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Palladium complex with tetrahydronaphthyl-substituted diimine ligand as a catalyst for polymerization of norbornenes and diazoacetates

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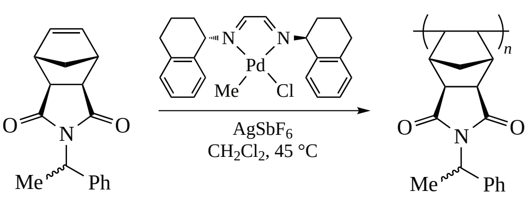
New methylpalladium chloride complex with bulky *N*,*N'*-bis(1,2,3,4-tetrahydro-1-naphthyl)-substituted glyoxal diimine ligand was obtained. This complex was found to be an efficient catalyst for vinyl-addition polymerization of norbornene derivative and for polymerization of a diazoacetate, giving polycarbenes with side polar functionalities.



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Diimine complexes of nickel and palladium are unique (pre)-catalysts for olefin polymerization among late transition metal-complexes since catalytic systems based on them can produce high-molecular weight products from ethylene and α-olefins.[1] In addition, palladium diimine complexes also exhibit low oxophilicity and good tolerance to various polar functionalities that make these complexes in demand in the synthesis of various polyolefins.[2] Since the first report describing the synthesis and usage of diimine palladium complexes as catalysts for olefin polymerization,[3] enormous numbers of such-type complexes were developed, and their olefin polymerization activity was estimated.[2(*c*),4] The activity of these complexes and the structure of resulting polymers (*e.g.*, the formation of a linear or branched polymers[5]) were tuned by the substitution at α-carbon atoms and/or by modifications of groups at the imine nitrogen atoms.[2(*b*),6] As monomers for studying the activity of such complexes and their olefin polymerization behavior, ethylene and α-olefins were generally used and relatively low attention was paid to the polymerization of other types of monomers over diimine palladium complexes.[7]

Cycloolefins, especially norbornene derivatives, represent an attractive group of monomers for preparing new polymeric materials with high glass transition temperatures, good chemical and thermal stability, and high transparency.[8] If vinyl-addition polymerization of unsubstituted norbornene is a well-developed process,[9] the involvement of norbornenes containing polar functionalities in this type of polymerization is a challenge[10] due to the absence of catalysts similar to well-defined Grubbs and Schrock catalysts for metathesis polymerization. Therefore, the search for new efficient catalytic systems for vinyl-addition polymerization of norbornene derivatives is highly demanded. Herein, we report the preparation of a new methylpalladium chloride complex bearing diimine ligand with bulky 1,2,3,4-tetrahydro-1-naphthyl groups and the estimation of its catalytic activity in vinyl-addition polymerization of *N*-substituted norbornene-5,6-dicarboximide. This type of monomers among norbornene derivatives was chosen due to the lack of the information about their vinyl-addition polymerization.

The desired diimine Pd-complex was obtained in two steps from glyoxal and (*S*)-(+)-1,2,3,4-tetrahydro-1-naphthylamine in a good yield (Scheme 1). The diimine ligand **1** was also isolated as an individual solid, and its structure was confirmed by X-ray analysis [Figure 1(*a*)].† Earlier compound **1** was described as a

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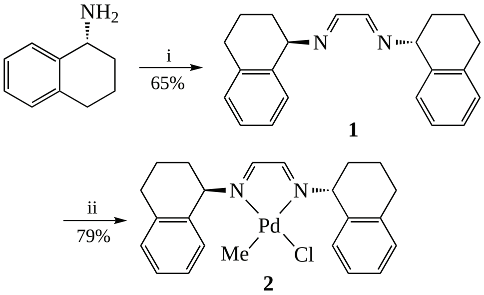
† Single crystals of **1** were grown by slow evaporation of a THF solution in argon, while those for **3**, by recrystallization from methanol.

Crystal data for **1**. $C_{22}H_{24}N_2$, M = 1265.72, monoclinic, space group $P2_1$, at 120 K: a = 13.968(3), b = 15.128(3) and c = 16.682(4) Å, β = 90.244(4)°, V = 3525.0(13) Å^3, Z = 8, d_{calc} = 1.192 g cm^{-3}, $F(000)$ = 1360. Intensities of 8499 reflections were measured with a Bruker APEX2 DUO CCD diffractometer [λ(MoKα) = 0.71073 Å, μ(MoKα) = 0.70 cm^{-1}, ω-scans, $2\theta < 60°$], and 3987 independent reflections (R_{int} = 0.0608) were used for the structure solution and refinement. Final R factors: R_1 = 0.0595 for 10645 observed reflections with $I > 2\sigma(I)$, wR_2 = 0.1358 and GOF = 0.985 for all the independent reflections.

Crystal data for **3**. $C_{17}H_{17}NO_2$, M = 267.31, triclinic, space group $P\bar{1}$, at 120 K: a = 5.4838(17), b = 10.566(3) and c = 11.825(4) Å, α = 99.867(4)°, β = 94.797(5)°, γ = 98.248(5)°, V = 663.9(4) Å^3, Z = 2, d_{calc} = 1.337 g cm^{-3}, $F(000)$ = 284. Intensities of 37502 reflections were measured with a Bruker APEX2 DUO CCD diffractometer [λ(MoKα) = 0.71073 Å, μ(MoKα) = 0.88 cm^{-1}, ω-scans, $2\theta < 60°$], and



Scheme 1 *Reagents and conditions*: i, glyoxal, Na_2SO_4, CH_2Cl_2, 0 °C; ii, (COD)Pd(Me)Cl, CH_2Cl_2, room temperature.

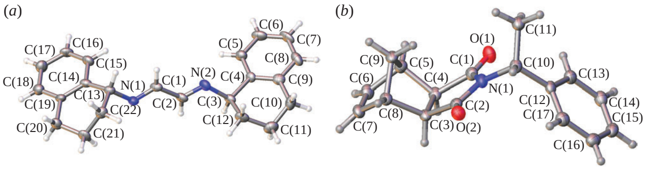
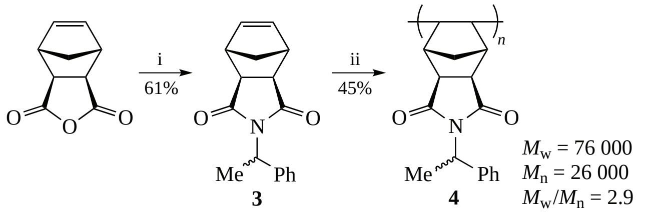


Figure 1 General view of (*a*) ligand **1** and (*b*) monomer **3** in representation of atoms *via* thermal ellipsoids at 50% probability level.

blood red oil.[11] The Pd-complex **2** and the ligand **1** were characterized by ^1H, ^{13}C and 2D NMR spectroscopy, mass spectrometry and elemental analysis that confirmed their structures.

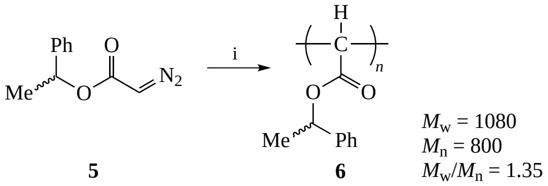
For the testing of catalytic properties of new complex **2** in vinyl-addition polymerization, a modified nadimide, racemic *N*-(1-phenylethyl)-*exo*-norbornene-5,6-dicarboximide **3**, was chosen as a model norbornene-type monomer (Scheme 2). This monomer combines in its structure the presence of both polar groups and bulky-substituents that make its polymerization an unusual task. Moreover, whereas vinyl-addition polymerization of most other norbornene derivatives has been actively studied,[10(*a*),15] there is a lack of information about vinyl-addition polymerization of nadimides and properties of the prepared polymers.[16] The target monomer **3** can be easily obtained from *cis*-5-norbornene-*exo*-2,3-dicarboxylic anhydride and racemic 1-phenylethylamine. The analogous monomers of both *exo*- and *endo*-configuration were described earlier.[17,18] It should be noted that *exo*-isomers of norbornene derivatives are usually more reactive in polymerization.[10(*a*)] Guiding by this, namely *exo*-derivative of the modified nadimide was prepared. The structure of compound **3** was confirmed by NMR spectroscopy, X-ray analysis [see Figure 1(*b*)][†] and mass spectrometry.



Scheme 2 *Reagents and conditions*: i, *rac*-PhCH(Me)NH_2, toluene, reflux; ii, **2**, CH_2Cl_2, $AgSbF_6$, 45 °C.

For the coordination vinyl-addition polymerization of a norbornene derivative, it is required that a Pd-complex have an open coordination site and a Pd–C bond.[10(*a*)] As it was expected without a cocatalyst, Pd-complex **2** did not catalyze the polymerization of **3** bearing polar and bulky groups (see Scheme 2). At the same time, after activation with $AgSbF_6$, the synthesized Pd-complex catalyzed vinyl-addition polymerization of **3** affording high-molecular weight polymer. According to ^1H and ^{13}C NMR spectroscopy, the obtained polymer did not contain HC=CH double bonds that suggests that the polymerization proceeded *via* vinyl-addition scheme. To the best of our knowledge, this is the first example of vinyl-addition polymerization of a nadimide over diimine Pd-complexes.

The catalytic activity of the obtained Pd-complex was also tested in another type of polymerization, which produces polycarbene from a diazoacetate monomer **5** (Scheme 3). This way of polymerization provides polymeric materials with low to moderate molecular weights and bearing ester group on each carbon atom of main chains in contrast to polyacrylates. Such polymers are considered as promising pour point depressants to fuels. The Pd-complex **2** catalyzed fast polymerization of diazoacetate **5** giving material **6** with the degree of polymerization of 4–5 and rather narrow molecular weight distribution. These results were confirmed by MALDI TOF analysis of the polymer (see Online Supplementary Materials, Figure S8).



Scheme 3 *Reagents and conditions*: i, **2**, THF, 25 °C.

Vinyl-addition polymers derived from nadimides can be considered as a promising alternative of polyimides for high performance applications like dielectric materials with high glass transition temperatures or membrane materials with enhanced chemical and thermal stability.[19] The synthesized polymer **4** is an amorphous substance, its WAXD pattern is represented by two broad peaks [Figure 2(*a*)] indicating some order in intra and inter-chains packing. The corresponding d-spacings (Table 1) are larger than the corresponding values for unsubstituted addition polynorbornene **7** and they are comparable with the same values for addition polynorbornene with silicon-containing side-chains of material **8**. The estimated fractional free volume for **4** by Askadskii method[20] using the polymer density was 15 ± 1%. Polymer **4** exhibited good thermal stability under an inert atmosphere and in air [Figure 2(*b*)]. Glass transition temperature was not observed by DSC for **4** till the beginning of the decomposition that evidences about high rigidity of polymer main chains in it. The properties of polymers

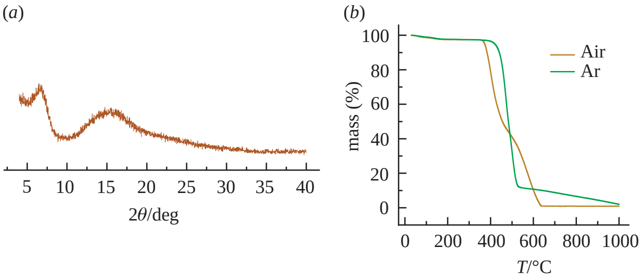
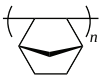


Figure 2 (*a*) WAXD pattern and (*b*) TGA curves for polymer **4**.

15371 independent reflections (R_{int} = 0.0978) were used for the structure solution and refinement. Final *R* factors: R_1 = 0.0616 for 2191 observed reflections with $I > 2\sigma(I)$, wR_2 = 0.1777 and GOF = 0.912 for all the independent reflections.

Using Olex2,[12] the structures were solved with the ShelXT[13] structure solution program using Intrinsic Phasing and refined with the XL[14] refinement package using Least-Squares minimisation. Positions of hydrogen atoms were calculated, and they all were refined in the isotropic approximation within the riding model.

CCDC 2065346 and 2065347 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.



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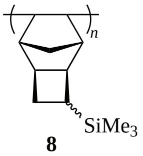

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Table 1 WAXD data for the addition polynorbornenes.

Polymer	$2\theta_1$/deg	$2\theta_2$/deg	d_1/Å	d_2/Å	Reference
7	10.0	18.5	8.8	4.7	21
4	7.0	15.5	12.6	5.7	This work
8	6.0	15.0	14.7	5.9	22

based on the synthesized monomers would be considered in future works.

In conclusion, a new methylpalladium chloride complex bearing diimine ligand was found to be an efficient catalyst for vinyl-addition polymerization of the nadimide and for oligomerization of diazoacetate producing the corresponding oligocarbene. The obtained polymeric and oligomeric products are interesting as dielectric and membrane materials, as well as pour point depressants to fuels, respectively.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2021.09.032.

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