Available online at www.sciencedirect.com
ScienceDirect
Journal of Organometallic Chemistry 692 (2007) 1353–1357
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

Complexation-induced conformational regulation of ferrocene-dipeptide conjugates to nucleate γ-turn-like structure

Toshiyuki Moriuchi, Takashi Fujiwara, Toshikazu Hirao *

Department of Applied Chemistry, Graduate School of Engineering, Osaka University, Yamada-oka, Suita, Osaka 565-0871, Japan

Received 7 September 2006; received in revised form 2 October 2006; accepted 2 October 2006
Available online 14 October 2006

Abstract

The complexation of the ferrocene-dipeptide conjugate bearing one dipeptide chain of heterochiral sequence (-L-Ala-D-Pro-NHPy) with $PdCl_2(MeCN)_2$ was demonstrated to afford the 2:1 *trans* palladium complex, which is present in the pseudo-helical conformation and γ-turn-like structure in the crystal structure through complexation and intramolecular hydrogen bonding. Furthermore, the left-handed pseudo-helical molecular arrangement was formed through a network of intermolecular hydrogen bonds.

Keywords: Bioorganometallic chemistry; Ferrocene; Dipeptide; Palladium complex; Hydrogen bond; γ-Turn

1. Introduction

Turns are a key structural motif in protein secondary structures [1]. Although considerable efforts have been devoted to the design of β-turn mimics [2,3], γ-turn mimicry has attracted less attention [2b,3b,3h,3i,4]. We have already demonstrated that a combination of the ferrocene scaffold as a central reverse-turn unit with the dipeptide chains (-L-Pro-L-Ala-NHPy) induces both inverse γ-turn-like and antiparallel β-sheet-like structures [5]. Metal ions have been known to exhibit a variety of properties in proteins, one of which is structural stabilization for biological function [6]. The incorporation of metal coordination sites into peptides has been investigated for the stabilization of secondary structures [7] and catalytic activities [8]. Recently, the research field of bioorganometallic chemistry, which is a hybrid area between biochemistry and organometallic chemistry, has received extensive interest. Bioconjugates composed of organometallic compounds and biomolecules such as amino acids and peptides have been investigated [9]. Ferrocenes are recognized to be a reliable scaffold for hydrogen bonding to have afforded the ferrocene-peptide conjugates as an artificially regulated system [5,10–12]. The advantage in the use of the -alanyl-proline heterochiral sequence as a dipeptide chain depends on a hydrogen bonding alanyl moiety and a sterically constrained proline as a well-known turn inducer, permitting a reverse-turn conformation [13]. We herein report the complexation-induced conformational regulation of the ferrocene-dipeptide monodentate ligand bearing one dipeptide chain of heterochiral sequence (-L-Ala-D-Pro-NHPy or -D-Ala-L-Pro-NHPy) to nucleate a γ-turn-like structure.

2. Results and discussion

The ferrocene-dipeptide conjugates **1**–**2** bearing one heterochiral dipeptide chain (-L-Ala-D-Pro-NHPy or -D-Ala-L-Pro-NHPy, respectively) were synthesized from (chlorocarbonyl)ferrocene and the corresponding dipeptide derivative [11e]. The complexation with metal ion is envisioned to stabilize and/or regulate secondary structures of peptide chains [7] and permit catalytic activities [8]. The complexation of the ferrocene-dipeptide conjugate **1** with 0.5 equiv. of $PdCl_2(MeCN)_2$ in acetonitrile afforded the 2:1 *trans* palladium complex **3** quantitatively. The single-crystal X-ray structure determination confirmed that the chirality-organized structure of the

* Corresponding author.
E-mail address: hirao@chem.eng.osaka-u.ac.jp (T. Hirao).

0022-328X/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2006.10.014

complex **3** is present in a pseudo-helical conformation through coordination to palladium and chirality organization based on intramolecular hydrogen bonds (N(1)···Cl(2), 3.362(5) Å; N(3)···O(2), 2.840(7) Å; N(23)···O(2), 2.814(7) Å), in which two ferrocene-dipeptide conjugates coordinate to the palladium center unsymmetrically (Fig. 1 and Tables 1–3). It should be noted that the NH adjacent to the pyridyl moiety of one peptide chain participates in the intramolecular hydrogen bonding with the CO of the Ala of the same peptide chain to nucleate a γ-turn-like structure. The torsion angles $\phi_2 = 84.7(9)°$ and $\psi_2 = -66.7(9)°$ of **3** indicate the γ-turn-like structure similar to an ideal γ-turn ($\phi_2 = 70$ to $85°$ and $\psi_2 = -60°$ to $-70°$) (Fig. 2). This

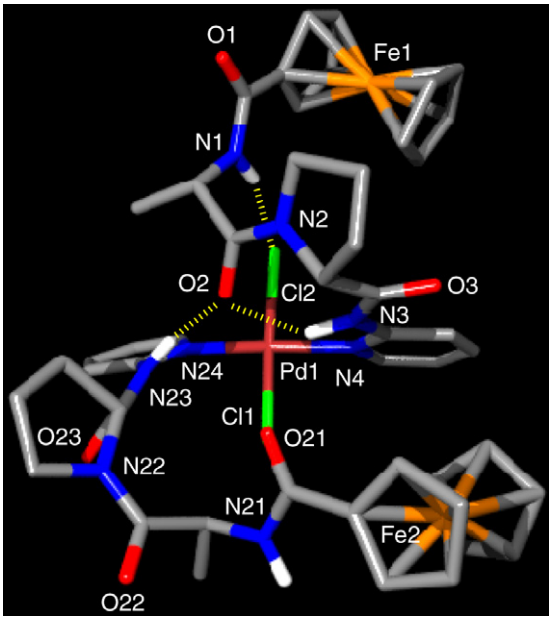


Fig. 1. Molecular structure of **3**.

Table 2
Hydrogen bonds for **3** and **4**

Crystal	Type [a]	Donor	Acceptor	D···A (Å)	D–H···A (°)
3	Intra	N(1)	Cl(2)	3.362(5)	163(4)
	Intra	N(3)	O(2)	2.840(7)	137(3)
	Intra	N(23)	O(2)	2.814(7)	170(4)
	Inter	N(21)	O(1a)	2.949(8)	170(5)
	Inter	N(21b)	O(1)	2.949(8)	170(5)
4	Intra	N(1)	Cl(2)	3.368(5)	163(4)
	Intra	N(3)	O2	2.843(7)	134(3)
	Intra	N(23)	O2	2.807(6)	172(2)
	Inter	N(21)	O(la)	2.940(7)	163(6)
	Inter	N(21b)	O(1)	2.940(7)	163(6)

[a] Inter, intermolecular; intra, intramolecular.

Table 3
Torsion angles (°) for **3** and **4**

	Angle[a]	**3**	**4**
ϕ_1	C(6)–N(1)–C(7a)–C(8)	−126.8(7)	126.7(7)
ψ_1	N(1)–C(7a)–C(8)–N(2)	75.4(7)	−74.4(7)
ω_1	C(7a)–C(8)–N(2)–C(9a)	178.6(6)	−178.5(6)
ϕ_2	C(8)–N(2)–(9a)–C(10)	84.7(9)	−84.6(8)
ψ_2	N(2)–C(9a)–C(10)–N(3)	−66.7(9)	66.8(8)
ϕ_1^*	C(26)–N(21)–C(27a)–C(28)	−74.1(9)	75.1(8)
ψ_1^*	N(21)–C(27a)–C(28)–N(22)	125.3(7)	−126.0(7)
ω_1^*	C(27a)–C(28)–N(22)–C(29a)	−7(1)	8(1)
ϕ_2^*	C(28)–N(22)–C(29a)–C(30)	76.0(9)	−75.9(9)
ψ_2^*	N(22)–C(29a)–C(30)–N(23)	−164.1(6)	163.5(6)

[a] Symbol used for torsion angles in peptides (IUPAC-IUB Commission on Biochemical Nomenclature).

chirality-organized structure is in sharp contrast to the crystal structure of **1**, in which an intermolecular hydrogen bonding network was observed instead of the intramolecular hydrogen bonds to induce a helically ordered molecular assembly [11i]. These findings suggest that the complexation with $PdCl_2(MeCN)_2$ induces the γ-turn-like structural regulation of the dipeptide chain through intramolecular hydrogen bonding in the crystal structure. Another interesting feature in the structure is

Table 1
Crystallographic data for **3** and **4**

	3 · CH_3CN	**4** · CH_3CN
Empirical formula	$C_{48}H_{52}N_8O_6Cl_2Fe_2Pd_1{\cdot}CH_3CN$	$C_{48}H_{52}N_8O_6Cl_2Fe_2Pd_1{\cdot}CH_3CN$
Formula weight	1167.04	1167.04
Crystal system	Orthorhombic	Orthorhombic
Space group	$P2_12_12_1$ (no. 19)	$P2_12_12_1$ (no. 19)
a (Å)	23.7306(6)	23.7117(6)
b (Å)	23.7755(6)	23.7726(6)
c (Å)	11.5004(3)	11.4953(3)
V (Å^3)	6488.6(3)	6479.8(3)
Z	4	4
D_{calc} (g cm^{-3})	1.195	1.196
μ(Mo Kα) (cm^{-1})	8.43	8.44
T (°C)	4.0	4.0
λ(Mo Kα) (Å)	0.71069	0.71069
R_1[a]	0.062	0.060
wR_2[b]	0.178	0.179

[a] $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$.
[b] $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$.

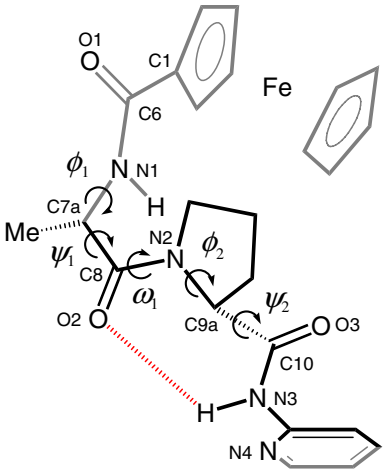


Fig. 2. Schematic representation of the definition of dihedral angles of **3**.

the dihedral angle, 29.4(3)°, between the least-squares planes of the coordinated pyridyl rings. The conformational regulation through intramolecular hydrogen bonding (Ala) and sterically constrained moieties (Pro) requires rotation of the pyridyl rings. Furthermore, each molecule is connected through intermolecular hydrogen bonds between the NH of the Ala and the CO adjacent to the ferrocene unit (another molecule) (N(21)···O(1a), 2.949(8) Å; N(21b)···O(1), 2.949(8) Å) to form a left-handed pseudo-helical molecular arrangement (Fig. 3).

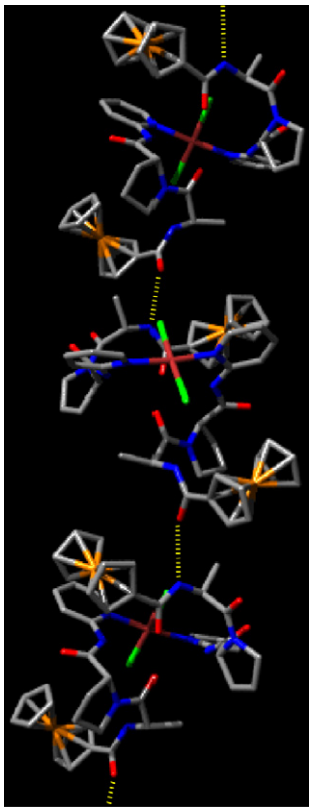
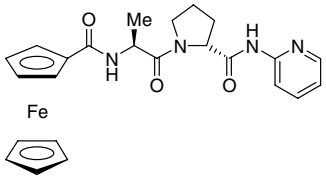
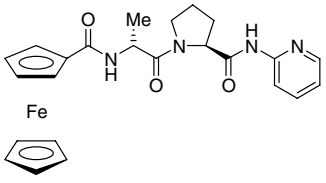


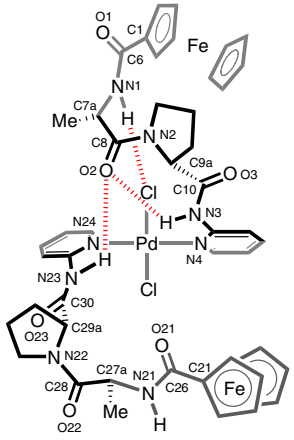
Fig. 3. A portion of a layer containing the helical-like ordered molecular assembly through a network of intermolecular hydrogen bonds in the crystal packing of **3**.



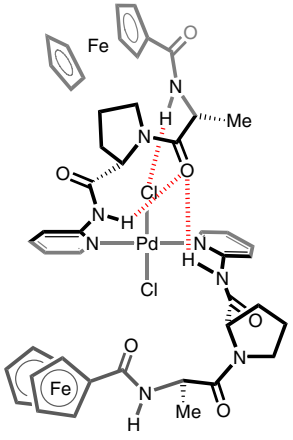
Fc(-L-Ala-D-Pro-NHPy)$_1$ **1**



Fc(-D-Ala-L-Pro-NHPy)$_1$ **2**



{Fc(-L-Ala-D-Pro-NHPy)$_1$}$_2$-PdCl$_2$ **3**



{Fc(-D-Ala-L-Pro-NHPy)$_1$}$_2$-PdCl$_2$ **4**

A good mirror imaged chirality-organized structure based on intramolecular hydrogen bonds (N(1)···Cl(2), 3.368(5) Å; N(3)···O(2), 2.843(7) Å; N(23)···O(2), 2.807(6) Å) was obtained in the 2:1 *trans* palladium complex **4** composed of the ferrocene-dipeptide conjugate **2** bearing one heterochiral dipeptide chain (-D-Ala-L-Pro-

NHPy). The opposite values of the torsion angles of **4** ($\phi_2 = -84.6(8)°$ and $\psi_2 = 66.8(8)°$) as compared with those of **3** were in agreement with the conformational isomer. An opposite helical molecular assembly, a right-handed pseudo-helical molecular arrangement, was also formed through intermolecular hydrogen bonds between the NH of the Ala and the CO adjacent to the ferrocene unit (another molecule) (N(21)···O(1a), 2.940(7) Å; N(21b)···O(1), 2.940(7) Å) in the crystal packing of the ferrocene **4**.

3. Conclusion

The complexation of the ferrocene-dipeptide conjugate bearing one dipeptide chain of heterochiral sequence (-L-Ala-D-Pro-NHPy) with $PdCl_2(MeCN)_2$ was demonstrated to induce conformational regulation of the dipeptide chain through complexation and chirality organization based on intramolecular hydrogen bonding, creating the γ-turn-like structure in the crystal structure. Furthermore, the palladium complex exhibited the helical-like ordered molecular assembly through a network of intermolecular hydrogen bonds in the crystal packing. Complexation and hydrogen bonds play a crucial role in regulating the three-dimensional structures. Studies on the application of chirality-organized structure to molecular recognition and asymmetric reaction are now in progress.

4. Experimental

4.1. General materials and experimental procedures

All reagents and solvents were purchased from commercial sources and were further purified by the standard methods, if necessary. Dipeptide derivatives were prepared according to the method reported in a previous paper by coupling of Boc-Ala-Pro-OH with 2-aminopyridine using EDCI, followed by removal of the *t*-butyloxycarbonyl protecting group [11e]. Melting points were determined on a Yanagimoto Micromelting Point Apparatus and were uncorrected. Infrared spectra were obtained with a JASCO FT/IR-480 Plus spectrometer. Mass spectra were run on a JEOL JMS-700 mass spectrometer.

4.2. General procedure for preparation of the palladium complexes *3* and *4*

A mixture of the ferrocene-dipeptide conjugate **1** (23.7 mg, 0.05 mmol) and $PdCl_2(MeCN)_2$ (6.49 mg, 0.025 mmol) was stirred in acetonitrile (8.0 mL) under argon at room temperature for 12 h. After evaporation of the solution, the palladium complex **3** was isolated quantitatively by recrystallization from acetonitrile/ether.

*Complex **3***: M.p. 201–203 °C (decomp.); IR (KBr) 3413, 3334, 3095, 2978,1713, 1634, 1576, 1516 cm^{-1}; FAB-MS *m/z* 1124 (M^+); Anal. Calc. for $C_{48}H_{52}N_8O_6Cl_2Fe_2Pd{\cdot}H_2O$: C, 50.39; H, 4.76; N, 9.79. Found: C, 50.07; H, 4.61; N, 9.71%.

*Complex **4***: M.p. 201–203 °C (decomp.); IR (KBr) 3413, 3334, 3095, 2978, 1713, 1634, 1576, 1516 cm^{-1}; FAB-MS *m/z* 1124 (M^+); Anal. Calc. for $C_{48}H_{52}N_8O_6Cl_2Fe_2Pd{\cdot}H_2O$: C, 50.39; H, 4.76; N, 9.79. Found: C, 50.25; H, 4.62; N, 9.72%.

4.3. X-ray structure analysis

All measurements for **3** and **4** were made on a Rigaku RAXIS-RAPID Imaging Plate diffractometer with graphite monochromated Mo Kα radiation. The structures of **3** and **4** were solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. The H atoms involved in hydrogen bonding were located in electron density maps. The remainder of the H atoms were placed in idealized positions and allowed to ride with the C atoms to which each was bonded. Crystallographic details are given in Table 1. Crystallographic data (excluding structure factors) for the structures reported in this paper.

Supplementary material

CCDC 620083 and 620084 contain the supplementary crystallographic data for **3** and **4**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

Acknowledgements

The authors thank the Analytical Center, Graduate School of Engineering, Osaka University, for the use of the NMR and MS instruments.

References

[1] (a) G.D. Rose, L.M. Gierasch, J.A. Smith, Adv. Prot. Chem. 37 (1985) 1;
(b) J. Kyte, Structure in Protein Chemistry, Garland, New York, 1995;
(c) C. Branden, J. Tooze, Introduction to Protein Structure, 2nd ed., Garland, New York, 1998.
[2] (a) For reviews on turn mimetics, see: A. Giannis, T. Kolter, Angew. Chem., Int. Ed. Engl. 32 (1993) 1244;
(b) R.M.J. Liskamp, Recl. Trav. Chim. Pays-Bas 113 (1993) 1–19;
(c) J.P. Schneider, J.W. Kelly, Chem. Rev. 95 (1995) 2169;
(d) P. Gillespie, J. Cicariello, G.L. Olson, Biopolymers 43 (1997) 191;
(e) S. Hanessian, G. McNaughton-Smith, H.-G. Lombart, W.D. Lubell, Tetrahedron 53 (1997) 12789;
(f) K.D. Stigers, M.J. Soth, J.S. Nowick, Curr. Opin. Chem. Biol. 3 (1999) 714.
[3] (a) For references after 2001, see: O. Langer, H. Kählig, K. Zierler-Gould, J.W. Bats, J. Mulzer, J. Org. Chem. 67 (2002) 6878;
(b) E.N. Prabhakaran, I.N. Rao, A. Boruah, J. Iqbal, J. Org. Chem. 67 (2002) 8247;

(c) F. Huang, W.M. Nau, Angew. Chem., Int. Ed. 42 (2003) 2269;
(d) J.M. Langenhan, I.A. Guzei, S.H. Gellman, Angew. Chem., Int. Ed. 42 (2003) 2402;
(e) M.H.V.R. Rao, S.K. Kumar, A.C. Kunwar, Tetrahedron Lett. 44 (2003) 7369;
(f) K.S. Rotondi, L.M. Gierasch, Biochemistry 42 (2003) 7976;
(g) G.M. Grotenbreg, M.S.M. Timmer, A.L. Llamas-Saiz, M. Verdoes, G.A. van der Marel, M.J. van Raaij, H.S. Overkleeft, M. Overhand, J. Am. Chem. Soc. 126 (2004) 3444;
(h) A. Trabocchi, D. Potenza, A. Guarna, Eur. J. Org. Chem. (2004) 4621;
(i) R.L. Beyer, H.N. Hoang, T.G. Appleton, D.P. Fairlie, J. Am. Chem. Soc. 126 (2004) 15096.

[4] (a) K.A. Newlander, J.F. Callahan, M.L. Moore, T.A. Tomaszek Jr., W.F. Huffman, J. Med. Chem. 36 (1993) 2321;
(b) J.F. Callahan, K.A. Newlander, J.L. Burgess, D.S. Eggleston, A. Nichols, A. Wong, W.F. Huffman, Tetrahedron 49 (1993) 3479;
(c) K. Burgess, K.-K. Ho, J. Am. Chem. Soc. 116 (1994) 799;
(d) T.P. Curran, N.M. Chandler, R.J. Kennedy, M.T. Keaney, Tetrahedron Lett. 37 (1996) 1933;
(e) K. Brickmann, P. Somfai, J. Kihlberg, Tetrahedron Lett. 38 (1997) 3651;
(f) J.M. Travins, F.A. Etzkorn, J. Org. Chem. 62 (1997) 8387;
(g) F.A. Etzkorn, J.M. Travins, S.A. Hart, in: A. Abell (Ed.), Advances Amino Acid Mimetics and Peptidomimetics, vol. 2, JAI Press Inc., Greenwich, 1999, pp. 125–163;
(h) A. Trabocchi, E.G. Occhiato, D. Potenza, A. Guarna, J. Org. Chem. 67 (2002) 7483;
(i) D. Yang, J. Qu, W. Li, D.-P. Wang, Y. Ren, Y.-D. Wu, J. Am. Chem. Soc. 125 (2003) 14452.

[5] T. Moriuchi, T. Nagai, T. Hirao, Org. Lett. 8 (2006) 31.

[6] (a) C.B. Anfinsen, J.T. Edsall, F.M. Richards, D.S. Eisenberg, Advances in Protein Chemistry, Academic Press, New York, 1991;
(b) W. Kaim, B. Schwederski, Bioinorganic Chemistry: Inorganic Elements in the Chemistry of Life, Wiley, New York, 1994.

[7] (a) For references after 1990, see: M. Lieberman, T. Sasaki, J. Am. Chem. Soc. 113 (1991) 1470;
(b) F. Ruan, Y. Chen, K. Itoh, T. Sasaki, P.B. Hopkins, J. Org. Chem. 56 (1991) 4347;
(c) B.A. Krizek, B.T. Amann, V.J. Kilfoil, D.L. Merkle, J.M. Berg, J. Am. Chem. Soc. 113 (1991) 4518;
(d) M.R. Ghadiri, C. Soares, C. Choi, J. Am. Chem. Soc. 114 (1992) 825;
(e) M.R. Ghadiri, M.A. Case, Angew. Chem., Int. Ed. Engl. 32 (1993) 1594;
(f) S.R. Gilbertson, G. Chen, M. McLoughlin, J. Am. Chem. Soc. 116 (1994) 4481;
(g) J.P. Schneider, J.W. Kelly, J. Am. Chem. Soc. 117 (1995) 2533;
(h) S.R. Gilbertson, R.V. Pawlick, Angew. Chem., Int. Ed. Engl. 35 (1996) 902;
(i) T. Yamamura, M. Arai, T. Yamane, T. Ukai, M. Ushiyama, H. Hirota, Bull. Chem. Soc. Jpn. 69 (1996) 2221;
(j) W.D. Kohn, C.M. Kay, B.D. Sykes, R.S. Hodges, J. Am. Chem. Soc. 120 (1998) 1124;
(k) M.J. Kelso, H.N. Hoang, T.G. Appleton, D.P. Fairlie, J. Am. Chem. Soc. 122 (2000) 10488;
(l) M.J. Kelso, H.N. Hoang, W. Oliver, N. Sokolenko, D.R. March, T.G. Appleton, D.P. Fairlie, Angew. Chem., Int. Ed. 42 (2003) 421.

[8] (a) D.L. Merkle, M.H. Schmidt, J.M. Berg, J. Am. Chem. Soc. 113 (1991) 5450;
(b) S.R. Gilbertson, S.E. Collibee, A. Agarkov, J. Am. Chem. Soc. 122 (2000) 6522.

[9] (a) G. Jaouen, A. Vessiéres, I.S. Butler, Acc. Chem. Res. 26 (1993) 361;
(b) R. Severin, R. Bergs, W. Beck, Angew. Chem., Int. Ed. 37 (1998) 1634;
(c) G. Jaouen, J. Organomet. Chem., Bioorganomet. Chem. (special issue) 589 (1999) 1–126.

[10] (a) R.S. Herrick, R.M. Jarret, T.P. Curran, D.R. Dragoli, M.B. Flaherty, S.E. Lindyberg, R.A. Slate, L.C. Thornton, Tetrahedron Lett. 37 (1996) 5289;
(b) T. Okamura, K. Sakauye, N. Ueyama, A. Nakamura, Inorg. Chem. 37 (1998) 6731;
(c) J.F. Gallagher, P.T.M. Kenny, M.J. Sheehy, Inorg. Chem. Commun. 2 (1999) 200;
(d) W. Bauer, K. Polborn, W. Beck, J. Organomet. Chem. 579 (1999) 269;
(e) H.-B. Kraatz, D.M. Leek, A. Houmam, G.D. Enright, J. Lusztyk, D.D.M. Wayner, J. Organomet. Chem. 589 (1999) 38;
(f) I. Bediako-Amoa, R. Silerova, H.-B. Kraatz, Chem. Commun. (2002) 2430;
(g) S. Maricic, U. Berg, T. Frejd, Tetrahedron 58 (2002) 3085;
(h) D.R. van Staveren, T. Weyhermüller, N. Metzler-Nolte, Dalton Trans. (2003) 210;
(i) T. Morita, S. Kimura, J. Am. Chem. Soc. 125 (2003) 8732;
(j) L. Barišić, M. Dropučić, V. Rapić, H. Pritzkow, S.I. Kirin, N. Metzler-Nolte, Chem. Commun. (2004) 2004;
(k) K. Heinze, M. Schlenker, Eur. J. Inorg. Chem. (2004) 2974;
(l) S.I. Kirin, D. Wissenbach, N. Metzler-Nolte, New J. Chem. 29 (2005) 1168;
(m) S. Chowdhury, K.A. Mahmoud, G. Schatte, H.-B. Kraatz, Org. Biomol. Chem. 3 (2005) 3018;
(n) K. Heinze, M. Beckmann, Eur. J. Inorg. Chem. (2005) 3450;
(o) S. Chowdhury, D.A.R. Sanders, G. Schatte, H.-B. Kraatz, Angew. Chem., Int. Ed. 45 (2006) 751.

[11] (a) A. Nomoto, T. Moriuchi, S. Yamazaki, A. Ogawa, T. Hirao, Chem. Commun. (1998) 1963;
(b) T. Moriuchi, A. Nomoto, K. Yoshida, T. Hirao, J. Organomet. Chem. 589 (1999) 50;
(c) T. Moriuchi, A. Nomoto, K. Yoshida, A. Ogawa, T. Hirao, J. Am. Chem. Soc. 123 (2001) 68;
(d) T. Moriuchi, A. Nomoto, K. Yoshida, T. Hirao, Organometallics 20 (2001) 1008;
(e) T. Moriuchi, K. Yoshida, T. Hirao, Organometallics 20 (2001) 3101;
(f) T. Moriuchi, K. Yoshida, T. Hirao, J. Organomet. Chem. 637–639 (2001) 75;
(g) T. Moriuchi, K. Yoshida, T. Hirao, J. Organomet. Chem. 668 (2003) 31;
(h) T. Moriuchi, K. Yoshida, T. Hirao, Org. Lett. 5 (2003) 4285;
(i) T. Moriuchi, T. Nagai, T. Hirao, Org. Lett. 7 (2005) 5265.

[12] (a) T. Moriuchi, T. Hirao, Chem. Soc. Rev. 33 (2004) 294;
(b) D.R. van Staveren, N. Metzler-Nolte, Chem. Rev. 104 (2004) 5931;
(c) S.I. Kirin, H.-B. Kraatz, N. Metzler-Nolte, Chem. Soc. Rev. 35 (2006) 348.

[13] D.S. Kemp, B.R. Bowen, Tetrahedron Lett. 29 (1988) 5081.