15-Membered Triolefinic Macrocycles − Catalytic Role of (*E*,*E*,*E*)-1,6,11-Tris(arenesulfonyl)-1,6,11-triazacyclopentadeca-3,8,13-triene Complexes of Palladium(0) in the Presence of Phosphanes

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The palladium(0) complexes of (*E*,*E*,*E*)-1,6,11-tris(arenesulfonyl)-1,6,11-triazacyclopentadeca-3,8,13-trienes deliver palladium to phosphanes with the generation of high concentrations of catalytically active species such as $Pd(PPh_3)_2$. After oxidation of the phosphanes, the palladium is reincorporated into the macrocycle, thus avoiding agglomeration and precipitation. These conclusions were reached by ^{31}P NMR, ^{19}F NMR, and electrospray ionization mass spectrometry studies of telomerization and Tsuji–Trost reactions.

Introduction

Palladium has emerged as a versatile catalytic metal in organic chemistry.[1] However, recovery of palladium species from processes occurring under homogeneous catalysis conditions is difficult, since phosphanes, the usual stabilizing ligands, oxidize to the corresponding phosphane oxides. The metal therefore irreversibly agglomerates, preventing reutilization in soluble form.

Nitrogen-containing 15-membered macrocycles featuring internal olefinic double bonds are unfrequent.[2] The few known examples from other groups contain only one double bond, and the key step for their preparation is metathesis.[3]

Macrocycles featuring endocyclic double bonds are endowed with peculiar abilities to coordinate late transition metals. Thus, the diverse configurational isomers of the 12-membered carbocycle cyclododeca-1,5,9-triene have a rich coordination chemistry, and their Ni^0 complexes have played fundamental roles in catalysis and in organo-nickel chemistry.[4] Other metals form complexes with cyclododecatrienes, including Cu^I,[5] Pd^{II},[6] Ag^I,[7] Rh^{III},[8] and Ru^{II}.[9] Related 12-membered carbocycles also form nickel^0 complexes.[10] In the upper limit of ring size, the 13-membered (*Z*,*E*,*Z*)-cyclotrideca-1,5,9-triene also forms a complex with Ag^I.[11] A special case is the complexation of Ag^I by [2.2.2]paracyclophanes, which occurs in an η^2 manner on each of the three benzene rings.[12] The related $[2_6]$(1,2,4,5)cyclophane (deltaphane) displays the same behavior.[12b] In contrast, (*Z*,*Z*,*Z*)-tribenz[12]annulene, the triunsaturated analogue of [2.2.2]orthocyclophane, coordinates Ag^I through the three olefins.[13] Outside of our contributions, metal complexes of macrocyclic triolefins with more than 13 members seems to be unknown.

Some of us have described the preparation of (*E*,*E*,*E*)-1,6,11-tris(arenesulfonyl)-1,6,11-triazacyclopentadeca-3,8,13-trienes **1** (Figure 1) from easily available arenesulfonamides and (*E*)-1,4-dibromo-2-butene.[14−17] Isomers of *E*,*E*,*Z* configuration are also accessible.[18] Both *E*,*E*,*E*[14,16,19] and *E*,*E*,*Z*[18] isomers are excellent ligands for palladium(0), platinum(0), and silver(I). Moreover, the palladium complexes of different macrocycles **1** are excellent catalysts in Suzuki-type cross-couplings.[14,16] The complexes can be recovered by column chromatography. A polystyrene anchored version is also active for the same cross-couplings and can be recovered by filtration and reused several times without noticeable lose of activity.[14] Recently it has been shown that the palladium(0) complex **2** (Ar^1 = Ar^2 = *p*-tolyl) is a reusable catalyst for hydroarylation of alkynes in ionic liquids.[20] Moreover, **2b** is inactive in the telomerization of butadiene with methanol. However, upon addition of two mol of triphenylphosphane (with respect to palladium-macrocycle complex) a catalytic species displaying high activity in the telomerization reaction was formed.

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After one run the phosphane was oxidized, but upon addition of fresh phosphane the catalytic activity was recovered. The process was successfully repeated several times.[21]

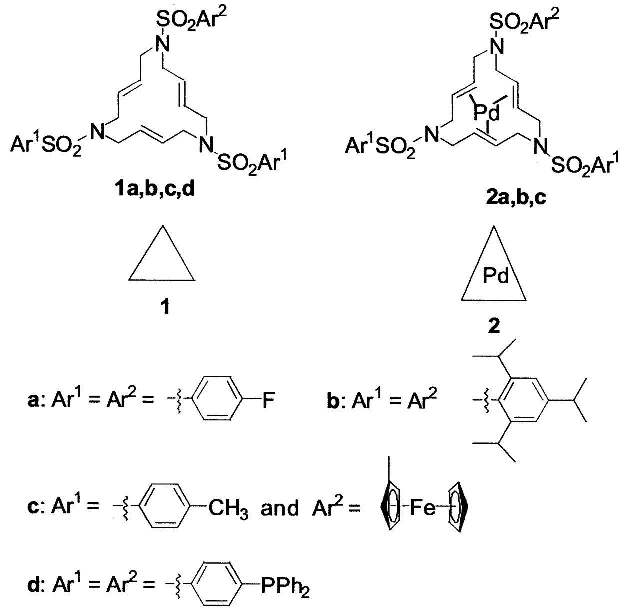


Figure 1. Macrocycles **1** and **2**

Intrigued by this telomerization behavior, we investigated its mechanistic significance. We present our conclusions in this paper.

Results and Discussion

We chose ^{31}P and ^{19}F NMR and electrospray ionization mass spectrometry as analytical tools to determine the fates of ligand **1**, complex **2**, and of ancillary phosphanes in the experiments to follow. In these experiments we have studied:

i. − the position of equilibrium when **2a** was mixed with triphenylphosphane or several bidentate phosphanes in different molar ratios,

ii. − the course of a typical Tsuji−Trost reaction between diphenylamine and cinnamyl carbonate in the presence of both **2a** and phosphanes,

iii. − the course of butadiene telomerizations in the presence of **2b** and phosphanes, and

iv. − the species formed when THF solutions of **2c** and triphenylphosphane or bidentate phosphanes were introduced into the ionization chamber of an electrospray ionization mass spectrometer.

The presence of fluorinated species **1a** and/or **2a** in the reaction mixtures was easily ascertainable by the appearance of a singlet at $\delta = -105.37$ (in $CDCl_3$), -111.17 (in THF), or -109.48 ppm (in DMF) for **1a**, and of two singlets at $\delta = -105.26$ and -105.43 (in $CDCl_3$), -111.14 and -111.22 (in THF), or -109.49 and -109.58 ppm (in DMF) of relative intensities 2:1 for **2a**. We had previously shown that complexes **2** present an averaged plane of symmetry bisecting one C−N−C angle and perpendicular to the plane defined by the three nitrogen atoms. Moreover, complexes **2** lack any C_3 axis of symmetry.[19,22] This means that two fluorine atoms in **2a** are isochronous and the third is anisochronous with respect to the other two. For the sake of brevity we have underlined this characteristic by the use of an isosceles triangle to represent **2** and an equilateral triangle to represent **1** (Figure 1).

The presence of different phosphorus species was determined by comparison of observed chemical shifts with those previously reported by other workers. Table 1 contains all pertinent data from the literature and from our own observations.

Macrocycles **1a** and **1d** had been reported previously.[17] Treatment of **1a** with $Pd_2(dba)_3$ in THF afforded **2a** (Scheme 1). Macrocycles **1b**[14,15] and **1c**,[16] as well as their complexes **2b**[14,19] and **2c**,[16] had also been described.

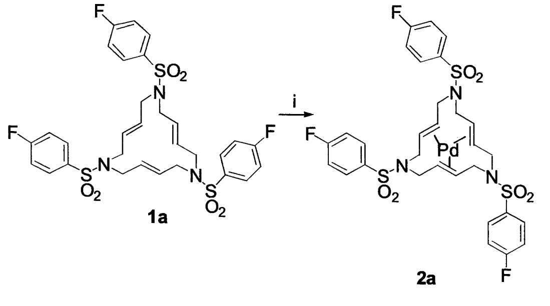
The general mechanistic conclusions of this paper are shown in Scheme 2. Palladium-macrocycle complexes **2** react with two mol of phosphane (or one mol of bidentate phosphane) to afford 14-electron species PdL_2 − the actual active species in palladium(0)-catalyzed reactions[1] − directly (Scheme 2). After catalysis comes to an end, if the phosphane is prone to oxidation (PPh_3 and dppb), palladium(0) reverts to the free macrocycle **1**, to be stored as complex **2**, ready for a new reaction requiring the addition of fresh phosphane but not fresh palladium. If, on the contrary, the phosphane is not easily oxidized (dppe and dppp), palladium remains as PdL_n, ready for a new reaction. This behavior has a clear advantage over the typical introduction of soluble palladium as $Pd(PPh_3)_4$ (**3a**), or other catalyst precursors. Thus, $Pd(PPh_3)_4$ exists in solution in equilibrium with $Pd(PPh_3)_3$ (**3b**) and with $Pd(PPh_3)_2$ (**3c**), plus free triphenylphosphane (Scheme 3). Whereas $Pd(PPh_3)_3$ is the predominant species in the equilibria, the truly active $Pd(PPh_3)_2$ species is only a minor component in the resulting equilibria.[23] In contrast, complexes **2** in the presence of two mol of PPh_3 quickly deliver high initial concentrations of $Pd(PPh_3)_2$.

Interaction between Complex 2a and Phosphanes. A ^{19}F NMR and ^{31}P NMR Study

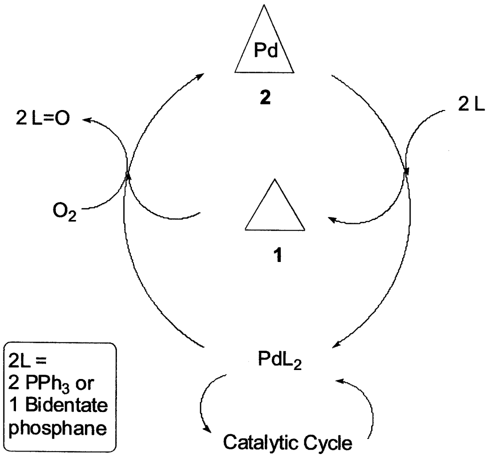
The conclusions of this part of the work depend on the correct interpretation of the ^{31}P NMR signals. NMR spectroscopic data of products **3−7** have been described in the literature, as have phosphorus signals of other pertinent compounds. These data are collected in Table 1. Tetrakis(triphenylphosphane)palladium (**3a**) gives a broad ^{31}P NMR signal. This is an indication of fast equilibria involving coordinatively unsaturated palladium species [$Pd(PPh_3)_n$, $n = 2$, 3 but mainly $n = 3$, Scheme 3].[23] Broad ^{31}P NMR signals have also been observed for dppb palladium complex **6**, both by us and by others.[30] Thus, product **6** is in equilibrium with other species. Whether or not the other species in equilibrium with **6** are open-chain species of type $(-Ph_2P-(CH_2)_4-PPh_2-Pd-)_x$ is not clear at present. Indeed, structure **6** requires a seven-membered ring, and more stable alternatives are probably possible.

Table 1. ^{31}P NMR spectroscopic data for pertinent compounds

Compound	^{31}P NMR spectroscopic data (δ and solvent)	Ref.
PPh_3	−5.6 (DMSO), −5.3 (THF), −4.1 (DMF)	this work
$O{=}PPh_3$	23.7 (THF)	this work
	30.5 ($CDCl_3$)	this work
	26.0 (DMF)	[24]
$Pd(PPh_3)_4$, **3a**	15.8 (THF)	[25]
	16.8 (br) at 10 mM (THF)	this work
	16.5 (br) at 20 mM (THF)	this work
	9 (br) (DMF)	[26]
	22.5 (br) (DMF)	[24]
$Pd(PPh_3)_4$ + 1 PPh_3	15.5 (br) (DMF)	[24]
$Pd(PPh_3)_4$ + 2 PPh_3	12.7 (br) (DMF)	[24]
$Pd(PPh_3)_4$ + 7 PPh_3	5.5 (br) (DMF)	[26]
$Pd(PPh_3)_3$, **3b**	20.5 (THF)	[25]
$Pd(PPh_3)_2$, **3c**	23.0−23.3 (THF)	[25]
$Pd(dba)(PPh_3)_2$	27.36, 25.53 (DMF)	[27]
$Ph_2P(CH_2)_2PPh_2$(dppe)	−12.6 (THF)	[28]
	−12.7 (THF)	this work
$Ph_2P(CH_2)_2P(O)Ph_2$(dppeO)	−11.5(d), 32.3(d) J = 48.0 ($CDCl_3$)	[29]
Pd(dppe)$_2$, **4**	30.4 (THF)	[28]
	30.6 (CH_2Cl_2)	[30]
	30.4 (THF)	this work
$Ph_2P(CH_2)_3PPh_2$(dppp)	−17.3 (THF)	[28]
	−17.6 (THF)	this work
$Ph_2P(CH_2)_3P(O)Ph_2$(dpppO)	−17.2, 32.0 ($CDCl_3$)	[29]
	31.2 [P(O)] (DMF)	[24]
$Ph_2P(O)(CH_2)_3P(O)Ph_2$(dpppO$_2$)	31.5 (DMF)	[24]
Pd(dppp)$_2$, **5**	4.0 (THF)	[28]
	4.2 (THF)	[30]
	3.8 (THF)	this work
$Ph_2P(CH_2)_4PPh_2$(dppb)	−17.1 (THF)	[28]
$Ph_2P(CH_2)_4P(O)Ph_2$(dppbO)	−16.5, 32.2 ($CDCl_3$)	[29]
	−16.2, 28.6 (THF)	this work
Pd(dppb)$_2$, **6**	12 (br) (CH_2Cl_2)	[30]
	5.0 (THF)	[28]
	10 (br) (THF)	this work
Pd(dppf)$_2$, **7**	7.4 (THF)	[28]
	6.4 (THF)	this work

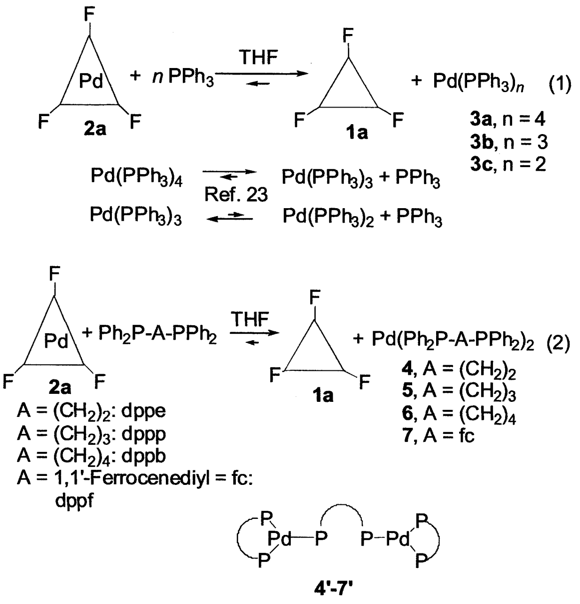


Scheme 1. Preparation of complex **2a**: i. $Pd_2(dba)_3$, THF, 80 °C



Scheme 2. Mechanistic role of macrocycles **1** and **2**

When complex **2a** (concd. ca. 10 mM) was mixed in the NMR tube with different amounts of triphenylphosphane in THF, macrocycle **1a** was formed (^{19}F NMR), together with bis(triphenylphosphane)palladium (**3c**) [^{31}P NMR, see Table 2 and Scheme 3, (1)]. Since **3c** reacts with more triphenylphosphane to afford $Pd(PPh_3)_3$ (**3b**), not all **2a** disappears. The data in Table 2 are informative with respect to the nature (value of n) of $Pd(PPh_3)_n$. Thus, only 60% of **1a** was formed for two mol of PPh_3, as a consequence of two consecutive equilibria, and ^{31}P NMR gave a broad peak (δ = 14−19). When greater quantities of PPh_3 were added, more complete conversion of **2a** into **1a** was observed, but



Scheme 3. Reactions between **2a** and phosphanes

^{31}P NMR revealed an upfield shift of the broad peak. Note that, according to literature data[25] (Table 1): the δ values for the phosphorus atoms in $Pd(PPh_3)_2$, $Pd(PPh_3)_3$, and $Pd(PPh_3)_4$ are ca. 23.1, 20.5, and 15.8 (br), respectively. This indicates that a **2a**/triphenylphosphane molar ratio of 1:2 gives a higher concentration of $Pd(PPh_3)_2$, or in any case higher than for ratios 1: >2.

Table 2. ^{31}P NMR spectroscopic data for mixtures of **2a** and PPh_3 in THF

Entry	Equiv of PPh_3	^{31}P NMR δ (ppm)	**1a** (%)[a]
1	2	14–19 (br)	60
2	3	11–16 (br)	63
3	4	5–16 (br)	80
4	6	7–17 (br)	100

[a] Determined by integration of ^{19}F NMR. The rest up to 100% is **2a**.

Additional evidence for the palladium transfer from **2a** to phosphanes was provided by ^1H NMR, which also showed the characteristic variation of chemical shifts of olefinic protons, upfield (δ < 5 ppm) for **2a** and downfield (δ > 5 ppm) for **1a**.

Similar experiments were performed with mixtures of **2a** and bidentate phosphanes (dppe, dppp, dppb, dppf) [see (2) in Scheme 3]. The equilibrium was shifted to the right in all cases, as evidenced by the signals of the macrocycle **1a** and of the complexes **4–7**. When, for instance, **2a** and dppe were mixed in a molar ratio of 1:1, 71% of **1a** was detected by ^{19}F NMR (Table 3). ^{31}P NMR gave a peak at δ = 30.4 ppm, agreeing with the value reported for $Pd(dppe)_2$, **4**.[28] Under equimolar conditions only 50% of **1a** would be expected to be formed. This phenomenon is repeated for all bidentate phosphanes. It could be due to the formation of species such as $Pd_{>1}(dppe)_2$ (for instance of type **4′**), which might produce broad signals, invisible in NMR. Only dppp showed behavior approaching what should be expected for the stoichiometry indicated in Scheme 3. In any case, the behavior is general.

Table 3. ^{31}P NMR spectroscopic data for mixtures of **2a** with bidentate phosphanes in THF

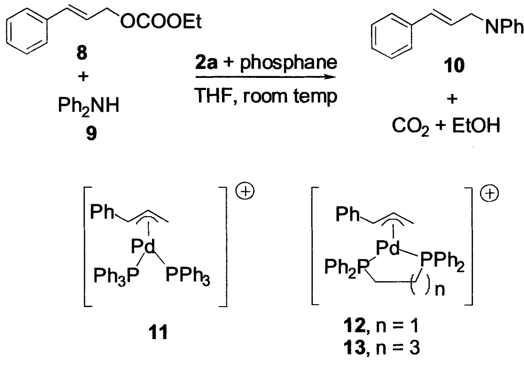
Entry	Moles of biphosphane	^{31}P NMR δ (ppm)	**1a** (%)[a]
1	dppe (1)	30.4 (**4**)[b]	71
2	dppp (1)	3.8 (**5**)[b]	56
3	dppb (1)	ca 10 (very br) (**6**)[b]	100
4	dppb (2)	Not observed	100
5	dppf (1)	6.4 (**7**)[b]	100

[a] Percentages of **1a** determined by ^{19}F NMR. [b] No other signals were visible in ^{31}P NMR.

We next checked the mechanistic role of complexes of general type **2** in two palladium-catalyzed reactions: allylation of diphenylamine with cinnamyl carbonate, and telomerization of butadiene with methanol.

Allylation of Diphenylamine with Cinnamyl Carbonate

Allylations of diphenylamine (**9**) with equimolar amounts of cinnamyl ethyl carbonate (**8**)[31] were performed in the NMR tube at the probe temperature. Macrocyclic complex **2a** was used as the palladium source in the presence of different quantities of PPh_3 or bidentate phosphanes (Scheme 4 and Table 4). Diphenylamine (0.2 M) and 5% molar palladium in the form of **2a** were dissolved in THF in the NMR tube under nitrogen atmosphere. In a typical experiment, no reaction had taken place after 5 days (Entry 1, Table 4). This was shown by ^1H NMR, since **8** and **10** have distinguishable spectra in the olefinic region. Upon addition of two mol of triphenylphosphane (with respect to Pd), however, the colorless solution turned yellow, the ^{19}F NMR signal of free macrocycle **1a** appeared while that of complex **2a** disappeared, and the ^{31}P NMR spectrum showed a broad peak centered at δ = 10 ppm, assigned to species $Pd(PPh_3)_n$ in fast equilibrium. After 24 hours the reaction was complete, ^{19}F NMR indicating mixtures of **1a** and **2a**, and ^{31}P NMR showing the presence of triphenylphosphane oxide, formed even under the inert atmosphere,



Scheme 4. Allylation of diphenylamine

Table 4. ^{19}F and ^{31}P NMR monitoring of Pd-catalyzed formation of **10** in THF

Entry	Palladium + phosphane	Time	^{19}F NMR products	^{31}P NMR δ (ppm)	Conversion
1	**2a**	5 days	only **2a**	–[a]	0%
	+ 2 PPh_3	immediately	only **1a**	10 (br)	–
	–	24 h	**1a** + **2a** (4:1)	18.8 (br), 24.8 ($OPPh_3$)	100%
	open air	–	only **2a**	24.8 ($OPPh_3$)	–
2	**2a** + 3 PPh_3	10 min	**1a** + **2a** (4:1)	29.0, 26.7, 24.9, 4–8 (br)	
	–	37 min	–	29.0, 26.7, 25.0, ca 10 (br)	–
	–	44 min	–	–	38–56%[b]
	–	1 day	–	26.7, 25.0, 24.4, 17–19 (br)	–
3	**3a**	9 min	NA[c]	28.9, 26.8, 24.6, 10–13 (br)	–
	–	20 min		28.9, 26.8, 24.6, 12–14 (br)	–
	–	41 min		28.9, 26.8, 24.6, 13–16 (br)	73%
4	$Pd_2(dba)_3$ + 2 PPh_3	10 min	NA	28.9, 26.8, 25.0, 24.6	–
		31 min		28.9, 26.8, 25.0, 24.6	–
		45 min		–	28%
5	**2a** + 1 dppe	6 min	only **1a**	30.3 (**4**)	–
		15 min	–	30.3, 46.0[d]/52.0[d] (**12**)	3%
		37 min	–	28.8, 29.3, 30.3, 46.0[d]/52.0[d] (**12**)	37%
		1 day	**1a** + **2a** (4:1)	30.1, 46.9/51.6, 55.4	71%
		6 days	**1a** + **2a** (1:3)	30.6 (**4**)	80%
6	**2a** + 1 dppb	11 min	only **1a**	−16.2/28.6 (dppbO), 17.3[e]/22.5[e] (**13**)	7%
		29 min	–	−16.2/28.6 (dppbO), 17.4[e]/22.5[e] (**13**)	9%
		1 day	–	–	59%
		2 days	**1a** + **2a** (1:2)	29.1	–
7	**2a** + 3 **1d**	10 min	only **1a**	8 (br) (see text), 24.1 (**1d** oxides)	–
		41 min	–	12 (br), 24.1	–
		1 day	–	20 (br), 24.1	100%

[a] Not registered. [b] Results from four different experiments. [c] Not applicable. [d] Doublet, $J = 40.3$ Hz. [e] Doublet, $J = 53.2$ Hz.

and a broad peak centered at 18.8. When the tube was opened to the ambient atmosphere, all the phosphorus was converted into triphenylphosphane oxide (δ = 24.8 ppm), while ^{19}F NMR showed *only* the presence of complex **2a**. These observations are fully consistent with the mechanistic proposal in Scheme 2.

Reactions performed in the presence of **2a** plus three mol of triphenylphosphane (Entry 2, Table 4), or only **3a** (Entry 3), or $Pd_2(dba)_3$ plus two mol of triphenylphosphane (Entry 4) gave similar results in terms of the intermediates involved. Indeed, three to four singlets were detected in the ^{31}P NMR spectra in all three cases. The chemical shifts are very close to those reported for π-allyl cationic intermediate **11**.[32] Another reaction similar to that of entry 4 but with 20% molar $Pd_2(dba)_3$ gave a ^{31}P NMR spectrum (in 35 min) consisting of two doublets of equal intensity at δ = 25.0 and 26.8 ppm (J = ca. 6 Hz) and a singlet at δ = 25.6 ppm. The two doublets are attributable to $Pd(dba)(PPh_3)_2$, as the chemical shifts are coincident with those reported.[27] The reaction in the presence of **2a** and dppe as catalyst source (Entry 5) gave a signal attributable to **4** at δ = 30.3 ppm and, simultaneously, only the signal of free macrocycle **1a** appeared, due to the complete transfer of palladium from **2a** to dppe. As the reaction progressed, two phosphorus doublets appeared, centered at δ = 46.0 and 52.0 ppm and with $J = 40.3$ Hz. These values are coincident with those reported for the tetrafluoroborate of **12**.[33] At the end of the reaction the signals of **2a** reappeared as a consequence of the slow transfer of palladium back to macrocycle **1a**. Similar results were obtained with dppb (Entry 6); in this case signals at δ = −16.2 and 28.6 ppm can be assigned to 1,4-bis(diphenylphosphane)butane monoxide.

One additional experiment consisted of the use of a precatalytic system made up of complex **2a** and the macrocyclic triphosphane **1d**[17] (Entry 7, Table 4). After a short time, only ligand **1a** was observed by ^{19}F NMR. The palladium is transferred to the peripheral phosphorus of **1d**, as indicated by broad peaks at variable chemical shifts in the ^{31}P NMR. Therefore, **1d** behaves similarly to simple triphenylphosphane.

Telomerization of Butadiene with Methanol

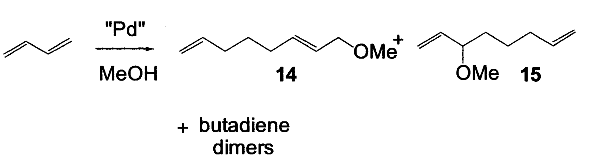
As mentioned in the introduction, complex **2b**, used alone, was ineffective for the telomerization of butadiene with methanol (Scheme 5, Table 5, entry 1).[21] In association with triphenylphosphane, however, it became efficient and the catalytic system was recoverable and then reusable, provided that fresh phosphane was added in each experiment[34] (Table 5, entries 2 and 3). For purposes of comparison, other catalyst precursors such as $Pd_2(dba)_3{\cdot}CHCl_3$ and $Pd(OAc)_2$ in association with an external ligand and without macrocycle, were also able to promote the reaction, but their activity dropped dramatically on recycling, even with addition of phosphane (Table 5, entries 4 and 5). Since the nature of the ligand often plays a crucial role in telomerization,[35] we briefly investigated this parameter. Among the phosphanes tested with $Pd_2(dba)_3$ as precursor, the best activities were presented by tris(*p*-tolyl)phosphane and

Table 5. Catalysts efficiency and recycling in telomerization of butadiene with methanol

Entry[a]	Pd + Phosphane[b]	Runs	T.O.F. [h^{-1}]	Conv. %	Selectivity (%) 14	15	Dimers
1	**2b** + PPh_3 (0)	1	60	3	16	0	84
2	**2b** + PPh_3 (3)	1	1360	68	72	16	12
	(recycling)+ PPh_3 (0)	2	820	41	85	7	8
3	Run 1 (Entry 2)	1	1360	68	72	16	12
	(recycling) + PPh_3 (3)	2	1740	87	80	14	6
	(recycling) + PPh_3 (3)	3	1400	70	79	14	7
	(recycling) + PPh_3 (3)	4	1500	75	81	14	5
4	$Pd_2(dba)_3$ + PPh_3 (3)	1	920	46	73	9	18
	(recycling) + PPh_3 (3)	2	180	9	67	10	23
	(recycling) + PPh_3 (3)	3	20	1	0	0	100
5	$Pd(OAc)_2$ + PPh_3 (3)	1[c]	2000	75	82	11	7
	(recycling) + PPh_3 (3)	2	300	15	80	7	13
	(recycling) + PPh_3 (3)	3	0	0	−	−	−
6	$Pd_2(dba)_3.CHCl_3$ + P(*p*-tolyl)$_3$ (2)	1[c]	2533	95	88	7	5
7	$Pd_2(dba)_3.CHCl_3$ + Et_2NPPh_2 (3)	1[d]	2940	98	84	6	8

[a] Reaction conditions: Pd/MeOH/C_4H_6 = 1:6000:4000; $2.5 \cdot 10^{-2}$ mmol Pd, starting butadiene pressure = 4 bar, 60 °C. The catalysts were recovered after distillation under reduced pressure of the products of first runs and directly reused. [b] In parentheses, mol of phosphane (or amine) per mol of palladium. [c] Reaction time: 0.75 h. [d] Reaction time: 0.66 h.

N,*N*-diethylaminodiphenylphosphane[36] (entries 6 and 7). Ligand basicity due to the presence of a nitrogen atom, introducing a new coordination site, could be a relevant factor.[37] The role of the macrocycle **1b** in maintaining the catalytic activity is clear in Table 6: whatever the precursor [$Pd_2(dba)_3 \cdot CHCl_3$ or $Pd(OAc)_2 \cdot$phosphane], we observed efficient recycling when the initial run was carried out in the presence of **1b**, although we have no explanation for the drop in activity in run 4 of entry 2. The TOFs of the first run were lower when **1b** was present than in its absence (Table 5), suggesting an induction period for the formation of the active catalyst. Indeed, in the second run, the TOF was enhanced. After reaction catalyzed by the active palladium-phosphane species is complete, the stability of **1b** permits recovery of the metal, avoiding precipitation. The oxidation of the phosphane in this process is not detrimental for the palladium(0). In fact, the recovered material, active in recycling experiments, contains the complex **2b** and something else. Thus, after distillation of the reaction product of Entry 3 (Table 5), ^1H and ^{31}P NMR spectra of the solid residue show the presence of free **1b** and $Pd(PPh_3)_n$ without any trace of metallic palladium. However, the same residue after 12 h at reflux in THF under air atmosphere quantitatively afforded **2b** and Ph_3PO, as indicated by NMR.



Scheme 5. Telomerization of butadiene with methanol

Interaction between Complex 2c and Phosphanes − An ESI-MS Study

Further evidence of the formation of **3b**, **3c**, **4**, **6**, and **7** when macrocycles **2** react with phosphanes was gained by an ESI-MS study of the reactions between complex **2c**[16] and several phosphanes in THF. Since ESI-MS is a soft ionization mass spectrometry,[38] its ability to detect ionic species in solution provides a convenient technique for direct observation of reaction intermediates.[39] In order to study the interactions between complex **2c** and phosphanes, mixtures of **2c** with different amounts of several phosphanes (PPh_3, dppe, dppb, and dppf) in anhydrous and degassed THF were analyzed by positive ion ESI-MS. After some experimentation, a cone voltage of 30 eV and quenching with aqueous 1% trifluoroacetic acid were found to permit better detection of PdL_x species. Peaks due to species containing palladium were immediately identifiable by the characteristic isotope distribution of the metal. Identification of species was aided by comparison of observed and calculated isotope distribution patterns, the latter calculated with the *Isoform* program. ESI-MS data are summarized in Table 7.

In entries 1−3 a solution of $Pd(PPh_3)_4$ (**3a**) in THF was investigated. A small cluster of peaks at m/z = 889−899, consistent with $Pd(PPh_3)_3$ (**3b**), was detected. A more intense cluster of peaks at m/z = 740−750 was observed when TFA was added to the sample (entry 2). This cluster is consistent with the incorporation of the anionic group (CF_3COO^-) originating from the solvent into the PdL_2 complex, [$Pd(PPh_3)_2$ (**3c**) + $CF_3COO]^+$.[40] When TFA was substituted for CH_3COONH_4 (entry 3) the above cluster disappeared and a new cluster was observed at m/z = 686−696, corresponding to [$Pd(PPh_3)_2$ (**3c**) + $CH_3COO]^+$.

Table 6. Catalyst recycling in the presence of **1b** in telomerization of butadiene with methanol

Entry[a]	Pd + ligands[b]	Run	T.O.F. h^{-1}	Conv. %	Selectivity (%)		
					14	**15**	Dimers
1	$Pd_2(dba)_3$[c] + **1b** (1) + PPh_3 (3)	1	1360	68	88	6	6
	recycling + PPh_3 (3)	2	1760	88	82	13	5
	recycling + PPh_3 (3)	3	1680	84	81	11	8
	recycling + PPh_3 (3)	4	1700	85	84	8	8
2	$Pd(OAc)_2$ + **1b** (1) + PPh_3 (3)	1	420	21	81	10	9
	recycling + PPh_3 (3)	2	1120	56	82	14	4
	recycling + PPh_3 (3)	3	1100	55	80	11	9
	recycling + PPh_3 (3)	4	500	25	80	9	11
3	$Pd_2(dba)_3$[c] + **1b** (1) + P(*p*-Tol)$_3$ (3)	1	940	47	81	12	7
	recycling + P(*p*-Tol)$_3$ (3)	2	2000	100	87	11	2
	recycling + P(*p*-Tol)$_3$ (3)	3	1580	79	83	12	5
	recycling + P(*p*-Tol)$_3$ (3)	4	1800	90	85	12	3
4[d]	$Pd_2(dba)_3$[c] + **1b** (1) + Et_2NPPh_2 (3)	1	2340	78	78	12	10
	recycling + Et_2NPPh_2 (3)	2	3000	100	84	7	9
	recycling + Et_2NPPh_2 (3)	3	2850	95	80	10	10
	recycling + Et_2NPPh_2 (3)	4	2910	97	86	6	8

[a] Reaction conditions for the first runs: $2.5 \cdot 10^{-2}$ mmol Pd; Pd/**1b**/phosphane/MeOH/C_4H_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 addition of phosphane, methanol, and butadiene in each recycling experiment. [b] Moles of phosphane (or amine) per mol of palladium. [c] $Pd_2(dba)_3.CHCl_3$. [d] Reaction time: 40 min.

The major peak in the mass spectra in all cases (entries 1−3) is at *m*/*z* = 644−654, corresponding to a doubly positively charged species. At a cone voltage of 50 eV the cluster was only observed at low intensity, and it disappeared upon further increasing the cone voltage to 100 eV. The observation of that cluster down to high cone voltage suggests that the doubly charged species may be an aggregate ion. In ESI-MS it is well known that higher values of cone voltage may be useful for minimization of aggregates of ions.[39b−39c]

When triphenylphosphane was mixed with complex **2c** (entries 4 and 5) in THF and upon addition of TFA, clusters corresponding to species $Pd(PPh_3)_2$ (**3c**) and $Pd(PPh_3)_3$ (**3b**) were identified in the spectrum. Unexpectedly, an increase in the number of equivalents of PPh_3 (entry 5) did not change the relative intensities of the clusters. An unassigned cluster at *m*/*z* = 644−654 was also observed.

Similar experiments were performed with mixtures of **2c** and bidentate phosphanes (dppe, dppb, and dppf). In the case of dppe (entries 6 and 7) the ESI-MS spectrum showed an intense cluster at *m*/*z* = 899−909, consistent with species $Pd(dppe)_2$ (**4**). Two new clusters at *m*/*z* = 915−925 and *m*/*z* = 932−942 could also be observed as weak ions, consistent with single or double oxidation of a phosphane function, respectively. Again, an adduct with trifluoroacetate anion was also observed at *m*/*z* = 1012−1022, and an unknown doubly charged aggregate at *m*/*z* = 829−839 was detected as a major peak at 30 eV. When four equivalents of dppe were used (entry 7), the relative proportion of the PdL_2 species **4** increased at the expense of the doubly charged ion.

The positive ion spectra for mixtures of **2c** with dppb (entry 8) and dppf (entries 9−11) also gave species corresponding to $Pd(Ph_2P{-}A{-}PPh_2)_2$, similarly to that observed with dppe. With dppb, a cluster at *m*/*z* = 955−965 assigned to $[Pd(dppb)_2]$ (**6**) was observed, together with an intense peak corresponding to the oxidation of a phosphorous atom (entry 8). Again, the most intense peak in the spectrum was a doubly positively charged species at *m*/*z* = 547−557. In the case of phosphane dppf (entries 9−11), $[Pd(dppf)_2]$ (**7**) at *m*/*z* = 1211−1221, plus the cluster attributable to [Pd(dppf){dppf(O)}] at *m*/*z* = 1227−1237 were detected. An additional cluster at *m*/*z* = 675−685 at half-mass separation was observed, showing behavior similar to that in the above cases. Finally, when working at higher voltage (50 eV), clusters due to Pd(dppf) and an oxidation derivative were observed (entry 11). It is difficult to say whether Pd(dppf) was already in the original sample or whether it was generated by fragmentation from **7** in the mass spectrometer. A general feature of all these spectra is the disappearance of the doubly positively charged species when the skimmer cone voltage is increased.

Macrocyclic complex **2c** and its corresponding free ligand **1c** could not be detected in the spectra of crude reaction mixtures with phosphanes, possibly because the ionization process of PdL_x species was easier than for **2c** and **1c**. However, mass spectra of pure **1c** and **2c** have been routinely registered and reported elsewhere.[16]

We can conclude that ESI-MS provides complementary confirmation for the formation of PdL_x species, in good agreement with NMR spectroscopic observations.

Conclusion

This work started from an observation concerning the potential of the 15-membered macrocycles **1** for the recycling of active catalytic palladium species for the telomeriz-

Table 7. Electrospray mass spectroscopic data for mixtures of **2c** with phosphanes

Entry	Sample[a]	Detected species[b]
1	**3a**[c]	**3b**, m/z = 889−899; m/z = 644−654[d]
2	**3a**	**3b**, m/z = 889−899; [**3c** + CF_3COO]$^+$, m/z = 740−750; m/z = 644−654[d]
3	**3a**[e]	**3b**, m/z = 889−899; [**3c** + CH_3COO]$^+$, m/z = 686−696; m/z = 644−654[d]
4	**2c** + 2 PPh_3	**3b**, m/z = 889−899; [**3c** + CF_3COO]$^+$, m/z = 740−750; m/z = 644−654[d]
5	**2c** + 6 PPh_3	**3b**, m/z = 889−899; [**3c** + CF_3COO]$^+$, m/z = 740−750; m/z = 644−654[d]
6	**2c** + 2 dppe	m/z = 829−839[d]; **4**, m/z = 899−909; [Pd(dppe){dppe(O)}]$^+$, m/z = 915−925; [Pd{dppe(O)}{dppe(O)}]$^+$, m/z = 932−942; [**4** + CF_3COO]$^+$, m/z = 1012−1022
7	**2c** + 4 dppe	m/z = 829−839[d]; **4**, m/z = 899−909; [Pd(dppe)(dppe(O))]$^+$, m/z = 915−925; [Pd{dppe(O)}{dppe(O)}]$^+$, m/z = 932−942; [**4** + CF_3COO]$^+$, m/z = 1012−1022
8	**2c** + 4 dppb	m/z = 547−557[d]; **6**, m/z = 955−965; [Pd(dppb){dppb(O)}]$^+$, m/z = 971−981; [Pd{dppb(O)}{dppb(O)}]$^+$, m/z = 987−997
9	**2c** + 2 dppf	m/z = 675−685[d]; **7**, m/z = 1211−1221; [Pd(dppf){dppf(O)}]$^+$, m/z = 1227−1237
10	**2c** + 4 dppf	m/z = 675−685[d]; **7**, m/z = 1211−1221; [Pd(dppf){dppf(O)}]$^+$, m/z = 1227−1237
11[f]	**2c** + 4 dppf	[Pd(dppf) + H]$^+$, m/z = 658−668; m/z = 675−685[d]; [Pd(dppf)$(O)_2$], m/z = 689−699.

[a] All the solutions were prepared in anhydrous and degassed THF and quenched with aqueous 1% trifluoroacetic acid (TFAA). Samples were investigated by use of a CH_3CN/H_2O mobile phase. [b] Reported clusters are from lowest to highest mass observed (calculated) in isotope envelope. [c] This sample was without additives. [d] Unassigned. [e] Ammonium acetate was added to the sample. [f] Spectrum determined at 50 eV.

ation of butadiene with methanol, these species being generated from various Pd^{II} or Pd^0 precursors.[21]

The modification of the macrocyclic structure by attachment of a fluorine atom on the aryl group, as in **1a**, has enabled the behavior of the corresponding complex **2a** in the presence of phosphanes to be elucidated, through multinuclear NMR studies. Similar results were obtained from an ESI-MS study with complex **2c**. We have shown that the turnover of the catalytic system in the telomerization of butadiene and in the Tsuji−Trost allylation requires the presence of external phosphane ligands, producing low-valence active $Pd(PPh_3)_n$. At the end of the reaction, the macrocyclic ligand **1** recovers and stabilizes palladium(0) to afford stable and soluble complexes **2**. This permits recycling of the metal and reconstitution of the catalytic system after addition of fresh phosphane.

Experimental Section

General Remarks: Macrocycles **1** were prepared as described.[15−17] Melting points were determined with a Kofler apparatus and are uncorrected. IR spectra were recorded with a Nicolet FT-IR 510 ZDX instrument. NMR spectra were recorded with a Bruker-Analytik AC 250 machine. ^1H NMR (250 MHz) chemical shifts are reported relative to $CHCl_3$ at δ = 7.26 ppm and to tetramethylsilane at δ = 0.00 ppm, ^{13}C NMR shifts (62.5 MHz) are reported relative to chloroform at δ = 77.00 ppm and tetramethylsilane at δ = 0.0 ppm. ^{19}F NMR (223 MHz) and ^{31}P (101 MHz) NMR chemical shifts are expressed relative to trifluoroacetic acid and to phosphoric acid, respectively. Mass spectra (EIMS) were obtained with a Hewlett−Packard 5989A spectrometer and determined at an ionizing voltage of 70 eV; relevant data are listed as m/z (%). MALDI-TOF spectra were recorded on a BIFLEX spectrometer (Bruker−Franzen Analytik) equipped with a pulsed nitrogen laser (337 nm), operating in positive-ion reflector mode, and using 19 kV acceleration voltage. Matrices (α-cyanocinnamic acid) were prepared at 5 mg/mL in THF. Analytes were dissolved at concentrations of between 0.1 and 5 mg/mL in THF or chloroform. Elemental analyses were determined at the "Servei d'Anàlisi Química de la Universitat Autònoma de Barcelona".

Gas phase chromatographs of the telomerization mixtures were recorded on a HP 6890 chromatograph equipped with a flame ionization detector and a HP 3395 integrator under the following conditions: DB1 capillary column (length: 25 m, diameter 0.32 mm), nitrogen as vector gas (0.4 bar), temperature of injector and detector: 250 °C, temperature of the oven: isotherm 50 °C-2 minutes, then 50−250 °C (5 °C/min.); nonane as internal standard.

Electrospray mass spectrometry analyses were recorded on a Navigator quadrupole mass spectrometer (Finnigan AQA ThermoQuest) equipped with an electrospray ion source. The instrument was operated in the positive ion mode (ESI+) at a probe tip voltage of 3 kV. The samples were dissolved in anhydrous and degassed THF. The solution, typically of an approximate concentration of 4 mM, could be further treated by the addition of 1−2 drops of a 0.1% M TFA aqueous solution. The samples were introduced into the mass spectrometer ion source directly through a Rheodyne injector with a 20 μL sample loop. The mobile phase flow (150 μL/min of 70:30 v/v CH_3CN/H_2O) was delivered by a P2000 HPLC pump (ThermoQuest) to the vaporization nozzle of the electrospray ion source (170 °C) and nitrogen was employed as both a drying and a nebulizing gas. Skimmer cone voltages were varied between 10 and 100 eV. Spectra were typically an average of 10−20 scans. Theoretical isotope patterns were calculated by use of the *Isoform* program and used to aid in assignment.

(*E*,*E*,*E*)-1,6,11-Tris[(4-fluorophenyl)sulfonyl]-1,6,11-triazacyclopentadeca-3,8,13-trienepalladium(0) (2a): A solution of $Pd_2(dba)_3$ (0.26 g, 0.28 mmol) in THF (2 mL) was added at 80 °C to a solution of **1a**[17] (0.35 g, 0.51 mmol) in THF (3 mL). The red color disappeared within minutes, and the mixture was stirred for another 30 min at room temp. The solution was then diluted with hexane (40 mL), with stirring. The formed precipitate was filtered off, washed with hexane (2 × 5 mL), and dried (0.40 g, quantitative), m.p. (dec) 180 °C. IR (KBr): ṽ = 1593, 1494, 1340, 1169, 1154 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 1.68−1.85 (m, 4 H), 2.84 (t, J =

12.2 Hz, 2 H), 3.12 (dd, J = 11.1, 10.9 Hz, 2 H), 3.80 (m, 2 H), 4.04 (m, 2 H), 4.60−4.70 (m, 4 H), 4.81 (d, J = 14.3 Hz, 2 H), 7.20 (m, 6 H), 7.84 (m, 6 H) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 45.0, 47.8, 48.9, 77.6, 79.3, 82.4, 116.8 (d, J = 22.9 Hz), 130.0 (d, J = 8.6 Hz), 134.7, 164.5 (d, J = 249.9 Hz) ppm. ^{19}F NMR (CDCl$_3$): δ = −105.43 (s, 1 F), −105.26 (s, 2 F) ppm. MALDI-TOF MS: *m*/*z*: 787.8 [M + H]$^+$, 809.8 [M + Na]$^+$, 825.8 [M + K]$^+$. $C_{30}H_{30}F_3N_3O_6PdS_3$ (788.20): calcd. C 45.72, H 3.84, N 5.33, S 12.20; found C 45.71, H 3.72, N 5.30, S 11.83.

General Procedure for the Telomerization of Butadiene with MeOH: The catalytic system (palladium source and phosphane) was introduced into the autoclave, which was equipped with a magnetic stirrer bar. After three purges (vacuum-argon), the degassed solution of MeOH (6 mL) and nonane (internal GC standard, 128 mg) were introduced under argon. The autoclave was then cooled to −20 °C in a bath of acetone/liquid nitrogen. The butadiene (9 mL, condensed at −20 °C in a Schlenk tube) was carefully transferred into the autoclave under argon. The system was then heated in an oil bath at 60 °C for the times listed in the tables. At the end of the reaction, the autoclave was cooled to room temperature and carefully opened under a hood to avoid possible resulting butadiene emanation. The reaction products were recovered by distillation at 40 °C under reduced pressure (10^{-2} Torr).

Recycling Procedure: After the above distillation, the resulting solid residue was reused after addition of phosphane and reactants without any further treatment.

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