Improved Catalytic Activity of Cyclopentadienylcobalt in the Preparation of Pyridines from Acetylenes and Nitriles

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(Received April 22, 1985)

Synopsis.   The catalytic activity of cyclopentadienyl-cobalt increases greatly upon introducing a methoxy-carbonyl group into the cyclopentadienyl ring, and by carring out the reaction with a vigorous exclusion of oxygen. Among the precursors we have examined, the most active one was [Co(Cp^z)(cot)] (Cp^z=methoxycarbonyl-substituted cyclopentadienyl; cot=cyclooctatetraene) which can generate the active species at 100 °C.

In 1973, we reported that the cyclopentadienyl-cobalt (CpCo) species catalyzed cyclocotrimerization of alkynes with the C≡N triple bond of nitriles to give substituted pyridines (Eq. 1).[1]

$$2R^1C\equiv CH + R^2C\equiv N \longrightarrow$$

R^1=H, alkyl, aryl: R^2=alkyl, aryl   (1)
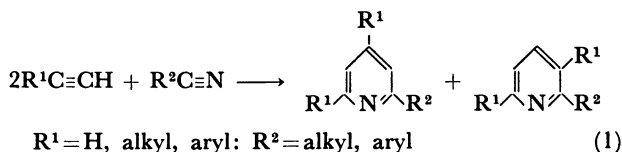
The "CpCo" species can be generated from several precursors such as CpCo(diene),[2] Cp$_2$Co,[3] and CpCo(CO)$_2$.[4] Entry into the catalytic cycle is also possible by starting from cobaltacyclopentadiene complexes.[1] The mechanism of Reaction 1 (involving the metallacycle intermediate) has been fairly well understood.[5]

The catalytic activity of cobalt, in terms of pyridine moles produced per g-atom Co, has been reported to be 190,[1] 200,[4] and 400.[6] Recently, Bönnemann and coworkers have used η^6-borinato in place of the Cp ligand, thereby improving the catalytic activity to ca. 2100 for the cooligomerization of HC≡CH with CH$_2$=CHCN.[7]

We have found that the catalytic activity of cobalt with the easily available η^5-Cp ligand can be greatly enhanced by (1) the exclusion of oxygen, (2) introduction of a CO$_2$Me group to the Cp ligand, and (3) lowering the reaction temperature. The test reaction that we employed was the cotrimerization of methylacetylene with acetonitrile (R^1=R^2=Me in Reaction 1). In order to check the maximum activity of the catalyst, we carried out the reaction in the presence of a large amount of the reactant so that the conversions would not exceed 80%. When all three of the above conditions are satisfied, the catalytic activity reaches as high as ca. 4000 moles of trimethylpyridine per g-atom Co.

The effect of oxygen on the reaction is shown in Fig. 1. When the reaction mixture is carefully degassed by use of a vacuum line, even the conventional CpCo(1,5-cod) exhibits high catalytic activity (ca. 2200 at 130 °C). However, its activity drops sharply when an increasing amount of oxygen is added to the system. A (η^5-C$_5$H$_4$CO$_2$Me)Co (abbreviated as Cp^{z}Co) analogue has a higher
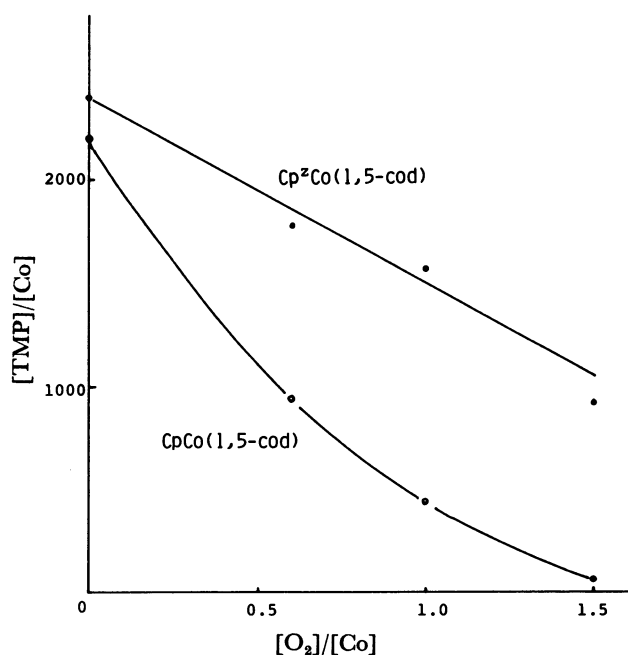

Fig. 1. Higher resistance of the Cp^{z}Co system towards deactivation by added oxygen.
[TMP]: amount of obtained trimethylpyridine, [Co]: amount of the catalyst used.
Reaction condition: 130 °C, 16 h.

resistance toward oxygen, and still maintains a reasonable catalytic activity (950) even in the presence of an excess amount of oxygen.

The other advantage of using Cp^{z}Co(1,5-cod) is that the reaction is much faster than for the case of the parent CpCo(1,5-cod), as evidenced by the time-conversion curves (A and B) in Fig. 2. A part of this phenomena must arise from an easier release of the 1,5-cod ligand from Cp^{z}Co(1,5-cod) than from CpCo(1,5-cod), i.e. a faster generation of the active species in the former system. We have measured the reaction rate for the exchange of the complexed and free diene: Cp^{z}Co(1,5-cod) was found to release the diene 10-times faster than CpCo(1,5-cod) in an acetonitrile solution.

When the reaction temperature was lowered from 130 to 100 °C, the catalytic activity by use of Cp^{z}Co(1,5-cod) markedly increased while the reaction rate decreased (curve C). The reaction rate at this lower temperature can be improved by employing cyclooctatetraene (cot), an easier leaving ligand, instead of 1,5-cod (curve D). In contrast, the catalytic activity of CpCo saturates at around 2000, even when CpCo(cot) is used as the precursor and the reaction is carried out at 100 °C (curve E). The difference observed in curves D and E implies that the Cp^{z}Co system either has a higher reactivity regarding
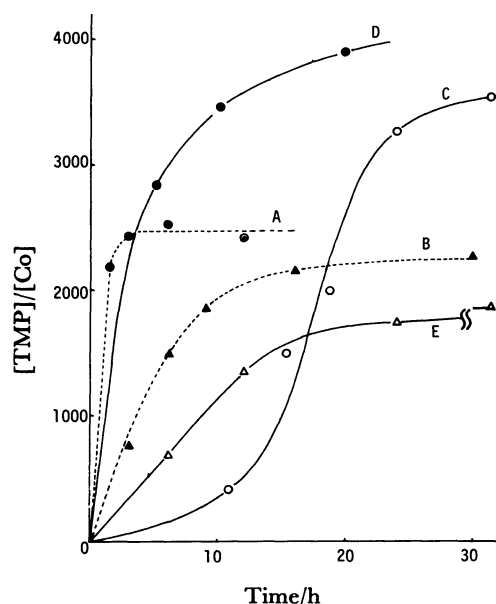
Fig. 2. Comparison of catalytic activity of CpCo and Cp²Co systems.
[TMP]: amount of obtained trimethylpyridine, [Co]: amount of the catalyst used.
A: Cp Co(1,5-cod) 130 °C, B: CpCo(1,5-cod) 130 °C, C: Cp Co(1,5-cod) 100 °C, D: Cp²Co(cot) 100 °C, E: CpCo(cot) 100 °C.

cooligomerization or a higher resistance to de-activation than the parent CpCo system.

Experimental

Column chromatography was carried out using Sumitomo alumina KCG-30 under a nitogen atmosphere. GLC analyses were performed at 110 °C on a Shimadzu GC-8A equipped with a 0.3×300-cm glass column packed with 15% PEG-20M on Uniport-HP. Tetradecane was used as an inner reference to determine the amount of each product.

(η⁵-Methoxycarbonylcyclopentadienyl)(η⁴-1,5-cyclooctadiene)-cobalt(Cp′Co(1,5-cod)): Sodium methoxycarbonylcyclopenta-dienide was prepared, according to a method from the literature,[8] (from sodium cyclopentadienide (7 mmol in 4 ml THF) and dimethyl carbonate (1 ml) by heating at reflux temperature for 1 h). Under a nitrogen atmosphere and at room temperature, the cyclopentadienide solution was transferred all at once into a flask (100 ml) containing a benzene solution (20 ml) of chlorotris(triphenylphos-phine)cobalt (4.4 g, 5 mmol) and 1,5-cyclooctadiene (2 ml). The flask was stoppered and vigorously shaken. A dark-red color immediately developed. The reaction mixture was allowed to stand overnight and was then filtered through a short column of alumina (25×25 mm) by the aid of additional benzene (10 ml). The filtrate was concentrated to ca. 10 ml and after the addition of hexane (20 ml), it was kept at room temperature overnight. Colorless crystals were formed and discarded, and the solution was chromatographed on alumina (deactivated by addition of 5% of H₂O, 25×200 mm). The column was washed with hexane and then with a 4/1 mixture of hexane/benzene. An orange-red band was eluted by a 1/1 mixture of hexane/benzene. The eluate was concentrated almost to dryness. The residue was dissolved in hexane (5 ml) and

was kept in a refrigerator overnight to yield orange-brown crystals of the title compound. They were recrystallized from hexane; yield: 0.78 g (54%); mp 86—87 °C.

C₁₅H₁₉O₂Co   Calcd   C 62.07   H 6.60
(290.25)   Found   62.13   6.59

IR (Nujil): ν=1720, 1700 cm⁻¹ (ester). ¹H-NMR (CDCl₃/TMSint): δ=1.6, 2.4, 3.6 (C₈H₁₂); 3.95 (CH₃); 4.40, 5.03 (C₅H₄) ppm.

(η⁵-Methoxycarbonylcyclopentadienyl)(η⁴-cyclooctatetraene)-cobalt(Cp′Co(cot)): This compound can be prepared in the same manner as above, using cyclooctatetraene (1 ml) in place of cyclooctadiene. Red-brown crystals; yield: 0.46 g (32%); mp 67—68 °C.

C₁₅H₁₅O₂Co   Calcd   C 62.95   H 5.28
(286.22)   Found   62.84   5.25

IR (Nujol): ν=1720, 1700 cm⁻¹ (ester). ¹H-NMR (CD₂Cl₂): δ=3.64 (=CH-, coordinated); 3.90 (CH₃); 4.55, 5.11 (C₅H₄); 5.56 (=CH-, uncoordinated).

Cotrimerization of Methylacetylene with Acetonitrile: Crystals of Cp′Co(cot) (28.6 mg) were dissolved in benzene (40 ml) under argon (this solution can be stored in a refrigerator for several months without any decomposition). A portion of this solution (1 ml) was transferred by syringe to an ampule. The ampule was connected to a vacuum line. The solution was degassed by three freeze-pump-thaw cycles. In another ampule containing benzene (1.5 ml) and acetonitrile (2.5 ml), methylacetylene (ca. 1.3 g) was condensed by bubbling through the gas at 0 °C. The second ampule was attached to a vacuum line and the mixture was degassed by three cycles of freeze-pump-thaw. Finally it was distilled into the first ampule containing the cobalt complex. The ampule was sealed and heated to 100 °C for 20 h. Unreacted reactants and the solvent were evaporated under a reduced pressure (25 mmHg (1 mmHg=133.322 Pa)) and the oily residue (1.43 g) was subjected to an GLC analysis. The products were 1,3,5-trimethylbenzene (0.30 mmol), 1,2,4-trimethylbenzene (1.69 mmol), 2,4,6-trimethyl-pyridine (5.12 mmol), and 2,3,6-trimethylpyridine (4.65 mmol). Trimethylpyridine was isolated upon extracting it from an ethereal solution of the residue using an 18% HCl aquous solution. After neutralization with KOH, the pyridine was again extracted with ether. Drying of the solution with Na₂SO₄ and evaporation of the ether under a reduced pressure gave a colorless oil (1.04 g) which was a 51/46 mixture of 2,4,6- and 2,3,6-trimethylpyridine. Other runs can be performed similarly.

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