol product						
TON	543	153 (126[d])	37 (10[c])	390	445	519
ee	56%	63% (68%[d])	41% (13%[c])	45%	30%	40%
Conv.	89%	25% (60%[d])	6% (17%[c])	64%	73%	86%
Time	12 h	12 h (12 h[d])	24 h (12 h[c])	24 h	12 h	12 h
Alcohol product						
TON	12 (60[c])	555	464	415	43(49[c])	210
ee	45% (46%[c])	72%	41%	59%	54% (50%[c])	0
Conv.	2% (>99%[c])	91%	76%	68%	7% (81%[c])	78%
Time	12 h (12 h[c])	12 h	12 h	24 h	1 h (3 h[c])	24 h
Alcohol product						
TON	12 (16[c])	37 (60[c])	512	153 (149[d])	549	421
ee	47% (68%[c])	52% (50%[c])	66%	20% (25%[d])	66%	68%
Conv.	2% (26%[c])	6% (>99%[c])	84%	25% (71%[d])	90%	69%
Time	12 h (24 h[c])	12 h (3 h[c])	12 h	24 h (24 h[d])	24 h	24 h
Alcohol product						
TON	201 (92[d])	55 (55[c])	262	390	336	
ee	78% (72%[d])	41% (24%[c])	54%	80%	91%	
Conv.	33% (44%[d])	9% (90%[c])	43%	64%	55%	
Time	24 h (12 h[d])	12 h (12 h[c])	12 h	12 h	12 h	

[a] General conditions for **a**: [**a**] = 6.79×10^{-4} M, [KO*t*Bu] = 5.52×10^{-3} M, [ketone] = 0.422 M, [*i*PrOH] = 12.4 M, 25 °C. The absolute configurations were obtained by gas chromatography or HPLC by comparison to known standards. The conversion was calculated based on GC analysis, which was calibrated by comparing with a working curve. [b] Conditions for **b**: [**b**] 6.79×10^{-4} M, [KO*t*Bu] = 5.52×10^{-3} M, [ketone] = 0.422 M, [*i*PrOH] = 12.4 M, 25 °C. [c] Conditions for **a**: [**a**] 6.79×10^{-4} M, [KO*t*Bu] = 5.52×10^{-3} M, [ketone] = 0.042 M, [*i*PrOH] = 12.4 M, 25 °C. [d] Conditions for **a**: [**a**] 6.79×10^{-4} M, [KO*t*Bu] = 5.52×10^{-3} M, [ketone] = 0.141 M, [*i*PrOH] = 12.4 M, 25 °C.

value in the beginning. This value is slightly superior to these catalysts of chiral salen–Co(II) complexes and cobalt complex with tetradentate aminophosphine ligand[10,14] in asymmetric reduction. There is totally no reactivity of **b** in the hydrogenation. Different performance between **a** and **b** on hydrogenation could be explained withby the different structure between **a** and **b**. We postulated that **a** was activated by excess base to afford **a1** containing an amido-ene(amido) ligand (Scheme 2). The conversion of amine(imine) to amido-ene(amido) ligand by base has been demonstrated by Morris et al. in iron-based complexes.[12] Similar to the case of iron,[15] to elucidate the function of ligands on catalytic performance, DFT calculations at the B3LYP/LANL2DZ level were employed to study the electronic structures. It turned out that the SOMO-1 of **a1** possesses 10.9 % cobalt character and 29.4 % amido N atom character (Figure 4). This suggests the N atom underwentundergoes a process of π donation with the metal d orbital to some extent, i.e. ligand-to-metal π donation. In addition, the same SOMO-1 orbital also contains 2.0 % CH=CH–N ene(amido) π^* character, indicating the existence of a π-backdonation interaction with the ene(amido) group. The similar mechanism has been demonstrated in iron-based catalysts recently by our group.[15] The multicomponent SOMO-1 orbital could be regarded as a hybrid orbital where the negative charge from the amido N atom could be relayed to the vacant ene(amido) π^*-antibonding orbitals via a cobalt d orbital to avert high electron density on the cobalt center. In the case of iron, this electron density transfer was assumed to reduce the high electron density on the metal center, so as to stabilize the complex against decomposition.[15] This π-backdonation interaction does not occur on **b1** due to lack of ene(amido) π^*-antibonding orbitals (see supporting information section for details).



Scheme 2. The proposed reactions of cobalt pre-catalysts **a** and **b** with 2 equiv. of KO*t*Bu to produce the putative amido complexes of **a1** and **b1**.

Complex **a** could hydrogenate a wide range of ketones. Unfortunately, when substituents were introduced on the benzenephenyl ring of acetophenone, *ee* values decreased more or less for most substrates. Good conversions were obtained on hydrogenation of acetophenones which contain electron donor groups. When substituent groups were replaced by electron withdrawing groups, the catalytic efficiency decreased under the identical general conditions. The *ee* value of 68 % was furnished on hydrogenation of 3′-bromoacetophenone, slightly more than the result reported by Zhang et al.[10] Hydrogenation of 3′-(trifluoromethyl)acetophenone exhibited an excellent conversion once ratio of pre-catalyst to substrate was improved. Relative low conversion of hydrogenation of 3,5-bis(trifluoromethyl)acetophenone was obtained due to stronger electron absorption capacity of substituents.

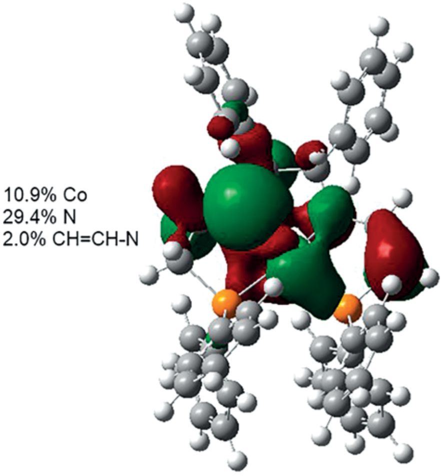


Figure 4. Qualitative molecular SOMO-1 orbital diagram of complex a1 obtained from restricted DFT calculations at the B3LYP/LANL2DZ level.

Moderate *ee* value(72 %) and high conversion (91 %) were obtained on hydrogenation of propiophenone, and these values have advantage over asymmetric borohydride reduction.[14] A moderate *ee* value of 66 % was obtained on reduction of 1-acetonaphthone, morehigher than Tomohiko's result,[16] and the reduced product can be used for the synthesis of (+)-compactin and 1233A.[17] A good *ee* value of 78 % was achieved on hydrogenation of 1-tetralone, and this value is better than the reported result of Co-catalyzed borohydride reduction.[18] Fortunately, when 2-chlorobenzophenone was used as feedstock, the corresponding alcohol was obtained with 91 % *ee* value, much more than the result of Co-catalyzed borohydride reduction,[19] and the enantiopurity erosion did not happened in this reaction. But when chlorine substituent was replaced by methyl, *ee* value was cut down to 80 % on hydrogenation of 2-methylbenzophenone, slightly lower than the result of hydroboration.[20] Finally, hydrogenation of alkyl-alkyl ketone was also performed. When 3-methyl-2-butanone was selected as substrate, product was obtained with an *ee* value of 41 %.

Conclusion

A new cobalt(II) complex bearing amine(imine)diphosphine PN(H)NP ligand for asymmetric transfer hydrogenation of ketones was developed. This catalyst could prompt asymmetric transfer hydrogenation of a wide range of ketones under very mild conditions after being activated by base and exhibited a maximum *ee* value of up to 91 %. The electronic structure studies based on DFT calculations revealed that a π-backdonation interaction between the cobalt d orbital and the π^* antibonding orbitals of amido-ene(imido) group is a key factor to enable its catalytic properties.

Experimental Section

General Comments

NMR spectra were recorded at ambient temperature and pressure using BRUKER AVANCE III, ^{31}P (242 MHz). The ^{31}P NMR spectra were referenced to 85 % H_3PO_4 (0 ppm). The electrospray ionization mass spectrometry (ESI-MS) data were collected on an Xevo G2-XS QTOFMS of mass spectrometer with an ESI source at the Instrumental Analysis Center of Shanghai Jiao Tong University. Single-crystal X-ray diffraction data were collected using a Nonius Kappa-CCD diffractometer with Mo-K_α radiation (λ = 0.71073 Å) at Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences.

Deposition Numbers 2013827 (for **a**) and 2014174 (for **b**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

Synthesis of Complex a: In an argon glovebox, a solution of diphenylphosphino-acetaldehyde hydrochloride dimer (353.6 mg, 0.67 mmol) in 10 mL of MeOH was added into a suspension of NaOMe (71.9 mg, 1.3mmol) in 5 mL of MeOH with stirring in a 100 mL of Schlenk flask. Then the solution of $PN(H)N(H_2)$[11] ligand (about 82 % purity, 750.0 mg, 1.44 mmol) in 30 mL of MeOH was added into the Schlenk flask. Finally, the solution of cobalt(II) bromide hydrate (291.6 mg, 1.3 mmol) in 10 mL of MeOH was added into the mixture solution, and dark brown solution was obtained. The solution was condensed to 10 mL after stirring for 3 h and filtered through a syringe filter with PTFE membrane (pore size 0.225 µm). Then the rest of solvent was removed under vacuum, and brown solid was obtained and transferred into a new flask. Subsequently, 50 mL of acetone was poured into the flask with stirring to dissolve the solid. The solution was stirred for further 12 h, and the precipitate appeared in the bottom of flask. Pure complex **a** (432.0 mg, 35 % yield) was collected by filtering with filter paper in glovebox, washing with acetone twice. The complex **a** was dissolved with 4 mL of dichloromethane, and acetone was let to slowly diffuse into the solution to afford brown crystals of **a**, which is suitable for X-ray diffraction. HRMS (ESI-TOF, CH_2Cl_2) *m/z* calculated for [($C_{42}H_{40}Br_2CoN_2P_2$)]: 853.0350, found 853.0345. FTIR (ATR, cm^{-1}): 3047w, 3008w, 2851w, 1624w, 1486w, 1453m, 1432s, 1187w, 1094s, 1073m, 1020w, 994w, 966m, 849w, 742s, 685s, 642s, 575s, 525s. Anal. Calcd for $C_{42}H_{40}Br_2CoN_2P_2$: C, 59.11 %, H, 4.72 %, N, 3.28 %; found C, 59.23 %, H, 4.77 %, N, 3.32 %.

Synthesis of Complex b: In an argon glovebox, 1.60 g of $PN(H)N(H)P$[13] ligand (about 60 % purity, 1.50 mmol) was dissolved in MeOH (30 mL) in a 100 mL Schlenk flask. Then the solution of cobalt(II) bromide hydrate (344 mg, 1.6mmol) in 20 mL of MeOH was added into the flask. Dark brown solution was obtained and stirred for further 3 h. Then solvent was removed under vacuum, and brown solid was obtained. After that, 50 mL of acetone was poured into the flask to dissolve the solid. The solution was stirred for further 12 h, and the precipitate appeared in the bottom of flask. Pure complex **b** (361.0 mg, 28 % yield) was collected by filtering with filter paper in glovebox, washing with acetone twice. The complex **b** was dissolved with 4 mL of dichloromethane, and acetone was let to slowly diffuse into the solution to afford brown crystals of **b**, which is suitable for X-ray diffraction. HRMS (ESI-TOF, CH_2Cl_2) *m/z* calculated for [($C_{42}H_{42}Br_2CoN_2P_2$)]: 855.0506, found 855.0490. FTIR (ATR, cm^{-1}): 3054w, 2963w, 2873w, 2368w, 1699m, 1581w, 1482w, 1449m, 1432s, 1354w, 1183m, 1094s, 1069m, 1020w, 959m, 916m, 845m, 803w, 735s, 689s, 628s, 557s. Anal. Calcd for $C_{42}H_{42}Br_2CoN_2P_2$: C, 58.97 %, H, 4.95 %, N, 3.27 %; found C, 59.08 %, 4.97 %, 3.30 %.

Computational Details

Geometry optimizations and frequency calculations were performed with the Gaussian09 program package using a series of functionals and basis sets in the vacuum state. Optimized ground states were found to have no imaginary frequencies while transition states had only one imaginary frequency. A tightly converged criterion (1×10^{-8} E_h in energy, 1×10^{-7} E_h in density change, and 1×10^{-7} in the maximum element of the DIIS error vector) was used for the self-consistent-field calculations. A pruned (99,590) integration grid was used for density functional theory calculations. Three dimensional visualizations of calculated structures were generated by ChemCraft. The analysis of MO compositions was performed using the natural atomic orbitals method. Orbitals from the Gaussian calculations were plotted with the ChemCraft program.

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