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15-Membered macrocyclic triolefin: role in recovering active palladium catalyst for the telomerization of butadiene with methanol

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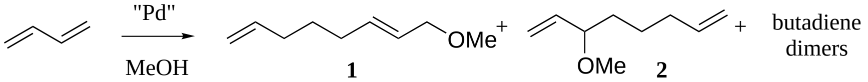
Abstract—The 15-membered macrocyclic triolefin **Ma** stabilizes a Pd(0) catalyst, active and recyclable in telomerization of butadiene with methanol. This Pd catalyst is generated from different Pd(0) or Pd(II) sources associated with phosphanes. © 2001 Elsevier Science Ltd. All rights reserved.

Recently, palladium(0) complexes of 15-membered macrocyclic triolefins, represented in Fig. 1 as **Pd-Ma**, have been synthezised[1] and shown to be efficient and recoverable catalysts for Suzuki-type cross-coupling reactions.[2] We were interested in using such a recoverable catalytic system in telomerization of butadiene in the presence of nucleophiles such as methanol[3] (Eq. (1)); this transformation remains of interest due to the possible use of linear octadienyl derivates as building blocks in the synthesis of natural products.[4] Many homogeneous zerovalent and bivalent palladium complexes excel in efficiency and selectivity in telomerization,[3,5] whose mechanism has been recently revisited.[6] However, no example of soluble recyclable systems seems to be reported. Only polymer-bound palladium complexes could be easily separated from a reaction mixture and reused with some loss of the activity[7] or with its preservation.[8] We present here our first results in recycling a soluble catalyst starting from different palladium sources associated with the free triolefinic macrocycle **Ma**.



(1)

We started our studies with **Pd-Ma** as catalyst (Table 1, entries 1–7) and compared the results with those observed by using $Pd_2(dba)_3 \cdot CHCl_3$ (noted below **Pd-dba**) as catalytic precursor (Table 1, entries 8–11), or $Pd(OAc)_2$ (Table 1, entry 12). **Pd-Ma** exhibited no efficiency without added phosphane (entry 1). The butadiene conversion was enhanced in the presence of

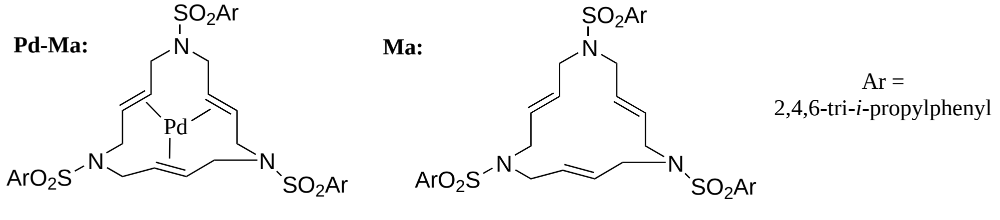


Figure 1. Structures of Pd-catalyst and macrocyclic ligand.

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Table 1. Telomerization of butadiene with methanol in the presence of Pd catalysts[a]

Entry	'Pd'-phosphane (equiv./Pd)	Time (h)	T.O.N.	T.O.F. (h^{-1})	Conv. (%)	Selectivity (%)		
						1	**2**	Dimers[b]
1	**Pd-Ma**	1	60	60	3	16	0	84
2	**Pd-Ma**-PPh$_3$ (1)	1	980	980	49	81	8	11
3	**Pd-Ma**-PPh$_3$ (1)	2	1380	690	69	86	8	6
4	**Pd-Ma**-PPh$_3$ (1)	3	1440	480	72	88	6	6
5	**Pd-Ma**-PPh$_3$ (2)	1	1180	1180	59	76	14	10
6	**Pd-Ma**-PPh$_3$ (3)	1	1360	1360	68	72	16	12
7	**Pd-Ma**-P(*p*-tol)$_3$ (3)	0.75	1180	1573	59	78	17	5
8	**Pd-dba**[c]-PPh$_3$ (2)	1	1420	1420	71	86	8	6
9	**Pd-dba**[c]-PPh$_3$ (3)	1	920	920	46	73	9	18
10	**Pd-dba**[c]-P(*o*-tol)$_3$ (2)	1.25	1900	1520	95	89	3	8
11	**Pd-dba**[c]-P(*p*-tol)$_3$ (2)	0.75	1900	2533	95	88	7	5
12	Pd(OAc)$_2$-PPh$_3$ (3)	0.75	1500	2000	75	82	11	7

[a] Reaction conditions: Pd/MeOH/C$_4$H$_6$ = 1/6000/4000; 2.5×10^{-2} mmol Pd, starting butadiene pressure = 4 bar, 60°C.

[b] 1,3,7-Octatriene and 4-vinylcyclohexene constitute essential dimers.

[c] **Pd-dba** = Pd$_2$(dba)$_3$·CHCl$_3$.

triphenylphosphane: when PPh$_3$/Pd = 1, the reaction took place but needed more than 1 h (entries 2–4). A ratio PPh$_3$/Pd = 3 seemed a good compromise to reach a fair butadiene conversion (entries 2/5/6). The conversion was similar by using **Pd-Ma**/3PPh$_3$ or **Pd-dba**/2PPh$_3$, but the selectivity to the linear ether was lower with the former catalyst (entries 6/8). As already mentioned,[3,6] we observed in all these experiments, the crucial effect of the added phosphane and of its amount on the course of the reaction. The performance of the second catalytic system (with **Pd-dba** as precursor) was higher for PPh$_3$/Pd = 2 (entries 8/9) and the order of efficiency of phosphanes was P(*p*-tolyl)$_3$ ≥ P(*o*-tolyl)$_3$ > PPh$_3$ (Table 1, entries 8/10/11), which could probably be correlated with the ligand basicity.[9] The use of Pd(II) as Pd(OAc)$_2$ associated with 3 equiv. of triphenylphosphane was also quite satisfying (Table 1, entry 12).

Concerning recycling, the systems based on **Pd-dba** or Pd(OAc)$_2$ lost their activity and selectivity, even in the presence of added phosphane in the recycling experiment (Table 2, entries 3–5). The activity of **Pd-Ma** also dropped in the absence of added phosphane in each run (Table 2, entry 1); but in the presence of added phosphane (entry 2), the activity was recovered and even enhanced when compared to the first run. This could suggest an effect of **Ma** in the formation of new telomerization active species.

This latter observation led us to test the possibility of recycling by association of **Pd-dba** or Pd(OAc)$_2$ with both a phosphane and the free macrocycle **Ma** (Table 3). We were delighted to observe the ability of **Ma** in the recovering of active Pd(0) species. With **Pd-dba**/**Ma**/3PPh$_3$, conversion and selectivity were higher in the first run (Table 3, entry 2) compared to that of the

Table 2. Catalyst recycling in telomerization of butadiene with methanol[a]

Entry	'Pd'-phosphane (equiv./Pd)[b]	Runs	T.O.F. (h^{-1})	Conv. (%)	Selectivity (%)		
					1	**2**	Dimers
1	**Pd-Ma**-PPh$_3$ (0)	1[c]	1360	68	72	16	12
		2	820	41	85	7	8
2	**Pd-Ma**-PPh$_3$ (3)	1[c]	1360	68	72	16	12
		2	1740	87	80	14	6
		3	1400	70	79	14	7
		4	1500	75	81	14	5
3	**Pd-dba**-PPh$_3$ (2)	1[c]	1420	71	86	8	6
		2	100	5	63	8	29
4	**Pd-dba**-PPh$_3$ (3)	1[c]	920	46	73	9	18
		2	180	9	67	10	23
		3	20	1	0	0	100
5	Pd(OAc)$_2$-PPh$_3$ (3)	1[c]	2000	75	82	11	7
		2	300	15	80	7	13
		3	0	0	–	–	–

[a] Reaction conditions of Table 1, except the catalysts, which were recovered after distillation under reduced pressure of the products of first runs and directly reused.

[b] Added phosphane (2 or 3 equiv./Pd except entry 1) in each recycling experiment.

[c] For clarity, results of Table 1 have been mentioned.

Table 3. Catalyst recycling in the presence of **Ma** in telomerization of butadiene with MeOH[a]

Entry	‘Pd’-ligands (equiv./Pd)	Runs	T.O.F. (h^{-1})	Conv. (%)	Selectivity (%)		
					1	**2**	Dimers
1[b]	**Pd-dba**+PPh$_3$ (3)	1	920	46	73	9	18
2	**Pd-dba**+**Ma** (1) +PPh$_3$ (3)	1	1360	68	88	6	6
		2	1760	88	82	13	5
		3	1680	84	81	11	8
		4	1700	85	84	8	8
3	**Pd-dba**+P(p-tol)$_3$ (3)	1	1540	77	90	5	5
4	**Pd-dba**+**Ma** (1) +P(p-tol)$_3$ (3)	1	940	47	81	12	7
		2	2000	100	87	11	2
		3	1580	79	83	12	5
		4	1800	90	85	12	3
5[b]	Pd(OAc)$_2$+PPh$_3$ (3)	1	2000	75	82	11	7
6	Pd(OAc)$_2$+**Ma** (1) +PPh$_3$ (3)	1	420	21	81	10	9
		2	1120	56	82	14	4
		3	1100	55	80	11	9
		4	500	25	80	9	11

[a] Reaction conditions of the first runs: 2.5×10^{-2} mmol of Pd; Pd/Ma/phosphane/MeOH/C$_4$H$_6$=1/1/3/6000/4000; 60°C; 1 h; starting butadiene pressure=4 bar. The catalysts were recovered in each run after distillation of the products under reduced pressure. They were reused after adding phosphane (3 equiv./Pd), methanol and butadiene in each recycling experiment.

[b] For clarity, the results of Table 1 have been mentioned.

same precursor system without added macrocycle (entry 1); furthermore the catalyst recycling was highly efficient (entry 2, runs 2–4). Such an improvement of the first run was not observed when PPh$_3$ was exchanged for P(p-tol)$_3$ (entries 3/4) or when **Pd-dba** was replaced by Pd(OAc)$_2$ (entries 5/6); however, effective catalyst recycling has also been observed.

Work is currently underway to determine the nature of the active species. Nevertheless, we have already observed that after four runs (Table 3, entry 2) distillation of the telomerization products, refluxing of the resulting solid for 12 h in THF and concentrating, the introduced palladium is quantitatively recovered as **Pd-Ma**, as indicated by NMR.

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References

1. Cerezo, S.; Cortès, J.; Lago, E.; Molins, E.; Moreno-Mañas, M.; Parella, T.; Pleixats, R.; Torrejón, J.; Vallribera, A. *Eur. J. Inorg. Chem.* **2001**, 1999–2006.
2. Cortés, J.; Moreno-Mañas, M.; Pleixats, R. *Eur. J. Org. Chem.* **2000**, 239–243.
3. Reviews: (a) Tsuji, J. *Adv. Organomet. Chem.* **1979**, *17*, 141–193; (b) Tsuji, J. *Palladium Reagents and Catalysis*; Wiley: Chichester, 1995; pp. 422–449.
4. Reviews: Tsuji, J. *Pure Appl. Chem.* **1979**, *51*, 1235–1241 and **1981**, *53*, 2371–2378.
5. For recent examples: (a) Camargo, M.; Dani, P.; Dupont, J.; de Souza, R. F.; Pfeffer, M.; Tkatchenko, I. *J. Mol. Catal. A: Chem.* **1996**, *109*, 127–131; (b) Bouachir, F.; Grenouillet, P.; Neibecker, D.; Poirier, J.; Tkatchenko, I. *J. Organomet. Chem.* **1998**, *569*, 203–215; (c) Benvenutti, F.; Carlini, C.; Marchionna, M.; Patrini, R.; Raspolli Galetti, A. M.; Sbrana, G. *J. Mol. Catal. A: Chem.* **1999**, *140*, 139–155; (d) Basato, M.; Crociani, L.; Benvenutti, F.; Raspolli Galetti, A. M.; Sbrana, G. *J. Mol. Catal. A: Chem.* **1999**, *145*, 313–316.
6. Vollmüller, F.; Krause, J.; Klein, S.; Mägerlein, W.; Beller, M. *Eur. J. Inorg. Chem.* **2000**, 1825–1832.
7. (a) Kaneda, K.; Kurosaki, H.; Terasawa, M.; Imanaka, T.; Teranishi, S. *J. Org. Chem.* **1981**, *46*, 2356–2362; (b) Benvenutti, F.; Carlini, C.; Marchionna, M.; Patrini, R.; Raspolli Galetti, A. M.; Sbrana, G. *J. Mol. Catal. A: Chem.* **1999**, *139*, 177–187.
8. Benvenutti, F.; Carlini, C.; Raspolli Galetti, A. M.; Sbrana, G.; Marchionna, M.; Patrini, R. *J. Mol. Catal. A: Chem.* **1999**, *137*, 49–63.
9. Benvenutti, F.; Carlini, C.; Lami, M.; Marchionna, M.; Patrini, R.; Raspolli Galetti, A. M.; Sbrana, G. *J. Mol. Catal. A: Chem.* **1999**, *144*, 27–40.