propene results in formation of the 2-oxametallacyclopentane species 7 as a mixture of two isomers.[15] Compound 7 was observed as a minor component in the formation of 6. The major isomer of metallacycle 7 contains the methyl group attached to the carbon atom bound to the titanium metal center (i.e. the 5-methyl regioisomer). A single-crystal X-ray diffraction analysis of 6[16] shows some similarities to the structure of 1. The η^2-bound benzophenone lies perpendicular to the O–Ti–O planes, making both aryloxide ligands equivalent. Although many η^2-aldehyde derivatives of the group 4 metals are known,[17] compound 6 represents the first structurally characterized monomeric η^2-ketone complex of a group 4 metal. The C–O distance of 1.397 (8) Å in 6 is slightly longer than the value of 1.338 (2) Å in the zirconocene η^2-ketene complex $[Cp^*_2Zr(OCCH_2)(py)]$.[18]

Acknowledgment. We thank the National Science Foundation (Grant CHE-8915573) for support of this research.

Supplementary Material Available: Tables of crystal data and data collection parameters, positional parameters, general temperature factors, and bond distances and angles for 1 and 6 (41 pages). Ordering information is given on any current masthead page.

OM920049G

---

(15) ^1H NMR (C_6D_6, 30 °C) for 7: 5-methyl isomer, δ 6.7–7.5 (aromatics), 3.25 (dd), 2.94 (dd, C*H*$_2$), 1.88 (m, C*H*Me), 0.60 (d, CH*Me*); 4-methyl isomer, δ 6.7–7.5 (aromatics), 3.69 (M, C*H*Me), 1.12 (dd), 0.99 (dd, C*H*$_2$), 0.93 (d, CH*Me*). Selected ^{13}C NMR (C_6D_6, 30 °C; only 5-methyl isomer assignable): δ 159.7 (ipso O*Ar″*), 149.4, 148.6 (ipso OC*Ph*$_2$), 95.4 (Ti*C*HMe), 89.8 (O*C*Ph$_2$), 59.0 (*C*H$_2$), 21.8 (TiCH*Me*).

(16) X-ray crystal data for $TiC_{52}H_{45}O_3P$ (6) at −75 °C: $a = 9.910$ (1) Å, $b = 10.757$ (3) Å, $c = 19.942$ (3) Å, $\alpha = 89.23$ (2)°, $\beta = 76.73$ (1)°, $\gamma = 82.50$ (2)°, $Z = 2$, $d_{calcd} = 1.290$ g cm^{-3} in space group $P\bar{1}$ (No. 2). Of the 5364 unique data collected with Mo Kα radiation ($4° \leq 2\theta \leq 45°$), the 2585 with $I > 3\sigma(I)$ were used in the final refinement to yield $R = 0.059$ and $R_w = 0.065$. Hydrogen atoms were placed in ideal positions and were not refined.

(17) (a) Manriquez, J. M.; McAlister, D. R.; Sanner, R. D.; Bercaw, J. E. *J. Am. Chem. Soc.* **1978**, *100*, 2716. (b) Wolczanski, P. T.; Bercaw, J. E. *Acc. Chem. Res.* **1980**, *13*, 121. (c) Roddick, D. M.; Bercaw, J. E. *Chem. Ber.* **1989**, *122*, 1579. (d) Kropp, K.; Skibbe, V.; Erker, G.; Kruger, C. *J. Am. Chem. Soc.* **1983**, *105*, 3353. (e) Erker, G.; Hoffman, U.; Zwettler, R.; Betz, P.; Kruger, C. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 630. (f) Erker, G.; Sosna, F.; Hoffman, U. *J. Organomet. Chem.* **1989**, *372*, 41. (g) Erker, G.; Czisch, P.; Schuland, R.; Angermund, K.; Kruger, C. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 364.

(18) Moore, E. J.; Straus, D. A.; Armantrout, J.; Santarsiero, B. D.; Grubbs, R. H.; Bercaw, J. E. *J. Am. Chem. Soc.* **1983**, *105*, 2068.

Paramagnetic Decamethylbimetallocenes

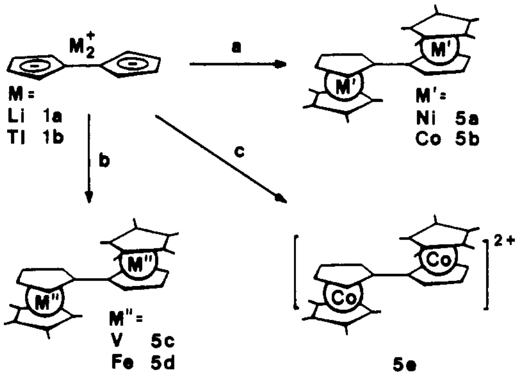
Peter Hudeczek and Frank H. Köhler*

Anorganisch-chemisches Institut der Technischen Universität München, Lichtenbergstrasse 4,
D-8046 Garching, Germany

Received February 4, 1992

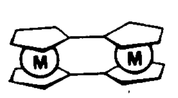
Summary: The paramagnetic decamethylbimetallocenes $(Cp^*M)_2C_{10}H_8$ have been synthesized for M = Ni, Co, and V together with the diamagnetic reference compounds having M = Fe and Co$^+$. The potentials of four electron transfers for Ni and Co$^+$ and of two for Fe (cyclic voltammetry) imply similar intramolecular interaction for all bimetallocenes. ^1H NMR spectroscopy shows paramagnetism for Co and V and antiferromagnetism for Ni.

Scheme I[a]

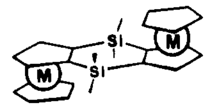


[a] Legend: (a) M = Li, Cp*Ni(acac), or Cp*Co(acac), THF, −78 °C; (b) M = Li, Cp*Li and $VCl_2(THF)_n$ or Cp*Na and $Fe_2Cl_4(THF)_3$, THF, 25 °C; (c) M = Tl, $[Cp^*CoCl]_2$, THF, −35 °C, NH_4PF_6.

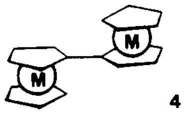
The chemistry of organometallic π-complexes derived from the fulvalene dianion (1) has experienced a remarkable renaissance because it allows the assembly of at least two metal fragments in close proximity.[1] What makes such an arrangement attractive is the study of conceivable successive stoichiometric or catalytic reactions at two metal centers, a reactivity that may be different from that of mononuclear π-complexes, and the interaction between the two metals that has been studied by various methods.[1] Our interest in fulvalene complexes is focused on the latter area and dates back to the investigation of bis(fulvalene)dimetal compounds 2, which in the case of Cr, V, and Ni show sizable antiferromagnetic coupling[2] rather than diamag-



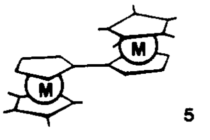
2



3



4



5

---

(1) Recent examples are: (a) Herberhold, M.; Brendel, H.-D.; Thewalt, U. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1652. (b) Schottenberger, H.; Ingram, G.; Obendorf, D.; Tessadri, R. *Synlett* **1991**, 905. (c) Jutzi, P.; Schnittger, J.; Neumann, B.; Stammler, H.-G. *J. Organomet. Chem.* **1991**, *410*, C13. (d) Webb, R. J.; Geib, S. J.; Staley, D. L.; Rheingold, A. L.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1990**, *112*, 5031. (e) Watanabe, M.; Kawata, S.; Sano, H.; Motoyama, I. *J. Organomet. Chem.* **1990**, *399*, 301. (f) McGovern, P. A.; Vollhardt, K. P. C. *Synlett* **1990**, 493. (g) Rausch, M. D.; Spink, W. C.; Conway, B. G.; Rogers, R. D.; Atwood, J. L. *J. Organomet. Chem.* **1990**, *383*, 227. (h) Wielstra, Y.; Gambarotta, S.; Spek, A. L.; Smeets, W. J. J. *Organometallics* **1990**, *9*, 2142. (i) Dong, T.-Y.; Hwang, M.-Y.; Hsu, T.-L.; Schei, C.-C.; Yeh, S.-K. *Inorg. Chem.* **1990**, *29*, 80. (j) Davis, J. H., Jr.; Sinn, E.; Grimes, R. N. *J. Am. Chem. Soc.* **1989**, *111*, 4784. (k) Astruc, D.; Guillin, J.; Varret, F.; Trautwein, A. X.; Villeneuve, G. *J. Am. Chem. Soc.* **1989**, *111*, 5800. (l) McManis, G. E.; Nielson, R. M.; Weaver, M. J. *Inorg. Chem.* **1988**, *27*, 1827. (m) Herrmann, W. A.; Andrejewski, D.; Herdtweck, E. *J. Organomet. Chem.* **1987**, *319*, 183. (n) Schwarzhans, K. E.; Scholz, W. *Monatsh. Chem.* **1987**, *118*, 875.

0276-7333/92/2311-1773$03.00/0

Table I. Cyclic Voltammetry Data for 5a,d,e[a]

	$E_{1/2}$, mV		
	5a[b]	**5d**[d]	**5e**[e]
M_2^{2-}/M_2^{-}			−1805[f]
M_2^{-}/M_2			−1310[g]
M_2/M_2^{+}	320	935	−455
M_2^{+}/M_2^{2+}	705	1310	−25
M_2^{2+}/M_2^{3+}	1305[c]		
M_2^{3+}/M_2^{4+}	1495[c]		

[a] In EtCN, 0.1 M n-Bu_4NPF_6, Pt disk; $E_{1/2}$ relative to internal $Cp_2Co^{0/+}$. [b] −21 °C, scan rate 200 mV s^{-1}, ΔE_p = 65 mV. [c] Scan rate 50 mV s^{-1}, ΔE_p = 125 and 65 mV. [d] 22 °C, scan rate 50–400 mV s^{-1}, ΔE_p = 60–70 mV. [e] −21 °C, scan rate 200 mV s^{-1}, ΔE_p = 80–90 mV. $E_{1/2}$ measured relative to internal $Cp_2Fe^{0/+}$ and calculated relative to $Cp_2Co^{0/+}$ with $E_{1/2}$ = −1345 mV at −25 °C. [f] Chemically not fully reversible, ΔE_p = 170–245 mV. [g] ΔE_p = 130 mV.

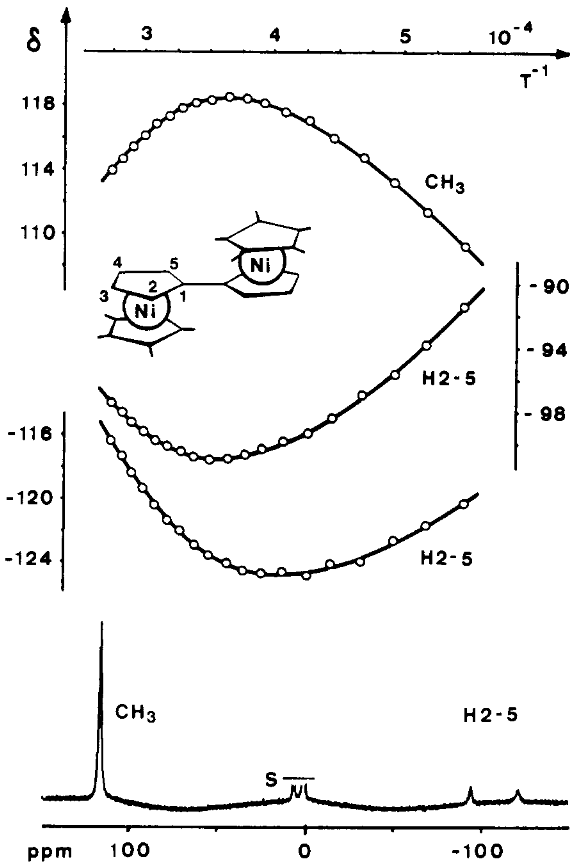


Figure 1. (Bottom) ^1H NMR spectrum of **5a** in toluene-d_8 at −59.3 °C (S = solvent). (Top) Curie plot of the paramagnetically shifted resonances. $\delta^{para}(^1H)$ is abbreviated as δ and given in ppm.

netism.[3] The other limit, i.e. almost negligible spin coupling, is realized when the metallocenes are separated by two silyl groups as in **3**.[4] The magnetic tuning range between these extremes might be accessible by the bimetallocenes **4**, for which no systematic metal-dependent study existed before we started our work.[5] Since methylation often increases the stability of metallocenes,[6] we have set out to investigate the decamethylbimetallocenes **5** rather than **4**. In parallel work Astruc and co-workers[7] have isolated some interesting diamagnetic examples of **5**, among them **5d,e** (described below) and the mixed-valence species **5d**$^+$.

The syntheses of the decamethylbimetallocenes are summarized in Scheme I. Thus, the reaction of **1a**[8] with Cp*Ni(acac)[9] or Cp*Co(acac)[9] in THF at −78 °C gave, after crystallization from hexane, microcrystals of decamethylbinickelocene (**5a**;[10] violet, 15% yield) or decamethylbicobaltocene (**5b**;[10] brown, 19% yield), respectively. The corresponding decamethylbivanadocene (**5c**) and decamethylbiferrocene (**5d**), which was needed as a diamagnetic reference compound, were obtained by reacting a mixture of **1a** and Cp*M (M = Li, Na) in THF at 25 °C with solvated vanadium(II) chloride[11] and $Fe_2Cl_4(THF)_3$, respectively. Crystallization from hexane gave brown microcrystals of **5c**[10] in 25% yield, while **5d**[10] was isolated as orange crystals after medium-pressure liquid chromatography in 4% yield. The reaction of $[Cp^*CoCl]_2$[12] with **1b**[1g] in THF at −35 °C resulted in a green mixture. Aqueous workup, precipitation with NH_4PF_6, and recrystallization from acetonitrile/ether yielded yellow crystals of **5e**$(PF_6)_2$[10] (79%), leaving behind thallium as a gray powder. The trans conformation of **5** was shown for **5d** and the Rh^+ analogue by X-ray crystallography,[7] as has been found previously for non-methylated bimetallocenes.[13]

Cyclic voltammetry of **5a,d,e** showed seven different redox states (Table I). **5a,d** could be oxidized stepwise to give a tetra- and dication, respectively, while **5e** showed four reductions. Some electron transfers (ET's) were quasi-reversible, and the most anodic ET of **5e** was chemically not fully reversible (cf. Table I). The two ET's involving a given mixed-valence ion are well separated ($\Delta E_{1/2}$ = 190–495 mV), thus indicating an interaction

---

(2) Köhler, F. H.; Doll, K.-H.; Prössdorf, W.; Müller, J. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 151.

(3) (a) Smart, J. C.; Pinsky, B. L. *J. Am. Chem. Soc.* **1977**, *99*, 956. (b) Smart, J. C.; Pinsky, B. L.; Friedrich, M. F.; Day, V. W. *J. Am. Chem. Soc.* **1979**, *101*, 4371. (c) Smart, C. J.; Pinsky, B. L. *J. Am. Chem. Soc.* **1980**, *102*, 1009.

(4) Atzkern, H.; Hiermeier, J.; Kanellakopulos, B.; Köhler, F. H.; Müller, G.; Steigelmann, O. *J. Chem. Soc., Chem. Commun.* **1991**, 997.

(5) (a) Hudeczek, P. Diplomarbeit, Techische Universität München, 1990. The magnetism of biferrocene cations has been studied by: (b) Cowan, D. O.; Candela, G. A.; Kaufmann, F. *J. Am. Chem. Soc.* **1971**, *93*, 3889. (c) Morrison, W. H., Jr.; Krogsund, S.; Hendrickson, D. N. *Inorg. Chem.* **1973**, *12*, 1998. (d) Morrison, W. H., Jr.; Hendrickson, D. N. *Inorg. Chem.* **1975**, *14*, 2331.

(6) Robbins, J. L.; Edelstein, N.; Spencer, B.; Smart, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 1882 and literature cited therein.

(7) Rittinger, S.; Buchholz, D.; Delville-Desbois, M.-H.; Linarès, J.; Varret, F.; Boese, R.; Zsolnai, L.; Huttner, G.; Astruc, D. *Organometallics* **1992**, *11*, 1454.

(8) Smart, J. C.; Curtis, C. J. *Inorg. Chem.* **1977**, *16*, 1788.

(9) Bunel, E. E.; Valle, L.; Manriquez, J. M. *Organometallics* **1985**, *4*, 1680.

(10) (a) The yields of **5a–c** were 54, 58, and 45%, respectively, after standard workup of the reaction mixture. This included stripping of the solvent, extraction of the solid remainder with hexane, and removal of hexane under reduced pressure and of decamethylmetallocene by sublimation. Crystallization twice from hexane gave the materials subjected to elemental analysis in yields indicated in the text. **5e**$(PF_6)_2$ was obtained similarly after extracting the solid remainder with water, precipitating with NH_4PF_6, and drying (95% yield before recrystallization). Since **5d** was only needed as a NMR reference compound, its synthesis and chromatographic separation were not optimized. In the mass spectrum of **5a** MH^+ was the base peak; in those of **5b–d** M^+ was the base peak; the calculated and experimental peak patterns were in good agreement. All new compounds gave satisfactory elemental analyses. **5d**: ^1H NMR (C_6D_6) δ = 1.72 (s, 30 H, CH_3), 3.73 (vt, 4 H, H2/5[10b]), 3.66 (vt, 4 H, H3/4[10b]); ^{13}C NMR (C_6D_6) δ = 83.23 (C_5Me_5), 80.23 (C1), 68.36 (C3/4[10c]), 71.73 (C2/5[10c]), 11.01 (C_5Me_5). **5e**: ^1H NMR (CD_3CN) δ = 1.95 (s, 30 H, CH_3), 5.55 (vt, 4 H, H2/5), 5.48 (vt, 4 H, H3/4); ^{13}C NMR (CD_3CN) δ = 99.73 (C_5Me_5), 93.48 (C1), 84.08 (C3/4), 89.76 (C2/5), 10.36 (C_5Me_5); assignments analogous to those of **5d**. (b) Assignment analogous to: Izumi, T.; Kasahara, A. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 1955. (c) Assignment based on a CH-COSY spectrum.

(11) Köhler, F. H. In *Organometallic Synthesis*; King, R. B., Eisch, J. J., Eds.; Elsevier: Amsterdam, **1988**; Vol. 4, p 15.

(12) Kölle, U.; Khouzami, F.; Fuss, B. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 131.

(13) (a) MacDonald, A. C.; Trotter, J. *Acta Crystallogr.* **1964**, *17*, 872. (b) Konno, M.; Hyodo, S.; Iijima, S. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 2327. (c) Geib, S. J.; Rheingold, A. L.; Dong, T.-Y.; Hendrickson, D. N. *J. Organomet. Chem.* **1986**, *312*, 241.

between the metallocenes which, in the case of the iron derivatives, is more pronounced for **5d** ($\Delta E_{1/2}$ = 345 mV) than for the silyl-bridged compound **3** with M = Fe ($\Delta E_{1/2}$ = 210 mV[14]).

While **5d,e** are diamagnetic, the paramagnetic compounds **5a,b,c** showed striking differences when studied by ^1H NMR spectroscopy. The paramagnetic ^1H NMR shifts at 298 K[15] of **5b** (δ^{para}_{298} = −39.3/−60.4 (H2–5), 36.7 (CH_3)) and of **5c** (δ^{para}_{298} = 319 (H2–5), 111.1 (CH_3)) are very similar to those found for substituted mononuclear cobaltocenes and vanadocenes.[16] In particular, the signals for H2–5 of **5c** are not resolved, as is found for many other vanadocenes.[16] It follows that **5b,c** have two and six unpaired electrons, respectively, and that the electron spin coupling is very small. This has been confirmed by a temperature-dependence study, according to which the δ^{para} values closely follow the Curie law.

In contrast, the ^1H NMR spectrum of **5a** (Figure 1) is much different from what is known for substituted nickelocenes.[16] The signal shifts of H2–5 (δ^{para}_{298} = −122.1/−100.6) and of CH_3 (δ^{para}_{298} = 117.9) are only about half as big as usual, and the signals are much narrower. The temperature dependence of the proton signal shifts is also shown in Figure 1. There is no linear correlation of δ^{para} with $1/T$ and, hence, a strong deviation from Curie behavior. Instead, all absolute shift values increase with the temperature after passing through a minimum. This is characteristic of a strong antiferromagnetic coupling. The coupling can be adjusted by substitution. Thus, for the parent binickelocene $(CpNi)_2C_{10}H_8$[5a] the signal shifts of H2–5 (δ^{para}_{298} = −160.7/−132.8) and of Cp (δ^{para}_{298} = −140.8) are also far from those of simple nickelocenes. However, the proton signals of the fulvalene ligand are more shifted than in the case of **5a**, which means that the antiferromagnetic coupling is somewhat smaller.

Unlike the predominantly Coulombic interaction between the metallocene moieties, which are rather similar (cyclic voltammetry), the magnetic exchange varies. In the decamethylbimetallocenes the latter effect is so pronounced that the influence of the metal on the magnetism may be studied conveniently. We are currently extending this work to other paramagnetic bimetallocenes.

Acknowledgment. We thank Dr. J. Blümel for the COSY spectrum. Financial support for this work was provided by the Deutsche Forschungsgemeinschaft, the Pinguin-Stiftung, and the Fonds der Chemischen Industrie.

OM9200621

---

[14] Atzkern, H.; Hiermeier, J.; Köhler, F. H.; Steck, A. *J. Organomet. Chem.* **1991**, *408*, 281.

[15] The signal shifts were measured relative to the solvent signal and calculated relative to the corresponding signal shifts of **5d**. Shifts to low frequency have a negative sign.

[16] (a) Köhler, F. H.; Geike, W. A. *J. Organomet. Chem.* **1987**, *328*, 35. (b) Köhler, F. H.; Doll, K.-H. *Z. Naturforsch., B* **1982**, *37*, 144. (c) Köhler, F. H.; Doll, K.-H.; Prössdorf, W. *J. Organomet. Chem.* **1982**, *224*, 341. (d) Köhler, F. H. *J. Organomet. Chem.* **1976**, *110*, 235. Note that we have changed the sign convention since.

Formation, Fragmentation, and Isomerization of Azatitanacycle Rings Supported by Aryloxide Ligation

John E. Hill, Phillip E. Fanwick, and Ian P. Rothwell*

Department of Chemistry, Purdue University, 1391 Brown Building, West Lafayette, Indiana 47907

Received January 2, 1992

Summary: The ethylene complex $[(Ar''O)_2Ti(\eta^2\text{-}C_2H_4)(PMe_3)]$ (Ar″O = 2,6-diphenylphenoxide) reacts with $PhCH_2N{=}CHPh$ to produce the 2-azatitanacyclopentane complex $[(Ar''O)_2Ti(CH_2CH_2CHPhNCH_2Ph)]$, which undergoes coupling reactions with alkynes and benzonitrile to produce new azametallacycles with loss of ethylene.

The last few years have seen an expansion of interest in the chemistry of transition-metal metallacyclic compounds.[1] In the case of the group 4 metals extremely useful synthetic methodologies have been built up around the formation and reactivity of metallacycle rings containing the metallocene (Cp_2M) subunit.[2-6] Recently our group has been exploring the reactivity of unsaturated

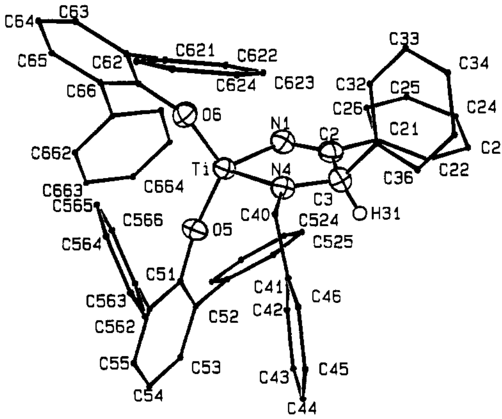


Figure 1. ORTEP view of **4** emphasizing the central coordination sphere. Selected bond distances (Å) and angles (deg): Ti–O(5), 1.816 (2); Ti–O(6), 1.829 (2); Ti–N(1), 1.910 (2); Ti–N(4), 1.886 (2); N(1)–C(2), 1.277 (3); C(2)–C(3), 1.529 (4); C(3)–N(4), 1.466 (3); O(5)–Ti–O(6), 124.10 (8); N(1)–Ti–N(4), 81.9 (1).

---

[1] (a) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finkey, R. G. *Principles and Applications of Organotransition Metal Chemistry*; 2nd ed.; University Science Books: Mill Valley, CA, 1987; Chapter 9. (b) Ingrosso, G. In *Reactions of Coordinated Ligands*; Brateman, P. S., Ed.; Plenum Press: New York, London, 1986; Vol. 1, p 639. (c) Schore, N. E. *Chem. Rev.* **1988**, *88*, 1081. (d) Negishi, E. *Chem. Scr.* **1989**, *29*, 457. (e) Chappell, S. D.; Cole-Hamilton, J. *Polyhedron* **1982**, *1*, 739. (f) Negishi, E. *Pure Appl. Chem.* **1981**, *53*, 2333. (g) Erker, G.; Kruger, C.; Muller, G. *Adv. Organomet. Chem.* **1985**, *24*, 1. (h) Hessen, B.; Teuben, J. H. *J. Organomet. Chem.* **1988**, *358*, 135. (i) Yasuda, H.; Tatsumi, K.; Nakamura, A. *Acc. Chem. Res.* **1985**, *18*, 120.

0276-7333/92/2311-1775$03.00/0