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- [6] The hydrolysis of the alkenylphosphonates was easy. For instance, heating a mixture of **2a**, 1 mL of 37% HCl, and 1 mL of 1,4-dioxane at 98 °C for 2 h and removal of volatiles left a crude hydrolysis product nearly quantitatively. Recrystallization from acetone/chloroform gave an analytically pure white material, m.p. 147–149 °C (Lit.: 142–142.5 °C; C. E. Griffin, T. D. Mitchell, *J. Org. Chem.* **1965**, 30, 1935).
- [7] It is interesting to compare the regioselectivity with the palladium-catalyzed addition of H–P(O)Ph₂ to terminal alkynes. The reaction generally forms linear adducts. However, 1-ethynylcyclohexene was an exceptional alkyne, which did not conform to the general regiochemical trend and gave the branched adduct; see: L.-B. Han, N. Choi, M. Tanaka, *Organometallics* **1996**, 15, 3259.
- [8] Hydrogen phosphonates exist in two tautomeric forms, HP(O)(OR)₂ and P(OR)₂(OH), the former being thermodynamically more favored under ambient conditions. They coordinate, like tertiary phosphanes, to transition metals to form complexes, which have been used as catalysts in organic reactions. a) D. M. Roundhill, R. P. Sperline, W. B. Beaulieu, *Coord. Chem. Rev.* **1978**, 26, 263. Although not known for [RhCl(PPh₃)₃], oxidative additions of H–P bonds to a few rhodium complexes have appeared in the literature. b) M. A. Bennett, T. R. B. Mitchell, *J. Organomet. Chem.* **1985**, 295, 223; c) A. Varshney, G. M. Gray, *J. Organomet. Chem.* **1990**, 391, 415.
- [9] Although it could not be detected in this particular reaction, another PPh₃-free rhodium complex **7**, displaying ³¹P NMR signals at δ = 126–128, was also formed when a large excess of **1** was used. Pure **6** and **7** have not been isolated yet. However, as confirmed by ³¹P NMR spectroscopy, a mixture of these complexes could be generated when [RhCl(cod)]₂ was mixed with **1** (see ref. [8b]).
- [10] The P^V(O)(OR')₂ and P^{III}(OH)(OR')₂ ligands in complexes **4** and **5** are not distinguishable. They are linked together by hydrogen bonds such as Rh[P(O)(OR')₂][P(OH)(OR')₂], as suggested by X-ray diffraction (see below). In this context, complex **5** is envisioned on the basis of the ³¹P NMR spectrum to adopt a pseudo-*fac* configuration. See Supporting Information for the detailed NMR data.
- [11] Interestingly, the conversion of **4** to **3** in toluene was much slower than in CH₂Cl₂; **4** was still present in the solution even after 4 h of heating at 60 °C (3/4 ≈ 2.8/1).
- [12] Allowing the solution to stand at room temperature overnight regenerated **4** to a small extent (4/3 ≈ 8/92).
- [13] Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-150935. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).
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- [17] The equilibrium between **3**, **4**, and **5** was confirmed separately. Mixing **5** (7.3 mg) with PPh₃ (2 equiv) in CD₂Cl₂ (0.5 mL) at room temperature generated a mixture of all three species (3/4/5 = 1/0.38/0.29) after 20 h.
- [18] Since the detailed structures of **6** and **7** are not known, the true amounts of these species in the mixture cannot be evaluated. The ratio given in Table 2 is a provisional value, calculated on the basis of an arbitrary assumption that only one molecule of **1** ligates Rh.
- [19] Attempted isolation of **8** failed, but the structure is evidenced by its NMR spectra (CD₂Cl₂). The ¹H NMR spectrum displays a signal for

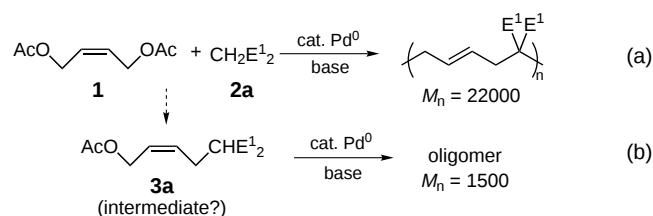
olefinic proton H^a at δ = 4.63 (dd, *J* = 16.6, *J*(H,Rh) = 4.6 Hz). The ¹H–¹H COSY technique confirms that another olefinic proton H^b is hidden at δ ~ 7.4 in the mass of phenyl proton signals. The large coupling constant indicates an *E* configuration of the double bond. The ³¹P NMR spectrum also conforms to the structure in showing a dd signal at δ = 29.0 (*J*(P,P) = 25.0, *J*(P,Rh) = 112.0 Hz, PPh₃) and a dt signal at δ = 56.3 (*J*(P,P) = 25.0, *J*(P,Rh) = 184 Hz, P(O)).

- [20] A mixture of these complexes in CD₂Cl₂ (molar ratio 3/4/5 = 1.0/1.3/1.7), generated by the reaction of [RhCl(PPh₃)₃] with an excess of **1** (6 equiv), was allowed to react with phenylacetylene (10 equiv) at room temperature. Complex **5** was completely consumed in 26 min, and **8** and **2a** were observed (molar ratio of 3/4/5/8/2a = 1.0/1.3/0/3.2/8.8).

Mechanistic Rationale of a Palladium-Catalyzed Allylic Substitution Polymerization—Carbon–Carbon Bond-Forming Polycondensation out of Stoichiometric Control by Cascade Bidirectional Allylation**

Nobuyoshi Nomura, Ko Tsurugi, and Masahiko Okada*

Palladium-catalyzed allylic alkylation has been the subject of intensive research in carbon–carbon bond-forming processes since its discovery,^[1] and it was recently extended to an allylic substitution polymerization^[2] (Scheme 1a, E¹ = CO₂Et) in which the use of bis(diphenylphosphanyl)butane (dppb) was indispensable. In a survey of recent studies on palladium-catalyzed allylation reactions,^[1b–f] π-allylpalladium(II) complex intermediates were extensively



Scheme 1. Palladium-catalyzed allylic substitution polymerization (E¹ = CO₂Et).

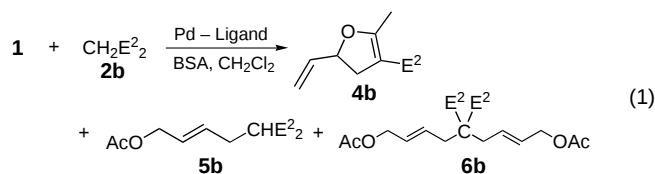
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investigated to reveal the origins of the regio-, stereo-, and enantioselectivity. However, transient olefin– L_nPd^0 complexes have not gained much attention, except for a few discussions on asymmetric recognition and induction.^[3–5] Herein we show that the reactions of olefin– L_nPd^0 complexes play a crucial role in successful polymerizations (Scheme 1 a), and that polymerization selectively proceeds by means of a cascade bidirectional allylation mechanism. Our preliminary results concerning the first example of a carbon–carbon bond-forming polycondensation out of stoichiometric control are also presented based on the mechanistic rationale.

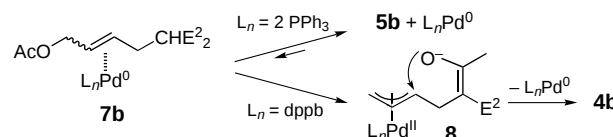
We prepared the bifunctional monomer **3a** ($E^1 = CO_2Et$, Scheme 1 b), which possessed both electrophilic and nucleophilic sites. There appeared to be two advantages in the use of **3a** instead of the two-component system of **1** and **2a**: 1) the stoichiometric control of polycondensation could be avoided, so that a polymer with a higher molecular weight should be formed; 2) under the same polymerization conditions, a half turnover number of Pd catalyst could lead to the same molecular weight of polymer (Scheme 1 a) in a shorter time. However, the polymerization of **3a** was quite sluggish and the number-average molecular weight (M_n) was estimated at only 1500 under the identical conditions^[6] (Scheme 1 b). We were surprised at this result, since **3a** was believed to be an initial intermediate.^[7]

To clarify the polymerization mechanism, we examined the model reaction between **1** and acetylacetone (**2b**, [Eq. (1)], $E^2 = COMe$). Various ligands were used in the reactions,



which were monitored by TLC and quenched soon after the quantitative consumption of **1**, or after 24 h (Table 1). Although no clear relationships between the catalytic activities and selectivity of the products were found, both were highly dependent on the ligand used. For example, dppb was found to be the most efficient ligand (Table 1, entry 4), and dppf and PPh_3 showed moderate catalytic activities (Table 1, entries 5 and 6). Other ligands were much less effective in this

reaction (Table 1, entries 1–3, 7, and 8). The main difference between using dppb and PPh_3 was the major product that was formed: both acetate groups of **1** reacted with L_nPd^0 to afford cyclic compound **4b** in the case of dppb^[7] (Table 1, entry 4), whereas in the presence of the PPh_3 system, one acetate group reacted selectively to produce **5b** and **6b** (Table 1, entry 6). The fact that **5b** hardly cyclized under the same conditions as those in entry 4, suggested that the transient olefin– L_nPd^0 complex **7b**, which was the precursor of **5b**, should be the key complex in the catalytic reaction (Scheme 2).^[8] After the



Scheme 2. Mechanism for selective cyclization ($E^2 = come$).

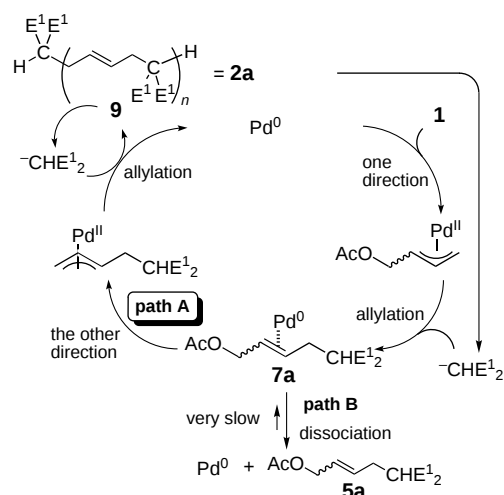
formation of **7b**, two pathways were possible. When PPh_3 was applied, **7b** selectively collapsed into **5b** and L_nPd^0 . The coordination of **5b** to L_nPd^0 was slow probably because of the steric effects of two bulky carbonyl groups introduced during the first allylation.^[9] In the dppb system, however, **7b** forms allylpalladium complex **8** at the other allylic terminal, and then intramolecular cyclization occurs (Scheme 2). Such a cascade mechanism is applicable to the polymerization reaction (Scheme 3). After the first allylation of **1**, **7a** selectively forms the allylpalladium(II) complex at the other allylic terminal when dppb is used (path A). The allylpalladium(II) complex is susceptible to intermolecular attack by the anion of **2a** to form **9**. Compound **9** is an equivalent of **2a**, and is involved in the catalytic polymerization cycle. Since **5a** showed considerably lower reactivity toward L_nPd^0 , a successful polymerization requires the high selectivity of path A and proceeds by means of the cascade bidirectional allylation mechanism. The manipulation of transient olefin– L_nPd^0 complexes, that is, controlling relative reaction rates between oxidative addition (path A) and dissociation (path B), is essential for a successful polymerization.^[5]

It is possible that this C–C bond-forming polycondensation may occur out of stoichiometric control, which is the intrinsic drawback of polycondensation.^[10] When polymerization exclusively proceeds through path A, each molecule of **1** reacts with two molecules of **2a** (or subsequently, **9**). This

Table 1. Ligand effects in Equation (1).^[a]

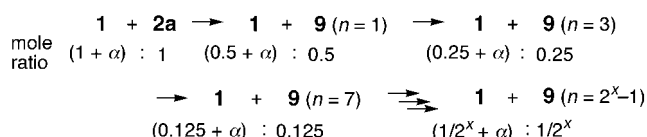
Entry	Ligand ^[b] (equiv. to Pd)	Time [h]	4b	Yield [%] ^[c] 5b	6b	Recovered [%] ^[c] 1
1	dppm (1)	24	–	–	–	93
2	dppe (1)	24	–	5	–	79
3	dppp (1)	24	traces	–	–	95
4 ^[d]	dppb (1)	1	82	–	–	0
5 ^[d]	dppf (1)	3	69	–	–	0
6 ^[d]	PPh_3 (2)	10	3	44	18	1
7	$P(o\text{-tolyl})_3$ (2)	24	–	–	–	92
8	bpy (1)	24	–	–	–	96

[a] All the reactions were carried out with **1** (0.50 mmol), **2b** (1.20 mmol), and BSA (3.0 mmol) in the presence of $[Pd_2(dba)_3]$ (1 mol %) and various ligands in CH_2Cl_2 (1 mL) at 25 °C. [b] $Ph_2P(CH_2)_nPPh_2$: dppm: $n = 1$, dppe: $n = 2$, dppp: $n = 3$, dppb: $n = 4$; dppf = 1,1'-bis(diphenylphosphanyl)ferrocene, bpy = 2,2'-bipyridine. [c] Yield after column chromatography. [d] Some oligomerization was also observed.



Scheme 3. Cascade bidirectional allylation mechanism.

means that all chains undergoing polymerization are always **9**, which has malonate functions at either terminal, and that the molecular number of **1** should be the same as that of **9** (Scheme 4, $\alpha = 0$). Then, even an excess of **1** ($\alpha > 0$) does not

Scheme 4. Polycondensation without stoichiometric control. n = average degrees of repeating unit.

affect the degree of polymerization, whereas polymerization will be terminated when **2a** is in excess ($\alpha < 0$, $1/2^x + \alpha = 0$). We examined the polymerization with different ratios of **1** and **2a** (Table 2). According to the widely accepted stoichiometric principle of polycondensation,^[10] the average degrees of polymerization (DPs) in both 1.0:1.1 and 1.1:1.0 of **1/2a** are expected to be the same (DP = 21). However, we obtained quite different DPs (estimated DPs, determined vs polystyrene standards): DP = 24 (**1/2a** 1.0:1.1); DP = 66 (**1/2a** 1.1:1.0) (Table 2, entries 1 and 2). When 1.3 equivalents of **1** are used,

Table 2. Polycondensation without stoichiometric control.^[a]

Entry	Ligand	Ratio (1/2a)	Expected DP ^[b]	Obtained DP ^[c]
1	dppb	1.0:1.1	21	24
2	dppb	1.1:1.0	21	66
3	dppb	1.3:1.0	7.7	50
4	dppb	1.5:1.0	5.0	46
5	dppb	2.0:1.0	3.0	37 ^[d]
6	PPh ₃	1.5:1.0	5.0	5.0 ^[e]

[a] All the reactions were carried out under the conditions described in ref. [6], except for the reaction temperature (25 °C). Crude samples from the reaction mixture were analyzed every 6 or 12 h until the values of M_n reached the upper limits. All polymer yields based on **1** (entry 1) or **2a** (entries 2–6) were nearly quantitative ($\geq 95\%$). [b] See ref. [10]. [c] Estimated by SEC (CHCl₃, polystyrene standard, Tosoh TSK gel G2000HXL, G3000HXL, and G5000HXL columns). [d] 45% of **1** (90% of the excess amount for **2a**) was recovered by column chromatography. [e] The DP was also estimated by ¹H NMR spectroscopy (DP = 5.0).

the DP is expected to decrease drastically to 7.7, whereas the observed DP remained quite high (DP = 50, Table 2, entry 3). Although a further excess of **1** gradually reduced the DPs in this system (Table 2, entries 4 and 5),^[11] an unexpectedly higher DP (≈ 12 -fold) was still obtained in the presence of two equivalents of **1**, and excess **1** was recovered (90%). In contrast, the PPh₃ system, which prefers path B, resulted in the same DP as expected based on general polycondensation (Table 2, entry 6). These results indicate that exclusive selectivity of the reaction pathways will overcome the stoichiometric principle of polycondensation. To the best of our knowledge, this is the first example of a C–C bond-forming polycondensation out of stoichiometric control, whereas there are two systems reported in bond-forming homogeneous polymerization.^[12, 13]

In summary, the mechanistic rationale of the palladium-catalyzed allylation polymerization was investigated, and a cascade bidirectional allylation mechanism was revealed. Further studies are underway to understand the conditions for manipulating olefin–L_nPd⁰ complexes. We are also investigating systems which will make C–C carbon–heteroatom bond-forming polycondensations out of stoichiometric control more practical.

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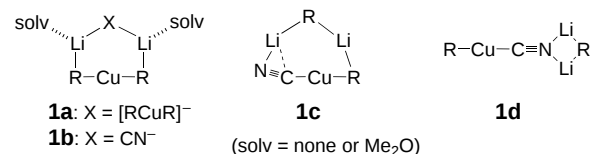
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- [11] Based on our mechanism, stoichiometric ratios should not affect DPs. The decreasing DPs might be caused by the lower selectivity in the presence of excess **1**, which accelerates the olefin–ligand exchange of **7**.
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Kinetic Reactivity of “Higher Order Cuprates” in S_N2 Alkylation Reactions**

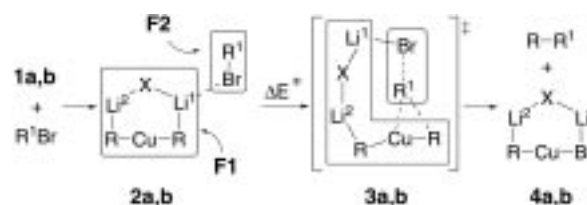
Eiichi Nakamura,* Masahiro Yamanaka, Naohiko Yoshikai, and Seiji Mori

Among a variety of organocopper reagents,^[1] “higher order” cyanocuprates have attracted much interest in the past years.^[2] Lipshutz originally offered this reagent to the synthetic society as a highly reactive substitute for the classical Gilman reagent, **1a** (denoted hereafter as series **a**



($R = Me$) throughout the text).^[3] The high reactivity was ascribed to a dianionic tricoordinated copper(II) structure,^[4] but this structure was soon challenged by Bertz.^[5] The structural debate ended recently and it was concluded that the Lipshutz reagent is not the tricoordinated species, but **1b** (denoted hereafter as series **b** throughout the text).^[6–8] The latter structure is essentially the same as that of the classical Gilman reagent **1a** except that the bridging group (X) in the Lipshutz reagent is a cyanide group instead of the $[RCuR]^-$ group, with which the Gilman reagent forms a dimeric copper structure.^[9] The Lipshutz reagent is therefore no more than a “lower order” cuprate, yet the fact still remains that it is often a more powerful nucleophile than a normal Gilman reagent. For instance, the Lipshutz reagent is the reagent of choice for S_N2 reactions, in which the Gilman and other lower order cuprates are far less reactive.^[10] Furthermore, the Lipshutz reagent shows some unusual reactivity, which suggests that a minute amount of alkyllithium is generated in equilibrium with the major $[R_2Cu]^-$ species.^[11] Thus the kinetic reactivity of the Lipshutz reagent is still an open question. We report herein density-functional studies on the S_N2 reaction of MeBr with the Lipshutz reagent **1b**, which suggest that **1b** could indeed be much more reactive than the Gilman reagent **1a**. The higher reactivity of **1b** has been ascribed both to the higher Lewis acidity of the $[LiCNLi]^+$ group, and to the energetically favorable structural change of the $[LiCNLi]^+$ moiety in the transition state (TS) of the reaction of **1b**. The studies also suggest that minor structural isomers of the Lipshutz reagent, **1c** and **1d**, might play a role in solution chemistry despite their low equilibrium concentration.^[8]

Previous studies have shown that the rate-determining step of the S_N2 reaction of the lithium organocuprate with MeBr is the C–Br bond cleavage stage (**3a, b**, Scheme 1), from which



Scheme 1. Substitution reaction between $R_2CuLi \cdot LiX$ ($R = Me$, series **a**: $X = RCuR$, series **b**: $X = CN$) and $R'Br$ ($R' = Me$).

the potential surface goes steeply downhill to the alkylation product.^[12, 13] The energy profile of the bromide displacement in series **a** and **b**, and the 3D structures of the stationary points are shown in Figures 1 and 2.^[14a] As shown in Figure 1, the activation energy from the initial coordination complex (CP, **2b**) to the displacement TS (**3b**) for the major species of the Lipshutz reagent **1b** is 3.8 kcal mol^{−1} smaller than that for the Gilman dimer **1a**.^[15, 16]

Where is the origin of this small but finite difference in the activation energies between series **a** and **b**? The answer to this question was probed by fragment energy analysis^[17] (Scheme 1 and Table 1) through the dissection of the CPs

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