Inorg. Chem. **2007**, *46*, 2968–2970

Inorganic Chemistry
Communication

Proton-Induced Cis–Trans Conversion of a Platinum(II) Center Coordinated by L-Cysteinatocobalt(III) Metalloligands

Zentaro Matsumoto, Takashi Aridomi, Asako Igashira-Kamiyama, Tatsuya Kawamoto, and Takumi Konno*

Department of Chemistry, Graduate School of Science, Osaka University, Toyonaka, Osaka 560-0043, Japan

Received February 10, 2007

Treatment of Λ_{L}-[Co(L-cys-*N*,*S*)(en)$_2$]$^+$ (L-H$_2$cys = L-cysteine) with $[PtCl_4]^{2-}$ in water, followed by the addition of acid, gave an S-bridged $Co^{III}_2Pt^{II}$ trinuclear complex ([**1**]$^{4+}$), which was reversibly converted to its deprotonated complex ([**2**]$^{2+}$) in an aqueous solution. While [**1**]$^{4+}$ formed only a trans isomer, [**2**]$^{2+}$ existed as a mixture of trans and cis isomers. The selective formation of a cis isomer was achieved by treatment of [**1**]$^{4+}$ or [**2**]$^{2+}$ with phthalic acid in water, which afforded a unique $Co^{III}_4Pt^{II}_2$ hexanuclear complex ([**3**]$^{4+}$). Complex [**3**]$^{4+}$ was reverted back to [**1**]$^{4+}$ by treatment with aqueous HCl, accompanied by the complete cis-to-trans conversion.

In recent years, the design and control of the dynamics of molecules are a subject of increasing attention because of their potential utility in various applications such as molecular recognition and molecular switching.[1] One of the most well-known dynamics of molecules involves cis−trans isomerism, which has attracted great interest in many fields ranging from inorganic to organic and biological chemistry.[2] In particular, considerable research efforts have been paid for the control of cis−trans isomerism in square-planer d^8 metal complexes of palladium(II) and platinum(II).[3] To date, a number of coordination systems of palladium(II) and platinum(II) that show cis−trans conversion in response to thermal and/or photochemical factors have been reported.[4] Furthermore, recent studies have shown that allosteric interactions of alkali-metal cations or inorganic anions lead to cis−trans conversion in palladium(II) coordination systems.[5] On the other hand, similar allosteric interactions that induce cis−trans conversion have not been found in platinum(II) coordination systems so far, presumably because of the relative inertness of the platinum(II) coordination environment compared to the palladium(II) environment.[6] Thus, the finding of new external factors that govern cis−trans isomerism of platinum(II) systems is a challenging task that may contribute to the development of platinum-based pharmaceuticals and catalysts, as well as the fundamental coordination chemistry of platinum(II).[7] In this paper, we report on a novel dichloroplatinum(II) coordination system derived from $[PtCl_4]^{2-}$ and Λ_{L}-[Co(L-cys-*N*,*S*)(en)$_2$]$^+$ (L-H$_2$cys = L-cysteine) that can act as an S-donating chiral metalloligand having a free carboxylate group.[8] This system was found to exhibit novel cis−trans conversion induced by protonation/deprotonation of a distant carboxyl group in the metalloligand (Scheme 1). Another cis−trans conversion accompanied by the linkage of two platinum(II) centers with the use of phthalate is also reported.

---

* To whom correspondence should be addressed. E-mail: konno@ch.wani.osaka-u.ac.jp.

(1) (a) Kruppa, M.; König, B. *Chem. Rev.* **2006**, *106*, 3520. (b) Kinbara, K.; Aida, T. *Chem. Rev.* **2005**, *105*, 1377. (c) Kovbasyuk, L.; Krämer, R. *Chem. Rev.* **2004**, *104*, 3161.

(2) (a) Dugave, C.; Demange, L. *Chem. Rev.* **2003**, *103*, 2475. (b) Engel, P. S. *Chem. Rev.* **1980**, *80*, 99. (c) Lummis, S. C. R.; Beene, D. L.; Lee, L. W.; Lester, H. A.; Broadhurst, R. W.; Dougherty, D. A. *Nature* **2005**, *438*, 248. (d) Melnic, M.; Holloway, C. E. *Coord. Chem. Rev.* **2006**, *250*, 2261.

(3) (a) Aizawa, S.; Saito, K.; Kawamoto, T.; Matsumoto, E. *Inorg. Chem.* **2006**, *45*, 4859. (b) Koch, K. R.; Wang, Y.; Coetzee, A. *J. Chem. Soc., Dalton Trans.* **1999**, 1013. (c) Menozzi, E.; Busi, M.; Ramingo, R.; Campagnolo, M.; Geremia, S.; Dalcanale, E. *Chem.—Eur. J.* **2005**, *11*, 3136. (d) Smith, D. C., Jr.; Gray, G. M. *Inorg. Chem.* **1998**, *37*, 1791. (e) Murdoch, S. del P.; Ranford, J. D.; Sadler, P. J.; Berners-Price, S. J. *Inorg. Chem.* **1993**, *32*, 2249.

(4) (a) Hanekom, D.; McKenzie, J. M.; Derix, N. M.; Koch, K. R. *Chem. Commun.* **2005**, 767. (b) Vicente, J.; Arcas, A.; Gálvez-López, M.-D.; Jones, P. G. *Organometallics* **2006**, *25*, 4247. (c) Pelczar, E. M.; Nytko, E. A.; Zhuravel, M. A.; Smith, J. M.; Glueck, D. S.; Sommer, R.; Incarvito, C. D.; Rheingold, A. L. *Polyhedron* **2002**, *21*, 2409. (d) Cusumano, M.; Guglielmo, G.; Ricevuto, V.; Sostero, S.; Traverso, O.; Kemp, T. J. *J. Chem. Soc., Dalton Trans.* **1981**, 302. (e) Mok, C. Y.; Tan, S. G.; Chan, G. C. *Inorg. Chim. Acta* **1990**, *176*, 43.

(5) (a) Yam, V. W.-W.; Lu, X.-X.; Ko, C.-C. *Angew. Chem., Int. Ed.* **2003**, *42*, 3385. (b) Lu, X.-X.; Tang, H.-S.; Ko, C.-C.; Wong, J. K.-Y.; Zhu, N.; Yam, V. W.-W. *Chem. Commun.* **2005**, 767.

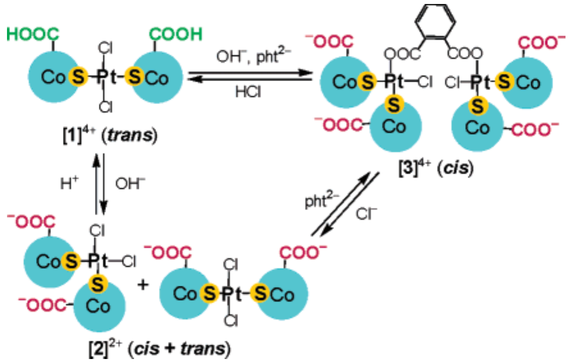
(6) (a) Hughes, R. P.; Meyer, M. A.; Tawa, M. D.; Ward, A. J.; Williamson, A.; Rheingold, A. L.; Zakharov, L. N. *Inorg. Chem.* **2004**, *43*, 747. (b) Appleton, T. G.; Clark, H. C.; Manzer, L. E. *Coord. Chem. Rev.* **1973**, *10*, 335. (c) Real, J.; Prat, E.; Polo, A.; Alvarez-Larena, A.; Piniella, J. F. *Inorg. Chem. Commun.* **2000**, *3*, 221. (d) Duran, J.; Brugat, N.; Polo, A.; Segura, C.; Real, J.; Fontrodona, X.; Benet-Buchholz, J. *Organometallics* **2003**, *22*, 3432.

(7) (a) Kostova, I. *Recent Pat. Anti-Cancer Drug Discovery* **2006**, *1*, 1. (b) Yamashita, F.; Kuniyasu, H.; Terao, J.; Kambe, N. *Inorg. Chem.* **2006**, *45*, 1399. (c) Anderson, G. K.; Cross, R. J. *J. Chem. Soc. Rev.* **1980**, *9*, 185.

(8) (a) Konno, T.; Yoshimura, T.; Aoki, K.; Okamoto, K.; Hirotsu, M. *Angew. Chem., Int. Ed.* **2001**, *40*, 1765. (b) Konno, T.; Kawamoto, T.; Kuwabara, R.; Yoshimura, T.; Hirotsu, M. *Chem. Lett.* **2002**, *31*, 304. (c) Aridomi, T.; Kawamoto, T.; Igashira-Kamiyama, A.; Konno, T. *Chem. Lett.* **2005**, *34*, 292.

10.1021/ic070265f CCC: $37.00

Scheme 1. Cis−Trans Conversion between $[\mathbf{1}]^{4+}$, $[\mathbf{2}]^{2+}$, and $[\mathbf{3}]^{4+}$



The reaction of a dark-brown aqueous solution of $\Lambda_{\rm L}$-[Co($\rm L$-cys-*N*,*S*)(en)$_2$]ClO$_4$[9] with K$_2$[PtCl$_4$] in a 2:1 molar ratio gave a red-brown solution, from which dark-red crystals ([**1**]Cl(ClO$_4$)$_3$) were isolated by the addition of aqueous HClO$_4$.[10] X-ray fluorescence spectrometry and elemental analytical data of this compound are in good agreement with a formula for a 2:1 adduct of $[\mathrm{Co(L\text{-}Hcys)(en)_2}]^{2+}$ and PtCl$_2$, and the presence of COOH groups is indicated by the IR spectrum that gives a ν(C═O) band at 1719 cm^{-1}.[11] The structure of [**1**]Cl(ClO$_4$)$_3$ was determined by single-crystal X-ray crystallography.[10] As shown in Figure 1, $[\mathbf{1}]^{4+}$ consists of two approximately octahedral $\Lambda_{\rm L}$-[Co($\rm L$-Hcys-*N*,*S*)(en)$_2$]$^{2+}$ units that are linked by a PtCl$_2$ moiety through Pt−S bonds, forming an S-bridged $\mathrm{Co^{III}{}_2Pt^{II}}$ trinuclear structure in [PtCl$_2${Co($\rm L$-Hcys-*N*,*S*)(en)$_2$}$_2$]$^{4+}$.[12] The coordination environment about the Pt$^{\rm II}$ atom is almost square-planar, coordinated by two S and two Cl atoms in a trans configuration [av Pt−S = 2.307(2) Å; Pt−Cl = 2.301(3) Å].

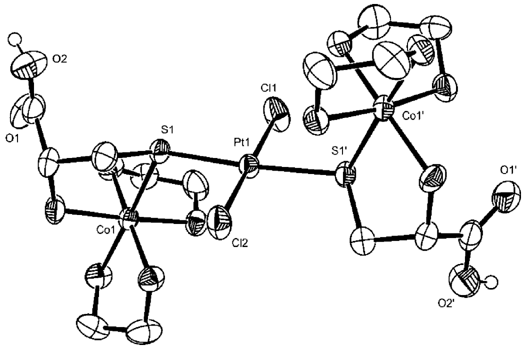


Figure 1. Perspective view of $[\mathbf{1}]^{4+}$.

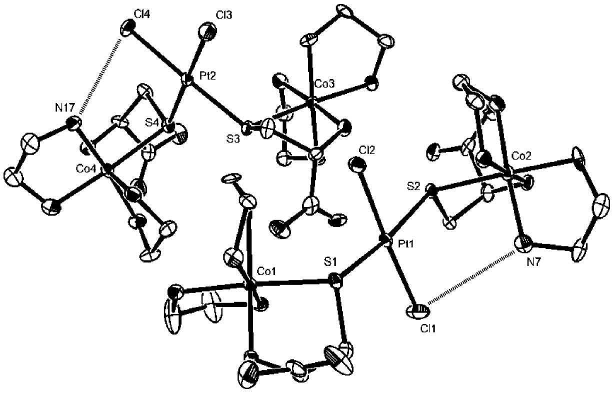


Figure 2. Perspective view of $[\mathbf{2}]^{2+}$. Hydrogen bonds are shown as dotted lines.

A similar 2:1 reaction of $\Lambda_{\rm L}$-[Co($\rm L$-cys-*N*,*S*)(en)$_2$]ClO$_4$ with K$_2$[PtCl$_4$] in water, followed by the addition of aqueous LiClO$_4$ instead of HClO$_4$, afforded dark-red crystals of [**2**]Cl$_{0.5}$(ClO$_4$)$_{1.5}$,[10] the absorption and circular dichroism spectral features of which are very similar to those of [**1**]Cl(ClO$_4$)$_3$. This compound was also obtained by the recrystallization of [**1**]Cl(ClO$_4$)$_3$ from water at pH ∼ 6.[10] It was shown that $[\mathbf{2}]^{2+}$ is a deprotonated form of $[\mathbf{1}]^{4+}$ by the IR spectrum that gives a ν(C═O) band at 1630 cm^{-1}, besides X-ray fluorescence spectrometry and elemental analysis. Single-crystal X-ray analysis revealed that $[\mathbf{2}]^{2+}$ contains cis and trans isomers of ($\Lambda_{\rm L}$)$_2$-[PtCl$_2${Co($\rm L$-cys-*N*,*S*)(en)$_2$}$_2$]$^{2+}$ (*cis*- and *trans*-$[\mathbf{2}]^{2+}$) in a 1:1 ratio (Figure 2).[10] The S-bridged $\mathrm{Co^{III}{}_2Pt^{II}}$ trinuclear structure in *trans*-$[\mathbf{2}]^{2+}$ is essentially the same as that of $[\mathbf{1}]^{4+}$, except two pendant carboxyl groups are deprotonated. However, it is noticed that the Pt−S bond distances in *trans*-$[\mathbf{2}]^{2+}$ [av 2.327(5) Å] are appreciably longer than those in $[\mathbf{1}]^{4+}$ [av 2.307(2) Å], although the Pt−Cl bond distances in $[\mathbf{1}]^{4+}$ [av 2.301(3) Å] and *trans*-$[\mathbf{2}]^{2+}$ [av 2.297(3) Å] are similar to each other. In *cis*-$[\mathbf{2}]^{2+}$, the Pt$^{\rm II}$ atom is coordinated by two S and two Cl atoms in a square-planar geometry, like the Pt$^{\rm II}$ atom in *trans*-$[\mathbf{2}]^{2+}$, but two S atoms occupy cis positions, despite the bulkiness of the $\Lambda_{\rm L}$-[Co($\rm L$-cys-*N*,*S*)(en)$_2$]$^+$ units. The Pt−Cl bond distances in *cis*-$[\mathbf{2}]^{2+}$ [av 2.326(4) Å] are ca. 0.03 Å longer than those in *trans*-$[\mathbf{2}]^{2+}$. This is indicative of the stronger trans influence due to thiolato donors relative to that due to chloro donors. Compatible with this, the Pt−S bond distances in *cis*-$[\mathbf{2}]^{2+}$ [av 2.283(4) Å] are shorter than those in *trans*-$[\mathbf{2}]^{2+}$.

The ^{13}C NMR spectrum of [**2**]Cl$_{0.5}$(ClO$_4$)$_{1.5}$ in D$_2$O (pH ∼ 6) exhibits two sets of carbon signals in a ca. 1:1 intensity ratio, consistent with the presence of cis and trans isomers in [PtCl$_2${Co($\rm L$-cys-*N*,*S*)(en)$_2$}$_2$]$^{2+}$ (Figure 3). Notably, the intensity ratio of two sets of signals varied upon lowering of the solution pH, and only one set of signals appeared at pH ∼ 1 after 2 days. The same ^{13}C NMR spectral behavior was observed for [**1**]Cl(ClO$_4$)$_3$ in D$_2$O, giving two sets of signals with equal intensity at pH ∼ 6 and a single set of signals at pH ∼ 1. These results clearly indicate that $[\mathbf{1}]^{4+}$ and $[\mathbf{2}]^{2+}$ are interconvertible with each other by changing the solution pH, accompanied by cis−trans conversion. It is considered that the S-bridged $\mathrm{Co^{III}{}_2Pt^{II}}$ structure prefers the trans configuration owing to the bulkiness of two Co$^{\rm III}$ metalloligands, as evidenced by the selective formation of a trans isomer for $[\mathbf{1}]^{4+}$. The comparison of the crystal structures of $[\mathbf{1}]^{4+}$ and *trans*-$[\mathbf{2}]^{2+}$ indicates that the Pt−S bonds are elongated by the deprotonation of two Co$^{\rm III}$ metalloligands. This is suggestive of the increase of the mutual trans influence due to thiolato donors by the deprotonation, which induces trans-to-cis conversion to generate the 1:1 mixture of cis and trans isomers for $[\mathbf{2}]^{2+}$.

---

(9) Freeman, C.; Moore, C. J.; Jackson, W. G.; Sargeson, A. M. *Inorg. Chem.* **1978**, *17*, 3513.

(10) See the Supporting Information.

(11) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*; Wiley: New York, 1997.

(12) In a crystal of [**1**]Cl(ClO$_4$)$_3$, each $\mathrm{Co^{III}Pt^{II}Co^{III}}$ trinuclear cation is connected with two neighboring trinuclear cations through two NH···O═C hydrogen bonds (3.026 Å) to form a 1D chain structure.

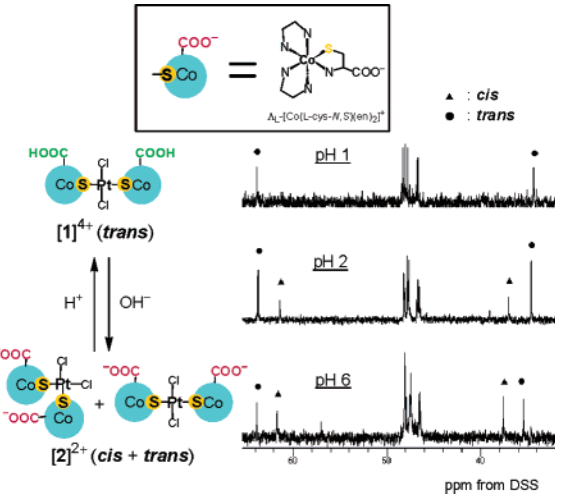


Figure 3. ^{13}C NMR spectra of [**2**]$^{2+}$ in D_2O adjusted to pH = 1, 2, or 6. Each spectrum was measured 2 days later after the adjustment of the pH.

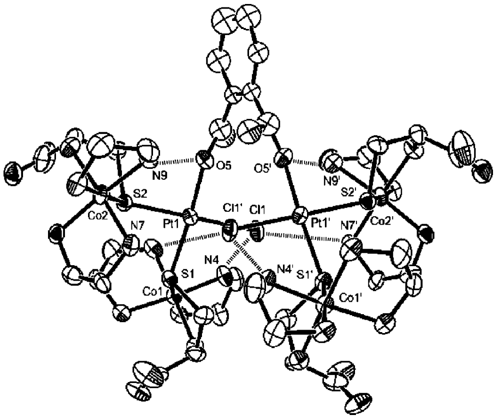


Figure 4. Perspective view of [**3**]$^{4+}$. Hydrogen bonds are shown as dotted lines.

To create an S-bridged $Co^{III}{}_2Pt^{II}$ species that selectively produces a cis isomer, an aqueous solution of [**2**]$Cl_{0.5}(ClO_4)_{1.5}$ was reacted with phthalic acid, which has been shown to act as a O,O′-chelating ligand toward a platinum(II) center,[13] in a 1:1 molar ratio at pH ~ 6. When the resulting dark-red reaction solution was allowed to stand at room temperature, after the addition of aqueous $NaClO_4$, dark-red crystals of [**3**]$(ClO_4)_4$ were isolated.[10] This compound was also obtained by the reaction of [**1**]$Cl(ClO_4)_3$ with phthalic acid under similar conditions.[10] The presence of fully deprotonated L-cysteinate and phthalate ligands in [**3**]$(ClO_4)_4$ was confirmed by IR and NMR spectroscopies. However, the elemental analytical data were not consistent with the formula for an expected 2:1:1 adduct but for a 4:2:1 adduct of [Co(L-cys-*N*,*S*)$(en)_2]^+$, $[PtCl]^+$, and phthalate. The structure of [**3**]$^{4+}$ was established by X-ray analysis for [**3**]$(SO_4)_2$, which was isolated by using aqueous Na_2SO_4 instead of aqueous $NaClO_4$.[10] As shown in Figure 4, [**3**]$^{4+}$ consists of two S-bridged $Co^{III}{}_2Pt^{II}$ trinuclear units of [PtCl{Co(L-cys-*N*,*S*)$(en)_2\}_2]^{3+}$ and a phthalate ligand. The phthalate ligand bridges two Pt^{II} atoms with the use of two COO^- groups [Pt−O = 2.061(5) Å], completing a unique $Co^{III}{}_4Pt^{II}{}_2$ hexanuclear structure in $[(PtCl)_2$(pht-*O*,*O*′){Co(L-cys-*N*,*S*)$(en)_2\}_4]^{4+}$ (Pt⋯Pt = 4.510 Å). As far as we know, such a bridging coordination mode of phthalate toward platinum(II) centers has not been reported, and, furthermore, [**3**]$^{4+}$ is the first example of a structurally characterized platinum(II) species with phthalate. The Pt^{II} atom in each $Co^{III}{}_2Pt^{II}$ trinuclear unit adopts a square-planar geometry with a cis configuration, coordinated by two S atoms from two deprotonated Co^{III} metalloligands, besides Cl and O atoms. In [**3**]$^{4+}$, the Pt−S bond distances trans to the O atom [2.272(2) Å] are the same as those trans to the Cl atom [2.272(2) Å]. This implies that the trans influence due to a carboxylato donor of phthalate is comparable with that due to a chloro donor and is thus weaker than that due to a thiolato donor. Because the phthalate ligand has a bridging coordination mode, a trans configuration is also possible for each $Co^{III}{}_2Pt^{II}$ trinuclear unit. The selective isolation of the cis configurational $Co^{III}{}_2Pt^{II}$ units in [**3**]$^{4+}$ could be related to the presence of NH⋯Cl (3.185 Å) and NH⋯O (2.894 Å) hydrogen bonds in each $Co^{III}{}_2Pt^{II}$ unit, together with the weaker trans influence due to chloro and carboxylato donors. The presence of NH⋯Cl (3.186 Å) hydrogen bonds between the two $Co^{III}{}_2Pt^{II}$ units is also noticed in [**3**]$^{4+}$, which may account for the selective isolation of the cis configurational $Co^{III}{}_2Pt^{II}$ units. Here, it should be noted that [**3**]$^{4+}$ is convertible to [**1**]$^{4+}$ and [**2**]$^{2+}$ by treatment with HCl and NaCl, respectively, which was evidenced by NMR spectroscopy. This is indicative of cis-to-trans conversion of the platinum(II) center due to the replacement of a coligand from phthalate to chloride (Scheme 1).

In summary, we showed that $[PtCl_4]^{2-}$ readily reacts with Λ_L-[Co(L-cys-*N*,*S*)$(en)_2]^+$ to form an S-bridged $Co^{III}{}_2Pt^{II}$ trinuclear complex with a $[Pt^{II}Cl_2S_2]$ square plane bound by two $[Co^{III}N_5S]$ octahedrons. The $Co^{III}{}_2Pt^{II}$ trinuclear complex was successfully isolated as protonated and deprotonated forms, [**1**]$^{4+}$ and [**2**]$^{2+}$, which are interconvertible with each other by changes of the solution pH. Remarkably, [**2**]$^{2+}$ existed as a mixture of cis and trans isomers, while [**1**]$^{4+}$ formed only a trans isomer, representing the first example of cis−trans conversion of platinum(II) induced by the change of pH. Furthermore, the linkage of two deprotonated $Co^{III}{}_2Pt^{II}$ trinuclear molecules with phthalate afforded a $Co^{III}{}_4$-$Pt^{II}{}_2$ hexanuclear structure in [**3**]$^{4+}$ having cis configurational $[Pt^{II}ClOS_2]$ planes, which is reverted back to [**1**]$^{4+}$ by treatment with HCl. Thus, trans-to-cis and cis-to-trans conversions of the platinum(II) center with two Λ_L-[Co(L-cys-*N*,*S*)$(en)_2]^+$ metalloligands were fully controlled by the protonation/deprotonation of pendant carboxylate groups in combination with the choice of coligands, the result of which would provide a novel design concept for dynamic molecular systems.

Supporting Information Available: Crystallographic data in CIF format and detailed experimental and spectroscopic data in PDF format. This material is available free of charge via the Internet at http://pubs.acs.org.

IC070265F

---

(13) (a) Brunner, H.; Arndt, M. R.; Treittinger, B. *Inorg. Chim. Acta* **2004**, *357*, 1649. (b) Kumar, L.; Puthraya, K. H.; Srivastava, T. S. *Inorg. Chim. Acta* **1984**, *86*, 173. (c) Scherer, O. J.; Hussong, K.; Wolmershäuser, G. *J. Organomet. Chem.* **1985**, *289*, 215.