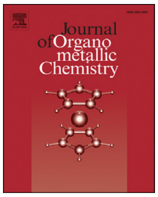
Journal of Organometallic Chemistry 804 (2016) 118–122

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem



Synthesis, structures, and norbornene polymerization behavior of palladium methyl complexes bearing N-heterocyclic carbene-sulfonate ligands

Minliang Li [a], Haibin Song [a], Baiquan Wang [a, b, c, *]

[a] State Key Laboratory of Elemento-Organic Chemistry, College of Chemistry, Nankai University, Tianjin 300071, People's Republic of China
[b] Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Nankai University, Tianjin 300071, People's Republic of China
[c] State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, People's Republic of China

ARTICLE INFO

Article history:
Received 14 October 2015
Received in revised form
26 December 2015
Accepted 31 December 2015
Available online 5 January 2016

Keywords:
Norbornene
Vinyl polymerization
NHC-sulfonate ligand
Palladium methyl complex

ABSTRACT

A series of N-heterocyclic carbene-sulfonate (NHC-sulfonate) palladium methyl complexes **2a**–**d** were synthesized from the reaction of NHC-sulfonate ligands with Ag_2O and $Pd_2(\mu\text{-Cl})_2Me_2(2,6\text{-lutidine})_2$ in good yields. All these complexes were fully characterized by ^1H and ^{13}C NMR, elemental analysis, and high-resolution mass spectrometry (HRMS). The molecular structure of the representative complex **2a** was also determined by single-crystal X-ray diffraction analysis. Upon activation with either methylaluminoxane (MAO) or $[Ph_3C]^+[B(C_6F_5)_4]^-$, all the palladium methyl complexes showed excellent catalytic activities [up to 10^8 g of polynorbornene (PNB) (mol of Pd)$^{-1}$ h^{-1}] in the vinyl polymerization of norbornene.

1. Introduction

In the last few decades, the polymerization of norbornene (NBE) has attracted much research interest. Polynorbornene (PNB) with different structures and properties can be obtained via three corresponding pathways: ring-opening metathesis polymerization (ROMP), cationic or radical polymerization, and vinyl polymerization [1]. In comparison to PNB prepared by ROMP and cationic or radical polymerization, vinyl-type PNB owns unique physical properties, such as high chemical resistance, good UV resistance, low dielectric constant, high glass transition temperature, excellent transparency, and good mechanical strength [1,2]. Therefore the vinyl polymerization of NBE has been the subject of many studies. The vinyl polymerization of NBE was first reported by Sartori et al. [3] in 1963 and subsequently great deals of transition metal complexes, such as titanium [4], zirconium [5], vanadium [6], chromium [7], iron [8], cobalt [9], rhodium and iridium [10], nickel [11], palladium [12], and copper [13], have been used as catalysts for NBE vinyl polymerization. However, in order to obtain this interesting class of polymers with new structures, the design of new catalysts for vinyl polymerization of NBE is still required.

Recently, a kind of phosphino-sulfonate ligands has received considerable attention. It was widely used for palladium-catalyzed polymerization of ethylene and copolymerization of ethylene with a variety of functionalized monomers [14]. The use of a stronger donor NHC in place of the phosphine may provide enhanced electronic unsymmetry and lower metal electrophilicity and will be potentially suitable for catalysis. However, reports of such sulfonate-tethered NHC complexes are really rare due to the difficulty in the synthesis of the ligands [15]. Nozaki's group reported the synthesis of the palladium alkyl complexes in which the NHC and sulfonate units were linked by a methylene spacer [16]. Jordan and co-workers reported saturated NHC-arenesulfonate palladium alkyl complexes and studied the dynamic properties and insertion reactivities [17]. More recently, we succeeded in developing a series of unsaturated NHC-sulfonate ligands and their C(sp^3), N-chelated and C(sp^2), N-chelated palladacycles, which showed high activities for the vinyl polymerization of norbornene in the presence of MAO. The Pd–C(sp^3) bond is more active for insertion of NBE than the Pd–C(sp^2) bond, as a result, the C(sp^3), N-chelated palladacycles showed higher activities by about one order of magnitude in

---

[*] Corresponding author. State Key Laboratory of Elemento-Organic Chemistry, College of Chemistry, Nankai University, Tianjin 300071, People's Republic of China.
E-mail address: bqwang@nankai.edu.cn (B. Wang).

http://dx.doi.org/10.1016/j.jorganchem.2015.12.045
0022-328X/

comparison with the C(sp^2), N-chelated palladacycles [18]. Compared with the Pd–C(sp^3) bond in C(sp^3), N-chelated palladacycles, the Pd–Me bond is more active and may possess higher activities. Herein, we synthesize and characterize a series of NHC-sulfonate palladium methyl complexes. The vinyl polymerization of norbornene with these complexes is also studied in the presence of MAO or $[Ph_3C]^+[B(C_6F_5)_4]^-$.

2. Results and discussion

2.1. Synthesis of NHC-sulfonate palladium methyl complexes

A series of NHC-sulfonate ligands were synthesized according to the literature [18]. Treatment of the NHC-sulfonate ligands with Ag_2O and $Pd_2(\mu\text{-}Cl)_2Me_2(2,6\text{-lutidine})_2$ yielded the desired NHC-sulfonate palladium methyl complexes in good yields (Scheme 1). All these complexes are fully characterized by ^1H and ^{13}C NMR, HRMS, and elemental analysis. In their ^1H NMR spectra, the signals of the Pd–CH_3 group show a sharp singlet and appeared at 0.10 (**2a**), 0.04 (**2b**), −0.03 (**2c**), and −0.03 (**2d**) ppm. The characteristic signals of the Pd–CH_3 group in their ^{13}C NMR spectra appeared at −15.1 (**2a**), −14.4 (**2b**), −14.9 (**2c**), and −15.0 (**2d**) ppm. For NHC-sulfonate palladium methyl complexes **2a–d**, only single isomer could be observed from the NMR spectra, which is different from Jordan's report [17].

The molecular structure of palladium methyl complex **2a** was determined by single crystal X-ray diffraction analysis. As shown in Fig. 1, complex **2a** possesses a seven-membered {C–O}Pd chelate ring, which adopts a twist-boat conformation [19] with an angle of 81.1(5)° between the Pd square plane [O(2)–Pd(1)–C(11)] and the backbone plane of the $\{C–O\}^-$ ligand [S(1)–C(19)–C(14)–N(2)]. The NHC ligand is rotated out of the Pd square plane by 68.1(8)°, as measured by the angle between the N(1)–C(11)–N(2) and O(2)–Pd(1)–C(11) planes. The 2,6-lutidine plane is nearly perpendicular to the Pd square plane [O(2)–Pd(1)–C(11)] with an angle of 86.9(3)°. The Pd–C(NHC) bond length is 1.980(2) Å, which is much shorter than the corresponding value in the saturated NHC-sulfonate palladium methyl complexes [17].

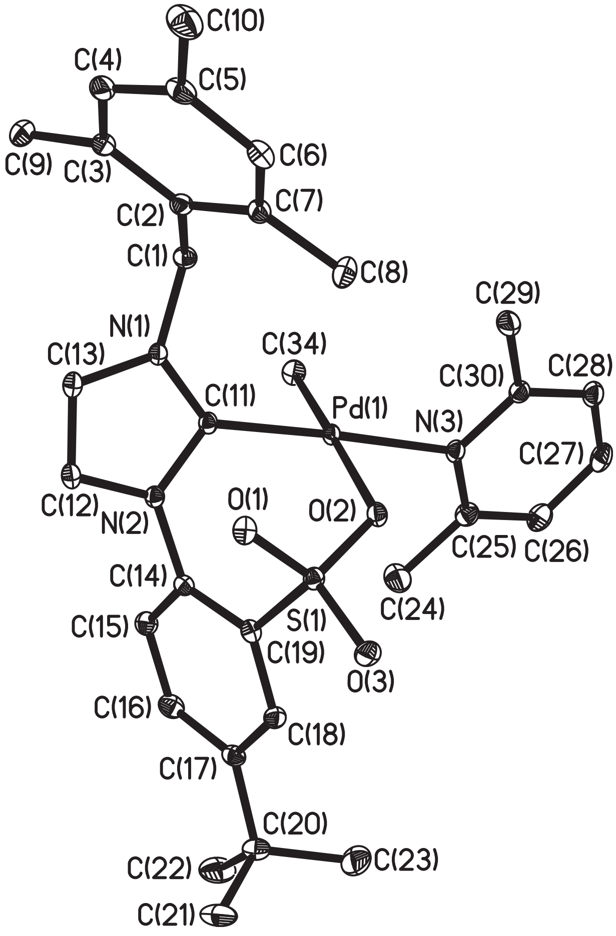


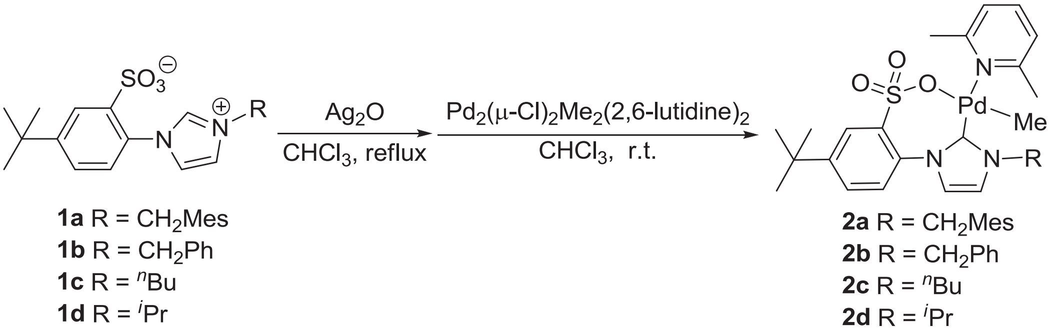
Fig. 1. ORTEP diagram of **2a**. Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Pd(1)–C(11) 1.980(2), Pd(1)–C(34) 2.034(3), Pd(1)–N(3) 2.112(2), Pd(1)–O(2) 2.2200(17), S(1)–O(1) 1.4469(18), S(1)–O(2) 1.4811(18), S(1)–O(3) 1.4514(18), C(11)–Pd(1)–C(34) 89.44(10), C(11)–Pd(1)–N(3) 176.53(9), C(34)–Pd(1)–N(3) 89.09(9), C(11)–Pd(1)–O(2) 91.78(8), C(34)–Pd(1)–O(2) 176.91(9), N(3)–Pd(1)–O(2) 89.54(7).

2.2. Norbornene polymerization

In order to explore the potential application of these N-heterocyclic carbene-sulfonate palladium methyl complexes, the vinyl polymerization of norbornene with these complexes was studied. Preliminary experiments were carried out with all of the NHC-sulfonate palladium methyl complexes in the absence of cocatalyst, but no polymer was obtained. In order to find suitable cocatalyst, complex **2a** was explored with various agents such as Et_2AlCl, Et_3Al, $^iBu_3Al$, MAO, and $[Ph_3C]^+[B(C_6F_5)_4]^-$. We found that both MAO and $[Ph_3C]^+[B(C_6F_5)_4]^-$ could efficiently activate the precatalyst.

2.2.1. Norbornene polymerization in the presence of MAO

Regarding the catalytic system with MAO, complex **2a** was typically investigated as a model precatalyst to optimize the polymerization parameters such as temperature, the molar ratio of Al/Pd, and time, and the detailed results were summarized in Table 1. The reaction temperature strongly affected the catalytic activity.



Scheme 1. Synthesis of the NHC-sulfonate palladium methyl complexes.