Journal of Organometallic Chemistry, 471 (1994) C6–C7

Preliminary Communication

C–O bond cleavage and oxidative addition of allyl carboxylate to ruthenium(0) complex. Isolation of (π-allyl)(trifluoroacetato)tris(triethylphosphine)ruthenium(II)

Sanshiro Komiya, Takashi Kabasawa, Koji Yamashita, Masafumi Hirano and Atsushi Fukuoka

Department of Applied Chemistry, Tokyo University of Agriculture and Technology, 2-24-16 Nakacho, Koganei, Tokyo 184 (Japan)

(Received September 29, 1993; in revised form December 22, 1993)

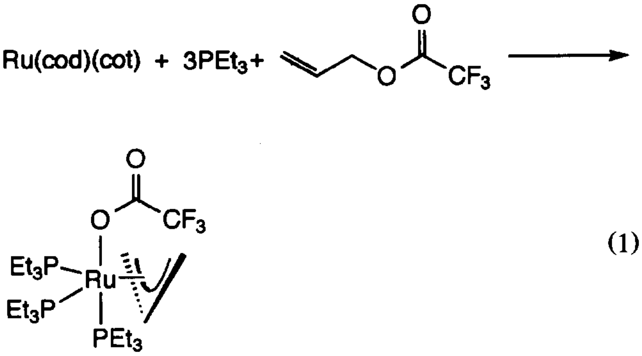
Abstract

(π-Allyl)(trifluoroacetato)tris(triethylphosphine)ruthenium(II) has been isolated by oxidative addition of allyl trifluoroacetate to Ru(cod)(cot) in the presence of triethylphosphine ligand.

Key words: Ruthenium; Phosphine; Allyl; Oxidative addition

The oxidative addition of esters to the low valent Group 10 transition metals such as Pd by a process involving C–O bond cleavage has been well documented, as the first step in catalytic allylations of organic compounds using allylic esters under neutral conditions; this has potential importance in organic synthesis [1,2]. In recent years, ruthenium complexes have also attracted attention as novel candidates in the catalytic chemoselective allylation of organic substrates using allyl acetates [3]. Although the mechanisms of the allylation are postulated to involve π-allylruthenium(II) species as an important key intermediate, there is so far no direct evidence for the formation of such species from allyllic esters, whereas the formation of π-allylruthenium(II) species by oxidative addition of reactive allyl halides to Ru^0 carbonyl is well known [3]. We previously reported an example of C–O bond oxidative addition in the presence of triethylphosphine of vinyl acetate to ruthenium(0) to give a *mer*-(vinyl)(acetato)tris(triethylphosphine)ruthenium(II) [4]. We now report the first example of C–O bond oxidative addition of allyl ester to the Ru^0 to give a (π-allyl)-(carboxylato)ruthenium(II) complex.

Allyl trifluoroacetate was introduced into a hexane solution of Ru(cod)(cot) in the presence of 3 equiv. of triethylphosphine and stirred for 16 h at room temperature. After evaporation of all volatile material, the residual orange oil was recrystallized from hexane to give pale yellow prisms of (π-allyl)(trifluoroacetato) tris(triethylphosphine)ruthenium(II) (**1**) (21%) [5*]. A similar π-allylruthenium(II) complex with trimethylphosphine (**2**) was also formed [6*].



(1)

The IR spectrum of **1** showed a strong asymmetric ν(OCO) band at 1680 cm^{-1}, the value suggesting the monodentate coordination mode of the trifluoroacetato ligand [7]. That the structure is trigonal bipyramidal containing a π-allyl entity for **1** as shown in the equation, was indicated by the following NMR analysis. ^{1}H NMR and H–H COSY spectra of **1** show characteristic pattern for the π-allyl metal complex: the *anti* and *syn* protons appear as a double doublet at δ 2.96 and a doublet at δ 3.25, respectively, and the methine proton as a double triple triplet at δ 4.38. *Anti* and methine protons involve couplings with one of the three P nuclei. The chemical shifts of these protons are observed at relatively higher magnetic field than the known tricarbonyl(π-allyl)ruthenium(II) complex, Ru (η^3-C$_3$H$_5$)(CO)$_3$X (X = OAc, OTf) [8], suggesting that the electron density on the π-allyl moiety in **1** is higher than that in the carbonyl analogue. Two sets of signals assignable to an apical and two equatorial PEt$_3$ ligands are observed in 1:2 ratio, where the geminal methylene protons in the equatorial PEt$_3$ ligands become magnetically nonequivalent to each other, since they are mutually diastereotopic. ^{31}P{^{1}H} NMR spectroscopy also shows a triplet and a doublet at 18.2 and 44.6 ppm from ext. H$_3$PO$_4$ in 1:2 ratio, confirming that the two P's lie at equatorial positions with a unique P at an apical position. The apical P nucleus

---

Correspondence to: Dr. S. Komiya.

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

0022-328X/94/$7.00
SSDI 0022-328X(94)24411-B

resonates at lower field than the equatorial ones, being consistent with strong electron withdrawal from the *trans* trifluoroacetato ligand. $^{13}C\{^1H\}$ NMR spectroscopy of **1** also shows characteristic signals for the π-allyl moiety. Methylene and methine carbons were observed at 47.1 (double triplet) and 94.8 (singlet) ppm, respectively. Both the carbonyl and trifluoromethyl carbons appear as a quartet by the coupling with three F nuclei. These NMR data are consistent with the proposed trigonal bipyramidal structure shown in eqn. (1).

When the synthesis of **1** was carried out in the presence of a small amount of moisture, **1** could not be isolated and a gradual evolution of propylene was observed. The proton source of the propylene gas was found to be water which is contaminated in the solvent, since the reaction in the presence of a small amount of D_2O liberated only C_3H_5D. In fact **1** is smoothly hydrolyzed in THF by a trace amount of water to liberate propylene in 45% yield at room temperature. The results suggest the strong nucleophilicity of the π-allyl moiety. Acidolysis of **1** with sulfuric acid released propylene in 59% yield. On the other hand, the reaction of Ru(cod)(cot) with a slight excess of allyl acetate in the presence of PEt_3 in hexane gave only an adduct Ru(cod)(cot)(PEt_3) under ambient conditions [9], whereas the reaction with excess allyl acetate at 50°C led to the gradual evolution of propylene gas. Though the isolation of the (π-allyl)(acetato)ruthenium(II) complex has not been achieved, the formation of propylene strongly supports the initial formation of a highly nucleophilic allylic ruthenium complex in solution.

Benzaldehyde reacted with **1** to give the corresponding homoallyl alcohol in 69% yield in THF at 50°C, whereas no reaction took place with dimethyl malonate under the same conditions, probably due to the high nucleophilicity of the allylic moiety induced by triethylphosphine ligands [6]. Further investigation concerning the structure and reactivities of **1** is now in progress.

Acknowledgments

We are grateful for financial support as a Grant-in-Aid for the Priority Areas from Ministry of Education, Science and Culture, Japan and to Prof. I. Shimizu and Mr. Y. Maruyama (Waseda University) for useful discussions.

References and notes

1 J.P. Collman, L.S. Hegedus, J.R. Norton and R.G. Finke, *Principles and Applications of Organotransition Metal Chemistry*, 2nd ed., University Science Books, Mill Valley, California, 1987.

2 (a) J. Tsuji, *Organic Synthesis with Palladium Compounds*, Springer-Verlag, Heidelberg, 1980, and references cited therein; (b) R.F. Heck, *Palladium Reagents in Organic Synthesis*, Academic Press, 1985.

3 (a) E.A. Seddon and K.R. Seddon, *The Chemistry of Ruthenium*, Elsevier, Oxford, 1984; (b) Y. Tsuji, T. Mukai, T. Kondo and Y. Watanabe, *J. Organomet. Chem., 369* (1989) C51; (c) T. Kondo, T. Mukai and Y. Watanabe, *J. Org. Chem., 56* (1991) 487; (d) T. Mitsudo, S.-W. Zhang, T. Kondo and Y. Watanabe, *Tetrahedron Lett., 33* (1992) 341; (e) I. Minami, I. Shimizu and J. Tsuji, *J. Organomet. Chem., 296* (1985) 269.

4 S. Komiya, J. Suzuki, K. Miki and N. Kasai, *Chem. Lett.*, (1987) 1287.

5 Yield, 21%. Mp = 110–111°C (dec.). Anal. Found: C, 44.41; H, 8.54. $C_{23}H_{50}F_3O_2P_3Ru$ calc.: C, 45.31; H, 8.27%. IR (KBr disk): 1680 cm^{-1} ($\nu(OCO)_{asym}$). ^1H NMR (C_6D_6): δ 0.60 (dt, 9H, $J = 12.2$, 7.6 Hz, apical-PCH_2CH_3), δ 1.02 (dt, 18H, $J = 12.4$, 7.5 Hz, eq-PCH_2CH_3), δ 1.11 (dq, 6H, $J = 14.2$, 7.6 Hz, apical-PCH_2CH_3), δ 1.77, 1.95 (dt, 6H each, $J = 14.2$, 7.5 Hz, eq-PCH_2CH_3), δ 2.96 (dd, 2H, $J = 11.4$, 3.0 Hz, *anti*-CH_2), δ 3.25 (d, 2H, $J = 7.2$ Hz, *syn*-CH_2), δ 4.38 (dtt, 1H, $J = 5.5$, 7.2, 11.4 Hz, CH). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 9.19 (s, apical-PCH_2CH_3), δ 9.92 (d, $J = 6.3$ Hz, eq-PCH_2CH_3), δ 22.0 (m, PCH_2CH_3), δ 47.12 (dt, $J = 18.3$, 9.4 Hz, CH_2), δ 94.82 (s, CH), δ 117.97 (q, $J = 291$ Hz, CF_3), δ 160.81 (q, $J = 34$ Hz, CO). $^{31}P\{^1H\{$ NMR (C_6D_6 from ext. H_3PO_4): δ 18.2 (d, $J = 34.7$ Hz, 2P), δ 44.6 (t, $J = 34.7$ Hz, 1P). ^{19}F NMR (C_6D_6 from ext. C_6F_6): δ −78.0 (s, CF_3). Unidentified orange oil was always contaminated. Repeated purification of **1** from hexane solution may be responsible for the low yield.

6 Formation of a PMe_3 analogue was confirmed by ^1H NMR spectroscopy: ^1H NMR (C_6D_6): δ 0.41 (d, 9H, $J = 8$ Hz, apical-PCH_3), δ 1.27 (d, 18H, $J = 7$ Hz, eq-PCH_3), δ 2.33 (dd, 2H, $J = 11$, 5 Hz, *anti*-CH_2), δ 2.90 (d, 2H, $J = 7$ Hz, *syn*-CH_2), δ 3.9 (m, 1H, CH). Syntheses and reactions of related (π-allyl)(bromo)ruthenium(II) complexes having trimethylphosphine ligands were recently reported: Y. Maruyama, I. Shimizu and A. Yamamoto, Abstr. No. 2E213, 65th National Meeting of Chem. Soc. Jpn., Tokyo, March 1993.; Y. Maruyama, I. Shimizu and A. Yamamoto, 40th Symp. Organomet. Chem. Jpn., A116, Sapporo, Oct. 1993.

7 S.D. Robinson and M.F. Uttley, *J. Chem. Soc., Dalton Trans.*, (1973) 1912.

8 G. Sbrana, G. Braca, F. Piacenti and P. Pino, *J. Organomet. Chem., 13*, (1968) 240; T. Kondo, H. Ono, T. Mitsudo and Y. Watanabe, 39th Symp. Organomet. Chem. Jpn., PA203, Abstr. p. 199, Tokyo, 1992; T. Kondo, N. Satake, H. Ono, T. Mitsudo and Y. Watanabe, 40th Symp. Organomet. Chem. Jpn., PA113, Sapporo, Oct. 1993.

9 B. Chaudret, G. Commenges and R. Poilblanc, *J. Chem. Soc., Chem. Commun.*, (1982) 1388; B. Chaudret and R. Poiblanc, *Organometallics, 4* (1985) 1722; R.S. Schrock and J. Lewis, *J. Am. Chem. Soc., 95* (1973) 4102.