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Template-Controlled Formation of an [11]ane-P_2C^{NHC} Macrocyclic Ligand at an Iron(II) Template

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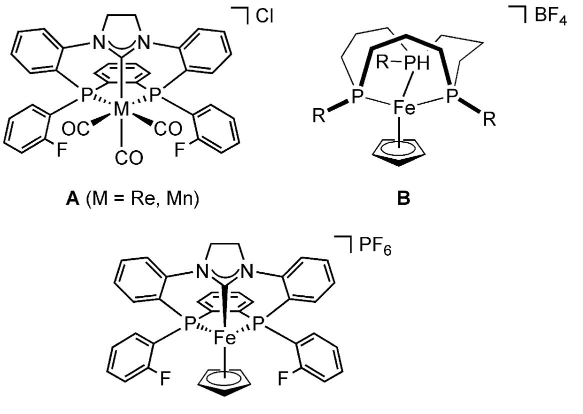
Complex [Fe(η^5-C_5H_5)(η^6-PhMe)]PF_6 reacts with 1,2-bis[bis(2-fluorophenyl)phosphanyl]benzene (**2**) in acetonitrile under irradiation for 6 h to give complex [Fe(η^5-C_5H_5)(**2**)(CH_3CN)]PF_6 ([**3**]PF_6). Reaction of [**3**]PF_6 with 1 equiv. of 2-azidoethyl isocyanide (**4**) yields complex [Fe(η^5-C_5H_5)(**2**)(**4**)]X ([**5**]X) (X = Br, PF_6). Staudinger reaction with PPh_3 at the azido function followed by hydrolysis of the iminophosphorane with HBr yields compound [**6**]X (X = Br^-, $PF_6{}^-$) with an NH,NH-stabilized NHC ligand. The *facially* coordinated NH,NH-stabilized NHC and the fluorinated diphosphane ligands were linked by *N*,*N′*-deprotonation of the NHC and nucleophilic attack of the nitrogen atoms at two C–F bonds, which gave – after anion exchange with NH_4PF_6 – complex [**1**]PF_6 bearing the macrocyclic [11]ane-P_2C^{NHC} ligand.

Introduction

The inherent stability of metal complexes with macrocyclic ligands makes them suitable for applications in which the macrocyclic framework has to withstand vigorous conditions.[1] N-Heterocyclic carbene (NHC)[2] and phosphane ligands[3] are known to form stable metal complexes, and this stability can be further enhanced by incorporation of these donor groups into macrocyclic ligands. We have prepared complexes of type **A** (Figure 1) bearing the *facially* coordinated mixed diphosphane–NHC macrocyclic ligand [11]ane-P_2C^{NHC} in a template synthesis at template centers such as {$Re^I(CO)_3$},[4] {$Mn^I(CO)_3$},[4] and {$CpRu^{II}$}.[5] A similar template strategy also enables the synthesis of complexes with the macrocyclic [16]ane-$P_2C^{NHC}{}_2$ ligand.[6]

So far the template synthesis of macrocycles with carbene donors involved the use of costly template metals like rhenium or ruthenium, wereas liberation of the macrocycle from the metal center proved difficult. In our search for more cost-efficient template metals we became interested in iron. Iron(II) has been used as template for the generation of P_3 macrocycles (**B**, Figure 1), which can be liberated from the metal center.[7] Here we describe the template-controlled formation of an [11]ane-P_2C^{NHC} macrocycle at a {$CpFe^{II}$} template leading to complex [**1**]PF_6.



A (M = Re, Mn)

B

[**1**]PF_6

Figure 1. Macrocyclic P_2C^{NHC} and P_3 ligands.

Results and Discussion

Our approach to the template-controlled synthesis of an [11]ane-P_2C^{NHC} ligand requires the coordination of a suitably substituted diphosphane and a reactive cyclic NH,NH-stabilized diaminocarbene in *facial* positions to the template metal center and their subsequent connection while coordinated.[4,5] A suitable diphosphane is 1,2-bis[bis(2-fluorophenyl)phosphanyl]benzene (**2**),[4a,8] which reacts with [Fe(η^5-C_5H_5)(η^6-PhMe)]PF_6[9] under irradiation in acetonitrile for 6 h to give complex [Fe(η^5-C_5H_5)(**2**)(CH_3CN)]PF_6 ([**3**]PF_6) (Scheme 1). A similar reaction has been described with [Fe(η^5-C_5H_5)(η^6-PhMe)]PF_6 and a related diphosphane.[10]

Complex [**3**]PF_6 was not isolated but instead was directly treated with 1 equiv. of 2-azidoethyl isocyanide (**4**)[11] in dichloromethane to give complex [**5**]PF_6 in 95% yield (note that the reaction of [**3**]PF_6 with isocyanide **4** in acetonitrile does not yield [**5**]PF_6). Complex [**3**]PF_6 was fully characterized by ^1H, ^{13}C, ^{19}F, and ^{31}P NMR, IR spectroscopy and MALDI mass spectrometry.

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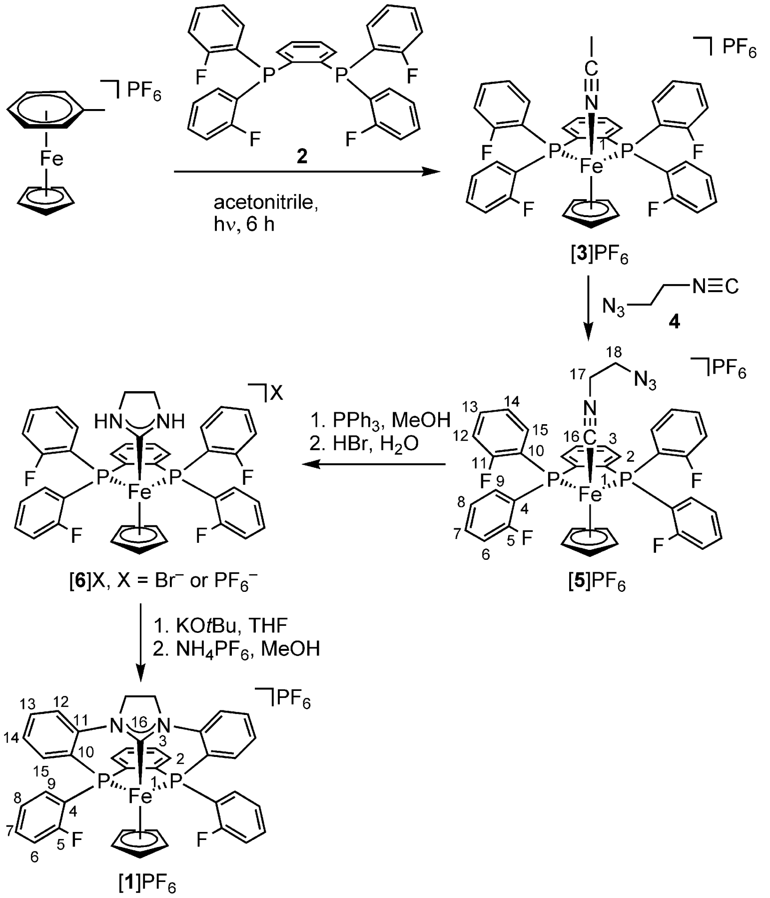

Scheme 1. Preparation of complexes [**5**](PF_6) and [**1**](PF_6) (the numbering refers to the assignment of the NMR resonances, see Experimental Section).

The signal for the isocyanide carbon atom (C-16) in the $^{13}C\{^1H\}$ NMR spectrum of [**3**]PF_6 appears at δ = 164.2 ppm with a $^2J(P,C)$ coupling constant of 28.0 Hz. All other resonances have been assigned based on 2D NMR spectroscopy. The IR spectrum of [**5**]PF_6 (in KBr) shows the isocyanide stretching frequency at $\tilde{\nu}$ = 2134 cm^{-1}, a lower wavenumber than observed for the free ligand **4** ($\tilde{\nu}$ = 2152 cm^{-1} in benzene).[11]

Such a decrease in wavenumber indicates backbonding from the metal center to the isocyanide and a concurrent slight deactivation of the isocyanide for a nucleophilic attack. A similar decrease in the wavenumbers has been observed in pentacarbonyl complexes of coordinated 2-hydroxyphenyl isocyanide, where enhanced $d\rightarrow\pi^*$ backbonding can lead to complete deactivation of the isocyanide group for an intramolecular nucleophilic attack by the hydroxy group.[12] The amino groups in coordinated 2-aminoethyl[5,11,13] or 2-aminophenyl isocyanides[14] are much more nucleophilic compared to hydroxy groups in 2-hydroxyphenyl isocyanide, and we were therefore convinced that in spite of the slight decrease in the C≡N wavenumber by coordination of the isocyanide, the conversion [**5**]PF_6 → [**6**]PF_6 would proceed upon reduction of the azido group in [**5**]PF_6 to the primary amine.

Various methods for the reduction of the azido group to a primary amine in coordinated 2-azido-functionalized isocyanides have been described.[5–7,13] From these we selected the Staudinger reaction for the conversion [**5**]PF_6 → [**6**]X (X = PF_6^-, Br^-) employing the sterically demanding phosphane PPh_3 to prevent substitution of the isocyanide in [**5**]PF_6. Complex [**5**]PF_6 was treated with PPh_3 in methanol, and the resulting iminophosphorane group was then hydrolyzed with HBr/H_2O to lead to the complex with the 2-aminoethyl isocyanide ligand, which is not stable but reacts under intramolecular nucleophilic attack of the amino group at the isocyanide carbon atom with formation of complex [**6**]X. Starting from the hexafluorophosphate salt [**5**]PF_6 and using HBr for the hydrolysis we obtained [**6**]X with both types of anions present. Due to this situation, compound [**6**]X was not isolated and purified. The crude reaction product was characterized instead. The MALDI mass spectrum showed a peak at m/z = 709 amu, which can be assigned to the cation [**6**]$^+$ or the corresponding complex with a non-cyclized 2-aminoethyl isocyanide ligand. However, the expected intramolecular cyclization of the 2-aminoethyl isocyanide ligand can be concluded from the absence of the absorption for the isocyanide stretching mode in the IR spectrum of [**6**]X. The resonance for the carbene carbon atom of the formed NH,NH-stabilized carbene ligand was observed at δ = 218 ppm [t, ^2J(P,C) = 24.6 Hz] in the $^{13}C\{^1H\}$ NMR spectrum of [**6**]X (in [D_6]dmso).

After removing the methanol solvent used for the generation of [**6**]X, the solid residue was dissolved in thf. Ring closure to give the [11]ane-P_2C^{NHC} macrocycle was accomplished by deprotonation of the nitrogen atoms of the NH,NH-stabilized carbene ligand in $[\mathbf{6}]^+$ with KO*t*Bu (Scheme 1). Ring-closure was completed within 24 h. After anion exchange with NH_4PF_6, compound [**1**]PF_6 was obtained in an overall yield of 74%.

Formation of the [11]ane-P_2C^{NHC} macrocycle can be concluded from the MALDI mass spectrum, which showed the formal loss of 2 equiv. of HF from $[\mathbf{6}]^+$ and formation of cation $[\mathbf{1}]^+$ with a peak at m/z = 669. The characteristic resonance for the carbene carbon atom was detected at δ = 222.3 ppm [t, ^2J(P,C) = 31.0 Hz] in the $^{13}C\{^1H\}$ NMR spectrum, which falls in the range described for $[Fe(\eta^5\text{-}C_5H_5)(NHC)L_2]^+$ cations.[15] In addition, the signal for the phosphorus atoms of the macrocyclic ligand was observed in the $^{31}P\{^1H\}$ NMR spectrum at δ = 89.8 ppm, and only one signal for the two remaining fluorine atoms was found in the ^{19}F NMR spectrum at δ = –96.1 ppm.

An X-ray diffraction analysis, performed with a crystal of the composition [**1**]PF_6·MeOH (obtained by evaporation of the solvent from a methanolic solution of [**1**]PF_6) unambiguously confirmed the formation of the [11]ane-P_2C^{NHC} macrocycle (Figure 2). Bond lengths and angles fall in the range described for related iron(II)–NHC complexes.[15,16]

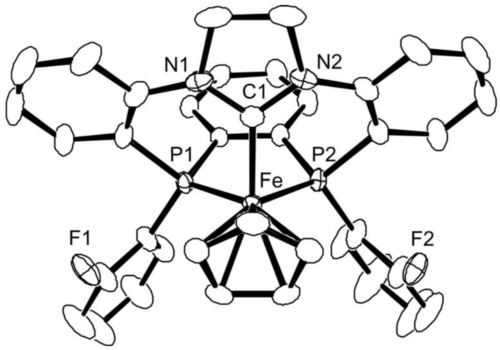

Figure 2. Structure of the cation $[\mathbf{1}]^+$ in [**1**]PF_6·MeOH (with hydrogen atoms omitted for clarity). Selected bond lengths [Å] and angles [°]: Fe–P1 2.1277(6), Fe–P2 2.1282(6), Fe–C1 1.895(2), range Fe–C_{Cp} 2.088(2)–2.097(2), N1–C1 1.363(3), N2–C1 1.361(3); P1–Fe–P2 88.13(2), P1–Fe–C1 86.90(7), P2–Fe–C1 85.99(7), N1–C1–N2 106.8(2).

Compared to transition metal complexes bearing the [11]ane-P_2C^{NHC} macrocycle (M = Re,[4] Mn,[4] Ru[5]), equivalent M–$C_{carbene}$ and M–P bond lengths reach a minimum in complex cation $[\mathbf{1}]^+$ (Table 1) caused by the small iron(II) cation. This geometric situation actually facilitates the formation of the macrocycle. The short Fe–$C_{carbene}$ and Fe–P bond lengths in $[\mathbf{1}]^+$ and presumably in the precursor complex cation $[\mathbf{6}]^+$ force the phosphane and carbene ligands closer together, thereby facilitating the formation of the two $N_{carbene}$–$C_{phosphane}$ bonds. Consequently, macrocycle formation $[\mathbf{6}]^+ \rightarrow [\mathbf{1}]^+$ proceeds with good yield in 1 d, whereas the same reaction takes much longer at the $\{Re(CO)\}^+$ (5 d) or $\{Mn(CO)_3\}^+$ (3 d) templates.

Table 1. Selected bond lengths and angles for complexes of the [11]ane-P_2C^{NHC} macrocycle.

Metal template	M–C_{NHC} [Å]	M–P [Å]	P–M–P [°]	Ref.
$\{Re(CO)_3\}^+$	2.172(4)	2.3957(13) 2.3985(14)	81.58(5)	[4b]
$\{Mn(CO)_3\}^+$	2.033(2)	2.2469(7) 2.2386(8)	84.64(2)	[4b]
$\{Ru(Cp)\}^+$	1.996(5)	2.2221(12) 2.2257(12)	84.89(4)	[5b]
$\{Fe(Cp)\}^+$	1.895(2)	2.1277(6) 2.1282(6)	88.13(2)	this study

Conclusion

We have demonstrated that the [11]ane-P_2C^{NHC} macrocycle can be generated at the low-cost $[Fe(\eta^5\text{-}C_5H_5)]^+$ template. In addition, short Fe–$C_{carbene}$ and Fe–P bond lengths at the iron(II) template facilitate the macrocycle formation compared to $\{Re(CO)_3\}^+$ and $\{Mn(CO)_3\}^+$ templates containing larger metal atoms. Given the current resurgence in iron-catalyzed reactions,[17,18] we believe that water-stable compounds like [**1**]PF_6 will find useful applications in catalysis. In addition, related triphosphane macrocycles have been generated at and liberated from the $\{Fe(\eta^5\text{-}C_5H_5)\}^+$ template. Therefore, it appears feasible to liberate the [11]ane-P_2C^{NHC} macrocycle from the $\{Fe(\eta^5\text{-}C_5H_5)\}^+$ template under generation of a new type of neutral, *facially* coordinating 6π-electron donor ligand.

Experimental Section

General Remarks: *Caution! Azide compound 4 can decompose vigorously upon uncontrolled heating!* Complex $[Fe(\eta^5\text{-}C_5H_5)(PhMe)]PF_6$[9] and ligand **4**[11] were prepared according to published procedures. Diphosphane **2**[4a] was obtained as described for similar compounds by Kyba.[8] See Scheme 1 for assignment of NMR spectra for complexes [**5**]PF_6 and [**1**]PF_6. Consistent microanalytical data were difficult to obtain due to the presence of fluoride (PF_6^- and fluorinated phenyl groups) in all complexes.

Synthesis of [Fe(Cp)(2)(4)]PF_6 ([5]PF_6): A solution of $[Fe(\eta^5\text{-}C_5H_5)(\eta^6\text{-}PhMe)]PF_6$ (33 mg, 0.09 mmol) and diphosphane **2** (50 mg, 0.10 mmol) in acetonitrile (30 mL) was irradiated with a high-pressure mercury lamp at ambient temperature for 6 h. The reaction solution, presumably containing the diphosphane complex [**3**]PF_6, was then transferred to a 100 mL Schlenk flask, and the solvent was removed under reduced pressure. The resulting solid was dissolved in dichloromethane (20 mL), and isocyanide **4** (13 mg, 0.14 mmol) was added. The reaction mixture was stirred for 12 h, after which the solvent was removed under reduced pressure. The residue was dissolved in dichloromethane (1 mL). Addition of diethyl ether (10 mL) to this solution led to precipitation of [**5**]PF_6 as an orange solid. Yield: 77 mg (0.09 mmol, 95%). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.89–7.77 (m, 4 H, 2-H, 3-H), 7.81–7.71 (m, 2 H, 15-H), 7.71–7.61 (m, 2 H, 9-H), 7.59–7.45 (m, 2 H, 6-H), 7.49–7.33 (m, 2 H, 14-H), 7.45–7.32 (m, 2 H, 12-H), 7.44–7.26 (m, 2 H, 13-H), 7.25–7.09 (m, 2 H, 8-H), 6.88–6.71 (m, 2 H, 7-H), 4.72 (s, 5

H, Cp-H), 3.08 (t, ^3J(H,H) = 5.2 Hz, 2 H, 17-H), 3.00 (t, ^3J(H,H) = 5.2 Hz, 2 H, 18-H) ppm. ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ = 164.2 [t, ^2J(C,P) = 28.0 Hz, C-16], 162.4 [d, ^1J(C,F) = 246.5 Hz, C-11], 161.8 [dd, ^1J(C,F) = 251.5 Hz, ^2J(C,P) = 3.8 Hz, C-5], 141.3 (m, C-1), 134.2 (s, C-15), 134.1 (m, C-9), 133.1 (m, C-2, C-7), 132.4 (s, C-3), 132.0 (s, C-13), 125.2 (br. s, C-14), 124.9 (br. s, C-8), 121.5−120.1 (m, C-4, C10), 116.6 (s, C-6), 116.5 (s, C-12), 82.6 (s, Cp-C), 48.7 (s, C-18), 44.1 (s, C-17) ppm. ^{31}P{^{1}H} NMR (162 MHz, CDCl$_3$): δ = 84.2 (s, ligand **2**-P), –144.2 (sept, PF$_6$) ppm. ^{19}F NMR (376 MHz, CDCl$_3$): δ = –98.8 (Ar-F), –99.8 (Ar-F), –70 (d, PF$_6$) ppm. IR (KBr): $\tilde{\nu}$ = 2134 (CN), 2136 (N$_3$), 2099 (N$_3$) cm^{-1}. MALDI-MS (positive ions): *m*/*z* (%) = 735 (100) [M – PF$_6$]$^+$.

Synthesis of [Fe(η^5-C$_5$H$_5$)([11]ane-P$_2$C$^{\text{NHC}}$)]PF$_6$ ([1]PF$_6$): To a solution of [**5**]PF$_6$ (56 mg, 0.64 mmol) in methanol (20 mL) was added dropwise a solution of PPh$_3$ (17 mg, 0.64 mmol) in methanol (20 mL) over 4 h. After stirring for 12 h, water (0.5 mL) and two drops of concentrated aqueous HBr were added. The mixture was stirred for 2 d. Subsequently, all solvents were removed under reduced pressure. An IR spectrum of the crude material obtained showed no resonances for isocyanide or azide groups anymore, and a MALDI mass spectrum showed a peak for the cation [**6**]$^+$ at *m*/*z* = 709 amu. The resonance for the carbene carbon atom of [**6**]$^+$ was detected at δ = 218 ppm [t, ^2J(P,C) = 24.6 Hz]. These data confirm the formation of [**6**]X, which was, however, not isolated due to the presence of two different anions (PF$_6^-$ and Br$^-$). To the crude dry [**6**]X were added KO*t*Bu (28 mg, 0.25 mmol) and thf (20 mL). The mixture was stirred for 1 d. The thf was then removed under reduced pressure. The solid residue was dissolved in dichloromethane and filtered. Removal of the dichloromethane solvent gave an orange solid. This solid was dissolved in MeOH (5 mL), and a solution of NH$_4$PF$_6$ (32 mg, 0.20 mmol) in H$_2$O (1 mL) was added. After stirring for 1 min, complex [**1**]PF$_6$ was precipitated by addition of water (15 mL). The solid was collected by filtration and dried under reduced pressure to give [**1**]PF$_6$ as a yellow-orange powder. Yield: 38 mg (0.53 mmol, 82%). ^{1}H NMR (400 MHz, [D$_6$]-dmso): δ = 7.73–7.64 (m, 2 H, 3-H), 7.69–7.59 (m, 2 H, 7-H), 7.64–7.57 (m, 2 H, 9-H), 7.56–7.48 (m, 2 H, 2-H), 7.54–7.46 (m, 2 H, 13-H), 7.52–7.39 (m, 2 H, 6-H), 7.49–7.40 (m, 2 H, 12-H), 7.41–7.32 (m, 2 H, 14-H), 7.27–7.18 (m, 2 H, 8-H), 6.89–6.74 (m, 2 H, 15-H), 4.59 [dd, ^2J(H,H) = 7.0 Hz, ^3J(H,H) = 2.7 Hz, 2 H, NC*H*HC*H*HN], 4.19 (s, 5 H, Cp-H), 3.51 [dd, ^2J(H,H) = 7.0 Hz, ^3J(H,H) = 2.7 Hz, 2 H, NCH*H*CH*H*N] ppm. ^{13}C{^{1}H} NMR (100 MHz, [D$_6$]dmso): δ = 222.3 [t, ^2J(C,P) = 31 Hz, C-16], 162.3 [d, ^1J(C,F) = 246.9 Hz, C-5], 144.5 [t, ^2J(C,P) = 6.0 Hz, C-11], 143.4 (pseudo-t, C-1), 134.2 [d, ^3J(C,F) = 8.7 Hz, C-7], 132.8 (br. s, C-15), 132.8 (s, C-3), 131.7 (m, C-9), 131.2 (m, C-2), 129.3 (s, C-13), 125.7 (br. s, C-8), 124.6 (s, C-14), 120.2 (s, C-12), 119.4 (m, C-4), 116.8 [d, ^2J(C,F) = 22.9 Hz, C-6], 81.1 (s, Cp-C), 49.1 (s, NCH$_2$CH$_2$N) ppm. ^{31}P{^{1}H} NMR (162 MHz, [D$_6$]dmso): δ = 89.8 (s, [11]ane-P$_2$C$^{\text{NHC}}$-P), –144.2 (sept, PF$_6$) ppm. ^{19}F NMR (376 MHz, [D$_6$]dmso): δ = –96.1 ([11]ane-P$_2$C$^{\text{NHC}}$-F), –70 (d, PF$_6$) ppm. MALDI-MS: *m*/*z* (%) = 669 (100) [M – PF$_6$]$^+$.

Crystal Data for [1]PF$_6$·MeOH: C$_{39}$H$_{33}$F$_8$FeN$_2$OP$_3$, M = 846.43, monoclinic, $P2_1/n$, a = 13.5480(6), b = 15.6393(7), c = 18.6503(8) Å, β = 110.8560(10)°, V = 3692.7(3) Å^3, T = 153(2) K, λ = 0.71073 Å, Z = 4, ρ = 1.522 g cm^{-3}, μ = 0.614 mm^{-1}, 28638 data measured, 10658 unique data (R_{int} = 0.0258), R = 0.0479, wR = 0.1326 for 8212 contributing reflections [$I \geq 2\sigma(I)$], refinement against $|F^2|$ with anisotropic thermal parameters for all non-hydrogen atoms and hydrogen atoms on calculated positions (no hydrogen position were calculated for the methanol molecule in the asymmetric unit, which is also disordered). CCDC-771185 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

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[1] See, for instance: M. Ranocchiari, A. Mezzetti, *Organometallics* **2009**, *28*, 1286–1288.

[2] a) F. E. Hahn, M. C. Jahnke, *Angew. Chem.* **2008**, *120*, 3166–3216; *Angew. Chem. Int. Ed.* **2008**, *47*, 3122–3172; b) O. Kaufhold, F. E. Hahn, *Angew. Chem.* **2008**, *120*, 4122–4126; *Angew. Chem. Int. Ed.* **2008**, *47*, 4057–4061.

[3] P. C. J. Kamer, P. W. N. M. van Leeuwen, J. N. H. Reek, *Acc. Chem. Res.* **2001**, *34*, 895–904 and references cited therein.

[4] a) O. Kaufhold, A. Stasch, P. G. Edwards, F. E. Hahn, *Chem. Commun.* **2007**, 1822–1824; b) O. Kaufhold, A. Stasch, T. Pape, A. Hepp, P. G. Edwards, P. D. Newman, F. E. Hahn, *J. Am. Chem. Soc.* **2009**, *131*, 306–317.

[5] a) O. Kaufhold, A. Flores-Figueroa, T. Pape, F. E. Hahn, *Organometallics* **2009**, *28*, 896–901; b) A. Flores-Figueroa, O. Kaufhold, A. Hepp, R. Fröhlich, F. E. Hahn, *Organometallics* **2009**, *28*, 6362–6369.

[6] A. Flores-Figueroa, T. Pape, K.-O. Feldmann, F. E. Hahn, *Chem. Commun.* **2010**, *46*, 324–326.

[7] P. G. Edwards, K. M. Abdul Malik, L.-l. Ooi, A. J. Price, *Dalton Trans.* **2006**, 433–441.

[8] a) E. P. Kyba, S.-T. Liu, R. L. Harris, *Organometallics* **1983**, *2*, 1877–1879; b) E. P. Kyba, M. C. Kerby, S. P. Rines, *Organometallics* **1986**, *5*, 1189–1194.

[9] M. Lautens (Ed.), *Science of Synthesis*, Georg Thieme Verlag, *Stuttgart* **2001**, vol, 1, pp. 749–750.

[10] T. Albers, P. G. Edwards, *Chem. Commun.* **2007**, 858–860.

[11] F. E. Hahn, V. Langenhahn, T. Pape, *Chem. Commun.* **2005**, 5390–5392.

[12] a) F. E. Hahn, M. Tamm, *J. Organomet. Chem.* **1993**, *456*, C11–C14; b) F. E. Hahn, M. Tamm, T. Lügger, *Angew. Chem.* **1994**, *106*, 1419–1421; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1356–1359; c) F. E. Hahn, M. Tamm, *Organometallics* **1995**, *14*, 2597–2600; d) M. Tamm, F. E. Hahn, *Coord. Chem. Rev.* **1999**, *182*, 175–209.

[13] A. Flores-Figueroa, O. Kaufhold, K.-O. Feldmann, F. E. Hahn, *Dalton Trans.* **2009**, 9334–9342.

[14] a) F. E. Hahn, V. Langenhahn, N. Meier, T. Lügger, W. P. Fehlhammer, *Chem. Eur. J.* **2003**, *9*, 704–712; b) F. E. Hahn, C. García Plumed, M. Münder, T. Lügger, *Chem. Eur. J.* **2004**, *10*, 6285–6293; c) F. E. Hahn, V. Langenhahn, T. Lügger, T. Pape, D. Le Van, *Angew. Chem.* **2005**, *117*, 3825–3829; *Angew. Chem. Int. Ed.* **2005**, *44*, 3759–3763.

[15] P. Buchgraber, L. Toupet, V. Guerchais, *Organometallics* **2003**, *22*, 5144–5147.

[16] a) A. A. Danopoulos, D. Pugh, H. Smith, J. Saßmannshausen, *Chem. Eur. J.* **2009**, *15*, 5491–5502; b) B. Liu, Q. Xia, W. Chen, *Angew. Chem.* **2009**, *121*, 5621−5624; *Angew. Chem. Int. Ed.* **2009**, *48*, 5513–5516.

[17] C. Bolm, *Nature Chem.* **2009**, *1*, 420.

[18] a) R. H. Morris, *Chem. Soc. Rev.* **2009**, *38*, 2282–2291; b) L. Ackermann, R. Vicente, A. R. Kapdi, *Angew. Chem.* **2009**, *121*, 9976–10011; *Angew. Chem. Int. Ed.* **2009**, *48*, 9792−9826.

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