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# Effect of Diene Ligands in the Rhodium-Catalyzed Polymerization of Phenylacetylene

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ABSTRACT: The effect of various diene ligands, namely 1,5-cyclooctadiene (cod), 2,5-norbornadiene (nbd), *endo*-dicyclopentadiene (dcp), tetrafluorobenzobarrelene (tfb), and tetrachlorobenzobarrelene (tcb), was examined in the Rh-catalyzed polymerization of phenylacetylene, aiming at the development of novel active catalysts. The new tfb catalyst $[(tfb)RhCl]_2$ **4** and tcb catalyst $[(tcb)RhCl]_2$ **5** are more active than the corresponding conventional cod catalyst **1** and nbd catalyst **2**. For example, catalyst **4** (polymer yield = 92−100%) was more active than **2** (polymer yield = 69−81%) when employed in polar solvents (THF, $C_2H_5OH$, $CH_3CN$, and DMF). This is attributable to the high $\pi$-acidity of tfb compared to other ligands, as evidenced by its significantly low LUMO energy (0.21 eV), and a considerably large upfield shift of olefinic protons in **4** ($\Delta\delta = 3.10$ ppm). Consequently, a strong back-donation from filled 4d orbitals of Rh to LUMO of tfb renders the Rh metal highly electron-deficient in catalyst **4,** facilitating the coordination of monomer to Rh metal and alkyne insertion, leading to higher catalytic activity of **4** than that of **2**.

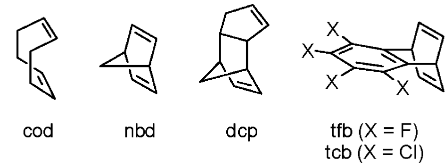
## Introduction

Design and development of novel catalyst systems for the polymerization of substituted acetylenes have been an active area of research in the last few years, and various transition metal catalysts from groups 4−10 have been developed for this purpose.[1−15] Research in this direction is motivated by the potential applications of formed polymers in various fields such as photonics, nonlinear optics, electrical conductors, gas separation membranes, stimuli-responsive materials, liquid crystals, and organic light-emitting diodes.[16−24] Rh catalysts efficiently polymerize monosubstituted acetylenes[15] such as phenylacetylene and its ring-substituted derivatives,[25−33] propiolic esters,[34−39] and *N*-propargylamides.[40−44] The low oxophilicity of Rh catalysts allows the polymerization of monomers carrying polar functional groups,[45−50] and the polymerization can also be carried out in protic solvents such as alcohols,[27,28] amines,[29] and even in water[31] and ionic liquids[30] to selectively produce stereoregular polymers with cis−transoidal main chain structure.[25−27]

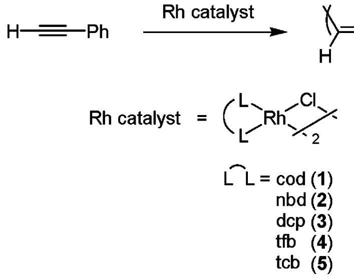
Many of the Rh catalysts for the polymerization of monosubstituted acetylenes contain cyclic diene ligands, and the most commonly used are 2,5-norbornadiene (nbd) and 1,5-cyclooctadiene (cod), which remain firmly bound to Rh metal, thus inhibiting the decomposition of propagating species.[15] Previous studies have revealed that Rh catalysts with a nbd ligand display higher activity than their cod counterparts and also afford higher-molecular-weight polymers.[25,26,29,32] A probable explanation for this finding is more facile coordination of acetylenic monomers to the nbd-based propagating species, leading to their higher activity.

In a search for more active Rh catalysts, we investigated *endo*-dicyclopentadiene (dcp), tetrafluorobenzobarrelene (tfb), and tetrachlorobenzobarrelene (tcb) as potential diene ligands for Rh catalysts in the polymerization of phenylacetylene, as shown in Chart 1 and Scheme 1. Both tfb and tcb ligands gave highly active Rh catalysts, $[(tfb)RhCl]_2$ (**4**) and $[(tcb)RhCl]_2$ (**5**), whose activity surpassed a conventional effective catalyst, $[(nbd)RhCl]_2$ (**2**).

**Chart 1. Structure of Diene Ligands.**



**Scheme 1. Polymerization of Phenylacetylene with Rh Catalysts 1−5.**



## Experimental Section

**Materials.** Phenylacetylene was purchased (Aldrich) and distilled over $CaH_2$ under reduced pressure before use. Solvents (Wako, Japan) employed for the synthesis of ligands and catalysts and for polymerization were purified before use by the standard procedures. Alkali metal amides and alkylating agents as cocatalysts and other reagents were commercially obtained and used without further purification. Catalysts **1** and **2** were synthesized according to the methods described in the literature.[51] Tetrafluorobenzobarrelene (tfb) and tetrachlorobenzobarrelene (tcb) were also synthesized by following the reported methods.[52,53] Rh catalysts **3**−**5** (**5**: new compound) were synthesized by modifying the reported procedures. The detailed procedures for their synthesis are described below.

***endo*-Dicyclopentadiene Rhodium(I) Chloride Dimer (3).** $RhCl_3{\cdot}3H_2O$ (263 mg, 1.0 mmol) was dissolved in a mixture of ethanol (15 mL) and water (3.0 mL), and *endo*-dicyclopentadiene (1.0 mL, excess) was added to the above solution. The reaction

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mixture was stirred for 30 min at room temperature and then refluxed for 3 h. The formed yellow precipitate was filtered and washed three times with methanol and purified by recrystallization from $CH_2Cl_2/CH_3OH$ to give **3** (49 mg, yield 18%) as brown solid. The $^1H$ and $^{13}C$ NMR spectral data agreed with the reported results.[54]

**Tetrafluorobenzobarrelene Rhodium(I) Chloride Dimer (4).** This compound was synthesized and purified by the same method as for **3** by using tetrafluorobenzobarrelene (452 mg, 2.0 mmol) instead of *endo*-dicyclopentadiene. Yield 84%. The $^1H$ and $^{13}C$ NMR spectral data agreed with the reported results.[55]

**Tetrachlorobenzobarrelene Rhodium(I) Chloride Dimer (5).** This compound was prepared and purified by a method similar to that of **4**. Yield 80%, mp 188.0−189.0 °C. IR (KBr): 3072, 3010, 2917, 1612, 1591, 1537, 1477, 1307, 1170, 1136, 970, 807, 771, 715. $^1H$ NMR (400 MHz, $CDCl_3$, 25 °C) $\delta$: 5.85 (brs, 2H, bridgehead CH), 3.81 (brs, 4H, ═CH). $^{13}C$ NMR (100 MHz, $CDCl_3$, 25 °C) $\delta$: 137.21 (Ar), 132.52 (Ar), 126.03 (Ar), 51.70 (d, $^1J_{Rh-C} = 10.7$ Hz, ═CH), 45.12 (d, $^2J_{Rh-C} = 3.3$ Hz, bridgehead CH). Anal. Calcd for $C_{24}H_{12}Cl_{10}Rh_2$: C, 33.49%; H, 1.41%; Cl, 41.19%. Found: C, 33.44%; H, 1.43%; Cl, 41.22%.

**Instruments.** The number- and weight-average molecular weights ($M_n$ and $M_w$, respectively) and polydispersity indices ($M_w/M_n$) of polymers were measured by GPC at 40 °C with a Jasco PU-980/RI-930 chromatograph; eluent THF, columns KF-805 (Shodex) × 3, molecular weight limit up to $4 \times 10^6$, flow rate 1 mL/min, calibrated with polystyrene standards. $^1H$ and $^{13}C$ NMR spectra were observed on a JEOL EX-400 spectrometer and IR spectra were recorded on a Shimadzu FTIR-8100 spectrophotometer. Elemental analyses were performed at the Microanalytical Center of Kyoto University. Melting points were determined by a Yanaco MP-50859 melting point apparatus.

**Polymerization.** All of the polymerizations were carried out under an Ar atmosphere in a Schlenk tube equipped with a three-way stopcock. A typical polymerization procedure is as follows: A toluene solution (2.0 mL) of phenylacetylene (2.5 mmol) was added to a toluene solution (3.0 mL) of $[(tfb)RhCl]_2$ (**4**) (10 $\mu$mol) with/without cocatalysts. Polymerization was carried out at 30 °C for a given time indicated in the footnotes of each table. The formed polymer was isolated by precipitation in a large amount of methanol, filtered with a glass filter, and dried under vacuum to constant weight.

## Results and Discussion

**Polymerization of Phenylacetylene with Catalysts 1−5.** Polymerization of phenylacetylene with catalysts **1**−**5** was carried out in toluene for 1 min in the presence of 1 equiv of $Et_3N$ to Rh atom at a monomer-to-rhodium ratio ($[M]_0/[Rh]$) of 250 (Table 1). Cod catalyst **1** gave poly(phenylacetylene) with a number-average molecular weight ($M_n$) of 22 000 in only 5% yield, while the nbd counterpart **2** displayed much higher activity to provide poly(phenylacetylene) in 69% yield ($M_n$ = 118 000) under the same conditions, in accordance with the reported results.[27−29] Catalyst **3**, which possesses an *endo*-dicyclopentadiene (dcp) ligand, showed even lower catalytic activity than the cod catalyst **1** and afforded polymer only in a trace amount.[56] On the other hand, both catalysts **4** and **5**, which have tetrafluorobenzobarrelene (tfb) and tetrachlorobenzobarrelene (tcb) ligands, respectively, polymerized phenylacetylene in quantitative yield into higher-molecular-weight polymers (**4**: $M_n$ = 281 000, **5**: $M_n$ = 227 000) than with the nbd catalyst **2**,[57] thus implicating higher activity of catalysts **4** and **5** than the well-known nbd catalyst **2**. To the best of our knowledge, this is the first example of any diene ligand exhibiting higher catalytic activity than the well-known nbd ligand in the Rh-catalyzed polymerization of phenylacetylene.

**Table 1. Polymerization of Phenylacetylene with Rh Catalysts 1−5**[a]

| | | polymer[b] | | |
|---|---|---|---|---|
| run | catalyst | yield (%) | $M_n$[c,d] | $M_w/M_n$[c] |
| 1 | 1 | 5 | 22 000 | 2.16 |
| 2 | 2 | 69 | 118 000 | 1.85 |
| 3 | 3 | trace | | |
| 4 | 4 | 100 | 281 000 | 1.70 |
| 5 | 5 | 100 | 227 000 | 1.79 |

[a] In toluene, 30 °C, 1 min; $[\text{phenylacetylene}]_0 = 0.50$ M, $[Rh] = 2.0$ mM, $[Et_3N]/[Rh] = 1.0$. [b] Methanol-insoluble product. [c] Determined by GPC (THF, PSt). [d] The theoretical $M_n$ of poly(phenylacetylene) is 25 000 assuming quantitative initiation efficiencies for all runs.

**Table 2. Effect of Solvents in the Polymerization of Phenylacetylene with $[(tfb)RhCl]_2$ and $[(nbd)RhCl]_2$**[a]

| | $[(tfb)RhCl]_2$ (**4**) | | | $[(nbd)RhCl]_2$ (**2**) | | |
|---|---|---|---|---|---|---|
| solvent | yield[b] (%) | $M_n$[c] | $M_w/M_n$[c] | yield[b] (%) | $M_n$[c,d] | $M_w/M_n$[c] |
| benzene | 16 | 37 000 | 1.93 | 0 | | |
| toluene | 31 | 58 000 | 1.88 | 0 | | |
| $CHCl_3$ | 25 | 49 000 | 2.27 | trace | | |
| $CH_2Cl_2$ | 21 | 54 000 | 2.34 | trace | | |
| $ClCH_2CH_2Cl$ | 19 | 41 000 | 2.64 | trace | | |
| THF | 100 | 236 000 | 2.12 | 69 | 68 000 | 3.36 |
| $C_2H_5OH$ | 100 | 165 000 | 2.21 | 81 | 73 000 | 2.43 |
| $CH_3CN$ | 100 | 113 000 | 3.03 | 75 | 102 000 | 3.53 |
| DMF | 92 | 92 000 | 2.58 | 70 | 65 000 | 2.89 |
| $(C_2H_5)_3N$ | 100 | 291 000 | 1.72 | 100 | 160 000 | 1.83 |

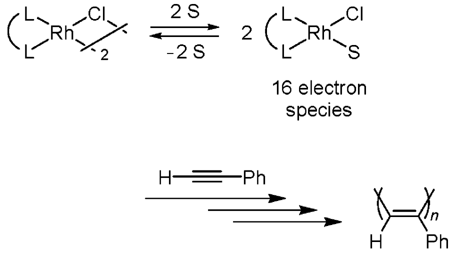
[a] At 30 °C, 24 h; $[\text{phenylacetylene}]_o = 0.50$ M, $[Rh] = 2.0$ mM. [b] Methanol-insoluble product. [c] Determined by GPC (THF, PSt). [d] The theoretical $M_n$ of poly(phenylacetylene) is 25 000 assuming quantitative initiation efficiencies for all runs.

The conventional Rh catalysts **1** and **2** are known to polymerize monosubstituted acetylenes in a stereospecific fashion to produce polymers with cis−transoidal main chain structure.[25−44] The $^1H$ NMR spectra of the polymers obtained with catalysts **4** and **5** displayed a sharp peak at 5.84 ppm due to the olefinic proton of the main chain. The cis contents, calculated from the integration ratio of olefinic protons to aromatic protons, were almost quantitative, manifesting a high level of stereoregularity in the polymerization catalyzed by **4** and **5**. This result also indicates that the change in the environment around Rh resulting from a change in the diene ligand does not influence the stereochemical outcome of this polymerization.

**Comparison of $[(tfb)RhCl]_2$ (4) and $[(nbd)RhCl]_2$ (2) Catalysts.** The features of highly active $[(tfb)RhCl]_2$ catalyst **4** were investigated in detail; at first, polymerization of phenylacetylene was carried out by using $[(tfb)RhCl]_2$ (**4**) and $[(nbd)RhCl]_2$ (**2**) in various solvents, whose results are listed in Table 2. In aromatic and chlorinated solvents such as benzene, toluene, $CHCl_3$, $CH_2Cl_2$, and $ClCH_2CH_2Cl$, catalyst **2** alone was ineffective even after 24 h polymerization. On the other hand, catalyst **4** was slightly active in these solvents to afford polymers with reasonable molecular weights ($M_n > 10^4$) in low yields (16−31%), presumably due to slow bridge cleavage of **4** in nonpolar solvents in the presence of phenylacetylene.

It is known that polar solvents efficiently induce the formation of active species from a catalyst precursor **2** to afford high-molecular-weight poly(phenylacetylene) in high yield;[27−29] e.g., polymerization proceeded homogeneously in THF to provide high-molecular-weight polymer ($M_n$ = 68 000) in 69% yield (Table 2). In the case of catalyst **4**, the polymerization system also remained homogeneous, and interestingly, polymer having much higher molecular weight ($M_n$ = 236 000) was quantitatively formed. When $C_2H_5OH$, $CH_3CN$, and DMF were used as polymerization solvents, polymer precipitated out during polymerization for both catalysts. In the case of catalyst **2**, the

**Scheme 2. Formation of 16-Electron Species from [(L−L)RhCl]$_2$ in Polar Solvents.**



(S = THF, CH$_3$CN, DMF, DMSO, Et$_3$N)

polymer yields were appreciable (70−81%) and the molecular weights were high ($M_n$ = 65 000−102 000). On the other hand, **4** exhibited improved catalytic performance to provide poly(phenylacetylene) having higher molecular weights ($M_n$ = 92 000−165 000) in better yields (92−100%), indicating that **4** is more active as a catalyst than **2**. The high activities displayed by both catalysts **2** and **4** in polar solvents is probably an outcome of bridge splitting induced by the coordination of the solvent to Rh to form 16-electron species, as shown in Scheme 2.

It is noted that poly(phenylacetylene) with high molecular weight ($M_n$ = 160 000) is quantitatively produced in triethylamine (Et$_3$N) (Table 2) with catalyst **2** in accordance with the reported results.[27−29] The result is well explained in terms of higher dissociating ability of Et$_3$N than THF, C$_2$H$_5$OH, CH$_3$CN, and DMF to form a 16-electron mononuclear complex [(nbd)RhCl(Et$_3$N)] from dinuclear complex [(nbd)RhCl]$_2$ (**2**).[29] Catalyst **4** in Et$_3$N also afforded in quantitative yield poly(phenylacetylene), whose molecular weight ($M_n$ = 291 000) was higher than that obtained with catalyst **2**, thus manifesting the superior catalytic performance of **4** over **2**. The structural resemblance of **4** with **2** suggests a same role for Et$_3$N in both cases, i.e., bridge cleavage of dinuclear [(diene)RhCl]$_2$ to form a 16-electron mononuclear complex [(diene)RhCl(Et$_3$N)], which acts as the precursor for the formation of active species (Scheme 2).[29]

In a previous study, our research group has found the rate enhancement of polymerization of phenylacetylene with catalyst **2** in the presence of strong alkylating agents.[58] Whereas polymerization hardly proceeded in toluene with catalyst **2** alone, addition of 1 equiv of either $n$-C$_4$H$_9$Li or (C$_2$H$_5$)$_3$Al to the Rh atom considerably accelerated the polymerization to give high-molecular-weight polymer ($M_n$ = 296 000−336 000) in 75% yield (Table 3). $n$-C$_4$H$_9$Li and (C$_2$H$_5$)$_3$Al exerted strong cocatalytic effect in combination with catalyst **4** as well to afford higher-molecular-weight polymers ($M_n$ = 312 000−395 000) in quantitative yield. However, relatively weak alkylating agents such as (C$_2$H$_5$)$_2$AlCl, ($n$-C$_4$H$_9$)$_4$Sn, and (C$_2$H$_5$)$_3$SiH were only slightly useful for both catalysts **2** and **4**. The strong alkylating agents react with [(diene)RhCl]$_2$ to form Rh-alkyl species, and insertion of phenylacetylene into the Rh−C bond is more facile than into the Rh−Cl bond, thus explaining the high catalytic activity observed with these cocatalysts.[58]

More recently, we have found a remarkable cocatalytic effect of alkali metal amides in conjunction with catalyst **2** in the polymerization of phenylacetylene.[59] The alkali metal amides (MN(SiMe$_3$)$_2$; M = Li, Na, K, and LiN(CHMe$_2$)$_2$) along with catalyst **2** polymerized phenylacetylene to give high molecular polymers ($M_n$ = 270 000−396 000) in quantitative yield (Table 4). These cocatalysts were equally effective for catalyst **4** as for catalyst **2**, and the molecular weights of formed polymers ($M_n$ = 361 000−487 000) were slightly higher than those with catalyst **2** ($M_n$ = 270 000−396 000). The excellent performance of alkali metal amides as cocatalysts is attributed to their ability to cleave [(diene)RhCl]$_2$ complexes (diene: nbd (**2**), tfb (**4**)) in an irreversible fashion to generate 14-electron Rh-amide complexes [(diene)Rh(NR$_2$)] (R: CHMe$_2$, SiMe$_3$), which induce extremely rapid polymerization of phenylacetylene on account of their electronically unsaturated and sterically open structure.[59,60]

**Table 3. Effect of Various Alkylating Agents in the Polymerization of Phenylacetylene with [(tfb)RhCl]$_2$ and [(nbd)RhCl]$_2$[a]**

| | [(tfb)RhCl]$_2$ (**4**) | | | [(nbd)RhCl]$_2$ (**2**) | | |
|---|---|---|---|---|---|---|
| cocatalyst | yield[b] (%) | $M_n$[c] | $M_w/M_n$[c] | yield[b] (%) | $M_n$[c,d] | $M_w/M_n$[c] |
| none[d] | 31 | 58 000 | 1.88 | 0 | | |
| $n$-C$_4$H$_9$Li | 100 | 395 000 | 2.23 | 75 | 336 000 | 2.31 |
| (C$_2$H$_5$)$_3$Al | 100 | 312 000 | 2.31 | 75 | 296 000 | 2.51 |
| (C$_2$H$_5$)$_2$AlCl | 52 | 69 000 | 2.02 | 0 | | |
| ($n$-C$_4$H$_9$)$_4$Sn | 43 | 64 000 | 1.93 | 3 | | |
| (C$_2$H$_5$)$_3$SiH | 39 | 58 000 | 1.91 | 0 | | |

[a] In toluene, 30 °C, 1 h; [phenylacetylene]$_o$ = 0.50 M, [Rh] = 2.0 mM, [cocat]/[Rh] = 1.0. [b] Methanol-insoluble product. [c] Determined by GPC (THF, PSt). [d] Polymerization time 24 h. [d] The theoretical $M_n$ of poly(phenylacetylene) is 25 000 assuming quantitative initiation efficiencies for all runs.

**Table 4. Effect of Alkali Metal Amides in the Polymerization of Phenylacetylene with [(tfb)RhCl]$_2$ and [(nbd)RhCl]$_2$[a]**

| | [(tfb)RhCl]$_2$ (**4**) | | | [(nbd)RhCl]$_2$ (**2**) | | |
|---|---|---|---|---|---|---|
| cocatalyst | yield[b] (%) | $M_n$[c] | $M_w/M_n$[c] | yield[b] (%) | $M_n$[c,d] | $M_w/M_n$[c] |
| none[d] | 31 | 58 000 | 1.88 | 0 | | |
| LiN(CHMe$_2$)$_2$ | 100 | 487 00 | 1.72 | 100 | 396 000 | 1.53 |
| LiN(SiMe$_3$)$_2$ | 100 | 361 000 | 2.01 | 100 | 270 000 | 1.92 |
| NaN(SiMe$_3$)$_2$ | 100 | 397 000 | 1.92 | 100 | 297 000 | 1.91 |
| KN(SiMe$_3$)$_2$ | 100 | 414 000 | 1.77 | 100 | 310 000 | 1.84 |

[a] In toluene, 30 °C, 1 h; [phenylacetylene]$_o$ = 0.50 M, [Rh] = 2.0 mM, [cocat]/[Rh] = 1.0. [b] Methanol-insoluble product. [c] Determined by GPC (THF, PSt). [d] Polymerization time 24 h. [d] Polymerization time 24 h. [d] The theoretical $M_n$ of poly(phenylacetylene) is 25 000 assuming quantitative initiation efficiencies for all runs.

**Regarding the Reason for High Activity of Catalysts 4 and 5.** According to the results stated above, it is obvious that various diene ligands behave differently in the polymerization of phenylacetylene catalyzed by [(diene)RhCl]$_2$ complexes. The nbd ligand is more effective than the cod ligand in accordance with the generally observed trend,[61,62] while dcp ligand was least active among the present ligands (Table 1). On the other hand, the tfb and tcb ligands gave rise to catalysts **4** and **5**, respectively, which were more active than the other catalysts **1**−**3**. The order of the effectiveness of the present diene ligands in the polymerization of phenylacetylene catalyzed by [(diene)RhCl]$_2$ is: tfb∼tcb > nbd > cod > dcp. We envisioned that different behavior of diene ligands in the Rh-catalyzed polymerization of phenylacetylene arises due to difference in their $\pi$-acidities.

The bonding in a metal−alkene complex is explained according to the Dewar−Chatt−Duncanson model, which states that d$^n$ metal−alkene bonding ($n \geq 2$) comprises two components: $\sigma$-donation from the filled alkene $\pi$ orbital (HOMO) to a metal-acceptor orbital, and back-donation from a filled metal d orbital to the vacant alkene $\pi$* orbital.[63−66] The outcome of this back-donation is the reduction of electron density at the metal center, thus enhancing its electrophilic character. The extent of the back-donation increases with the increase in the $\pi$-acidity of the alkene, which is defined as the ability of a ligand to accept electrons in the vacant lowest unoccupied molecular

**Table 5. $^1$H NMR Data of Diene Ligands and Rh Catalysts 1−5[a]**

| diene | $\delta_{\text{olefinic}}$ (ppm) | $\delta_{[(\text{diene})\text{RhCl}]_2}$ (ppm) | $\Delta\delta$ (ppm) |
|---|---|---|---|
| cod | 5.56 | 4.20 | 1.36 |
| nbd | 6.82 | 3.93 | 2.89 |
|  | 5.48 | 6.11, 4.22 | −0.63, 1.26 |
| dcp[68] | 5.95 | 4.66 | 1.29 |
| tfb | 6.92 | 3.82 | 3.10 |
| tcb | 6.90 | 3.81 | 3.09 |

[a] Measured in $CDCl_3$ at 25 °C, with tetramethylsilane (TMS) as an internal reference standard.

**Table 6. LUMO Energies of Diene Ligands[a]**

| diene | LUMO energy (eV) |
|---|---|
| cod | 0.90 |
| nbd | 0.79 |
| dcp | 1.09 |
| tfb | 0.21 |
| tcb | 0.48 |

[a] Calculated by PM3 using Spartan 04 program.

orbitals (LUMO) from filled d orbitals of metal.[67] The $\pi$-acidity of alkene can be estimated by measuring the upfield shift of olefinic protons in a metal−alkene complex relative to uncomplexed alkene. A higher $\pi$-acidity of an alkene is reflected in a larger upfield shift of olefinic protons in a metal−alkene complex and vice versa. Another useful parameter for deciding the $\pi$-acidity of an alkene is the LUMO energy of alkene. Because back-donation is an event involving d−$\pi^*$ overlap, a more effective overlap is expected from an alkene of lower LUMO energy (i.e., higher $\pi$-acidity).

The chemical shifts of olefinic protons in the dienes coordinating to Rh in catalysts **1**−**5** relative to those in the free dienes namely, cod, nbd, dcp, tfb and tcb, are shown in Table 5. In all cases, olefinic protons in Rh complexes were upfield shifted compared to uncomplexed diene ligands. The $\Delta\delta$ of nbd catalyst **2** (2.89 ppm) was higher than that of cod catalyst **1** (1.36 ppm). The upfield shift of olefinic protons was the smallest (∼1.29 ppm) in the least active catalyst **3**.[68] On the other hand, tfb and tcb, which were the most effective ligands, displayed the largest upfield shifts of their olefinic protons in the corresponding Rh complexes (**4**: $\Delta\delta = 3.10$ ppm, **5**: $\Delta\delta = 3.09$ ppm). These results indicate that $\pi$-acidities of tfb and tcb are higher than those of other ligands. It is noteworthy that the $\pi$-acidity follows the same order (tfb∼tcb > nbd > cod > dcp) as the catalytic activity of the corresponding complexes **1**−**5** (tfb **4**∼tcb **5** > nbd **2** > cod **1** > dcp **3**).

The semiempirical PM3 calculations were performed to estimate the energies of the lowest unoccupied molecular orbitals (LUMO) of the diene ligands, whose results are depicted in Table 6. These calculations have brought forth that the LUMO energy of dcp (1.09 eV) was the highest, while those of tfb and tcb were the lowest (tfb: 0.21 eV, tcb: 0.48 eV) among the present diene ligands (cod: 0.90 eV, nbd: 0.79 eV). According to these results, tfb should be the most $\pi$-acidic among the present diene ligands.

The high $\pi$-acidity of tfb ligand is reminiscent of a strong back-donation, which results in a significant drift of electron density from filled 4d orbitals of Rh to LUMO of tfb ($\pi^*$ orbital of tfb, in this case). This renders the Rh metal in catalyst **4** electron-deficient, thus facilitating the coordination of monomer to it. The lower $\pi$-acidity of the nbd ligand suggests a weaker back-donation in the nbd Rh complex **2** than in the corresponding tfb complex **4**. Thus Rh atom in **2** should be less electrophilic than that of **4**, which makes the coordination of monomer to Rh atom of **2** relatively less facile. This explains the higher activity of tfb catalyst **4** than that of nbd catalyst **2**. The $\pi$-acidity of dcp ligand is the lowest, as evidenced by the smallest upfield shift of olefinic protons in **3** (∼1.29 ppm, Table 5)[68] and the highest LUMO energy of dcp (1.09 eV, Table 6). These observations indicate that back-donation from Rh to dcp in complex **3** is even weaker than that in cod complex **2**, thus explaining its lowest activity among **1**−**5**. It is reasonable to ascribe the difference in the catalytic activity of catalysts **1**−**5** to the different $\pi$-acidic character of their diene ligands; however, stability of the propagating species and the effect of the energy barrier for the vinyl migration step to the coordinated monomer for each catalyst must be considered by further experiments.

## Conclusions

The present study has revealed that the tfb- and tcb-containing Rh complexes $[(\text{tfb})\text{RhCl}]_2$ **4** and $[(\text{tcb})\text{RhCl}]_2$ **5** display higher catalytic activity than the corresponding conventional cod and nbd catalysts (**1** and **2**, respectively). A detailed study of the polymerization of phenylacetylene with catalysts **2** and **4** in various polar and nonpolar solvents indicates that **4** is a more active catalyst than **2**. Strong alkylating agents and alkali metal amides efficiently work as cocatalysts in conjunction with catalysts **2** and **4** and higher-molecular-weight polymers are formed in the case of catalyst **4**. These observations find their explanation in the higher $\pi$-acidity of tfb than that of nbd as evidenced by its significantly low LUMO energy (0.21 eV) and a very large upfield shift of olefinic protons in **4** (3.10 ppm). The high $\pi$-acidity of tfb ligand induces a considerable back-donation from filled 4d orbitals of Rh to LUMO of tfb, rendering the Rh metal in catalyst **4** highly electron-deficient. This leads to a more facile coordination of monomer with Rh metal in catalyst **4**, resulting in its higher catalytic activity.

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## References and Notes

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(56) Catalyst **3** is not altogether ineffective; in the presence of more effective cocatalysts such as alkali metal amides ($\text{LiN}(i\text{-Pr})_2$) or strong alkylating agents ($n\text{-C}_4\text{H}_9\text{Li}$, etc.), it can polymerize phenylacetylene in appreciable yield (50−60%) to afford polymer with a molecular weight on the order of $10^4$.

(57) Monodentate olefins, ethylene and cyclooctene, and bidentate olefins, such as 1,3-butadiene, 1,4-cyclohexadiene, 1,4-benzoquinone, tetramethyl-1,4-benzoquinone, hexachloro-1,3-cyclopentadiene, hexachloronorbornadiene-1,2-dicarboxylic acid dimethyl ester, tetraphenylcyclopentadienone, and 1,3,5,7-cyclooctatertraene, were hardly effective to induce polymerization of substituted acetylenes.

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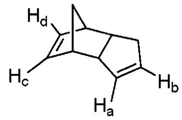
(68) All of the four olefinic protons in *endo*-dicyclopentadiene (dcp) are nonequivalent, hence, a separate signal for each proton should be observed. However, chemical shifts of $H_a$ and $H_b$ are very close to each other and they are observed as one broad mutiplet around 5.48 ppm. For the same reason, $H_c$ and $H_d$ are also observed as one broad multiplet around 5.95 ppm. In the $[(\text{dcp})\text{RhCl}]_2$ (**3**), both $H_c$ and $H_d$ are upfield shifted to the same extent and are observed as one signal around 4.66 ppm. However, geometric arrangement of $H_a$ is quite different from $H_b$ in Rh complex **3**, which gives rise to upfield shift of one proton ($H_a$ or $H_b$) and downfield shift of other ($H_a$ or $H_b$). For more details, see ref 15.



*endo*-Dicyclopentadiene

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