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HIGHLY SELECTIVE COTRIMERIZATION OF OLEFINS CATALYZED BY PHOSPHINATED POLYSTYRENE RESIN-ANCHORED $PdCl_2$-$AgBF_4$

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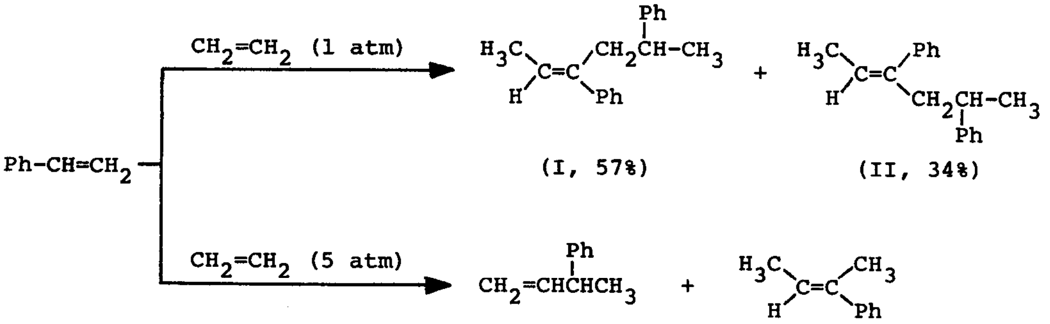
Codimerization of olefins with transition metal complexes has been extensively studied. Little is known, however, concerning cotrimerization of olefins.[1] In the course of the study on heterogenized transition metal catalysts using organic polymer,[2] we found that $PdCl_2$ anchored to polystyrene resin catalyzed selectively cotrimerization of styrenes and ethylene or propylene and had a high reactivity for styrene, compared with homogeneous Pd complexes.[3] This is the first example of cotrimerization of monoolefins as far as we know.

The polymer-Pd complex (A) was prepared by the reaction of polymeric diphenylbenzylphosphine (no cross-linking) with $PdCl_2$.[2]
Found: C, 53.88; H, 4.36; Cl, 11.76; P, 6.55%

In the absence of additive $AgBF_4$, the complex (A) showed no catalytic activity. A mixture of styrene (6.4 g, 62 mmol), the polymer complex (A) (300 mg, 0.64 mg-atom of Pd), $AgBF_4$ (142 mg, 0.64 mmol) and chloroform (16 ml) was stirred under 1 atm of ethylene at 50°C for 4.5 hr. The complex could be easily separated from the resulting mixture. The filtrate was gas-chromatographed. Styrene was completely consumed and gave selectively cotrimers (I, II; 91%). Distillation gave 5.7 g of the cotrimers, bp 113°C(1 mmHg).[4] On the other hand, under 5 atm of ethylene, 1:1 adducts of styrene and ethylene (III, IV) gave the almost quantitative yield.[4]



(I, 57%)

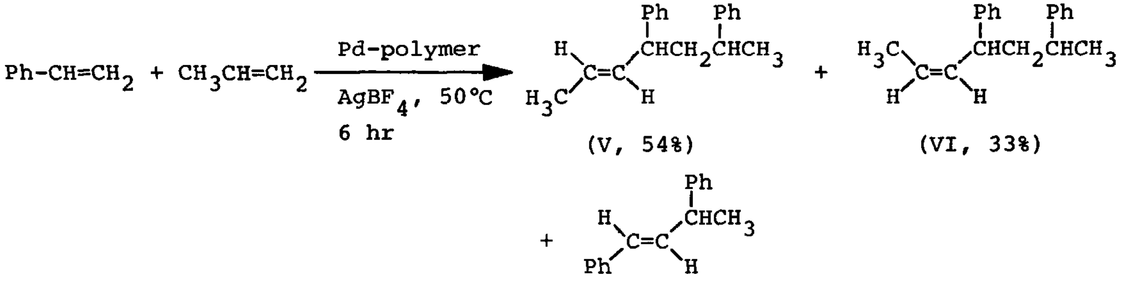
(II, 34%)

(III, 95%)

(IV, 4%)

All above oligomers contain internal phenyl groups. It is interesting that oligomers of ethylene could not be detected under the reaction conditions. The complex filtered off showed the catalytic activity without adding $AgBF_4$ anew. Other compounds were tried as additives. $AgPF_6$ and $AgClO_4$ were active but AgOAc, $AgNO_3$, AgCl, $BF_3 \cdot OEt_2$, and $AlCl_3$ showed no activity. The fact indicates that the function of the additive may be removal of a chlorine ligand to form a cationic Pd complex.[5]

In the reaction of styrene and propylene (1 atm), a similarly selective cotrimerization could be also observed.[4] It is noteworthy that the cotrimers containing branched methyl group could not be detected.



(V, 54%)

(VI, 33%)

(VII, 5%)

This catalyst system also induced the homodimerization of styrene, ethylene or propylene. Styrene gave VII (90% after 1 hr). The dimerization rate of ethylene or propylene, however, was slow under an atmospheric pressure.

In addition, the corresponding homogeneous system, $PdCl_2(PPh_3)_2$-$AgBF_4$ catalyzed no dimerization.

References and Notes

1. a) P.Heimbach and G.Wielke, Justus Liebigs Ann. Chem., <u>727</u>, 183 (1969). b) P.Heimbach, H.Selbeck, and E.Troxler, Angew. Chem., Int. Ed., <u>10</u>, 659 (1971).
2. a) K.Kaneda, M.Terasawa, T.Imanaka, and S.Teranishi, Chem. Lett., 1005 (1975). b) K.Kaneda, T.Uchiyama, M.Terasawa, T.Imanaka, and S.Teranishi, ibid, 449 (1976).
3. M.G.Barlow, M.J.Bryant, R.M.H.Haszeldine, and A.G.Mackie, J. Organomet. Chem., <u>21</u>, 215 (1970).
4. All these new compounds gave satisfactory elemental analysis and spectral (IR, NMR, and Mass) data.
5. Recently, it has been reported that Pt, Ni cationic complexes catalyzed dimerization of olefins. a) A.Renzi, A.Panunzi, and A.Vitagliano, Chem. Comm., 47 (1976). b) T.Koike, K.Kawakami, K.Maruya, T.Mizoroki, and A.Ozaki, Chem. Lett., 551 (1977).