drides, which then transfer hydride ion intramolecularly. The conversion of **13** to **15** is particularly noteworthy since it involves the formal addition of hydride ion to the concave face of a highly hindered unsaturated ketone.

In summary, we have demonstrated that high degrees of regio- and stereocontrol can be achieved through the use of alkoxide assisted nucleophilic additions. Further mechanistic details about these processes, as well as the application of the ligand assisted nucleophilic additions to the synthesis of complex target molecules, will be the subject of future reports.

Acknowledgment. We thank V. Paragamian for helpful discussions. D. Liotta acknowledges the support of the National Institutes of Health (GM-26908) and McNeil Pharmaceutical.

Supplementary Material Available: Experimental details for the preparation of enone **8** including full spectroscopic and X-ray crystallographic data (5 pages). Ordering information is given on any current masthead page.

Insertion of $(\eta^5\text{-}C_5Me_5)(PMe_3)Ir$ into the C–H Bonds of Functionalized Organic Molecules: A C–H Activation Route to 2-Oxa- and 2-Azametallacyclobutanes, Potential Models for Olefin Oxidation Intermediates

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Several important transition-metal-based systems are known that are capable of oxidizing alkenes to epoxides and aldehydes.[1] One of the most important is cytochrome P-450; smaller systems involving porphyrins and other chelating ligands have been used as models for these biological oxidations.[2] Several mechanisms have been postulated for such transformations,[3] but one of the most intriguing and often invoked[4] involves four-membered 2-oxametallacyclobutanes as crucial intermediates. In spite of this, and the fact that the oxametallacyclobutane postulate is controversial,[5] only a small number of such metallacycles (or their nitrogen analogues) have been prepared and characterized.[6] We report here a novel route to 2-oxa- and 2-azametallacyclobutanes[7] that has developed from our C–H activation research. This has yielded the first simply substituted members of this class of complexes and has given us an opportunity to begin an investigation of their chemistry.

In studies aimed at determining the relative rate of insertion of the C–H activating species[8] $(\eta^5\text{-}C_5Me_5)(PMe_3)Ir$ into C–H versus other types of X–H bonds, we carried out the photolysis of $Cp^*(PMe_3)IrH_2$ (complex **1** illustrated in Scheme I) in *tert*-butylamine. This gives typically 90% conversion (NMR) to the new alkyl hydride $Cp^*(PMe_3)Ir(CH_2CMe_2NH_2)H$ (**2a**). No trace of the amido hydride $Cp^*(PMe_3)Ir(NH\text{-}t\text{-}Bu)H$, which would result from insertion into the N–H bond, was observed. Compound **2a** was too sensitive to isolate in pure form, but it was characterized fully by spectroscopic techniques. In addition to the expected ^1H and ^{13}C signals, it has a characteristic Ir–H resonance at δ −17.81 ppm in the ^1H NMR spectrum. Similarly, irradiation of **1** in *tert*-butyl alcohol gives 95% conversion to the alkyl hydride $Cp^*(PMe_3)Ir(CH_2CMe_2OH)H$ (**2b**, $\delta_{Ir-H} = -17.76$). Once again, only C–H insertion occurs; no formation of the O–H insertion product $Cp^*(PMe_3)Ir(O\text{-}t\text{-}Bu)H$ was detected.

It is possible that the alkoxy hydride $Cp^*(PMe_3)Ir(O\text{-}t\text{-}Bu)H$ and the amido hydride $Cp^*(PMe_3)Ir(NH\text{-}t\text{-}Bu)H$ are being produced, but their formation from $Cp^*(PMe_3)Ir$ is reversible (either thermally or photochemically), and the alkyl hydrides **2a** and **2b** are the thermodynamic rather than the kinetic products of these reactions. Unfortunately, we have not yet been able to prepare these O–H and N–H insertion products independently so that we might test their stability to the reaction conditions. If these species are not being formed, however, we are led to the somewhat surprising conclusion[9] that insertion of $Cp^*(PMe_3)Ir$ into C–H bonds is completely favored over insertion into either O–H or N–H bonds.

Realizing that complexes **2a** and **2b** contain the structural elements needed to form 2-oxa- and 2-azametallacyclobutanes, we sought a method for effecting dehydrogenative ring closure. This was achieved by a chlorination/nucleophilic cyclization sequence. Treatment of the nitrogen compound **2a** with 1 equiv of chloroform in benzene for several days led to the formation of the air-stable cyclic salt **4** in 80% yield. Presumably this reaction takes place via uncyclized precursor **3a**, which rapidly undergoes ring closure under the reaction conditions. Compound **4** is extremely hygroscopic. Crystals of **4** suitable for an X-ray diffraction study were obtained as the dihydrate by crystallization from toluene/hexamethyldisiloxane, and analysis of the data confirmed the proposed structure.[10] An ORTEP diagram of the

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(1) For some specific examples and leading references, see: (a) Chong, A. O.; Sharpless, K. B. *J. Org. Chem.* **1977**, *42*, 1587. (b) Sheldon, R. A.; Van Doorn, J. A. *J. Catal.* **1973**, *31*, 427. (c) Mimoun, H.; Mignard, M.; Brechot, P.; Saussine, L. *J. Am. Chem. Soc.* **1986**, *108*, 3711. (d) Chaumette, P.; Mimoun, H.; Saussine, L.; Fischer, J.; Mitschler, A. *J. Organomet. Chem.* **1983**, *250*, 291. (e) Sheldon, R. A.; Kochi, J. K. *Metal Oxidations of Organic Compounds*; Academic Press: New York, 1981. (f) Mijs, W. J.; DeJonge, C. R. H. I., Eds. *Organic Synthesis by Oxidation with Metal Compounds*; Plenum Press: New York, 1986.

(2) (a) Groves, J. T.; Subramanian, D. V. *J. Am. Chem. Soc.* **1984**, *106*, 2177. (b) Groves, J. T. In *Advances in Inorganic Biochemistry*; Eichorn, G. L., Marzilli, L. G., Eds.; Elsevier: New York, 1979; pp 119–145. (c) Renaud, J.-P.; Battioni, P.; Bartoli, J. F.; Mansuy, D. *J. Chem. Soc., Chem Commun.* **1985**, 888 and references cited therein.

(3) See, for example: (a) Strukul, G.; Michelin, R. A. *J. Am. Chem. Soc.* **1985**, *107*, 7563. (b) Gould, E. S.; Hiatt, R. R.; Irwin, K. C. *J. Am. Chem. Soc.* **1968**, *90*, 4573. (c) Srinivasan, K.; Perrier, S.; Kochi, J. K. *J. Mol. Catal.* **1986**, *36*, 297. (d) Sheng, M. N.; Zajacek, J. G. *J. Org. Chem.* **1970**, *35*, 1839. (e) Jorgenson, K. A.; Hoffmann, R. *Acta. Chem. Scand.* **1986**, *B40*, 411.

(4) See, for example: (a) Collman, J. P.; Brauman, J. I.; Meunier, B.; Raybuck, S. A.; Kodadek, T. *Proc. Natl. Acad. Sci. U.S.A.* **1984**, *81*, 3245. (b) Collman, J. P.; Kodadek, T.; Raybuck, S. A.; Brauman, J. I.; Papazian, L. M. *J. Am. Chem. Soc.* **1985**, *107*, 4343. (c) Collman, J. P.; Brauman, J. I.; Meunier, B.; Hayashi, T.; Kodadek, T.; Raybuck, S. A. *Ibid.* **1985**, *107*, 2000. (d) Rappe, A. K.; Goddard, W. A. *J. Am. Chem. Soc.* **1982**, *104*, 3287. (e) Girardet, M.; Meunier, B. *Tetrahedron Lett.* **1987**, *2955*. (f) Mock, W. L.; Bieniarz, C. *Organometallics* **1985**, *11*, 1917. (g) Sharpless, K. B.; Teranishi, A. Y.; Bacvkvall, J.-E. *J. Am. Chem. Soc.* **1977**, *99*, 3120. (h) Groves, J. T.; Avaria-Neisser, G. E.; Fish, K. M.; Imachi, M.; Kuczkowski, R. L. *J. Am. Chem. Soc.* **1986**, *108*, 3837. (i) Walba, D. M.; DePuy, C. H.; Grabowski, J. J.; Bierbaum, V. M. *Organometallics* **1984**, *3*, 498.

(5) For recent discussions and leading references, see: (a) Traylor, T. G.; Miksztal, A. R. *J. Am. Chem. Soc.* **1987**, *109*, 2770. (b) Lee, R. W.; Nakagaki, P. C.; Balasubramanian, P. N.; Bruice, T. C. *Proc. Natl. Acad. Sci. U.S.A.* **1988**, *85*, 641. 2-Oxametallacyclobutanes have also been proposed as intermediates in metal-mediated reactions of epoxides: see, for example: (c) Milstein, D.; Calabrese, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 3773 and references cited therein. (d) Alper, H.; Arzoumanian, H.; Petrignani, J.-F.; Saldana-Maldonado, M. *J. Chem. Soc., Chem. Commun.* **1985**, 340.

(6) (a) Bennett, C. R.; Bradley, D. C. *J. Chem. Soc., Chem. Commun.* **1974**, 29. (b) Simpson, S. J.; Turner, H. W.; Andersen, R. A. *Inorg. Chem.* **1981**, *20*, 2991. (c) Hawkins, S. M.; Hitchcock, P. B.; Lappert, M. F.; Rai, A. K. *J. Chem. Soc., Chem. Commun.* **1986**, 1689. (d) Schlodder, R.; Ibers, J. A.; Lenarda, M.; Graziani, M. *J. Am. Chem. Soc.* **1974**, *96*, 6893. (e) Lenarda, M.; Ros, R.; Traverso, O.; Pitts, W. D.; Bradley, W. H.; Graziani, M. *Inorg. Chem.* **1977**, *16*, 3178. (f) Miyashita, A.; Ishida, J.; Nohira, H. *Tetrahedron Lett.* **1986**, 2127.

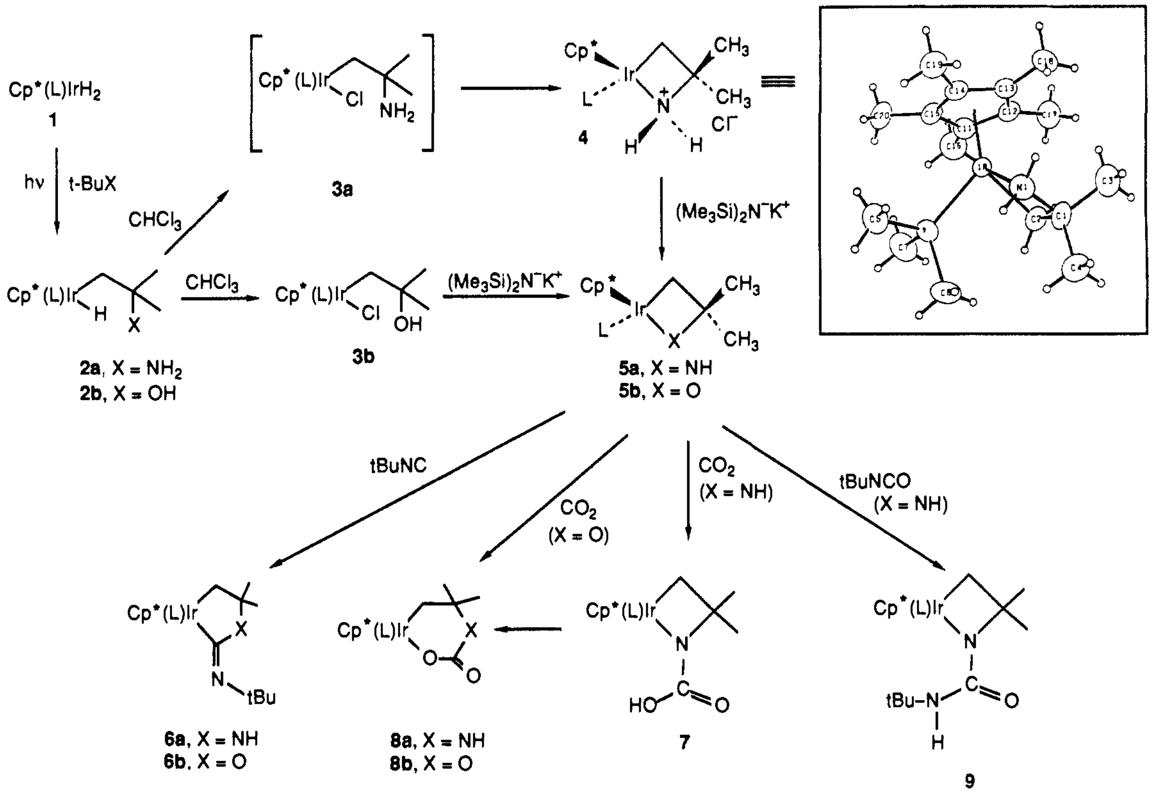
(7) 2-Azametallacyclobutanes may be involved as intermediates in the metal-catalyzed conversion of aziridines to β-lactams; cf.: Alper, H.; Urso, F.; Smith, D. J. H. *J. Am. Chem. Soc.* **1983**, *105*, 6737.

(8) (a) Bergman, R. G. *Science (Washington, D.C.)* **1984**, *223*, 902. (b) Buchanan, J. M.; Stryker, J. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 1537.

(9) For recent discussions of this problem, and examples of apparent preferences for O–H and N–H insertion in other systems, see: (a) Hillhouse, G. L.; Bercaw, J. E. *J. Am. Chem. Soc.* **1984**, *106*, 5472. (b) Casalnuovo, A. L.; Calabrese, J. C.; Milstein, D. L. *Inorg. Chem.* **1987**, *26*, 973. (c) Huang, S.; Homan, R. W.; Gross, M. L. *Organometallics* **1986**, *5*, 1857. (d) Chiu, K. W.; Jones, R. A.; Wilkinson, G.; Galas, A. M. R.; Hursthouse, M. B.; Abdul Malik, K. M. *J. Chem. Soc., Dalton Trans.* **1981**, 1204.

0002-7863/88/1510-3704$01.50/0

Scheme I



[Cp* = η^5-C_5Me_5; L = PMe_3]

metallacycle is included in Scheme I. The water molecules and chloride ions incorporated in the unit cell form an interesting hydrogen bonding network with the cationic metal complex; two additional ORTEP diagrams illustrating the packing of water molecules, chloride ions and iridium cations in the crystal are provided with the Supplementary Material.

Ammonium salt **4** is the conjugate acid of the target neutral 2-azametallacyclobutane. Attempted deprotonation with several bases gave only intractable materials, but ultimately it was discovered that treatment of **4** with the hindered base $(Me_3Si)_2N^-K^+$ at −40 °C in toluene led to the formation of a single new complex, as determined by ^{1}H NMR spectroscopy. After removal of solvent in vacuo and extraction into pentane, Cp*(PMe_3)Ir(CH_2CMe_2NH) (**5a**) was obtained as a yellow, air-sensitive solid in 95% isolated yield. This material, too sensitive for elemental analysis, was characterized by ^{1}H and ^{13}C NMR spectrometry (see Supplementary Material), IR spectrometry (ν_{NH} = 3415 cm^{-1}), and high resolution mass spectrometry (calculated for the two iridium-containing isotopomers: 475.1984; 473.1960; found: 475.1987; 473.1950).

It was also found possible to replace the hydride in alcohol **2b** with a chloride ligand. In this case, however, reaction of **2b** with 1 equiv of chloroform in benzene led to the uncyclized alkyl chloride Cp*(PMe_3)Ir(CH_2CMe_2OH)Cl (**3b**) as yellow, air-stable crystals. This material was isolated in 85% yield and fully characterized by elemental analysis and spectroscopic techniques (IR: ν_{OH} = 3421 cm^{-1}; other data provided as Supplementary Material). Treatment of **3b** with a slight excess of $(Me_3Si)_2N^-K^+$ in benzene at room temperature gave the neutral 2-oxametallacyclobutane **5b** as yellow crystals in 95% yield and this material was fully characterized. Compound **5b**, like its nitrogen-containing counterpart **5a**, is extremely air-sensitive both in solution and in the solid state.

Preliminary investigation of the chemistry of the aza- and oxametallacyclobutanes **5a** and **5b** indicates that they are quite reactive toward electrophilic organic compounds. For example, reaction of **5a** with *tert*-butyl isocyanide results in rapid insertion of the organic molecule into the metal–nitrogen bond, giving complex **6a** in greater than 90% isolated yield. Evidence that insertion has taken place into the M–N rather than the M–C bond is provided by the ^{13}C NMR spectrum. The methylene carbon (δ 25.2 ppm) retains a phosphorus–carbon coupling of 7.3 Hz, typical for a P–M–C linkage in this system. The isonitrile carbon resonance appears as a doublet at 155.6 ppm (J_{P-C} = 14.4 Hz). Also, a characteristic C═N stretching absorption is observed at 1563 cm^{-1}.

Treatment of **5a** with *tert*-butyl isocyanate leads to the immediate formation of a new, yellow, air-stable material in nearly quantitative yield; spectral and analytical data are consistent with its assignment as the substituted urea **9**. Evidence that metallacycle **5a** behaves as an organic amine in its reaction with isocyanate, rather than undergoing insertion into the M–N bond, is found in the ^{13}C NMR spectrum. The methylene carbon resonance appears at −10.3 ppm, typical for a four-membered metallacycle in this and related Cp*(PMe_3)Rh systems.[11] Complex **9** also exhibits a C═O stretching absorption at 1601 cm^{-1} in the infrared spectrum as well as a ^{13}C NMR resonance at 159.5 ppm.

Metallacycle **5a** also reacts with carbon dioxide. Reaction occurs over several days at room temperature to give the metallaurethane **8a** in 80% yield. A C═O stretching absorption is observed at 1626 cm^{-1} in the infrared spectrum as well as a resonance in the ^{13}C NMR spectrum at 162.6 ppm. Interestingly, an intermediate can be detected when the reaction is monitored by ^{1}H NMR spectrometry. This material forms immediately on mixing of CO_2 with **5a** at room temperature and is then converted slowly to **8a** on standing in solution. Due to the reactivity of this material we have not been able to isolate it. It exhibits a broad resonance at 12.71 ppm in the ^{1}H NMR spectrum and a carbonyl absorbance in the IR at 1605 cm^{-1}. We suggest that, analogous to reaction with isocyanate, the initial product is the carbamic

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(10) The structure was determined by Dr. F. J. Hollander of the UC Berkeley College of Chemistry X-ray diffraction facility (CHEXRAY). Details of the structure determination are provided as Supplementary Material.

(11) Periana, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 7346.

acid derivative **7**, which slowly rearranges to the insertion product **8a**.

Oxygen-substituted metallacycle **5b** also undergoes insertion reactions. Addition of carbon dioxide to a benzene solution of **5b** leads to rapid insertion into the metal–oxygen bond, giving metallacarbonate **8b** as the exclusive product by ^{1}H NMR spectrometry (isolated as a yellow powder; 80% yield; ν_{CO} = 1644 cm^{-1}). No intermediate analogous to that observed with **5a** was detected. On treatment with *tert*-butyl isocyanide, **5b** gives mainly insertion product **6b**. The isonitrile reacts much less rapidly with **5b** than with **5a**; the reaction requires heating at 45 °C for several days to reach completion. Reaction of **5b** with *tert*-butyl isocyanate is more complex and leads to a mixture of products.

Although insertion of organic molecules into the M–O and M–N bonds of metallacyclobutanes **5a** and **5b** occurs readily, our attempts to find conditions under which aziridine or epoxide are extruded have so far not met with success. However, there are many situations in which a given type of complex resists reductive elimination when it incorporates a third-row metal but is much more reactive when it incorporates a first- or second-row metal. We therefore plan to extend our studies of 2-oxa and 2-aza-metallacyclobutanes to rhodium and cobalt, so that the chemistry of these materials can be compared with that observed with iridium.

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Supplementary Material Available: Spectroscopic and analytical data for complexes **2a**, **2b**, **4**, **5a**, **5b**, **6a**, **6b**, **7**, **8a**, **8b**, and **9** and details of the structure determination for complex **4**, including experimental description, ORTEP drawings showing full atomic numbering and packing in the crystal, crystal and data collection parameters, general temperature factor expressions (B's), root-mean-square amplitudes, positional parameters and their estimated standard deviations, and intramolecular distances and angles (20 pages); table of observed and calculated structure factors for **4** (17 pages). Ordering information is given on any current masthead page.

Rapid, Reversible Intramolecular C–H Oxidative Addition and Hydrogen Exchange in a Heterodinuclear "Early–Late" Transition-Metal Complex

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Information about how C–C and C–H bonds are formed and cleaved by systems utilizing two transition metals having very different electronic properties[1] should be obtainable by studying early–late dinuclear complexes having alkyl and hydride ligands attached to both metal centers. So far, however, very few complexes of this type have been described.[2] In this paper we wish to report the synthesis and chemistry of such a system involving tantalum and platinum (complex **3** in Scheme I). We have observed a transformation in which the methyl group bound to Ta undergoes intramolecular C–H insertion at an adjacent Pt center, leading to the new bis-μ-methylene hydride (**5**). Mechanistic studies provide evidence that this insertion is stereospecific, rapid, and reversible.

Bridging methylene complex **3** was synthesized[3] in 71% yield by reaction of $Cp_2(CH_3)Ta(CH_2)$ (**1**)[4] with $(PMe_3)_2Pt(C_2H_4)$, and its geometry was unambiguously determined in a single-crystal X-ray diffraction study (Scheme I).[5] The Ta–CH_3 and μ-CH_2 groups reside on the same side of the metal–metal bond. Addition of excess PMe_3 to **3** in toluene at room temperature caused instantaneous formation of $Pt(PMe_3)_4$[6] and regeneration of mononuclear methylene complex **1**, as determined by ^{1}H and ^{31}P NMR analysis. To our knowledge, this is the first reported example of fragmentation of a μ-alkylidene complex to give an isolable mononuclear alkylidene complex.[7-9] In the absence of added ligand, however, thermal decomposition of **3** occurred in benzene over several hours at 40 °C to give a mixture of **1**, $Pt(PMe_3)_4$, and a new bis-Cp-containing product in a 1:1:2 ratio. An identical mixture of products was obtained within an hour upon photolysis of **3**. Spectrometric and X-ray diffraction studies[5] (see Scheme I for ORTEP and line drawings) identified the new material as **5**: a bis-μ-methylene hydride complex formed by oxidative addition of a tantalum–methyl C–H bond across the platinum center. ^{1}H NMR observations identified a terminal hydride ligand in **5**, oriented cis to one of the bridging methylene groups and trans to the other.

Kinetic and isotope labeling experiments revealed the following information about the interconversions of complexes **1**, **3**, and **5**: (a) The thermal conversion of **3** to **5** is a smooth first-order process ($k = 3.3 \times 10^{-4}$ s^{-1} in benzene at 40 °C), with $\Delta H^{\ddagger} = 23.4 \pm 0.4$ kcal/mol and $\Delta S^{\ddagger} = 0.4 \pm 0.5$ eu.[10] (b) ^{1}H NMR spin saturation transfer experiments[11] demonstrated that μ-CH_2/hydride exchange in **5** occurs,[12] but interchange takes place with only the hydrogens on the CH_2 group cis to the hydride. The

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[1] Some leading references: (a) Ferguson, G. S.; Wolczanski, P. T. *Organometallics* **1985**, *4*, 1601; *J. Am. Chem. Soc.* **1986**, *108*, 8293. (b) Casey, C. P.; Palermo, R. E.; Rheingold, A. L. *J. Am. Chem. Soc.* **1986**, *108*, 549. (c) Sartain, W. J.; Selegue, J. P. *Organometallics* **1987**, *6*, 1812. (d) Ichikawa, M.; Lang, A. J.; Shriver, D. F.; Sachtler, W. M. H. *J. Am. Chem. Soc.* **1985**, *107*, 7216. (e) Dai, C. H.; Worley, S. D. *J. Phys. Chem.* **1986**, *90*, 4219. (f) Somorjai, G. A. *Catal. Rev. Sci. Eng.* **1978**, *18*, 173. (g) Arai, T.; Maruya, K.; Domen, K.; Onishi, T. *J. Chem. Soc., Chem. Commun.* **1987**, 1757. (h) Scott, J. P.; Budge, J. R.; Rheingold, A. L.; Gates, B. C. *J. Am. Chem. Soc.* **1987**, *109*, 7736 and references cited therein. (i) Garden, D.; Kemball, C.; Whan, D. A. *J. Chem. Soc., Faraday Trans. 1* **1986**, 3113. (j) Baiker, A.; Gasser, D.; Lenzner, J. *J. Chem. Soc., Chem. Commun.* **1987**, 1750 and references therein. (k) Sinfelt, J. H. *Bimetallic Catalysts: Discoveries, Concepts and Applications*; Wiley: New York, 1983. (l) *Metal-Support and Metal-Additive Effects in Catalysis*; Imelik, B., et al., eds.; Elsevier: New York, 1982.

[2] For recent examples, see: (a) Park, J. W.; Mackenzie, P. B.; Schaefer, W. P.; Grubbs, R. H. *J. Am. Chem. Soc.* **1986**, *108*, 6402. (b) Bruno, J. W.; Huffman, J. C.; Green, M. A.; Caulton, K. G. *J. Am. Chem. Soc.* **1984**, *106*, 8310.

[3] Bridging alkylidene complexes without alkyl groups or hydrides have been prepared earlier by this technique; see, for example: (a) Ashworth, T. V.; Howard, J. A. K.; Laguna, M.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1980**, 1593. (b) Howard, J. A. K.; Mead, K. A.; Moss, J. R.; Navarro, R.; Stone, F. G. A.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1981**, 743. (c) Williams, G. D.; Lieszkovszky, M.-C.; Mirkin, C. A.; Geoffroy, G. L. *Organometallics* **1986**, *5*, 2228.

[4] Schrock, R. R.; Sharp, P. R. *J. Am. Chem. Soc.* **1978**, *100*, 2389.

[5] The structure was determined by Dr. F. J. Hollander of the UC Berkeley College of Chemistry X-ray Diffraction Facility (CHEXRAY). Details of the structure determination are provided as Supplementary Material.

[6] Mann, B. E.; Musco, A. *J. Chem. Soc., Dalton Trans.* **1980**, 776.

[7] This type of fragmentation has been proposed to account for intermolecular scrambling in μ-methylenedicobalt systems: Theopold, K. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 464.

[8] Both direct and indirect observations of μ-alkylidene ligands unbridging to a terminal position have been reported, see: Messerle, L.; Curtis, M. D. *J. Am. Chem. Soc.* **1982**, *104*, 889 and references therein.

[9] It has been proposed that Tebbe's reagent, $Cp_2Ti(Cl)CH_2AlMe_2$, reacts via the intermediacy of $Cp_2Ti{=}CH_2$: (a) Tebbe, F. N.; Parshall, G. W.; Ovenall, D. W. *J. Am. Chem. Soc.* **1979**, *101*, 5074. (b) Howard, T. R.; Lee, J. B.; Grubbs, R. H. *J. Am. Chem. Soc.* **1980**, *102*, 6876.

[10] Error limits are based on the standard deviations of the calculated slope and intercept of a least-square fit to the Eyring plot.

[11] (a) Martin, M. L.; Martin, G. J.; Delpuech, J.-J. *Practical NMR Spectroscopy*; Heyden & Sons Inc.: Philadelphia, PA, 1980; pp 315–321. (b) Faller, J. W. In *Determination of Organic Structures by Physical Methods*; Nachod, F. C., Zuckerman, J. J., Eds.; Academic Press: New York, 1973; Vol. 5, Chapter 2.

[12] Exchange between μ-CH_2 and μ-H groups has been previously observed in homonuclear systems: (a) Calvert, R. B.; Shapley, J. R. *J. Am. Chem. Soc.* **1977**, *99*, 5225. (b) Heinekey, D. M., unpublished results.

0002-7863/88/1510-3706$01.50/0