

Ortho-Phosphinobenzenesulfonate: A Superb Ligand for Palladium-Catalyzed Coordination–Insertion Copolymerization of Polar Vinyl Monomers

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CONSPECTUS

Ligands, Lewis bases that coordinate to the metal center in a complex, can completely change the catalytic behavior of the metal center. In this Account, we summarize new reactions enabled by a single class of ligands, phosphine–sulfonates (*ortho*-phosphinobenzenesulfonates). Using their palladium complexes, we have developed four unusual reactions, and three of these have produced novel types of polymers.

In one case, we have produced linear high-molecular weight polyethylene, a type of polymer that group 10 metal catalysts do not typically produce. Secondly, complexes using these ligands catalyzed the formation of linear poly(ethylene-*co*-polar vinyl monomers). Before the use of phosphine–sulfonate catalysts, researchers could only produce ethylene/polar monomer copolymers that have different branched structures rather than linear ones, depending on whether the polymers were produced by a radical polymerization or a group 10 metal catalyzed coordination polymerization. Thirdly, these phosphine–sulfonate catalysts produced nonalternating linear poly(ethylene-*co*-carbon monoxide). Radical polymerization gives ethylene-rich branched ethylene/CO copolymers copolymers. Prior to the use of phosphine–sulfonates, all of the metal catalyzed processes gave completely alternating ethylene/carbon monoxide copolymers. Finally, we produced poly(polar vinyl monomer-*alt*-carbon monoxide), a copolymerization of common polar monomers with carbon monoxide that had not been previously reported.

Although researchers have often used symmetrical bidentate ligands such as diimines for the polymerization catalysis, phosphine–sulfonates are unsymmetrical, containing two nonequivalent donor units, a neutral phosphine, and an anionic sulfonate. We discuss the features that make this ligand unique. In order to understand all of the new reactions facilitated by this special ligand, we discuss both the steric effect of the bulky phosphines and electronic effects. We provide a unified interpretation of the unique reactivity by considering of the net charge and the enhanced back donation in the phosphine–sulfonate complexes.



Introduction

In homogeneous metal catalysis, the development of new ligands has played an essential role because they can dramatically alter catalyst activity as well as selectivity of the products. This aspect is especially important in

polymerization catalysis where the control of monomer composition and polymer microstructure affects the physical properties of the products. In this Account, we focus our attention on one class of ligand, phosphine–sulfonates, which have established synthetic routes toward

unprecedented polymeric materials made from polar vinyl monomers.

Polar vinyl monomers such as methyl acrylate, vinyl acetate, and acrylonitrile are inexpensive and widely used monomers in radical, anionic, and cationic polymerization. Incorporation of these monomers into polyolefins such as high density polyethylene would change their physical properties such as adhesion, dyeability, printability, and compatibility. Until recently, however, the metal-catalyzed coordination–insertion polymerization of the basic polar vinyl monomers remained unsolved.^{1,2}

A major challenge to incorporating polar vinyl monomers in coordination–insertion polymerization is the strong coordination of functional groups of the monomers to the Lewis acidic metal center. The catalysts that are most often utilized for coordination–insertion polymerization, especially for polyolefin production, are based on early transition metals such as group 4–6 metals. Due to the highly Lewis acidic nature of these early transition metals, however, they

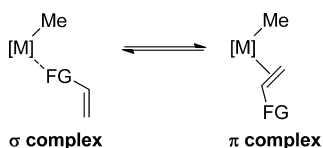


FIGURE 1. σ - and π -coordination of polar vinyl monomers to a metal center.

tend to form stable σ -complexes with the functional groups of polar monomers, thus preventing the formation of the π -complex needed for activation of the C=C double bond (Figure 1). An additional serious problem is beta-X elimination of $[M]CH_2CHXR$ species formed by 1,2 insertion of the polar $CH_2=CHX$ monomer, which produces deactivated $M-X$ complexes. Owing to the lack of catalysts capable of incorporating polar monomers into linear polyethylene, the ethylene/polar monomer copolymers were limited to the ones with different types of branched structures produced by either a radical copolymerization or by a palladium-catalyzed copolymerization using diimine ligands reported by Brookhart and co-workers.^{3–5}

Since the 1960s, nickel complexes bearing anionic chelating $[P-O]$ ligands were successfully applied as ethylene oligomerization catalysts.⁶ Murray et al. first synthesized *ortho*-phosphinobenzenesulfonate ligands, exemplified by $Ar_2P(C_6H_4\text{-}ortho\text{-}SO_3^-)$, which subsequently became one of the most successful class of ligands developed by Union Carbide/UOP for the nickel-catalyzed ethylene oligomerization producing linear 1-alkenes.^{7a–c} Further studies on ethylene oligomerization and ethylene/CO copolymerization were executed mostly by industrial researchers.² In 2002, Drent et al. reported first in an academic journal that neutral Pd(II) catalysts generated in situ from phosphonium–sulfonate ligands copolymerized ethylene and methyl acrylate to produce linear copolymers.⁸ Subsequently, intensive

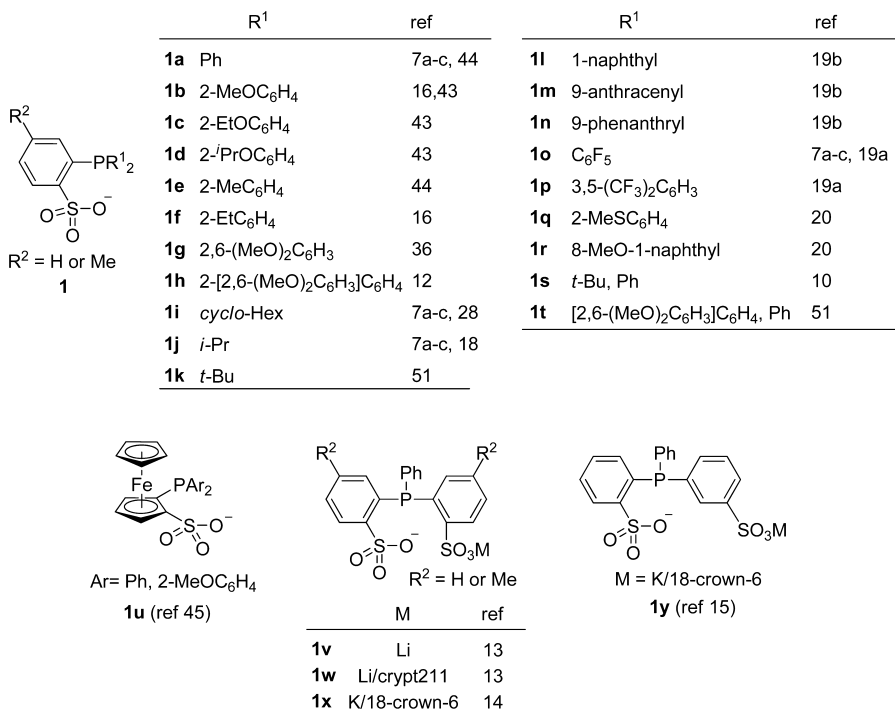


FIGURE 2. Examples of phosphine–sulfonate ligands.

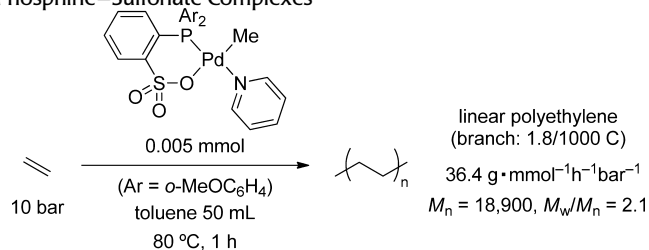
studies have focused on the unique characteristics of this class of catalysts. Thus far, several unprecedented types of polymers using polar monomers including acrylates, vinyl acetate, acrylonitrile, and carbon monoxide were produced by this catalyst system.^{2,9}

In this Account, we briefly overview the new types of polymerizations established by this superb ligand, phosphine–sulfonate: (1) ethylene homopolymerization, (2) ethylene/polar monomer copolymerization, (3) nonalternating ethylene/carbon monoxide copolymerization, and (4) polar monomer/carbon monoxide alternating copolymerization. Next, we provide a unified interpretation for the unique polymerization reactions involving polar vinyl monomers. The contents are focused on palladium chemistry and the body text does not include other metal complexes.¹⁰ Some examples of phosphine–sulfonate ligands thus far reported are listed in Figure 2.

1. Ethylene Homopolymerization

By using palladium phosphine–sulfonate catalysts, highly linear polyethylenes are produced without any activator

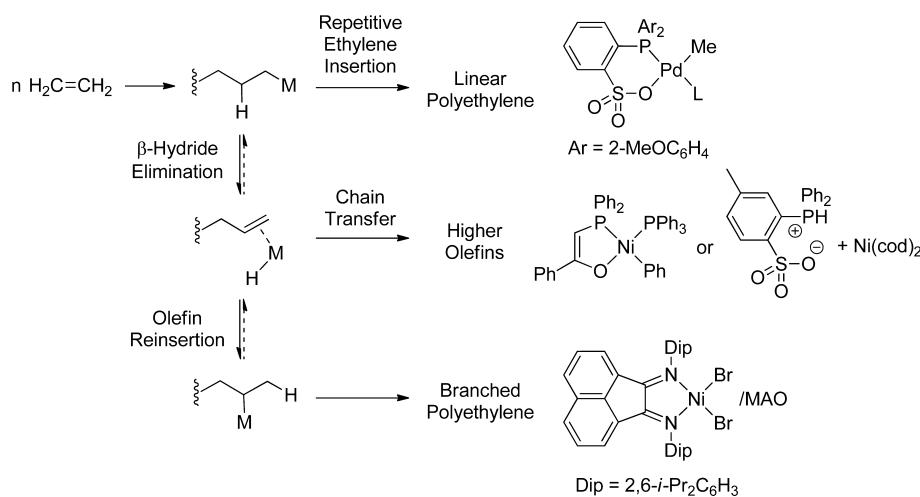
SCHEME 1. Ethylene Homopolymerization Catalyzed by Palladium Phosphine–Sulfonate Complexes¹⁶

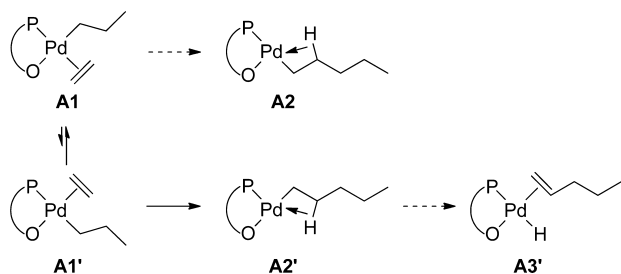


or noncoordinating counterions.¹¹ Under typical reaction conditions (Scheme 1), the polymerization proceeds with the activity of 10^{-1} – 10^2 g(polymer)·mmol⁻¹(Pd) h⁻¹ bar⁻¹, and the resulting polyethylene has molecular weights of 10^3 – 10^5 with highly linear structures within the range of 1–10 branches per 1000 carbons. Thus far, palladium complexes with ligand **1h** give the highest activity (985 g·mmol⁻¹ h⁻¹ bar⁻¹) and molecular weight (M_n = 227 000).¹² Phosphine–sulfonate ligands bearing additional coordinating group(s) tend to form multinuclear species due to the intermolecular coordination of the additional coordinating group. For example, a complex with **1v** formed a tetranuclear cubic structure containing Li–SO₃ bridges and it gave polyethylene with high molecular weight (M_w = 1 000 000).¹³ Similar aggregation was suggested for **1y** in toluene for ethylene homopolymerization and for ethylene/methyl acrylate copolymerizations.¹⁴ Sequestration of the Li⁺ cation in **1v** by Crypt211 to generate a free sulfonate group in **1w** resulted in a dramatic increase in the chain transfer rate and the formation of ethylene oligomers. Coordination of B(C₆F₅)₃ to a sulfonate oxygen of (**1f**)Pd(Me) also resulted in a substantial decrease in the molecular weight of the polyethylene produced by this catalyst.¹⁵

The feature of palladium phosphine–sulfonate catalysts is compared with other group 10 metal catalysts (Scheme 2). With nickel [P–O] catalysts, C₄–C₂₀ ethylene oligomers are generally formed by repetitive ethylene insertion to alkyl-metal species followed by β -hydride elimination and release of 1-alkenes (Scheme 2, middle line).^{6,7} On the other hand, Brookhart's catalysts,³ nickel or palladium complexes with bulky diimines, afford highly branched and

SCHEME 2. Ethylene Oligomerization and Polymerization Catalyzed by Group 10 Metal Complexes



SCHEME 3. Ethylene Polymerization Using Palladium Phosphine–Sulfonates

high-molecular-weight polyethylene. The formation of high-molecular-weight polyethylene with a branched structure can be attributed to the suppression of chain transfer, which results in effective reinsertion of the eliminated olefin to the metal–hydride bond without preference of regioselectivity (Scheme 2, bottom line). In contrast, in the case of palladium/phosphine–sulfonate, it was suggested that retardation of the β -hydride elimination step is one reason why the catalysts provided linear polyethylene (Scheme 2, upper line).^{17,18} It is also proposed that the β -hydride elimination from alkylpalladium and reinsertion of the eliminated alkene plays a major role, especially under low ethylene pressures. In such a case, either regioselective olefin reinsertion from PdH(1-alkene) to *normal*-alkylpalladium species or preferable ethylene insertion to *normal*-alkylpalladium (Scheme 2, upper line) over *iso*-alkylpalladium (Scheme 2, bottom line) could be the origin of the linear polyethylene production. Furthermore, protection of the apical position of the palladium center was proposed to prevent the olefin complex from chain transfer.^{19–21} For example, as the steric protection at the axial positions increases in the series **1r** < **1b** < **1q**, the molecular weight of the polyethylene increases from 1×10^3 to 500×10^3 g/mol.²⁰ A similar substituent effect was reported in the original report from Union Carbide on the nickel phosphine–sulfonate catalyst for ethylene oligomerization.^{7b}

Density functional theory (DFT) calculations provided insight into the polymerization mechanism operated by the unsymmetrical phosphine–sulfonate ligand (Scheme 3). Due to the much stronger *trans* influence of phosphine than sulfonate, isomer **A1** having the alkyl group at *trans* to the sulfonate is more stable than isomer **A1'** with alkyl group at *trans* to the phosphine. The ethylene insertion takes place from the less stable isomer **A1'** rather than the more stable **A1**, which is consistent to the report on nonsymmetric diphosphines and phosphine–phosphinite ligands.²² The β -hydride elimination from **A2'** to **A3'** is highly unfavorable, which is unique for the unsymmetrical phosphine–sulfonate ligand.

TABLE 1. Copolymerization of Ethylene with Polar Monomers to Produce Functionalized Linear Polyethylenes

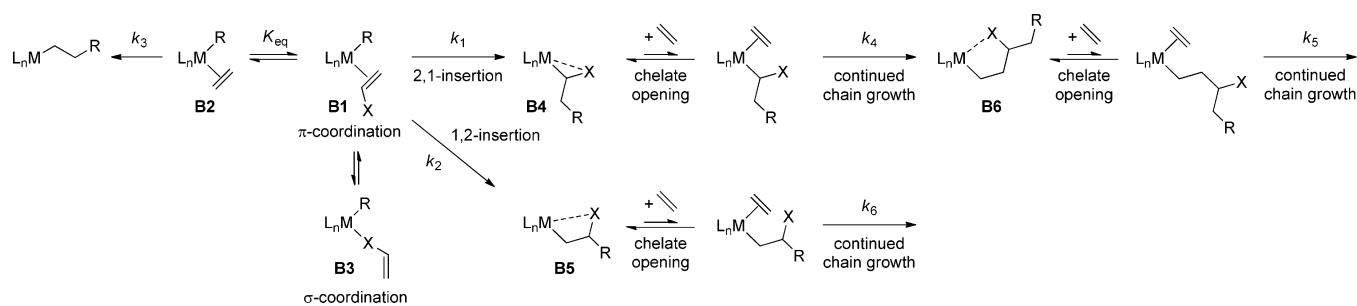
FG	L ¹	$M_n/10^{-3}$	incorporation 1/(m+1) %
COOMe	1b, 1h	~41.2	~52
COOH	1b	6–8	3–10
OAc	1i	5–11	0.6–1.9
CN	1b	~12.3	2–9
F	1a, 1b, 1f	4.5–14.5	0.1–3.6
OBu	1b	0.9–4.8	1–7
C(=O)NH ⁱ Pr	1b	1.2–1.3	3.2–4.1
<u>NC(=O)(CH₂)₃</u>	1b	3.0–4.2	0.3–2.6

2. Ethylene/Polar Monomer Copolymerization

The polar vinyl monomers (CH₂=CHX) so far incorporated into linear polyethylene chain by palladium phosphine–sulfonate catalysts are as follows: acrylates (X = CO₂R),^{8,12,14,23–25} acrylic acid (X = CO₂H),^{24,26,27} vinyl acetate (X = OAc),²⁸ acrylonitrile (X = CN),^{14,29} methyl vinyl ketone (X = COMe),³⁰ vinyl fluoride (X = F),³¹ vinyl ethers (X = OR),³² acrylamide (X = CONR₂),^{25,33} *N*-vinylpyrrolidone,³³ and vinylsulfones (X = SO₂R).³⁴ These catalysts can also incorporate allyl monomers,³⁵ functionalized norbornenes,^{27,36} and maleic anhydride.²⁷

The representative results are summarized in Table 1. The copolymerizations are carried out either in neat monomer or in a toluene solution of the polar monomer under ethylene pressure of 0.1–3.0 MPa at 60–100 °C. The copolymers thus obtained have a highly linear structure in which the number of Me branches on the backbone of the copolymer was very low. It should be noted that the catalytic activity sharply drops in the copolymerization with polar monomers when compared to the ethylene homopolymerization, by the 2–3 orders of magnitude, on average. Significant influence of the stabilizing base in phosphine–sulfonate-based complexes on the activity of these catalysts was reported. When the reaction is initiated by a complex [P–O]PdMe(L²) where L² represents a coordinating ligand to stabilize the complex, the dissociation of L² is crucial to attain higher activity. The relative order for the ability for dissociation was estimated to be 2,6-lutidine < Bu₃P=O < DMSO < Ph₃P=O.³⁷

The molecular weight and polar monomer incorporation ratio varies depending on the monomers. Methyl acrylate

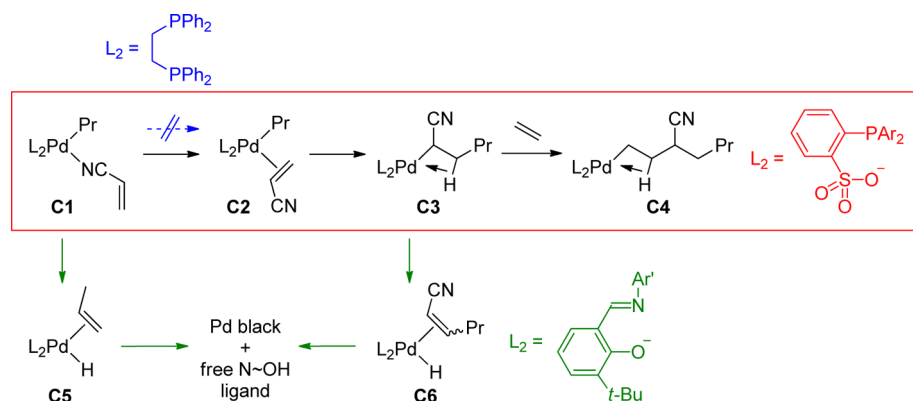
SCHEME 4. General Mechanistic Features of Ethylene/Polar Vinyl Monomer Copolymerizations by Palladium(II)/Phosphine–Sulfonate Complexes

was the first reported example of ethylene/polar monomer copolymerization by palladium/phosphine–sulfonate system.⁸ The incorporation of up to 52 mol % methyl acrylate was demonstrated, and homo-oligomerization of methyl acrylate by coordination–insertion mechanism was also observed.²³ Even acrylic acid is applicable to the copolymerization with ethylene and the content of acrylic acid could be varied between 3.0 and 9.6 mol %.^{26,27} Another important ester monomer, vinyl acetate, was successfully copolymerized with ethylene with vinyl acetate incorporation level of 0.6–1.9% using palladium/alkylphosphine–sulfonate complexes, either a mixture of Pd(dba)₂ and **[1i]H**, or isolated complexes **[(1i)PdMe]** (L = 2,6-lutidine, DMSO).²⁸ Higher M_n and incorporation ratio was achieved by using allyl acetate in place of vinyl acetate.³⁵ It is worth noting that the utilization of methacrylates is still a challenging issue.³⁸

In addition to ester monomers, the copolymerization of ethylene with acrylonitrile was realized to afford ethylene-rich linear copolymers of M_n up to 12,300 with acrylonitrile incorporation ratio of 2–9%.²⁹ Among vinyl halides, vinyl fluoride could be copolymerized with ethylene with **(1a, 1b, 1f)PdMe(pyridine)** producing highly linear polyethylene structures with molecular weights of $M_n = 4,500$ –14,500 with low incorporation of vinyl fluoride (0.09–3.6%).^{31a} Very recently, the first incorporation of vinyl chloride into a polyethylene via a clear insertion mechanism was accomplished using ligands **1i** and **1s**. Here, 2,1-insertion of vinyl chloride is competitive with ethylene insertion into Pd–H species, but not regarding incorporation in the growing polymer chain. This yields polymers with CH₃CHCl-endgroups (≤ 0.4 mol % incorporated vinyl chloride, $M_n = 3,900$ –14,400).^{31b} Vinyl ethers such as CH₂=CHOR (R = *t*-Bu, Et, Bu, Ph) were successfully copolymerized with ethylene by **(1b)PdMe(pyridine)** to give highly linear polyethylene containing 1–7% VE ($M_n = 900$ –4800).³² Various acrylamides and *N*-vinylpyrrolidone were also successfully incorporated in the main chain of linear polyethylene with various incorporation ratios.^{25,33}

A fairly comprehensive mechanistic picture of the decisive steps in these copolymerization reactions has emerged (Scheme 4).^{23,25,39} A combination of experimental (especially variable temperature NMR studies) and theoretical investigations revealed that, for electron-deficient polar vinyl monomers, H₂C=CHX copolymerization is inhibited by (1) chelating σ -X coordination of the last or penultimate incorporated repeat unit (**B4**, **B5**, and **B6**) that competes with π -olefin coordination for further chain growth, (2) slower insertion (k_4) into the α -X-substituted alkylpalladium formed by 2,1-insertion of comonomer (species **B4**) relative to nonsubstituted ethylene insertion products, and (3) σ -X coordination of free monomer via the functional group (**B3**), as already alluded to in Figure 1. While chelate opening (point 1) can be promoted by increasing the concentration of both monomers, thus more efficiently forming a copolymer of a given composition, this obviously does not apply to σ -X versus π -olefin coordination of the free monomer (point 3). The overall inhibition of polymerization by σ -coordination of functional groups qualitatively follows the trend ester < sulfones < nitrile \approx amides < sulfoxide.²⁵

Note that the reactions shown in Scheme 4 are all reversible deactivation steps that inhibit but do not fully shut down the copolymerization by palladium phosphine–sulfonate catalysts. Most recently, a range of irreversible deactivation reactions was also found to occur under polymerization conditions. Additionally, exchange of the P-bound aryl groups of the phosphinesulfonate for the growing alkyl chain results in formation of additional new active species.⁴⁰ For electron poor vinyl monomers, 2,1-insertion (k_1) is generally preferred over 1,2 insertion (k_2).² This selectivity can be overridden by appropriate bulky substituents, which destabilize the transition state of 2,1-insertion.⁴¹ However, bulky substituents also appear to disfavor incorporation of polar monomer versus ethylene with these catalysts (K_{eq} and k_1 , k_2 vs k_3) as a general trend.

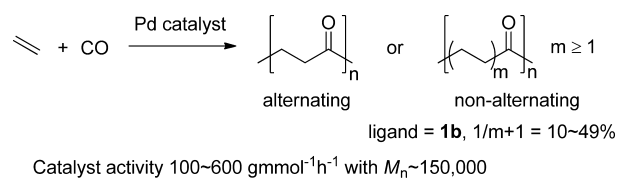
SCHEME 5. Comparison of Phosphine–Sulfonate, dppe, and Imine–Phenolate Ligands in the Insertion of Acrylonitrile to Alkylpalladium Species

The advantage of phosphine–sulfonate ligand over bisphosphine or imine–phenolate ligands was speculated on with the aid of DFT studies for the ethylene/acrylonitrile copolymerization (Scheme 5).³⁹ The most stable species was σ -acrylonitrile complex **C1** (=B3) and the highest energy transition state was the ethylene insertion to the α -cyanoalkylpalladium species, which is **C3** (=B4) to **C4** (=B6). The isomerization of σ -acrylonitrile complex **C1** (=B3) to π -complex **C2** (=B1) was easier with phosphine–sulfonate than with a bisphosphine ligand dppe, due to the more electron rich nature of the metal center in the neutral complex. Although this also applied to the imine–phenolate complex, in the case of imine–phenolate, the β -hydride elimination from **C1** to **C5** or from **C3** to **C6** resulted in the reductive O–H elimination causing catalyst decomposition to the free phenol ligand.

3. Nonalternating Ethylene/CO Copolymerization

While ethylene-rich highly branched ethylene/CO copolymers were obtained via radical copolymerization, the metal-catalyzed ethylene/CO copolymerization generally produces completely alternating linear copolymers (Figure 3, the left product).⁴² Since the completely alternating γ -polyketone generally suffers from low processability due to its insolubility in common solvents and very high T_m (≈ 260 °C), incorporation of a small amount of propylene in addition to ethylene is often used for the production of melt processable copolymers. The nonalternating, ethylene rich linear ethylene/CO copolymer (Figure 3, the right product) is expected to be a substitute for such ethylene/propylene/CO terpolymers.

The first example of nonalternating linear ethylene/CO copolymer having successive ethylene incorporation was reported by Drent et al.⁴³ By using a mixture of Pd(OAc)₂ and

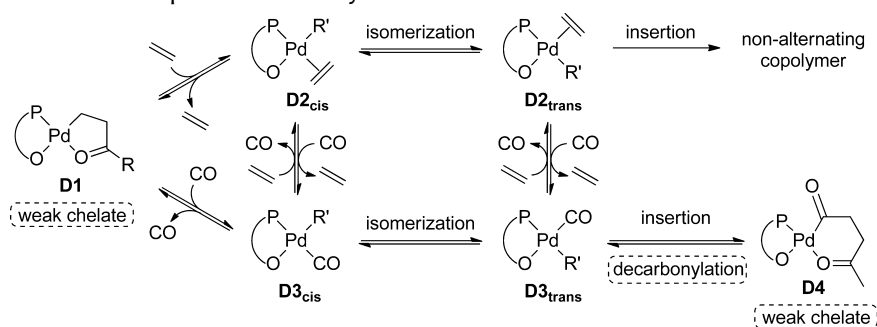
**FIGURE 3.** Alternating and nonalternating ethylene/CO copolymers.

a phosphine–sulfonate ligand (**1b**, **1d**), the CO content in the produced ethylene/CO nonalternating copolymers could be varied in range of 42–49%. A subsequent investigation showed that the usage of well-defined single component catalysts can enhance the ethylene incorporation and achieve a higher degree of nonalternation. The lower nonalternation selectivity in the former case is due to the formation of bischelated [P–O]₂Pd complexes, which favor the production of strictly alternating ethylene/CO copolymer.⁴⁴ In contrast to the [P–O]-chelated complexes, the resulting nonchelated bisphosphine complex is only capable of the alternating copolymerization.

Since the discovery, many investigations on nonalternating linear ethylene/CO copolymerization have been performed based on phosphine–sulfonate ligands.^{45–48} For example, the introduction of a bulkier *o*-alkoxy group or *o*-methyl group on the aryl substituent led to a significant increase in the amount of ethylene incorporation into the copolymer up to 90%.⁴⁷ Copolymers with CO contents of 35%⁴⁴ and 10%⁴⁷ exhibited melting temperatures of 220 and 118 °C, respectively.

The origin of the multiple ethylene units was investigated through experimental^{46,48} and theoretical⁴⁹ studies (Scheme 6). The formation of multiple ethylene units can be understood as a result of ethylene insertion into the five-membered palladacycle **D1**. This insertion is facilitated for neutral palladium phosphine–sulfonate complexes relative to

SCHEME 6. Plausible Explanations for Multiple Insertion of Ethylene



cationic palladium dppp species because formation of Pd–O chelates by coordination of the carbonyl group on the growing polymer chain is less favorable in the former case. This difference is manifested in two ways: (i) The relative stability of chelate complexes **D1** is lower than that of the corresponding cationic complexes bearing a dppp ligand and opening of the chelate structure of **D1** by ethylene is therefore easier.^{46,49} The ratio of the binding affinities of carbon monoxide and ethylene to the palladium chelate complex **D1** was also determined by NMR spectroscopy to be ~50:1 at 25 °C in the phosphine–sulfonate-based system, which is unusually smaller than that in cationic complexes (~10⁴:1).⁴⁸ (ii) The decarbonylation of Pd–acyl complexes bearing a phosphine–sulfonate ligand (**D4**) is more favorable than that of cationic Pd–acyl complexes bearing a dppp ligand due to the relative instability of the six-membered chelate structure (**D4**) in the former case.^{48,49} Furthermore, double ethylene insertion does not necessarily result in chain transfer for palladium phosphine–sulfonate catalysts.²

4. Polar Monomer/CO Alternating Copolymerization

Another unique feature of the palladium phosphine–sulfonate complex is that the catalyst mediates alternating copolymerization of polar monomers with CO, which had never been accomplished by any other method. The alternating copolymer of vinyl acetate and CO was first obtained using a mixture of Pd(dba)₂ and phosphonium–sulfonate (**1a**, **1b**).⁵⁰ The head-to-tail selectivity was found to be less controlled, which suggests that insertion of vinyl acetate into the acyl–palladium bond may occur in both the 2,1- and 1, 2-mode. In the following report, it was found that the regio- and stereoselectivity of the vinyl acetate/CO copolymerization can be enhanced by using a *P*-chiral phosphine–sulfonate (**1t**).⁵¹ The optically active ligand **1t** enabled

SCHEME 7. Asymmetric Alternating Copolymerization of Vinyl Acetate/CO and Methyl Acrylate/CO

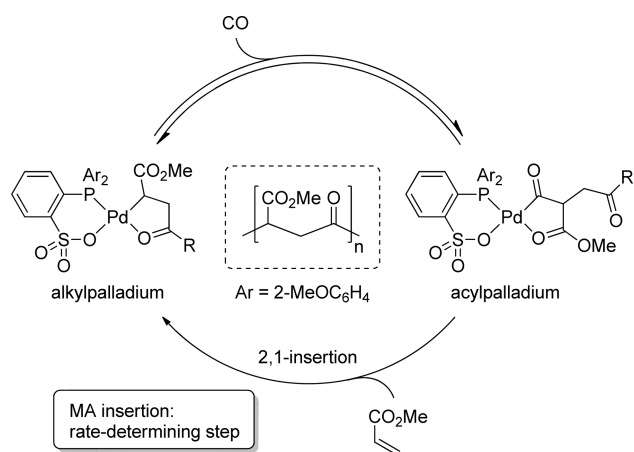
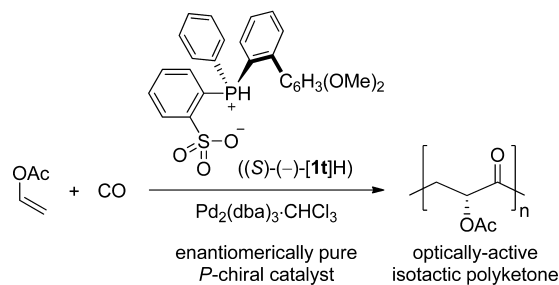
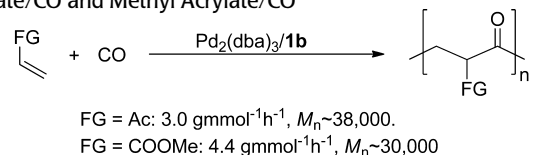
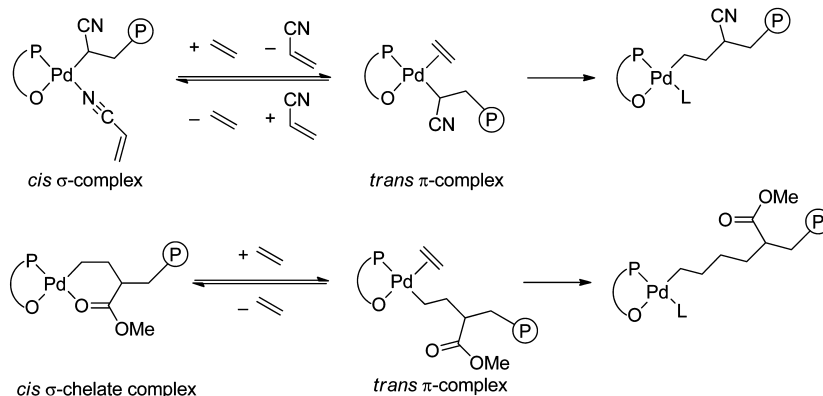


FIGURE 4. Summary of the mechanism of the copolymerization of methyl acrylate with CO.

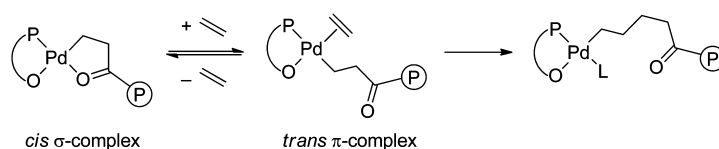
the asymmetric copolymerization of vinyl acetate/CO (Scheme 7). The alternating copolymerization of methyl acrylate with CO was also accomplished by using the same catalytic system.^{51,52} Unlike vinyl acetate/CO, the regio-chemistry was strictly regulated in both of **1b** and **1t**,

SCHEME 8. Key Steps in the Unique Reactions First Realized by Palladium Phosphine–Sulfonate Systems

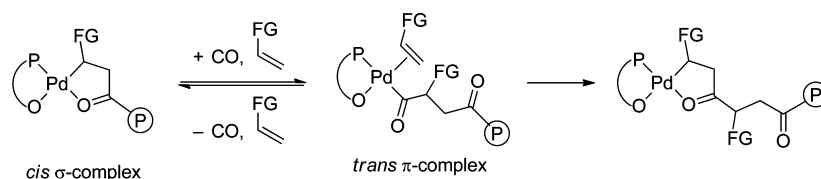
Section 2. Copolymerization of polar vinyl monomers (e.g. acrylonitrile; methyl acrylate) with ethylene



Section 3. Non-alternating copolymerization of ethylene with CO



Section 4. Copolymerization of polar vinyl monomers (methyl acrylate or vinyl acetate) with CO



implying that the insertion of methyl acrylate into the acyl–palladium bond occurs only in the 2,1-insertion mode.

The mechanism for the alternating copolymerization of methyl acrylate with carbon monoxide catalyzed by palladium phosphine–sulfonate complexes is summarized in Figure 4.⁵² Experimental and theoretical investigations suggested that the coordination–insertion of carbon monoxide into alkylpalladium complex is reversible. After coordination of methyl acrylate, insertion takes place exclusively in 2,1-fashion resulting in the regiocontrolled structure of the copolymer. The rate-determining step is the olefin insertion step as is often the case with copolymerization of olefins with CO.

5. What is Special about Phosphine–Sulfonate Ligands?

In this section, we provide a brief overview of the mechanistic features of the palladium phosphine–sulfonate system and identify several issues which may be important for its characteristic reactivity. Comparisons with cationic palladium complexes bearing diphosphine or α -diimine ligands are mainly considered. Scheme 8 summarizes the key steps

of the polymerization reactions which were never achieved without palladium phosphine–sulfonates, as discussed in sections 2–4. We focus our attention on the fact that the most stable intermediates in these reactions are “*cis* σ -complexes” and the key insertion reactions proceed from “*trans* π -complexes”, where “*cis*” and “*trans*” denote the location of alkyl group relative to phosphorus atom.

In the copolymerization of polar vinyl monomers with ethylene (section 2), ethylene insertion was possible even in the presence of heteroatom coordination (free monomer, multinuclear aggregated complexes, or intramolecular chelation in the insertion products). The ethylene insertion takes place from the “*trans* π -complex” which is in equilibrium with the more stable “*cis* σ -complex”. The palladium phosphine–sulfonate system also enabled the nonalternating copolymerization of ethylene with CO (section 3). This is because ethylene insertion can take place from the most stable chelate complex, “*cis* σ -complex” via the intermediate “*trans* π -complex”. In polar monomer/CO copolymerization (section 4), the rate-determining step is the olefin insertion step and other steps (CO coordination–insertion and

olefin coordination) were under equilibrium. In turn, the reaction starts from the most stable "cis σ -complexes" and "trans π -complexes" are formed under equilibrium, which is prerequisite for the olefin insertion. The *cis*–*trans* isomerization seems to occur readily in all of these reactions.¹⁸ In addition to the isomerization of *tetra*-coordinated species, *cis*–*trans* isomerization can take place concomitantly with ligand exchange via *penta*-coordinate complexes when π -ligands are involved.⁵³

The foregoing discussion highlights the key role that the "trans π -complexes" play in monomer insertion for phosphine–sulfonate palladium catalysts. Because of their

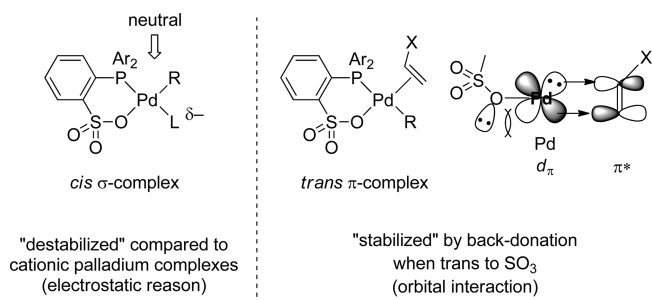


FIGURE 5. Plausible interpretation of the features of palladium phosphine–sulfonate system. L = heteroatom ligand, X = H or functional groups, and R = alkyl or acyl.

early transition state characters, stabilization of the "trans π -complexes" should also stabilize the subsequent olefin insertion transition states, those are the rate-determining transition states, in all reactions drawn in Scheme 8. In addition, the stabilization of "trans π -complexes" leads to the increase in their concentration.

In this context, two factors that affect the relative stability of the "trans π -complexes" in phosphine–sulfonate systems can be considered: charge effects and orbital interactions. For further discussion, it is important to note that electrostatic factors (charge) and the orbital interaction effects can be separated theoretically by energy decomposition analysis (EDA)⁵⁴ as well as by the Klopman–Salem equation.⁵⁵

We first discuss electrostatic effects. The stability of σ -heteroatom-coordinated complexes of neutral palladium complexes is lower than that of their cationic analogues.² Thus, the net neutral charge of phosphine–sulfonate complexes promotes dissociation of σ -heteroatom-coordinated ligands from the "cis σ -complex" (Figure 5, left).³⁹ This can be considered as "destabilization" of "cis σ -complexes", that is, relative "stabilization" of "trans π -complexes", electrostatically.⁵⁶

Next, we discuss orbital interaction effects. π -Back-bonding interactions may also influence the stability of the "trans

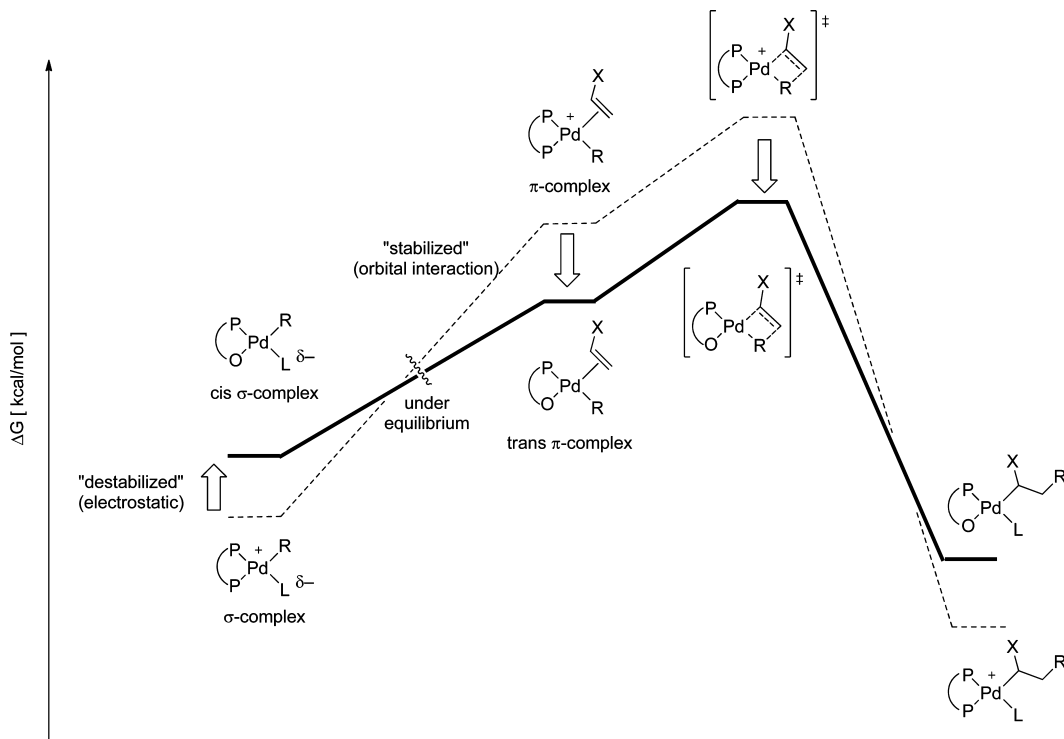


FIGURE 6. Potential energy surfaces of simplified reaction sequences by palladium phosphine–sulfonate (bold line) and palladium diphosphines (dotted line). L = heteroatom ligand, X = H or functional groups, and R = alkyl or acyl. The influence of electrostatic factor in "cis σ -complex" and orbital interaction in "trans π -complex" is described.⁵⁶

π -complex." The back-donation from palladium to π -acceptor monomers such as olefins and CO is enhanced when the *trans* ligand is sulfonate (Figure 5, right, "*trans* π -complex").⁵² The efficient back-donation found in a "*trans* π -complex" was attributed to a stereoelectronic effect of the sulfonate moiety. In other words, the SO₃ group does not withdraw the π -electrons from palladium but, instead, repulsion between lone pairs on the ligated oxygen and π -electrons of palladium facilitates the back-donation to π -acceptor monomers. In contrast, when the *trans* ligand is phosphine ("*cis* π -complex"), the degree of back-donation is similar to that of a cationic palladium dppe complex.⁵² In addition, the TS for the subsequent olefin insertion is lowered in the phosphine–sulfonate complex because formation of an alkylpalladium bond at *trans* to the sulfonate is favorable owing to the weaker *trans* influence of a sulfonate than that of a phosphine.

A simplified potential energy surface for these reactions for neutral phosphine–sulfonate and cationic diphosphine systems is provided in Figure 6. The stable "*cis* σ -complex" is "destabilized" in the phosphine–sulfonate system by the electrostatic effect noted above. In other words, the dissociation of L (heteroatom ligand) is facilitated. In addition, the intermediate "*trans* π -complex", is "stabilized" in the phosphine–sulfonate system by back-donation from palladium to the π -acceptor monomer. By these two effects, the concentration of "*trans* π -complex" is increased in the case of phosphine–sulfonate. This is beneficial for the next insertion step which is promoted because of its early transition state character. In addition, strong acidity of the conjugate acid of the anionic ligand may be essential to prevent catalyst decomposition via β -hydride elimination (Scheme 5).³⁹

Conclusion and Outlook

Since the advent of palladium phosphine–sulfonate catalysts, syntheses of various novel polymers were accomplished. We overviewed these reactions to reach unified interpretations: the unique reactivity originates from the neutral net charge and the enhanced back-donation. In addition to these charge effect and orbital interaction effect mainly discussed in this account, the steric effects of bulky phosphines also play a key role in productivity, molecular weight of the polymer, and regio- and stereoselectivity as discussed in sections 2–4. Clearly, finding catalysts where reaction rates, productivities, and molecular weights are sufficiently high for commercial viability is a still remaining challenge in this field. To date, several novel ligands have been synthesized inspired by the knowledge of phosphine–sulfonate ligands replacing either the phosphine or the

sulfonate moieties by other groups. Very recently, cationic diphosphine monoxide ligands were reported as an alternative to the phosphine–sulfonate to mediate the copolymerization of ethylene and polar monomers.⁵⁷ Further studies to reveal the common features between the phosphine–sulfonates and biphosphine monoxide would open the next stage of ligand design.

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FOOTNOTES

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