Synthesis of anionic methylpalladium complexes with phosphine–sulfonate ligands and their activities for olefin polymerization†

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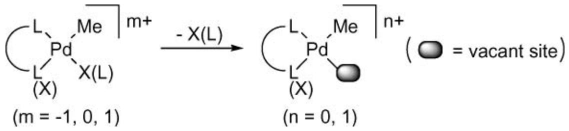
Reaction of diarylphosphinobenzene-2-sulfonic acids with tertially amines, followed by addition of [PdMeCl(cod)], provided anionic methylpalladium(II) complexes with bidentate phosphine–sulfonate ligands, which show high activity for copolymerization of ethylene with methyl acrylate.

Olefin polymerization with late transition-metal complexes has attracted much interest[1] due to their lower oxophilicity relative to early transition metals, and many catalysts have been developed to polymerize various olefins and to copolymerize non-polar olefins with carbon monoxide[2] or with polar olefins.[3] In order to achieve higher activity and further understanding of the reaction mechanism, structurally-characterized organometallic complexes have been isolated in many cases before the polymerization. In the case of palladium catalysts with bidentate ligands, the corresponding monomethyl complexes[4] have generally been recognized as convenient catalyst precursors, because simple generation (Scheme 1) of a vacant site at the *cis*-position to the methyl group, followed by coordination of an olefin, would readily initiate the coordination polymerization. These methylpalladium complexes have also been frequently used for mechanistic investigation of the copolymerization.

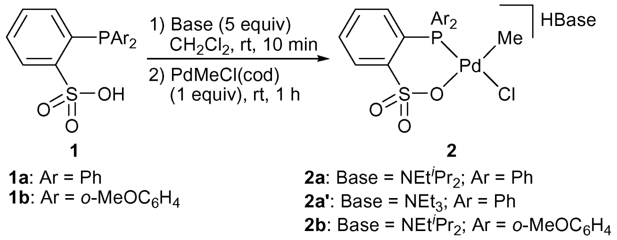


Scheme 1 Generation of a vacant site on monomethyl palladium complexes with bidentate ligands.

In the past decade, significant efforts have been devoted to developing late transition-metal catalysts capable of producing highly functionalized polymers by copolymerization of non-polar olefins with readily-available polar olefins. For example, Brookhart's diimine palladium complexes can copolymerize ethylene or propylene with polar vinyl monomers such as methyl acrylate.[3c,d] The copolymers produced were highly branched and methyl acrylate was incorporated only at the chain end.

In 2002, Pugh and coworkers have developed palladium catalysts which can produce unique polymers such as a highly linear copolymer of ethylene and alkyl acrylates[5a] and a non-perfectly alternating copolymer of ethylene and CO.[5b] In their reports, the palladium catalysts were formed *in situ* by combination of diarylphosphinobenzene-2-sulfonic acid with $Pd(dba)_2$ or $Pd(OAc)_2$. Very recently, Rieger *et al.* reported the first examples of structurally-characterized palladium complexes with bidentate phosphine–sulfonate ligands, which gave higher catalytic activity and a higher number of extra ethylene insertions in the non-perfectly alternating copolymerization of ethylene and CO.[6] To improve the catalyst system, our group has concurrently attempted to synthesize palladium complexes with diarylphosphinobenzene-2-sulfonic acids. Herein we report the first synthesis of methylpalladium(II) complexes with bidentate phosphine–sulfonate ligands. Preliminary results for the copolymerization of ethylene and methyl acrylate are also described.

Treatment of diphenylphosphinobenzene-2-sulfonic acid **1a** with diisopropylethylamine in dichloromethane, followed by addition of PdMeCl(cod), afforded the anionic methylpalladium complex **2a** in 94% yield (Scheme 2).[7] Similarly, the reaction of *o*-methoxyphenyl substituted ligand **1b** gave methylpalladium complex **2b** in 92% yield. When triethylamine was used instead of diisopropylethylamine for the reaction of **1a**, the corresponding methylpalladium complex **2a′** was also obtained in 89% yield.



Scheme 2 Preparation of anionic methylpalladium(II) complexes with phosphine–sulfonate ligands.

The structure of **2a′** was determined by X-ray crystallography‡ to reveal that the phosphine–sulfonate ligand coordinates to palladium in a bidentate fashion, similar to Rieger's dicyclopentadienylethoxy palladium complex (Fig. 1). The palladium complex adopts a square planar geometry and the methyl group is located at the *trans*-position to the oxygen atom of the sulfonate. It is interesting that a chloride ion is bound to the palladium to form an anionic methylpalladium complex, considering simple loss of the chloride ion would give a neutral complex. The synthesis of **2a** can also be performed in acetonitrile, meaning that acetonitrile did not replace the chloride ion on the palladium. Anionic methylpalladium(II) complexes are relatively rare, and as far as we

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† Electronic supplementary information (ESI) available: Synthetic procedures and characterization data for **2a**, **2a′** and **2b**; X-Ray data for **2a′**. See DOI: 10.1039/b512452m

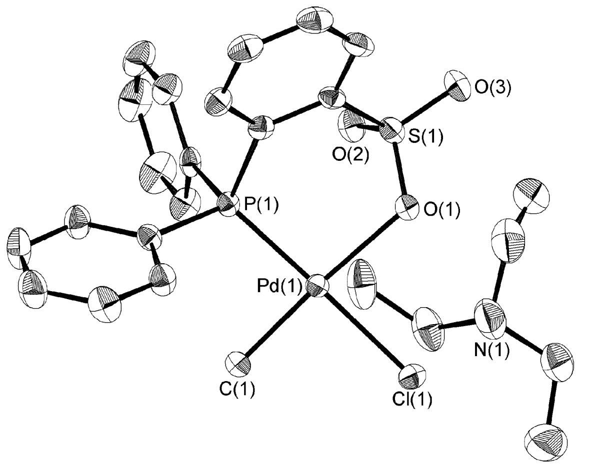
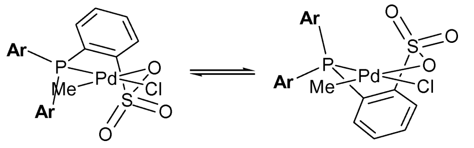


Fig. 1 Structure of complex **2a′**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at the 50% probability level. Selected bond lengths (Å) and angles (Å): Pd(1)–C(1) 2.051(4); Pd(1)–O(1) 2.184(3); Pd(1)–P(1) 2.2195(12); Pd(1)–Cl(1) 2.3997(12); Cl(1) · · · N(1) 3.268(5).

know, all of the previously reported examples possess a dianionic ligand and a methyl group on palladium.[8] The nitrogen atom of the ammonium ion is in close contact with the chloride (3.27 Å) and the ammonium hydrogen should be located at a reasonable position for a hydrogen bond with the chloride ligand.

Notable temperature dependence was observed in the ^{1}H NMR spectra of complex **2b**. At room temperature the two methoxy groups of **2b** gave one sharp singlet at 3.58 ppm, which split into two broad signals at 3.49 and 3.66 ppm on cooling at −60 °C. This behavior can be accounted for by considering the conformational interchange of the aryl groups which are arranged in an unsymmetric structure as disclosed by the crystallographic study on complex **2a′** (Scheme 3).



Scheme 3 Conformational interchange of the aryl groups of **2b**.

Copolymerization of ethylene and methyl acrylate was then investigated with catalyst **2** (Table 1). When the copolymerization was carried out at 80 °C with NaBAr$^f_4$, **2b** showed higher activity than **2a**, as is consistent with Pugh's result (entry 2, 3).[5a,9,10] Screening of additives such as NaBAr$^f_4$ and AgOTf was performed to examine the effectiveness in removing the chloride ion from the palladium metal of **2b**. Effect of the additives on the copolymerization was quite notable. For example, the catalytic activity of the copolymerization with NaBAr$^f_4$ at 80 °C (entry 2) was twice as high as that reported by Pugh with Pd(dba)$_2$ and **1b** in the same reaction conditions,[5a] while the reactions with AgOTf or no additive showed much lower activities (entry 6, 8). However, the highest comonomer incorporation was observed with no additive, and particularly, the reaction at 80 °C provided the copolymer with 16% of methyl acrylate incorporated in the polymer chain (entry 8). An increase in reaction temperature generally leads to an enhancement in catalytic activity and a reduction of polymer molecular weight, but no gain or a decrease in the activity was observed at high temperature possibly due to decomposition of the catalyst (entry 1, 6, 8). The highest molecular weight (12 500) was obtained in the reaction with no additive at 50 °C for 72 h. Addition of galvinoxyl had little influence on the activity of the reaction with no additive at 80 °C, while significantly reduced activity (4 g mmol^{-1} h^{-1}) was observed for the reaction with NaBAr$^f_4$. Espinet and co-workers have reported that galvinoxyl not only serves as a radical trap but can react with a Pd–H bond.[11] The observed reduction of activity with NaBAr$^f_4$ can be attributed to the frequent chain transfer reaction *via* β-hydride elimination and generation of a Pd–H bond, relative to those in the reaction with no additive.

In conclusion, the first syntheses of methylpalladium(II) complexes with phosphine–sulfonate bidentate ligands were achieved. An X-ray structure of **2a′** revealed that the complexes were rare examples of anionic methylpalladium(II) complexes. We further examined the copolymerization of ethylene and methyl acrylate with the catalysts and found interesting effects of additives on the catalytic activity, the molecular weight and the degree of methyl acrylate incorporation. These preliminary copolymerization results indicate that further examination of additives, ligands, bases used to prepare the catalysts, and reaction conditions would lead to an improved catalyst system for production of the unique highly linear copolymer of ethylene and methyl acrylate.

Table 1 Copolymerization of ethylene and methyl acrylate with **2**[a]

Entry	Catalyst	Additive	Temp/°C	Yield/g	Activity/g mmol^{-1} h^{-1}	TOF/h^{-1}[b]	Methyl acrylate incorporation (mol%)[c]	M_n	M_w/M_n
1	**2b**	NaBAr$^f_4$ (0.01 mmol)	90	2.59	17	490	13	3200	1.64
2	**2b**	NaBAr$^f_4$ (0.01 mmol)	80	2.61	17	490	13	4100	1.87
3	**2a**	NaBAr$^f_4$ (0.01 mmol)	80	0.94	6.3	200	7	2700	1.46
4	**2b**	NaBAr$^f_4$ (0.01 mmol)	70	2.00	13	400	9	6200	1.54
5	**2b**	NaBAr$^f_4$ (0.01 mmol)	60	1.40	9.3	290	8	6100	2.44
6	**2b**	AgOTf (0.02 mmol)	80	0.49	3.3	90	14	2400	1.54
7	**2b**	AgOTf (0.02 mmol)	60	0.96	6.4	180	14	4500	1.61
8	**2b**	None	80	0.24	1.6	43	16	4500	1.61
9	**2b**	None	70	0.30	2.0	55	15	6800	1.61
10	**2b**	None	50	0.19	1.3	35	14	8500	2.11
11	**2b**[d]	None	50	0.57	0.8	22	13	12 500	1.79

[a] Conditions: 0.01 mmol of catalyst **2**; ethylene pressure, 3.0 MPa; 2.5 mL of methyl acrylate; solvent, 2.5 mL of toluene; reaction time, 15 h. [b] TOF (turnover frequency): mol olefin/(mol Pd·h). [c] Determined by ^{1}H NMR spectroscopy. [d] Copolymerization was carried out for 72 h.

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Notes and references

‡ Crystal data for **2a′**: $C_{25}H_{33}ClNO_3PPdS$, $M = 600.40$, monoclinic, $a = 14.186(6)$ Å, $b = 10.679(5)$ Å, $c = 17.678(8)$ Å, $\beta = 92.549(2)°$, $V = 2675.5(19)$ Å^3, $T = 120(2)$ K, space group $P2_1/c$, $Z = 4$, μ(Mo-Kα) = 0.958 mm^{-1}, 14896 reflections measured, 4364 unique ($R_{int} = 0.0255$) which were used in all calculations. The final w$R(F_2)$ was 0.1208 (all data). CCDC reference number 283231. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b512452m

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9 The ^{1}H NMR spectrum of the volatile materials collected by vaccum transfer of the crude mixture showed no byproduct such as oligomers of ethylene and/or methyl acrylate.

10 The activity of the reaction with **2b** for 3 h was 29 g mmol^{-1} h^{-1}. The copolymerization reaction slows down as it proceeds and the amounts of the remaining monomers decrease.

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