

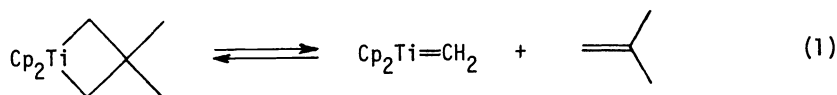
PREPARATION OF HETERONUCLEAR BRIDGING METHYLENE COMPLEXES

P. B. Mackenzie, K. C. Ott, and R. H. Grubbs

Contribution No. 6398 from the Laboratories of Chemistry
 California Institute of Technology
 Pasadena, California 91125

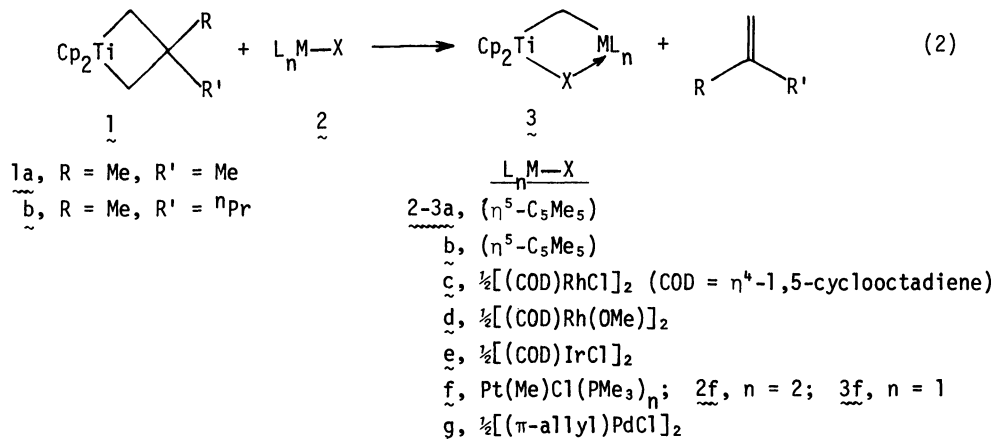
Abstract - The reactions of the titanacyclobutane complexes ($\eta^5\text{-C}_5\text{H}_5$)₂TiCH₂CRR'CH₂ (**1a**, R = R' = Me; **1b**, R = Me, R' = Pr) with M-X compounds (M = Ti, Zr, Rh, Ir, Pd, Pt; X = Cl, OMe) have been investigated. The titanacyclobutanes have been found to react as sources of ($\eta^5\text{-C}_5\text{H}_5$)₂TiCH₂, giving ($\eta^5\text{-C}_5\text{H}_5$)₂Ti($\mu\text{-CH}_2$)($\mu\text{-X}$)ML_n (L_n = ancillary ligands) products. Several such complexes have been isolated as crystalline solids; however, only ($\eta^5\text{-C}_5\text{H}_5$)₂Ti($\mu\text{-CH}_2$)($\mu\text{-X}$)Rh($\eta^4\text{-1,5-cyclooctadiene}$) is stable in solution at 25°C. The complex ($\eta^5\text{-C}_5\text{H}_5$)₂Ti($\mu\text{-CH}_2$)($\mu\text{-Cl}$)Ti($\eta^5\text{-C}_5\text{Me}_5$)Cl was found to react with CO to form the bridging ketene complex ($\eta^5\text{-C}_5\text{H}_5$)₂Ti- μ,η^2 (C,O)-(OCCH₂)Ti($\eta^5\text{-C}_5\text{Me}_5$)Cl₂.

The reactive titanium methylene complex, ($\eta^5\text{-C}_5\text{H}_5$)₂TiCH₂, can be generated from a number of precursors. These include adducts with Lewis acids such as R₂AlCl¹, ZnI₂² and MgBr₂³ as well as those with olefins⁴ and acetylenes.⁵



For most applications, the olefin adducts serve as the cleanest source of this reactive intermediate (eq. 1).⁶ Organic applications of these reagents have been recently reviewed.⁷

We have found that ($\eta^5\text{-C}_5\text{H}_5$)₂TiCH₂CRR'CH₂ (**1**) reacts with M-X complexes **2** (X = Cl, OMe) to give methylene bridged bimetallic products **3** (eq. 2).



Compounds **3a-3e** have been isolated as crystalline, air sensitive solids; **3f** and **3g** have only been observed spectroscopically (*vide infra*). Characteristically⁸ low field ¹H and ¹³C NMR resonances are observed for the bridging methylene group in all cases (Table 1). Carbon-rhodium coupling is observed with the TiCH₂Rh compound **3c**; similarly, the methylene proton resonances of **3f** are split by coupling to ¹⁹⁵Pt and ³¹P.

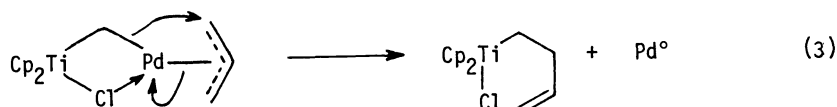
Whereas **3c** and **3d** are quite robust, being unaffected by heating at 60°C in benzene for 24 h, most of the other complexes decompose over several hours at 25°C in benzene. The decomposition pathways have in general not been elucidated. It has, however, been established that the decomposition of **3f** is accelerated by added phosphine. Since phosphine is liberated in the synthesis of **3f** from **2f**, attempts to isolate **3f** have been hampered by this instability and have not yet been successful.

TABLE 1. ^1H and ^{13}C NMR parameters of the bridging methylenes*

Compound	^1H	^{13}C
	(Chemical shifts in ppm relative to TMS)	
3a	6.61	219.6 $^1\text{J}_{\text{C-H}}$ 116 Hz
3b	6.63 (CD_2Cl_2)	--
3c	7.48	186.5 $^1\text{J}_{\text{C-H}}$ 128 Hz $^1\text{J}_{\text{C-Rh}}$ 20 Hz
3d	7.21	--
3e	7.95	180.0 $^1\text{J}_{\text{C-H}}$ 137 Hz
3f	8.09 $^2\text{J}_{\text{Pt-H}}$ 39.0 Hz $^3\text{J}_{\text{P-H}}$ 5.1 Hz	
3g	8.18 AB pattern, $J = 7.4$ Hz 7.75	

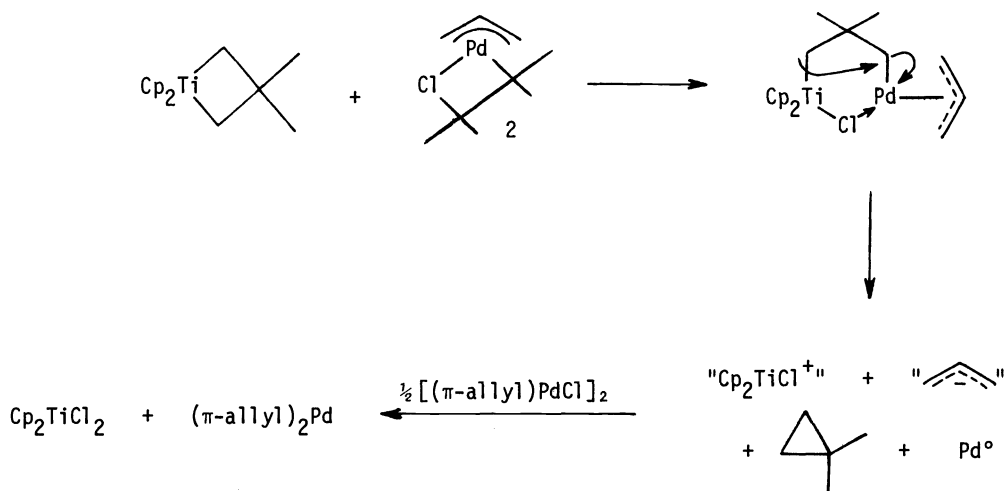
*All spectra were obtained for C_6D_6 solutions unless otherwise noted.

The reaction of **1a** with $[(\pi\text{-allyl})\text{PdCl}]_2$ is complex, in part because the methylene bridged product **3g** is unstable, decomposing to Pd metal and a C_5H_5 containing species, tentatively identified as $(\eta^5\text{-C}_5\text{H}_5)_2\text{Ti}(\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2)\text{Cl}$. It is presumed that these products are formed via reductive coupling of the bridging methylene and π -allyl groups (eq. 3). A similar step has been proposed to describe the reaction of Grignard reagents with $(\pi\text{-allyl})\text{Ni}$ complexes.⁹



The reaction of **1a** with $[(\pi\text{-allyl})\text{PdCl}]_2$ is further complicated by the appearance of 1,1-dimethylcyclopropane and $(\pi\text{-allyl})_2\text{Pd}$ as side products. We speculate that these products are formed via a 1,5-dimetallapentane intermediate¹⁰ (Scheme 1) which reductively eliminates 1,1-dimethylcyclopropane, forming Pd metal and (ultimately) $(\pi\text{-allyl})_2\text{Pd}$ and $(\eta^5\text{-C}_5\text{H}_5)_2\text{TiCl}_2$.

SCHEME 1. A reaction sequence for the production of 1,1-dimethylcyclopropane and $(\pi\text{-allyl})_2\text{Pd}$ in the reaction of **1a** with **2g**

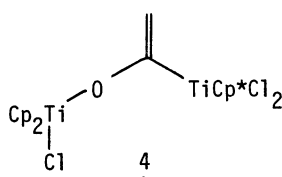


1,1-Dimethylcyclopropane is also formed in the reaction of **1a** with $[(\text{CO})_2\text{RhCl}]_2$, in approximately 60% yield. Isobutene (~40%) and unidentified intractable organometallic species are the only other products. This reaction contrasts markedly with the analogous $[(\eta^4\text{-}1,5\text{-cyclooctadiene})\text{RhCl}]_2$ reaction which cleanly gives the methylene bridged product and no 1,1-dimethylcyclopropane. When the product of the latter reaction, **3c**, is treated with CO, 1,5-cyclooctadiene is liberated and two new peaks appear in the ^1H NMR of the bridging methylene region. These new peaks quickly disappear with concomitant precipitation of an intractable brown-black material. If the species responsible for the transient peaks are in fact $\text{TiCH}_2\text{Rh}(\text{CO})_x$ compounds, then these observations suggest that such species are unstable.

If a methylene bridged species is formed in the reaction of **1a** with $[(\text{CO})_2\text{RhCl}]_2$ but rapidly decomposes, it is reasonable to speculate that the 1,1-dimethylcyclopropane is formed via methylene transfer to isobutene. We discount this possibility because treatment of **3c** with CO in the presence of isobutene did not generate any 1,1-dimethylcyclopropane, even though $\text{TiCH}_2\text{Rh}(\text{CO})_x$ species are apparently formed.

Compounds **3d** and **3e** also give intractable organometallic products upon reaction with CO. The fate of the CH_2 fragment in these reactions has not been determined.

Compound **3a** reacts with CO to form the bridging ketene complex **4**.¹¹ This complex, which is unstable, was also prepared by reaction of $(\eta^5\text{-C}_5\text{Me}_5)\text{TiCl}_3$ with the ketene complex $(\eta^5\text{-C}_5\text{H}_5)_2\text{Ti}(\eta^2\text{-OCCH}_2)$.¹²



The ligand substitution and general reaction chemistry of **3c** is being examined.

REFERENCES

1. F. N. Tebbe, G. W. Parshall and G. S. Reddy, *J. Am. Chem. Soc.*, **100**, 3611 (1978).
2. J. J. Eisch and A. Piotrowski, *Tetrahedron Lett.*, 2043 (1983).
3. J. W. Bruin, G. Schat, O. S. Akkerman and F. Bickelhaupt, *Tetrahedron Lett.*, **24**, 3935 (1983).
4. J. B. Lee, K. C. Ott and R. H. Grubbs, *J. Am. Chem. Soc.*, **104**, 7491 (1982).
5. R. J. McKinney, T. Tulip, D. Thorn, T. S. Coolbaugh and F. N. Tebbe, *J. Am. Chem. Soc.*, **103**, 5584 (1981).
6. J. R. Stille and S. Buchwald, Unpublished results.
7. K. A. Brown-Wensley, S. L. Buchwald, L. Cannizzo, L. Clawson, S. Ho, D. Meinhart, J. R. Stille, D. Straus, and R. H. Grubbs. *Pure & Appl. Chem.*, in press.
8. W. A. Herrman, "The Methylene Bridge", *Adv. Organomet. Chem.*, **20**, 159 (1982).
9. H. Felkin, C. Chuit, C. Frajerman, G. Roussi, G. Swierczewski, *J. Organomet. Chem.*, **127**, 371 (1977).
10. K.H. Theopold and R. G. Bergman have observed cyclopropane formation from a 1,2-dicobaltacyclopentane and have proposed the involvement of an intermediate analogous to the depicted 1,5-dimetallapentane: *J. Am. Chem. Soc.*, **102**, 5694 (1980).
11. ^1H NMR (CD_2Cl_2): C_5H_5 δ 6.41 (s), Z-vinyl proton δ 4.30 (s), C_5Me_5 δ 2.25 (s); ^{13}C gated decoupled NMR (CD_2Cl_2 , -20°C): $\text{C}=\text{CH}_2$ δ 215.1 (dd, $J = 10$ Hz), $\text{C}=\text{CH}_2$, δ 132.1 (dd, $J = 155$ Hz), C_5H_5 δ 117.1 (d of m, $J = 177$ Hz), C_5Me_5 δ 107.3 (br s), C_5Me_5 δ 13.0 (q, $J = 127$ Hz). Difference ^1H NOE spectroscopy, CD_2Cl_2 , -20°C : Irradiation of the C_5Me_5 resonance enhanced the downfield vinylic resonance at δ 4.69. Irradiation of the C_5H_5 resonance did not enhance either of the vinylic proton resonances.
12. D. A. Straus, Unpublished results.