

Synthesis and structure of dipalladium complexes containing cyclooctatetraene and bicyclooctatrienyl ligands

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Received 6 September 2007; received in revised form 2 October 2007; accepted 2 October 2007

Available online 9 October 2007

Abstract

The reaction of a substitutionally labile dipalladium(I) complex $[\text{Pd}_2(\text{CH}_3\text{CN})_6][\text{BF}_4]_2$ (**1**) with 1,3,5,7-cyclooctatetraene (COT) in acetonitrile afforded $[\text{Pd}_2(\mu-\eta^3:\eta^3\text{-C}_8\text{H}_8)(\text{CH}_3\text{CN})_4][\text{BF}_4]_2$ (**2**). The reaction of **2** with COT in acetonitrile yielded $[\text{Pd}_2(\mu-\eta^3:\eta^3\text{-C}_{16}\text{H}_{16})(\text{CH}_3\text{CN})_4][\text{BF}_4]_2$ (**4**), where COT is dimerized via C–C bond formation. Complexes **2** and **4** were structurally characterized by X-ray diffraction analyses. In dichloromethane, COT isomerized to styrene at room temperature in the presence of catalytic amount of **1**, **2**, or **4**.

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Keywords: Palladium; Cyclooctatetraene; Dinuclear complexes

1. Introduction

Coordination behavior of 1,3,5,7-cyclooctatetraene (COT) has been intensively studied, since COT shows diverse binding modes to mono-, di-, and trinuclear metal moieties. In organopalladium chemistry, coordination of COT to Pd^{II} or Pd^0 has been well characterized (Scheme 1) [1–4]. The COT ligand in a “tub” conformation binds a mononuclear Pd^{II} center through a bidentate manner (Scheme 1, A). On the other hand, it is known that the COT ligand in a nearly planar conformation coordinates to Pd^0L_2 moieties (Scheme 1, B and C). The coordination behavior of COT to a Pd–Pd bonded moiety has also been examined in our group. Recently, we reported that the COT ligand coordinates to a triangular tripalladium core (Scheme 1, D) or a rhombic tetrapalladium core in face-capping manners [5,6]. Thus, COT acts as the ligand for the metal sheet sandwich complexes [7]. Herein, we wish to report that the dinuclear addition of a $[\text{Pd}_2\text{L}_n]^{2+}$ moiety

to COT (1 equiv.) takes place to yield a $\mu-\eta^3:\eta^3\text{-COT}$ half-sandwich complex $[\text{Pd}_2(\mu-\eta^3:\eta^3\text{-C}_8\text{H}_8)(\text{CH}_3\text{CN})_4][\text{BF}_4]_2$ (**2**). Complex **2** reacts with COT to give the bicyclooctatrienyl dipalladium complex $[\text{Pd}_2(\mu-\eta^3:\eta^3\text{-C}_{16}\text{H}_{16})(\text{CH}_3\text{CN})_4][\text{BF}_4]_2$ (**4**).

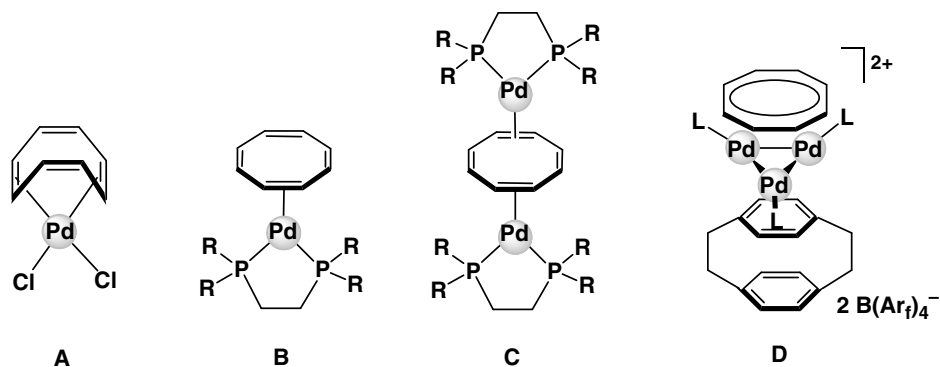
2. Results and discussion

The reaction of a homoleptic acetonitrile dipalladium(I) complex $[\text{Pd}_2(\text{CH}_3\text{CN})_6][\text{BF}_4]_2$ (**1**) [8] with COT (1 equiv.) in acetonitrile afforded $[\text{Pd}_2(\mu-\eta^3:\eta^3\text{-C}_8\text{H}_8)(\text{CH}_3\text{CN})_4][\text{BF}_4]_2$ (**2**) in 92% isolated yield as a mixture of two isomers (isomer ratio = 72/28) (Eq. (1)). ^1H NMR spectra of each isomer of **2** in acetone- d_6 at -90°C showed eight resonances for the COT protons. Upon warming the sample, all of the signals broadened, and at 25°C , one very broad signal was observed at $\delta = 5.5$ ppm.

A single crystal of **2** suitable to X-ray diffraction analysis was obtained by recrystallization from CH_3CN /toluene. The molecular structure of **2** was shown in Fig. 1. Two Pd atoms are bound to the same face of the COT ligand. The distance between two Pd atoms (3.57 Å) is out of the range of normal Pd–Pd bonds. The coordination mode of

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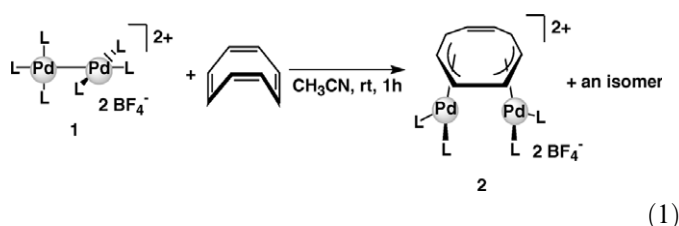
E-mail address: tetsu@chem.eng.osaka-u.ac.jp (T. Murahashi).



Scheme 1.

the COT ligand is the bi- η^3 -allyl mode, while the structure is C_1 symmetric (Figs. 1 and 2), being consistent with the ^1H NMR signal pattern observed at -90°C . It was previously reported that the related bi- η^3 -allyl complex $[(\mu\text{-}\eta^3\text{-}\eta^3\text{-RCH=CH-CH=CH-CHR})\text{Pd}_2(\text{CH}_3\text{CN})_4][\text{BF}_4]_2$ (**3**, R = Ph or *t*-Bu) is formed by the reaction of complex **1** and 1,6-disubstituted 1,3,5-trienes, where two η^3 -allyl moieties are chemically equivalent with each other according to the NMR analyses as well as the X-ray structure analyses [9–11]. The unsymmetrical bi- η^3 -allyl structure in complex **2** is probably due to the close proximity of the two $[\text{Pd}(\text{CH}_3\text{CN})_2]$ moieties. It should be mentioned that the C_8 ring of the COT ligand in **2** creases at $\text{C}2\cdots\text{C}5$ (Fig. 2), although the COT ligand in **2** may be attributable to the COT^{2-} ligand. Furthermore, there is the bond length alternation at the uncoordinated region ($\text{C}6\text{--}\text{C}7\text{--}\text{C}8\text{--}\text{C}1$) (1.47(1) Å/1.33(1) Å/1.48(1) Å). These suggest the electronic delocalization over the C_8 ring of the COT^{2-} ligand is not so large. The structure of another isomer is elusive at

this stage. Since complex **3** was formed from **1** and trienes as a mixture of *syn*- and *anti*-dinuclear addition products [10], a possible structure of another isomer of **2** is the *anti*-adduct, in which each Pd atom is bound to an opposite face of the C_8 ring.



When complex **2** was treated with COT (excess) in CD_3CN , the bicyclooctatrienyl complex **4** was formed almost quantitatively in the NMR monitoring experiment (Eq. (2)). Complex **4** was isolated in 65% yield after recrystallization from CH_3CN /toluene. A single crystal suitable to the X-ray diffraction analysis was obtained by recrystallization from CH_3CN / Et_2O . The molecular structure of **4** is shown in Fig. 3. In complex **4**, COT was dimerized via the formation of $\text{C}6\text{--}\text{C}6'$ bond, and each cyclooctatrienyl ring coordinates to a palladium moiety in a η^3 -coordination mode. The relative position of the η^3 -coordinated $[\text{PdL}_2]$ moiety and the $-\text{C}_8\text{H}_8[\text{PdL}_2]$ substituent with respect to a cyclooctatrienyl ring is *syn*. This is reasonably understood by the *syn*-insertion of an olefin part of the COT to the $\text{Pd}\text{--}\text{C}\text{--}\sigma$ bond of the σ -allyl complex which may be formed by allyl $\pi\text{--}\sigma$ transformation of one of the η^3 -allyl palladium moieties of **2**. Several bicyclooctatrienyl transition metal complexes are known to be prepared from COT [12–14].

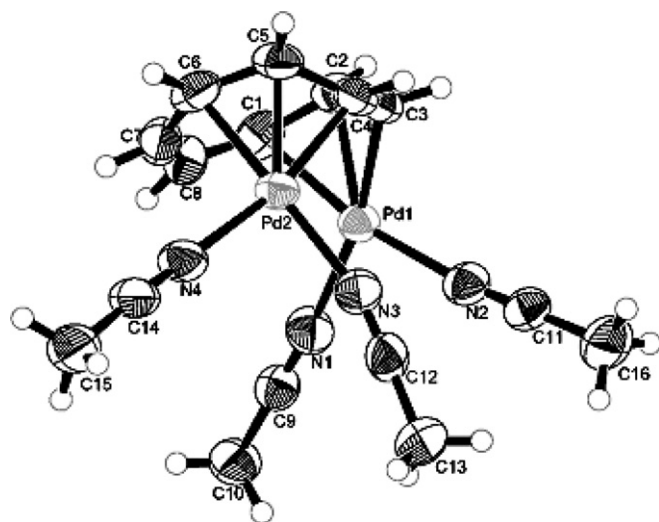
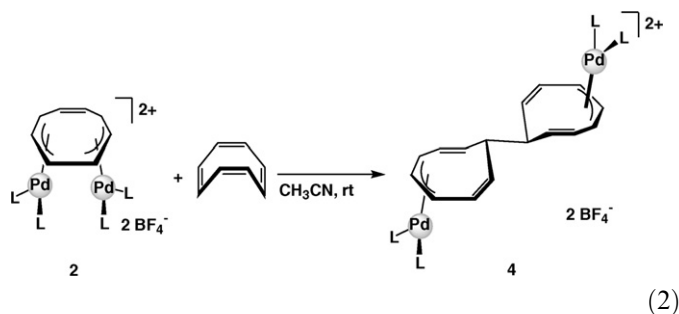


Fig. 1. ORTEP drawing of $[(\mu\text{-}\eta^3\text{-}\eta^3\text{-C}_8\text{H}_8)\text{Pd}_2(\text{CH}_3\text{CN})_4][\text{BF}_4]_2$ (**2**) (50% probability ellipsoids, BF_4^- anions were omitted for clarity). Selected bond lengths (Å): Pd1–C1 2.162(9), Pd1–C2 2.109(8), Pd1–C3 2.132(8), Pd2–C4 2.148(8), Pd2–C5 2.106(8), Pd2–C6 2.155(8), Pd1–N1 2.102(7), Pd1–N2 2.116(8), Pd2–N3 2.073(8), Pd2–N4 2.120(7), C1–C2 1.41(1), C2–C3 1.43(1), C3–C4, 1.48(1), C4–C5 1.43(1), C5–C6 1.41(1), C6–C7 1.47(1), C7–C8 1.33(1), C8–C1 1.48(1).

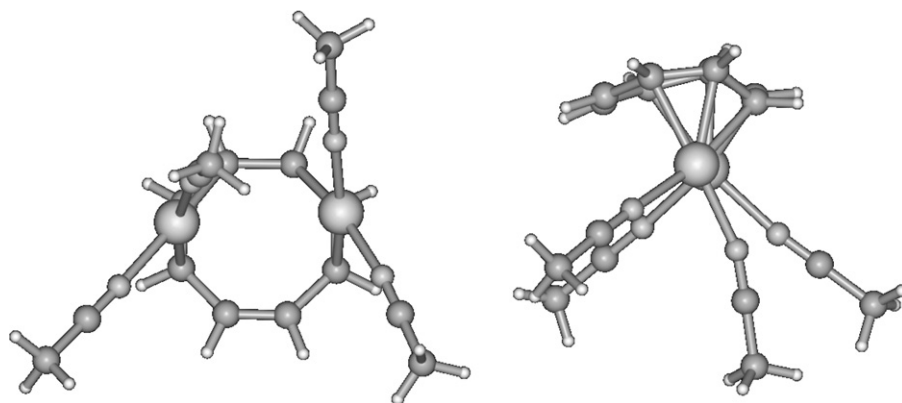


Fig. 2. Bottom and side views of complex 2.

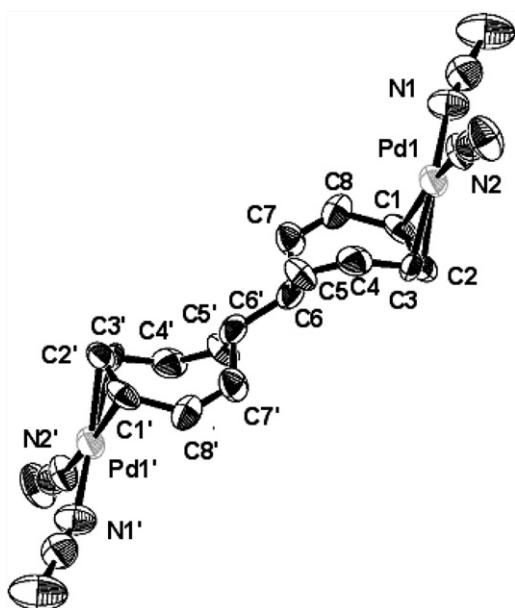
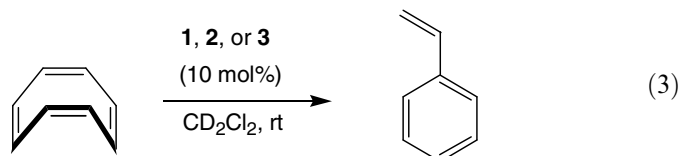


Fig. 3. ORTEP drawing of $[(\mu\text{-}\eta^3\text{-}\eta^3\text{-C}_{16}\text{H}_{16})\text{Pd}_2(\text{CH}_3\text{CN})_4][\text{BF}_4]_2$ (**4**) (50% probability ellipsoids, BF_4^- anions were omitted for clarity). Selected bond lengths (Å): Pd1–C1 2.12(2), Pd1–C2 2.12(2), Pd1–C3 2.15(2), Pd1–N1 2.11(1), Pd1–N2 2.09(2), C1–C2 1.40(3), C2–C3 1.42(3), C3–C4 1.45(3), C4–C5 1.35(2), C5–C6 1.55(2), C6–C6' 1.54(3).

When the reaction of **1** with COT was carried out in CD_2Cl_2 , the formation of **2** or **3** was not observed. Instead, gradual isomerization of COT to styrene proceeded at room temperature. The isomerization was catalyzed by 10 mol% of **1** (84% after 144 h), **2** (87% after 120 h), or even **4** (75% after 80 h), while mononuclear cationic η^3 -allyl palladium complex $[\text{Pd}(\eta^3\text{-C}_3\text{H}_5)(\text{CH}_3\text{CN})_2][\text{BF}_4]$, mononuclear dicationic complex $[\text{Pd}(\text{CH}_3\text{CN})_4][\text{BF}_4]_2$, and $\text{Pd}_2(\text{dba})_3$ did not catalyze the isomerization from COT to styrene in the same condition. It is known that isomerization of COT to styrene proceeds at high temperature [15]. Furthermore, Cope and Burg reported isomerization of halocyclooctatetraene to 2-halostyrene at 100 °C in high yield [16], where bicyclo[4.2.0]octatriene (**A**) is the intermediate [17–

19]. In the reaction shown in Eq. (3), bicyclo[4.2.0]octatriene (**A**) is presumably formed by a catalytic action of a dipalladium species. A possible catalytic cycle is shown in Fig. 4. 1,2-Dipalladated cyclooctatriene (**B**) may be tautomerized with the bicyclo[4.2.0]octadiene (**C**) from which the transolefination [10] and Pd-promoted 1,3-hydrogen shift [20] may afford the bicyclo[4.2.0]octatriene (**A**).



In summary, it has been proven that a dinuclear addition of a $[\text{Pd}_2\text{L}_n]^{2+}$ moiety to COT proceeds in acetonitrile to afford the $\mu\text{-}\eta^3\text{:}\eta^3\text{-COT}$ dipalladium(II) complex. In the presence of excess COT, $\mu\text{-}\eta^3\text{:}\eta^3\text{-C}_{16}\text{H}_{16}$ dipalladium(II) complex is eventually formed. In dichloromethane, the dipalladium complexes catalyze the isomerization of COT to styrene at room temperature.

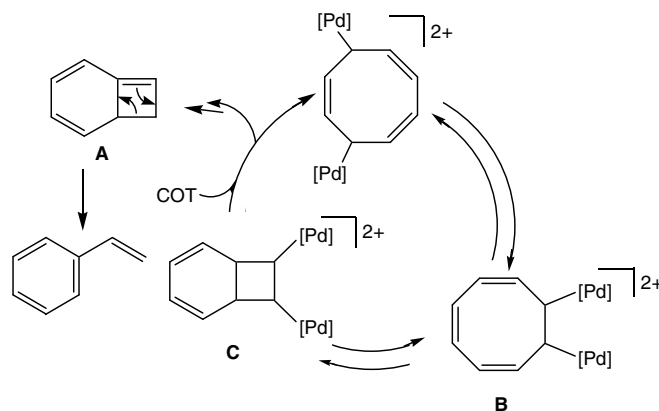


Fig. 4. A possible cycle for the isomerization of COT to styrene at room temperature.

3. Experimental

3.1. General consideration

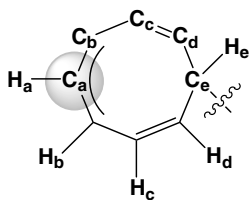
All manipulations were conducted under a nitrogen atmosphere using standard Schlenk or drybox techniques. ^1H and ^{13}C nuclear magnetic resonance spectra were recorded on JEOL GSX-270S and JEOL AL-400 spectrometers. Elemental analyses were performed at the Analytical Center, Faculty of Engineering, Osaka University. X-ray crystal data were collected by Rigaku RAXIS-RAPID Imaging Plate diffractometer. All solvents used in this work were distilled prior to use. Toluene was distilled from sodium benzophenone ketyl, CH_2Cl_2 , CH_3CN , CD_2Cl_2 , and CD_3CN from CaH_2 . All commercially available reagents were distilled and degassed prior to use.

3.2. Synthesis of $[\text{Pd}_2(\mu\text{-}\eta^3\text{:}\eta^3\text{-C}_8\text{H}_8)(\text{CH}_3\text{CN})_4][\text{BF}_4]_2$ (**2**)

To a CH_3CN solution of $[\text{Pd}_2(\text{CH}_3\text{CN})_6][\text{BF}_4]_2$ (**1**) (126 mg, 0.20 mmol) [8] was added COT (22.0 mg, 0.21 mmol), and the mixture was stirred for 1 h at room temperature. The reaction mixture was filtered and toluene was added to the filtrate. Crystallization at -20°C gave reddish orange microcrystals of **2** (121 mg, 92% yield). ^1H NMR (acetone- d_6 , -90°C) for **2**. For major isomer; $\delta = 6.20\text{--}5.90$ (m, 4H), 5.54 (m, 1H), 5.38 (m, 1H), 5.17 (m, 1H), 3.27 (br m, 1H), 2.64 (br s, 6H), 2.45 (br s, 6H). For minor isomer; $\delta = 6.25\text{--}5.85$ (m, 4H), 5.71 (m, 1H), 5.5 (overlap), 5.29 (m, 1H), 3.12 (br s, 1H). Anal. Calc. for $\text{C}_{16}\text{H}_{20}\text{N}_4\text{B}_2\text{F}_8\text{Pd}_2$: C, 29.35; H, 3.08; N, 8.56. Found: C, 29.10; H, 3.00; N, 8.40%.

3.3. Synthesis of $[\text{Pd}_2(\mu\text{-}\eta^3\text{:}\eta^3\text{-C}_{16}\text{H}_{16})(\text{CH}_3\text{CN})_4][\text{BF}_4]_2$ (**4**)

To a CH_3CN solution of $[\text{Pd}_2(\text{CH}_3\text{CN})_6][\text{BF}_4]_2$ (**1**) (126 mg, 0.20 mmol) was added COT (104 mg, 1.0 mmol), and the mixture was stirred for 14 h at room temperature. The reaction mixture was filtered and the benzene was added to the filtrate to give a pale yellow precipitate. Recrystallization from CH_3CN /toluene at -20°C gave yellow crystals of **4** (98 mg, 65% yield). ^1H NMR (CD_3CN , 25°C) for **4**: $\delta = 6.01$ (dd, $J = 10.5$ Hz, $J = 5.4$ Hz, H_c), 5.79 (dd, $J = 10.5$ Hz, $J = 7.0$ Hz, H_d), 5.73 (dd, $J = 8.6$ Hz, $J = 5.1$ Hz, H_b), 4.70 (t, $J = 8.6$ Hz, H_a), 2.43 (br m, H_e), 2.23 (s, CH_3CN). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_3CN) for **4**: $\delta = 137.5$ (s, C_d), 127.7 (s, C_c), 98.7 (s, C_e), 79.0 (s, C_b), 45.2 (s, C_a). Anal. Calc. for $\text{C}_{24}\text{H}_{28}\text{N}_4\text{B}_2\text{F}_8\text{Pd}_2$: C, 37.98; H, 3.72; N, 7.38. Found: C, 37.70; H, 3.58; N, 7.10%.



3.4. X-ray structure analyses of **2** and **4**

Crystal data for **2**: $\text{C}_{16}\text{H}_{20}\text{N}_4\text{B}_2\text{F}_8\text{Pd}_2$, $M = 654.77$, space group $P\bar{1}$ (no. 2), $a = 10.1953(4)$ Å, $b = 11.3646(4)$ Å, $c = 11.4885(7)$ Å, $\alpha = 68.468(5)^\circ$, $\beta = 73.328(5)^\circ$, $\gamma = 86.334(3)^\circ$, $V = 1184.9(1)$ Å³, $Z = 2$, $F(000) = 636$, $D_{\text{calc}} = 1.835$ g/cm³, $\mu(\text{Mo K}\alpha) = 15.91$ cm⁻¹, 289 variables refined with 4036 reflections collected at 273 K with $I > 3\sigma(I)$ to $R = 0.043$.

Crystal data for **4**: $\text{C}_{24}\text{H}_{28}\text{N}_4\text{B}_2\text{F}_8\text{Pd}_2$, $M = 758.92$, space group $P2_1/n$ (no. 14), $a = 6.7545(2)$ Å, $b = 10.130(1)$ Å, $c = 21.498(2)$ Å, $\beta = 97.970(4)^\circ$, $V = 1456.7(2)$ Å³, $Z = 2$, $F(000) = 748$, $D_{\text{calc}} = 1.730$ g/cm³, $\mu(\text{Mo K}\alpha) = 13.08$ cm⁻¹, 181 variables refined with 1345 reflections collected at 213 K with $I > 3\sigma(I)$ to $R = 0.080$.

Appendix A. Supplementary material

CCDC 662513 and 662514 contain the supplementary crystallographic data for **2** and **4**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2007.10.004](https://doi.org/10.1016/j.jorganchem.2007.10.004).

References

- [1] P.M. Maitlis, P. Espinet, M.J.H. Russell, in: G. Wilkinson, F.G.A. Stone, E.W. Abel (Eds.), *Comprehensive Organometallic Chemistry*, vol. 6, Pergamon Press, New York, 1982 (Chapter 38.9).
- [2] H.P. Fritz, H. Keller, *Chem. Ber.* 95 (1962) 158.
- [3] (a) H. Frye, K. Ernest, J. Viebrock, *Z. Naturforsch. B* 20 (1965) 269; (b) D.J. Mabbott, B.E. Mann, P.M. Maitlis, *J. Chem. Soc., Dalton Trans.* (1977) 294; (c) N.C. Baenziger, C.V. Goebel, T. Berg, J.R. Doyle, *Acta Crystallogr., Sect. B* 34 (1978) 1340.
- [4] F. Schager, K.-J. Haack, R. Mynott, A. Rufinska, K.-R. Pörschke, *Organometallics* 17 (1998) 807.
- [5] T. Murahashi, N. Kato, T. Uemura, H. Kurosawa, *Angew. Chem., Int. Ed.* 46 (2007) 3509.
- [6] T. Murahashi, M. Fujimoto, Y. Kawabata, R. Inoue, S. Ogoshi, H. Kurosawa, *Angew. Chem., Int. Ed.* 46 (2007) 5440.
- [7] T. Murahashi, M. Fujimoto, M. Oka, Y. Hashimoto, T. Uemura, Y. Tatsumi, Y. Nakao, A. Ikeda, S. Sakaki, H. Kurosawa, *Science* 313 (2006) 1104.
- [8] T. Murahashi, T. Nagai, T. Okuno, T. Matsutani, H. Kurosawa, *Chem. Commun.* (2000) 1689.
- [9] T. Murahashi, T. Nagai, Y. Mino, E. Mochizuki, Y. Kai, H. Kurosawa, *J. Am. Chem. Soc.* 123 (2001) 6927.
- [10] T. Murahashi, H. Nakashima, T. Nagai, Y. Mino, T. Okuno, M.A. Jalil, H. Kurosawa, *J. Am. Chem. Soc.* 128 (2006) 4377.
- [11] T. Murahashi, T. Nagai, H. Nakashima, S. Tomiyasu, H. Kurosawa, *Chem. Lett.* (2006) 754.
- [12] R.P. Aggarwal, N.G. Connelly, B.J. Dunne, M. Gilbert, A.G. Orpen, *J. Chem. Soc., Dalton Trans.* (1991) 1.
- [13] R. Goddard, S.A.R. Knox, R.F.D. Stansfield, F.G.A. Stone, M.J. Winter, P. Woodward, *J. Chem. Soc., Dalton Trans.* (1982) 147.
- [14] R. Goddard, P. Woodward, *J. Chem. Soc., Dalton Trans.* (1979) 661.

- [15] J. Stapersma, I.D.C. Roop, G.W. Klumpp, *Tetrahedron* 38 (1982) 2201.
- [16] A.C. Cope, M. Burg, *J. Am. Chem. Soc.* 74 (1952) 168.
- [17] R. Huisgen, W.E. Konz, *J. Am. Chem. Soc.* 92 (1970) 4102.
- [18] W.E. Konz, W. Hechtel, R. Huisgen, *J. Am. Chem. Soc.* 92 (1970) 4104.
- [19] R. Huisgen, W.E. Konz, G.E. Gream, *J. Am. Chem. Soc.* 92 (1970) 4105.
- [20] P.M. Maitlis, P. Espinet, M.J.H. Russell, in: G. Wilkinson, F.G.A. Stone, E.W. Abel (Eds.), *Comprehensive Organometallic Chemistry*, vol. 6, Pergamon Press, New York, 1982 (Chapter 38.7).