

HPLC, HRMS, optical rotation) with an authentic sample.

In summary, an efficient synthetic route to the aminopolyol **2** is described. This compound may be selectively N-acylated to provide any of the homologous tunicamycin antibiotics in pure form as well as a series of related structures of potential utility as biological probes.

**Acknowledgment.** This research was generously supported by the National Science Foundation, ICI Americas Inc., and Glaxo Inc. D.Y.G. acknowledges a doctoral fellowship from the Natural Sciences and Engineering Research Council of Canada.

**Supplementary Material Available:** Procedures for the synthesis of **5**, *N*-BOC-2',3'-bis(allyloxycarbonate)-protected uridine 5'-aldehyde, and (*E*)-13-methyltetradecenoic acid and a summary of spectral and analytical data for all synthetic intermediates (42 pages). Ordering information is given on any current masthead page.

### Transformation of an Alkynyl Thioether into a Disubstituted Acetylene by Combination with a Chromium Carbene

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Although the combination of acetylenes with metal carbenes like **1** is a wellspring of organic structures,<sup>1</sup> few of the acetylenes previously studied have been substituted at their triple bonds by atoms other than carbon or hydrogen. Alkynyl ethers give the *p*-methoxyphenol products of the Dötz reaction.<sup>2</sup> Ynamines give pentacarbonyl (1-amino-2-propenylidene)chromiums,<sup>3</sup> and, after heating, indenenes.<sup>3c,4</sup> Bis(diphenylphosphino)acetylene after heating also gives indenenes.<sup>5</sup> (Trimethylsilyl)acetylene gives the normal Dötz product and bis(trimethylsilyl)acetylene a ketene.<sup>6</sup> We report here that, as pictured in eq 1, when the acetylene is an alkynyl thioether, a precursor easily obtained,<sup>7</sup> the structure of the product, despite the enormous variety previously formed from metal carbenes and acetylenes,<sup>1</sup> is of a kind not seen before.<sup>8,9</sup>

(1) Leading references: (a) McCallum, J. S.; Kunng, F.-A.; Gilbertson, S. R.; Wulff, W. D. *Organometallics* **1988**, *7*, 2346. (b) Bos, M. E.; Wulff, W. D.; Miller, R. A.; Chamberlin, S.; Brandvold, T. A. *J. Am. Chem. Soc.* **1991**, *113*, 9293. (c) Wulff, W. D. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: New York, 1991; Vol. 5, p 1065 ff. (d) Katz, T. J.; Yang, G. X.-Q. *Tetrahedron Lett.* **1991**, *32*, 5895. (e) Katz, T. J.; Sivavec, T. M. *J. Am. Chem. Soc.* **1985**, *107*, 737. (f) Hoye, T. R.; Rehberg, G. M. *J. Am. Chem. Soc.* **1990**, *112*, 2841. (g) Harvey, D. F.; Lund, K. P.; Neil, D. A. *Tetrahedron Lett.* **1991**, *32*, 6311. (h) Herndon, J. W.; Tumer, S. U.; Schnatter, W. F. K. *J. Am. Chem. Soc.* **1988**, *110*, 3334. (i) Grotjahn, D. B.; Dötz, K. H. *Synlett* **1991**, 381. (j) Schwindt, M. A.; Miller, J. R.; Hegedus, L. S. *J. Organomet. Chem.* **1991**, *413*, 143. (k) Katz, T. J.; Lee, S. J. *J. Am. Chem. Soc.* **1980**, *102*, 422.

(2) (a) Yamashita, A.; Toy, A. *Tetrahedron Lett.* **1986**, *27*, 3471. Other metal carbenes behave similarly: (b) Yamashita, A. *J. Am. Chem. Soc.* **1985**, *107*, 5823. (c) Yamashita, A.; Seahill, T. A.; Toy, A. *Tetrahedron Lett.* **1985**, *26*, 2969. (d) Yamashita, A.; Toy, A.; Ghazal, N. B.; Muchmore, C. R. *J. Org. Chem.* **1989**, *54*, 4481. The tungsten analogue with ethoxyacetylene is said to give the pentacarbonyl (1-ethoxy-3-phenyl-2-propenylidene)tungsten: (e) Casey, C. P.; Polichnowski, S. W.; Shusterman, A. J.; Jones, C. R. *J. Am. Chem. Soc.* **1979**, *101*, 7282.

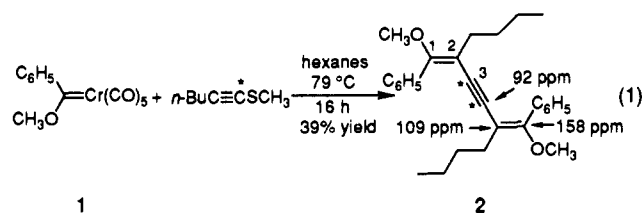
(3) (a) Dötz, K. H.; Kreiter, C. G. *Organomet. Chem.* **1975**, *99*, 309. (b) Dötz, K. H. *Chem. Ber.* **1977**, *110*, 78. (c) Dötz, K. H.; Pruskil, I. *Chem. Ber.* **1978**, *111*, 2059. (d) Fischer, H.; Dötz, K. H. *Chem. Ber.* **1980**, *113*, 193. (e) Dötz, K. H.; Kreiter, C. G. *Chem. Ber.* **1976**, *109*, 2026.

(4) (a) Dötz, K.-H.; Neugebauer, D. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 851. (b) Review: Dötz, K. H. In *Reactions of Coordinated Ligands*; Braterman, P. S., Ed.; Plenum: New York, 1986; Vol. 1, Chapter 4.

(5) (a) Dötz, K. H.; Pruskil, I.; Schubert, U.; Ackermann, K. *Chem. Ber.* **1983**, *116*, 2337. (b) Cambie, R. C.; Rutledge, P. S.; Tercel, M.; Woodgate, P. D. *J. Organomet. Chem.* **1986**, *315*, 171.

(6) Dötz, K. H.; Fügen-Köster, B. *Chem. Ber.* **1980**, *113*, 1449.

(7) 1-Alkyne + *n*-BuLi in THF at -78 °C, followed by (MeS)<sub>2</sub> Brandsma, L. *Preparative Acetylene Chemistry*, 2nd ed.; Elsevier: New York, 1988; p 132.



The structure of **2** (analyzed as C<sub>28</sub>H<sub>34</sub>O<sub>2</sub>) is revealed by its NMR spectra,<sup>10</sup> showing equal numbers of phenyl, methoxy, and butyl groups, and four quaternary carbons, the phenyl (resonating at  $\delta$  134.51) and three others (resonating at  $\delta$  158.23, 108.94, and 92.20). These last are assigned to C-1, C-2, and C-3 on the basis of analogies.<sup>11</sup> The experiment that identified the structure is one in which C-1 of the precursor (starred in eq 1) is replaced by <sup>13</sup>C. The only resonance in the product that intensifies is the one at 92 ppm, and the only ones split by coupling to the <sup>13</sup>C are those at 109 and 158 ppm. The split peaks appear as AA'X "triplets", the separations of the outer lines (which should equal  $J_{AX} + J_{A'X}$ ) being 102.5 Hz for the former resonance and 10.5 Hz for the latter. For there to be only one major splitting, the labeled carbons in **2** must be acetylenic. That they are is also demonstrated by the magnitude of the 102.5 Hz splitting, which identifies a bond between carbons that are sp and sp<sup>2</sup> hybridized.<sup>16</sup> That the butyl and phenyl groups are not interchanged is shown by the 5.6 Hz coupling (collapsed by irradiating  $\delta_H$  2.25) between the allylic methylene protons and C-3. This is considerably larger than that of known four-bond HCC=CC couplings.<sup>20,21</sup> The stereochemistry about the double bond is shown by the 5% NOE of the carbon resonance at 92 ppm when either  $\delta_H$  7.55 (the *o*-phenyl protons) or 2.25 is irradiated and the lack of NOE when the resonance irradiated is  $\delta_H$  3.37 (the OCH<sub>3</sub>).<sup>22</sup>

(8) 1-(Methylthio)-1-propyne and pentacarbonyl [ethoxy(phenyl-ethynyl)methylene]tungsten, the only alkynyl thioether and metal carbene previously combined, at 40 °C inserted the acetylene into the C=M bond. Fischer, H.; Meisner, T.; Hofmann, J. *J. Organomet. Chem.* **1990**, *397*, 41.

(9) The reaction of 1-(methylthio)-1-octyne analogous to eq 1 is described in the supplementary material.

(10) <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz):  $\delta$  0.88 (t, 7.1 Hz, 6 H), 1.34 (m, 8 H), 2.25 (t, 7.4 Hz, 4 H), 3.37 (s, 6 H), 7.27 (m, 6 H), 7.54 (m, 4 H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz):  $\delta$  14.01, 22.49, 29.94, 30.79, 58.22, 92.20, 108.94, 127.75, 128.18, 128.95, 134.51, 158.23.

(11) C-1: calcd is 160.3 ppm (ref 12); the analogous carbon in the lactone of 4-methoxy-4-*p*-tolyl-2-(3-hydroxypropyl)-but-3-enoic acid resonates at 157.0 ppm (ref 1a) and in (*Z,Z*)-1,6-diphenyl-1,6-bis(phenylthio)hexa-1,5-dien-3-yne at 147.5 ppm (ref 13). This last compound also provides analogies for the resonance of C-3 (96.4 ppm) and the UV spectrum. Its  $\lambda_{max}$  in CH<sub>3</sub>CN (372 nm, log  $\epsilon$  = 4.45) plus increments for replacing RS by RO (48 nm, ref 14) and adding two alkyls (+10 nm) implies that  $\lambda_{max}$  for **2** should be 334 nm. Found (in 95% EtOH) is 328 nm (log  $\epsilon$  = 4.20). C-2: 101 ppm is calculated by adding to the chemical shift of  $\alpha$ -methoxystyrene (81.71 ppm) increments for the butyl and ethynyl substituents (ref 12) and 14.9 ppm for the deconjugating effect of a substituent cis to methoxy (ref 15).

(12) Pretsch, E.; Clerc, T.; Seibl, J.; Simon, W. *Tables of Spectral Data for Structure Determination of Organic Compounds*, 2nd ed.; Springer-Verlag: New York, 1989; p C85 ff.

(13) Zschunke, A.; Mügge, C.; Hintzsche, E.; Schroth, W. *J. Prakt. Chem.-Zsch. Z.* **1992**, *334*, 141.

(14) Scott, A. I. *Interpretation of the Ultraviolet Spectra of Natural Products*; Pergamon Press: New York, 1964; Table 2.

(15) (a) Taskinen, E. *Tetrahedron* **1978**, *34*, 425. (b) Strobel, M. P.; Andrieu, C. G.; Paquer, D.; Vazeux, M.; Pham, C. C. *Nouv. J. Chim.* **1980**, *4*, 101.

(16) Equations for  $J_{AX}$  (ref 17) and for  $J_{A'X}$  (ref 18) when summed imply that  $(\%S_A)(\%S_X) = 1617$ , similar to the ideal  $(50)(33\frac{1}{3}) = 1667$ . In two phenylacetylenes  $J_{AX} + J_{A'X}$  is 104 Hz (ref 19), while a substitution of *t*-Bu for Ph reduces the sum to 77 Hz (ref 19b).

(17) Frei, K.; Bernstein, H. J. *J. Chem. Phys.* **1963**, *38*, 1216.

(18) Lambert, J.; Klessinger, M. *Magn. Reson. Chem.* **1987**, *25*, 456.

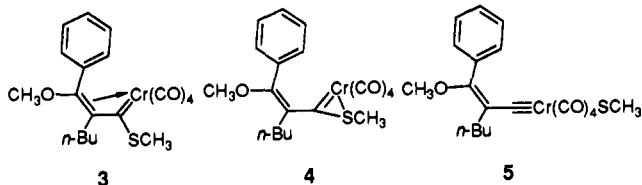
(19) (a) Hansen, P. E.; Poulsen, O. K.; Berg, A. *Org. Magn. Reson.* **1975**, *7*, 405. (b) Kamińska-Trela, K.; Biedrzycka, Z.; Machinek, R.; Knieriem, B.; Lüttke, W. *J. Organomet. Chem.* **1986**, *314*, 53.

(20) Hansen, P. E. *Prog. Nucl. Magn. Reson. Spectrosc.* **1981**, *14*, 175, Table 10.

(21) Three-bond H-C couplings are this size. (a) Karabatsos, G. J.; Orzech, C. E., Jr. *J. Am. Chem. Soc.* **1965**, *87*, 560. (b) Vogeli, U.; von Philipsborn, W. *Org. Magn. Reson.* **1975**, *7*, 617. (c) Hansen, M.; Jakobsen, H. J. *J. Magn. Reson.* **1975**, *20*, 520.

(22) Neuhaus, D.; Williamson, M. P. *The Nuclear Overhauser Effect in Structural and Conformational Analysis*; VCH Publishers: New York, 1989.

The transformation of **1** into **2** probably involves species related to metal carbene **3**, analogous to presumed intermediates in the Dötz and other reactions.<sup>1</sup> Yet although it has (*E*)-stereochemistry,<sup>1a</sup> **3** does not yield a naphthol or an indene. The reason we propose is that it is diverted by the adjacent sulfur atom, as pictured in structure **4**, to **5**, which transforms into **2** either by dimerizing or by combining with **3**.<sup>23</sup> This accords with the



propensity of heteroatoms to bridge carbon–metal bonds,<sup>25</sup> the facility with which structures  $Z(\text{Et}_2\text{N})\text{C}=\text{Cr}(\text{CO})_5$  convert to  $(\text{Et}_2\text{N})\text{C}=\text{Cr}(\text{CO})_4\text{Z}$  (*Z* is Se, Te, Cl, Br, I, Sn, and Pb),<sup>26</sup> the ready dimerizations of metal carbenes to acetylenes<sup>27</sup> and their derivatives,<sup>28,29</sup> and the instability of (alkylthio)methylenechromium pentacarbonyls.<sup>30</sup> In this connection, note that the metal carbene adds to the acetylene in the direction that should be favored electronically,<sup>8</sup> that is, in the way it adds to ynamines<sup>3a–d</sup> but not, seemingly,<sup>2a,31</sup> to most alkoxyacetylenes.<sup>2</sup>

The transformation may be useful in mechanistic analysis for it is one of only two<sup>1c</sup> that appear to trap the presumed 2-propenyldiene–metal precursor of products like phenols and indenes.<sup>1a,b</sup> It may also lead to new ways to couple molecules, for it suggests that chromium (alkyl- and arylthio)carbenes<sup>30</sup> in general may link to give acetylenes. The relevant previous work is ambiguous. On the one hand there is an assertion that they do link,<sup>32</sup> while on the other a structure related to **3** gave a 1-(alkylthio)indene instead.<sup>33,34</sup>

(23) The eliminated  $[\text{Cr}(\text{CO})_4\text{SCH}_3]_2$  is not known, but the  $\text{SePh}^{24a}$  and  $\text{Me}_2\text{P}$  analogues<sup>24b</sup> are, as is  $[\text{W}(\text{CO})_4\text{SPh}]_2$ .<sup>24c</sup>

(24) (a) Röhl, W.; Fischer, E. O.; Neugebauer, D.; Schubert, U. Z. *Naturforsch B: Anorg. Chem. Org. Chem.* **1982**, *37B*, 1274. (b) Vahrenkamp, H. *Chem. Ber.* **1978**, *111*, 3472 and references therein. (c) Lucas, C. R.; Newlands, M. J.; Gabe, E. J.; Lee, F. L. *Can. J. Chem.* **1987**, *65*, 898.

(25) By S: (a) Doyle, R. A.; Angelici, R. J. *J. Am. Chem. Soc.* **1990**, *112*, 194 and references therein. (b) Kreissl, F. R.; Keller, H. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 904. (c) Schenk, W. A.; Rüb, D.; Burschka, C. J. *Organomet. Chem.* **1987**, *328*, 305. (d) By S, Se, and Te: Werner, H. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 927 and references therein. By O: (e) Adams, H. A.; Bailey, N. A.; Cahill, P.; Rogers, D.; Winter, M. J. *J. Chem. Soc., Chem. Commun.* **1983**, 831. By P: (f) Rathke, J. W.; Muettterties, E. L. *J. Am. Chem. Soc.* **1975**, *97*, 3272. (g) Karsch, H. H.; Klein, H.-F.; Schmidbauer, H. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 637. (h) Lindner, E.; Neese, P.; Hiller, W.; Fawzi, R. *Organometallics* **1986**, *5*, 2030 and references therein. (i) Gibson, V. C.; Graimann, C. E.; Hare, P. M.; Green, M. L. H.; Bandy, J. A.; Grebenik, P. D.; Prout, K. J. *J. Chem. Soc., Dalton Trans.* **1985**, 2025. (j) Young, S. J.; Olmstead, M. M.; Knudsen, M. J.; Schore, N. E. *Organometallics* **1985**, *4*, 1432. (k) Etienne, M.; Choukroun, R.; Basso-Bert, M.; Dahan, F.; Gervais, D. *Nouv. J. Chim.* **1984**, *8*, 531.

(26) (a) Fischer, E. O.; Himmelreich, D.; Cai, R.; Fischer, H.; Schubert, U.; Zimmer-Glasser, B. *Chem. Ber.* **1981**, *114*, 3209 and references cited therein. (b) Fischer, H.; Fischer, E. O.; Cai, R.; Himmelreich, D. *Chem. Ber.* **1983**, *116*, 1009.

(27) (a) Fischer, E. O.; Ruhs, A.; Plabst, D. Z. *Naturforsch B: Anorg. Chem. Org. Chem.* **1977**, *32B*, 802. (b) McDermott, G. A.; Mayr, A. *J. Am. Chem. Soc.* **1987**, *109*, 580.

(28) (a) Kim, H. P.; Angelici, R. J. *Adv. Organomet. Chem.* **1987**, *27*, 51. (b) Buhro, W. E.; Chisholm, M. H. *Adv. Organomet. Chem.* **1987**, *27*, 311.

(29) For couplings of alkoxy- and aminocarbynes see: (a) Vrtis, R. N.; Lippard, S. J. *Isr. J. Chem.* **1990**, *30*, 331. (b) Vrtis, R. N.; Liu, S.; Rao, C. P.; Bott, S. G.; Lippard, S. J. *Organometallics* **1991**, *10*, 275. (c) Filipou, A. C.; Grünleitner, W.; Völkl, C.; Kiprof, P. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1167. (d) Carnahan, E. M.; Lippard, S. J. *J. Chem. Soc., Dalton Trans.* **1991**, 699. (e) Carnahan, E. M.; Lippard, S. J. *J. Am. Chem. Soc.* **1990**, *112*, 3230. (f) Mayr, A.; Bastos, C. M. *J. Am. Chem. Soc.* **1990**, *112*, 797.

(30) The chromium derivatives decompose at or below room temperature. Their tungsten analogues are more stable. (a) Fischer, E. O.; Leopold, M.; Kreitner, C. G.; Müller, J. *Chem. Ber.* **1972**, *105*, 150. (b) Lam, C. T.; Senoff, C. V.; Ward, J. E. H. *J. Organomet. Chem.* **1974**, *70*, 273. (c) Reference 2d. (d) Parlier, A.; Rudler, H.; Alvarez, C. J. *Organomet. Chem.* **1989**, *379*, 271. (e) Reference 8.

(31) The conclusion may be invalidated if the electronically favored adduct [the (1-alkoxy-2-propenyldiene)chromium] does not give the Dötz product.

(32) Dötz, K. H.; Leue, V. *J. Organomet. Chem.* **1991**, *407*, 337.

**Acknowledgment.** We thank the National Science Foundation for partial support (CHE 85-13274) and Diego Hoic and Shuhao Shi for help.

**Supplementary Material Available:** Preparative details, <sup>1</sup>H and <sup>13</sup>C NMR spectra of unlabeled **2** (the later with and without proton couplings), and <sup>13</sup>C NMR spectra of labeled **2**, showing <sup>13</sup>C couplings, and proton–carbon NOEs (6 pages). Ordering information is given on any current masthead page.

(33) (a) Raubenheimer, H. G.; Kruger, G. J.; Marais, C. F.; Otte, R.; Scott, F. S. *Appl. J. Chem.* **1987**, *40*, 207. (b) Raubenheimer, H. G.; Kruger, G. J.; Linford, L.; Marais, C. F.; Otte, R.; Hattingh, J. T. Z.; Lombard, A. *J. Chem. Soc., Dalton Trans.* **1989**, 1565.

(34) The only metal-mediated transformations previously recorded for alkynyl thioethers are polymerizations by Mo, W, and Ni catalysts,<sup>35</sup> additions of organocoppers<sup>36</sup> and tantalum derivatives,<sup>37</sup> coordination to transition metals,<sup>38</sup> and the insertion of 1-(methylthio)-1-propyne into a tungsten carbene.<sup>8</sup>

(35) (a) Masuda, T.; Matsumoto, T.; Yoshimura, T.; Higashimura, T. *Macromolecules* **1990**, *23*, 4902. (b) Matsumoto, T.; Masuda, T.; Higashimura, T. *J. Polym. Sci., Part A: Polym. Chem.* **1991**, *29*, 295. (c) Richter, A. M.; Richter, J. M.; Beye, N.; Fanghänel, E. *J. Prakt. Chem.* **1987**, *329*, 811.

(36) (a) Normant, J. F.; Alexakis, A. *Synthesis* **1981**, 841. (b) Rao, S. A.; Knochel, P. *J. Am. Chem. Soc.* **1991**, *113*, 5735. (c) Vermeer, P.; de Graaf, C.; Meijer, J. *Recl. Trav. Chim. Pays-Bas* **1974**, *93*, 24.

(37) Takai, K.; Miyai, J.; Kataoka, Y.; Utimoto, K. *Organometallics* **1990**, *9*, 3030.

(38) (a) Mo: Beevor, R. G.; Green, M.; Orpen, A. G.; Williams, I. D. *J. Chem. Soc., Dalton Trans.* **1987**, 1319. (b) Zr: Van Wageningen, B. C.; Livinghouse, T. *Tetrahedron Lett.* **1989**, *30*, 3495. (c) Ru: Miller, D. C.; Angelici, R. J. *Organometallics* **1991**, *10*, 79.

## Detection of a $\sigma$ -Complex in the Reaction of Cobalt Atoms with Methane

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Received July 27, 1992

Revised Manuscript Received November 11, 1992

Although the occurrence of two-electron, three-center  $\text{M} \cdots \text{H} \cdots \text{C}$  bonds is now well-established for a large number of organometallic complexes in which the C–H bonds of a bound ligand interact with the metal center,<sup>1</sup> there is less evidence for the coordination of free hydrocarbon C–H bonds to transition-metal species.<sup>2–5</sup> These weak interactions are thought to be important in C–H activation.<sup>6–8</sup> The most direct evidence for alkane complexes came from the early work of Perutz and Turner<sup>2</sup> on  $\text{M}(\text{CO})_5$  fragments bound to alkanes in low-temperature matrices. Alkane complexes

(1) (a) Brookhart, M.; Green, M. L. H. *J. Organomet. Chem.* **1983**, *250*, 395. (b) Timmers, F.; Brookhart, M. *Organometallics* **1985**, *4*, 1365. (c) Calvert, R. B.; Shapley, J. R. *J. Am. Chem. Soc.* **1978**, *100*, 7726.

(2) Perutz, R. N.; Turner, J. J. *J. Am. Chem. Soc.* **1975**, *97*, 4791.

(3) Bullock, R. M.; Headford, C. E. L.; Kegley, S. E.; Norton, J. R. *J. Am. Chem. Soc.* **1985**, *107*, 727.

(4) Periana, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 7332.

(5) Gould, G. L.; Heinekey, D. M. *J. Am. Chem. Soc.* **1989**, *111*, 5502.

(6) Crabtree, R. H.; Holt, E. M.; Lavin, M.; Morehouse, S. M. *Inorg. Chem.* **1985**, *24*, 1986. (b) Crabtree, R. H. *Chem. Rev.* **1985**, *85*, 245.

(7) (a) Chamberlain, L. R.; Rothwell, I. P.; Huffman, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 1502. (b) Buchanan, J. M.; Stryker, J. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 1537. (c) Stoutland, P. O.; Bergman, R. G. *J. Am. Chem. Soc.* **1985**, *107*, 4581. (d) Thompson, M. E.; Bercaw, J. E. *Pure Appl. Chem.* **1984**, *56*, 1. (e) Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1984**, *106*, 1650; **1985**, *107*, 620. (f) Hoyana, J. K.; Graham, W. A. G. *J. Am. Chem. Soc.* **1982**, *104*, 3722. Hoyana, J. K.; McMaster, A. D.; Graham, W. A. G. *J. Am. Chem. Soc.* **1983**, *105*, 7190. (g) Graham, W. A. G. *J. Organomet. Chem.* **1986**, *300*, 81. (h) Baudry, D.; Ephritikhine, M.; Felkin, H.; Zakrzewski, J. *J. Organomet. Chem.* **1984**, *272*, 391. (i) Park, J. W.; Mackenzie, P. B.; Schaefer, W. P.; Grubbs, R. H. *J. Am. Chem. Soc.* **1986**, *108*, 6402.

(8) (a) Koga, N.; Obara, S.; Kitaura, K.; Morokuma, K. *J. Am. Chem. Soc.* **1985**, *107*, 7109. (b) Fitzpatrick, N. J.; McGinn, M. A. *J. Chem. Soc., Dalton Trans.* **1985**, 1637.