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Nucleophilic Substitution at the Central Allyl Carbon Atom of a (π-Allyl)platinum Complex

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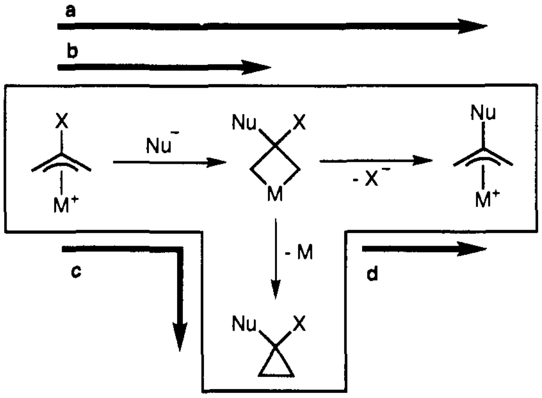
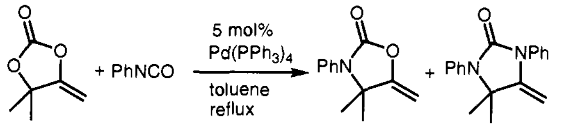
The nucleophilic attack at the central carbon of the π-allyl ligand attached to transition metals has attracted a great deal of attention in recent years. In contrast to the usual nucleophilic attack at allyl termini to give allylated products,[1] this process converts (π-allyl)metal complexes into various metallacyclobutanes[2] and in some cases leads to the formation of cyclopropane derivatives through reductive elimination from metallacyclobutanes.[3] Scheme 1 outlines the nucleophilic attack at the central carbon of the allyl moiety in (π-allyl)metal complexes and transformation of the metallacyclobutane formed in that manner. Courses b and c have been well documented.[2,3] Course d has been exemplified in the reversible hydride addition and elimination of an (η^3-allyl)tungsten complex[4] and in the dissociation of the bond at the β-carbon of the metallacycle.[2l,5] In all of these examples, the central group X (in Scheme 1) was a hydrogen atom or, in one case, an alkyl group. For the π-allyl moiety wherein X is an appropriate leaving group, it is expected that nucleophilic substitution (i.e., consecutive reactions via course a) may take place. In this communication, we report the first examples of platinum-catalyzed and -promoted reactions involving consecutive reactions via course a in Scheme 1.

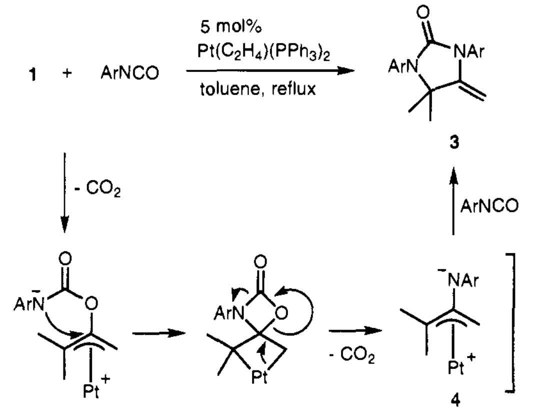
Scheme 1



In the course of our study on catalytic reactions involving an oxatrimethylenemethane–palladium (OTMM–Pd) complex, [η^3-$CH_2C(O)CH_2$]PdL_2, we obtained unexpected products resulting from bond breaking between a central carbon and an oxygen. The reaction of 5,5-dimethyl-4-methylene-1,3-dioxolan-2-one (**1**), a precursor for OTMM, with phenyl isocyanate in the presence of $Pd(PPh_3)_4$ catalyst in toluene at reflux afforded cyclic urea **3a** in 19% yield as a byproduct together with cyclic carbamate **2a** in 78% yield (eq 1).[6] We thought that this byproduct **3a** was likely to arise via a metallacyclobutane intermediate resulting from the nucleophilic attack at the central carbon. If so, the use of a platinum complex as the catalyst should be more effective for the selective formation of urea **3** since it has been known that the formation of a dialkylplatinum (i.e., a platinacyclobutane in the present case) is more favorable than that of a palladium complex.[7] As expected, the platinum-catalyzed reaction proceeded to give urea **3** as the sole product (eq 2). The reactions were carried out on the scale of **1** (2 mmol), ArNCO (4 mmol), and $Pt(C_2H_4)(PPh_3)_2$ (0.1 mmol) in toluene (5 mL) at reflux. In the reaction of **1** with PhNCO for 1 h, **3a** was obtained in 82% yield. Reactions with other aromatic isocyanates (Ar = 4-MeC_6H_4, 4-$MeOC_6H_4$, 4-ClC_6H_4, and 4-$NO_2C_6H_4$) afforded the corresponding cyclic ureas **3b** (1 h, 54%), **3c** (2 h, 45%), **3d** (2 h, 89%), and **3e** (2 h, 95%), respectively. The most likely mechanism for this reaction is the following: (i) intramolecular nucleophilic attack of nitrogen anion, initially generated by the addition of OTMM–Pt to the isocyanate, at the central carbon of the allyl moiety to give a metallacycle; (ii) decarboxylation from the metallacycle leading to azatrimethylenemethane–platinum (ATMM–Pt) (**4**); (iii) [3 + 2]cycloaddition of **4** and another molecule of the isocyanate to produce **3**, as has been observed for the formation of **2a**. The platinum complex also catalyzed the reaction of **1** with 1 equiv of diphenylcarbodiimide (PhN=C=NPh) to afford cyclic urea **3a** as the sole product in



1 **2a** **3a** (1)



3 **4** (2)

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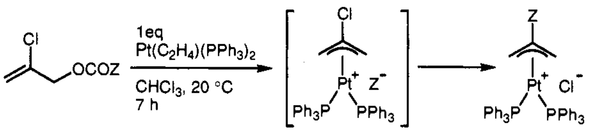
48% yield.[8] This result can be rationally explained in terms of the similar mechanism given in eq 2 with the cleavage of the carbon–oxygen bond but without decarboxylation.

The treatment of isolated OTMM–Pt, [η^3-$CH_2C(O)CH_2$]Pt($(PPh_3)_2$ (**5**),[9] with 1 equiv of *p*-toluenesulfonyl isocyanate afforded ATMM–Pt, [η^3-$CH_2C(NTs)CH_2$]$Pt(PPh_3)_2$ (**6**),[11] in 78% yield (eq 3). This result provides evidence of the intervention of ATMM–Pt in the catalytic reaction of **1** with isocyanates to give urea **3**. The result also represents the first example of a stoichiometric intramolecular reaction of course a in Scheme 1.

(3)

5 **6** (78%)

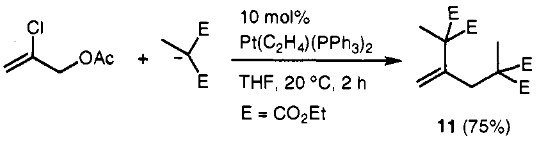
Further examples of stoichiometric nucleophilic substitution are as follows. The reaction of 2-chloro-2-propenyl ethyl carbonate (**7a**)[12] with a stoichiometric amount of $Pt(C_2H_4)(PPh_3)_2$ in $CHCl_3$ at 20 °C afforded (η^3-2-ethoxyallyl)bis(triphenylphosphine)platinum chloride (**9a**) in 48% yield[13] (eq 4). Similarly, the treatment of 2-chloro-2-propenyl *N,N*-diethylcarbamate (**7b**)[12] gave [η^3-2-(diethylamino)allyl]bis(triphenylphosphine)platinum chloride (**9b**) in 77% yield[13] (eq 4). In these reactions, oxidative addition of **7a** or **7b** to a zero-valent platinum followed by decarboxylation gives **8a** and **8b**, respectively. Then, **9a** and **9b** are produced by the substitution of chloride by ethoxide and diethylamide, respectively, in **8a** and **8b** via metallacyclobutanes (i.e., platinacyclobutanes) at the crossroads of Scheme 1.[15]



(4)

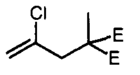
7a; Z = OEt
b; Z = NEt$_2$
8
9a (48%)
9b (77%)

Catalytic reactions using carbon nucleophiles were envisioned to enhance the synthetic utility of the present methodology. The reaction of 2-chloro-2-propenyl acetate (0.5 mmol) with sodium diethyl methylmalonate (2 mmol) in the presence of 10 mol % $Pt(C_2H_4)(PPh_3)_2$ in THF at 20 °C exclusively afforded a doubly alkylated product, **11**, in 75% yield (eq 5), while the catalytic reaction using $Pd(PPh_3)_4$ instead of the platinum complex gave a usual monoalkylated product, **12** (89% yield), as the sole product with chloride remaining intact. Conversion of **12** to **11** in a platinum-catalyzed reaction was not observed. These results lend support to a mechanism involving nucleophilic substitution at the π-allyl center of the platinum complex as a key step. Interestingly, platinum-catalyzed reaction of 2-chloro-2-propenyl acetate (0.5 mmol) with sodium ethyl benzoylacetate (1 mmol) in THF at reflux temperature for 6 h gave 3-(ethoxycarbonyl)-2-phenyl-4-methylfuran (**13**) in 69% yield (eq 6). The central attack on (η^3-2-chloroallyl)platinum(II) would give 1-benzoyl-1-(ethoxycarbonyl)trimethylenemethane–Pt, which undergoes enolate *O*-cyclization[16] followed by exo to endo double-bond isomerization leading to **13**.

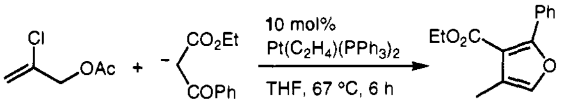


(5)

11 (75%)



12



(6)

13 (69%)

In the reactions presented here, the platinum behaves as an electron sink with a function similar to that of a carbonyl group in the addition/elimination mechanism for the reaction of an acid chloride with alkoxide.

Supplementary Material Available: Typical experimental procedures and spectral data of products (5 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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[8] In the case of palladium-catalyzed reaction, 4,4-dimethyl-5-methylene-3-phenyl-2-(phenylimino)oxazolidine (68%) and cyclic urea **3a** (17%) were obtained.[6]

[9] OTMM–Pt complex **5** was prepared by the reaction of ethyl 2-acetoxy-2-propenyl carbonate[10] with $Pt(C_2H_4)(PPh_3)_2$ in C_6H_6 at room temperature. Note that the OTMM–Pd and –Pt complexes have hybrid η^3 and η^2 character, the latter being greater in the case of Pt complexes. For examples, see: Fawcett, J.; Henderson, W.; Jones, M. D.; Kemmitt, R. D. W.; Russell, D. R.; Lam, B.; Kang, S. K.; Albright, T. A. *Organometallics* **1989**, *8*, 1991. Kemmitt, R. D. W.; Mason, S.; Moore, M. R.; Fawcett, J.; Russell, D. R. *J. Chem. Soc., Chem. Commun.* **1990**, 1535. Ohsuka, A.; Fujimori, T.; Hirao, T.; Kurosawa, H.; Ikeda, I. *J. Chem. Soc., Chem. Commun.* **1993**, 1039.

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[12] Compounds **7a** and **7b** were prepared from 2-chloropropen-1-ol, and ethyl chloroformate or *N,N*-diethyl chloroformamide, respectively. The data for **7a** and **7b** are provided in the supplementary material.

[13] The yields of **9** were determined by the treatment of **9** with $AgBF_4$ leading to the corresponding tetrafluoroborate salts **10a** and **10b**[14] (not shown in the text). Structural data for **9** and **10** are provided in the supplementary material.

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