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EDGE ARTICLE

Co(I) complexes with a tetradentate phenanthroline-based PNNP ligand as a potent new metal-ligand cooperation platform

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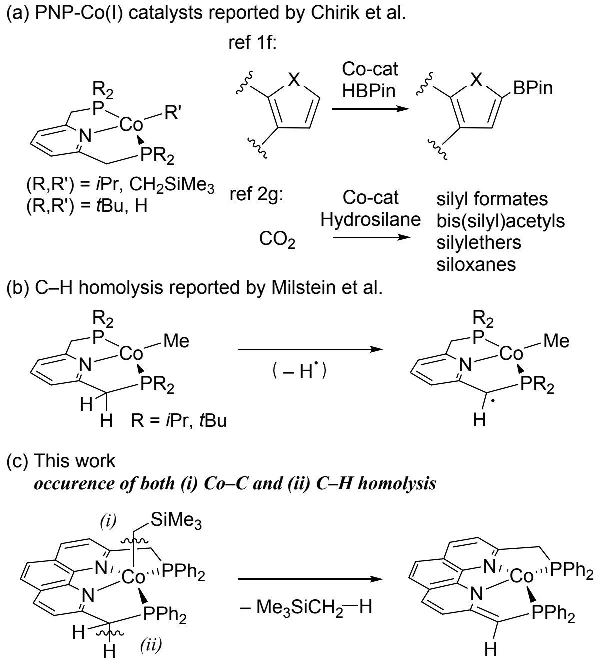
Nai-Yuan Jheng,[a,b] Yusuke Ishizaka,[a,b] Yuki Naganawa,[b] Akira Sekiguchi,[b] and Yumiko Nakajima*[a,b]

A series of low spin cobalt(I) complexes bearing a tetradentate phenanthroline-based PNNP ligand (2,9-bis((diphenylphosphanyl)methyl)-1,10-phenanthroline), [CoCl(PNNP)] (**1**), [CoMe(PNNP)] (**2**) and [Co(CH_2SiMe_3)(PNNP)] (**3**), were synthesized and structurally identified. Complex **3** underwent structural rearrangement of the PNNP skeleton upon heating to form [Co(PNNP')] (**4**), which is supported by an asymmetrical PNNP' ligand with a dearomatized phenanthroline backbone. Mechanistic studies supported that the transformation from **3** to **4** was initiated by homolysis of either a Co–CH_2SiMe_3 bond or a benzylic C–H bond. Complex **4** achieved H–H bond cleavage of H_2 (1 atm) at ambient temperature, to form [Co(PNNP'')] (**6**), in which two H atoms were incorporated in the endocyclic double bond of the PNNP'' ligand backbone.

Introduction

Low valent cobalt complexes play an important role as key active species in various catalytic reactions,[1] activation of small molecules,[2] etc. In this field, extensive studies have been performed using multidentate ligands, which effectively stabilize the reactive metal centres and are helpful to perform detailed mechanistic studies.[1e-h,2a,2d,3] Among these studies, Co(I) complexes with a tridentate pincer ligand, which coordinates with a metal centre in a meridional fashion, have drawn a great deal of attention due to their unique electronic properties and diverse reactivities. For example, in 2001, one important benchmark was made by Brookhart, Gibson, et al; they developed bis(imino)pyridine (PDI)-coordinated Co(I) methyl complex [CoMe(PDI)],[4] which is nowadays recognized as the key intermediate in the first late-transition-metal olefin polymerization.[5] These studies opened up a new application pathway for Co(I)-alkyl complexes. Chirik's group further expanded the chemistry of PDI-coordinated Co(I)-alkyl complexes to reveal their intrinsic electronic structures and achieved various catalytic reactions, in which Co(I)-alkyls play a pivotal role.[1f,1h,1i] The utility of the pyridine-based PNP pincer ligand (PNP = 2,6-bis((dialkylphosphanyl)methyl)pyridine) has also been reported in Co(I)-catalysed C–H borylation and CO_2 reduction (Scheme 1a).[1f,2g] In 2013, Milstein et al. reported the formal loss of an H radical via benzylic C–H homolysis of the PNP-pincer ligand in a Co(I) methyl complex (Scheme 1b).[6] A detailed mechanistic study revealed that the occurrence of benzylic C–H scission in PNP-Co(I) methyl complex is mediated via novel long-range metal-ligand cooperation (MLC), which is possibly attributable to the characteristic radical properties of a Co complex.



Scheme 1 Unique metal-ligand cooperation (MLC) of Co(I) complexes.

As a result, this study brought a new axis to Co(I) chemistry, specifically introduction of the MLC concept, which has thus far brought some significant breakthroughs in, mainly, precious metal catalysis. However, as far as we know, studies on MLC of

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[a] *Graduate School of Pure and Applied Sciences, University of Tsukuba 1-1-1 Tennoudai, Tsukuba, Ibaraki 305-8577, Japan. E-mail: yumiko-nakajima@aist.go.jp*

[b] *Interdisciplinary Research Center for Catalytic Chemistry (IRC3), National Institute of Advanced Industrial Science and Technology (AIST), 1-1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan.*

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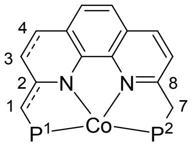
Table 1 Selected bond distances and spectroscopic data of **1**, **4**, **5**, and **6**

	Selected bond lengths (Å)						δ_H (ppm) (C_6D_6)	δ_P (ppm) (C_6D_6)	
	C1–C2	C2–C3	C3–C4	C7–C8	P1–C1	P2–C7			
1	1.491(10)	1.405(10)	1.397(11)	1.461(11)	1.847(8)	1.856(7)	4.17 (PCH_2) 5.23 (PCH_2)	55.6 (PCH_2)	
4	1.377(3)	1.451(2)	1.358(3)	1.494(3)	1.788(2)	1.867(2)	3.08 (PCH_2) 4.33 (PCH)	38.2 (PCH) 52.8 (PCH_2)	
5	1.361(7)	1.451(7)	1.354(7)	1.357(7)	1.776(5)	1.777(5)	4.68 (PCH)	33.9 (PCH)	
6	1.388(8)	1.487(8)	1.453(10)	1.472(8)	1.809(6)	1.862(5)	3.25 (PCH_2) 4.64 (PCH)	44.5 (PCH) 55.6 (PCH_2)	

Co complexes are still extremely limited probably due to the complicated paramagnetic nature of Co species.[7] In important prior works, we developed a novel low-valent Fe system supported by a tetradentate phenanthroline-based PNNP ligand (2,9-bis((diphenylphosphanyl)methyl)-1,10-phenanthroline), which was originally prepared by Ziessel.[8] The PNNP ligand coordinates with a metal centre via rigid meridional coordination fashion and exhibits strong donating ability. Owing to these properties, the PNNP ligand acts as a strong-field ligand, and we successfully isolated a series of reactive PNNP-supported Fe complexes as stable diamagnetic species and demonstrated MLC in the system.[9] Motivated by these results, we expanded the concept of the PNNP ligand to Co(I) chemistry. Herein, we describe synthesis of PNNP-Co(I) alkyl complexes as a well-defined diamagnetic species. We found that the PNNP-Co system exhibits a unique structural transformation behaviour, which correlates with dearomatization of the phenanthroline backbone of the PNNP ligand (Scheme 1c). Furthermore, MLC-mediated H–H bond cleavage, using a Co(I) system, was achieved, demonstrating the unprecedented role of the PNNP-backbone as a hydrogen reservoir.

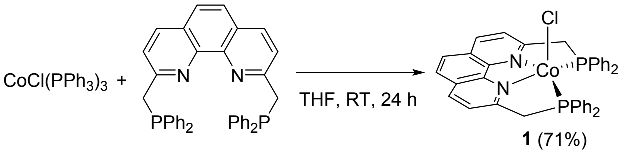
Results and discussion

Synthesis of PNNP-supported Co(I) alkyl complexes

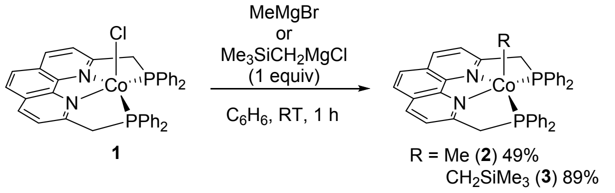
Introduction of the PNNP ligand on the Co metal was achieved by the reaction of [$CoCl(PPh_3)_3$] with 1 equiv of PNNP at ambient temperature to form [CoCl(PNNP)] (**1**) as a green precipitate. After washing with Et_2O to remove excess PPh_3, **1** was obtained in 71% isolated yield (Scheme 2).

Complex **1** is a diamagnetic species and identified using NMR spectroscopy. In a $^{31}P\{^1H\}$ NMR spectrum, **1** exhibits one singlet at 55.6 ppm, supporting a symmetrical structure of **1** with a mirror plane that bisects the Co atom and the phenanthroline moiety. Two benzylic CH_2 groups exhibit one set of diastereotopic signals at 4.17 (m) ppm and 5.23 (m) ppm. A single-crystal X-ray diffraction study was performed to support the five-coordinate square pyramidal structure of **1**, which exhibits typical bond lengths around the Co metal (Table 1, Fig. S22).[1f,1h,1k,2h]

In an attempt to synthesize a Co(I) alkyl complex, the reaction of **1** with MeMgBr (1 equiv) was performed. On the treatment of MeMgBr, complex **1** immediately transferred to the corresponding methyl complex [CoMe(PNNP)] (**2**) (Scheme 3). Complex **2** was thermally unstable and transferred to unidentified compounds gradually at ambient temperature. Due to this stability problem, isolated yield of **2** was 49% after a simple purification procedure by passing through a Celite pad. The reaction of **1** with Me_3SiCH_2MgCl (1 equiv) similarly proceeded, resulting in the formation of [$Co(CH_2SiMe_3)(PNNP)$] (**3**) as a sole product (Scheme 3). Complex **3** is more stable than **2**, and **3** was isolated in 89% yield. Single crystals of neither **2** nor **3** could be obtained; these complexes have not been characterized by X-ray crystallography. On the other hand, complexes **2** and **3** were fully identified by NMR spectroscopy. Complexes **2** and **3** exhibit one singlet at 76.9 ppm and 75.7 ppm in the $^{31}P\{^1H\}$ NMR spectrum, respectively. Complex **2** exhibits one triplet at –0.36 ppm ($^3J_{PH}$ = 3.3 Hz), which is assignable to the Me group attached to the Co atom. The CH_2SiMe_3 group of **3** appears as one singlet at –0.60 ppm and one triplet at –0.57 ppm ($^3J_{PH}$ = 4.4 Hz).



Scheme 2 Synthesis of **1**.



Scheme 3 Synthesis of **2** and **3**.

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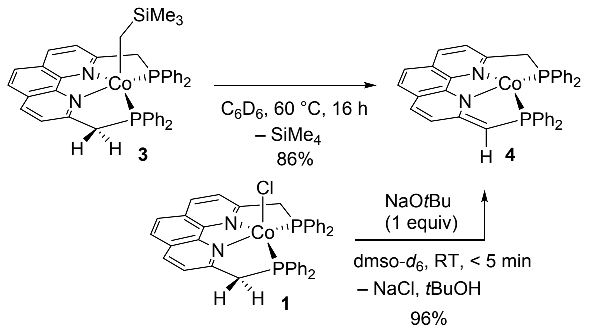
Spontaneous dearomatization of the PNNP backbone via MLC

With well-defined Co(I) alkyl complexes **2** and **3** in hand, we next set out for the reactivity investigation of these complexes. It is well known that low-coordinate Co(I) species are a good platform for C–H bond cleavage.[1d,1e,2a,3g] In this context, Chirik's group reported that PNP-Co(I) alkyl [CoMe(PNP)] successfully underwent an oxidative addition reaction of benzene upon heating at 80 °C.[3e] Different from the PNP-Co(I) system, **2** transferred to an unidentified complex mixture after leaving in benzene at ambient temperature for a few hours (vide infra). Transformation of **3** proceeded at slower rate but cleanly to form a four-coordinate Co(I) complex supported by an asymmetrical PNNP' ligand with a dearomatized phenanthroline backbone [Co(PNNP')] (**4**) as the sole product. At 60 °C, the reaction completed within 16 h to form **4** in 86% isolated yield (Scheme 4). In this reaction, concomitant formation of $SiMe_4$ was also confirmed by following the reaction using ^1H NMR spectroscopy.



Scheme 4 Synthesis of **4**.

In previous studies on pincer Ru[10] and Rh[11] systems, dearomatization of the ligand backbone often proceeds via deprotonation under basic conditions. Likewise, **4** was alternatively synthesized by the simple deprotonation reaction starting from **1** and NaO^{t}Bu as a base. Thus, the reaction of **1** with NaO^{t}Bu (1 equiv) proceeded at room temperature to afford **4** selectively in 96% yield. Complex **4** exhibited two phosphorus signals at 38.2 ppm and 52.8 ppm, which are assignable to the PCH and PCH_2 moieties, respectively. In the ^1H NMR spectrum of **4**, the PCH_2 group exhibits one doublet at 3.08 ppm due to the coupling with a phosphorus atom ($^2J_{PH}$ = 12 Hz). The exomethylene hydrogen (PCH) appeared at 4.35 ppm as a broad signal. Thus, a dearomatized asymmetrical PNNP' ligand system is supported.

The structure of **4** was confirmed by a single-crystal X-ray diffraction study (Figure 1). The Co–C, Co–P and Co–N bonds exhibit similar values to those in previously reported structurally analogous Co(I) complexes.[1f,1h,1k,2h] The C7–C8 bond length is 1.494(3) Å, which is in the typical range of a C–C single bond. In contrast, the C1–C2 bond length at the other side arm is shorter, 1.377(3) Å, reflective of its double-bond character (Table 1). The C3–C4 bond exhibits a similar bond length, 1.358(3) Å, whereas the adjacent C2–C3 bond exhibits a single-bond character with a bond length of 1.451(2) Å. These values strongly support the dearomatized phenanthroline backbone structure of **4**. The P1–C1 bond (1.788(2) Å) is shorter than the P2–C7 bond (1.867(2) Å) due to the sp_2-bond character around the C1 atom. The trend has also been reported in similar transition-metal complexes bearing a dearomatized PNNP, PNP, or bipyridine-based PNN ligand (6-((dialkylphosphanyl)methyl)-2,2'-bipyridine).[9b, 12]

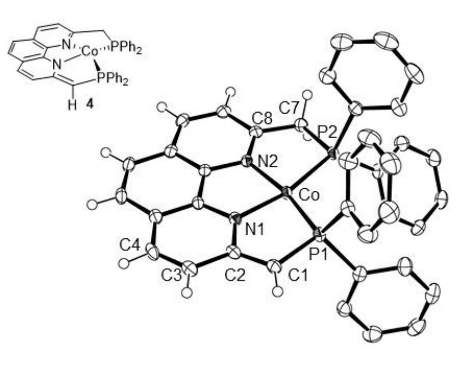


Fig. 1 ORTEP drawing of **4** with 50% probability ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Co–P1, 2.1876(6); Co–P2, 2.1433(5); Co–N1, 1.9016(14); Co–N2, 1.9033(15); P1–Co–P2, 109.03(2); P1–Co–N1, 83.15(5); N1–Co–N2, 82.88(6); N2–Co–P2 84.58(5).

The sharp contrast between **4** and the conventional Ru- and Rh-MLC systems is the occurrence of the spontaneous structural transformation of the PNNP ligand motif at elevated temperature.[10,11] Related to this, Milstein et al. recently reported the MLC-mediated benzylic C–H homolysis in a PNP-Co(I) methyl complex as shown in Scheme 1b.[6] In this system, the occurrence of C–H homolysis was experimentally evidenced by H· abstraction using proper radical scavengers. Thus, we examined the reactivity of **3** towards TEMPO (2,2,6,6-tetramethylpiperidin-1-yl)oxyl) as a radical trap, to shed light on the mechanism of the transfer from **3** to **4**. A C_6D_6 solution containing **3** and excess TEMPO (4 equiv) was left to stand at 60 °C for 1 h. The ^1H NMR analysis of the reaction mixture revealed the formation of both TEMPO-H (major) and TEMPO-alkyl (minor), which were accompanied by a trace of Me_4Si (molar ratio TEMPO-H/TEMPO-alkyl = 7/1) (Scheme 5). This result is indicative that the transformation from **3** to **4** is triggered by the benzylic C–H homolysis.[13] On the other hand, formation of TEMPO-alkyl also supported the occurrence of spontaneous homolytic Co–alkyl bond dissociation, which successfully follow the benzylic H abstraction by $\cdot CH_2SiMe_3$ to form **4** as well as Me_4Si. It is to be mentioned that formation of a new Co complex **5** as well as some unidentified paramagnetic products were also confirmed in the reaction of **3** with TEMPO (Scheme 5). Trace amount of **5** was isolated from the resulting reaction mixture, in pure form, with hexane, and identified using NMR spectroscopy. In its $^{31}P\{^1H\}$ NMR spectrum, **5** exhibits one singlet signal at 33.9 ppm. In the ^1H NMR spectrum, the alkyl group was observed at –0.17 ($SiMe_3$) and –0.29 (CH_2) ppm. The PCH signals appear as a singlet at 4.68 ppm with the integral intensity of 2H. Consistent with this, two PCH groups appear equivalently at 82.7 ppm in the $^{13}C\{^1H\}$ NMR. Thus, we assigned **5** to a Co(III) alkyl complex with a symmetrically double-deprotonated PNNP ligand. A single crystal of **5** was obtained from cold hexane solution. Thus, the structure of **5** was confirmed by X-ray diffraction study (Figure 2). The

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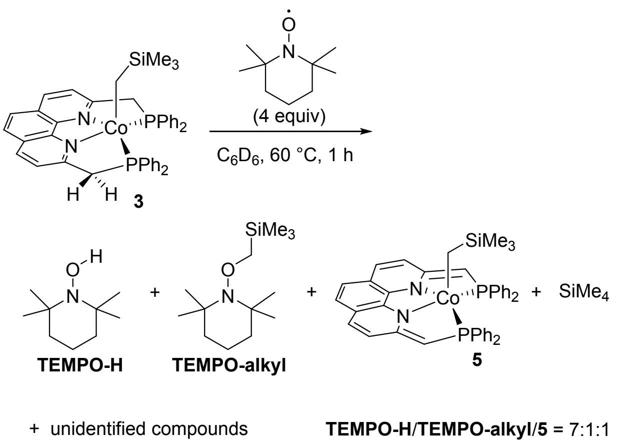
crystallographic data demonstrated the double bond character of both C1–C2 and C7–C8 bonds (Table 1). The formation of **5** is likely achieved by double benzylic C–H homolysis, which could be induced by TEMPO.



Scheme 5 Reaction of **3** with TEMPO.

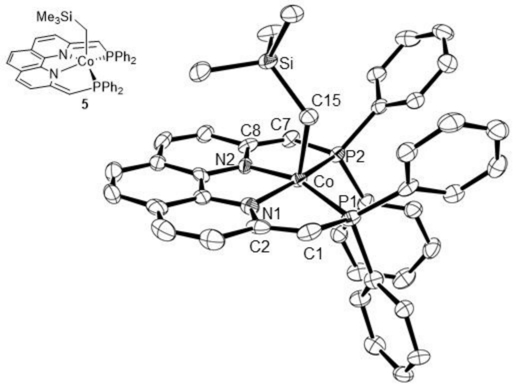
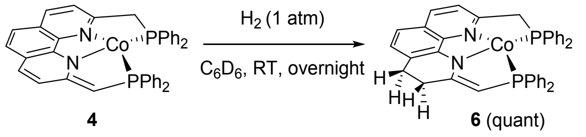


Fig. 2 ORTEP drawing of **5** with 50% probability ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Co–C15, 2.017(5); Co–P1, 2.2196(15); Co–P2, 2.2207(15); Co1–N1, 1.894(4); Co–N2, 1.884(4); P1–Co–P2, 110.68(6); P1–Co–N1, 82.02(14); N1–Co–N2, 83.31(19); N2–Co–P2 82.36(13).

Reversible H–H bond cleavage by 4

Because the aromatization/dearomatization sequence of the ligand backbone is nowadays recognized as a good motif for bond cleavage mediated by MLC, it was expected that **4** would also be active towards bond cleavage. Indeed, our preliminary experimental results revealed that **4** reacted with 1 atm of H_2 to cleave a H–H bond (Scheme 6).



Scheme 6 H–H bond cleavage by **4**.

To our surprise, two H atoms, formed during the reaction, were incorporated in the endocyclic double bond of the ligand backbone. The structure of **6** was successfully confirmed by single-crystal X-ray diffraction analysis (Figure 3). Thus, both C2–C3 and C3–C4 bonds exhibit typical single-bond lengths, 1.487(8) and 1.453(10), respectively. The dihedral angle of C2–C3–C4–C5 is –34.0(9) °, supporting the non-planar structure of the PNNP’’ backbone. Other bond lengths and angles of the PNNP’’-backbone in **6** are similar to those in **4**. Hence, the occurrence of further deterioration of the conjugated ligand backbone in **6** was evidenced.

In the ^{1}H NMR spectrum of **6**, the PNNP’’ ligand exhibits four doublet signals in the aromatic region. In addition, there are two triplet signals at 2.89 and 2.67 ppm with the integral intensity of 2H, assigned to the methylene hydrogens attached to the C3 or C4 atoms. Two phosphorus signals were observed at 44.5 and 55.6 ppm in the ^{31}P{^{1}H} NMR spectrum. All these spectral data support the asymmetric structure of **6**, which, in turn, is supported by PNNP’’ ligand that has a hydrogenated phenanthroline backbone. Interestingly, reversibility of the H_2 activation by **4** was supported by a preliminary experiment. Thus, heating C_6D_6 solution of **6** at 110 °C for 16 h lead to the partial conversion of **6** to **4** (24% NMR yield). This result strongly supports the unique properties of the PNNP-Co(I) system as a H_2 reservoir. Furthermore, the aromatization/dearomatization sequence of the ligand backbone was demonstrated trough these reactions, suggesting a utility of the PNNP-Co(I) system as a potent new MLC platform. Indeed, Milstein et al. previously reported this kind of hydrogenation of the conjugated phenanthroline backbone, as a new mode of MLC, within a PNNP-Ru system.[14]

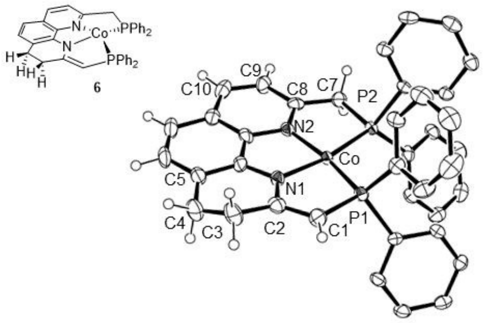


Fig. 3 ORTEP drawing of **6** with 50% probability ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Co1–P1, 2.1588(14); Co1–P2, 2.1202(14); Co1–N1, 1.898(4); Co1–N2, 1.884(4); P1–Co1–P2, 107.49(6); P1–Co1–N1, 83.64(15); N1–Co1–N2, 83.59(19); N2–Co1–P2 85.15(13); C2-C3-C4-C5, -34.0(9); C7-C8-C9-C10, -179.1(5).

Conclusions

In this study, a series of PNNP-Co(I) complexes were synthesized as stable diamagnetic species and fully identified. In this PNNP-Co(I) system, diverse structural transformation of the PNNP ligands, which related to the unique MLC behavior, was demonstrated. First, PNNP-Co(I) alkyl complex **3** undergoes a structural transformation of the ligand backbone via long-range MLC upon heating, affording **4** with a dearomatized phenanthroline scaffold. The reaction is initiated by homolysis of either the Co–alkyl bond or the benzylic C–H bond. Second, **4**

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undergoes reversible H–H bond cleavage, where the phenanthroline backbone of **4** behaves as a hydrogen reservoir, to form **6**. It is of great interest that **6** still has two vacant sites, which could further react with substrates. Overall, we have successfully established a new reactive Co(I) platform, which exhibits both a reactive Co(I) centre and potent diverse MLC properties. Further study to develop novel catalytic reactions is now under way in our laboratory.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

The acknowledgements come at the end of an article after the conclusions and before the notes and references.

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13 As have been discussed in ref 6, formation of free H· is unlikely since such the reaction should be extremely endothermic. We suppose that the benzylic C–H homolysis is facilitated in the presence of TEMPO, which can act as a H atom acceptor.

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Graphical and textual abstract for the Table of Contents

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A cobalt(I) alkyl complex bearing a tetradentate phenanthroline-based PNNP ligand undergoes dearomatization of the ligand backbone skeleton upon heating. The resulting complex cleavages H–H, resulting in the incorporation of two H atoms into the endocyclic double bond of the ligand backbone.