

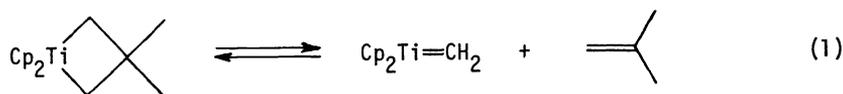
PREPARATION OF HETERONUCLEAR BRIDGING METHYLENE COMPLEXES

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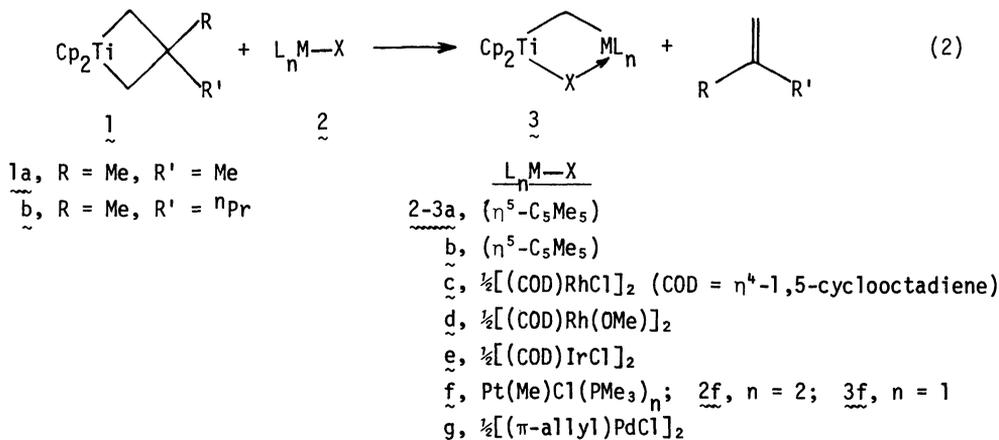
Abstract - The reactions of the titanacyclobutane complexes ($\eta^5\text{-C}_5\text{H}_5$)₂TiCH₂CRR'CH₂ (**1a**, R = R' = Me; **1b**, R = Me, R' = Pr) with M-X compounds (M = Ti, Zr, Rh, Ir, Pd, Pt; X = Cl, OMe) have been investigated. The titanacyclobutanes have been found to react as sources of ($\eta^5\text{-C}_5\text{H}_5$)₂TiCH₂, 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.

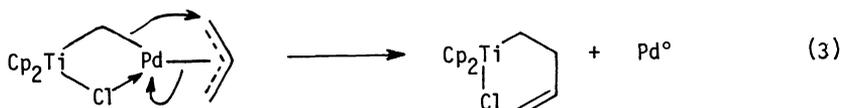
Whereas **3c** and **3d** are quite robust, being unaffected by heating at 60°C in benzene for 24 h, most of the other complexes decompose over several hours at 25°C in benzene. The decomposition pathways have in general not been elucidated. It has, however, been established that the decomposition of **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	

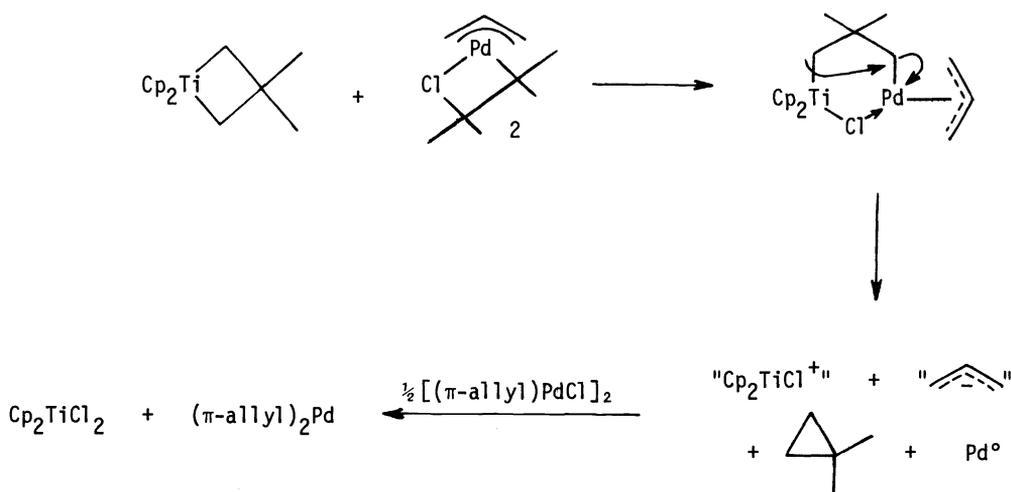
*All spectra were obtained for C_6D_6 solutions unless otherwise noted.

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**

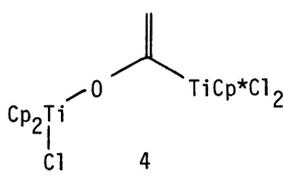


1,1-Dimethylcyclopropane is also formed in the reaction of **1a** with $[(\text{CO})_2\text{RhCl}]_2$, in approximately 60% yield. Isobutene (~40%) and unidentified intractable organometallic species are the only other products. This reaction contrasts markedly with the analogous $[(\eta^4\text{-}1,5\text{-cyclooctadiene})\text{RhCl}]_2$ 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.

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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.
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