Organometallics **2000,** *19,* 4666−4668

Fluxional Behavior of Indenyl-Derived Ytterbocene(II) Complexes. The $SiHR_2$ Group as a NMR Spectroscopic Probe

Michael G. Klimpel, Wolfgang A. Herrmann, and Reiner Anwander*

Anorganisch-chemisches Institut, Technische Universität München, Lichtenbergstrasse 4, D-85747 München, Germany

Received April 18, 2000

Summary: Indenyl-derived ytterbocene(II) complexes $[1\text{-}(SiHR_2)\text{-}2\text{-}R'\text{-}C_9H_5]_2Yb(L)_2$ *(R* = *Me,* C_6H_5*; R′* = *H, Me; L* = *donor ligand) have been synthesized via silylamine elimination from* $Yb[N(SiMe_3)_2]_2(THF)_2$ *and the indene derivatives in hexane at ambient temperature. The "SiH-decorated" silyl substituents assist in the examination of the fluxional behavior of the stereoisomers in solution, the ratio and interconversion of which are affected by the size and ring position of the substituents as well as the type of donor ligand, e.g., THF vs TMEDA.*

Ytterbocene(II) and samarocene(II) complexes gained considerable interest in the field of rare earth-mediated α-olefin and ring-opening polymerization.[1] Various derivatives comprising *ansa*- and nonlinked cyclopentadienyl and indenyl systems as well as heteroleptic complexes[2−7] were ascribed high catalytic efficiency occurring via a novel bisinitiator mechanism.[8] It is known that the interconversion of stereoisomers, implied chemically and thermally through rotation and epimerization processes, significantly affects the stereospecifity of olefin transformations.[9] To better examine such fluxional phenomena, our interest was drawn to the design of specially functionalized indenyl derivatives of the diamagnetic ytterbium(II) center.[10] We report here the synthesis of ytterbocene(II) complexes via a silylamine elimination reaction.[11] Moreover, the indenyl-bonded $SiHR_2$ group (R = Me, Ph) is exploited as a sensitive probe for dynamic NMR investigations.

New silyl-substituted indenes $1\text{-}(SiHMe_2)C_9H_7$ (**1**),[12] $1\text{-}[SiH(C_6H_5)_2]C_9H_7$ (**2**), and $1\text{-}(SiHMe_2)\text{-}2\text{-}Me\text{-}C_9H_6$ (**3**) were prepared according to common salt metathesis procedures from lithiated indene and the corresponding chlorosilanes in THF/ether. $Yb[N(SiMe_3)_2]_2(THF)_2$ (**4**)[13] reacts with **1** and **2** in hexane to form the dark red compounds $[1\text{-}(SiHMe_2)C_9H_6]_2Yb(THF)_2$ (**5**) and $[1\text{-}\{SiH(C_6H_5)_2\}C_9H_6]_2Yb(THF)_2$ (**6**), respectively, in yields >90% (Scheme 1).[14−16]

---

* Corresponding author. Fax: +49 89 289 13473. E-mail: reiner.anwander@ch.tum.de.

[1] For a recent review, see: Yasuda, H. *Top. Organomet. Chem.* **1999**, 2, 255−283.

[2] Evans, W. J.; Bloom, I.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 6507−6508. (b) Evans, W. J.; Katsumata, H. *Macromolecules* **1994**, *27*, 2330−2332. (c) Evans, W. J.; Katsumata, H. *Macromolecules* **1994**, *27*, 4011−4013. (d) Evans, W. J.; DeCoster, D. M.; Greaves, J. *Organometallics* **1996**, *15*, 3210−3221.

[3] (a) Yamamoto, H.; Yasuda, H.; Yokota, K.; Nakamura, A.; Kai, Y.; Kasai, N. *Chem. Lett.* **1988**, 1963−1966. (b) Yasuda, H.; Yamamoto, H.; Yamashita, M.; Yokota, K.; Nakamura, A.; Miyake, S.; Kai, Y.; Kanehisa, N. *Macromolecules* **1993**, *26*, 7134−7143.

[4] Jiang, T.; Shen, Q.; Lin, Y.; Jin, S. *J. Organomet. Chem.* **1993**, *450*, 121−124.

[5] Ihara, E.; Noduno, M.; Katsura, K.; Adachi, Y.; Yasuda, H.; Yamagashira, M.; Hashimoto, H.; Kanehisa, N.; Kai, Y. *Organometallics* **1998**, *17*, 3945−3956.

[6] (a) Knjazhanski, S. Ya.; Nomerotsky, I. Yu.; Bulychev, B. M.; Belsky, V. K.; Soloveichik, G. L. *Organometallics* **1994**, *13*, 2075−2078. (b) Knjazhanski, S. Ya.; Kalyuzhnaya, E. S.; Elizalde Herrera, L. E.; Bulychev, B. M.; Khvostov, A. V.; Sizov, A. I. *J. Organomet. Chem.* **1997**, *531*, 19−25. (c) Knjazhanski, S. Ya.; Elizalde Herrera, L. E.; Cadenas, G.; Bulychev, *J. Organomet. Chem.* **1998**, *568*, 33−40.

[7] (a) Hou, Z.; Tezuka, H.; Zhang, Y.; Yamazaki, H.; Wakatsuki, Y. *Macromolecules* **1998**, *31*, 8650−8652. (b) Zhang, Y.; Hou, Z.; Wakatsuki, Y. *Macromolecules* **1999**, *32*, 939−941.

[8] Boffa, l. S.; Novak, B. M. *Macromolecules* **1994**, *27*, 6993−6995.

[9] For a recent review, see: Brintzinger, H.-H.; Fischer, D.; Mülhaupt, R.; Rieger, B.; Waymouth, R. M. *Angew. Chem.* **1995**, *107*, 1255−1283; *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1143−1170.

[10] For structurally characterized Ln(II) indenyl complexes, see: (a) Jin, J.; Jin, Z.; Wie, G.; Chen, W. *J. Struct. Chem. (Jiegou Huaxue)* **1993**, *12*, 24. (b) Evans, W. J.; Gummersheimer, T. S.; Boyle, T. J.; Ziller, J. W. *Organometallics* **1994**, *13*, 1281−1284. (c) Khvostov, A. V.; Bulychev, B. M.; Belsky, V. K.; Sizov, A. I. *J. Organomet. Chem.* **1999**, *584*, 164−170. (d) Qian, C.; Li, H.; Sun, J.; Nie, W. *J. Organomet. Chem.* **1999**, *585*, 59−62.

[11] Further nonsalt metathesis routes to lanthanidocene(II) complexes comprise: (a) Fischer, E. O.; Fischer, H. *Angew. Chem.* **1964**, *76*, 52. (b) Hammel, H.; Weidlein, J. *J. Organomet. Chem.* **1990**, *388*, 75−87. (c) Watson, P. L.; Whitney, J. F.; Harlow, R. L. *Inorg. Chem.* **1981**, *20*, 3271−3278. (d) Deacon, G. B.; Newnham, R. H. *Aust. J. Chem.* **1985**, *38*, 1757−1765. (e) Wang, S.; Yu, Y.; Ye, Z.; Qian, C.; Huang, X. *J. Organomet. Chem.* **1994**, *464*, 55−58. (f) Qian, C.; Zou, G.; Sun, J. *J. Organomet. Chem.* **1998**, *566*, 21−28.

[12] Eppinger, J.; Spiegler, M.; Hieringer, W.; Herrmann, W. A.; Anwander, R. *J. Am. Chem. Soc.* **2000**, *122*, 3080−3096.

[13] (a) Andersen, R. A.; Boncella, J. M. *Organometallics* **1985**, *4*, 205−207. (b) Boncella, J. M. Ph.D. Thesis, University of California, Berkeley, 1982.

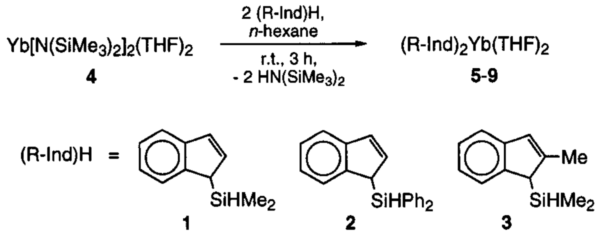
[14] Complexes **5**−**9** were synthesized analogously (see Supporting Information). Complex **5**: in a glovebox, indene **1** (349 mg, 2.00 mmol) and complex **4** (638 mg; 1.00 mmol) were dissolved in hexane (20 mL) and stirred at ambient temperature. The initially orange solution turned dark red within 3 min. After 3 h the reaction mixture was centrifugated, leaving a small amount (<5%) of dark brown, insoluble residue. Product **5** was obtained as dark red needles by crystallization of the hexane fraction at −40 °C (500 mg, 75%). IR (Nujol): 2081 s (Si−H), 1244 m, 1156 m, 1027 m, 968 m, 878 m, 722 s, 661 w, 440 w cm^{-1}. Anal. Calcd for $C_{30}H_{42}O_2Si_2Yb$: C, 54.28; H, 6.38. Found: C, 53.50; H, 6.36. ^1H NMR (C_6D_6, 25 °C): Major isomer (67%): δ 7.59 (dd, $^3J_{H,H} = 6.9$ Hz, 2H, indenyl), 7.36 (dd, $^3J_{H,H} = 7.7$ Hz, 2H, indenyl), 6.99 (m, 2H, Indenyl), 6.81 (m, 2H, indenyl), 6.28 (m, 2H, indenyl), 5.14 (sp, $^3J_{H,H} = 3.6$ Hz, 2H SiH), 2.99 (s, 8H, THF I), 1.24 (s, 8H, THF II), 0.71 (d, $^3J_{H,H} = 3.6$ Hz, 6H, SiMe I), 0.54 (d, $^3J_{H,H} = 3.6$ Hz, 6H, SiMe II). Minor isomer (33%): δ 7.64 (dd, $^3J_{H,H} = 8.0$ Hz, 2H, indenyl), 7.33 (dd, $^3J_{H,H} = 5.9$ Hz, 2H, indenyl), 6.88 (m, 2H indenyl), 6.80 (m, 2H indenyl), 6.33 (dd, 2H, indenyl), 4.94 (sp, $^3J_{H,H} = 3.3$ Hz, 2H, SiH), 2.99 (s, 8H, THF I), 1.24 (s, 8H, THF II), 0.51 (d, $^3J_{H,H} = 3.3$ Hz, 6H, SiMe I), 0.44 (s, $^3J_{H,H} = 3.3$ Hz, 6H, SiMe II). ^{13}C NMR (C_6D_6, 25 °C): δ 134.9, 131.8, 127.3, 121.9, 121.7, 118.4, 99.7, 99.2, 97.6, 69.4, 25.3, 1.3, −1.2, −2.5. Although well-shaped crystals of complex **5** could be obtained, attempts to mount the crystals for diffraction studies were frustrated by the fact that they readily redissolved upon warming to ambient temperature. For the synthesis of the *N*-MeIm and TMEDA derivatives **10** and **11** a slight excess of the free donor ligand was added to the reaction mixtures.

[15] The ytterbocene(II) complexes reported here can also be synthesized according to our extended silylamide route starting from $Yb[N(SiHMe_2)_2]_2(THF)_x$. The latter complex constitutes the preferred synthetic precursor compound to *ansa*-ytterbocene(II) complexes (Klimpel, M. G.; Anwander, R. A., 12. Tage der Seltenen Erden, December 3−5, 1999, Hamburg, Germany).

[16] Anwander, R. *Top. Organomet. Chem.* **1999**, *2*, 1−61.

10.1021/om000324w CCC: $19.00
Publication on Web 10/12/2000

Scheme 1. Synthesis of Ytterbium Indenyl Complexes via Silylamine Elimination



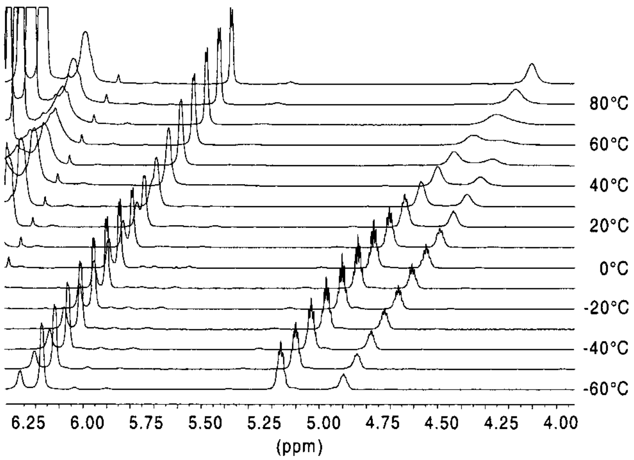


Figure 1. Selected resonances of the variable-temperature 400 MHz ^{1}H NMR spectra for **5** (toluene-d_8, coalescence temperature 40 °C).

After recrystallization from toluene/THF, the room-temperature ^{1}H NMR spectra of these complexes show the presence of two isomers in the ratio of 2:1 (**5**) and 3:2 (**6**), readily detectable by their SiH signals in benzene-d_6 and tetrahydrofuran-d_8 (δ_{SiH}: **5**, 5.14−4.94; **6**, 6.02−5.88). Signal integrals indicate an R-Ind:THF ratio of 1:1, consistent with the composition established by microanalysis. The SiH stretching vibrations were detected at 2081 (**5**) and 2111 (**6**) cm^{-1}. A variable-temperature NMR study in toluene-d_8 revealed the coalescense of these doubled sets of signals at elevated temperature depending on the steric bulk of the silyl substituents. This dynamic behavior is representatively shown for complex **5** in Figure 1, reinforcing the role of the SiH moiety as a powerful NMR spectroscopic probe. The importance of a silyl group in the 1-position for the occurrence of two complex isomers at ambient temperature was further shown by the ^{1}H NMR spectra of [1-(SiHMe$_2$)-2-Me-C$_9$H$_5$]$_2$Yb(THF)$_2$ (**7**), (C$_9$H$_7$)$_2$Yb(THF)$_2$ (**8**), and [2-Me-C$_9$H$_6$]$_2$Yb(THF)$_2$ (**9**), synthesized analogously. While the latter two complexes do not show any signal coalescence in toluene-d_8 within the temperature range of −100 to 90 °C, the 1,2-substituted derivative **7**, like the complexes **5** and **6**, diplays two signals in the ratio of 1:1 at ambient temperature, which coalesce at 50 °C.

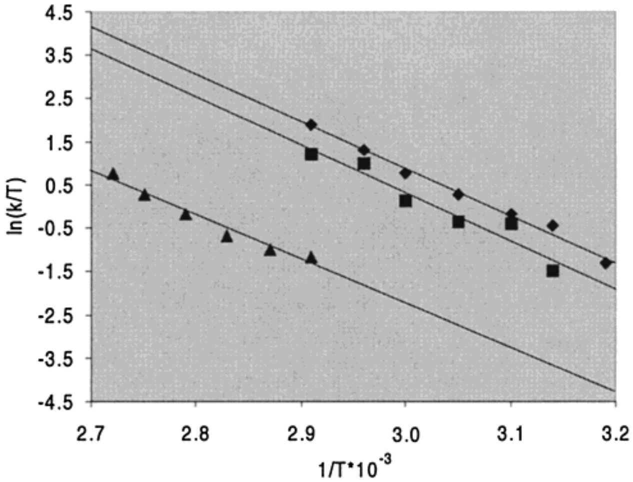


Figure 2. Eyring plot for complexes **5** (◆), **10** (■), and **11** (▲) (cf. Table 1).

Table 1. Activation Parameters of Compounds 5, 10, and 11 Obtained from Line Shape Analysis[17,a]

complex[b]	T_c (K)	$\Delta G^‡(T)$ (kcal mol^{-1})	$\Delta H^‡$ (kcal mol^{-1})	$\Delta S^‡$ (cal K^{-1} mol^{-1})
(R-Ind)$_2$Yb(THF)$_2$ (**5**)	313	15.4 ± 1.6	19.9 ± 0.8	14.1 ± 2.4
(R-Ind)$_2$Yb(*N*-MeIm)$_2$ (**10**)	318	15.7 ± 1.4	20.0 ± 0.7	13.4 ± 2.4
(R-Ind)$_2$Yb(TMEDA) (**11**)	343	17.1 ± 1.6	19.8 ± 0.8	7.9 ± 2.1

[a] NMR spectra recorded on a JEOL JNM-GX-270 instrument. [b] R-Ind = 1-(SiHMe$_2$)C$_9$H$_6$.

Such a fluxional behavior can alternatively be interpreted as a pseudo *rac*/*meso* isomerism or an interconversion of rotational isomers. To get more information about this isomerization process, we performed a line shape analysis according to the procedures of *Shanan-Atidi* and *Piette/Anderson* for unequally populated isomers.[17] The Eyring plots and the activation parameters $\Delta H^‡$, $\Delta G^‡$, and $\Delta S^‡$ derived herefrom (Figure 2, Table 1) support a dissociative mechanism, involving initial separation of a donor ligand (e.g., THF) followed by a hindered rotation of the indenyl ligands about the Yb−centroid (Cp) axis.

The line shape treatment led to a free energy parameter $\Delta G^‡$ of 15.4 ± 1.6 kcal/mol for complex **5**. The high coalescence temperature of 80 °C of the SiHPh$_2$-substituted derivative **6** excluded an adequate line shape analysis. Surprisingly, the activation enthalpy and entropy barriers $\Delta H^‡$ and $\Delta S^‡$, respectively, are markedly higher than expected for an exclusive rotation of the 1-functionalized indenyl ligand about the Yb−centroid (Cp) axis. For comparison, a $\Delta G^‡$ rotation of 8.3 kcal/mol (−70 °C) and 13.1 kcal/mol (−27.5 °C) were obtained for bulky U(C$_8$H$_6$*t*Bu$_2$-1,4) and Fe(C$_5$H$_3$*t*Bu$_2$-1,3),[18] while the energy barrier $\Delta H^‡$ for the cyclopentadienyl ring rotation in Fe(Cp)(C$_5$H$_4$CMe$_2$Et) was determined as 1.39 ± 0.23 kcal/mol.[19] However, a dissociation enthalpy of 20 kcal/mol for complex **5** seems to be far too low for indenyl dissociation according to a classical epimerization process. For comparison, the dissociation enthalpy for the cyclopentadienyl ligands in Yb(Cp)$_3$ derived from a mass spectrometric study is ca. 55 kcal/mol.[20] Therefore, we postulate the following scenario. Generation of a sterically unsaturated transition state [(R-Ind)$_2$Yb(THF)$_x$, $x < 2$] due to donor ligand displacement should require less than 10 kcal/mol (cf., the bond disruption enthalpy for the Sm(II)−THF bond was determined as 7.3 kJ/mol from a iodonolytic titration calorimetry[21]). Subsequently, the decreased steric crowding of the

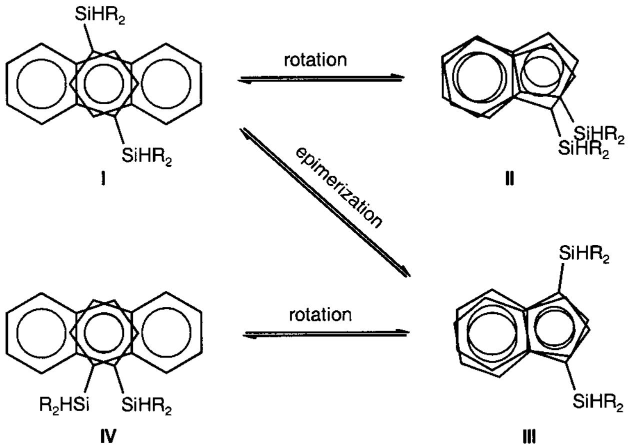
---

[17] (a) Shanan-Atidi, H.; Bar-Eli, U. H. *J. Phys. Chem.* **1970**, *74*, 961−963. (b) Piette, L. H.; Anderson, W. A. *J. Chem. Phys.* **1959**, *30*, 899−908.

[18] Luke, W. D.; Streitwieser, A., Jr. *J. Am. Chem. Soc.* **1981**, *103*, 3241−3243.

[19] Mann, B. E.; Spencer, C.; Taylor, B. F.; Yavari, P. *J. Chem. Soc., Dalton Trans.* **1984**, 2027−2028.

Scheme 2. Possible Indenyl–Indenyl Ligand Transpositions



metal center favors the hindered rotation of the indenyl ligands about the Yb–centroid (Cp) vector. The moderately positive activation entropies $\Delta S^\ddagger$ are in good agreement with an increased particle number in the transition state, i.e., donor dissociation. To prove the importance of initial donor dissociation, a variable-temperature NMR study of complex **5** was also performed in a mixture of toluene-d_8/tetrahydrofuran-d_8 (ca. 3:1): the two well-separated SiH signals (δ 5.01, 4.76) did not coalesce below 60 °C. Further evidence for such a dissociative mechanism was obtained from the activation entropies of complexes $[1\text{-}(SiHMe_2)C_9H_6]_2Yb(N\text{-}MeIm)_2$ (**10**) and $[1\text{-}(SiHMe_2)C_9H_6]_2Yb(TMEDA)_2$ (**11**) synthesized from complex **5** and the corresponding stronger donating and chelating ligands 1-methylimidazole and TMEDA, respectively. Accordingly, the TMEDA derivative exhibits a significantly smaller activation entropy (Table 1) corresponding to the dissociation of one donor moiety in the transition state.

MM2 force field calculations employing nonsubstituted $(Ind)_2Yb(THF)_2$ as the starting geometry[10d] are also supportive of such a rotational process. The steric energies of the interconversion of four highly symmetric rotational isomers of the $[1\text{-}(SiHMe_2)C_9H_6]_2Yb(THF)_2$ fragment were determined (Scheme 2 ; the metal center and the THF molecules are not shown for clarity). The rotational interconversions **I** → **II** and **III** → **IV** display one global maximum and several minima [ΔE_{steric}(minima) 1–2 kcal/mol]. Figure 3 shows the potential surface of the **I** → **II** interconversion along with the ball-and-stick drawings of two minimum rotational isomers. Interestingly, the high energies of the maxima do not originate from steric hindrance between the two silyl groups but from close contacts between silyl groups and THF donor molecules.[22]

These preliminary results show that bis(indenyl) metallocene complexes of the divalent rare earth metals can be straightforwardly synthesized according to the silylamide route in high yields and purity. Due to the steric crowding of 1-functionalized silylindenyl complexes, two isomers are formed which coalesce at elevated temperature in noncoordinating solvents. Although this dynamic behavior cannot be unambigeously established at this time, a reasonable fluxional process involving donor ligand dissociation followed by hindered rotation of the indenyl ligand is suggested. A similar fluxional behavior in unbridged 2-arylindene zirconocene complexes is exploited for the synthesis of elastomeric polypropylene ("Waymouth system").[23] Finally we have demonstrated that SiH-decorated silyl groups are valuable spectroscopic probes.

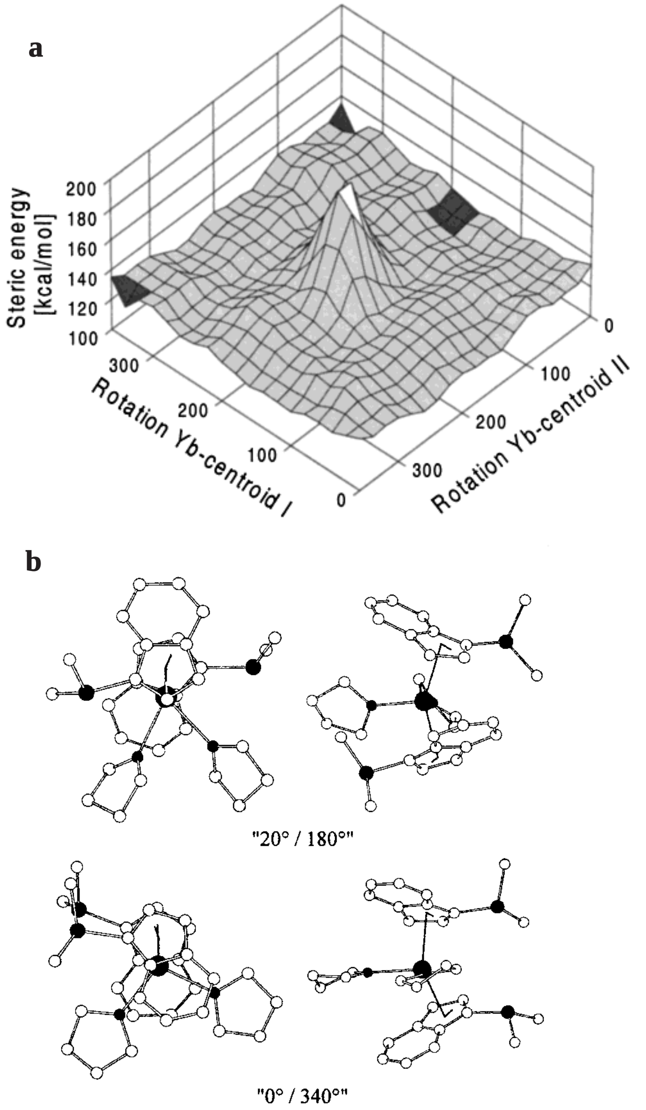


Figure 3. (a) Potential surface for the isomerization process **I** → **II**. (b) Top and side views of the calculated molecular structures of low-energy isomers "20°/180°" and "0°/340°". These isomers are indicated on the potential surface in dark color.

Supporting Information Available: Full experimental details for ligands **1**, **2**, and **3** and complexes **5**–**11**; steric energies for rotational isomers **I**–**IV**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM000324W

---

(20) Thomas, T. J.; Hayes, R. G. *J. Organomet. Chem.* **1970**, *23*, 487–489.

(21) Nolan, S. P.; Stern, D.; Marks, T. J. *J. Am. Chem. Soc.* **1989**, *111*, 7844–7853.

(22) Watson, P. L.; Whitney, J. F.; Harlow, R. L. *Inorg. Chem.* **1981**, *20*, 3271–3278.

(23) (a) Coates, G. W.; Waymouth, R. M. *Science* **1995**, *267*, 217–219. (b) Witte, P.; Lal, T. K.; Waymouth, R. M. *Organometallics* **1999**, *18*, 4147–4155.