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Preparation, Structures, and Electrochemical Properties of Silaplatinacyclohexadienes with Ferrocenyl Pendant Groups

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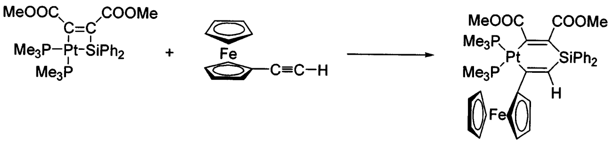
Summary: The reactions of ethynylferrocene with $\mathrm{Pt(CZ{=}CZ\text{-}SiPh_2)(PMe_3)_2}$ *(Z = COOMe) and with* $\mathrm{Pt(SiHPh_2)_2(PMe_3)_2}$ *form the six-membered silaplatinacycles,* $\mathrm{Pt(CZ{=}CZ\text{-}SiPh_2\text{-}CH{=}CFc)(PMe_3)_2}$ *(**1**) and* $\mathrm{Pt(CFc{=}CH\text{-}SiPh_2\text{-}CH{=}CFc)(PMe_3)_2}$ *(**2**, Fc = ferrocenyl), respectively. Electrochemical measurement and spectroscopic analyses of the oxidation product of **2** indicate a mixed valence of two ferrocene units.*

Introduction. Many synthetic organic reactions promoted by transition metal complexes involve intermediate metallacycles with four- to six-membered rings.[1,2] Kinetic stability of the metal−carbon bond of these compounds is mainly attributed to the restricted conformation of the ring system, which prevents free rotation of the M−C and C−C bonds and retards the decomposition of the complexes via reductive elimination or β-hydrogen elimination. The five-membered cobaltacycles having two ferrocenyl groups, prepared from 2:1 addition of ethynylferrocene to a Co(I) complex, exhibit the electrochemical interaction between the ferrocenyl centers.[3] Four-membered silametallacyclobutenes[4−7] have been proposed to react with unsaturated molecules, such as alkynes, leading to the formation of a C−Si bond. The reaction of phenylacetylene with $\mathrm{Pt(SiHMe_2)_2(PEt_3)_2}$ produces the silaplatinacyclohexadiene, which has been considered to involve the intermediate silaplatinacyclobutene and its ring expansion by an alkyne.[8] In this study, the reactions of an alkyne with the silaplatinacyclobutene that was recently isolated by our group[9] are applied to introduce ferrocenyl groups to the silaplatinacycles. Structural and electrochemical properties of the obtained complexes are discussed.

Results and Discussion. $\mathrm{Pt(CZ{=}CZ\text{-}SiPh_2)(PMe_3)_2}$ (Z = COOMe)[9b] reacts with equimolar ethynylferrocene at 60 °C in toluene to produce the six-membered metallacycle containing a ferrocenyl pendant group, $\mathrm{Pt(CZ{=}CZ\text{-}SiPh_2\text{-}CH{=}CFc)(PMe_3)_2}$ (**1**, Fc = ferrocenyl) (eq 1), which is isolated by recrystallization from THF−hexane in 63% yield. The reaction of excess ethynylferrocene with $\mathrm{Pt(SiHPh_2)_2(PMe_3)_2}$ in toluene affords the six-membered Pt complex with two ferrocenyl groups at the α-carbon of the metal center, $\mathrm{Pt(CFc{=}CH\text{-}SiPh_2\text{-}CH{=}CFc)(PMe_3)_2}$ (**2**), as shown in eq 2. Complex **2**, which is precipitated during the reaction, is isolated in 62% yield as an orange powder by filtration of the solvent. Equation 2 probably involves the initial formation of the 4-sila-3-platinacyclobutene via equimolar reaction of the bis(diphenylsilyl)platinum complex with ethynylferrocene followed by ring expansion triggered by insertion of another ethynylferrocene molecule into the Pt−Si bond, similarly to eq 1. Evidence of the intermediate four-membered metallacycle was not found in the NMR spectra of the reaction mixture.



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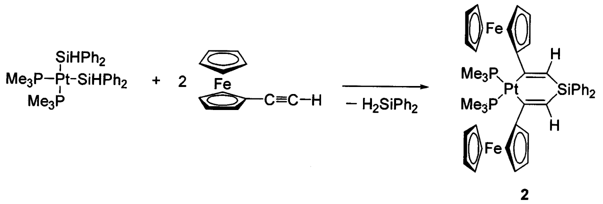

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[1] Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*, 2nd ed.; University Science: Sausalito, CA, 1987; p 459.

[2] (a) Cámpora, J.; Palma, P.; Carmona, E. *Coord. Chem. Rev.* **1999**, *193−195*, 207. (b) Jennings, P. W.; Johnson, L. L. *Chem. Rev.* **1994**, *94*, 2241.

[3] (a) Ohkubo, A.; Fujita, S.; Ohba, K.; Aramaki, K.; Nishihara, H. *J. Chem. Soc., Chem. Commun.* **1992**, 1553. (b) Murata, Y.; Hoshi, T.; Matsuoka, I.; Nankawa, T.; Kurihara, M.; Nishihara, H. *J. Inorg. Organomet. Polym.* **2000**, *10*, 209. (c) Nishihara, H. *Bull. Chem. Soc. Jpn.* **2001**, *74*, 19. See also: Yamada, Y.; Mizutani, J.; Kurihara, M.; Nishihara, H. *J. Organomet. Chem.* **2001**, *637*, 80.

[4] (a) Okinoshima, H.; Yamamoto, K.; Kumada, M. *J. Am. Chem. Soc.* **1972**, *94*, 9263. (b) Yamamoto, K.; Okinoshima, H.; Kumada, M. *J. Organomet. Chem.* **1971**, *27*, C31.

[5] (a) Seyferth, D.; Vick, S. C.; Shannon, M. L.; Lim, T. F. O.; Duncan, D. P. *J. Organomet. Chem.* **1977**, *135*, C37. (b) Seyferth, D.; Duncan, D. P.; Vick, S. C. *J. Organomet. Chem.* **1977**, *125*, C5. (c) Seyferth, D.; Shannon, M. L.; Vick, S. C.; Lim, T. F. O. *Organometallics* **1985**, *4*, 57.

[6] Sakurai, H.; Kamiyama, Y.; Nakadaira, Y. *J. Am. Chem. Soc.* **1977**, *99*, 3879.

[7] (a) Ishikawa, M.; Ohshita, J.; Ito, Y.; Iyoda, J. *J. Am. Chem. Soc.* **1986**, *108*, 7417. (b) Ohshita, J.; Isomura, Y.; Ishikawa, M. *Organometallics* **1989**, *8*, 2050.

[8] Yamashita, H.; Tanaka, M.; Goto, M. *Organometallics* **1992**, *11*, 3227. See also: Eaborn, C.; Metham, T. N.; Pidcock, A. *J. Organomet. Chem.* **1977**, *131*, 377.

[9] (a) Tanabe, M.; Yamazawa, H.; Osakada, K. *Organometallics* **2001**, *20*, 4451. (b) Tanabe, M.; Osakada, K. *J. Am. Chem. Soc.* **2002**, *124*, 4550.

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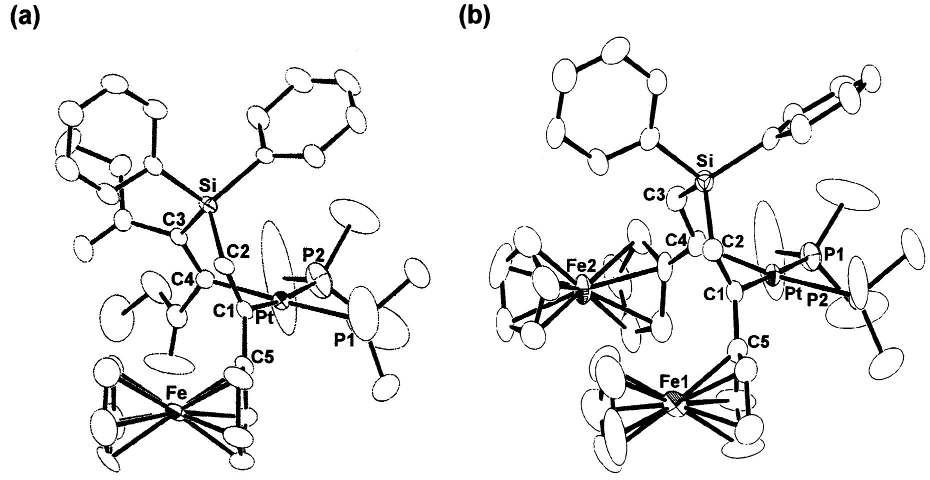

Figure 1. OTREP drawing of (a) **1** and (b) **2** with 30% thermal ellipsoidal plots. Hydrogen atoms were omitted for simplicity. Selected bond distances (Å) and angles (deg) for **1**: Pt−P1 2.315(3), Pt−P2 2.314(3), Pt−C1 2.067(7), Pt−C4 2.055(7), C1−C2 1.33(1), C1−C5 1.48(1), C2−Si 1.840(8), Si−C3 1.880(7), C3−C4 1.33(1), P1−Pt−P2 95.3(1), P1−Pt−C1 87.5(2), P1−Pt−C4 171.9(2), P2−Pt−C1 173.9(2), P2−Pt−C4 91.8(2), C1−Pt−C4 85.1(3), Pt−C1−C5 118.1(6), Pt−C1−C2 118.7(6), C2−C1−C5 123.2(7), C1−C2−Si 119.0(6), C2−Si−C3 102.4(3), Si−C3−C4 117.0(6), C3−C4−Pt 121.6(6). Selected bond distances (Å) and angles (deg) for **2**: Pt−P1 2.329(4), Pt−P2 2.331(4), Pt−C1 2.08(1), Pt−C4 2.04(1), C1−C2 1.32(2), C1−C5 1.48(2), C2−Si 1.82(1), Si−C3 1.86(1), C3−C4 1.34(2), P1−Pt−P2 94.7(1), P1−Pt−C1 177.4(3), P1−Pt−C4 91.5(4), P2−Pt−C1 87.8(3), P2−Pt−C4 168.0(4), C1−Pt−C4 86.2(5), Pt−C1−C5 116.9(9), Pt−C1−C2 119.4(9), C2−C1−C5 124(1), C1−C2−Si 120(1), C2−Si−C3 103.4(6), Si−C3−C4 119(1), C3−C4−Pt 119(1).

Figure 1 depicts the molecular structures of **1** and **2**. The boat conformation of the six-membered rings, formed by cis addition of the Pt−Si bond to the alkyne, makes the Si and Pt centers closer; the Pt···Si distances of **1** and **2** are 3.28 and 3.27 Å, respectively. The ferrocenyl groups of the complexes are situated at a site opposite to the silyl group on the coordination plane of the Pt center. The conformation of the six-membered metallacyclic ring and the orientation of the ferrocenyl pendants are quite similar between **1** and **2**. The distance between the two Fe centers of **2** is approximately 6.0 Å. The NMR spectra of the complexes are also consistent with the structure confirmed by X-ray crystallography.

The cyclic voltammogram of **1** in Figure 2a shows a single reversible ferrocene−ferrocenium redox at $E_{1/2} = -0.06$ V (vs Ag^+/Ag), which is lower than that of ferrocene ($E_{1/2} = 0.15$ V vs Ag^+/Ag). Complex **2** exhibits two redox waves as shown in parts b and c in Figure 2; two reversible oxidation and reduction peaks are observed at $E_{1/2} = -0.08$ and 0.07 V ($\Delta E = 0.15$ V) (vs Ag^+/Ag) at −40 °C. The electrochemical reactions ($E_{ox} = -0.03$ and 0.08 V vs Ag^+/Ag) lack reversibility at 15 °C due to concomitant chemical oxidation of the product at that temperature. The two reversible peaks at the low temperature indicate the presence of two mixed valence ferrocene units.[10] The absorption spectra of **2** under electrochemical oxidation conditions, measured by a flow electrolysis technique,[11] indicate a stepwise increase of the absorption of ferrocenium (380 nm) upon electrolysis at −0.20 and 0.15 V. This is in accordance with the mixed valence state of the Fe(II)−Fe(III) species. The difference between the two potentials reflects the magnitude of the interaction. Recently, Ribou et al. reported electrochemical communication between two ferrocenyl units through a π-conjugated organic bridge.[12] The difference of the redox potential of **2** ($\Delta E = 0.15$ V) is between those of 1,2-diferrocenyl-

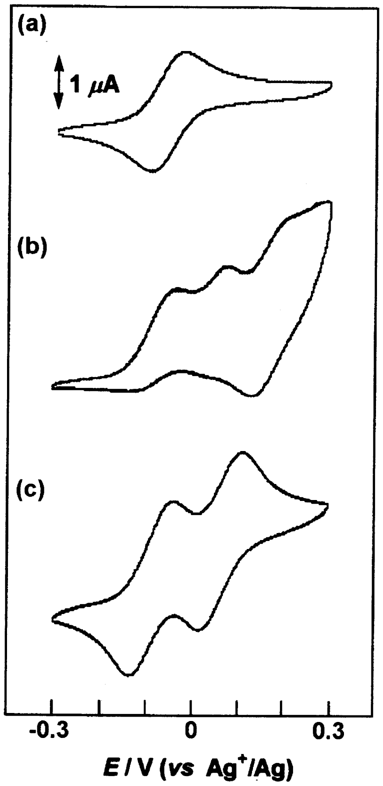

Figure 2. Cyclic voltammograms of (a) 0.22 mM of **1** at 15 °C, (b) 0.52 mM of **2** at 15 °C, and (c) 0.52 mM of **2** at −40 °C in CH_2Cl_2 solutions containing Et_4NBF_4 (0.10 M) (scan rate = 0.1 V s^{-1}). **1**: $E_{1/2} = -0.06$ V. **2** at −40 °C: $E_{1/2} = -0.08$ and 0.07 V ($\Delta E = 0.15$ V).

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[10] (a) Cowan, D. O.; Levanda, C.; Park, J.; Kaufman, F. *Acc. Chem. Res.* **1973**, *6*, 1. (b) Levanda, C.; Bechgaard, K.; Cowan, D. O. *J. Org. Chem.* **1976**, *41*, 2700.

[11] (a) Nakao, H.; Hayashi, H.; Okita, K. *Anal. Sci.* **2001**, *17*, 545. (b) Sakano, T.; Horie, M.; Osakada, K.; Nakao, H. *Bull. Chem. Soc. Jpn.* **2001**, *74*, 2059.

ethylene (0.17 V) and 1,4-diferrocenylbutadiene (0.13 V). Thus, the ferrocenyl groups of **2** communicate with each other through the nonconjugated metallacyclic part of the complex.

Experimental Section: (a) General Methods. All manipulations of the complexes were carried out using standard Schlenk techniques under an argon or a nitrogen atmosphere. Hexane, toluene, and THF were distilled from sodium/benzophenone and stored under nitrogen. NMR spectra (^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H}) were recorded on a JEOL EX-400 spectrometer. Peak positions of the ^{31}P{^{1}H} NMR spectra were referenced to an external 85% H_3PO_4. Elemental analyses were carried out with a Yanaco MT-5 CHN autocorder. Cyclic voltammetry was measured in CH_2Cl_2 solution containing 0.10 M Et_4NBF_4 with ALS Electrochemical Analyzer Model-600A. The measurement was carried out in a standard one-compartment cell under inert gas equipped with an Ag^+/Ag reference electrode, a platinum-wire counter electrode, and a platinum disk working electrode. $Pt(SiHPh_2)_2(PMe_3)_2$,[13] $Pt(CZ{=}CZ\text{-}SiPh_2)(PMe_3)_2$,[9b] and ethynylferrocene[14] were prepared according to the literature method. Et_4NBF_4 for the electrochemical measurement was recrystallized from methanol before use.

(b) Preparation of $Pt(FcC{=}CH\text{-}SiPh_2\text{-}CZ{=}CZ)(PMe_3)_2$ (Fc = ferrocenyl, Z = COOMe) (1). A solution of $Pt(CZ{=}CZ\text{-}SiPh_2)(PMe_3)_2$ (124 mg, 0.18 mmol) and ethynylferrocene (43 mg, 0.21 mmol) in toluene (5 mL) was stirred at 60 °C for 48 h. The solvent was removed under reduced pressure. Hexane was added to the residue, which caused separation of an orange solid. The product was collected by filtration, washed with hexane two times (3 mL), and dried in vacuo. Recrystallization from THF−hexane gave **1** as orange crystals (102 mg, 63%). Anal. Calcd for $C_{36}H_{44}FeO_4P_2PtSi$: C, 49.04; H, 5.03. Found: C, 48.87; H, 5.15. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.00 (d, P(CH_3), 9H, ^2J(HP) = 8.4 Hz, ^3J(HPt) = 19.6 Hz), 1.20 (d, P(CH_3), 9H, ^2J(HP) = 8.4 Hz, ^3J(HPt) = 17.2 Hz), 3.26 (s, 3H, OCH_3), 3.78 (s, 3H, OCH_3), 4.09 (m, 1H, C_5H_4), 4.13 (s, 6H, Cp and one proton signal of C_5H_4 group), 4.43 (m, 1H, C_5H_4), 4.64 (m, 1H, C_5H_4), 7.08 (dd, 1H, =C*H*, ^4J(HP) = 2.4, 19.2 Hz, ^3J(HPt) = 116.7 Hz), 7.27−7.31 (m, 6H, C_6H_5-*m* and -*p*), 7.45 (m, 2H, C_6H_5-*o*), 7.76 (m, 2H, C_6H_5-*o*). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 16.6 (d, P(CH_3)$_3$, *J*(CP) = 11.0 Hz), 17.0 (d, P(CH_3)$_3$, *J*(CP) = 12.9 Hz), 50.5 (OCH_3), 51.2 (OCH_3), 66.1 (d, C_5H_4-2, ^4J(CP) = 5.5 Hz, ^3J(CPt) = 29.5 Hz), 67.0 (C_5H_4-3), 67.8 (C_5H_4-3), 70.1 (Cp), 71.2 (C_5H_4-2, ^3J(CPt) = 49.6 Hz), 97.1 (apparent triplet, C_5H_4-1, ^3J(CP) = 7.3 Hz, ^2J(CPt) = 40.4 Hz), 120.7 (d, Si*C*(H)=, ^3J(CP) = 3.6 Hz, ^2J(CPt) = 16.6 Hz), 127.2 (C_6H_5-*m*), 127.3 (C_6H_5-*m*), 128.3 (C_6H_5-*p*), 128.4 (C_6H_5-*p*), 135.0 (C_6H_5-*o*), 135.8 (C_6H_5-*o*), 137.9 (C_6H_5-*i*), 140.1 (C_6H_5-*i*), 141.8 (br, Si*C*(Z)=), 171.5 (d, PtC*C*=O, ^3J(CP) = 10.9 Hz, ^2J(CPt) = 107.4 Hz), 176.1 (d, SiC*C*=O, ^4J(CP) = 5.5 Hz, ^3J(CPt) = 20.2 Hz), 183.7 (dd, Pt*C*=, ^2J(CP) = 11.0, 106.5 Hz), 193.6 (dd, Pt*C*=, ^2J(CP) = 11.0, 101.0 Hz). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ −28.8 (d, ^2J(PP) = 15.5 Hz, *J*(PPt) = 1681 Hz), −27.8 (d, ^2J(PP) = 15.5 Hz, *J*(PPt) = 2185 Hz).

Table 1. Crystallographic Data and Details of Refinement for 1 and 2

	1	2
chemical formula	$C_{36}H_{44}O_4FeP_2PtSi$	$C_{42}H_{48}Fe_2P_2PtSi$
formula wt	881.71	949.66
cryst syst	triclinic	triclinic
space group	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)
a, Å	11.983(6)	12.496(4)
b, Å	15.284(4)	14.876(2)
c, Å	10.600(2)	11.432(3)
α, deg	100.60(2)	102.56(2)
β, deg	97.21(3)	108.54(8)
γ, deg	75.38(3)	87.958(2)
V, Å^3	1839.9	1965.3
Z	2	2
μ, mm^{-1}	4.331	4.404
F(000)	880	948
D_{calcd}, g cm^{-3}	1.591	1.605
cryst size, mm	0.32 × 0.40 × 0. 56	0.16 × 0.28 × 0.58
2θ range, deg	5.0−55.0	5.0−55.0
scan rate, deg min^{-1}	16	16
no. of unique reflns	8842	9029
no. of used reflns ($I > 3\sigma(I)$)	6999	6507
no. of variables	406	433
R	0.052	0.070
R_w	0.051	0.074

(c) Preparation of $Pt(FcC{=}CH\text{-}SiPh_2\text{-}CH{=}CFc)(PMe_3)_2$ (2). To a toluene (7 mL) solution of ethynylferrocene (542 mg, 2.5 mmol) was added $Pt(SiHPh_2)_2(PMe_3)_2$ (737 mg, 1.0 mmol) at room temperature. After the mixture was stirred for 12 h at 60 °C, an orange solid was gradually generated. The product was collected by filtration, washed with toluene two times (2 mL) and hexane (3 mL), and dried in vacuo. Yield 607 mg (62%). Recrystallization from THF−hexane gave red crystals for X-ray crystallography. Anal. Calcd for $C_{42}H_{48}Fe_2P_2PtSi$: C, 53.12; H, 5.09. Found: C, 53.30; H, 5.04. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.87 (d, P(CH_3), 18H, ^2J(HP) = 7.9 Hz, ^3J(HPt) = 16.8 Hz), 4.07 (m, 2H, C_5H_4), 4.13 (m, 2H, C_5H_4), 4.19 (s, 10H, Cp), 4.43 (m, 2H, C_5H_4), 4.47 (m, 2H, C_5H_4), 7.15 (d, 2H, =C*H*, ^4J(HP) = 15.6 Hz, ^3J(HPt) = 123.9 Hz), 7.23 (m, 3H, C_6H_5-*m* and -*p*), 7.35 (m, 3H, C_6H_5-*m* and -*p*), 7.66 (m, 4H, C_6H_5-*o*). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 17.1 (m, P(CH_3)$_3$), 66.2 (C_5H_4-3), 66.8 (C_5H_4-3), 68.7 (C_5H_4-2, ^3J(CPt) = 29.4 Hz), 69.7 (Cp), 70.5 (C_5H_4-2, ^3J(CPt) = 46.0 Hz), 101.8 (apparent triplet, C_5H_4-1, ^3J(CP) = 7.4 Hz, ^2J(CPt) = 55.0 Hz), 125.6 (Si*C*=, ^2J(CPt) = 22.0 Hz), 126.9 (C_6H_5-*m*), 127.5 (C_6H_5-*p*), 127.6 (C_6H_5-*m*), 128.1 (C_6H_5-*p*), 135.0 (C_6H_5-*o*), 135.8 (C_6H_5-*o*), 141.1 (C_6H_5-*i*), 142.8 (C_6H_5-*i*), 189.0 (dd, Pt*C*=, ^2J(CP) = 11.0, 110.1 Hz). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ −28.7 (*J*(PPt) = 1782 Hz).

(d) Crystal Structure Determination. Crystals of **1** and **2** were mounted in glass capillary tubes under Ar. Intensities were collected for Lorentz and polarization effects on a Rigaku AFC-5R automated four-cycle diffractometer by using Mo Kα radiation (λ = 0.71069 Å) and the ω−2θ scan method, and an empirical absorption correction (Ψ scan) was applied. Calculations were carried out by using the program package teXsan

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[12] Ribou, A.-C.; Launay, J.-P.; Sachtleben, M. L.; Li, H.; Spangler, C. W. *Inorg. Chem.* **1996**, *35*, 3735.

[13] Kim, Y.-J.; Park, J.-I.; Lee, S.-C.; Osakada, K.; Tanabe, M.; Choi, J.-C.; Koizumi, T.; Yamamoto, T. *Organometallics* **1999**, *18*, 1349−1352.

[14] Doisneau, G.; Balavoine, G.; Fillebeen-Khan, T. *J. Organomet. Chem.* **1992**, *425*, 113.

for Windows. Atomic scattering factors were obtained from the literature.[15] A full-matrix least-squares refinement was used for non-hydrogen atoms with anisotoropic thermal parameters. Hydrogen atoms were located by assuming the ideal geometry and included in the structure calculation without further refinement of the parameters. Crystallographic data and details of refinement of **1** and **2** were summarized in Table 1.

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Supporting Information Available: Crystallographic data for **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[15] *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. 4.