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Cationic cyclopalladated complexes: new catalyst precursors for the telomerization of butadiene with alcohols

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Abstract

The cationic cyclopalladated complexes derived from *N,N*-dimethylbenzylamine **4**, *N*-benzylidene-(*S*)-(−)-α-methylbenzylamine **5** and 8-methyl quinoline **6** have been prepared and their properties as catalyst precursors for the telomerization of butadiene with methanol were investigated. The butadiene conversion was 60–70% for the three complexes and a mixture of butadiene dimers and telomers containing 2, 4 and 6 butadiene units were formed. The product selectivity is strongly influenced by the nature of the cyclopalladated complex. Thus, with complex **6** the C16 and C24 telomers were formed preferentially (more than 85%). On the other hand, with complex **4** the amount of butadiene dimers is greater than 40%. Complex **6** is also active for the telomerization of other aliphatic alcohols, but in these cases the 1- and 3-alkoxy octadiene telomers were produced preferentially.

Keywords: Cyclopalladated complexes; Palladium; Telomerization; Butadiene; Alcohols

1. Introduction

It is well known that the telomerization of butadiene with alcohols catalyzed by palladium compounds affords in most of the cases 1- and 3-alkoxy octadienes [1,2]. However, in few cases, high telomers containing 3 to 6 butadiene units were also observed when (η^3-allyl)palladium derivatives were employed as catalyst precursors [3–5]. It was also demonstrated that besides the nature of the palladium complex, the molar ratio butadiene:alcohol, the temperature and the reaction time have a remarkable influence on the selectivity of these reactions [5]. We have recently shown that cyclopalladated complexes are able to catalyze the telomerization of isoprene with methanol [6]. We thought that these metallocyclic complexes could be also good catalyst candidates for the telomerization of butadiene with alcohols. Moreover, due to the great variety of cyclopalladated complexes [7] available, it will be possible to study the influence of the nature of the palladated ligand on the selectivity of this reaction. In this paper

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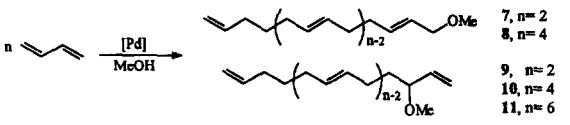
we present our results concerning the use of a selection of these metallocyclic species as catalyst precursors for the telomerization of butadiene with a series of alcohols.



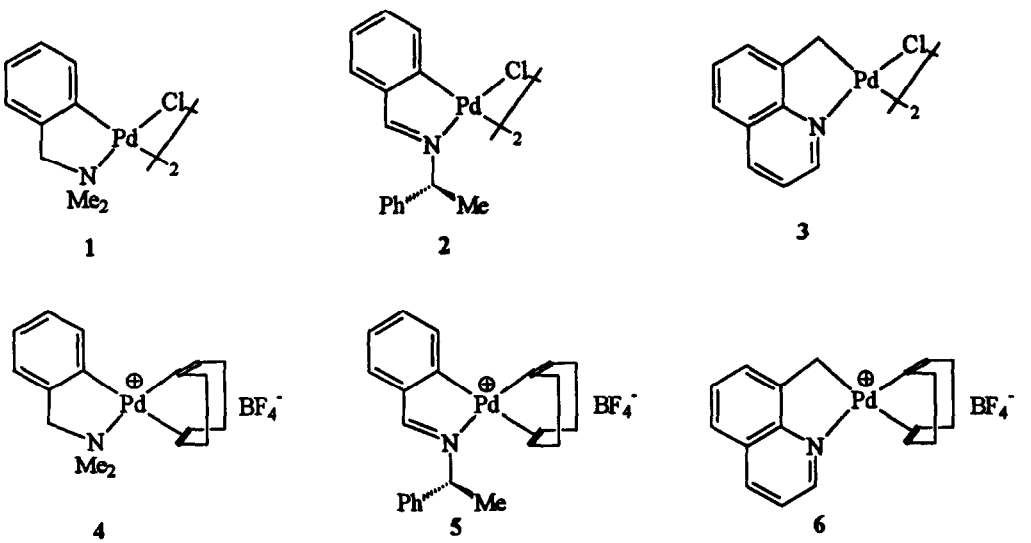
Scheme 2.

2. Results and discussion

The palladium complexes used in this study are depicted in Scheme 1. The dimeric complexes **1–3** can be prepared by published procedures [6,8]. The cationic complexes *N,N*-dimethylbenzylamine **4** and *N*-benzylidene-(*S*)-(−)-α-methylbenzylamine **5** were synthesized (70–90%) through abstraction of the Cl^- anions from the dimers **1** and **2**, respectively, by silver tetrafluoroborate in the presence of 1,5-cyclooctadiene. On the other hand, the simple action of sodium tetrafluoroborate with complex **3** in the presence of 1,5-cyclooctadiene affords compound 8-methyl quinoline **6** in 95% yield. The assignment of the structures of compounds **4** and **5** were based on their spectroscopic data and elemental analysis (see Experimental section). However, due to the poor solubility of compound **6** in non-coordinating solvents, its ^1H NMR spectrum was performed in acetonitrile-d_3 or in DMSO-d_6. It shows the characteristic resonances of the methylene–quinoline ring and those of the free 1,5-cyclooctadiene unit.

The results obtained in the telomerization of butadiene with methanol catalyzed by complexes **4–6** (see Scheme 2) are summarized in Table 1.

In all of these reactions a mixture of telomers obtained almost exclusively with an even number of butadiene units were detected. The 1- and 3-methoxy octadienes **7** and **9** and hexadecatetraenes telomers **8** and **10** were formed, the telomer **7** being the major isomer in the C8 fraction and 3-methoxy compound **10**, in the fraction of C16 derivatives. However, the 3-methoxy isomer **11** of the telomer containing butadiene units was the only one detected by ^1H NMR. It is also important to note that only traces of butadiene dimers were formed when the neutral dimeric complexes **1–3** were used as



Scheme 1.

Table 1
Telomerization of butadiene with MeOH

Complex	Butadiene		Telomer selectivity (%)		
	Conversion (%)	Dimers (%)	$MeOC_8^2$	$MeOC_{16}^4$	$MeOC_{24}^6$
4	60	26	16	13	5
5	65	3	20	15	27
6	70	2	7	25	36
6 [a]	55	30	21	4	–
6 [b]	20	18	2	–	–

Reaction conditions: [Complex] = 0.11 mmol; $[C_4H_6]$ = 150 mmol; [MeOH] = 37.5 mmol; CH_2Cl_2 5 ml; 60°C; 6 h. The upper indices denote the number of double bonds.
[a] Addition of 0.11 mmol of PPh_3.
[b] Addition of 0.11 mmol of $P(nBu)_3$.

the catalyst precursors. This clearly indicated that the presence of two easily accessible vacant coordination sites on the palladium center is a prerequisite for the occurrence of the telomerization reaction.

It is clear from Table 1 that the cationic cyclopalladated complexes **4–6** are able to catalyze the telomerization of butadiene with methanol and that the butadiene conversion is not influenced by the nature of cyclopalladated ligand. However, the selectivity is dramatically influenced by the nature of the palladium catalyst precursor. Thus only traces of butadiene dimers are produced with complexes **5** and **6** as compared with the formation of telomers. On the other hand, the formation of butadiene dimers are favored in the case of complex **4**. It is also important to note that the C24 derivative **11** is formed preferentially with the complexes **5** and **6**. The addition of triphenylphosphine or tri(n-butyl)phosphine reduces both the butadiene conversion and the formation of telomers of higher nuclearity. This is probably due to the competition for the vacant coordination sites on the metal center, between the phosphines and the butadiene.

The temperature and the time of reaction also have a marked influence on the product selectivity. With **6** as catalyst precursor, more than 45% of C24 derivatives were obtained when the reaction was carried out at 80°C, for 8 h and with a molar ratio of MeOH:butadiene of 0.25.

The catalyst precursor **6** is also active for the telomerization with other aliphatic alcohols. However, the butadiene conversions decreases significantly with increasing the steric hindrance of the alkyl group. Thus, under the same reaction conditions used in Table 1, the conversion for the telomerization with n-propanol, n-butanol, isopropanol, isobutanol and tert-butanol were 47, 42, 25, 23 and 7%, respectively. In all cases, 1- and 3-alkoxy octadienes were formed almost exclusively. A noticeable exception was observed for tert-butanol for which only butadiene dimers were detected.

The results presented in this paper indicate that cyclopalladated ligand exerts a strong influence on the product selectivity in the telomerization of butadiene with methanol. Moreover, they also strongly suggest that these ligands should be present on the catalytic active palladium species. The formation of almost solely telomers containing even numbers of butadiene molecules also suggests that the reaction presumably proceeds via condensation of C8 units, as was already pointed out earlier for the telomerization of alcohols by cationic (η^3-allyl)palladium derivatives [5].

3. Experimental

3.1. General

All manipulations were performed under dry, oxygen-free argon using standard techniques. All solvents were dried and distilled under argon prior to use. Infrared (Nujol mulls) spectra were recorded in the region 4000–400 cm^{-1} using a Mattson 3020 FTIR spectrophotometer. The ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded at 200.13 and 50.32 MHz, respectively, using a Varian VXR-200 instrument. Proton and carbon shifts (δ/ppm, J/Hz), are positive downfield relative to external $SiMe_4$.

Elemental analyses were carried out by the 'Central Analítica IQ/UFRGS' (Porto Alegre, Brazil). Mass spectra were obtained with a GC–MS HP5988A (EI, 70 eV). The reaction products were analyzed by gas chromatography on a Varian 3400 chromatograph equipped with an OV1 column 30 m × 0.25 mm × 0.2 μm, and FID detector; N_2 was the carrier (1 ml/min); the temperature program was from 50°C (5 min) to 180°C (15 min) at a heating rate of 10°C/min.

The compounds **1** [8], **2** [6] and **3** [8] were prepared by procedures described in literature. All other reagents were obtained from commercial sources and were used as received without further purification.

3.2. Complex 4

A solution of silver tetrafluoroborate (0.2 g, 1 mmol) in 15 ml of dichloromethane was added to a solution of **1** (0.28 g, 1 mmol) and 1,5-cyclooctadiene (1.1 ml) in 15 ml of dichloromethane at room temperature. The reaction mixture is than filtered through a Celite plug to remove AgCl and remaining light yellow solution is concentrated to ca. 3 ml under reduced pressure. Addition of hexanes (50 ml) gives an light yellow solid which as recovered by filtration, washed with hexanes (3 × 25 ml) and dried in vacuum (0.38 g, 88%).

Calculated for $C_{17}H_{24}BF_4NPd$: C = 46.86; H = 5.52; N = 3.22. Found: C = 45.66; H = 5.40; N = 3.17. IR (Nujol mulls): 1057 cm^{-1} ν (BF_4); ^1H NMR ($CDCl_3$): 7.12–7.57 (m, 5H, aromatics); 5.51 (d, 4H, HC=CH); 2.92 (s, 6H, NMe_2); 2.73 (m, 8H, H_2C–CH_2).

4. Complex 5

This compound was obtained in 70% yield by a similar procedure as used above for complex **4** starting from compound **2**.

IR (Nujol): ν (C=N) 1608 cm^{-1}, 1055 cm^{-1} ν (BF_4^-). ^1H NMR ($CDCl_3$, 200 MHz) 1.70 (d, 3H, CH_3, ^3J = 6.6 Hz), 2.02–2.22; 2.22–2.82 (m, 8H, CH_2 cod), 4.87–4.99 (m, 1H, C*H* cod) 5.17 (q, 1H, C*H*Me, ^3J = 6.5 Hz), 5.71–5.81 (m, 1H, *C*H cod), 5.84–6.01 (m, 2H, C*H* cod), 6.70–6.73 (m, 1H, C*H* arom), 7.07–7.42 (m, 7H, C*H* arom), 7.47–7.57 (m, 1H, C*H* arom), 8.40 (d, 1H, C*H*=N, ^4J = 1.41 Hz)). ^{13}C-{^1H}NMR ($CDCl_3$) δ 21.6 CH_3), 2.70–2.90 (4 C, CH_2), 65.5 (*C*H–Me), 110.6 (*C*H, cod), 111.3 (C*H*, cod), 123.0 (*C*H, cod), 124.9 (C*H*, cod), 123.03; 123.90; 126.19; 126.90; 127.34; 128.38; 128.39; 130.38; 131.07 (C arom), 139.9(C_{ipso}-C=N); 145.7(C_{ipso}-C–N); 156.0(C_{ipso}-Pd), 176.5 (*C*=N).

5. Complex 6

An yellow suspension of the dimeric cyclopalladated compound **3** (0.7 g, 2.5 mmol), 1.5 ml of 1,5-cyclooctadiene and sodium tetrafluoroborate (0.35 g, 3.2 mmol) in 50 ml of methanol was stirred for 6 h at room temperature. The white solid thus formed was recovered by filtration, washed with methanol (3 × 50 ml) and dried in vacuum (1.0 g, 91%). Calculated for $C_{18}H_20NBF_4Pd$: C = 48.74; H = 4.54; N = 3.16. Found: C = 48.86; N = 4.36; N = 2.87. IR (Nujol mulls): 1059 cm^{-1} ν (BF_4); ^1H NMR (CD_3CN): 8.62–7.50 (m, 6H, aromatics); 3.82 (s, 2H, CH_2) and 5.55 (s, 4H, CH=CH); 2.36 (s, 8H, CH_2–CH_2) for the H of free 1,5-cyclooctadiene.

5.1. Catalytic experiments

Butadiene (8.1 g, 150 mmol), methanol (37.5 mmol), palladium compound (0.015 mmol) and dichloromethane (5 ml) is introduced into a glass-lined 100 ml stainless steel autoclave under argon. The reaction mixture was stirred magnetically and the autoclave heated at 60°C for 6 h. It was then cooled down and the excess of butadiene was vented through a cold trap. The butadiene conversion and the product selec-

tivity were determined by capillary gas chromatography using undecane as internal standard.

The C8, C16 and C24 derivatives were separated by fraction distillation under reduced pressure and their structures were assigned by CG–MS and by comparing their ^{1}H and ^{13}C NMR spectra with those that was described in the literature [9].

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