A new method for the conversion of allyl alcohol into π-allyl species promoted by nucleophilic interaction with a CO ligand†

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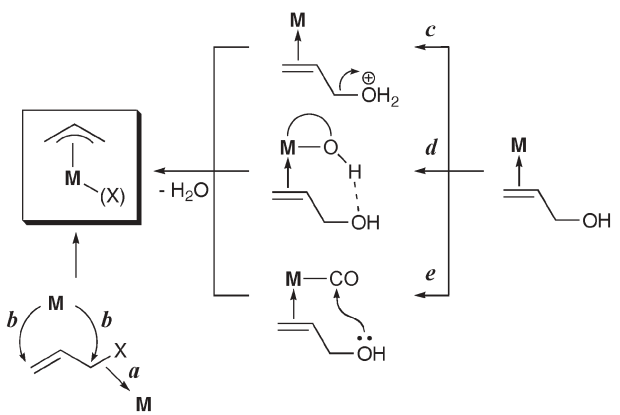
Upon treatment with an iridium carbonyl complex, $[(PN)Ir(CO)_2]^+$, allyl alcohol can be smoothly converted into π-allyliridium species at ambient temperature *via* nucleophilic interaction of the alcohol with a CO ligand followed by C(allyl)–O bond cleavage in the resultant protonated allyloxycarbonyl intermediate.

A wide variety of stoichiometric and catalytic transformations of allyl compounds mediated by transition metal species have been developed and utilized as indispensable tools in organic synthesis. π(η^3)-Allyl species are regarded as the key intermediates of the transformations,[1] and various allyl sources such as halides and ester derivatives have been employed to extend the synthetic utility of the transformations. Activation of allyl alcohol has attracted increasing attention due to economical and environmental advantages but only a limited number of conversions of allyl alcohol into π-allyl species have been reported so far.[2] Although, to date, a couple of methods for activation of allyl alcohol have been established as summarized in Scheme 1, the concerted oxidative addition (*path a*) and the S_N2-type mechanisms (*path b*) are not always applicable to allyl alcohol because of the OH group being a bad leaving group. Another feasible approach is dehydration under acidic conditions. The dehydration, however, usually requires action of an excess amount of Lewis acid or severe reaction conditions, while rare examples of successful catalytic activation of allyl alcohol mediated by acidic hydrido species (*path c*) or a protic tether ligand (*path d*) have been reported.[2] During the course of our study on heterodinuclear complexes with P/N-based multidentate ligands,[3] we have found an unprecedented method for activation of allyl alcohol **1** on the iridium-carbonyl complex, $[(PN)Ir(CO)_2]^+$ $\mathbf{2}^+$ (PN = 2-diphenylphosphinomethylpyridine),[4,5] through interaction with a CO ligand (*path e*), which is applicable to a catalytic conversion.

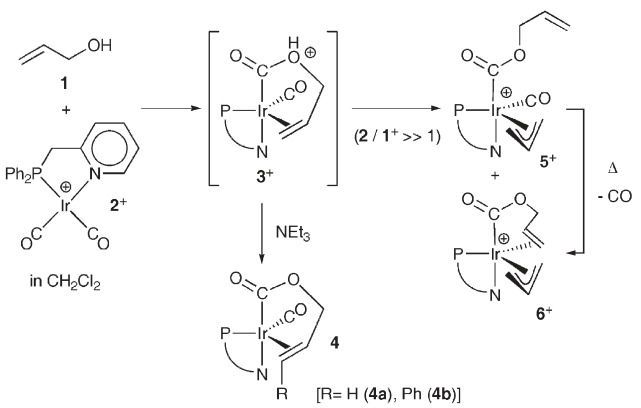


Scheme 1

Interaction of allyl alcohol **1** with the cationic iridium-carbonyl complex **2**·BF_4[5] at ambient temperature afforded different types of products depending on the reaction conditions (Scheme 2).

A 1 : 1 reaction gave an unstable intermediate $\mathbf{3}^+$, which was soon converted to a mixture (see below). Although $\mathbf{3}^+$ could not be characterized spectroscopically due to its instability, $\mathbf{3}^+$ turned out to be the protonated allyloxycarbonyl species as revealed by (1) deprotonation with NEt_3 (immediately after addition of **1**) leading to the neutral product **4a** (R = H; 61% isolated yield; consisting of two isomers)‡ and (2) comparison of **4a** with **4b** (R = Ph; 61% isolated yield)‡ derived from cinnamyl alcohol and characterized by X-ray crystallography (Fig. 1a).§[6,7] Complex **4b** contains the five coordinate, trigonal-bipyramidal Ir center, and the remarkable structural features are the chelating η^1-C(=O)–CH_2(η^2-CH=CHR) linkage resulting from (1) nucleophilic addition of the OH moiety in **1** to the CO ligand and (2) the η^2-coordination of the olefinic part. Appearance of a ν(C=O) vibration (1644 (**4a**), 1637 cm^{-1} (**4b**)) and upfield shift of the olefinic ^1H and ^{13}C NMR signals are consistent with this structure.

On the other hand, when a mixture of **1** and **2**·BF_4 was left for a longer time (1 h) (in particular, in the presence of an excess amount of **1**), a mixture of products was obtained, from which two major species, **5**·BF_4 (72% isolated yield when **1**/**2**·BF_4 = 20) and **6**·BF_4,¶ were isolated and characterized by X-ray crystallography



Scheme 2

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† Electronic supplementary information (ESI) available: X-ray structural data for **4b**, **5**·BF_4 and **6**·BF_4. See DOI: 10.1039/b601143h

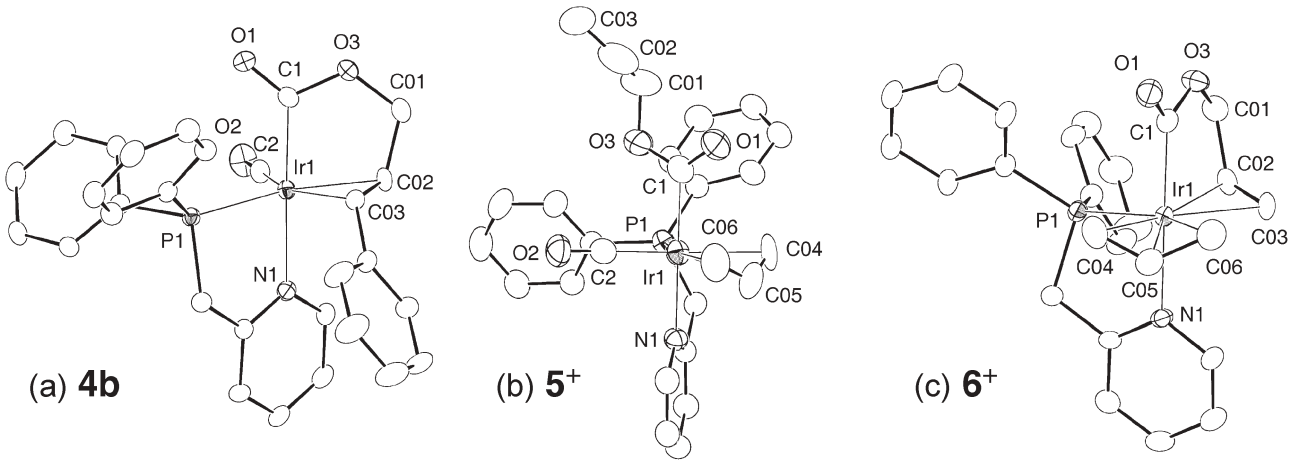
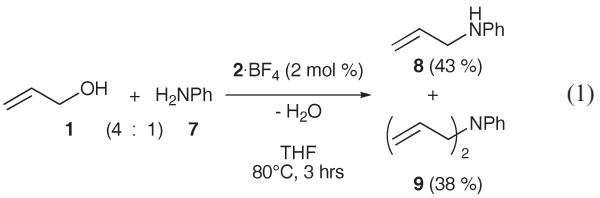


Fig. 1 ORTEP plots of **4b**, $\mathbf{5}^+$ and $\mathbf{6}^+$ drawn with thermal ellipsoids at the 30% probability level.

(Fig. 1b,c)§ and ^{1}H and ^{31}P NMR.‡ It is notable that (1) $\mathbf{5}\cdot BF_4$ and $\mathbf{6}\cdot BF_4$ contain two allyl units, one is the η^3-allyl ligand and the other is the non- ($\mathbf{5}\cdot BF_4$) or η^2-coordinated allyloxycarbonyl ligand ($\mathbf{6}\cdot BF_4$), and (2) the η^3-allyl ligands result from oxidative addition of **1**. It was confirmed that thermolysis of $\mathbf{5}\cdot BF_4$ caused decarbonylation leading to $\mathbf{6}\cdot BF_4$.

Comparison of the structures of $\mathbf{3}^+$ (**4**) and $\mathbf{5}^+$ strongly suggests that the η^3-allyl ligand in $\mathbf{5}^+$ is formed *via* C(allyl)–O bond cleavage of the η^2-coordinated allyloxy moiety ($\mathbf{3}^+ \rightarrow \mathbf{A}$) followed by dehydrative condensation with a second molecule of **1** (Scheme 3). The unstable intermediate $\mathbf{3}^+$ should be formed by η^2-coordination of **1** ($\mathbf{1} + \mathbf{2}^+ \rightarrow \mathbf{B}$) followed by nucleophilic interaction between the OH group in **1** and the Lewis acidic CO moiety. Cationic five-coordinate (η^2-olefin)Ir complexes like **B** have precedents[8] and the rather strong η^2-coordination of the olefinic part in **1** (**B**) should assist the subsequent intramolecular interaction between the OH and CO groups leading to $\mathbf{3}^+$. Thus it is remarkable that the present study reveals a new method for conversion of allyl alcohol **1** into η^3-allyl species ($\mathbf{5}^+$ and $\mathbf{6}^+$) under mild reaction conditions (at ambient temperature), which involves oxidative addition *via* heterolytic C–O bond cleavage of the protonated allyloxycarbonyl intermediate $\mathbf{3}^+$ (*path e* in Scheme 1).

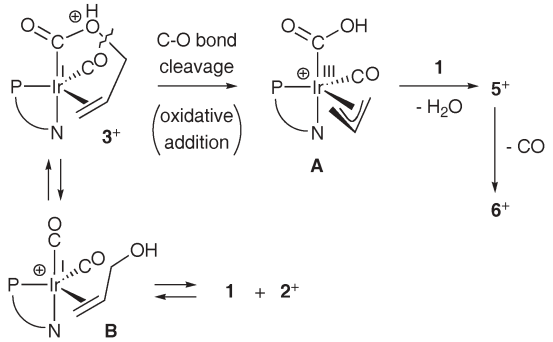
These results, in particular, the C–O bond cleavage under mild conditions, suggest that the iridium complexes appearing in this communication may show activity for catalytic conversion of allyl alcohol **1**. As expected, the iridium complexes ($\mathbf{2}\cdot BF_4$, $\mathbf{5}\cdot BF_4$ and $\mathbf{6}\cdot BF_4$) were active for catalytic allylation of aniline **7** with **1**[2a,b] to produce a mixture of mono- (**8**) and diallylaniline (**9**) (eqn. 1).[6] The reaction at 80 °C in the presence of a catalytic amount of **2** (2 mol%) was completed within 3 h. The catalytic activity of the decarbonylated species $\mathbf{6}\cdot BF_4$ was slightly better than those of $\mathbf{2}\cdot BF_4$ and $\mathbf{5}\cdot BF_4$.



(1)

In conclusion, we have demonstrated a novel method for conversion of allyl alcohol into an η^3-allyl species under mild reaction conditions (*path e* in Scheme 1), which can be extended to a catalytic allylation reaction with allyl alcohol. While carbonyl species have seldom been used as a catalyst precursor for conversion of allyl alcohol because of their apparently low ability with respect to oxidative addition (*cf.* nucleophilic phosphine complexes), the present result implies that (1) C–O bond oxidative addition of **1** is promoted by nucleophilic interaction of the OH group in **1** with the CO ligand and (2) the $[Ir(CO)]^+$ part in $\mathbf{2}^+$ serves as an effective Lewis acid to promote the OC–O bond formation as well as the subsequent C(allyl)–O bond cleavage, and thus cationic iridium-carbonyl complexes like $\mathbf{2}^+$ have a potential to serve as an effective catalyst for allylic transformations with allylic alcohol **1**. Extension of the catalytic reaction is now under study and the results will be reported in due course.

We thank Prof. Ryo Takeuchi (Aoyama Gakuin University) for fruitful discussions and Mr Kim Dong Hwan (Sunchon University, Korea) for his assistance with the catalytic study. A Monbukagakusho scholarship for C.D. from the Japanese Government is gratefully acknowledged. The present research is financially supported by the Japanese Government and the Japan Society for the Promotion of Science, which are gratefully acknowledged.

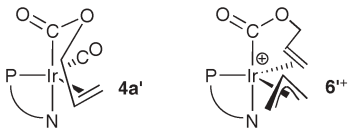


Scheme 3

Notes and references

‡ Selected spectroscopic data: **2**:[5] δ_P (in $CDCl_3$) 27.1, δ_H (in $CDCl_3$) 4.57 (2H, d, J = 12.0 Hz, PCH_2), 7.5–7.8 (11H, m), 7.95 (1H, t, J = 7.6 Hz, py),

8.93 (1H, d, py), δ_C (in $CDCl_3$) 40.9 (d, J = 35 Hz, PCH_2), 125–142 (py and Ph), 162.4 (d, J = 5 Hz, CO), FD-MS m/z = 526 (**2**), IR (KBr) 2085, 2018 (ν_{CO}), 1061 cm^{-1} (ν_{BF}); for **4a** (1 : 1 mixture of two isomers): δ_P (in $CDCl_3$) −2.05, −3.65, δ_H (in CD_2Cl_2; too complicated to be assigned) 0.82–0.86 (0.5H, m), 1.82 (0.5H, dt, J = 5.4 and 3.2 Hz), 1.71–1.76 (0.5H, m), 2.12–2.15 (1H, m), 3.08 (0.5H, dd, J = 9.6 and 2.7 Hz), 3.45–3.51 (0.5H, d, J = 9.7 Hz), 3.90 (0.5H, dd, J = 17.6 and 9.8 Hz), 4.2–4.4 (2.5 H, m), δ_C (in CD_2Cl_2) 20.9 (d, J = 8 Hz, CH_2=CH), 21.3 (d, J = 23 Hz, CH_2=CH), 41.1 (d, J = 7 Hz, =CH), 45.0 (d, J = 28 Hz, PCH_2), 45.3 (d, J = 31 Hz, PCH_2), 46.4 (d, J = 27 Hz, =CH), 69.5 (d, J = 3 Hz, OCH_2), 71.4 (d, J = 5 Hz, OCH_2), FD-MS m/z = 583 (**4a**), IR (KBr) 1961 (ν_{CO}), 1644 cm^{-1} ($\nu_{C=O}$); for **4b**: δ_P (in CD_2Cl_2) −3.10, δ_H (in CD_2Cl_2) 2.56 (1H, dd, J = 16.9 and 9.3 Hz, PhC*H*=), 3.53 (t, J = 8.0 Hz, CH_2O), 3.78 (1H, dd, J = 16.9 and 11.5 Hz, =C*H*CH_2), 3.9 (1H, m, CH_2O), δ_C (in CD_2Cl_2) 37.0 (d, J = 6 Hz, Ph–*C*H), 41.5 (d, J = 29 Hz, –$CHCH_2$), 44.48 (d, J = 28 Hz, CH_2P), FD-MS m/z = 659 (**4b**), IR (KBr) 1954 (ν_{CO}), 1637 cm^{-1} ($\nu_{C=O}$); for **5**·BF_4: δ_P (in $CDCl_3$) 0.97, δ_H (in $CDCl_3$) 3.40 (1H, d, J = 12.3 Hz, η^3-allyl), 3.63 (1H, dd, J = 13.7 and 6.1 Hz, η^3-allyl), 4.15–4.95 (6H, m), 5.00–5.17 (3H, m), 5.62 (1H, m, η^3-allyl), ESI-MS m/z = 624 (**5**$^+$), 556 (**6**$^+$-allyl), IR (KBr) 2057 (ν_{CO}), 1655 ($\nu_{C=O}$), 1084 cm^{-1} (ν_{BF}); for **6**·BF_4 (4 : 1 mixture of two isomers): δ_P (in $CDCl_3$) −6.0, −7.3 (major), δ_H (in $CDCl_3$) 3.05–3.90 (6H, m), 4.30–4.82 (5H, m), 5.62 (1H, m, η^3-allyl), IR (KBr) 1657 ($\nu_{C=O}$), 1081 cm^{-1} (ν_{BF}), ESI-MS m/z = 296 (**6**$^+$). Satisfactory ^{13}C NMR data for **5**·BF_4 and **6**·BF_4 could not be obtained due to their low solubility in organic solvents. The presence of the isomers hampered detailed spectroscopic characterization of **4a** and **6**$^+$. The isomer **6′**$^+$ could be detected as the minor component of the disordered structure (**6**$^+$: **6′**$^+$ = 0.8 : 0.2) and the structure of **4a′** was proposed taking into account the structure of **4b**.



§ X-ray data collections were carried out with a Rigaku RAXIS-IV imaging plate area detector at −60 °C. **4b**: $C_{29}H_{25}IrNO_3P$, fw = 658.72, monoclinic, space group $P2_1/n$, a = 10.4334(8) Å, b = 14.1368(9) Å, c = 16.992(1) Å, β = 94.627(4)°, V = 2498.0(3) Å^3, Z = 4, d_{calcd} = 1.751 g·cm^{-3}, $R1$ = 0.0346 (refined on F^2) for 4960 data ($I > 2\sigma(I)$) and 332 parameters. **5**·BF_4: $C_{26}H_{26}IrNO_3BF_4P$, fw = 710.49, monoclinic, space group $C2/c$, a = 33.60(1) Å, b = 10.959(2) Å, c = 15.568(5) Å, β = 112.406(8)°, V = 5298(2) Å^3, Z = 8, d_{calcd} = 1.781 g·cm^{-3}, $R1$ = 0.0633 (refined on F^2) for 4549 data ($I > 2\sigma(I)$) and 334 parameters. **6**·BF_4·CH_2Cl_2: $C_{26}H_{28}NO_2BF_4Cl_2PIr$, fw = 767.42, triclinic, space group P-1, a = 9.9562(9) Å, b = 11.5147(7) Å, c = 12.548(1) Å, α = 91.706(5)°, β = 103.789(3)°, γ = 91.982(5)°, V = 1395.2(2) Å^3, Z = 2, d_{calcd} = 1.827 g·cm^{-3}, $R1$ = 0.0494 (refined on F^2) for 5644 data ($I > 2\sigma(I)$) and 368 parameters. CCDC 296203–296205. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b601143h

¶ The isolated yield of **6**·BF_4 was variable and dependent on the solvent and crystallization condition. A better yield was obtained by the reaction in and slow crystallization from THF.

1 J. Tsuji, *Palladium Reagents and Catalysts: New Perspectives for the 21st Century*, Wiley, New York, 2004; J. Tsuji, *Transition Metal Reagents and Catalysts*, Wiley, New York, 2000; J. A. Davis, in *Comprehensive Organometallic Chemistry II*, ed. E. W. Abel, F. G. A. Stone and G. Wilkinson, Pergamon Press, Oxford, 1995, Vol. 9, p. 291; S. A. Godleski, in *Comprehensive Organic Synthesis*, ed. B. M. Trost and I. Fleming, Pergamon, New York, 1991, Vol. 3, p. 585; B. M. Trost and M. L. Crawley, *Chem. Rev.*, 2003, **103**, 2921.

2 (*a*) F. Ozawa, H. Okamoto, S. Kawagishi, S. Yamamoto, T. Minami and M. Yoshifuji, *J. Am. Chem. Soc.*, 2002, **124**, 10968; (*b*) F. Ozawa, T. Ishiyama, S. Yamamoto, S. Kawaguchi, H. Murakami and M. Yoshifuji, *Organometallics*, 2004, **23**, 1698; (*c*) H. Saburi, S. Tanaka and M. Kitamura, *Angew. Chem., Int. Ed.*, 2005, **44**, 1730; (*d*) C. García-Yebra, J. P. Janssen, F. Rominger and G. Helmchen, *Organometallics*, 2004, **23**, 545; (*e*) R. Takeuchi and M. Kashio, *J. Am. Chem. Soc.*, 1998, **120**, 8647. See also references cited therein.

3 (*a*) S. Tanaka and M. Akita, *Angew. Chem., Int. Ed.*, 2001, **40**, 2865; (*b*) S. Tanaka, C. Dubs, A. Inagaki and M. Akita, *Organometallics*, 2004, **23**, 317; (*c*) C. Dubs, A. Inagaki and M. Akita, *Chem. Commun.*, 2004, 2760; (*d*) S. Tanaka, C. Dubs, A. Inagaki and M. Akita, *Organometallics*, 2005, **24**, 163; (*e*) C. Dubs, T. Yamamoto, A. Inagaki and M. Akita, *Organometallics*, 2006, **25**, 1344; (*f*) C. Dubs, T. Yamamoto, A. Inagaki and M. Akita, *Organometallics*, 2006, **25**, 1359.

4 PN complexes: P. Braunstein, B. T. Heaton, C. Jacob, L. Manzi and X. Moise, *Dalton Trans.*, 2003, 1396; B. Åkermark, B. Krakenberger, S. Hansson and A. Vitagliano, *Organometallics*, 1987, **6**, 620.

5 Complex **2**·BF_4 was prepared by repeated carbonylation (1 atm)[3f] of [(PN)Ir(η^4-cod)]BF_4, which was obtained by treatment of (μ-Cl)$_2${Ir(η^4-cod)}$_2$ with the PN ligand[4] in the presence of $AgBF_4$.

6 In a previous paper,[3f] we reported (1) formation of a dinuclear allyloxycarbonyl species analogous to **4a** (but incorrectly assigned as the η^1-species because of lack of crystallographic structural information) and (2) allylation reaction of **7** with **1** catalyzed by heterodinuclear complexes such as [(OC)$_2$Ir(μ-PNNP)Pd(η^3-allyl)]$^+$ (PNNP = 3,5-bis(diphenylphosphinomethyl)pyrazolato). But the mechanism of the activation of **1** could not be clarified because of (1) the dinuclear system being too complicated to be studied in detail and (2) the presence of stereoisomers (*e.g.* four isomers for (allyl–OOC)(OC)Ir(μ-PNNP)Pd(η^3-allyl) corresponding to **4a**). Meanwhile the present result apparently supports the mononuclear mechanism at Ir or at Pd discussed in ref. 3f but the dinuclear mechanism cannot be always ruled out on the basis of different reaction features (*e.g.* effect of CO). Further study is needed to clarify the mechanism of the dinuclear system.

7 An example of an η^1:η^2-allyloxy carbonyl complex: R. J. Madhushaw, S. R. Cheruku, K. Narkunan, G.-H. Lee, S.-M. Peng and R.-S. Liu, *Organometallics*, 1999, **18**, 748.

8 A related five coordinate (η^2-olefin)iridium complex with the PN ligand, [(μ-η^2:η^2-cod){Ir(PN)(CO)$_2$}$_2$](BF$_4$)$_2$, was characterized by X-ray crystallography (see supporting information of ref. 3*e* (complex **6**)).