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Preliminary Communication

Convenient synthesis of [η^3-1-(formyl)allyl]- and [η^3-1-(dimethoxymethyl)allyl]palladium chlorides

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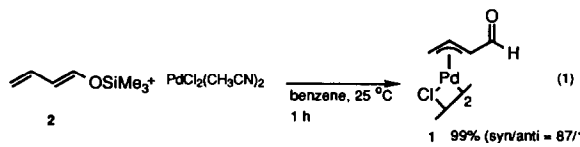
Abstract

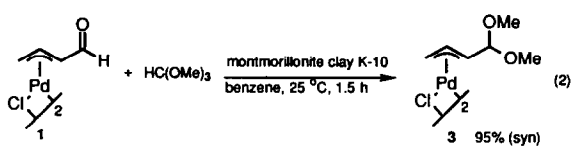
New type of (η^3-allyl)palladium complexes, [η^3-1-(formyl)allyl]palladium chloride and [η^3-1-(dimethoxymethyl)allyl]palladium chloride, were efficiently synthesized and subjected to aldol reaction with an enol silyl ether.

The aldol reaction is one of the most powerful methods for carbon–carbon bond formation in organic synthesis. Aldehydes and acetals have been commonly used as the electrophilic acceptor in the aldol reaction. The range of aldehydes and acetals capable of undergoing aldol reactions as well as the stereochemical course of the reaction have been well investigated, especially in the case of the reactants having α-substituents. However, there are few reports dealing with the reaction of substrates whose α-substitutents are metal moieties [1]. It was anticipated that such aldol reactions might show new possibilities based on the bound metal. Thus, we initiated a study to develop a method for the preparation of such metal complexes. We describe here efficient access to (η^3-allyl)palladium complexes in which an aldehyde or an acetal function is attached at the allylic terminal carbon.

The simplest formyl compound of this sort may be [η^3-1-(formyl)allyl]palladium chloride **1**. This complex **1** has been reported in the study of the reaction of $PdCl_2$ with 1-methoxybutadiene, but no experimental details were given except for its ^1H NMR data [2]. Having studied the reaction of Pd^{II} with a dienol silyl ether [3*], we examined the reaction of $PdCl_2(CH_3CN)_2$ with 1-siloxybutadiene **2** to obtain the desired complex **1** [4*]. Thus, treatment of dienol silyl ether **2** with $PdCl_2(CH_3CN)_2$ in dry benzene at room temperature for 1 h afforded [η^3-1-(formyl)allyl]palladium chloride **1** in a quantitative yield (99%, *syn*/*anti* = 87/13) (eqn. (1)) [5*].



When treated with trimethyl orthoformate and montmorillonite clay K-10 in dry CH_2Cl_2 [6] at room temperature for 1.5 h, **1** was converted into the desired complex, [η^3-1-(dimethoxymethyl)allyl]palladium chloride **3** (95%, only *syn* isomer) (eqn. (2)) [7*]. The exclusive formation of *syn* isomer will bring about some advantage from the viewpoint of organic synthesis.



We then just briefly examined the possibility of the use of an aldehyde complex **1** and an acetal complex **3** in aldol type of reactions. In these complexes or their activated forms, four sites are available, in principle, for nucleophilic attack, these being two terminal carbon atoms of the allyl part [8], a carbonyl or acetal carbon atom, and a metal center. Of the four sites, the acetal carbon atom of **3** was selectively attacked by an enol silyl ether as described below, while the complex **1** reacted only sluggishly under several types of standard reaction conditions. The acetal complex **3** reacted with the enol silyl ether **4** in the presence of Me_3SiOTf in CH_2Cl_2 at −78°C for 5 h, to give the aldol product **5** (62%, major/minor = 60/40) [9*]. The two isomers of **5** correspond to diastereomers with respect to β- and γ-positions of the carbonyl and both isomers exist in

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* Reference number with asterisk indicates a note in the list of references.

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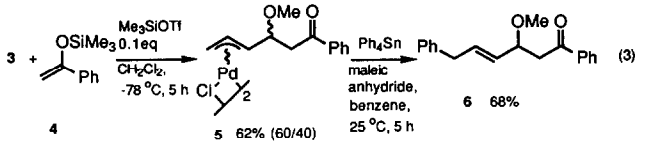
syn forms. Phenylation of **5** with Ph_4Sn in the presence of maleic anhydride [10] in dry benzene at 25°C for 5 h gave the *E*-olefin **6** (68%) exclusively (eqn. (3)) [11*]. An interesting possibility of intervention of a cationic palladium (1-methoxybutadiene) complex [12*], obtainable from **3** and Me_3SiOTf, is not clear at this time. In conclusion, it is expected that the development of convenient methods for the preparation of (η^3-allyl)palladium(II) having a formyl or an acetal group will provide unique opportunities in aldol and organometallic chemistry.



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References and notes

1 J. Ju, B. R. Reddy, M. Kham and K. M. Nicholas, *J. Org. Chem., 54* (1989) 5426; R. Tester, V. Varghese, A. M. Montana, M. Khan and K. M. Nicholas, *J. Org. Chem., 55* (1990) 186; C. Mukai, K. Nagai and M. Hanaoka, *Tetrahedron Lett., 30* (1989) 5623.

2 M. K. Andri, A. V. Krylov, N. E. Averochkin and A. P. Belov, *Koord. Khim., 10* (1984) 540.

3 The reaction of $PdCl_2$ with 1-silyl-1-(siloxy)butadiene was found to give [η^3-1-(silylcarbonyl)allyl]palladium chloride. S. Ogoshi, K. Ohe, N. Chatani, H. Kurosawa, Y. Kawasaki and S. Murai, *Organometallics, 9* (1990) 3021; S. Ogoshi, K. Ohe, N. Chatani, H. Kurosawa and S. Murai, *Organometallics, 10* (1991) 3183.

4 Molybdenum and ruthenium complexes analogous to **1** were also prepared by using the similar method. S. A. Benyunes, M. Green and M. J. Grimshire, *Organometallics, 8* (1989) 2268; S. A. Benyunes, J. P. Day, M. Green, A. W. Al-Saadoon and T. L. Waring, *Angew. Chem., Int. Ed. Engl., 29* (1990) 1416.

5 Synthesis of [η^3-1-(formyl)allyl]palladium chloride **1**. Under an atmosphere of nitrogen, dienol silyl ether **2** (1.53 g, 10 mmol) was added to the suspension of $PdCl_2(CH_3CN)_2$ (1.82 g, 7.1 mmol) in dry benzene (80 ml) at room temperature and the suspension was stirred for 1 h. The reaction mixture was concentrated *in vacuo* (5 mmHg) to give [η^3-1-(formyl)allyl]palladium chloride **1** in a quantitative yield (1.47 g, 99%, *syn*/*anti* = 87/13), m.p. 142–143°C dec. IR (KBr) 1699, 1695 cm^{-1}; ^{1}H-NMR (270 MHz, $CDCl_3$) **1**-*syn* δ 3.44 (d, J = 12.6 Hz, 1H), 3.86 (dd, J = 5.1, 10.9 Hz, 1H), 4.35 (d, J = 7.3 Hz, 1H), 5.97 (ddd, J = 12.6, 10.9, 7.3 Hz, 1H), 9.65 (d, J = 5.1 Hz, 1H), **1**-*anti* δ 3.97 (d, J = 13.7 Hz, 1H), 4.39 (d, J = 7.5 Hz, 1H), 5.02 (dd, J = 4.6, 5.7 Hz, 1H), 5.68 (ddd, J = 13.7, 7.5, 5.7 Hz, 1H), 9.02 (d, J = 4.6 Hz, 1H). Anal. Found: C, 23.09; H, 2.46; Cl, 16.64. C_4H_5OClPd calc.: C, 22.77; H, 2.39; Cl, 16.81%.

6 E. C. Taylor and C. Chang, *Synthesis*, (1977) 467.

7 Transformation of **1** into [η^3-1-(dimethoxymethyl)allyl]palladium chloride **3**. The complex **1** (1.06 g, 5 mmol), trimethyl orthoformate (7.5 g) and montmorillonite clay K-10 (5 g) were stirred in dry CH_2Cl_2 (25 ml) at room temperature for 1.5 h. The reaction mixture was filtered and concentrated to give yellow oil. The yellow oil was recrystallized with CH_2Cl_2/hexane to give [η^3-1-(dimethoxymethyl)allyl]palladium chloride **3** (1.24 g, 95%, only *syn* isomer), m.p. 105–108°C dec. ^{1}H-NMR (270 MHz, $CDCl_3$) δ 3.03 (d, J = 12.2 Hz, 1H), 3.34 (s, 3H), 3.43 (s, 3H), 3.58 (dd, J = 10.8, 2.2 Hz, 1H), 4.04 (d, J = 6.8 Hz, 1H), 4.63 (d, J = 2.2 Hz, 1H), 5.65 (ddd, J = 12.2, 10.8, 6.8 Hz, 1H). Anal. Found: C, 28.11; H, 4.33; Cl, 13.87. $C_6H_{11}O_2ClPd$ calc.: C, 28.04; H, 4.31; Cl, 13.79%.

8 B. M. Trost, *Acc. Chem. Res., 13* (1980) 385; J. Tsuji and I. Minami, *Acc. Chem. Res., 20* (1987) 140.

9 Aldol reaction of **3** with enol silyl ether. A solution of the acetal complex **3** (516 mg, 2 mmol) and an enol silyl ether **4** (384 mg, 2 mmol) in dry CH_2Cl_2 (5 ml) was cooled to −78°C and Me_3SiOTf (44.4 mg, 0.2 mmol) was added. The reaction mixture was stirred at −78°C for 5 h and warmed up to 25°C. Then, the mixture was washed with saturated aqueous $NaHCO_3$ solution (15 ml) and dried over $MgSO_4$ for 3 h. The residue was separated by column chromatography (silicagel 100–200 mesh, hexane/EtOAc = 2/1, R_f = 0.11) to give an aldol product **5** (426 mg, 62%, major/minor = 60/40), m.p. 61–63°C dec. IR (KBr) 1680 cm^{-1}; ^{1}H-NMR (270 MHz, $CDCl_3$) **5**-major δ 3.01 (d, J = 12.4 Hz, 1H), 3.34 (d, J = 5.4 Hz, 1H), 3.39 (d, J = 7.8 Hz, 1H), 3.46 (s, 3H), 3.86 (dd, J = 11.2, 4.2 Hz, 1H), 4.01 (ddd, J = 7.8, 5.4, 4.2 Hz, 1H), 4.02 (d, J = 6.6 Hz, 1H), 5.58 (ddd, J = 12.4, 11.2, 6.6 Hz, 1H), 7.3–8.1 (m, 5H); **5**-minor δ 2.96 (d, J = 13.1 Hz, 1H), 3.28 (d, J = 4.6 Hz, 1H), 3.53 (d, J = 6.8 Hz, 1H), 3.44 (s, 3H), 3.94 (dd, J = 11.2, 2.9 Hz, 1H), 4.01 (ddd, J = 6.8, 4.6, 2.9 Hz, 1H), 4.02 (d, J = 6.6 Hz, 1H), 5.58 (ddd, J = 13.1, 11.2, 6.6 Hz, 1H), 7.3–8.1 (m, 5H). Anal. Found: C, 44.94; H, 4.36. $C_{13}H_{15}OClPd$ calc.: C, 45.24; H, 4.38.

10 H. Kurosawa, S. Ogoshi, Y. Kawasaki, S. Murai, M. Miyoshi and I. Ikeda, *J. Am. Chem. Soc., 112* (1990) 2813.

11 Phenylation of **6**. To a solution of aldol product **5** (160 mg, 0.47 mmol) and maleic anhydride (91 mg, 0.93 mmol) in dry benzene (10 ml) was added Ph_4Sn (195 mg, 0.47 mmol) at 25°C and the reaction mixture was stirred for 5 h and concentrated. The residue was separated by column chromatography (silicagel 100-200 mesh, hexane/EtOAc = 6/1, R_f = 0.18) to give **6** (yield 68%). ^{1}H-NMR (270 MHz, $CDCl_3$) δ 2.96 (d, J = 5.1 Hz, 1H), 3.02 (d, J = 5.4 Hz, 1H), 3.27 (s, 3H), 3.33 (d, J = 7.3 Hz, 1H), 3.39 (d, J = 7.8 Hz, 1H), 4.26 (dddd, J = 7.8, 5.4, 5.1, 0.7 Hz, 1H), 5.47 (ddt, J = 15.1, 7.8, 1.5 Hz, 1H), 5.90 (dtd, J = 15.1, 6.8, 0.7 Hz, 1H), 7.1–7.4 (m, 5H), 7.5–8.0 (m, 5H).

12 (a) No aldol reaction occurred between **3** and **4** in the absence of Me_3SiOTf; (b) Treatment of analogous acetal-substituted (η^3-allyl)molybdenum complexes with HBF_4 led to isolation of cationic diene-molybdenum complexes, which in turn reacted with nucleophiles to give η^3-allyl complexes analogous to **5** [13].

13 S. Hasson, J. F. Miller and L. S. Liebeskind, *J. Am. Chem. Soc., 112* (1990) 9660.