Bis(azido)palladium(II) Complexes Bearing an (*R* or *S*)-(BINAP) Ligand: Synthesis, Structures, and Catalytic Application to Suzuki–Miyaura C—C Coupling Reactions

Sun Myeong Choi,[†] Sera Lee,[†] Yong-Joo Kim,[†,¶,*] Ji Hun Lee,[‡] Soon W. Lee,[‡] and Jun-Chul Choi[§,¶,*]

[†]*Department of Chemistry, Kangnung-Wonju National University, Gangneung 210-702, South Korea.*
**E-mail: yjkim@kangnung.ac.kr*
[‡]*Department of Chemistry, Sungkyunkwan University, Natural Science Campus, Suwon, South Korea*
[§]*National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Japan.*
**E-mail: junchul.choi@aist.go.jp*
[¶]*These authors contributed equally to this work.*
Received September 17, 2019, Accepted November 25, 2019

Keywords: BINAP, Palladium, Azido, Suzuki-Miyaura C—C coupling

Chiral ligand 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (BINAP) is widely utilized as an ancillary ligand for late-transition-metal complexes, especially for Ru and Rh metals, in asymmetric organic catalysis.[1,2] BINAP–Pd (II) complexes in particular have been intensively investigated as catalysts for reactions such as amination [3,4] and C—C coupling.[5–7] However, it is worth noting that BINAP–Pd(II) complexes containing a pseudohalogen ligand have not been reported to exhibit C—C coupling activity, probably because of their poor solubility or low catalytic activity.

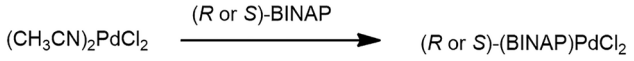
Our research group has continually investigated the synthesis and catalytic properties of group 10 metal-pseudohalogen complexes.[8] As an extension of our investigations into the scope of these complexes, we decided to prepare BINAP–Pd(II) complexes containing an azido ligand as a pseudohalogen group, expecting to find catalytic activity in Suzuki–Miyaura C—C coupling reactions. We report herein the synthesis, structures, and catalytic activity of these complexes.

Our target complexes, chiral (BINAP)–Pd–bis(azido) complexes, could be prepared in two steps. First, the BINAP–Pd(II) chloro complexes, [(*R*)-(BINAP)$PdCl_2$] (**1**), [(*S*)-(BINAP)$PdCl_2$] (**2**), and [(*R*)-(Tolyl-BINAP)$PdCl_2$] (**3**), were prepared in quantitative yields by substitution of the acetonitrile ligands of [$(CH_3CN)_2PdCl_2$] with BINAP, as shown in Scheme 1.

In the second step, complexes **1**–**3** were treated with aqueous NaN_3 to afford the corresponding Pd(II) azido complexes in high yields (**4**–**7** in Scheme 2). Isolated products were characterized by spectroscopy (IR and NMR) and X-ray diffraction. The IR spectra of complexes **4**–**7** exhibit characteristic azide bands at 2028–2036 cm^{-1}. These azido complexes are readily solvated in CH_2Cl_2 or THF. Figures 1 and 2 show the molecular structures of *cis*-{(*R*)-BINAP)}bis(azido)palladium(II) (**4**) and *cis*-{(*S*)-BINAP)}bis(azido) palladium(II) (**5**). The ORTEP drawings clearly show the (*R*)- or (*S*)-form of the complex. The naphthalene rings on the BINAP ligand are perpendicular to each other, inducing the C_2 symmetry required for the complexes to be chiral. To the best of our knowledge, these are the first examples in which the structures of both the (*R*)- and (*S*)-forms of the chiral (BINAP)Pd(II) azido complexes have been determined. The Pd—N_3 bond lengths (2.07 Å) agree well with those of known Pd azido complexes. [9,10]

We examined the dipolar cycloaddition of the azido ligands in complexes **4** and **6** with organic isothiocyanates [R–NCS; R = Ph, (*S*)-(+)-CH(CH_3)Ph, Me_3Si], with the expectation of affording five-membered heterocyclic rings in the products. Consistent with our expectation, these complexes undergo dipolar addition to phenyl or 1-phenyl ethyl iosthiocyanates to afford bis(*S*-coordinated tetrazole–thiolato) Pd(II) complexes **8** and **9** (Eq. 1 in Scheme 3). Heating was required for the reaction to proceed, which agrees well with previous reports, in which the preparation of Pd(II) azido complexes containing chelating ligands demands more vigorous conditions for small molecule insertion than that of bis(tertiary phosphine)–Pd (II) azido complexes.[11] In contrast, room-temperature reactions with trimethylsilyl isothiocyanate (TMS–NCS) proceeded slowly to give the ligand-substituted bis(isothiocyanato) Pd(II) complexes **10** (Eq. 2 in Scheme 3). The progress of the above reactions can be readily monitored by the disappearance of the IR absorption band of the starting compounds (**6** and **7**) at ca. 2028 cm^{-1}, indicating the formation of the *S*-coordinated tetrazole–thiolato products (**8** and **9**). In addition, the appearance of characteristic symmetric and asymmetric NCS bands at 2107–2108 and 2078–2080 cm^{-1}, respectively, can be used to confirm the formation of isothiocyanato complexes, [(*S*)-(Tol-BINAP)Pd$(NCS)_2$] (**10**) (Eq. 2 in Scheme 3). The independent reaction of complex **6** with an aqueous KSCN also

ISSN (Print) 0253-2964 | (Online) 1229-5949



Scheme 1. Ligand exchange with BINAP.

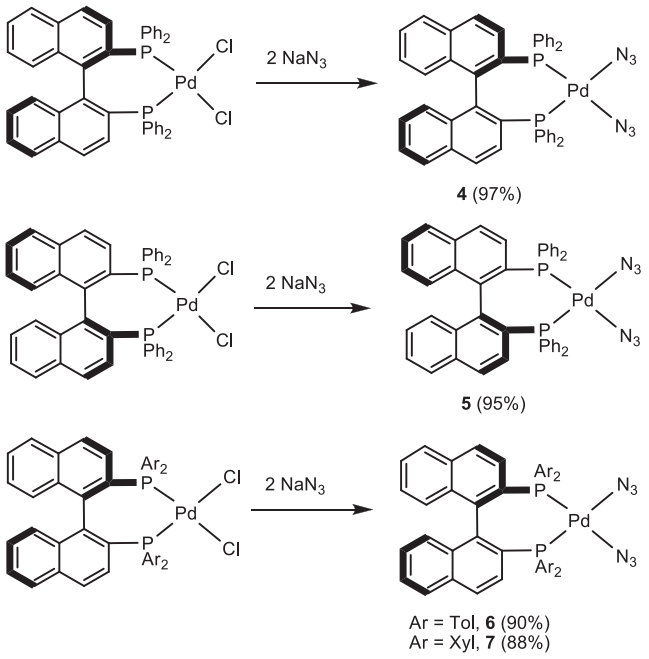
afforded complex **10** in high yield without the formation any linkage isomers.

Figure 3 shows the molecular structure of complex **9**. Two tetrazole moieties lie above and below the molecular plane, defined by phosphorus and two sulfur atoms. As expected, the chirality of the BINAP ligand in complexes **4** and **9** is the same (Figures 1 and 3).

Many (BINAP)Pd complexes are widely employed as catalysts for asymmetric organic reactions. However, the utility of neutral (BINAP)Pd-catalyzed C─C coupling reactions as compared with that of ionic (BINAP)Pd complexes has not been reported. In this context, we examined the applicability of the (BINAP)Pd-pseudohalogen complexes prepared in this study for catalyzing Suzuki–Miyaura C─C coupling reactions.

To optimize the reaction, the coupling was performed under various conditions in the presence of Pd catalyst (complex **4**, 1 or 0.5 mol %) as shown in Table 1. Entry 6 shows the highest isolated yield of the biaryl product with a small quantity of the (BINAP)Pd catalyst and a short reaction time. Therefore, we applied this optimized condition to various combinations of aryl bromides and phenyl boronic acid (entry 1–9) as well as aryl boronic acids (entry 10–13) as seen in Scheme 4 and Table 2.

Table 2 shows relatively high yields when our (BINAP)Pd complex was used for aryl bromides containing either activated or deactivated aryl groups, with the exception of entry 13, which afforded the homo coupled product. In the case of entry 13, the expected product of the C─C cross-coupling



Scheme 2. Synthesis of (BINAP)Pd(II) azides.

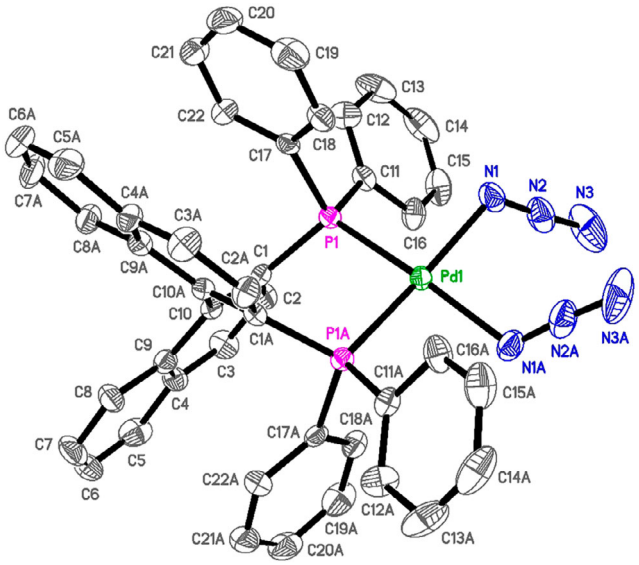


Figure 1. Molecular structure of compound **4**·2(CH_2Cl_2). Atoms labeled with "a" are related to the corresponding numbered atoms by a two-fold rotation. Two co-crystallized dichloromethane molecules are omitted for clarity. Selected bond lengths (Å) and bond angles (°): Pd1–N1 2.070(5), Pd1–P1 2.267(1), N1–N2 1.185(8), N2–N3 1.157(10); N1#1–Pd1–N1 89.4(3), N1#1–Pd1–P1 167.8 (2), N1–Pd1–P1 90.0(1), P1–Pd1–P1#1 93.17(6), N2–N1–Pd1 117.7(4), N3–N2–N1 176.5(8). Symmetry transformations used to generate equivalent atoms: A = $-x + 2$, y, $-z + 3/2$.

was not afforded, maybe because the electron-rich 4-pyridyl group hinders transmetallation necessary for the C─C cross-coupling by reductive elimination. Therefore, we believe that

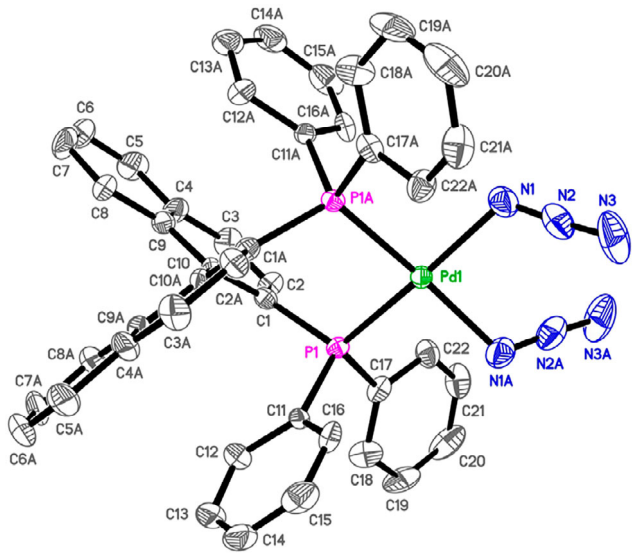
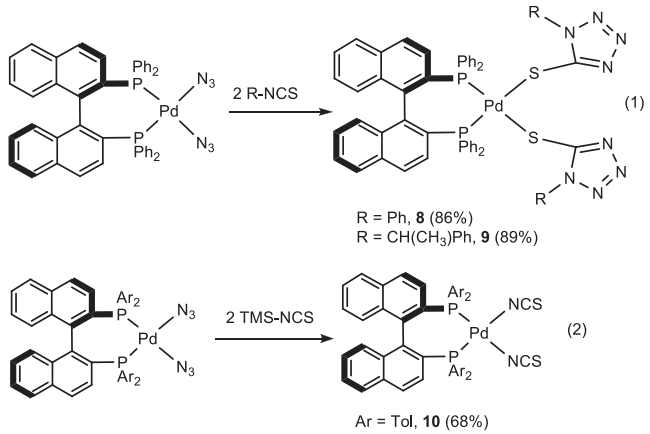


Figure 2. Molecular structure of compound **5**·2(CH_2Cl_2). Atoms labeled with "a" are related to corresponding numbered atoms by a two-fold rotation. Selected bond lengths (Å) and bond angles (°): Pd1–N1 2.071(6), Pd1–P1 2.268(1), N1–N2 1.194(9), N2–N3 1.169(10); N1A–Pd1–N1 90.7(3), N1A–Pd1–P1 89.15(17), N1–Pd1–P1 168.3(2), P1–Pd1–P1A 93.32(7), N2–N1–Pd1 117.0(5), N3–N2–N1 176.2(9). Symmetry transformations used to generate equivalent atoms: A = $-x + 1$, y, $-z + 1/2$.



Scheme 3. Reactions of (R-BINAP)Pd(II) azide with R-NCS.

instead of C─C cross-coupling, homo coupling to give 4,4′-diacetylbiphenyl occurs under present conditions.

These results suggest that neutral (BINAP)Pd(II) azide can be employed as efficient catalysts for Suzuki–Miyaura C─C coupling reactions.

In summary, new chiral Pd(II) azido complexes having an (*R*)- or (*S*)-(BINAP) ligand were synthesized and particularly in the case of the (*R*)- and (*S*)-forms of the chiral (BINAP)Pd (II) azido complexes were structurally characterized by spectroscopy and X-ray diffraction. The reactivity of these azido complexes towards organic isothiocyanates depended on the reaction conditions. These complexes were effective for catalyzing Suzuki–Miyaura C─C coupling reactions. We also reported the first example of Pd(II) pseudo-halogen complexes containing chiral BINAP ligands, a potential precursor for new types of heterocyclic tetrazole compounds, which can be useful in other palladium-catalyzed organic transformation.

Experimental

All manipulations of air-sensitive compounds were performed under N_2 or Ar using standard Schlenk-line techniques. The analytical laboratory at Kangwon National University at Samcheok carried out elemental analyses with Flash EA 1112 analyzers (Thermofisher Scientific, Bremen, Germany). X-ray reflection data were obtained at the Korea Basic Science Institute (Seoul, Korea). The $(CH_3CN)_2PdCl_2$ was prepared by a modified literature method.[13] Complexes [(*R*)-(BINAP)$PdCl_2$] (**1**), [(*S*)-(BINAP)$PdCl_2$] (**2**), and [(*R*)-(Tol-BINAP)$PdCl_2$] (**3**) were analogously prepared from the general ligand substitution using $[Pd(CH_3CN)_2Cl_2]$[13] with an equivalent of the corresponding BINAP ligands.[14]

Preparation of [(R)-(BINAP)Pd(N_3)$_2$] (4), [(S)-(BINAP)Pd(N_3)$_2$] (5), and [(R)-(Tol-BINAP)Pd(N_3)$_2$] (6). To a Schlenk flask containing **1** (0.315 g, 0.39 mmol) CH_2Cl_2 (3 mL) and a NaN_3 solution (0.077 g, 1.18 mmol) dissolved in H_2O (3 mL) were added in that order. After stirring for 18 h at room temperature, the solvent was evaporated to give a pale orange solid, which was extracted with CH_2Cl_2 and evaporated again to afford crude solids.

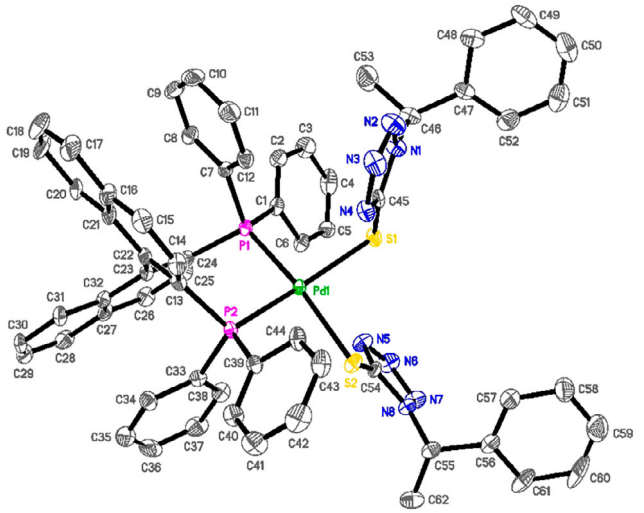


Figure 3. Molecular structure of compound **9**·2(CH_2Cl_2). Selected bond lengths (Å) and bond angles (°): Pd1–P2 2.273(1), Pd1–P1 2.296(1), Pd1–S2 2.387(1), S1–C45 1.720(5), S2–C54 1.714(4), N1–N2 1.345(5), N1–C45 1.356(6), N2–N3 1.284(6), N3–N4 1.359 (5), N4–C45 1.339(5), N5–C54 1.339(6), N5–N6 1.352(5), N6–N7 1.293(6), N7–N8 1.355(5), N8–C54 1.365(5); P2–Pd1–P1 92.70(4), P2–Pd1–S2 88.09(4), P1–Pd1–S2 165.09(4), S2–Pd1–S1 91.02(4).

Recrystallization from THF-diethyl ether or CH_2Cl_2-hexane gave orange solids of [(*R*)-(BINAP)Pd(N_3)$_2$] (**4**, 0.310 g, 97%). Single crystals for X-ray crystallography were grown from CH_2Cl_2-hexane at −35°C.

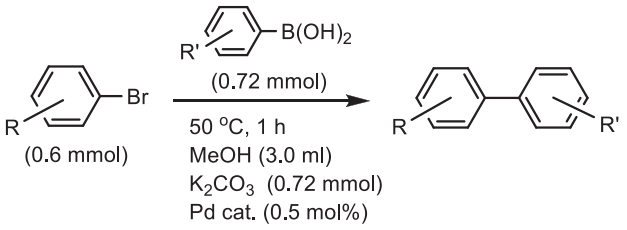
Complexes [(*S*)-(BINAP)Pd(N_3)$_2$] (**5,** 95%), and [(*R*)-(Tol-BINAP)Pd(N_3)$_2$] (**6**, 90%) were prepared analogously.

Reactions of Complexes 4 and 6 with R–NCS {(R = Ph), (S)-(+)-1-Phenylethyl, Trimethylsilyl}. To a Schlenk flask containing complex **4** (0.150 g, 0.18 mmol) THF (4 mL) and (*S*)-(+)-1-Phenylethyl isothiocyanate (48 μL, 0.41 mmol) were added in that order. After stirring for 18 h at 50°C, volatiles in the reaction mixture were evaporated under vacuum, and the resulting residues were washed with

Table 1. Optimization reactions for the Suzuki–Miyaura cross-coupling reactions of 4-bromo (or chloro) acetophenone with phenyl boronic acid.

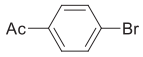
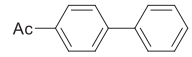
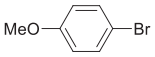
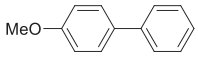
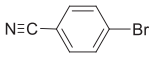
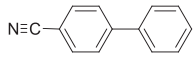
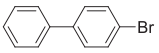
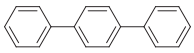
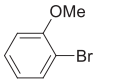
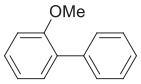
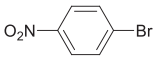
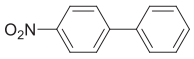
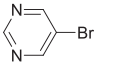
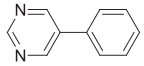
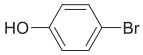
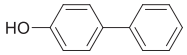
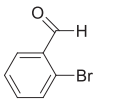
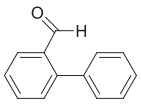
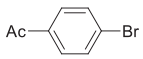
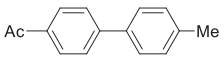
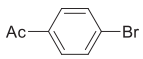
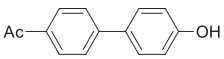
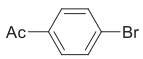
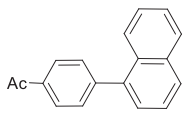
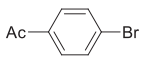
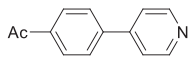
Entry	Solvent	Base	*R* (°C)	*t* (h)	Isolated yield (%)
1	MeOH	K_2CO_3	50	2.0	99
2	MeOH	Cs_2CO_3	50	2.0	64
3[a]	MeOH	K_2CO_3	50	1.0	31
4	MeOH	K_2CO_3	50	1.0	93
5	MeOH	Na_2CO_3	50	1.0	85
6[b]	MeOH	K_2CO_3	50	1.0	99
7[c]	MeOH	K_2CO_3	50	1.0	65
8[d]	MeOH	K_2CO_3	50	1.0	86

All 1 mol% unless stated.
[a] Under air.
[b] Cat. 0.5 mol %.
[c] 4-chloroacetophenone.
[d] Cat. is (BINAP)$PdCl_2$.



Scheme 4. Suzuki-Miyaura Cross-Coupling reactions.

Table 2. C─C coupling reactions of aryl bromide and aryl boronic acid.

Entry	Aryl bromide	Product	Isolated yield [%]
1			99
2			68
3			93
4			86
5			71
6			99
7			91
8			66
9			81
10			94
11			91
12			99
13[a]			50

[a] Homo coupling product, $CH_3C(O)$-C_6H_4-C_6H_4-$C(O)CH_3$.

hexane and diethyl ether. Recrystallization from CH_2Cl_2/(diethyl ether) gave orange crystals of [(*R*)-(BINAP)Pd{(SCN4(R)}2] (R = Ph) (**8**, 0.174 g, 86%).

Complexes, [(*R*)-(BINAP)Pd{(SCN4(R)}2] (R = CH(Me)Ph) (**9**, 89%), and [(*R*)-(Tol-BINAP)Pd$(NCS)_2$] (10, 68%) were analogously prepared.

General Procedure for Suzuki–Miyaura Cross-Coupling Reactions. For synthetic details and spectral data, see the Appendix S1 (Supporting Information).

X-Ray Structure Determination. Details on X-ray structure are described in Appendix S1.

Acknowledgments. This work was supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (NRF-2016R1D1A3B03932228).

Supporting Information. Additional supporting information may be found online in the Supporting Information section at the end of the article.

References

1. S. Akutagawa, *Appl. Cat. A.* **2019**, *21*, 1737.
2. T. Ohkuma, N. Kurono, In *Privileged Chiral Ligands and Catalysts*, Q.-L. Zhou Ed., Wiley-VCH, Verlag GmbH, Weinheim, **2011**, p. 1.
3. (a) J. F. Hartwig, *Pure Appl. Chem.* **2004**, *76*, 507. (b) M. Kawatsura, J. F. Hartwig, *J. Am. Chem. Soc.* **2000**, *122*, 9546. (c) L. M. Alcazar-Roman, J. F. Hartwig, A. L. Rheingold, L. M. Liable-Sands, I. A. Guzei, *J. Am. Chem. Soc.* **2000**, *122*, 4618.
4. J. W. Faller, J. C. Wilt, *Org. Lett.* **2005**, *7*, 633.
5. M. Shibaski, M. Sodeoka, J. Synth, *Org. Chem., Jpn.* **1994**, *52*, 956.
6. A. Lei, X. Zhang, *Org. Lett.* **2002**, *4*, 2285.
7. M. Ogasawara, H. Ngo, T. Sakamoto, T. Takahashi, W. Lin, *Org. Lett.* **2005**, *7*, 2881.
8. (a) K.-E. Lee, H.-T. Jeon, S.-Y. Han, J. Ham, Y.-J. Kim, S. W. Lee, *Dalton Trans.* **2009**, 6578. (b) Y.-J. Kim, J.-H. Lee, T. Kim, J. Ham, Z. N. Zheng, S. W. Lee, *Eur. J. Inorg. Chem.* **2012**, 6011. (c) H.-K. Kim, J.-H. Lee, Y.-J. Kim, Z. N. Zheng, S. W. Lee, *Eur. J. Inorg. Chem.* **2013**, *4958*. (d) K.-W. Kim, Y.-J. Kim, H. J. Lim, S. W. Lee, *Bull. Kor. Chem. Soc.* **2015**, *36*, 2952. (e) J.-H. Choi, K.-Y. Choi, Y.-J. Kim, H. J. Im, S. W. Lee, *Bull. Kor. Chem. Soc.* **2017**, *38*, 812.
9. B. Bendiksen, W. C. Riley, M. W. Babich, J. H. Nelson, R. A. Jacobson, *Inorg. Chim. Acta* **1982**, *57*, 29.
10. W. P. Fehlhammer, L. F. Dahl, *J. Am. Chem. Soc.* **1972**, *94*, 3377.
11. (a) Y.-J. Kim, Y.-S. Kwak, Y.-S. Joo, S. W. Lee, *J. Chem. Soc. Dalton Trans.* **2002**, 144. (b) Y.-J. Kim, J.-T. Han, S. Kang, W. S. Han, S. W. Lee, *Dalton Trans.* **2003**, 3357. (c) Y.-J. Kim, X. Chang, J.-T. Han, M. S. Lim, S. W. Lee, *Dalton Trans.* **2004**, 3699.
12. Y. K. Kang, D. Y. Kim, *Bull. Kor. Chem. Soc.* **2008**, *29*, 2093.
13. R. Doyle, P. E. Slade, H. B. Jonassen, *Inorg. Synth.* **1960**, *6*, 218.
14. A. C. Véron, M. Felber, O. Blacque, B. Spingler, *Polyhedron* **2013**, *52*, 102.

