severely overlapping resonances at 89.34 and 80.34, 42.93, 39.25, 38.64, 34.87, 33.67, 29.56, 23.11 (>CH's, $>CH_2$'s and CH_3's).

The probe temperature was slowly raised to −50 °C, and a third ^{13}C spectrum was recorded of the reaction mixture, viz., δ 210.57 and 208.30 (—C≡O's), 88.58 (η^5-Cp C's), 90.16 and 86.86 (η^2-(CH=CH's)), 39.16 (2, >CH's), 38.25 (>CH), 34.15, 32.11 and 28.52 ($>CH_2$'s), 23.45 (CH_3). We attribute these resonances to [*exo*(?)-η^2-(*exo*-4-methylbicyclo[3.2.1]oct-2-ene)dicarbonyl(η^5-cyclopentadienyl)iron(II)]$^+$, **21**$^+$.

The NMR tube containing the reaction mixture was removed from the probe and maintained at 0 °C overnight, and a fourth ^{13}C spectrum identical with that of *exo*-4-methylbicyclo[3.2.1]-oct-2-ene, **22**, was recorded.

Reaction of [η^1-2-(4-Methoxybicyclo[3.2.1]oct-2-enyl)]dicarbonyl(η^5-cyclopentadienyl)iron(II), 12, and Tetrafluoroboric Acid. Formation of [η^1-2-Bicyclo[3.2.1]oct-3-enylidene]dicarbonyl(η^5-cyclopentadienyl)iron(II) Tetrafluoroborate, 9$^+$BF$_4^-$. A nitrogen-blanketed solution of **12** (0.035 g, 0.111 mmol) in 0.6 mL of CD_2Cl_2 was cooled to −78 °C in a 5-mm NMR tube. To this cold solution was added 0.1 mL of HBF_4·Et_2O, the contents were mixed at −78 °C, the tube was placed in the precooled (−78 °C) probe of the NR-80, and the $^{13}C\{^1H\}$ NMR spectrum of the reaction mixture was determined. It is identical in all respects to that of **9**$^+$BF$_4^-$ formed when an ~3:2 mixture of **4** and **5** is protonated under similar conditions.

Acknowledgment. We thank Dr. Ron Garber and Helga Cohen for their help with the NMR coupling constant determinations. We are indebted to the National Science Foundation for support of this work in the form of a research grant to the principal investigator, CHE-8614928, and a grant, CHE-8904942, to the Department of Chemistry for the purchase of the 500-MHz NMR spectrometer. We are indebted to the NIH, which provided the Department under Instrumentation Grant, No. 1-510-RR02849, with funds for the purchase of the VG Analytical, Ltd., 70SQ high-resolution, double-focusing mass spectrometer and VG 11/250 data system used in this work.

Organolanthanide-Catalyzed Cyclodimerizations of Disubstituted Alkynes

H. J. Heeres, A. Heeres, and J. H. Teuben*

Groningen Center for Catalysis and Synthesis, Department of Chemistry, University of Groningen, Nijenborgh 16, 9747 AG Groningen, The Netherlands

Received September 29, 1989

The lanthanide alkyls $Cp_2^*LnCH(SiMe_3)_2$ (Ln = La, Ce) are efficient catalysts for the cyclodimerization of 2-alkynes MeC≡CR (R = Me, Et, *n*-Pr) to 1,2-disubstituted 3-alkylidenecyclobutenes. The first step in the reaction is a propargylic metalation of the α-methyl group, giving $Cp^*_2LnCH_2C{\equiv}CR$ compounds and free $CH_2(SiMe_3)_2$.

Various lanthanide alkyls and hydrides are active alkene polymerization catalysts.[1,2] In fact, Cp^*_2LnH (Ln = La, Nd, Sm, Lu)[2c] compounds appear to be the most active ethylene polymerization catalysts known to date. The bis(pentamethylcyclopentadienyl)lanthanides are excellent models for the study of alkene polymerization. Mechanistic studies with this class of compounds have led to a better understanding of polymerization pathways and related reactions such as termination and chain transfer.[2a] In contrast, relatively little is known about organolanthanide-catalyzed alkyne oligomerization and polymerization. The reported literature deals mainly with acetylene polymerization by Ziegler–Natta type systems.[3] Our interest in this area stems from the observation that Cp^*_2Y– and Cp^*_2Sc–alkyl species are active catalysts for the selective dimerization of α-alkynes to 2,4-disubstituted enynes.[4] In this communication we report the reactivity of some well-defined lanthanide alkyls with various disubstituted alkynes.

Reaction of $Cp^*_2LnCH(SiMe_3)_2$ (Ln = La, Ce) with an excess of 2-butyne (benzene-d_6, 2-butyne/$Cp^*_2LnCH(SiMe_3)_2$ ratio 20:1) results in the catalytic formation of a cyclic dimer: 1,2-dimethyl-3-ethylidenecyclobutene (**1**; eq 1, characterized by MS and ^1H and ^{13}C NMR methods).[5] The reaction proceeds to completion in ca. 10 h at

(1) The following abbreviations are used in this article: Cp* = η^5-C_5Me_5 ring, Ln = lanthanide or group 3 element, lw = line widths of NMR resonances at half-maximum.

(2) (a) Watson, P. L. *J. Am. Chem. Soc.* **1982**, *104*, 337. (b) Watson, P. L.; Parshall, G. W. *Acc. Chem. Res.* **1985**, *18*, 51. (c) Jeske, G.; Lauke, H.; Mauermann, H.; Swepston, P. N.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8091. (d) Evans, W. J. *Adv. Organomet. Chem.* **1985**, *24*, 131. (e) Parkin, G.; Bunel, E.; Burger, B. J.; Trimmer, M. S.; Van Asselt, A.; Bercaw, J. E. *J. Mol. Catal.* **1987**, *41*, 21.

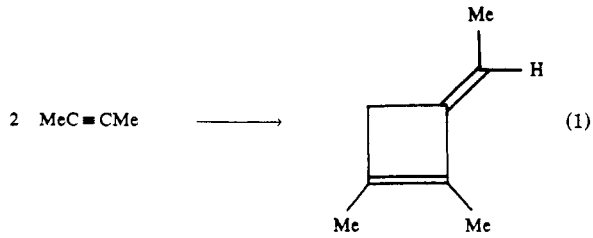
(3) (a) Shen, Z. *Inorg. Chim. Acta* **1987**, *140*, 7. (b) Bruzzone, M. In *Fundamental and Technological Aspects of Organo-f-Element Chemistry*; Marks, T. J., Fragala, J. L., Eds.; D. Reidel: Dordrecht, The Netherlands, **1985**; p 387.

(4) (a) Den Haan, K. H.; de Boer, J. L.; Teuben, J. H.; Spek, A. L.; Kojić-Prodić, B.; Hays, G. R.; Huis, R. *Organometallics* **1986**, *5*, 1726. (b) Thompson, M. E.; Baxter, S. M.; Bulls, A. R.; Burger, B. J.; Nolan, M. C.; Santarsiero, B. D.; Schaefer, W. P.; Bercaw, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 203.

(5) Cyclic dimer **1** was separated from the catalysts by vacuum transfer (25 °C, 0.01 mmHg) and obtained as a benzene-d_6 (or benzene) solution. Attempts to purify **1** by vacuum distillation (bp 38–40 °C, 24 mmHg) resulted in partial decomposition. Spectroscopic data for **1**: ^1H NMR (benzene-d_6) δ 4.96 (q, $^3J_{HH}$ = 6.6 Hz, 1 H, =C(*H*)Me), 2.72 (s, 2 H, CH_2), 1.66 (d, $^3J_{HH}$ = 6.6 Hz, 3 H, =C(H)*Me*), 1.61 (s, 3 H, Me), 1.51 (s, 3 H, Me); ^{13}C NMR (benzene-d_6) δ 141.3 (s), 140.4 (s), 139.2 (s), 102.5 (d, $^1J_{CH}$ = 153 Hz, =*C*(H)Me), 36.4 (t, $^1J_{CH}$ = 137 Hz, *C*H_2), 13.5 (q, $^1J_{CH}$ = 126 Hz, Me), 13.1 (q, $^1J_{CH}$ = 126 Hz, Me), 9.1 (q, $^1J_{CH}$ = 126 Hz, Me); MS $M^{\cdot+}$ = *m*/*e* 108. **1** slowly decomposes in air and must be stored under nitrogen. NMR and GC methods and a successful computer simulation of ^1H NMR spectra including all long-range proton–proton coupling constants suggest the formation of a single isomer. Attempts to determine the exact geometry of the ethylidene moiety by ^1H NOE difference measurements were not successful. However, 2D NOESY spectra display a clear NOESY cross-peak between the ring CH_2 and the ethylidene methyl group and imply that the latter is pointing toward the ring CH_2 protons.

0276-7333/90/2309-1508$02.50/0

80 °C, giving a turnover number of 2/h. Both NMR shifts



(1)

1

and coupling constants for 1 are in the range observed for various substituted cyclobutenes.[6] Especially informative is the downfield-shifted CH_2 group at δ 2.71 ppm (^{1}H NMR) and δ 36.5 ppm (^{13}C NMR).

NMR spectroscopy clearly indicates that the first step in the catalytic reaction is a fast and quantitative CH activation of an α-methyl group of 2-butyne, giving 2-butynyllanthanide compounds, $Cp^*_2LnCH_2C{\equiv}CMe$[7] and free $CH_2(SiMe_3)_2$ (eq 2).

$$Cp^*_2LnCH(SiMe_3)_2 + MeC{\equiv}CMe \rightarrow Cp^*_2LnCH_2C{\equiv}CMe + CH_2(SiMe)_3 \quad (2)$$

Ln = La (**2**), Ce (**3**)

Propargylic metalation, well-known for group 1, 2, 12, and 13 chemistry,[8] is unprecedented in organolanthanide and early-transition-metal chemistry. Generally, insertion of disubstituted alkynes in the metal–carbon bond is observed.[9]

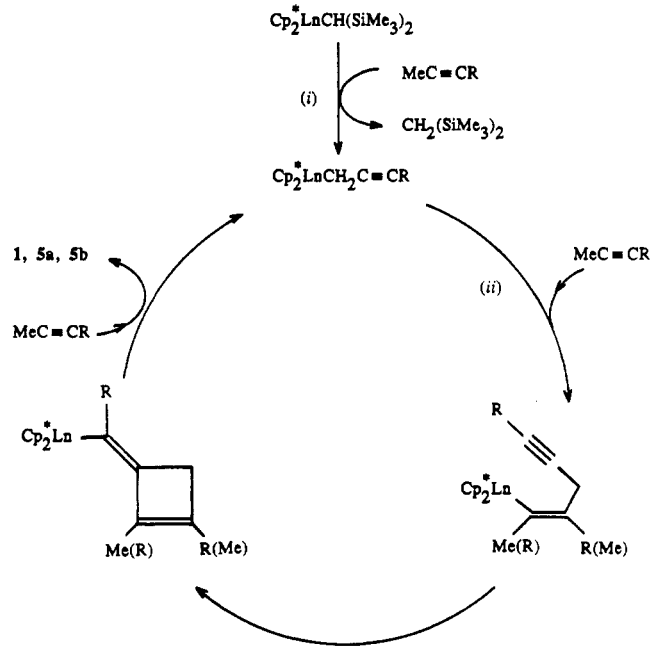
In contrast to the lanthanum and cerium derivatives, $Cp^*_2YCH(SiMe_3)_2$ is unreactive toward 2-butyne (benzene-d_6 solution, 12-fold excess of 2-butyne, 6 weeks at 80 °C). The yttrium analogue of **2** and **3**, $Cp^*_2YCH_2C{\equiv}CMe$ (**4**),[10] is accessible by the reaction of $(Cp^*_2YH)_2$ with 2-butyne in pentane (eq 3). However, **4** is also inactive for

$$(Cp_2{}^*YH)_2 + 2MeC{\equiv}CMe \rightarrow 2Cp_2{}^*YCH_2C{\equiv}CMe + 2H_2 \quad (3)$$

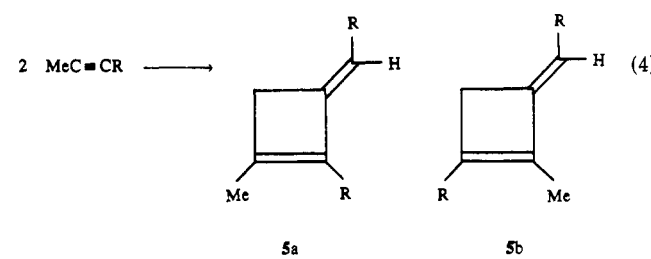
4

the cyclodimerization of 2-butyne (benzene-d_6, 10-fold excess of 2-butyne, 2 weeks at 50 °C, followed by 2 weeks at 80 °C). These differences in reactivity are likely to be steric in origin.[11]

Scheme I



Various disubstituted alkynes RC≡CMe were tested to determine the scope of this remarkable cyclodimerization. Catalytic dimerization was found for Ln = La, Ce and R = Et, *n*-Pr. GC/MS data for the lanthanum-catalyzed dimerizations of 2-pentyne and 2-hexyne indicate the presence of two major dimers (**5a** and **5b**), representing more than 93% of all oligomers present, in a 2.3:1 ratio for 2-pentyne and a 1.3:1 ratio for 2-hexyne. ^{1}H and ^{13}C NMR spectra show that both isomers are substituted cyclobutenes which differ with respect to the position of the alkyl substituents at the endocyclic double bond (eq 4).[12] The activities are 2.0 and 1.3 turnovers/day (50 °C) for 2-pentyne and 2-hexyne, respectively.



(4)

5a **5b**

The cerium-catalyzed reactions of 2-pentyne and 2-hexyne are more complicated, as is suggested by the presence of five dimers in the reaction mixture (GC/MS) with isomers **5a** and **5b** as the major products (2-pentyne, together 89%, 2.4:1 ratio; 2-hexyne 80% 2.4:1 ratio).[13]

Stoichiometric α-methyl CH activation without subsequent dimerization takes place for MeC≡CR with bulky R groups, e.g. $SiMe_3$ and *t*-Bu.[14] 3-Hexyne does not react, even when kept at 80 °C for 2 months. Hence, cyclo-

(6) (a) Butler, P. E.; Griesbaum, K. *J. Org. Chem.* **1968**, *33*, 1956. (b) Inoue, Y.; Itoh, Y.; Hashimoto, H. *Chem. Lett.* **1978**, 911. (c) Seebach, D.; Graf, B. *Angew. Chem.* **1968**, *13*, 532.

(7) $Cp^*_2LaCH_2C{\equiv}CMe$ (**2**): ^{1}H NMR (benzene-d_6) δ 2.30 (q, $^5J_{HH}$ = 2.9 Hz, 2 H, CH_2), 1.90 (s, 30 H, C_5Me_5), 1.67 (t, $^5J_{HH}$ = 2.9 Hz, 3 H, Me); ^{13}C NMR δ 139.7 (s, *C*≡C), 118.6 (s, C_5Me_5), 102.8 (s, C≡*C*), 50.8 (t, $^1J_{CH}$ = 155 Hz, *C*H_2), 10.4 (q, $^1J_{CH}$ = 125 Hz, C_5*Me*$_5$), 7.8 (q, $^1J_{CH}$ = 130 Hz, Me). $Cp^*_2CeCH_2C{\equiv}CMe$ (**3**): ^{1}H NMR (benzene-d_6, 21 °C) δ 2.5 (s, 30 H, lw = 14 Hz, C_5Me_5), −9.6 (s, 3 H, lw = 6 Hz, Me), −30.5 (s, 2 H, lw = 38 Hz, *C*H_2). The exact bonding of the $-CH_2C{\equiv}CMe$ groups is still under investigation. Analogous to the case for allylic compounds, a dynamic equilibrium ($M{-}CH_2C{\equiv}CR \rightleftarrows CH_2{=}C{=}C(R)M$[8b]) or a static intermediate η^3 structure is possible.

(8) (a) For example, the reaction of 2-butyne with *n*-BuLi in THF leads to clean monometalation and the formation of a $CH_2C{\equiv}CMe$ anion; see: Klein, J.; Becker, J. Y. *Tetrahedron* **1978**, *28*, 5385. (b) Moreau, J. L. In *The Chemistry of Ketenes, Allenes, and Related Compounds*; Patai, S., Ed.; Wiley: Chichester, England **1980**; Chapter 10, p 364. (c) Klein, J. In *The Chemistry of the Carbon-Carbon Triple Bond*; Patai, S., Ed.; Wiley: Chichester, England, **1978**, Chapter 9, p 343.

(9) (a) See ref 2d. (b) Evans, W. J.; Meadows, J. H.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1984**, *106*, 1291. (c) Evans, W. J. *Polyhedron* **1987**, *6*, 803. (d) Schwartz, J.; Labinger, J. A. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 333. (d) McDade, C.; Bercaw, J. E. *J. Organomet. Chem.* **1985**, *279*, 281.

(10) IR (KBr/Nujol): 2720 (w), 1975 (m), 1930 (w), 1230 (w), 1020 (m), 710 (m), 600 (w) cm^{-1}. ^{1}H NMR (benzene-d_6): δ 2.16 (q, $^5J_{HH}$ = 2.9 Hz, 2 H, *C*H_2), 1.92 (s, 30 H, C_5*Me*$_5$), 1.54 (t, $^5J_{HH}$ = 2.9 Hz, 3 H, Me). ^{13}C NMR (benzene-d_6): δ 137.3 (s, *C*≡C), 116.9 (s, C_5Me_5), 94.9 (d, J_{YC} = 8.0 Hz, C≡*C*), 42.0 (d of t, $^1J_{CH}$ = 154 Hz, J_{YC} = 8.1 Hz, CH_2), 11.0 (q, $^1J_{CH}$ = 125 Hz, C_5*Me*$_5$), 8.4 (q, $^1J_{CH}$ = 130 Hz, Me). Anal. Calcd for $C_{24}H_{35}Y$: C, 69.89; H, 8.55. Found: C, 69.54; H, 8.41.

(11) Ionic radii for Ln^{3+} (6-coordinate): La^{3+}, 1.03 Å; Ce^{3+}, 1.01 Å; Y^{3+}, 0.90 Å. See: Shannon, R. D. *Acta Crystallogr.* **1976**, *A32*, 751.

(12) NMR data are given in the supplementary material.

(13) No attempts have been made to characterize these three minor isomers.

(14) The reactions were carried out in sealed NMR tubes for the Ce–alkyl compound (benzene-d_6, $Cp^*_2CeCH(SiMe_3)_2$/2-alkyne ratios of 1:15). ^{1}H NMR for $Cp^*_2CeCH_2C{\equiv}CR$ (benzene-d_6, 25 °C): R = $-SiMe_3$, δ 2.96 (s, 30 H, lw = 23 Hz, C_5Me_5), −7.07 (s, 9 H, lw = 5 Hz, $SiMe_3$), −32 (s, 2 H, lw = 80 Hz, CH_2); R = *t*-Bu, δ 2.69 (s, 30 H, lw = 10 Hz, C_5Me_5), −10.4 (s, 9 H, lw = 16 Hz, *t*-Bu), CH_2 protons not observed.

dimerization seems limited to alkynes bearing (a) at least one α-methyl group and (b) a small second alkyl group.

The details of the mechanism remain to be elucidated, but a plausible route is given in Scheme I. One of the key steps (ii) is alkyne insertion in the Ln–CH_2 bond. The 2-alkynyl compounds **2** and **3** and their analogues are the only organolanthanide species that can be oserved during the catalytic dimerization (NMR), and this suggests that alkyne insertion in the M–C bond is rate-determining. This step also determines the selectivity, i.e. isomeric ratios, of the reactions with asymmetrical 2-alkynes.

Acknowledgment. We thank the PX-2 group at the Koninklijke/Shell-laboratorium, Amsterdam, for stimulating discussions and Dr. A. P. Bruins and E. van der Meulen for recording the GC/MS spectra. Financial support from Shell Research BV is gratefully acknowledged.

Supplementary Material Available: An experimental section containing details of the preparation and spectroscopic characterization of compounds (4 pages). Ordering information is given on any current masthead page.

Generation of the 19-Electron ("18 + δ") Adducts $CpMo(CO)_3(L_2\text{-}P)$ and $CpMo(CO)_2(L_2\text{-}P,P')$ (Cp = η^5-$CH_3C_5H_4$, η^5-C_5Ph_4H, η^5-C_5Ph_5; L_2 = 2,3-Bis(diphenylphosphino)maleic Anhydride). Crystal Structure of the $(\eta^5\text{-}C_5Ph_4H)Mo(CO)_2L_2$ Complex

Fei Mao, Cecelia E. Philbin, Timothy J. R. Weakley, and David R. Tyler*

Department of Chemistry, University of Oregon, Eugene, Oregon 97403

Received September 28, 1989

The 19-electron ("18 + δ") $CpMo(CO)_3(L_2\text{-}P)$ (Cp = η^5-$CH_3C_5H_4$, η^5-C_5Ph_4H) and $CpMo(CO)_2(L_2\text{-}P,P')$ (Cp = η^5-$CH_3C_5H_4$, η^5-C_5Ph_4H, η^5-C_5Ph_5) complexes were generated by irradiation of $Cp_2Mo_2(CO)_6$ and L_2 (L_2 is the chelating phosphine ligand 2,3-bis(diphenylphosphino)maleic anhydride) in CH_2Cl_2 or THF. ($L_2\text{-}P$ indicates one P atom of L_2 is coordinated; $L_2\text{-}P,P'$ indicates two P atoms are coordinated.) ESR and IR spectra of these complexes show that the odd electron is primarily localized on the L_2 ligand (L_2 has low-energy π^* orbitals), and therefore, these complexes are best described as 18-electron complexes with reduced ligands ("18 + δ" complexes). All of the complexes were spectroscopically characterized, but only the $(\eta^5\text{-}C_5Ph_4H)Mo(CO)_2(L_2\text{-}P,P')$ complex could be isolated. The mechanism of formation of these complexes involves the reaction of a photogenerated $CpMo(CO)_3$ radical with the L_2 ligand to form initially the $CpMO(CO)_3(L_2\text{-}P)$ species; this complex then reacts to give the $CpMo(CO)_2(L_2\text{-}P,P')$ molecule. The crystal structure of the $(\eta^5\text{-}C_5Ph_4H)Mo(CO)_2(L_2\text{-}P,P')$ complex was determined; the molecule has a four-legged piano-stool structure. In the solid state, the two phosphorus atoms are not equivalent because of the orientation of the C_5Ph_4H ring. The two phosphorus atoms are also magnetically inequivalent at room temperature in solution on the ESR time scale but become equivalent at 185 °C. The dynamic ESR spectra are attributed to η^5-C_5Ph_4H ring rotation. An analysis of the spectra led to the following activation parameters for rotation of the C_5Ph_4H ring: $\Delta H^\ddagger = 2.2 \pm 0.1$ kcal mol^{-1}, $\Delta S^\ddagger = -22.9 \pm 0.3$ cal K^{-1} mol^{-1}. Rotation of the η^5-C_5Ph_4H ring is hindered because of the severe steric interactions between the phenyl rings on the C_5 ring and the phenyl rings bonded to the phosphorus atoms. Electrochemical, infrared, NMR, and ESR data are reported for the complexes generated in this study.

The reaction of 17-electron organometallic radicals with two-electron-donor ligands yields 19-electron adducts.[1] The stability of the 19-electron adducts depends critically on their electronic structure. At one extreme of the stability range are 19-electron transition states in which the unpaired electron is primarily metal-localized in a M–L antibonding orbital.[1] Adducts such as this are involved in many of the associatively activated substitution reactions of 17-electron species.[2,3] At the other extreme of stability are the relatively stable adducts that are perhaps best described as 18-electron complexes with reduced ligands (so-called "18 + δ" complexes).[4] An example of this type of complex is the $Co(CO)_3L_2$ species (L_2 is the chelating phosphine ligand 2,3-bis(diphenylphosphino)-maleic anhydride):[5]

(1) Stiegman, A. E.; Tyler, D. R. *Comments Inorg. Chem.* **1986**, *5*, 215–245.
(2) Tyler, D. R. *Prog. Inorg. Chem.* **1988**, *36*, 125–194.
(3) Trogler, W. C. *Int. J. Chem. Kinet.* **1987**, *19*, 1025–1047.

(4) Prof. Ted Brown (University of Illinois) coined the term "18 + δ" to describe those 19-electron adducts that are essentially 18-electron complexes with reduced ligands. The term 18 + δ is preferred when the term "19-electron adduct" might lead to confusion about the electronic structure of the adduct. Examples of 18 + δ complexes are increasingly numerous; see: (a) Kaim, W. *Inorg. Chem.* **1984**, *23*, 504–505. (b) Creber, K. A. M.; Wan, J. K. S. *Transition Met. Chem.* **1983**, *8*, 253–254. (c) Creber, K. A. M.; Wan, J. K. S. *J. Am. Chem. Soc.* **1981**, *103*, 2101–2102. (d) Alberti, A.; Hudson, A. *J. Organomet. Chem.* **1983**, *241*, 313–319. (e) Maroney, M. J.; Trogler, W. C. *J. Am. Chem. Soc.* **1984**, *106*, 4144–4151. (f) Kaim, W.; Kohlmann, S. *Inorg. Chem.* **1986**, *25*, 3442–3448. (g) Kaim, W. *J. Organomet. Chem.* **1984**, *262*, 171–178. (h) Kaim, W. *Inorg. Chim. Acta* **1981**, *53*, L151–L153. (i) Kaim, W. *Inorg. Chem.* **1984**, *23*, 3365–3368. (j) Alegria, A. E.; Lozada, O.; Rivera, H.; Sanchez, J. *J. Organomet. Chem.* **1985**, *281*, 229–236.
(5) Fenske, D. *Chem. Ber.* **1979**, *112*, 363–375.

0276-7333/90/2309-1510$02.50/0