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Stereoselective Addition of Alcohol to Alkyne Catalyzed by Dicationic Platinum and Palladium Complexes

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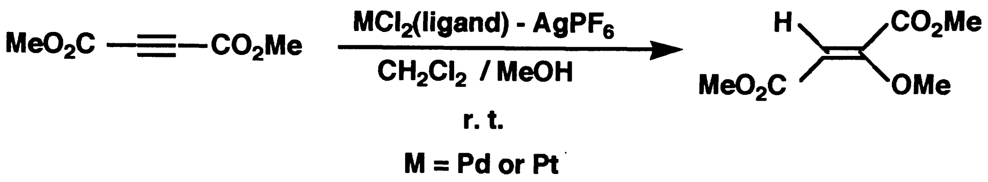
In the presence of the dicationic catalysts derived from $PtCl_2$(ligand) or $PdCl_2$(ligand) (ligand = $2PPh_3$, diphosphine) and excess $AgPF_6$ addition of MeOH to dimethyl acetylenedicarboxylate smoothly proceeded under mild conditions to give dimethyl methoxyfumarate selectively. The dicationic platinum catalysts were more catalytically active for the addition reaction than the corresponding palladium catalysts.

Nucleophilic addition of alcohol, water, amine etc., to acetylenic compounds affords a useful method for functionalization of a C-C triple bond.[1)] It has been reported that intramolecular addition of NH, OH, or COOH to an acetylenic moiety leading to heterocyclic compounds is catalyzed by Pd(II) complexes such as $PdCl_2$ or $Pd(OAc)_2$, but the intermolecular reaction does not proceed by the same catalysts.[2)] Parkins *et al.* reported that a doubly charged cationic palladium complex, $[Pd(PMe_2Ph)_2(solvent)_2]^{2+}$, catalyzes addition of water or MeOH to dimethyl acetylenedicarboxylate (DMAD) at room temperature but the corresponding platinum complex does not, due to the high stability of the Pt-C bond in the intermediate, a σ-vinyl platinum complex.[3)] We have found that both Pt(II) and Pd(II) dicationic complexes carrying PPh_3 or diphosphine ligands can promote facile stereoselective catalytic addition of alcohol to internal alkyne (eq1).



(eq 1)

Reaction of DMAD (5.0 mmol) with MeOH (1.0 mL, 25 mmol) in the presence of a catalytic amount of the platinum dicationic species (1 mol%),[4)] prepared *in situ* from $PtCl_2$(diphos) (0.05 mmol) and $AgPF_6$ (0.15 mmol), in CH_2Cl_2 (1.0 mL) at room temperature for 18 h gave dimethyl methoxyfumarate quantitatively. Representative results using several dicationic platinum and palladium complexes are summarized in Table 1. The corresponding neutral complex, $PtCl_2$(diphos) or $PdCl_2$(diphos), did not show any catalytic activity for the addition reaction under similar conditions. The reaction proceeded stereoselectively to give only the (*Z*)-isomer.[5)] All dicationic platinum catalysts which were examined showed high catalytic activity toward the addition reaction.

Catalytic activity of the palladium complex having a potentially tridentate ligand, POP (=$Ph_2P(CH_2)_2O(CH_2)_2PPh_2$), decreased extremely compared with that of the complex having diphos or dppt

Table 1. Addition of MeOH to DMAD catalyzed by MCl_2(ligand)-$AgPF_6$ system a)

Run	M	Ligand	Yield % b)
1	Pt	diphos	100
2		dppt	100
3		POP	100
4		$2PPh_3$	100
5	Pd	diphos	100
6		dppt	100
7		POP	8 c)
8		$2PPh_3$	89 c)

a) DMAD (5.0 mmol) was treated with MCl_2(ligand) (0.05 mmol) and $AgPF_6$ (0.15 mmol) in CH_2Cl_2 (1.0 mL) and MeOH (1.0 mL) at room temperature for 18 h.
b) GC yields.
c) DMAD was recovered.

(=$Ph_2P(CH_2)_5PPh_2$) (runs 7 vs 5, 6). σ-Vinyl complexes, [(POP)M{η^1-(*E*)-MeO_2CC=C(OMe)CO_2Me}] [PF_6] (M = Pd or Pt)6) where POP acted as a tridentate ligand, were obtained in high yields from the stoichiometric reaction, whereas for simple bidentate diphosphine, the corresponding σ-vinyl complexes could not be isolated. The isolated cationic σ-vinyl palladium complex did not show catalytic activity for the addition reaction under mild conditions. Thus, it is understood that the low catalytic activity shown by the Pd(II)-POP system is due to the formation of the stable σ-vinyl palladium complex. On the contrary, the analogous cationic σ-vinyl platinum complex itself also showed high catalytic activity for the reaction. The different reactivity is probably due to the differece of the softness between Pd(II) and Pt(II).

The dicationic platinum complex, prepared from $PtCl_2$(diphos) and $AgPF_6$, also catalyzed addition of MeOH to unactivated acetylene, 6-dodecyne or diphenylacetylene under mild conditions (room temperature, 18 h) to give 6-dodecanone (turnover number 10) or phenylacetophenone (turnover number 8), hydrolyzed compounds of the products, but the corresponding palladium complexes were inactive. Catalytic activity of these dicationic platinum complexes for the addition reaction was higher than that of the palladium complexes and the diphosphines were better ligands than monodentate phosphine. Further investigation on the mechanism, scope, and limitation for the present reaction is in progress.7)

References

1) R. C. Larock and W. W. Leong, "COMPREHENSIVE ORGANIC SYNTHESIS," ed by B. M. Trost and I. Fleming, Pergamon Press, Oxford (1991), Vol. 4, p.269.
2) K. Utimoto, *J. Syn. Org. Chem. Jpn.*, **45**, 112 (1987) and references cited therein.
3) A. Avshu, R. D. O'Sullivan, and A. W. Parkins, *J. Chem. Soc., Dalton Trans.*, **1983**, 1619.
4) The resulting AgCl did not affect the addition reaction. The same result was obtained when AgCl had been removed by firtration from the reaction mixture.
5) Addition of alcohol to alkynic acid ester catalyzed by trialkylphosphine gives vinyl ether with the opposite configuration, see J. Inanaga, Y. Baba, and T. Hanamoto, *Chem. Lett.*, **1993**, 241.
6) Preparation and propeties of the σ-vinyl complexes will be reported separately.
7) Recently addition of alcohol to alkyne catalyzed by a cuboidal $PdMo_3S_4$ cluster has been reported, see T. Wakabayashi, Y. Ishii, H. Nanikawa, T. Murata, Y. Mizobe, and M. Hidai, The 67th Annual Meeting of the Chemical Society of Japan, March 1994, 1H239; T. Murata, Y. Mizobe, H. Gao, Y. Ishii, T.Wakabayashi, F. Nakano, T. Tanase, S. Yano, M. Hidai, I. Echizen, H. Nanikawa, and S. Motomura, *J. Am. Chem. Soc.*, **116**, 3389 (1994).

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