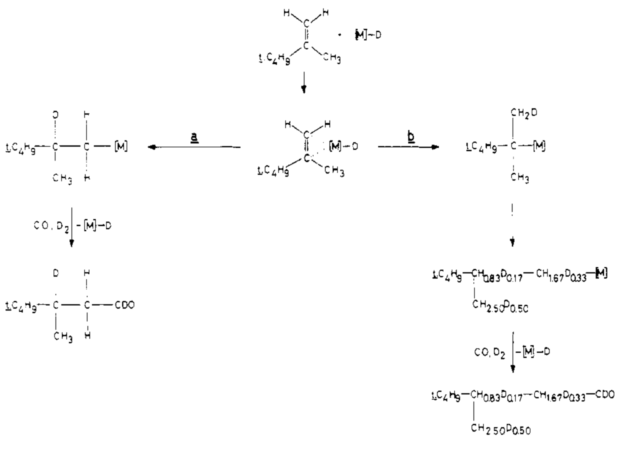
Chart I. Protium Content at the Different Carbon Atoms of 3,4,4-Trimethylpentanal Produced in the Deuterioformylation of 2,3,3-Trimethyl-1-butene by Rhodium and Cobalt Carbonyls

	$t\text{-}C_4H_9$—	CH—	CH_3	CH_2—CDO
$Co_2(CO)_8$	9.00	0.67	2.52	0.90
$Rh_4(CO)_{12}$	8.98	0.00	3.00	2.01

Scheme I



It follows, therefore, that in spite of practically exclusive formylation at the terminal carbon atom in 2,3,3-trimethyl-1-butene both by cobalt and rhodium carbonyls as the catalyst precursor, different pathways probably caused by different regioselectivities can be displayed by either catalyst in the first step of the reaction. A similar phenomenon could also be responsible for the extensive formylation (32%) of the methyl group in [1-^{14}C]-propene,[19,20] in the presence of $Co_2(CO)_8$. These results had previously been interpreted in terms of a rapid interconversion with considerable isomerization of π-olefin complexes. Alternatively, insertion of propylene into the H–Co bond could prevail with the addition of the metal atom to the internal carbon atom; equally probable β-elimination[21] from the two methyl groups should then bring about the high extent of formylation in position 3 of propylene.[19,20,22] A tentative rationalization has been proposed for such kind of attack, which has been called "anti-Markownikoff insertion".[23] However, the different reaction pathways observed using either rhodium or cobalt carbonyls as the catalyst precursors point out either that too much is still unknown for such rationalization or that the nature of the catalytic species formed from both metals is rather different.

Acknowledgment. This work was supported by the "Schweizerischer Nationalfonds zur Förderung der wissenschaftlichen Forschung".

---

(19) Piacenti, F.; Bianchi, M.; Frediani, P.; Matteoli, U.; Lo Moro, A. *J. Chem. Soc., Chem. Commun.* **1976**, 789.

(20) Piacenti, F.; Bianchi, M.; Frediani, P.; Matteoli, U.; Lo Moro, A. *Chim. Ind. (Milan)* **1976**, *58*, 759.

(21) Possible isotopic effects are disregarded on the basis of the same isomeric ratios of the aldehydes having been obtained with [1-^{14}C]propene and with unlabeled propene.

(22) Piacenti, F.; Pino, P.; Lazzaroni, R.; Bianchi, M. *J. Chem. Soc. C* **1966**, 488.

(23) Henrici-Olivé, G.; Olivé, S. *Top. Curr. Chemistry* **1976**, *67*, 107.

Synthesis and Structures of Titanaoxacyclobutanes

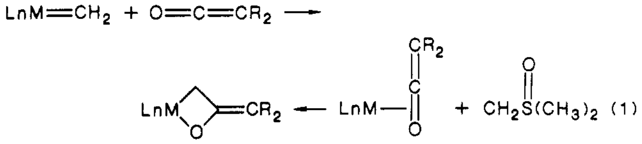
Suzzy C. Ho, S. Hentges, and Robert H. Grubbs*

Arnold and Mabel Beckman Laboratory of Chemical Synthesis,[†] *California Institute of Technology*
Pasadena, California 91125

Received September 17, 1987

Summary: Titanaoxacyclobutanes can be prepared by the addition of a ketene to a titanium methylene complex or by the addition of a methylene fragment to a titanium ketene complex. For example, the addition of 2 equiv of dimethylsulfoxonium methylide to titanocene chloro-acyl complexes yields titanaoxacyclobutanes. The first equivalent deprotonates the acyl to form the titanocene ketene complex which is trapped by the second equivalent of the methylide to yield the metallaoxacyclobutane. Both routes yield complexes that are stable to temperatures above 60 °C. Variable-temperature NMR studies show that the metallaoxacyclobutane ring is puckered with a barrier to inversion of 13–19 kcal/mol.

Metallaoxacyclobutanes have long been considered as intermediates in transition-metal-catalyzed olefin epoxidations and conversions of carbonyls to alkenes by metal alkylidenes.[1] To date, the major route to metallaoxacyclobutanes has been the reactions of high-valent, electron-rich, late transition metals with electron-deficient tetracyanooxiranes.[2] The analogous organic heteroatom complexes have also been observed in the olefin oxidation by SO_3 as well as in "Wittig" transformations.[4] We report here two independent routes to early-transition-metal metallaoxacyclobutanes: (1) reaction of a metal methylidene complex with an organic ketene and (2) coupling of a metal ketene complex with dimethylsulfoxonium methylide (eq 1).



Treatment of a yellow suspension of titanocene chloro-acyl complex 1[4] with an excess of dimethylsulfoxonium methylide[5] resulted in the instantaneous formation of a dark solution from which a red solid, 2, was isolated in 77% yield[6] (eq 2). The product is moderately air-sensitive and

---

[†] Contribution No. 7664.

(1) (a) Collman, J. P.; Brauman, J. L.; Meunier, B.; Hayashi, T.; Kodadek, T.; Raybuck, S. A. *J. Am. Chem. Soc.* **1985**, *107*, 200. (b) Groves, J. T.; Nenu, T. E. *Ibid.* **1983**, *105*, 5786. (c) Sharpless, K. B.; Teranishi, A. Y.; Bäckvall, J.-E. *Ibid.* **1977**, *99*, 3120. (d) Tebbe, F. N.; Parshall, G. W.; Reddy, G. S. *J. Am. Chem. Soc.* **1978**, *101*, 3611. (e) Pine, S. H.; Zahler, R.; Evans, D. A.; Grubbs, R. H. *Ibid.* **1980**, *102*, 3270. (f) Buchwald, S. L.; Grubbs, R. H. *Ibid.* **1983**, *105*, 5490. (g) Brown-Wensley, K. A. Ph.D. Thesis, California Institute of Technology, 1981.

(2) (a) Schlodder, R.; Ibers, J. A.; Lenarda, M.; Graziani, M. *J. Am. Chem. Soc.* **1974**, *96*, 6893. (b) Lenarda, M.; Ros, R.; Traverso, O.; Pitts, W. D.; Bradley, W. H.; Graziani, M. *Inorg. Chem.* **1977**, *16*, 3178.

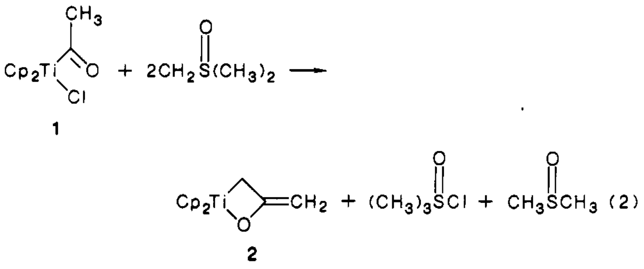
(3) (a) Naganame, M.; Okumura, O.; Noda, S.; Mori, A. *J. Chem. Soc., Chem. Commun.* **1973**, 841. (b) Uedejs, S.; Snoble, K. A. *J. Am. Chem. Soc.* **1973**, *93*, 4778.

(4) (a) Fachinetti, E.; Floriani, C. *J. Organomet. Chem.* **1974**, *71*, C5. (b) Bertelo, C. A.; Schwartz, J. *J. Am. Chem. Soc.* **1975**, *97*, 228.

(5) Corey, E. J.; Chaykovsky, M. *J. Am. Chem. Soc.* **1965**, *87*, 1353.

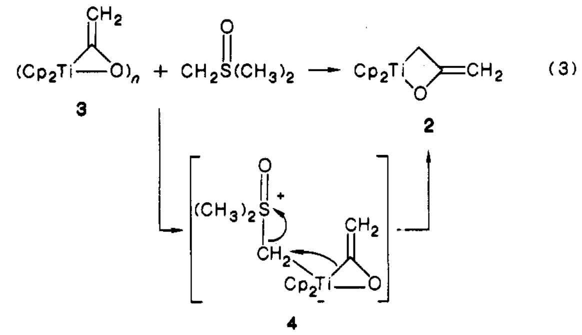
(6) To a cooled suspension of the chloro-acyl complex 1 (1.0 g, 3.9 mmol) in 20 mL of benzene was added 0.79 g (8.6 mmol) of neat dimethylsulfoxonium methylide by syringe. The resulting red solution was filtered through a medium frit packed with Celite (2 cm). The solvent was evaporated under vacuum to yield a brick-red solid that was washed with pentane and cold ether and then dried under vacuum overnight to yield 0.66 g (77%) of product 2. Protonolysis of 2 with anhydrous HCl yielded titanocene dichloride and acetone.

is stable in the solid state under an inert atmosphere. A cyclic, monomeric solution structure of **2** is supported by the spectral data[7] and the cryoscopic molecular weight.



(2)

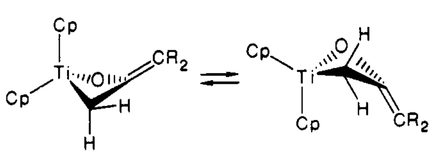
The stoichiometry of the reaction suggests the initial formation of the ketene complex **3** which reacts further with the excess ylide to form complex **2** and dimethyl sulfoxide. This is confirmed by direct treatment of the titanium ketene complex **3**[8] with dimethylsulfoxonium methylide (eq 3). The coupling of the methylene ylide and the ketene complex **3** is proposed to proceed through ionic intermediate **4** which rearranges and eliminates dimethyl sulfoxide.



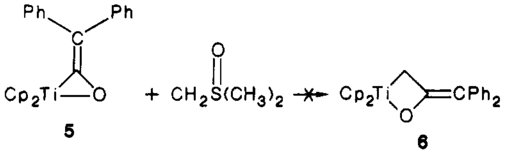
(3)

The diphenyl-substituted ketene complex **5**[9] gave intractable products (no detectable signals by ^{1}H NMR (eq 4)) on treatment with $Me_2S(O)CH_2$ under the same reaction conditions. The titanaoxacyclobutane **6**, however, can be obtained by heating a toluene solution of 3-*tert*-butyltitanacyclobutane **7** (a source of titanocene methylidene)[10] and diphenylketene at 80 °C for 10 min[11] (eq 5).

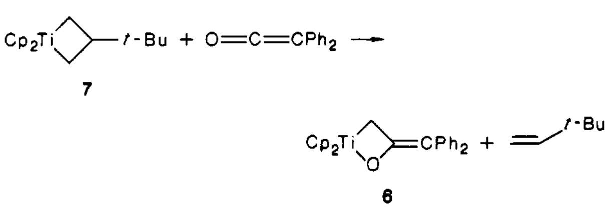
Scheme I



Analytically pure **6** was isolated in 71% yield.[12] Attempts to prepare **2** from **7** and ketene in an analogous reaction were unsuccessful.



(4)



(5)

Recrystallization of both **2** and **6** from a variety of solvents failed to yield crystals suitable for X-ray analysis. The solution structures of the titanaoxacyclobutanes were examined by dynamic ^{1}H NMR. At room temperature, only one signal was observed for both cyclopentadienyl rings of **2**. The titanium–methylene protons appeared as a broad signal that sharpened with increasing temperature. At −40 °C the methylene signal resolved into two doublets ($\Delta\nu$ = 87 Hz) with coupling constants of 10 Hz. At −60 °C the cyclopentadienyl resonances also appeared as two singlets ($\Delta\nu$ = 2 Hz).[13] The results suggest a puckered ring structures for complex **2**. Interconversion of the two degenerated puckered conformers by a ring flip is rapid at room temperature (Scheme I). The free energy of activation $\Delta G^{\ddagger}$ for this process was calculated to be 13.0 ± 0.2 kcal. In contrast, the ^{1}H NMR spectrum of **6** at room temperature exhibits two signals for the cyclopentadienyl ligands and two separated doublets for the titanium methylene protons (δ 2.54 and 1.91). Coalescence of the cyclopentadienyl resonances was achieved at 100 °C, and the $\Delta G^{\ddagger}$ was calculated to be 19.0 ± 0.2 kcal. The structural feature that leads to this high barrier to inversion is under investigation.[14] It has been proposed that puckering is due to donation of the electrons of the exo methylene double bond into the empty a_1 orbital on the titanium[15] as is seen in zironocene metallacyclopentenes.[16] We propose instead that the lone-pair electrons on oxygen can also donate into the empty a_1 orbital. Puckering of the metallaoxacycle ring is required for optimum orbital overlap.

It is surprising that these metallaoxacycles are thermally stable up to 100 °C. By comparison, the proposed me-

---

(7) **2**: mp 145–148 °C dec; ^{1}H NMR (C_6D_6, 90 MHz, 20 °C) δ 5.70 (s, 10 H), 3.73 (br s, 1 H), 3.64 (d, J = 1 Hz, 1 H), 1.80 (br s, 2 H); ^{13}C NMR (C_6D_6, 22.5 MHz) δ 182.6 (t, ^2J = 5 Hz), 113.2 (dm, ^1J = 174 Hz, ^3J = 6 Hz), 79.0 (dd, J = 155 Hz), 55.4 (dt, ^{13}J = 8 Hz, J = 129 Hz); IR (Nujol) 1588 cm^{-1} (C=C). Anal. Calcd for $C_{13}H_{14}OTi$: C, 66.88; H, 6.03; mol wt, 234. Found: C, 66.65; H, 5.98; mol wt, 240.

(8) Straus, D. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **1982**, *104*, 5499. The titanium ketene complex is known to exist in two different oligomeric forms with different colors (red and yellow) which are in equilibrium in solution. Reaction of the red Ti ketene isomer with sulfoxonium methylide proceeded instantaneously to give the metallaoxacyclobutane **2** while the yellow isomer gave the same product **2** at a much slower rate when treated with the ylide.

(9) Fachinetti, G.; Biran, D.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Am. Chem. Soc.* **1978**, *100*, 1921.

(10) Howard, T. R.; Lee, J. B.; Grubbs, R. H. *J. Am. Chem. Soc.* **1980**, *102*, 6876.

(11) A solution of 0.55 g (2.0 mmol) of 3-*tert*-butyltitanacyclobutane and 0.39 g (4.0 mmol) of diphenylketene in 4 mL of toluene was heated at 80 °C for 10 min. Purple-red solids precipitated. The dark green supernatant solution was removed by cannulation. The solid was washed with pentane and ether then dried under vacuum overnight (71% yield). Recrystallization from ether, dichloromethane, or toluene yielded **6** as thin plates. Complex **6** was first prepared from 3,3-dimethyltitanacyclobutane and diphenylketene at 0 °C in dichloromethane. Reaction of **6** with anhydrous HCl yielded titanocene dichloride and 1,1-diphenyl-2-propanone.

(12) **6**: mp 186–189 °C dec; ^{1}H NMR (C_6D_6, 90 MHz) δ 7.26 (m, 10 H), 5.89 (s, 5 H), 5.44 (s, 5 H), 2.54 (d, J = 10 Hz, 1 H), 1.91 (d, J = 10 Hz, 1 H); ^{13}C NMR (C_6D_6, 22.5 MHz) δ 55.1, 108.6, 113.3, 113.4, 124.8, 125.3, 131.5, 133.2, 144.4, 145.9, 178.0. Anal. Calcd for $C_{25}H_{22}OTi$: C, 77.72; H, 5.74. Found: C, 77.69; H, 5.76.

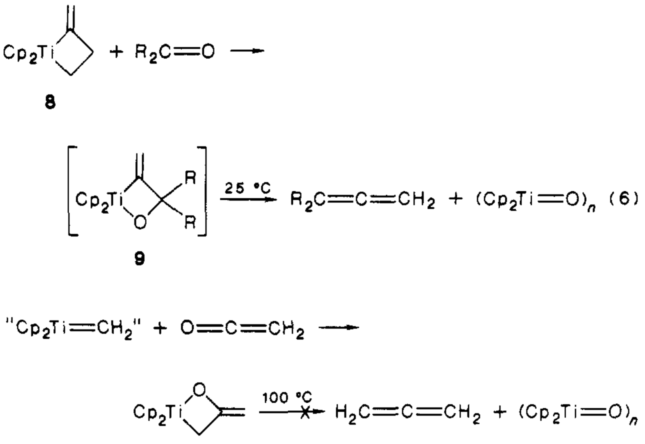
(13) **2**: ^{1}H NMR (CD_2Cl_2, 90 MHz, −60 °C) δ 5.86 (s, 5 H), 5.84 (s, 5 H), 3.38 (br s, 1 H), 3.28 (d, J = 1 Hz, 1 H), 2.23 (d, J = 10 Hz, 1 H), 1.24 (d, J = 10 Hz, 1 H).

(14) Anslyn, E. V.; Grubbs, R. H., unpublished results.

(15) (a) Tatsumi, K.; Yasuda, H.; Nakamura, A. *Isr. J. Chem.* **1983**, *23*, 145. (b) Hofmann, P.; Frede, M.; Stauffert, P.; Lasser, W.; Thewalt, U. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 712.

(16) (a) Erker, G.; Wicker, J.; Engel, K.; Rosenfeldt, F.; Dietrich, W.; Krüger, C. *J. Am. Chem. Soc.* **1980**, *102*, 6344. (b) Erker, G.; Engel, K.; Krüger, C.; Müller, G. *Organometallics* **1984**, *3*, 128.

tallaoxacycles in early metal olefin epoxidation and alkylidene transfer reactions have never been observed. Most striking is the comparison of the stable 3-alkylidene complexes **2** and **6** to the isomeric 2-methylene complexes such as **9** that are formed in the reaction of the precursor to $Cp_2Ti{=}C{=}CR_2$ (**8**) with ketones and aldehydes. Complex **9** is unstable at room temperature (eq 6).[17]



At least two major factors are considered to account for this difference. If the transition state for the cleavage of the metallaoxacycle is similar to that for the cleavage of the corresponding metallacyclobutanes, the ring must reach a planar geometry for the reaction to occur.[18] As indicated above, the 3-methylene-metallaoxacyclobutanes are puckered and there is a significant barrier to flattening. The 2-methylene isomers cannot pucker and maintain normal angles and bond distances. The differences in the barriers to planarity could account for a significant part of the difference in stabilities between the two isomers. In all the examples where **9** is a proposed intermediate, the β-carbon is substituted with alkyl groups. Substitution in this position has been shown to significantly destabilize the corresponding metallacyclobutanes[19] due to significant steric interactions between the β-substituent and the cyclopentadienyl ligands. Therefore, there is significantly greater relief of steric strain when **9** cleaves to allene and the titanocene oxide than when **2** or **6** reacts to yield the same products. We propose that these 3-alkylidene metallaoxacycles are more stable than the 2-alkylidene isomer due to the combined ability to pucker to increase bonding by donation of the oxygen lone pair electrons to the titanium center and to the absence of steric crowding due to the planar sp^2 β-carbon.

Acknowledgment. We wish to acknowledge the financial support of the Department of Energy (DE-FG03-85ER135452) and the National Science Foundation (CHE 8520517).

Registry No. **1**, 66320-88-5; **2**, 112681-97-7; **5**, 12099-30-8; **6**, 112681-98-8; **7**, 75687-68-2; $CH_2S(O)(CH_3)_2$, 70775-39-2; Cp_2TiCl_2, 1271-19-8; $O{=}C{=}CPh_2$, 525-06-4; $Cp_2TiCH_2C(CH_3)_2CH_2$, 80122-07-2; 1,1-diphenyl-2-propanone, 781-35-1; acetone, 67-64-1.

---

[17] Buchwald, S.; Grubbs, R. H. *J. Am. Chem. Soc.* **1983**, *105*, 5490.

[18] Anslyn, E. V.; Grubbs, R. H. *J. Am. Chem. Soc.* **1987**, *109*, 4880.

[19] Straus, D. A.; Grubbs, R. H. *Organometallics* **1982**, *1*, 1658.

Synthesis, Characterization, and Reactivity of Several Unusual Trinuclear Clusters Containing Either Rhodium or Cobalt and the Cyclopentadienyl or Pentamethylcyclopentadienyl Ligands

Craig E. Barnes* and Michelle R. Dial

Department of Chemistry, University of Tennessee
Knoxville, Tennessee 37996-1600

Received September 25, 1987

Summary: Exposure of various mono- and dinuclear carbonyl complexes of rhodium and cobalt to the bis(ethylene) complex $CpCo(C_2H_4)_2$ gives rise to several new trinuclear clusters of the form $(Cp^*M)_{3-n}(CpCo)_n(\mu_3\text{-}CO)_2$ (n = 1, 2; M = Co, Rh) in high yield. These 46e clusters exhibit paramagnetically shifted ^{1}H NMR spectra and readily engage in the reversible transfer of a cyclopentadienyl cobalt fragment to suitable organometallic acceptors.

Recently, a series of unsaturated trinuclear cluster complexes of the form $Cp^*_3MM'M''(\mu_3\text{-}CO)_2$ have been described which exhibit interesting electronic properties.[1,2] These complexes are unusual in that they contain three low-valent, electron-rich metals in a highly electron-deficient cluster arrangement (46 electron count). Depending on the metals and substitution on the cyclopentadienyl rings, several different high- and low-spin electron configurations have been reported for these complexes.[1a,2a–c] Herein we report on a broadly applicable synthetic methodology for the synthesis of a wide variety of this type of trinuclear cluster containing at least one CpCo fragment. Preliminary characterization of the electronic states of several new examples of these clusters is also presented along with initial investigations into their reactions with carbon monoxide and several organometallic complexes.

---

[1] (a) Herrmann, W. A.; Barnes, C. E.; Zahn, T.; Ziegler, M. L. *Organometallics* **1985**, *4*, 172–180. (b) Hörlein, R.; Herrmann, W. A.; Barnes, C. E.; Weber, C.; Krüger, C.; Ziegler, M. L.; Zahn, T. *J. Organomet. Chem.* **1987**, *321*, 257–272. (c) Herrmann, W. A.; Barnes, C. E.; Serrano, R.; Koumboris, B. *J. Organomet. Chem.* **1983**, *256*, C30–C34.

[2] (a) Green, M.; Hankey, D. R.; Howard, J. A. K.; Louca, P.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1983**, 757–758. (b) Bray, A. C.; Green, M.; Hankey, D.; Howard, J.; Johnson, O.; Stone, F. G. A. *J. Organomet. Chem.* **1985**, *281*, C12–C16. (c) Olsen, W. L.; Stacy, A. M.; Dahl, L. F. *J. Am. Chem. Soc.* **1986**, *108*, 7646–7656. (d) Carriedo, G. A.; Howard, J. A. K.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1984**, 1555–1561. (e) Barr, R. D.; Green, M.; Howard, J. A. K.; Marder, T. B.; Orpen, A. G.; Stone, F. G. A. *Ibid.* **1984**, 2757–2763. (f) Farrugia, L. J.; Jeffery, J. C.; Marsden, C.; Stone, F. G. A. *Ibid.* **1985**, 645–650. (g) Jeffery, J. C.; Marsden, C.; Stone, F. G. A. *Ibid.* **1985**, 1315–1321. (h) Barr, R. D.; Green, M.; Marsden, K.; Stone, F. G. A.; Woodward, P. *Ibid.* **1983**, 507–512. (i) Carriedo, G. A.; Howard, J. A. K.; Stone, F. G. A. *J. Organomet. Chem.* **1983**, *250*, C28–C32. (j) Brun, P.; Dawkins, G. M.; Green, M.; Miles, A. D.; Orpen, A. G.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1982**, 926–927. (k) Stone, F. G. A. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 89–99 and references therein. (l) Boag, N. M.; Green, M.; Mills, R. M. Pain, G. N.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1980**, 1171–1173. (m) Green, M.; Mills, R. M.; Pain, G. N.; Stone, F. G. A.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1982**, 1309–1319. (n) Green, M.; Howard, J. A. K.; Pain, G. N.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1982**, 1327–1331. (o) Mague, J. T. *J. Organomet. Chem.* **1986**, *305*, 1–198. (p) Bedard, R. L.; Rae, A. D.; Dahl, L. F. *J. Am. Chem. Soc.* **1986**, *108*, 5924–5932. (q) Bedard, R. L.; Dahl, L. F. *Ibid.* **1986**, *108*, 5933–5948. (r) Olson, W. L.; Dahl, L. F. *Ibid.* **1986**, *108*, 7657–7663. (s) Lawson, R. J.; Shapley, J. R. *Inorg. Chem.* **1978**, *17*, 772–774. (t) Jan, D.-Y.; Hsu, L.-Y.; Hsu, W.-L.; Shore, S. G. *Organometallics*, **1987**, *6*, 274–283. (u) Lauher, J. W. *J. Am. Chem. Soc.* **1986**, *108*, 1521–1531. (v) Zonnevylle, M. C.; Silvestre, J.; Hoffmann, R. *Ibid.* **1986**, *108*, 1509–1517. (w) Uchtman, V. A. *J. Am. Chem. Soc.* **1969**, *91*, 3763–3769. (x) Strouse, C. E.; Dahl, L. F. *Discuss. Faraday Soc.* **1969**, *No. 47*, 93–106. (y) Byers, L. R.; Uchtman, V. A.; Dahl, L. F. *J. Am. Chem. Soc.* **1981**, *103*, 1942–1951.

0276-7333/88/2307-0782$01.50/0