Cobalt–Carbon Bond Formation Reaction via Ligand Reduction of Porphycene–Cobalt(II) Complex and Its Noninnocent Reactivity

Taro Koide,† Isao Aritome,† Tatsuya Saeki,† Yoshitsugu Morita,§ Yoshihito Shiotani,‡ Kazunari Yoshizawa,§ Hisashi Shimakoshi,† and Yoshio Hisaeda†,‡,†,‡

†Department of Chemistry and Biochemistry, Graduate School of Engineering and ‡Institute for Materials Chemistry and Engineering, Kyushu University, Moto-o-oka 744, Nishi-ku, Fukuoka-shi, Fukuoka 819-0395, Japan
§Department of Applied Chemistry, Faculty of Science and Engineering, Chuo University, Kasuga 1-13-27, Bunkyo-ku, Tokyo 112-8551, Japan

Supporting Information

ABSTRACT: The interesting redox properties and reactivity of metalloporphycene have been studied for decades; however, the detailed experimental investigation on the reactivity and reaction mechanism under inert condition combined with theoretical calculations had not been performed so far. In this study, the novel reactivity of the reduced form of the cobalt porphycene with alkyl halides to form cobalt–carbon (Co–C) bonds was revealed. Under electrochemical reductive conditions, not the central cobalt, but the ligand was reduced and reacted with alkyl halides to afford the cobalt–alkyl complexes under N₂ atmosphere in a glovebox. The reaction mechanism was clarified by the combination of experimental and theoretical studies that the porphycene ligand works as a noninnocent ligand and allows the S_n2-type Co–C bond formation. This result provides us the possibility of the reaction triggered by the reduction of ligand with macrocyclic π-conjugated system, not by the reduction of metal.

INTRODUCTION

In general, transition-metal complexes, which work as catalysts reacting with organohalides, show a catalytic cycle that starts from the generation of a low-valent metal. Oxidative addition, transmetallation, and reductive elimination are the significant steps in these catalytic reactions.1 Especially, electrocatalytic reactions possess common mechanistic features such that the metal center accepts electrons from the working electrode by changing to a lower valence state and become an initiator of the catalytic reaction. Among them, the cobalt-catalyzed reactions have received increasing attention because of some advantages. One of the reasons is that cobalt is inexpensive compared to other transition metals, which show a high catalytic reactivity such as palladium, rhodium, etc. Another reason is that the cobalt catalyst is effective for the synthesis of complicated molecules because the cobalt-catalyzed reaction is a characteristic reaction with the generation of a radical intermediate by the homolytic cleavage of the cobalt–carbon (Co–C) bond.2–4 The Co–C bond formation process is the key step and mainly classified into the following three types by the valence of cobalt: (1) reaction of Co(I) with alkyl halide,2,5,6 (2) reaction of Co(II) with alkyl radical,7,8 and (3) reaction of Co(III) with nucleophile such as the Grignard reagent.9,10 We also reported the Co–C bond formation reaction using hydrophobic vitamin B₁₂ derivatives, which was initiated by the reduction of the cobalt center from Co(II) to the super nucleophilic Co(I).11,12 The reaction mechanisms of these reactions have also got attention.13 Aiming for further improvement, it is necessary to utilize not only the valence change of the cobalt, but also the effect of the ligands. Recently, there have been several examples of the reaction of cobalt complexes with redox-active ligands.14–19 In the case of cobalt(III) bis(amidophenolate), the cobalt center acts as a strong nucleophile and reacts with alkyl halides under gentle conditions to generate the Co–C bond without a valence change in the cobalt ion but with the one-electron oxidations of two amidophenolate ligands. The reaction mechanism was estimated to be the S_n2-type oxidative addition of alkyl halides to the Co(III) center. The redox-active ligands supply two electrons instead of the cobalt ion for the formation of the Co–C bond. In this reaction, the redox-active ligands played the role of an electron donor along with the reaction sequence.14

As a ligand of cobalt complex, we focused on porphycene, a tetrapyrrolic macrocycle and one of the structural isomers of porphyrin, which has been attracted increasing attention because of its intriguing properties such as low-energy absorption, small highest occupied molecular orbital (HOMO)–lowest unoccupied molecular orbital (LUMO) gap, strong emission, as well as rich coordination chemistry and its catalytic activity.20–25 The reduction potential of...
Porphycene is known to be anodically shifted compared to that of porphyrin due to the splitting of LUMO, which is degenerate in porphyrin, based on the symmetry lowering from porphyrin to porphycene ($D_{4h}$ to $D_{2h}$). Depending on this positive shift in the reduction potentials, the redox behavior of the Co(II) complex of porphycene is totally different from that of porphyrin. In the case of the porphyrin−Co complex, the one-electron reduction of the Co(II) complex affords the Co(I) complex. On the other hand, the radical anion of the Co(II) complex is known to be formed in the case of the porphycene−Co complex (Figure 1). The unique catalytic reactivity of the porphycene−cobalt complex was reported for the oxidation of vinyl ether into two corresponding different acetals under aerobic conditions. In this study, the electrochemical experiments of the porphycene−cobalt complex under anaerobic conditions (in glovebox, $O_2 < 3$ ppm) have been investigated. We found the formation and dissociation reaction of the Co−C bond via the redox of the noninnocent porphycene ligand. Although the reactivity of the reduced species of metalloporphycene has been investigated in several examples, this study gave information of fundamental reactivity and reaction mechanism of cobalt porphycene with alkyl halides under inert condition. The theoretical interpretation of the reaction also provides us the possibility of the reaction triggered by the reduction of ligand, not by the reduction of metal, using macrocyclic π-conjugated molecule.

**RESULTS AND DISCUSSION**

The cyclic voltammogram of the cobalt complex of $\beta$-tetra-$n$-propyl porphycene (Co(II)Pc) in tetrahydrofuran (THF) exhibited two reversible reduction processes at $-0.93$ and $-1.25$ V (vs Ag/AgCl), almost the same values as already reported (Figure 2a). The time-dependent spectral change in the UV−vis absorption spectrum was observed under electrochemical reductive conditions at $-1.2$ V (vs Ag/AgCl). The generation of the radical anion of the porphycene−Co(II) complex (Co(II)Pc$^{--}$) under reductive conditions was detected by spectroelectrochemistry in THF. The absorption peaks at 386 and 610 nm became weaker and new peaks at 731 nm and longer wavelengths appeared (Figure 2b), indicating that the reduction proceeded not at the central metal, but at the porphycene ligand, as already reported. The cyclic
voltammmogram and absorption spectra of Co(II)Pc in CH₂Cl₂ without total degassing are also known to show reversible redox waves and similar spectral changes.²⁰ The radical anion species was also observed by electron spin resonance (ESR) measurement. The ESR spectrum of the solution obtained from the bulk electrolysis of Co(II)Pc at −1.2 V (vs Ag/AgCl) in THF exhibits many well resolved hyperfine structures (g = 2.007, A = 0.68 G) (Figure 3). The spectrum is characteristic to that of the methylated complex CH₃−Co(III)Pc was also successfully afforded and isolated. On the basis of the ¹H NMR of CH₃−Co(III)Pc in CDCl₃, the signal at −5.0 ppm was assigned as the axial methyl group and the valence of the cobalt could be +3 (Figure 5). Hence, the formation of the Co−alkyl bond via

differentiation in the macrocyclic conjugation system of the porphycene ligand before and after the electrolysis. The observed absorption at the electrolysis resembled that of the reported porphycene with the Co−C bond.³¹,³² To identify the product, constant potential electrolysis was carried out in CH₂Cl₂ at −1.20 V (vs Ag/AgCl). CH₂Cl₂ was removed from the solution after the constant potential electrolysis under reduced pressure and the residue was purified by washing it with methanol/water = 2:1. The obtained product was successfully isolated and characterized by ¹H NMR and electron spray ionization time-of-flight mass spectra (ESI-TOF-MS). Methylene protons of the axial chloromethyl group were observed at −2.22 ppm because of the shielding effect due to the ring current of the 18π porphycene core (Figure 4). This result indicated that dichloromethane reacted with the reduced porphycene−cobalt complex and the covalent bond between the cobalt and chloromethyl group was formed at the axial position of the cobalt.

By using a similar procedure, the Co−CH₃ complex was prepared by the electrochemical reductive reaction of Co(II)Pc under the CH₃I coexisting condition in dimethylformamide (DMF) and analyzed by ¹H NMR and ESI-TOF-MS. The one electron reduced form of metalloporphycene (MPc⁺), which displays hyperfine couplings assigned to the four core nitrogens and the 16 peripheral protons (pyrrole β × 4, methine bridge × 4, propyl α × 8),²⁰,³⁰,³¹ indicating the generation of radical delocalized to the whole porphycene skeleton, thus the observed species was identified as Co(II)−Pc⁺. However, when the electrochemical reduction of Co(II)Pc was performed in CH₂Cl₂ under N₂ atmosphere in a glovebox, the electrochemical and spectral changes were totally different from those of the reaction in THF. Cyclic voltammogram showed irreversible behavior (Figure 2c) and no bathochromic shift was observed for both the Soret band and Q band, whereas the intensity of absorption bands at 592 and 384 nm was slightly decreased and increased, respectively (Figure 2d). This result implies that a chemical reaction occurred after the first reduction step, but there was little change in the macrocyclic conjugation system of the porphycene ligand before and after the electrolysis.

Figure 3. ESR spectrum of Co(II)Pc⁺⁺ in THF at room temperature.

Figure 4. ¹H NMR spectrum of CH₃Cl−Co(III)Pc in CDCl₃ (* shows the signal assigned as residual solvent).

Figure 5. ¹H NMR spectrum of CH₃−Co(III)Pc in CDCl₃ (* shows the signal assigned as residual solvent).

Figure 6. The electrochemical reductive reaction of Co(II)Pc was confirmed. Judging from the spectral change without the appearance of a low-energy absorption band due to the radical anion in the spectroelectrochemistry and the irreversible reduction process of Co(II)Pc in CH₂Cl₂, the reaction between the radical anion ([Co(II)Pc]⁺) and alkyl halides quickly proceeds after the generation of the radical anion (Scheme 1, Figure 6A). As the intermediate, small amount of highly nucleophilic Co(I) species could be considered as one possibility (Figure 6B). If there was a small ratio of electron transfer from the ligand to cobalt and generated [Co(I)Pc]− was the reactive species, the longer-wavelength absorption due to the covalent bond between the cobalt and chloromethyl group was formed at the axial position of the cobalt.

Free-radical migration from the porphycene ligand to the alkyl halide followed by the reaction with the Co(II) complex and halalkyl radical (Figure 6C) was also unlikely from the radical-trapping experiment described below. α-Phenyl-N-tert-butyl-nitron (PBN) was added as the radical-trapping reagent to the reaction system including Co(II)Pc and CH₃I at −1.2 V (vs Ag/AgCl). Though the reaction was traced by an ESR
measurement, no signal due to the CH$_3$-PBN radical was observed, probably due to the fast formation of the Co−C bond. Furthermore, the CH$_3$−Co(III)Pc could be even isolated from the solution containing PBN and characterized by $^1$H NMR. However, the ESR signal of the CH$_3$-PBN radical appeared by visible light irradiation after the electrolysis at −1.2 V (vs Ag/AgCl) for 2 h, indicating that the formation of the Co(III)−C bond under reductive conditions proceeded without the generation of the methyl radical. Therefore, the pathway through the Co(II) complex of porphycene radical anion is the most plausible (Figure 6A), and the homolytic dissociation of the Co(III)−C bond by light irradiation produces the Co(II) species and methyl radical (Figure 6ii).

We performed the density functional theory (DFT) calculations for the detailed analysis of the reaction mechanism. There are two possible electronic states for the one-electron reduced species of Co(II)Pc; i.e., the metal-reduced species, [Co(I)Pc]$^-\cdot$, or the ligand-reduced species, [Co(II)Pc]$. The energy level of the former one was estimated to be 21.2 kcal/mol higher than the latter one, thus the ligand-reduced radical anion species is dominant and the presence of metal-reduced Co(I) species is negligible (Figure 7). This is consistent with the experimental result that the reduction occurred not at the Co center, but at the porphycene ligand. The expected absorption spectrum from TD-DFT calculation also reproduced the long-wavelength absorption of the ligand-reduced radical anion species (Supporting Information (SI), Figure S12). The energy levels of the MOs, including HOMO-3, derived from the d$^z_2$ orbital of Co(II) center increase from ca. −6 to −2 V, along with the reduction of the porphycene ligand from neutral to the radical anion (SI, Figure S10). From the optimized positional relationship between the [Co(II)Pc]$^-\cdot$ and substrate (CH$_3$I) at the first step of the reaction (RC1 in Figure 7), the substrate approaches from a slightly diagonal position on the ligand, not just above the cobalt ion, might be because of the electrostatic interaction between

Figure 6. Consideration of the Co−C bond formation reaction via the reduction of Co(II)Pc. The colored rings and cobalt centers correspond to the models shown in Scheme 1. (i) First step of the reaction determined by spectroelectrochemistry and ESR. (A−C) Possible reaction mechanisms following to the first reduction step. (A) Reaction of [Co(II)Pc]$^-\cdot$ with alkyl halide. (B) Reaction of Co(I)Pc generated by the electron transfer from porphycene to cobalt center with alkyl halide. (C) Reaction of Co(II)Pc and alkyl radical formed by the radical migration from [Co(II)Pc]$^-\cdot$ to alkyl halide. (ii) Visible light irradiation to R-Co(III)Pc afforded Co(II)Pc and alkyl radical, which was trapped by α-phenyl-N-tert-butyl-nitron (PBN).
negatively charged porphycene ligand and slightly positively charged carbon due to the difference in electronegativity with halogen. Then, the activated cobalt center reacts with CH$_3$I to afford a product having the Co–C bond via the SN$_2$-like transition state (TS1). From the theoretical calculation of the spin density, the electron spin delocalized to the macrocyclic conjugation system of the porphycene at first, and partial electron transfer occurred from both the porphycene ligand and cobalt ion to CH$_3$I, indicating that the porphycene ligand took the electronic state between the radical anion and neutral at the transition state (TS1). More precisely, spin density moved onto the carbon atom of CH$_3$I from the ligand, and iodine atom, which is released as a leaving group of the SN$_2$-type reaction, became negatively charged without the electron spin (Figure 8). On the basis of the result, porphycene could be thought of as a noninnocent ligand whose reduction initiates the Co–C bond formation reaction. It is worthy to note that the reduced part and the reacted part are different. The reduction occurred at the porphycene ligand, but the following reaction proceeds at the central cobalt and affords the Co–C bond via TS1. The energy gap between the reaction complexes (RC1) and TS1 was estimated to be 15.0 kcal/mol that is possible to be

**Figure 7.** Energy diagrams and calculated models of the two possible reaction mechanisms of the Co–C bond formation reaction under reductive condition. Reaction processes shown in red and black lines correspond to route (A) and (B) in Figure 6.

**Figure 8.** (a) Schematic representation of the plausible reaction mechanism. (b) Calculated spin density representation of each step of the Co–C bond formation reaction. The table below is the summary of the charge and spin density distribution of each reaction step.
surpassed at room temperature. From these results, it could be concluded that the one-electron reduced species of the porphycene−Co(II) complex takes the radical anion form, which is highly reactive to form the Co(III)−C bond by the reaction with alkyli halides.

The chemical one-electron reduction of the porphycene−cobalt complex was also performed using decamethylcobaltocene, possessing a reduction potential of −1.44 V vs Ag/AgCl. The anion radical of the porphycene was formed and checked by the change in the absorption spectra. The spectral change induced by the reductant was similar to that observed by the electrochemical one-electron reduction in THF, indicating that it was not due to the change in the valence of the central metal ion, but the formation of the radical anion species of the porphycene ligand. When this reduction proceeded in CH2Cl2, the porphycene−Co−CH2Cl complex was generated and successfully isolated. The resembling Co−alkyl complexes were formed in THF by the chemical reduction and the following reaction with alkyli halides.

**CONCLUSIONS**

In summary, we found that the one-electron reduced species of the Co(II) porphycene, Co(II) porphycene radical anion, reacts with alkyli halides to form Co−C bonds under N2 atmosphere. The Co−C bond formation reaction discovered here is a new type of reactivity, which had not seen in the cobalt complexes. The reaction mechanism was clarified by the combination of experimental and theoretical studies. The ligand-reduced species of Co(II) porphycene was detected by photo-electrochemistry and ESR measurement, and the cobalt−alkyl complexes could be isolated after the constant potential electrolysis. DFT calculations revealed that the porphycene ligand works as a noninnocent ligand and afforded cobalt−alkyl complex by the S_{n}2-type reaction between cobalt center and substrate. Further investigation to construct a catalytic cycle by using a redox-active porphycene ligand is now underway in our group.

**EXPERIMENTAL SECTION**

**General Information.** Reagents and solvents of the best grade available were purchased from commercial suppliers and were used without further purification, unless otherwise noted. Dried dichloromethane (CH2Cl2) and DMF were obtained by distillation from CaH2 under N2 atmosphere. THF was dried by distillation from benzophenone/sodium under N2 atmosphere. NMR spectra were recorded on a Bruker Avance 500 MHz NMR spectrometer. The resonance frequencies are 500 and 125 MHz for 1H and 13C, respectively. Chemical shifts were reported as δ values in ppm relative to tetramethylsilane. High-resolution electron spray ionization time-of-flight mass spectra (HR-ESI-TOF-MS) were measured on JMS-T100LC-AccuTOF and microTOFQFI spectrometer (JEOL, Japan). Ultra-violet−visible−near-infrared (UV−vis−NIR) absorption spectra were recorded on U-3310 spectrometer (Hitachi, Japan) and V-670KS (JASCO, Japan). Electron spin resonance (ESR) measurement was carried out with a JES-FE1G X-band spectrometer (JEOL) equipped with an Advantest TR-5213 microwave counter and an Echo Electronics EFM-200 NMR field meter.

Redox potentials were measured by the cyclic voltammetry method on an ALS electrochemical analyzer model 630C in glovebox. Cyclic voltammetric measurements were carried out using 1.6 mm diameter platinum working electrode and platinum wire counter electrode in dehydrated solvents containing 0.1 M Bu4NPF6 as a supporting electrolyte under nitrogen atmosphere at room temperature. In this experiment, we employed a Ag/10 mM AgCl reference electrode. The reference electrode was separated from the bulk solution by a fritted-glass bridge filled with 0.1 M KCl aqueous solution.

**DFT Calculation.** We optimized local minima on the potential energy surfaces using the B3LYP method.35,34 To estimate excited states, TD calculations35 with the B3LYP method were performed using optimized structures. We used the TZVP (for Co, C, H, and N) basis36 and the SDD (for I) basis.37 Vibrational frequencies were systematically computed to ensure that on a potential energy surface each optimized geometry corresponds to a local minimum that has no imaginary frequency. The Gaussian 09 program package was used for all DFT calculations.

**Synthesis of TPrPc and Co(II)Pc.** TPrPc and Co(II)Pc were synthesized as described in the literature.39,27

**Synthesis of CH2Cl−Co(III)Pc and CH3−Co(III)Pc.** The electro-syntheses of CH2Cl−Co(III)Pc and CH3−Co(III)Pc were performed under N2 atmosphere and in the dark using the following procedure: 5.8 mg (11 μmol) of Co(II)Pc was dissolved in either 12 mL of CH2Cl2 or a mixture of 10 mL of DMF and 2 mL of CH3I containing 0.1 M TBABF4. Bulk electrolysis of the solution was performed at −1.2 V vs Ag/AgCl for 2 h using a divided cell system consist of a platinum mesh electrode as working, a zinc plate electrode as counter (sacrificial), and a cell guard 2400 film as a separator. After completion of electrolysis, the solution was transferred from the cell and the solvent was evaporated to dryness using a stream of N2 gas. The residue was dissolved in diethyl ether and the insolubles were removed by filtration. The resultant organic layer was evaporated under reduced pressure, and 1H NMR measurement was performed on the residual solid.

**CH2Cl−Co(III)Pc.** 1H NMR (500 MHz, CDCl3): δ 9.62 (s, 4H, Pc-β-H), 9.26 (s, 4H, Pc-meso-H), 4.07 (m, 8H, −CH2CH2CH2CH3), 2.42 (brm, −CH2CH2CH2CH3), 1.37 (t, 12H, J = 7.5 Hz, −CH2CH2CH2CH3), −2.22 (s, 2H, Co−CH2Cl); MS (positive mode): C_{32}H_{38}N_{4}Co ([M + H]+) m/z found: 585.45; calcd: 585.21.

**CH3−Co(III)Pc.** 1H NMR (500 MHz, CDCl3): δ 9.50 (s, 4H, Pc-β-H), 9.14 (s, 4H, Pc-meso-H), 4.02 (m, 8H, −CH2CH2CH2CH3), 2.41 (m, 8H, −CH2CH2CH2CH3), 1.37 (t, 12H, J = 7.3 Hz, −CH2CH2CH2CH3), −4.84 (s, 3H, Co−CH3); MS (positive mode): C_{33}H_{40}N_{4}Co ([M + H]+) m/z found: 551.25; calcd: 551.25.

**ASSOCIATED CONTENT**

Supporting Information

**Corresponding Author**

*E-mail: yhisatcm@mail.cstm.kyushu-u.ac.jp.*
ACKNOWLEDGMENTS

This work was partially supported by JSPS KAKENHI Grant Number JP16H01035 in Precisely Designed Catalysts with Customized Scaffolding and Grant Number JP16H04119, and by JSPS and PAN under the Research Cooperative Program Grant Number AJ179063(29-9111-t11). T.K. is grateful to the financial support by Izumi Science and Technology Foundation and Toyota Physical and Chemical Research Institute.

REFERENCES

(1) Metal-Catalyzed Cross-Coupling Reactions, 2nd ed.; de Meijere, A., Diederich, F., Eds.; Wiley-VCH: Weinheim, Germany, 2004; pp 1–916.

(2) Summers, J. S.; Petersen, J. L.; Stolzenberg, A. M. Comparison of the Structures of the Five-Coordinate Cobalt(II) Pyridine, Five-Coordinate Cobalt(III) Methyl, and Six-Coordinate Cobalt(III) Methyl Pyridine Complexes of Octaethylporphyrin. J. Am. Chem. Soc. 1994, 116, 7189–7195.

(3) Giedyk, M.; Goliszewska, K.; Gryko, D. Vitamin B12 catalysed reactions. Chem. Soc. Rev. 2015, 44, 3391–3404.

(4) Lexa, D.; Saveant, J.-M. The Electrochemistry of Vitamin B12. Acc. Chem. Res. 1983, 16, 235–243.

(5) Ogoshi, H.; Watanabe, E.; Koketsu, N.; Yoshida, Z. Synthesis and Properties of Organocobalt(III)octaethylporphyrins. Bull. Chem. Soc. Jpn. 1976, 49, 2529–2536.

(6) Zheng, G. D.; Yan, Y.; Gao, S.; Tong, S. L.; Gao, D.; Zhen, K. J. The Reaction Mechanism Of Alkyl Halides With Carbon Dioxide Catalyzed By 5,10,15,20-Tetraphenyl Porphyrin Cobalt (CoTPP).

(7) Wayland, B. I.; Gridnev, A. A.; Ittel, S. D.; Frydlic, M. Thermodynamic and Activation Parameters for a (Porphyrinoato)-cobalt-Alkyl Bond Homolysis. Inorg. Chem. 1993, 32, 3830–3833.

(8) Glod, G.; Angst, W.; Holliger, C.; Schwartzbach, R. Corrinoid-Mediated Reduction of Tetrachloroethene, Trichloroethene, and Trichlorofluoroethene in Homogeneous Aqueous Solution: Reaction Kinetics and Reaction Mechanisms. Environ. Sci. Technol. 1997, 31, 253–260.

(9) Li, B.; Wu, Z.-H.; Gu, Y.-F.; Sun, C.-L.; Wang, B.-Q.; Shi, Z.-J. Direct Cross-Coupling of C-H Bonds with Grignard Reagents through Cobalt Catalysis. Angew. Chem., Int. Ed. 2011, 50, 1109–1113.

(10) Zhu, X.; Su, J.-H.; Du, C.; Wang, Z.-L.; Ren, C.-J.; Niu, J.-L.; Song, M.-P. Cobalt(II)-Catalyzed Oxidative C-H Arylation of Indoles and Boronic Acids. Org. Lett. 2017, 19, 596.

(11) Hisaeda, Y.; Shimakoshi, H. Handbook of Porphyrin Science; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; World Scientific, 2010; Vol. 10, pp 313–370.

(12) Shimakoshi, H.; Tokunaga, M.; Baba, T.; Hisaeda, Y. Photochemical Dechlorination of DDT Catalyzed by a Hydrophobic Vitamin B12 and a Photosensitizer Under Irradiation with Visible Light. Chem. Commun. 2004, 1806–1807.

(13) Costentin, C.; Robert, M.; Savéant, J.-M. Does Catalysis of Reductive Dechlorination of Tetra- and Trichloroethylenes by Vitamin B12 and Corrinoid-Based Dehalogenases Follow an Electron Transfer Mechanism? J. Am. Chem. Soc. 2005, 127, 12154–12155.

(14) Smith, A. L.; Hardcastle, K. I.; Soper, J. D. Redox-Active Ligand-Mediated Oxidative Addition and Reductive Elimination at Small Planar Cobalt(III): Multielectron Reactions for Cross-Coupling. J. Am. Chem. Soc. 2010, 132, 14358–14360.

(15) Dzik, W. I.; van der Vlugt, J. I.; Reek, J. N. H.; de Bruin, B. Ligands that Store and Release Electrons during Catalysis. Angew. Chem., Int. Ed. 2011, 50, 3356–3358.

(16) Paul, G. C.; Ghorai, S.; Mukherjee, C. Monoradical-containing Four-coordinate Co(III) Complexes: Homolytic S-S and Se-Se Bond Cleavage and Catalytic Isocyanate to Urea Conversion under Sunlight. Chem. Commun. 2017, 53, 8022–8025.

(17) Bowman, A. C.; Milsmann, C.; Atienza, C. C. H.; Lobkovsky, E.; Wieghardt, K.; Chirik, P. J. Synthesis and Molecular and Electronic Structures of Reduced Bis(imino)pyridine Cobalt Dinitrogen Complexes: Ligand versus Metal Reduction. J. Am. Chem. Soc. 2010, 132, 1676–1684.

(18) Semproni, S. P.; Milsmann, C.; Chirik, P. J. Four-Coordinate Cobalt Pincer Complexes: Electronic Structure Studies and Ligand Modification by Homolytic and Heterolytic Pathways. J. Am. Chem. Soc. 2014, 136, 9211–9224.

(19) Lyaskovsky, V.; de Bruin, B. Redox Non-Innocent Ligands: Versatile New Tools to Control Catalytic Reactions. ACS Catal. 2012, 2, 270–279.

(20) Bernard, C.; Gisselbrecht, J.; Gross, M.; Vogel, E.; Laumann, M. Redox Properties of Porphyrines and Metalloporphyrines. A Comparison with Porphyrins. Inorg. Chem. 1994, 33, 2393–2401.

(21) Sánchez-García, D.; Sessler, J. L. Porphyrines: Synthesis and Derivatives. Chem. Soc. Rev. 2008, 37, 215–232.

(22) Hayashi, T.; Okazaki, K.; Shimakoshi, H.; Tani, F.; Naruta, Y.; Hisaeda, Y. Synthesis and Properties of Alkylperoxocobalt(III) Porphyrin and Porphycene. Chem. Lett. 2000, 29, 90–91.

(23) Anguera, G.; Sánchez-García, D. Porphyrines and Related Isomers: Synthetic Aspects. Chem. Rev. 2017, 117, 2481–2516.

(24) Waluk, J. Spectroscopy and Tautomerization Studies of Porphycenes. Chem. Rev. 2017, 117, 2447–2480.

(25) Ciącka, P.; Fita, P.; Liskowski, A.; Kijak, M.; Nonell, S.; Kuzuhara, D.; Yamada, H.; Radzewicz, C.; Waluk, J. Tautomerism in Porphycenes: Analysis of Rate-Affecting Factors. J. Phys. Chem. B 2015, 119, 2292–2301.

(26) Kadish, K. M.; Lin, X. Q.; Han, B. C. Chloride-Binding Reactions and Electrochemistry of (TPP)CoII and (TPP)CoIII in Dichloromethane. Inorg. Chem. 1987, 26, 4161–4167.

(27) Gisselbrecht, J. P.; Gross, M.; Köcher, M.; Laumann, M.; Vogel, E. Redox Properties of Porphyrines and Metalloporphyrines as Compared with Porphyrins. J. Am. Chem. Soc. 1990, 112, 8618–8620.

(28) Kadish, K. M.; Boulas, P. L.; Kisters, M.; Vogel, E.; Aukuloo, A. M.; D’Souza, F.; Guilard, R. Synthesis and Electrochemical Reactivity of σ-Bonded and N-Substituted Cobalt Porphyrines. Inorg. Chem. 1998, 37, 2693–2700.

(29) Hayashi, T.; Okazaki, K.; Urakawa, N.; Shimakoshi, H.; Sessler, J. L.; Vogel, E.; Hisaeda, Y. Cobaltporphyrines as Catalysts. The Oxidation of Vinyl Ethers via the Formation and Dissociation of Cobalt-Carbon Bonds. Organometallics 2001, 20, 3074–3078.

(30) Renner, M.; Forman, A.; Wu, W.; Chang, C.; Fajer, J. Electrochemical, Theoretical, and ESR Characterizations of Porphycenes. The σ Anion Radical of Nickel(II) Porphyrine. J. Am. Chem. Soc. 1989, 111, 8618–8621.

(31) Schlüpmann, J.; Huber, M.; Toporowicz, M.; Plate, M.; Köcher, M.; Vogel, E.; Levanon, H.; Mobius, K. Liquid-Phase ESR, ENDOR, and TRIPLE Resonance of Porphycene Anion Radicals. J. Am. Chem. Soc. 1990, 112, 6463–6471.

(32) Kadish, K. M.; Han, B. C.; Endo, A. Electrochemistry of Five- and Six-Coordinate σ-Bonded Cobalt Porphyrins. (TPP)Co(CH3)(py) and (TPP)Co(R) Where TPP Is the Dianion of Tetraphenylporphyrin and R = CH3, C2H5, or CH2Cl. Inorg. Chem. 1997, 36, 4502–4506.

(33) Becke, A. D. Density-functional Exchange-Energy Approximation with Correct Asymptotic Behavior. Phys. Rev. A 1988, 38, 3098–3100.

(34) Lee, C.; Yang, W.; Parr, R. G. Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. Phys. Rev. B 1988, 37, 785–789.
(35) Casida, M. E.; Jamorski, C.; Casida, K. C.; Salahub, D. R. Molecular Excitation Energies to High-Lying Bound States from Time-Dependent Density-Functional Response Theory: Characterization and Correction of the Time-Dependent Local Density Approximation Ionization Threshold. J. Chem. Phys. 1998, 108, 4439–4449.

(36) Schäfer, A.; Horn, H.; Ahlrichs, R. Fully Optimized Contracted Gaussian Basis Sets for Atoms Li to Kr. J. Chem. Phys. 1992, 97, 2571–2577.

(37) Hehre, W. J.; Ditchfield, R.; Pople, J. A. Self-Consistent Molecular Orbital Methods. XII. Further Extensions of Gaussian-Type Basis Sets for Use in Molecular Orbital Studies of Organic Molecules. J. Chem. Phys. 1972, 56, 2257–2261.

(38) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Keith, T.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian 09, revision D.01; Gaussian, Inc.: Wallingford, CT, 2013.

(39) Vogel, E.; Balci, M.; Pramod, K.; Koch, P.; Lex, J.; Ermer, O. Angew. Chem., Int. Ed. Engl. 1987, 26, 928–931.