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; $\nu_{CO} = 1644$ 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-$\mu$-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 $\mu$-$CH_2$ 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 $\mu$-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-$\mu$-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 $\mu$-$CH_2$/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 $\mu$-methylenedicobalt systems: Theopold, K. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 464.

[8] Both direct and indirect observations of $\mu$-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.

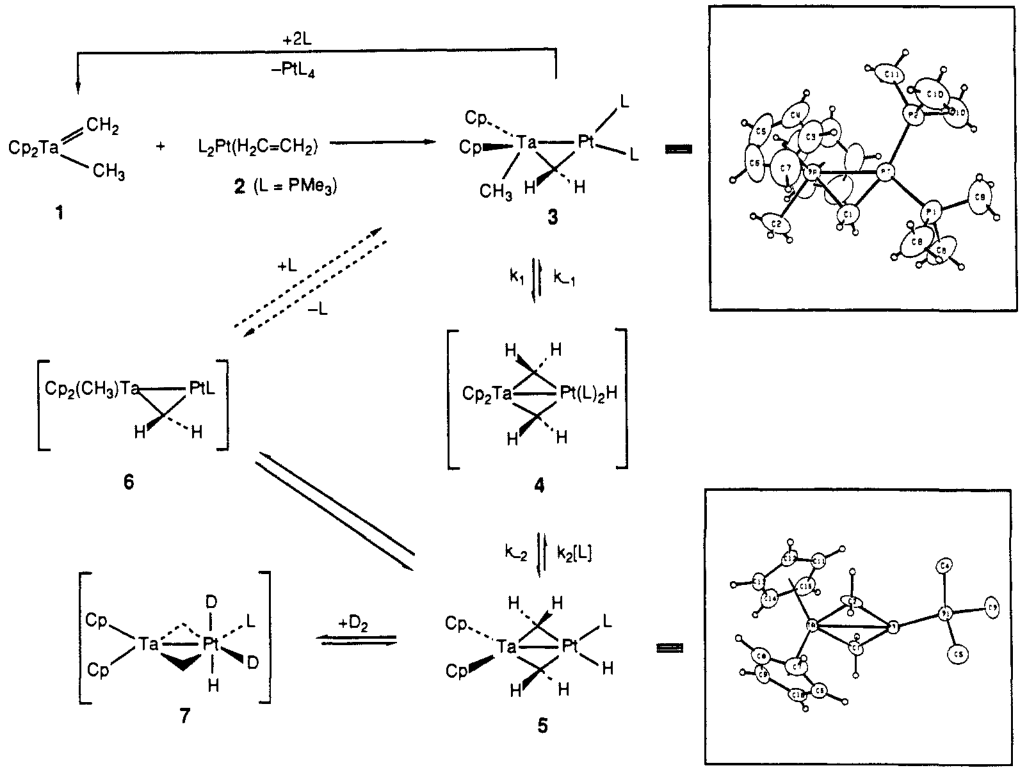
[10] Error limits are based on the standard deviations of the calculated slope and intercept of a least-square fit to the Eyring plot.

[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 $\mu$-$CH_2$ and $\mu$-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

**Scheme I**



activation parameters for this process are 18.2 ± 0.4 kcal/mol and −0.1 ± 1.1 eu for $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, respectively.[10] We suggest an intermediate closely resembling **6** to account for this exchange.[13] (c) In $C_6D_6$ at 20 °C, complex **5** undergoes exchange of hydrogen with $D_2$ at the hydride position and at a $\mu$-$CH_2$ position. However, as observed in the saturation transfer experiments, the $CH_2$ group cis to the hydride undergoes exchange rapidly; deuterium is incorporated much more slowly into the trans $CH_2$ group. We suggest that the rapid cis exchange occurs by incorporation of D into the platinum–hydride position via intermediate **7** followed by scrambling into the cis $CH_2$ group via the **5**/**6** equilibrium, discussed above. The stereoselectivity of the $\mu$-$CH_2$ exchange requires that the Pt-bound D and L ligands retain their stereochemistry in **7**.[14] (d) The overall conversion of **1** to **5** is completely reversible. Thus, reaction of **5** with $PMe_3$ proceeded smoothly at room temeperature over several hours, affording excellent yields of **1** (86%) and $Pt(PMe_3)_4$ (95%). Disappearance of **5** in the presence of an excess of $PMe_3$ at −50 °C cleanly obeyed pseudo-first-order kinetics but was *substantially faster than the* **5** *to* **6** *interconversion whose rate was measured, as discussed above, using saturation transfer techniques.*[15] A plot of the observed rate constant $k_{obsd}$ versus the concentration of $PMe_3$ was linear and showed no evidence for saturation behavior at high $[PMe_3]$, indicating that the rate law for this process is second order overall: first order in [**5**] and first order in $[PMe_3]$.

Our observation that the $PMe_3$-induced conversion of **5** back to **1** (which, undoubtedly, proceeds via the initial formation of **3**) takes place more rapidly than the conversion of **5** to **6** requires that intermediate **6**, although in equilibrium with **5**, is not the lowest energy reaction pathway in the **5** to **3** interconversion. Instead, $PMe_3$ adds initially, most likely[16] leading to Pt-bonded phosphine adduct **4**, and reductive elimination to **3** occurs in a second step. This conclusion is significant with respect to the mechanism of the "forward" reaction, the decomposition of **3** to produce **5**. The principle of microscopic reversibility demands that because (in the presence of $PMe_3$) the fastest **5** to **3** conversion proceeds via intermediate **4**, the most rapid **3** to **5** conversion must also proceed by this route.[17] Due to the stereochemical arrangement of the ligands in **3**, it is likely that an intramolecular isomerization step places the methyl group in the proximity of the Pt atom prior to the C–H oxidative addition.

Work is continuing on the chemistry of $\mu$-methylene complexes **3** and **5** and on the reactions of tantalum alkylidene complex **1** with other coordinatively unsaturated late transition-metal complexes.

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**Supplementary Material Available:** Spectroscopic and analytical data for **3** and **5**, experimental details of the X-ray diffraction studies of **3** and **5**, including crystal and data collection parameters, tables of positional parameters, general temperature factors, and intramolecular distances and angles (13 pages); listing of observed and calculated structure factors (55 pages). Ordering information is given on any current masthead page.

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(13) As noted by a referee, this species could have either a classical Ta-bound $CH_3$ group or one in which a C–H bond is weakly coordinated to the Pt center. Cf. (a) Brookhart, M.; Green, M. L. H. *J. Organomet. Chem.* **1983**, *250*, 395. (b) Calvert, R. B.; Shapley, J. R. *J. Am. Chem. Soc.* **1978**, *100*, 7726.

(14) Although this seems to us to be the most reasonable mechanism, our data do not allow us to distinguish between this pathway and an alternative one, suggested by a referee, in which $D_2$ reacts directly at the $CH_2$ group.

(15) Direct comparison of these rates was possible by extrapolating the data from the spin saturation transfer experiments to −50 °C. At this temperature, the rate constant for the **5** + $PMe_3$ reaction is 2.2 ± 0.1 × $10^{-4}$ $[PMe_3]$ $s^{-1}$; the extrapolated **5** $\rightleftharpoons$ **6** exchange rate constant is 6.1 ± 6.4 × $10^{-6}$ $s^{-1}$.

(16) (a) Braterman, P. S.; Cross, R. J.; Young, G. B. *J. Chem. Soc., Dalton Trans.* **1976**, 1306; **1976**, 1310; **1977**, 1892. (b) Packett, D. L.; Syed, A.; Trogler, W. C. *Organometallics* **1988**, *7*, 159.

(17) The near-zero value for $\Delta S^{\ddagger}$ (0.4 ± 0.5 eu) in the **3** to **5** interconversion is also consistent with a nondissociative rate-determining step.