Pergamon

Tetrahedron Letters, Vol. 38, No. 46, pp. 8025-8026, 1997

0040-4039/97 $17.00 + 0.00

PII: S0040-4039(97)10220-9

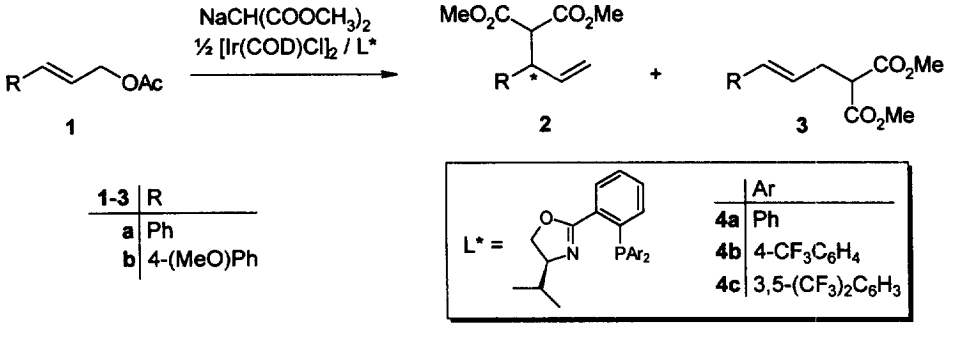
First Enantioselective Alkylations of Monosubstituted Allylic Acetates Catalyzed by Chiral Iridium Complexes

Jörg P. Janssen and Günter Helmchen*

Institut für Organische Chemie der Universität, Im Neuenheimer Feld 270, D-69120 Heidelberg, Germany

Abstract: Monoaryl allylic acetates were alkylated with sodium dimethylmalonate in the presence of iridium complexes of chiral phosphinooxazolines as catalysts to give branched products regioselectively in excellent yields with up to 95 % ee. © 1997 Elsevier Science Ltd.

Currently, asymmetric allylic substitutions are being intensely studied. One variant of great potential for organic synthesis is the reaction with monosubstituted allylic derivatives **1** with regioselectivity in favor of the branched, chiral products **2** (cf. Scheme 1). However, linear substitution products **3** are formed with typical Pd based catalysts, except in the special cases R = CH_3[1a], R = CH_2O^-[1b] and (MOP)Pd catalyst for R = aryl[1c]. In contrast, Mo and W catalysts[2] generally favor branched products. Very recently it was discovered that this is also true for alkylations with a catalyst formed from $[Ir(COD)Cl]_2$ and $P(OPh)_3$[3]. We are now able to report the first asymmetric allylic alkylations with Ir catalysts.



Scheme 1

Allylic acetates were alkylated with dimethyl malonate using a modified published procedure worked out for achiral Ir catalysts[3]. With 4 mol % of the catalysts $[Ir(COD)Cl]_2$ + **4**, aryl-substituted substrates furnished branched products **2a,b** in good yields with > 90 % enantiomeric excess (Table 1). With ligand **4a** the reaction was relatively slow and non-selective. Electron withdrawing substituents (**4b**) are beneficial as was already reported for the achiral catalysts. Steric effects are also important; this is demonstrated by the relatively unsatisfactory performance of ligand **4c**. The results with ligand **4b** indicate that Ir catalysts possess great potential for asymmetric allylic substitutions. We are currently extending this work in several directions.

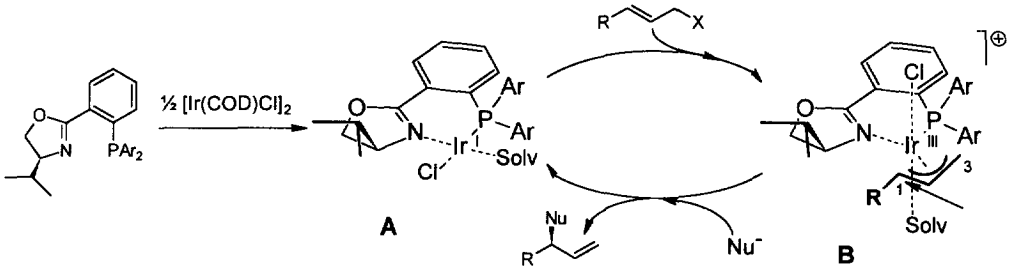
Table 1. Enantioselective Allylic Alkylations of 1-Substituted Allylic Acetates.[a]

Entry	Substrate	Ligand	Yield [%]	Ratio of **2**:**3**	% ee of **2**[b]
1	**1a**	**4a**	61	92:8	30 (*R*)
2	**1a**	**4b**	99	95:5	**91** (*R*)
3	**1a**	**4c**	95	89:11	84 (*R*)[c]
4	**1b**	**4a**	89	99:1	72 (*R*)
5	**1b**	**4b**	98	99:1	**95** (*R*)
6	**1b**	**4c**	71	93:7	62 (*R*)[c]

[a] General procedure: A solution of 2.0 mmol of **1**, 0.08 mmol of **4** and 26.9 mg (0.04 mmol) of $[Ir(COD)Cl]_2$ in 1.0 ml of abs. THF was added to 6 ml of a 1.0 M solution of sodium dimethylmalonate in abs. THF. After stirring for 24 h under nitrogen at reflux the reaction mixture was diluted with ether, extracted with water, dried and concentrated *in vacuo*. Flash chromatography (silica gel, hexane/ethyl acetate 9:1) gave a mixture of **2** and **3**.

[b] The ee of the products was determined by HPLC using a 25 cm DAICEL CHIRACEL® OJ column with 5 cm precolumn [**2a**: hexane/*i*-PrOH 93:7, $t_R(S) = 42$ min, $t_R(R) = 48$ min; **2b**: hexane/*i*-PrOH 95:5, $t_R(S) = 73$ min, $t_R(R) = 79$ min]. Absolute configurations were determined by comparison with published data[2-4].

[c] Reaction time: two days.



Scheme 2

A tentative rationalization of our results is given in Scheme 2. Key intermediate is a π-allyl-Ir(III) complex **B** formed from the Ir(I) complex **A** by oxidative addition. A variety of similar π-allyl-Ir(III) complexes derived from Vaska's complex were structurally characterized; they typically display octahedral coordination with co-planar arrangement of the planes IrC-1C-3, concerning the allyl moiety, and IrPP (or IrNN), concerning donor centers of additional ligands[5]. In complex **B**, we assume the substituent R to be oriented away from the large aryl groups at phosphorus. Attack of the nucleophile at the allylic carbon *trans* to phosphorus is expected to be preferred, as found for (phosphino-oxazoline)Pd complexes[6]. The superior results with the better electron donating methoxy-substituted substrate **1b** suggests that regioselectivity is due to charge control.

Acknowledgements. This work was by supported by the Deutsche Forschungsgemeinschaft (SFB 247) and the Fonds der Chemischen Industrie. We thank Degussa AG for iridium salts. The excellent technical assistance of B. Nowak is gratefully acknowledged.

REFERENCES

1. (a) T. Hayashi, K. Kishi, A. Yamamoto, Y. Ito, *Tetrahedron Lett.* **1990**, 1743; (b) B.M. Trost, R.C. Bunt, *Angew. Chem. Int. Ed. Engl.* **1996** , *35*, 99-102; (c) T. Hayashi, M. Kawatsura, Y. Uozumi, *J. Chem. Soc., Chem. Commun.* **1997**, 561-562.
2. B.M. Trost, G.B. Tometzki, M.-H. Hung, *J. Am. Chem. Soc.* **1987**, *109*, 2176 and literature cited; G. Lloyd-Jones, A. Pfaltz, *Angew. Chem. Int. Ed. Engl.* **1995**, 34, 462-464; *Z. Naturforsch.* **1995**, *50b*, 361-367.
3. R. Takeuchi, M. Kashio, *Angew. Chem. Int. Ed. Engl.* **1997**, 36, 263-265.
4. J.W. Faller, C. Lambert, M. R. Mazzieri, *J. Organomet. Chem.* **1990**, *383*, 161-177.
5. J.A. Kaduk, A.T. Poulos, J.A. Ibers, *J. Organomet. Chem.* **1977**, *127*, 245-360; R.H. Hsu, J.-T. Chen, G.-H. Lee, Y. Wang, *Organometallics* **1997**, *16*, 1159-1166.
6. J. Sprinz, M. Kiefer, G. Helmchen, M. Reggelin, G. Huttner, O. Walter, L. Zsolnai, *Tetrahedron Lett.* **1994**, 1523-1526.

(*Received in Germany* 17 *September* 1997; *accepted* 18 *September* 1997)