Available online at www.sciencedirect.com
ScienceDirect
Mendeleev Commun., 2021, **31**, 478–480

Mendeleev Communications

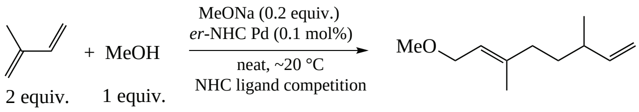
NHC Pd^{II} complexes for the solvent-free telomerization of isoprene with methanol

Sergey A. Rzhevskiy, Maxim A. Topchiy, Vasilii N. Bogachev, Alexandra A. Ageshina, Lidiya I. Minaeva, Grigorii K. Sterligov, Mikhail S. Nechaev and Andrey F. Asachenko*

A. V. Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, 119991 Moscow, Russian Federation. E-mail: aasachenko@ips.ac.ru

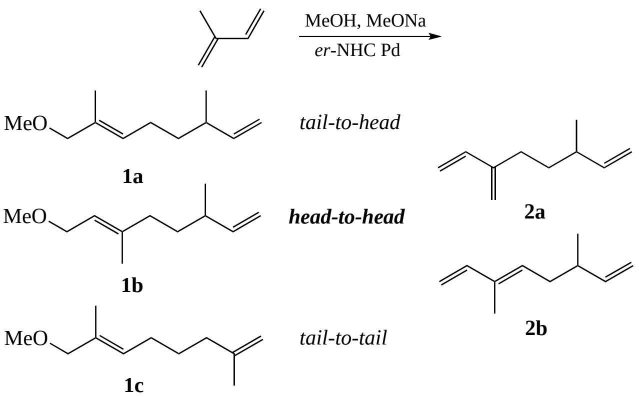
DOI: 10.1016/j.mencom.2021.07.013

A comparative study of N-heterocyclic carbene Pd complexes in the head-to-head isoprene telomerization with methanol revealed significant impact of ligand structure as well as axial group structure on the catalyst activity. Some *N,N′*-diaryl substituted imidazol-2-ylidene, imidazolidin-2-ylidene and expanded-ring tetrahydropyrimidin-2-ylidene and tetrahydrodiazepin-2-ylidene based ligands were tested to explore the fundamental correlations between structure (ring carbene size along with the substituent sterical and electronic properties) and catalytic activity.



Keywords: isoprene, telomerization, methanol, palladium catalysis, solvent-free reactions, N-heterocyclic carbenes, ligands.

The telomerization reactions, implied as oligomerization of mono- and dienes with the wide array of small molecules, most often of nucleophilic nature, are well studied and have the major synthetic potential and flexibility in a variety of applications.[1] The telomerization process is already used in industry, *e.g.*, linear 1-octanol is obtained in the Kuraray telomerization of butadiene with water followed by double bond reduction[2], while 1-octene is produced in the Dow Chemical Company by reduction of 1-methoxyocta-2,7-diene synthesized, in turn, by telomerization of butadiene with methanol.[3] Isoprene is a common diene produced in a very large scale all over the world and used practically in all spheres of industry and national economy.[4] Since isoprene is less reactive than butadiene, its telomerization represents a good challenge. Regarding the fact that isoprene molecule is non-symmetric, its telomerization can in principle afford four different products from two diene units (Scheme 1, tail-to head **1a**, head-to-head **1b**, tail-to-tail **1c** and head-to-tail, not shown). Non-symmetric nucleophile unit can also react by two different positions, which would ultimately bring about eight different telomers. Nucleophile nature highly affects the process selectivity,[5] which can be controlled by varying solvent, catalyst ligand and reaction conditions.[6] Dimers of type **2a** and **2b** depriving nucleophile unit can be also formed.



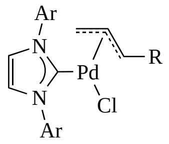
Scheme 1

Palladium(II) N-heterocyclic carbene complexes[7] have been by far the most widely employed in the isoprene telomerization.[5(c),8] We have recently reported that NHC (N-heterocyclic carbene) complexes of gold(I), copper(I) and palladium(II) showed better activity as pre-catalysts compared to common used NHC complexes in different important catalyzed reactions.[9]

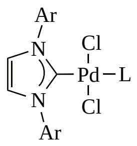
In the course of our ongoing interest on the development of new NHC-based metal complexes for the application in catalytic reactions, herein we report on our comparative study of influence of *er*-NHC Pd complexes **3–8** on the outcome of the isoprene telomerization with methanol. The telomerization was performed under environmentally benign conditions in accordance with the green-chemistry principles.[10]

Initially we have tested NHC Pd complexes **6–8** with saturated five-, six- and seven-membered ring carbene backbone bearing mesityl (Mes**)** and 2,6-diisopropylphenyl (Dipp**)** substituents at the nitrogen atoms. The reaction was carried out under atmospheric pressure at room temperature and in the absence of solvent (Table 1).[6(c)] It was found out that the expansion of the ring (entries 1, 2 *vs*. 3, 4 and 5, 6) together with the growth of the sterical effect of the N-substitutes (entries 1, 3, 5 *vs*. 2, 4, 6) caused decrease in the catalytic activity and, consequently, drop in the isoprene conversion. Less bulky complex **6b** (entry 1) exhibited higher activity and selectivity.

Further on, we have varied structure of the five-membered Pd–NHC complexes with Mes substituent on the nitrogen atom. It was demonstrated that upon transition from saturated SIMes-complex **6b** (Table 2, entry 1) to unsaturated IMes analogue **3b** (entry 2) little improvement in selectivity took place. Use of complex **4c** bearing auxiliary ligand SPhos (entry 3) led to the decrease in the catalytic activity, while the application of 3-chloropyridine ligand in catalyst **4b** on the contrary improved



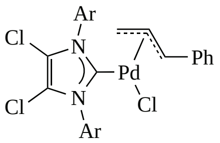
3a–d, **3′a**,**b**



4a–c

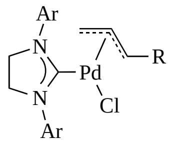
3a Ar = 2,6-$Pr^i_2C_6H_3$, R = Ph
3′a Ar = 2,6-$Pr^i_2C_6H_3$, R = H
3b Ar = 2,4,6-$Me_3C_6H_2$, R = Ph
3′b Ar = 2,4,6-$Me_3C_6H_2$, R = H
3c Ar = 2,6-$(Ph_2CH)_2$-4-$MeOC_6H_2$, R = Ph
3d Ar = 2,6-$(Ph_2CH)_2$-4-MeC_6H_2, R = Ph

4a Ar = 2,6-$Pr^i_2C_6H_3$, L = 3-chloropyridine
4b Ar = 2,4,6-$Me_3C_6H_2$, L = 3-chloropyridine
4c Ar = 2,4,6-$Me_3C_6H_2$, L = SPhos



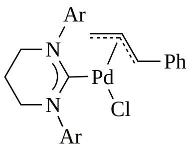
5

Ar = 2,6-$Pr^i_2C_6H_3$



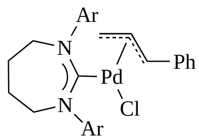
6a,**b**, **6′a**

6a Ar = 2,6-$Pr^i_2C_6H_3$, R = Ph
6′a Ar = 2,6-$Pr^i_2C_6H_3$, R = H
6b Ar = 2,4,6-$Me_3C_6H_2$, R = Ph



7a,**b**

7a Ar = 2,6-$Pr^i_2C_6H_3$
7b Ar = 2,4,6-$Me_3C_6H_2$



8a,**b**

8a Ar = 2,6-$Pr^i_2C_6H_3$
8b Ar = 2,4,6-$Me_3C_6H_2$

Table 1 Comparison of *er*-NHC Pd complexes in isoprene telomerization with methanol.[a]

Entry	Catalyst	Conversion (%)	GC yield (%)				
			1a	1b	1c	2a	2b
1	**6b**	100	19.1	51.2	1.2	0	3.7
2	**6a**	91	3.6	15.6	0.4	4	10
3	**7b**	41	0.2	16	0.1	1	1.1
4	**7a**	42	0.4	9.4	0.1	4.7	3.8
5	**8b**	35	0	2.8	0	0.3	0.4
6	**8a**	15	0.4	4.5	0.1	4.2	1.2

[a]Reaction conditions: MeOH (1 equiv.), MeONa (2 mol%), catalyst (0.1 mol%), isoprene (2 equiv.), room temperature, 72 h.

Table 2 Five-membered Mes-substituted Pd–NHC complexes in the isoprene telomerization.[a]

Entry	Catalyst	Conversion (%)	GC yield (%)				
			1a	1b	1c	2a	2b
1	**6b**	100	19.1	51.2	1.2	0	3.7
2	**3b**	100	22.3	51.7	1.62	0	3
3	**4c**	30	1.6	12	0	1	0.7
4	**4b**	100	24.4	58.7	1.7	0	3.3
5	**3′b**	100	21.6	58.9	1.4	0	3

[a]Reaction conditions: MeOH (1 equiv.), MeONa (2 mol%), catalyst (0.1 mol%), isoprene (2 equiv.), room temperature, 72 h.

it (entry 4). Replacement of the cinnamyl leaving group by allyl in catalyst **3′b** (entries 1, 2 *vs.* 5) had a small positive effect on the product yields.

Since testing the less active catalysts can usually help to specify the effects of the pre-catalyst structure on the reaction outcome, the additional experimental series involving less active

Table 3 Detailed comparison of five-membered SIPr and IPr NHC Pd complexes in the isoprene telomerization.[a]

Entry	Catalyst	Conversion (%)	GC yield (%)				
			1a	1b	1c	2a	2b
1	**3′a**	100	6.3	26.7	0.6	0	9.3
2	**6′a**	100	4.3	18.3	0.54	0	11.7
3	**3a**	100	5.8	24.1	0.6	0	9
4	**6a**	91	3.6	15.6	0.4	4	10
5	**3c**	35	0.3	0.2	0	1.1	0.9
6	**3d**	17	0.2	0.2	0	0.8	0.7
7	**4a**	100	8.2	24	0.9	0	9.4
8	**5**	46	3.15	6.25	0.17	3.2	4.6

[a]Reaction conditions: MeOH (1 equiv.), MeONa (2 mol%), catalyst (0.1 mol%), isoprene (2 equiv.), room temperature, 72 h.

IPr and SIPr Pd complexes with Dipp substituents were performed (Table 3). Once again the experiments revealed the advantages of unsaturated IPr over saturated SIPr complexes in activity (see Table 3, entries 1 *vs.* 2 and 3 *vs.* 4), and the advantage of allyl leaving group over the cinnamyl one (entries 1 *vs.* 3 and 2 *vs.* 4). As it was indicated, allyl group could be changed for 3-chloropyridine auxiliary ligand with the minor selectivity fall (entries 1 *vs.* 7). It was additionally demonstrated that the increase in the steric bulkiness of ligand core leads to the dramatical drop in the catalyst activity (entries 3 *vs.* 5 and 6). The presence of electron-withdrawing chlorine atoms in the imidazole ring also disproves the catalytic activity (entries 3 *vs.* 8).

In conclusion, we have performed the comparative study of the NHC Pd complexes in the isoprene telomerization with methanol and revealed the fundamental relationship between structure and catalytic activity. The ring expansion, the sterical effect of the bulky substitutes, the SPhos and 3-chloropyridine auxiliary ligands and the presence of acceptor groupings in the imidazole ring lead to decrease in the catalytic activity. The best results were achieved with the use of complex **3′b**, which allowed us to assume that the right carbene structure, along with the small leaving group would demonstrate acceptable activity and selectivity. The current results can be used as the basis for further development of environmentally friendly procedure of isoprene telomerization.

Maxim A. Topchiy, Vasilii N. Bogachev, Alexandra A. Ageshina, Grigorii K. Sterligov and Andrey F. Asachenko are thankful to Russian Science Foundation (RSF) for financial support (grant no. 19-73-10185). Part of this work was carried out by Sergey A. Rzhevskiy, Lidiya I. Minaeva and Mikhail S. Nechaev as part of the A. V. Topchiev Institute of Petrochemical Synthesis (TIPS) Russian Academy of Sciences (RAS) State Program. This work was performed using the equipment of the Shared Research Center 'Analytical center of deep oil processing and petrochemistry of TIPS RAS'.

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2021.07.013.

References

1 (*a*) A. Behr, M. Becker, T. Beckmann, L. Johnen, J. Leschinski and S. Reyer, *Angew. Chem., Int. Ed.*, 2009, **48**, 3598; (*b*) N. D. Clement, L. Routaboul, A. Grotevendt, R. Jackstell and M. Beller, *Chem. – Eur. J.*, 2008, **14**, 7408; (*c*) B. Cornils, *J. Mol. Catal. A: Chem.*, 1999, **143**, 1; (*d*) E. J. Smutny, *J. Am. Chem. Soc.*, 1967, **89**, 6793; (*e*) S. Takahashi, T. Shibano and N. Hagihara, *Tetrahedron Lett.*, 1967, **8**, 2451; (*f*) A. Zapf and M. Beller, *Top. Catal.*, 2002, **19**, 101.

2 L. Messerle, *J. Am. Chem. Soc.*, 1998, **120**, 2209.
3 P. W. N. M. van Leeuwen, N. D. Clément and M. J.-L. Tschan, *Coord. Chem. Rev.*, 2011, **255**, 1499.
4 U. Asghar and A. Masoom, *Am. J. Chem. Eng.*, 2020, **8**, 1.
5 (*a*) L. I. Zakharkin, E. A. Petrushkina, N. P. Aksenova, T. N. Konstantinova and T. V. Bavrina, *Dokl. Akad. Nauk*, 2001, **379**, 402 (in Russian); (*b*) R. Benn, P. W. Jolly, R. Mynott and G. Schenker, *Organometallics*, 1985, **4**, 1136; (*c*) R. Jackstell, A. Grotevendt, D. Michalik, L. El Firdoussi and M. Beller, *J. Organomet. Chem.*, 2007, **692**, 4737.
6 (*a*) E. A. Petrushkina, D. V. Khomishin, N. E. Mysova, A. V. Orlinkov, V. N. Kalinin, A. B. Ponomarev, I. A. Godovikov, Ya. V. Zubavichus and A. A. Veligzhanin, *Moscow Univ. Chem. Bull*., 2007, **62**, 276 (*Vestn. Mosk. Univ. Khim*., 2007, 337); (*b*) E. A. Petrushkina and D. V. Khomishin, in *Pheromones: Theories, Types and Uses*, ed. I. M. Gregory, Nova Science Publishers, New York, 2010, pp. 125–164; (*c*) I. Maluenda, M.-T. Chen, D. Guest, S. M. Roe, M. L. Turner and O. Navarro, *Catal. Sci. Technol.*, 2015, **5**, 1447; (*d*) T. A. Faßbach, A. J. Vorholt and W. Leitner, *ChemCatChem*, 2019, **11**, 1153; (*e*) S. M. Maddock and M. G. Finn, *Organometallics*, 2000, **19**, 2684; (*f*) D. S. Suslov, M. V. Bykov, M. V. Belova, P. A. Abramov and V. S. Tkach, *J. Organomet. Chem.*, 2014, **752**, 37.
7 A. V. Astakhov, S. B. Soliev and V. M. Chernyshev, *Russ. Chem. Bull., Int. Ed*., 2020, **69**, 2073 (*Izv. Akad. Nauk, Ser. Khim*., 2020, 2073).
8 (*a*) *N-Heterocyclic Carbenes in Transition Metal Catalysis and Organocatalysis*, ed. C. S. J. Cazin, Springer Science, Heidelberg, 2011; (*b*) *N-Heterocyclic Carbenes: From Laboratory Curiosities to Efficient Synthetic Tools*, ed. E. S. Díez-González, RSC Publishing, London, 2010; (*c*) *N-Heterocyclic Carbenes: Effective Tools for Organometallic Synthesis*, ed. S. P. Nolan, Wiley-VCH, Weinheim, 2014.
9 (*a*) E. L. Kolychev, A. F. Asachenko, P. B. Dzhevakov, A. A. Bush, V. V. Shuntikov, V. N. Khrustalev and M. S. Nechaev, *Dalton Trans.*, 2013, **42**, 6859; (*b*) O. S. Morozov, A. V. Lunchev, A. A. Bush, A. A. Tukov, A. F. Asachenko, V. N. Khrustalev, S. S. Zalesskiy, V. P. Ananikov and M. S. Nechaev, *Chem. – Eur. J.*, 2014, **20**, 6162; (*c*) M. A. Topchiy, A. A. Ageshina, P. S. Gribanov, S. M. Masoud, T. R. Akmalov, S. E. Nefedov, S. N. Osipov, M. S. Nechaev and A. F. Asachenko, *Eur. J. Org. Chem.*, 2019, 1016.
10 (*a*) P. S. Gribanov, G. A. Chesnokov, M. A. Topchiy, A. F. Asachenko and M. S. Nechaev, *Org. Biomol. Chem.*, 2017, **15**, 9575; (*b*) G. A. Chesnokov, P. S. Gribanov, M. A. Topchiy, L. I. Minaeva, A. F. Asachenko, M. S. Nechaev, E. V. Bermesheva and M. V. Bermeshev, *Mendeleev Commun.*, 2017, **27**, 618; (*c*) P. S. Gribanov, G. A. Chesnokov, P. B. Dzhevakov, N. Yu. Kirilenko, S. A. Rzhevskiy, A. A. Ageshina, M. A. Topchiy, M. V. Bermeshev, A. F. Asachenko and M. S. Nechaev, *Mendeleev Commun.*, 2019, **29**, 147.

Received: 17th February 2021; Com. 21/6454