

Regioselective Attack of a Soft Carbon Nucleophile and Hydrogen Sulfide at the Central Carbon of a β -Substituted η^3 -Allyl To Respectively Form η^3 -TMM and New Metallacyclic Thiacyclobutane Complexes[†]

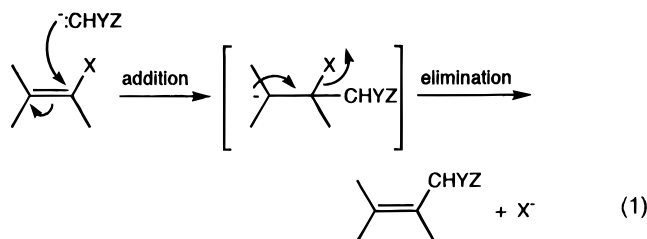
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Summary: The cationic β -substituted allyl complexes $\{Pt(PPh_3)_2[\eta^3-CH_2C(OE)CH_2]\}^+$ ($E = \text{silyl, alkyl, acyl}$) undergo the substitution of the carbon nucleophile for OE at the allyl central carbon to transform into η^3 -TMM complexes or undergo addition by hydrogen sulfide to yield new metallathiacyclobutane complexes.

Substitution reactions using carbon nucleophiles are of great importance in organic chemistry, because they not only can construct the C–C bonds but also can alter the functionality.² It is known that nucleophilic substitution at an sp^2 carbon is generally difficult. This can be explained by the fact that such reactions often proceed via a tetrahedral mechanism, also called an addition–elimination mechanism, as illustrated in eq 1.³ A recently developed example is the Pt(0)-catalyzed

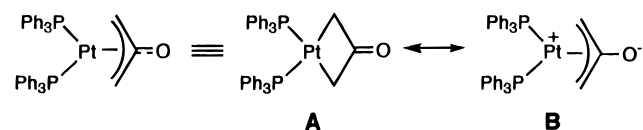


double substitution reaction of $CH_2C(Cl)CH_2OAc$, in which the replacement of chloride by a carbon nucleophile in an allyl intermediate is considered to be the key step.⁴

To take advantage of our discovery of the convenient synthesis of η^3 -oxa-TMM by adding water to a novel η^3 -propargyl/allenyl complex,^{5,6} we find that the electrophilic addition of η^3 -oxa-TMM readily generates the 2-siloxy-, 2-alkoxy-, and 2-(acyloxy)- η^3 -allyl complexes.⁷ Such allyl complexes provide rare stoichiometric examples of regioselective nucleophilic attack by a carbon

nucleophile or hydrogen sulfide at the allyl central carbon, yielding important η^3 -TMM complexes and new metallathiacyclobutane complexes, respectively.

The η^3 -oxatrimethylenemethane complex can be envisaged to have the resonance forms of metallacyclobutanone (**A**) and η^3 -2-oxyallyl (**B**). Such a structure



implies that the oxygen atom of the η^3 -oxyallyl group should exhibit nucleophilicity.^{5–9} We first tested the reactivity of the η^3 -oxa-TMM complex $Pt(PPh_3)_2[\eta^3-CH_2C(O)CH_2]$ (**1**) toward electrophiles. Complex **1** can be protonated by HCO_2H ($pK_a = 3.74$) or stronger acids to form the corresponding hydroxyallyl complex, but not by a weaker acid such as $PhCO_2H$ ($pK_a = 4.19$). Addition of ionic electrophiles such as Me_3SiOTf and Ph_3CBF_4 to complex **1** yields the first η^3 -2-siloxyallyl and η^3 -2-(trityloxy)allyl complexes $\{Pt(PPh_3)_2[\eta^3-CH_2C(OE)CH_2]\}^+(X)$ ($E = SiMe_3, X = OTf$ (**2**); $E = CPh_3, X = BF_4$ (**3a**)). Both **2** and **3a** tend to decompose upon recrystallization and have been characterized by NMR techniques.

Treatment of **1** with mild neutral organic electrophiles such as EtI , $iPrI$, CH_2CHCH_2Br , $MeC(O)Br$, and $PhC(O)Br$ leads to the formation of the cationic η^3 -2-alkoxyallyl complexes $\{Pt(PPh_3)_2[\eta^3-CH_2C(OR)CH_2]\}^+(X)$ ($R = Et$ (**3b**), iPr (**3c**), allyl (**3d**)^{10,11} and η^3 -2-(acyloxy)allyl complexes $\{Pt(PPh_3)_2[\eta^3-CH_2C(O_2CR)CH_2]\}^+(Br)$ ($R = Me$ (**4a**), Ph (**4b**)) respectively (Scheme 1). $PhBr$, PhI , and $tBuI$ do not react with **1** even at $60^\circ C$. These results can be explained by an S_N2 mechanism in which the relatively strong C–X bond of aryl halides and the steric hindrance of $tBuI$ are unfavorable to the substitution process. The electrophilic addition of η^3 -oxa-TMM affords an alternative methodology for the synthesis of central-carbon-substituted allyl complexes.

The common allyl ligands are known to be prone to nucleophilic attack at the terminal carbon. In contrast,

[†] η^3 -TMM denotes the η^3 -trimethylenemethane complexes $M[\eta^3-CH_2C(CR_1R_2)CH_2]$. We use η^3 -oxa-TMM and η^3 -aza-TMM to stand for the η^3 -oxatrimethylenemethane complex $M[\eta^3-CH_2C(O)CH_2]$ and η^3 -azatrimethylenemethane complex $M[\eta^3-CH_2C(NR)CH_2]$, respectively.¹

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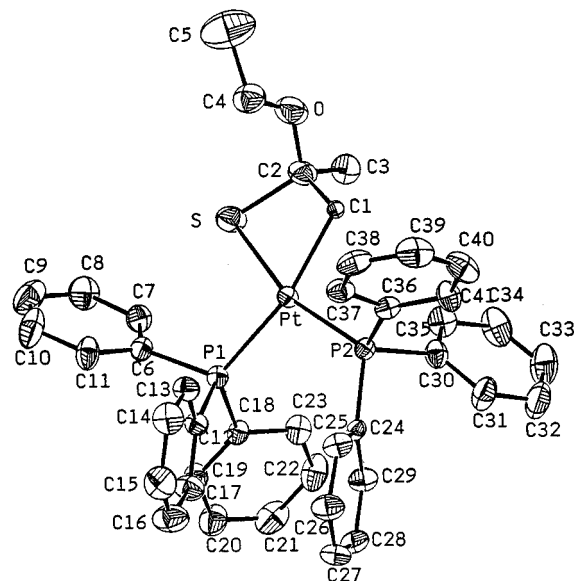
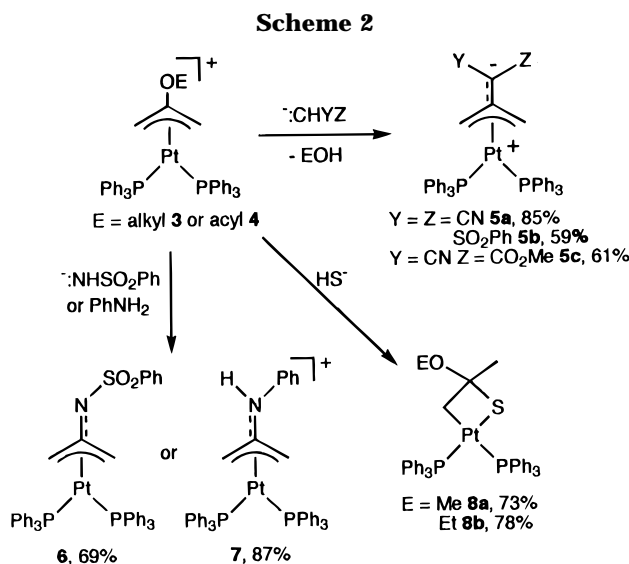
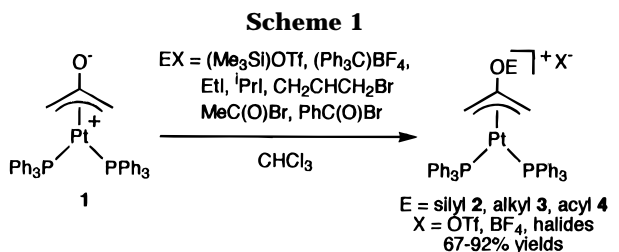


Figure 1. ORTEP drawing of Pt(PPh₃)₂[η³-CH₂C(OEt)(Me)S] (**8a**). All hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Pt-P1, 2.304(3); Pt-P2, 2.256(3); Pt-S, 2.304(3); Pt-C1, 2.157(8), C1-C2, 1.57(1); S-C2, 1.83(1), C2-C3, 1.61(2); C2-O, 1.35(1); ∠P1-Pt-P2, 101.98(9); ∠C1-Pt-S, 73.6(2); ∠Pt-C1-C2, 94.3(5); ∠Pt-S-C2, 83.0(4); ∠C1-C2-S, 103.6(7).

structure of **8a** (in Figure 1) shows that the metallathiacyclobutane ring folds a dihedral angle of 25.2(8)° against the C1-S axis. The distance of 2.76(1) Å between the Pt and C2 atoms is beyond the normal bonding range. The formation of such new compounds apparently results from the nucleophilic addition of sulfide to the allyl carbon and platinum.¹⁶ The formation of metallathiacyclobutane supports the notion that the aforementioned reactions of substitution undergo an addition-elimination mechanism. Facile nucleophilic attack at the central allyl carbon of the β-substituted η³-allyl adds a new feature to allyl chemistry.

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Supporting Information Available: Text giving detailed experimental and spectral data for all compounds and a fully labeled ORTEP drawing and tables of all crystal data, bond lengths and angles, atomic coordinates, and thermal parameters for **8a** (12 pages). Ordering information is given on any current masthead page.

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cationic η³-allyl species with the oxygen-bound substituent at the central carbon are subject to regioselective nucleophilic attack at the central carbon. In the typical cases, the 2-(benzyloxy)allyl complex **4b** readily undergoes replacement of the acyloxy group by the soft carbon nucleophile Na[CHYZ] to transform into the important η³-TMM products Pt(PPh₃)₂[η³-CH₂-C(CYZ)CH₂] (Y = Z = CN (**5a**), SO₂Ph (**5b**); Y = CO₂Me, Z = CN (**5c**)) in high yields. Among these products, **5c** cannot be prepared by reacting the η³-propargyl/allenyl complex with Na[CH(CN)(CO₂Me)].¹² In an analogous sense, the reactions of **4b** with Na[NHSO₂-Ph] or aniline yield the η³-aza-TMM complex Pt(PPh₃)₂[η³-CH₂C(NSO₂Ph)CH₂] (**6**) or the N-phenylated η³-aza-TMM complex {Pt(PPh₃)₂[η³-CH₂C(NHPh)CH₂]}(Br) (**7**), respectively (Scheme 2).^{13,14} Similar substitution reactions of {Pt(PPh₃)₂[η³-CH₂C(OPh)CH₂]}(BF₄) (**3e**) with carbanion and amide also lead to the η³-TMM and η³-aza-TMM products, respectively. Aniline, however, does not react with **3e**. The substitution reactions of the central-carbon-substituted allyl complexes serve as a pragmatic complementary synthetic access to the η³-TMM or η³-aza-TMM species via the formation of a C=C bond or a C=N bond, respectively.

In the reactions of 2-alkoxyallyl cations with hydrogen sulfide, we obtain the new complexes of metallathiacyclobutane,¹⁵ [Pt(PPh₃)₂[η³-CH₂C(OR')(Me)S] (R' = Et (**8a**), ⁱPr (**8b**)) (Scheme 2). The incorporation of sulfide at the allyl central carbon accompanied by proton transfer creates a stereogenic carbon. The single-crystal

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