A Copper(I) Complex with Chelating 1,5-Hexadiene

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Studies on 1,5-hexadiene complexes of the d^{10} metals nickel(0), palladium(0), and copper(I) reveal significant variations in the coordination of the 1,5-hexadiene. Whereas nickel(0) and bulky monodentate ligands L form trigonal-planar complexes of type $LNi(R,S\text{-}\eta^2,\eta^2\text{-}C_6H_{10})$,[1,2] nickel(0) and smaller monodentate ligands L give tetrahedral complexes of the type $L_2Ni(R,R/S,S\text{-}\eta^2,\eta^2\text{-}C_6H_{10})$ as a pair of enantiomers.[3] With chelating donor ligands and 1,5-hexadiene as a *chelating* ligand,[4] tetrahedral nickel(0) complexes $(R_2PC_2H_4PR_2)Ni(R,R/S,S\text{-}\eta^2,\eta^2\text{-}C_6H_{10})$ (pair of enantiomers)[3] and $(RN{=}CHCH{=}NR)Ni(R,S\text{-}\eta^2,\eta^2\text{-}C_6H_{10})$[5] with different local symmetries[2] of the diene ligand have been observed. In contrast, mononuclear palladium(0) appears to form only trigonal-planar enantiomeric complexes of type $(R_2PC_2H_4PR_2)Pd(R/S\text{-}\eta^2\text{-}C_6H_{10})$. These are fluxional complexes and exchange coordinated and uncoordinated double bonds via a $(R_2PC_2H_4PR_2)Pd(R,R/S,S\text{-}\eta^2,\eta^2\text{-}C_6H_{10})$ transition state.[6]

Because of the variety of coordination modes encountered for 1,5-hexadiene bound to nickel(0) or palladium(0), we were interested in discovering whether copper(I) would also form a complex with a chelating 1,5-hexadiene ligand and in establishing what the local symmetry of the coordination would be. Until now, acyclic dienes have only been found to coordinate to copper(I) in a bridging fashion.[7] Here we report a copper(I) trifluoromethanesulfonate complex with a chelating, $R,R/S,S\text{-}\eta^2,\eta^2$-bonded 1,5-hexadiene ligand exhibiting C_2 symmetry.

The starting material for the synthesis of the 1,5-hexadiene complex was the toluene copper(I) trifluoromethanesulfonate complex, $Cu(OSO_2CF_3)\cdot{}^1/_2C_6H_5CH_3$ (**1**),[8,9] which was prepared similarly to the benzene derivative $Cu(OSO_2CF_3)\cdot{}^1/_2C_6H_6$[10] by the stoichiometric reaction of Cu_2O with trifluoromethanesulfonic anhydride in toluene at 0 °C. Complex **1** is the preferred starting material, since it is prepared more easily than the benzene derivative, avoids the necessity of using boiling benzene as solvent, and is very soluble in toluene at low temperatures. Although **1** appears to be less stable than the benzene analogue, the isolated complex as well as its toluene solution may be stored at 20 °C. As for the benzene complex,[8,10] solid **1** presumably consists of dinuclear moieties with copper ions bound to different sides of a bridging toluene ligand.

When a solution of **1** (10 mmol of Cu) in a mixture of toluene (3 mL) and 1,5-hexadiene (2 mL) is cooled from 0 to −78 °C, (1,5-hexadiene)copper(I) trifluoromethanesulfonate (**2**) separates out (eq 1). After recrystallization from toluene, washing with

$$\underset{\mathbf{1}}{Cu(OSO_2CF_3)\cdot{}^1/_2C_6H_5CH_3} \xrightarrow{\text{1,5-hexadiene/toluene}} \underset{\mathbf{2}}{(R,R/S,S\text{-}\eta^2,\eta^2\text{-}C_6H_{10})Cu(OSO_2CF_3)} \quad (1)$$

cold pentane, and drying under vacuum, large white needles of **2** are isolated in 42% yield (1.24 g).[11] Solid **2** (mp 71 °C) is stable at room temperature in an inert atmosphere but rapidly decomposes when exposed to air. It has not been possible to vaporize the compound in the mass spectrometer. The compound dissolves well in toluene, CH_2Cl_2, and diethyl ether without discernible displacement of the 1,5-hexadiene ligand. However, THF, pyridine, and HMPTA readily displace the diene ligand in **2** when added to the solutions mentioned above (^1H NMR).

Several displacement reactions with alkenes were undertaken in order to determine the relative stability of the coordination of 1,5-hexadiene to the copper(I) center. A mixture of **2** and 1,5-hexadiene dissolved in CD_2Cl_2 exhibits in the ^1H NMR spectrum (200 MHz) at −80 °C only one set of 1,5-hexadiene signals. Thus a rapid exchange of 1,5-hexadiene ligands and free substrate has to be assumed to proceed even at low temperatures. Addition of 1,5-cyclooctadiene (cod) in slight excess to an ethereal solution of **2** leads to the displacement of hexadiene and formation of $[Cu(cod)_2]SO_3CF_3$;[10] the opposite reaction is not observed. Obviously, 1,5-hexadiene is less strongly coordinated to copper(I) than cod. This can also be deduced from the fact that in **2** the triflate ligand is coordinated to the copper atom, whereas cod forms the ion $[Cu(cod)_2]^+$. A 1,6-heptadiene derivative of stoichiometry $(C_7H_{12})Cu(OSO_2CF_3)$ (**3**)[12] can be obtained by a synthesis similar to that for **2**. The binding mode of the diene ligand has not yet been established for this compound. When 1,5-hexadiene is added to an ethereal or toluene solution of the 1,6-heptadiene derivative **3**, the latter is converted into the 1,5-hexadiene complex **2**. These displacement reactions show that

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(1) L = $(c\text{-}C_6H_{11})_3P$, iPr_3P, $(2,6\text{-}Me_2C_6H_3O)_3P$: (a) Henc, B.; Jolly, P. W.; Salz, R.; Stobbe, S.; Wilke, G.; Benn, R.; Mynott, R.; Seevogel, K.; Goddard, R.; Krüger, C. *J. Organomet. Chem.* **1980**, *191*, 449. (b) Michaelis, S. Dissertation, Universität Bochum, 1991. Michaelis, S.; Pörschke, K.-R. Unpublished results.

(2) The notations *R* and *S* refer to the configurations of the β-C atoms of terminally coordinated double bonds, which are asymmetric due to the coordination of the alkene to the metal center (Paiaro, G. *Organomet. Chem. Rev., Sect. A* **1970**, *6*, 319). For *chelating α,ω-dienes* the stereomers *R,S*, *R,R*, and *S,S* are conceivable, of which, however, generally only the "meso-form" (*R,S*) or the racemate (*R,R/S,S*) is encountered for a certain complex. The *R,S* mode implies a C_s-symmetrical, "U-shaped" coordination of the diene to the metal center, whereas in the *R,R/S,S* conformers the diene ligand is of local C_2 symmetry with a "zigzag" shape.

(3) Mynott, R.; Pörschke, K.-R.; Lutz, F.; Krüger, C. Manuscript in preparation.

(4) Besides the complexes with chelating 1,5-hexadiene, mononuclear complexes with η^2-bonded and dinuclear complexes with $\mu\text{-}\eta^2,\eta^2$-bonded 1,5-hexadiene ligands are known for nickel(0), as for palladium(0): Pörschke, K.-R.; Pluta, C.; Proft, B.; Lutz, F.; Krüger, C. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1992**, *47*.

(5) Bonrath, W.; Pörschke, K.-R.; Michaelis, S. *Angew. Chem.* **1990**, *102*, 295; *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 298.

(6) Krause, J.; Bonrath, W.; Pörschke, K.-R. *Organometallics* **1992**, *11*, 1158.

(7) (a) Butadiene: Hendra, P. J.; Powell, D. B. *Spectrochim. Acta* **1962**, *18*, 1195. Cook, B. W.; Miller, R. G. J.; Todd, P. F. *J. Organomet. Chem.* **1969**, *19*, 421. (b) Other conjugated dienes: Håkansson, M. Dissertation, University of Göteborg, 1990. Håkansson, M.; Jagner, S.; Walther, D. *Organometallics* **1991**, *10*, 1317. (c) 1,4-Pentadiene: See ref 7b. (d) 1,5-Hexadiene: See ref 13. Oliinik, V. V.; Zavalii, P. Yu.; Mys'kiv, M. G.; Fundamenskii, V. S. *Kristallografiya* **1986**, *31*, 284; *Sov. Phys.—Crystallogr. (Engl. Transl.)* **1986**, *31*, 168; *Chem. Abstr.* **1986**, *104*, 234742m. (e) 1,7-Octadiene: Håkansson, M.; Wettström, K.; Jagner, S. *J. Organomet. Chem.* **1991**, *421*, 347.

(8) The compound has been prepared previously but not isolated: Dines, M. B.; Bird, P. H. *J. Chem. Soc., Chem. Commun.* **1973**, 12.

(9) **1**: To a suspension of Cu_2O (357 mg, 2.5 mmol) in toluene (3 mL) is added $(CF_3SO_2)_2O$ (1.7 g, 6 mmol) at 0 °C. Upon stirring (4 h), the oxide dissolves, the red color disappears, and some product precipitates. This reaction mixture may be used for further reactions. Isolation of pure **1** is achieved by dissolving the precipitate in additional toluene (10 mL) at 20 °C, filtration through a capillary, and cooling the clear solution to −78 °C, whereupon the product separates. Recrystallization from toluene affords white crystals, which are washed with small portions of cold pentane and dried under vacuum at −30 °C. The yield (830 mg, 1.60 mmol) is low (32%) due to the high solubility of the compound, also at low temperature. Anal. Calcd for $C_9H_8Cu_2F_6O_6S_2$ (M_r = 517.4): C, 20.89; H, 1.56; Cu, 24.56. Found: C, 20.79; H, 1.58; Cu, 24.60.

(10) Salomon, R. G.; Kochi, J. K. *J. Chem. Soc., Chem. Commun.* **1972**, 559; *J. Am. Chem. Soc.* **1973**, *95*, 1889.

(11) **2**: Anal. Calcd for $C_7H_{10}CuF_3O_3S$ (M_r = 294.8): C, 28.52; H, 3.42; Cu, 21.56. Found: C, 28.54, H, 3.45; Cu, 21.45. Synthesis and spectroscopic characterization are as described in the text.

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the chelating coordination of 1,5-hexadiene to copper(I) is intermediate between those of 1,6-heptadiene (weaker) and cod (stronger).

In the IR spectrum of **2** the $=$C—H stretching modes of the coordinated olefinic double bonds ($\nu(=CH_2)_{sym,as}$ 3080, 2990 cm^{-1}) are essentially unchanged as compared to those of free 1,5-hexadiene.[13] A C$=$C stretching vibration band found at 1580 cm^{-1} is discernibly shifted to lower wavenumbers as compared to that of the free substrate (1640 cm^{-1}). The olefinic wagging vibration $\rho(=CH_2)$ appears at 940 cm^{-1} and is shifted to higher wavenumbers relative to the free substrate band (910 cm^{-1}), as is expected.[14]

In the ^{1}H NMR spectrum (400 MHz, CD_2Cl_2) of **2** at 27 °C, the signals of the olefinic protons [δ 5.96 (–CH$=$), 5.19 ($=CH_EH$), 5.07 ($=CHH_Z$)] and the methylene protons (δ 2.42) are sharp and low-field-shifted to those of the free substrate (δ 5.81, 4.99, 4.92, 2.14); at −80 °C, these shifts are partially reversed (δ 5.90, 5.03, 4.96, 2.35) and the methylene signal is broad. In the ^{13}C NMR spectrum (50.3 MHz, CD_2Cl_2, 27 °C), three sharp 1,5-hexadiene signals are observed [δ 130.4 ($=$CH–), 104.6 ($H_2C=$), 36.1 (–CH_2–)], of which the olefinic resonances are shifted to high field as compared to those of free 1,5-hexadiene (δ 138.4, 114.7, 33.5).

The observation of only *one* ^{1}H methylene signal, its splitting pattern (at 27 °C), and temperature dependence (broad at −80 °C) are of special interest. The signal observed at 27 °C is evidently identical at different magnetic fields (400 and 200 MHz) and for different solvents (CD_2Cl_2 and toluene-d_8). Thus the signal must be attributed either to equivalent protons or to the fact that nonequivalent protons are practically isochronous.

For a C_2- (or C_s-) symmetrically and *statically* bound 1,5-hexadiene ligand, the geminal methylene protons –CH_aH_b– should be different and for the –C_2H_4– fragment two temperature-independent resonances with an AA′BB′ proton coupling pattern are expected due to the chirality of the metal-bound $=$CH– carbon atoms. If these resonances are nearly isochronous, resolution of the signals might not be achieved but the spectra should be different at different magnetic fields, which is contrary to the observation. Since it is unlikely that the geminal methylene proton signals are exactly isochronous for various solvents, it can be deduced that the protons are equivalent due to a rapid exchange of the methylene proton sites; i.e., the bonding of the 1,5-hexadiene ligand in **2** is *fluxional* at 27 °C. When the temperature is lowered, the signal broadens due to slower exchange, but the limiting spectrum has not been obtained.

Such an exchange of proton sites might proceed by an intermolecular exchange of coordinated 1,5-hexadiene or an exchange of coordinated and trace amounts of free 1,5-hexadiene (see above). However, an *intramolecular* mechanism can also be envisaged by which, starting with, e.g., a chelating *R,R*- (C_2-symmetrical) η^2,η^2-bonded 1,5-hexadiene ligand, one Cu–alkene coordination bond is cleaved, the free alkene double bond is recoordinated from the reverse side, thereby passing through an *R,S*- (C_s-symmetrical) coordination mode of the 1,5-hexadiene ligand, and the process is repeated for the second Cu–alkene coordination bond, ending with an *S,S*-η^2,η^2-bonded 1,5-hexadiene ligand (Figure 1). In analogy to our findings for related nickel(0)[4] and palladium(0)[6] 1,5-hexadiene complexes, this mechanism seems to us to be most likely for the copper(I) complex **2** as well.

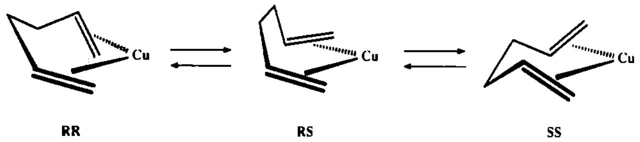

Figure 1. Proposed dynamics of the 1,5-hexadiene coordination in **2**.

Table I. Crystallographic Data for **2**

$C_7H_{10}CuF_3O_3S$
fw 294.8
$a = 6.843\ (1)$ Å
$b = 18.748\ (2)$ Å
$c = 8.905\ (1)$ Å
$\beta = 107.43\ (1)°$
$V = 1089.9$ Å^3
$Z = 4$
space group $P2_1/n$ (No. 14)
$T = 20$ °C
$\lambda = 0.710\,69$ Å
$\rho_{calcd} = 1.80$ g cm^{-3}
$\mu = 22.17$ cm^{-1}
transm coeff = 0.5354–0.7543
$R = 0.050$, $R_w = 0.060$[a]

[a] $R = (\sum||F_o| - |F_c||)/\sum|F_o|$; $R_w = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$.

Table II. Atomic Coordinates and Isotropic Thermal Parameters (Å^2) for **2**

atom	*x*	*y*	*z*	U_{eq}[a]
Cu	0.1067 (1)	0.1907 (1)	0.3798 (1)	0.052 (1)
S	0.3502 (2)	0.1676 (1)	0.7581 (1)	0.051 (1)
F1	0.3965 (7)	0.0459 (2)	0.6337 (5)	0.123 (4)
F2	0.6733 (6)	0.1015 (3)	0.7363 (7)	0.133 (5)
F3	0.5244 (7)	0.0503 (2)	0.8832 (5)	0.119 (4)
O1	0.1680 (6)	0.1430 (2)	0.7835 (5)	0.079 (3)
O2	0.3273 (6)	0.1998 (2)	0.6064 (2)	0.061 (2)
O3	0.4852 (7)	0.2069 (2)	0.8869 (4)	0.082 (3)
C1	0.2988 (11)	0.2059 (4)	0.2309 (9)	0.084 (6)
C2	0.2617 (11)	0.1391 (5)	0.2349 (10)	0.099 (7)
C3	0.1079 (12)	0.0907 (4)	0.1304 (8)	0.095 (6)
C4	−0.0279 (11)	0.0591 (3)	0.2100 (9)	0.089 (5)
C5	−0.1355 (11)	0.1153 (4)	0.2804 (10)	0.096 (6)
C6	−0.1294 (9)	0.1234 (4)	0.4214 (9)	0.084 (5)
C7	0.4951 (10)	0.0870 (3)	0.7522 (8)	0.074 (5)

[a] $U_{eq} = {}^1/_3 \sum_i\sum_j U_{ij} a_i^* a_j^* \vec{a}_i \cdot \vec{a}_j$.

X-ray Structure Determination. Details of data collection and structure solution are summarized in Table I.[15] Atomic coordinates are listed in Table II, and Table III contains selected bond lengths and angles. A picture of the molecule showing the atomic labeling scheme is shown in Figure 2.

Complex **2** exists as parallel chains of (1,5-hexadiene)Cu(SO_3CF_3) units related by an *n*-glide plane in the crystal. The conformation of the central $[Cu(SO_3CF_3)]_n$ skeleton is similar to that observed for bis(cyclooctene)copper(I) triflate,[16] and the rms deviation of the central chain atoms between the two structures is 0.15 Å. Here, however, the similarity ends. Whereas the (cyclooctene)$_2$Cu^I cations are connected by the bridging triflate anions with one short and one long Cu–O contact [2.049 (4), 2.433 (4) Å], in **2** the Cu–O distances are approximately equal [2.101 (4), 2.135 (4) Å]. An explanation can be found in the arrangement of the olefin C$=$C bonds about the Cu atoms. In the (cyclooctene)$_2$Cu^I complex the two C$=$C bonds and one oxygen atom of the triflate anion are arranged in an almost trigonal fashion about the copper atom (rms deviation 0.08 Å). In **2**,

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(12) **3**: To the slurry of **1** (10.0 mmol) in toluene (0 °C) is added 1,6-heptadiene (3 mL) resulting in a clear solution. At −78 °C white crystals deposit, which are isolated, washed with cold pentane, and dried under vacuum: yield 830 mg (27%). Anal. Calcd for $C_8H_{12}CuF_3O_3S$ (M_r = 308.8): C, 31.12; H, 3.92; Cu, 20.58. Found: C, 31.08; H, 4.09; Cu, 20.58. ^{1}H NMR (400 MHz, −80 °C, CD_2Cl_2): δ 5.46 ($=$CH–), 4.65 ($=CH_EH$), 4.60 ($=CHH_Z$), 2.42 and 1.70 ($=$CH—CH_aH_b–), 1.91 and 1.75 (–CH_aH_b–). ^{1}H NMR (200 MHz, 27 °C): δ 5.55 ($=$CH–), 4.76 ($=CH_EH$), 4.69 ($=CHH_Z$), 2.15 ($=$CH—CH_2–), 1.90 (–CH_2–). ^{13}C NMR (50.3 MHz, 27 °C, CD_2Cl_2): δ 123.7 ($=$CH–), 94.6 ($=CH_2$), 33.6 ($=$CH—CH_2–), 27.5 (–CH_2–). Presumably, the structure of **3** in solution is dynamic, similar to that of **2**.

(13) Hendra, P. J.; Powell, D. B. *Spectrochim. Acta* **1961**, *17*, 909.

(14) The out-of-plane bending force constants are expected to increase upon coordination because of the repulsive forces between the ligand atoms and the metal atom: Grogan, M. J.; Nakamoto, K. *J. Am. Chem. Soc.* **1966**, *88*, 5454.

(15) In addition to several locally written programs, the following programs were used: TRACER by Lawton and Jacobson for cell reduction; DATAP by Coppens, Leiserowitz, and Rabinovich for data reduction; Sheldrick's SHELX-76 for Fourier calculations and initial least-squares refinement; GFMLX, a modified version of BDLS, by Hirshfeld, Coppens, Leiserowitz, and Rabinovich for subsequent full-matrix least-squares refinement; Davis' DAESD for bond distance and angle calculations; and Johnson's ORTEP for the molecular diagram.

(16) Budzelaar, P. H. M.; Timmermans, P. J. J. A.; Mackor, A.; Spek, A. L.; Duisenberg, A. J. M. *Acta Crystallogr.* **1987**, *C43*, 2298.

Table III. Selected Distances (Å) and Angles (deg) for **2**

Cu–O2	2.135 (4)	Cu–C1	2.148 (7)
Cu–C2	2.132 (8)	Cu–C5	2.157 (8)
Cu–C6	2.168 (7)	Cu–O3*	2.101 (4)
S–O1	1.410 (4)	S–O2	1.445 (4)
S–O3	1.441 (4)	S–C7	1.818 (6)
C1–C2	1.280 (11)	C2–C3	1.487 (11)
C3–C4	1.454 (11)	C4–C5	1.525 (11)
C5–C6	1.253 (12)		

O3*–Cu–C6	101.8 (2)	O3*–Cu–C5	110.4 (2)
O3*–Cu–C2	134.9 (3)	O3*–Cu–C1	102.6 (2)
O3*–Cu–O2	94.2 (1)	C6–Cu–C5	33.7 (3)
C6–Cu–O2	103.7 (2)	C5–Cu–C2	85.1 (3)
C2–Cu–C1	34.8 (3)	C1–Cu–O2	100.5 (2)
O3–S–O2	113.2 (2)	O3–S–O1	115.3 (3)
O2–S–O1	115.7 (3)	S–O2–Cu	134.3 (2)
Cu*–O3–S	127.5 (2)	C2–C1–Cu	71.9 (5)
C3–C2–C1	133.5 (8)	C3–C2–Cu	105.5 (5)
C1–C2–Cu	73.3 (5)	C4–C3–C2	112.4 (7)
C5–C4–C3	112.1 (6)	C6–C5–C4	128.4 (8)
C6–C5–Cu	73.6 (5)	C4–C5–Cu	102.5 (5)
C5–C6–Cu	72.7 (5)		

however, the coordination about the copper atom is approximately tetrahedral and the 1,5-hexadiene acts as a chelating ligand. The 1,5-hexadiene groups assume a C_2-symmetrical conformation, with *R*,*R*- and *S*,*S*-η^2,η^2-bonded diene ligands alternating along the $[Cu(SO_3CF_3)]_n$ skeleton. The mode of coordination of the hexadiene to the metal can be conveniently described by the angle subtended at the metal by the midpoints of the two double bonds (113.8°), the average distance from the metal to these points (mean 2.06 Å), and the rotation of the olefinic bonds out of the plane defined by the metal atom and their midpoints (mean 30°); the distance of the double-bond midpoints ["span" of the Cu(I)-bound diene ligand] is 3.44 Å. Both complexes show nearly equal Cu–C distances [**2**: mean 2.15 (2) Å].

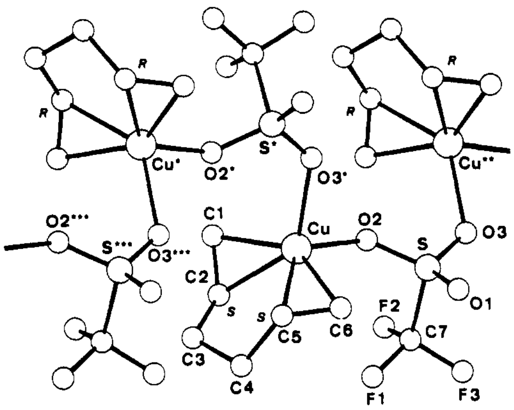

Figure 2. Molecular structure of $[(R,R/S,S\text{-}\eta^2,\eta^2\text{-}1,5\text{-hexadiene})Cu(SO_3CF_3)]_n$ (**2**).

The conformation adopted by the 1,5-hexadiene is very similar to that observed for other d^{10} tetrahedrally coordinated metals with chelating 1,5-hexadiene.[3] The conformation is also similar to that calculated by molecular modeling[17] for the free molecule with the double bonds in a cisoid arrangement. In the calculated molecule, the corresponding values are 124°, 1.89 Å, and 35°, respectively, for a pseudoatom placed at the intersection of the normals to the planes of the double bonds (calculated distance between the midpoints of the double bonds: 3.34 Å). The fact that the 1,5-hexadiene ligand in **2** can adopt the energetically favored conformation supports the stabilization of the complex.

Supplementary Material Available: Listings of crystal data and data collection parameters, H atom coordinates, thermal parameters, distances, and angles (4 pages). Ordering information is given on any current masthead page.

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(17) SYBYL 5.41, Tripos Associates, Inc., St. Louis, MO. Force field: Tripos (Version 5.2). Minimizing algorithm: BFGS. Convergence criterion: rms gradient less than 0.01 kcal mol^{-1} Å^{-1}. Nonbonded cutoff: 8 Å.