Steric Control of Oxidative Trimerization of Alkynyl Ligands in Trimethylphosphane Palladium Complexes

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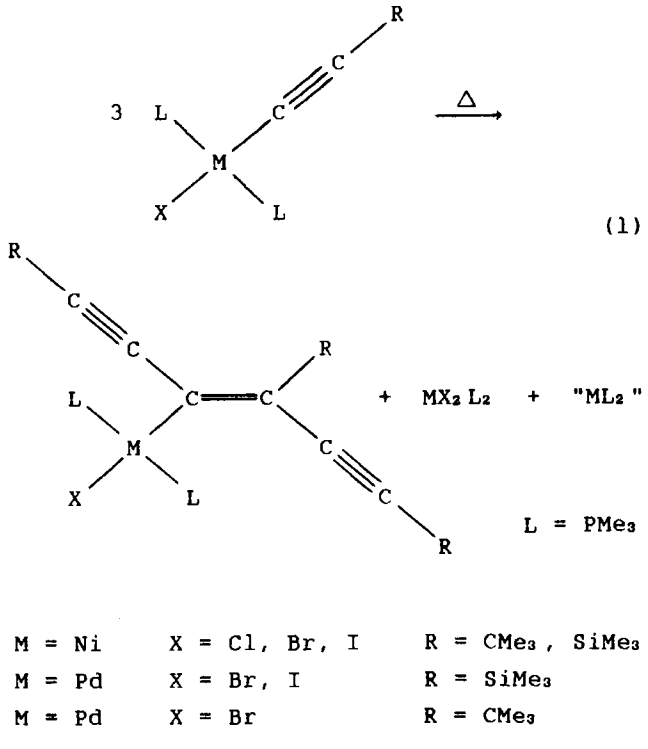
Alkynylpalladium compounds *trans*-PdX(C≡C−R)(PMe_3)$_2$ [R = CMe_3, X = Cl (**1**), I (**19**); R = CMe_2OH, X = Cl (**2**), Br (**10**), I (**11**); R = *c*-Hex, X = Cl (**3**), Br (**12**), I (**13**); R = $CHMe_2$, X = Br (**4**); R = CH_2SiMe_3, X = Cl (**5**), Br (**14**), I (**15**); R = COOEt, X = Br (**6**), I (**7**); R = Ph, X = Cl (**8**), I (**17**); R = *n*-Pr, X = N_3 (**16**), I (**20**); R = *n*-Hex, X = I (**21**); R = $SiPh_3$, X = Br (**22**)] and *trans*-PdX(C≡C−R)(PBu_3)$_2$ [R = $SiMe_3$, X = Cl (**9**), I (**18**)] as well as *trans*-PdX(C≡C−R)(PPh_3)$_2$ [R = CMe_3, X = Br (**23**); R = CH_2SiMe_3, X = Br (**24**), I (**25**)] are prepared by known methods. Thermal decomposition between 120 and 160°C results in a selective transformation only with trimethylphosphane complexes **1**, **2**, **10**–**13**, and **19**. Oxidative trimerization of the alkynyl groups C≡C−CMe_2R' and C≡C−(*c*-Hex) affording the enediynyl compounds *trans*-PdX[C(C≡C−CMe_2R')=C(C≡C−CMe_2R')CMe_2R'](PMe_3)$_2$ [R' = Me, X = Cl (**26**), I (**27**); R' = OH, X = Cl (**28**), Br (**29**), I (**30**)] and *trans*-PdX{C[C≡C−(*c*-Hex)]=C[C≡C−(*c*-Hex)](*c*-Hex)}(PMe_3)$_2$ [X = Br (**31**), I (**32**)] appears to be controlled by balanced steric demands of phosphorus and alkynyl substituents. The steric control is investigated by melting transformable monoalkynyl complex *trans*-PdI(C≡C−CMe_2OH)(PMe_3)$_2$ (**11**) with non-transformable[*] complex *trans*-PdI[C≡C−(*n*-Pr)](PMe_3)$_2$ (**20**) to give a mixture (**A**) of transformed complexes with mixed substituents R. Similar results are obtained in other mixtures, when transformable PdBr(C≡C−$SiMe_3$)(PMe_3)$_2$[1] is heated with the non-transformable complexes PdBr[C≡C−(*n*-Pr)](PMe_3)$_2$[1] and **20** (mixture **B**) or transformable PdBr[C≡C−(*c*-Hex)](PMe_3)$_2$ (**12**) with non-transformable PdBr[C≡C−(*n*-Pr)](PMe_3)$_2$[1] (mixture **C**).

Monoalkynylpalladium halides containing two trimethylphosphane ligands can be thermally transformed into enediynyl compounds in analogy to the corresponding nickel systems[2], if sterically non-demanding phosphane units on the metal and bulky CMe_3 or $SiMe_3$ substituents on the alkylnyl group are provided[1]. By this method enediynyl compounds become accessible, which are not or only in low yields obtainable by other methods. In recent years, enediynyl compounds have been investigated, because some undergo Bergman cyclization[3] showing effects as antitumor antibiotics[4].

While the heavier halide ions X favor the reaction in the order Cl < Br < I, transformation is blocked by bulkier triorganophosphane or alkynyl ligands. As an influence of inductive effects of substituents R is not observed[5] steric control is obvious.

Using published methods[1,2], we have synthesized a large number of alkynyl compounds of palladium and report on experiments of oxidative trimerization in the melt under aspects of stereoselectivity.



Syntheses of Alkynylpalladium Halides

The method of dehydrohalogenation by using a tertiary amine is most widely applied and gives highest total yields, although the reaction according to Equation (2) is usually less productive than the final step in the oxidative substitution described in Equation (4).

[*] Here and in the following "non-transformable" refers to the pure complexes.

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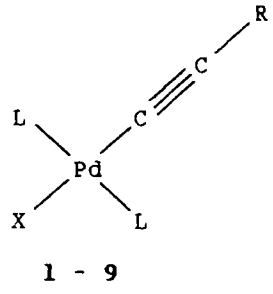
$$PdX_2L_2 + HC{\equiv}CR + NEt_3 \xrightarrow[48 - 81\%]{EtOH}$$



+ $HNEt_3X$ (2)

1 - 9

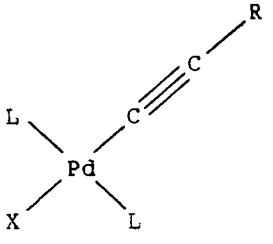
	L
1 - 8	PMe_3
9	PBu_3

	R	X
1	CMe_3	Cl
2	CMe_2OH	Cl
3	cyclo-Hex	Cl
4	$CHMe_2$	Br
5	CH_2SiMe_3	Cl

	R	X
6	COOEt	Br
7	COOEt	I
8	Ph	Cl
9	$SiMe_3$	Cl

A convenient complement is provided by the transhalogenation reaction according to Equation (3).

$$PdCl(C{\equiv}CR)L_2 + NaX \xrightarrow[85 - 96\%]{EtOH}$$



+ NaCl (3)

10 - 18

	L
10 - 17	PMe_3
18	PBu_3

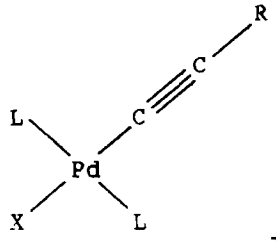
	R	X
10	CMe_2OH	Br
11	CMe_2OH	I
12	c-Hex	Br
13	c-Hex	I
14	CH_2-$SiMe_3$	Br

	R	X
15	CH_2-$SiMe_3$	I
16	n-Pr	N_3
17	Ph	I
18	$SiMe_3$	I

When selectivity or yield of the dehydrohalogenation reaction (Equation 2) is low, alkynylpalladium halides are conveniently prepared by oxidative substitution according to Equation (4).

The new complexes crystallize from weakly polar solvents and are mostly air-stable in the solid state. When some of the compounds (**6**, **7**, **14**–**16**, **20**, **21**) at 20°C turn black within three weeks in daylight, such decomposition reaction usually does not indicate a transformation given by Equation (1). Only the compounds **1**, **2**, **10**–**13**, and **19** in the melt at 120–160°C undergo an oxidative trimerization of alkynyl groups according to Equation (5).

$$PdL_4 + X\text{-}C{\equiv}C\text{-}R \xrightarrow[86 - 95\%]{Et_2O}$$



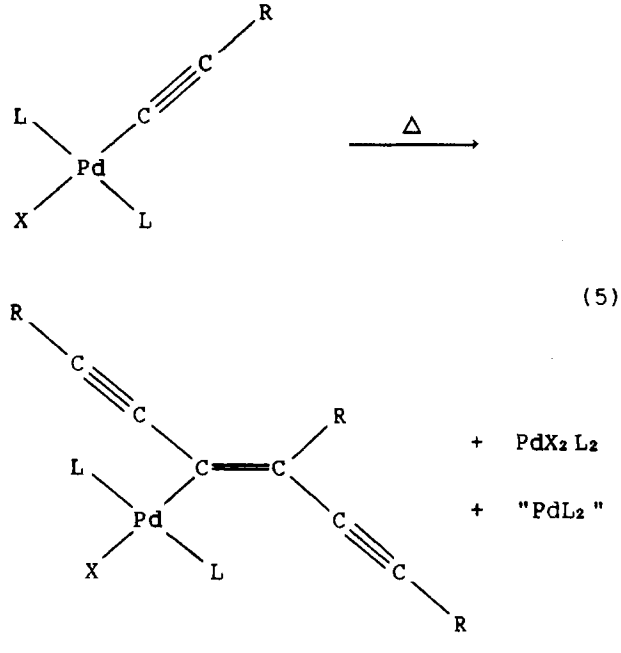
+ 2 L (4)

19 - 25

	L
19 - 22	PMe_3
23 - 25	PPh_3

	R	X
19	CMe_3	I
20	n-Pr	I
21	n-Hex	I
22	$SiPh_3$	I

	R	X
23	CMe_3	Br
24	CH_2-$SiMe_3$	Br
25	CH_2-$SiMe_3$	I



(5)

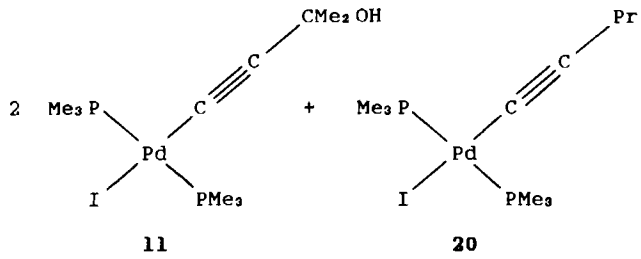
26 - 32 L = PMe_3

	R	X
26	CMe_3	Cl
27	CMe_3	I
28	CMe_2OH	Cl
29	CMe_2OH	Br

	R	X
30	CMe_2OH	I
31	c-Hex	Br
32	c-Hex	I

In order to investigate the mechanics of steric control and the limits of reactivity transformable monoalkynyl complexes are molten with non-transformable monoalkynyl complexes.

An excess of transformable **11** is kept with non-transformable **20** for 2 h at 115–120°C. A red-brown oil **A** separates containing different transformed complexes in statistical distribution [Equation (6)].



11 **20** (6)

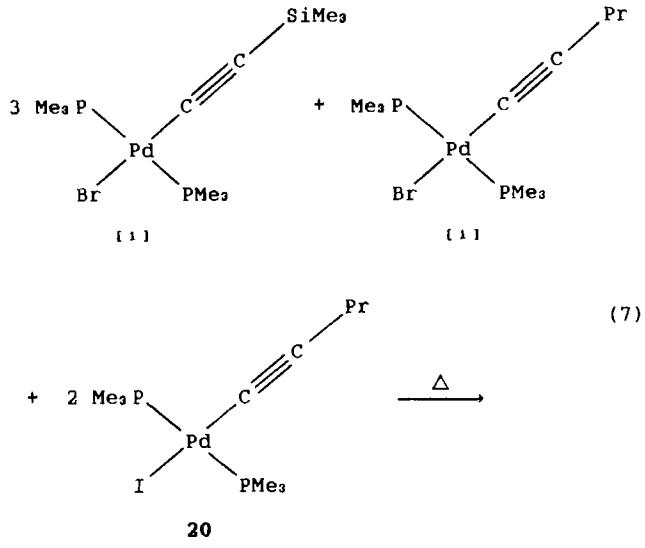
$\xrightarrow{\Delta}$ **A** + $PdI_2(PMe_3)_2$ + "$Pd(PMe_3)_2$"

Equiv.	A	PdI[C(C≡C-R)=C(C≡C-R)R](PMe3)2
0.17	PdI[C(C≡C-CMe2OH)=C(C≡C-CMe2OH)CMe2OH](PMe3)2	**30**
0.33	PdI{C[C≡C-(n-Pr)]=C(C≡C-CMe2OH)CMe2OH}(PMe3)2[a]	**33**
0.33	PdI{C[C≡C-(n-Pr)]=C[C≡C-(n-Pr)]CMe2OH}(PMe3)2[a]	**34**
0.17	PdI{C[C≡C-(n-Pr)]=C[C≡C-(n-Pr)](n-Pr)}(PMe3)2	**35**

R = CMe_2OH, n-Pr [a] The substituents R appear to be distributed at random

In another reaction 3 equivalents of PdBr(C≡C–$SiMe_3$)$(PMe_3)_2$[1] are heated with 1 equivalent of PdBr[C≡C–(*n*-Pr)]$(PMe_3)_2$[1] and 2 equivalents of **20**. The resulting red brown oil **B** contains different transformed complexes in statistical distribution [Equation (7)].

These results led us to investigate the catalytic activity of a selected transformable complex. One equivalent of transformable **12** is heated with 11 equivalents of non-transformable PdBr[C≡C–(*n*-Pr)]$(PMe_3)_2$[1] [Equation (8)] to yield a red-brown oil **C** containing different transformed complexes with the remarkable product distribution shown below.



(7)

B + 2 $PdX_2(PMe_3)_2$ + 2 "$Pd(PMe_3)_2$"

Equiv.	B	PdX[C(C≡C-R)=C(C≡C-R)R](PMe3)2
0.30	PdBr[C(C≡C-SiMe3)=C(C≡C-SiMe3)(SiMe3)](PMe3)2	[1]
0.50	PdBr[C(C≡C-SiMe3)=C(C≡C-SiMe3)(n-Pr)](PMe3)2[a]	**36**
0.46	PdBr{C(C≡C-SiMe3)=C[C≡C-(n-Pr)](n-Pr)}(PMe3)2[a]	**37**
0.27	PdBr{C[C≡C-(n-Pr)]=C[C≡C-(n-Pr)](n-Pr)}(PMe3)2	**38**
0.19	PdI[C(C≡C-SiMe3)=C(C≡C-SiMe3)(SiMe3)](PMe3)2	[1]
0.08	PdI[C(C≡C-SiMe3)=C(C≡C-SiMe3)(n-Pr)](PMe3)2[a]	**39**
0.12	PdI{C(C≡C-SiMe3)=C[C≡C-(n-Pr)](n-Pr)}(PMe3)2[a]	**40**
0.08	PdI{C[C≡C-(n-Pr)]=C[C≡C-(n-Pr)](n-Pr)}(PMe3)2	**35**

X = Br, I; R = $SiMe_3$, n-Pr

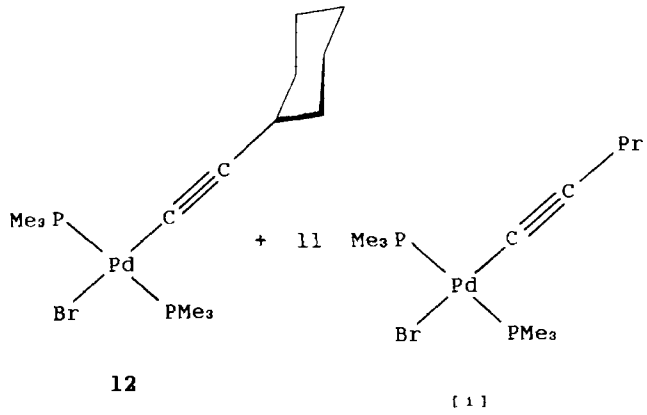
[a] The substituents R appear to be distributed at random

Table 1. Cone angles of alkynyl groups (C≡C–R)

R	Cone angle [°]	R	Cone angle [°]
COOEt	42	$CHMe_2$	66
Ph	57	CH_2-$SiMe_3$	66
n-Pr	58	$SiMe_3$	70
n-Bu	58	CMe_2OH	73
n-Hex	58	CMe_3	76
c-Hex	64	$SiPh_3$	87

Discussion

The oxidative trimerization is suppressed outside a region of shielding by space-filling alkynyl substituents. A quantitative estimate of steric effects in PR_3 ligands is based on the cone angle obtained by Tolman[6] from space-filling models. Considering similar metal-to-phosphorus bond distances {228 pm in nickel(0) complexes and 231 pm in *trans*-PdBr[C(C≡C–CMe_3)=C(C≡C–CMe_3)(CMe_3)]$(PMe_3)_2$[1]} the literature value of Θ(PMe_3) = 118° is suitable in the present case. Same arguments can be referred to for an



(8)

$\xrightarrow{\Delta}$ C + 4 $PdBr_2(PMe_3)_2$ + 4 "$Pd(PMe_3)_2$"

Equiv.	C	$PdBr[C(C{\equiv}C\text{-}R){=}C(C{\equiv}C\text{-}R)R](PMe_3)_2$
0.21	$PdBr\{C[C{\equiv}C\text{-}(c\text{-}Hex)]{=}C[C{\equiv}C\text{-}(c\text{-}Hex)](c\text{-}Hex)\}(PMe_3)_2$	**32**
1.65	$PdBr\{C[C{\equiv}C\text{-}(c\text{-}Hex)]{=}C[C{\equiv}C\text{-}(c\text{-}Hex)](n\text{-}Pr)\}(PMe_3)_2$ [a]	**41**
1.09	$PdBr\{C[C{\equiv}C\text{-}(c\text{-}Hex)]{=}C[C{\equiv}C\text{-}(n\text{-}Pr)](n\text{-}Pr)\}(PMe_3)_2$ [a]	**42**
1.05	$PdBr[C\{C{\equiv}C\text{-}(n\text{-}Pr)]{=}C[C{\equiv}C\text{-}(n\text{-}Pr)](n\text{-}Pr)\}(PMe_3)_2$	**38**

R = c-Hex, n-Pr

[a] The substituents R appear to be distributed at random

Table 2. Synthesis of alkynylpalladium halides by method a)

No.	PdX_2L_2 [mg] [mmol]	HC≡C-R [mg] [mmol]	Yield [mg] [mmol]/[%]	mp. [°C]	Habitus
1	1880	480	1590	149	white
	5.71	5.84	4.24/74		needles
2	2170	560	1670	122	white
	6.59	6.66	4.43/67		needles
3	2700	890	2660	140	white
	8.19	8.19	6.63/81		needles
4	2690	440	1640	108-	yellow
	6.43	6.46	4.04/63	109	needles
5	1520	820	1320	113	white
	4.61	4.65	3.26/71		platelets
6	1750	400	1120	129	white
	4.18	4.08	2.57/61		needles
7	1500	290	680	97	orange yel-
	2.93	2.96	1.41/48		low needles
8	1250	390	760	177-	white
	3.79	3.82	1.93/51	179	needles
9	2240	380	1310	10	yellow
	3,85	3,87	2.04/53		oil

Table 3. Synthesis of alkynylpalladium halides by method b)

No.	$PdCl(C{\equiv}C\text{-}R)(PR_3)_2$ [mg] [mmol]	NaX [mg] [mmol]	Yield [mg] [mmol]/[%]	mp. [°C]	Habitus
10	2000	18400	2100	126	pale yellow
	5.30	179.0	4.98/94		needles
11	2100	29320	2460	116	yellow
	5.59	195.6	5.25/94		needles
12	1560	22150	1630	119-	pale yellow
	3.89	147.8	3.68/95	121	needles
13	1670	28060	1920	115	pale yellow
	4.16	187.2	3.90/94		needles
14	720	10930	740	94-	white
	1.77	106.2	1.65/93	96	platelets
15	1010	22390	1160	88	white
	2.49	149.4	2.34/94		platelets
16	1210	20600	1050	81-	white
	3.35	317	2.86/85	82	needles
17	1180	15230	1120	173-	white
	2.42	101.6	2.30/95	174	needles
18	1540	19690	1690	> -25	orange yel-
	2.39	131.4	2.30/96		low Oil

Table 4. Synthesis of alkynylpalladium halides by method c)

No.	$Pd(PR_3)_4$ [mg] [mmol]	HC≡C-R [mg] [mmol]	Yield [mg] [mmol]/[%]	mp. [°C]	Habitus
19	960	500	990	149	white
	2.34	2.40	2.12/91		needles
20	1800	300	910	115-	white
	4.30	4.40	2.24/52	116	needles
21	790	470	820	15	red
	1.92	1.99	1.66/86		oil
22	980	920	1330	169	pale yel-
	2.38	2.53	2.14/90		low powder
23	1580	560	960	170-	light yel-
	1.37	1.43	1.21/88	171	low powder
24	1220	210	820	153	light yel-
	1.06	1.10	1.00/94		low powder
25	1200	250	860	144-	light yel-
	1.04	1.05	0.99/95	145	low powder

Table 5. Thermal transformation of **1**, **2**, **10**–**13**, and **19** by method d)

No.	$PdX(C{\equiv}C\text{-}R)(PMe_3)_2$ [mg] [mmol]	No.	Yield [mg] [mmol]/[%]	mp. [°C]	Habitus
1	1020	**26**	200	144	yellow
	2.72		0.38/14		ashlers
19	1930	**27**	210	142	yellow
	4.14		0.34/08		ashlers
2	1210	**28**	290	48-	brown
	3.21		0.53/17	50	needles
10	1420	**29**	550	114	brown
	3.37		0.94/28		needles
11	1980	**30**	560	151-	brown
	4.23		0.89/21	155	ashlars
12	800	**31**	360	69-	red brown
	1.80		0.55/31	73	ashlars
13	1720	**32**	740	58	red brown
	3.49		1.05/30		ashlars

estimate of steric demand in alkynyl ligands, because plausible values for all bond lengths in the M–C≡C–R axis are also similar to those in the M–C≡N–R axis of isocyanides[7] (Table 1). Before a reasonable connection between reactivity and bulkiness in isocyanide insertion reactions or likewise in oxidative trimerization of alkynyl groups can be established, it is sufficient for our working hypothesis to find a trend in steric requirements on the basis of published

Table 6. Elemental analyses of compounds **1**–**32**

No.	formula	mass calcd.	m/e (%) M^+ found	Calcd. C	Calcd. H	Found C	Found H
1	$C_{12}H_{27}ClP_2Pd$	375.2	376(90)[a]	38.42	7.25	38.77	7.19
2	$C_{11}H_{25}ClOP_2Pd$	377.1	378(84)	35.03	6.68	35.79	6.79
3	$C_{14}H_{29}ClP_2Pd$	401.2	400(100)	41.91	7.29	42.05	7.29
4	$C_{11}H_{25}BrP_2Pd$	405.6	406(24)[b]	32.57	6.21	32.61	6.33
5	$C_{12}H_{29}ClP_2PdSi$	405.3	404(100)	35.56	7.21	35.77	7.12
6	$C_{11}H_{23}BrO_2P_2Pd$	435.6	436(49)	30.33	5.32	30.95	5.49
7	$C_{11}H_{23}IO_2P_2Pd$	482.6	482(76)[c]	24.05[d]	4.49[d]	24.01	4.66
8	$C_{14}H_{33}ClP_2Pd$	395.2	394(100)	42.55	5.87	42.65	6.01
9	$C_{29}H_{63}ClP_2PdSi$	643.7	642(73)	54.11	9.87	53.74	9.69
10	$C_{11}H_{25}BrOP_2Pd$	421.6	422(38)[e]	31.34	5.98	30.93	6.01
11	$C_{11}H_{25}IOP_2Pd$	468.6	468(100)	28.20	5.38	28.28	5.37
12	$C_{14}H_{29}BrP_2Pd$	445.7	446(95)	37.73	6.56	38.06	6.60
13	$C_{14}H_{29}IP_2Pd$	492.7	492(41)	34.13	5.93	33.84	5.70
14	$C_{12}H_{29}BrP_2PdSi$	449.7	450(28)	32.05	6.50	32.56	6.49
15	$C_{12}H_{29}IP_2PdSi$	496.7	496(34)[f]	29.02	5.89	29.63	5.94
16	$C_{11}H_{25}N_3P_2Pd$	367.7	367(33)[g]	-	-	-	-
17	$C_{14}H_{33}IP_2Pd$	486.6	486(17)[h]	34.56	4.76	33.87	4.69
18	$C_{29}H_{63}IP_2PdSi$	735.2	734(100)	47.38	8.64	47.73	8.54
19	$C_{12}H_{27}IP_2Pd$	466.6	466(21)	30.89	5.83	31.20	5.95
20	$C_{11}H_{25}IP_2Pd$	452.6	452(17)[i]	29.19	5.57	29.58	6.03
21	$C_{14}H_{31}IP_2Pd$	494.7	494(23)[j]	33.99	6.32	34.37	6.86
22	$C_{26}H_{63}BrP_2PdSi$	621.9	622(2)	50.21	5.35	50.90	5.48
23	$C_{42}H_{89}BrP_2Pd$	792.1	-	63.69	4.96	63.60	4.85
24	$C_{42}H_{81}BrP_2PdSi$	822.2	-	61.36	5.03	60.98	5.11
25	$C_{42}H_{81}IP_2PdSi$	869.1	-	58.04	4.76	58.18	4.41
26	$C_{24}H_{45}ClP_2Pd$	537.5	538(8)	39.94[k]	7.37[k]	39.93	7.35
27	$C_{24}H_{45}IP_2Pd$	628.9	628(97)[l]	38.81[m]	6.56[m]	38.77	6.40
28	$C_{21}H_{39}ClO_3P_2Pd$	543.4	[n]	-	-	-	-
29	$C_{21}H_{39}BrO_3P_2Pd$	587.8	[o]	42.91	6.69	43.01	6.84
30	$C_{21}H_{39}IO_3P_2Pd$	634.8	[o]	41.67[q]	6.34[q]	41.67	6.26
31	$C_{30}H_{51}BrP_2Pd$	660.0	658(99)	54.59	7.79	54.48	7.75
32	$C_{30}H_{51}IP_2Pd$	707.0	706(25)	50.97	7.27	50.40	7.21

[a] 538(3) $PdCl[C(C{\equiv}CCMe_3){=}C(C{\equiv}CCMe_3)(CMe_3)](PMe_3)_2^+$. – [b] 538(2) $PdBr[C(C{\equiv}CCHMe_2){=}C(C{\equiv}CCHMe_2)(CHMe_2)]PMe_3^+$, 420(20) $PdBr_2(PMe_3)_2^+$. – [c] 512(98) $PdI_2(PMe_3)_2^+$. – [d] Calcd. for **7** (75%) containing $PdI_2(PMe_3)_2$ (25%). – [e] 570(29) $PdBr\{C[C{\equiv}CCMe_2(OH)]{=}C[C{\equiv}CCMe_2(O)](CMe_2)\}(PMe_3)_2^+$. – [f] 718(14) $PdI[C(C{\equiv}CCH_2SiMe_3){=}C(C{\equiv}CCH_2SiMe_3)(CH_2SiMe_3)](PMe_3)_2^+$, 512(11) $PdI_2(PMe_3)_2^+$. – [g] 392(14) $Pd[C{\equiv}C(n\text{-}Pr)]_2(PMe_3)_2^+$. – [h] 512(54) $PdI_2(PMe_3)_2^+$. – [i] 512(3) $PdI_2(PMe_3)_2^+$. – [j] 712(10) $PdI\{C[C{\equiv}C(n\text{-}Hex)]{=}C[C{\equiv}C(n\text{-}Hex)](n\text{-}Hex)\}(PMe_3)_2^+$, 512(17) $PdI_2(PMe_3)_2^+$. – [k] Calcd. for **26** (90%) containing **1** (10%). – [l] 806(13) $Pd[C(C{\equiv}CCMe_3){=}C(C{\equiv}CCMe_3)(CMe_3)]_2(C{\equiv}CCMe_3)(CMe_3)(PMe_3)^+$, 674(17) $PdI_2(C{\equiv}CCMe_3)_2(PMe_3)_2^+$. – [m] Calcd. for **27** (53%) containing **19** (47%). – [n] 526(86) $PdCl\{C[C{\equiv}CCMe_2(OH)]{=}C[C{\equiv}CCMe_2(O)](CMe_2)\}(PMe_3)_2^+$. – [o] 570(91) $PdBr\{C[C{\equiv}CCMe_2(OH)]{=}C[C{\equiv}CCMe_2(O)](CMe_2)\}(PMe_3)_2^+$. – [p] 616(100) $PdI\{C[C{\equiv}CCMe_2(OH)]{=}C[C{\equiv}CCMe_2(O)](CMe_2)\}(PMe_3)_2^+$. – [q] Calcd. for **30** (94%) containing **11** (6%).

estimates (remote cone angle[7]). The values $64° < \Theta < 76°$ (Table 1) give the limits of bulkiness for a dominating reaction according to Equation (5). As experiments with mixtures of monoalkynyl complexes show, the trimerization reaction in general is accessible not only for compounds with bulky substituents within the given limits but also for alkynyl compounds with less bulky substituents. The products of trimerization below a cone angle of 64° can be detected by mass spectrometry but cannot be isolated from a multitude of decomposition products as with nickel[8]. The presence of small or larger amounts of bulky alkynyl compounds seems to activate the reaction within certain limits.

From these experimental findings we derive the following view of steric control in the reaction according to Equation (1).

1. A close approach of two complex molecules followed by halide transfer. This step requires sterically non-demanding phosphane ligands and is favored by heavier halide ions.

2. Formation of a coordinated vinylidene intermediate. The high reactivity of this hypothetical fragment is controlled by shielding substituents at the β-C atom, specifically allowing insertion into a M–C bond.

3. Steric control by bulky shielding substituents is still sufficient at higher ratios of monoalkynyl complexes with less bulky substituents. High ratios of non-transformable monoalkynyl complexes lead to a non-statistical product distribution with a relatively higher ratio of the enediynyl of the transformable compound.

Experimental

All materials were handled under dry argon. Melting points and decomposition temperatures were obtained from sealed capillaries and are uncorrected. – Trimethylphosphane[9] was prepared from

Table 7. Characteristic IR (Nujol) and NMR (298 K, Me_4Si external reference, $\delta = 0$) data for complexes **1**–**32**

No.	IR ν(C≡C) [cm^{-1}]	solvent	^{1}H NMR (300 MHz) δPC$\underline{H}_3$ (J_{PH})	δP$\underline{C}H_3$ (J_{PC})	^{13}C NMR (75.4 MHz) δPd$\underline{C}$	δPd$C\equiv\underline{C}$
1	2118 w	D_6-acetone	1.48 s	14.3 s	79.3	113.4
2	2130 m[a]	D_6-acetone	1.48 s	14.5 s	84.3	111.7
3	2138 w	C_6D_6	1.10 t'(7.3)	14.3 t'(32.3)	81.6[b]	109.1[c]
	2113 w					
4	2132 w	CD_2Cl_2	1.52 t'(7.3)	15.6 t'(32.3)	81.4	111.1
5	2112 m	D_6-acetone	1.41 s	14.7 t'(30.3)	79.5	100.3
6	2103 vs	D_6-acetone	1.59 s	15.1 t'(31.7)	99.1	154.4
7	2101 vs	D_6-acetone	1.69 t'(7.6)	17.0 t'(33.8)	98.6	[d]
8	2105 vs	D_6-acetone	1.58 t'(7.5)	14.8 t'(32.5)	98.9	110.8
9	2035 vs	C_6D_6	[e]	26.8 t'(33.5)[f]	119.3[g]	110.7[c]
	2020 vs					
10	2128 m[a]	CD_2Cl_2	1.52 t'(6.4)	15.4 t'(32.1)	86.9[g]	110.5
11	2106 m[a]	D_6-acetone	1.66 t'(7.5)	17.2 t'(33.4)	89.8[g]	110.0[c]
12	2128 vw	C_6D_6	1.28 t'(7.2)	15.3 t'(32.0)	84.3[g]	109.1[c]
	2096 vw					
13	2138 vw	C_6D_6	1.35 t'(7.3)	17.2 t'(32.8)	87.7[b]	107.5[b]
	2100 vw					
14	2139 m	D_6-acetone	1.52 s	15.5 s	81.7	99.9
15	2170 w	D_6-acetone	1.59 t'(7.5)	17.5 t'(32.5)	86.0	99.5
16	2136 w[h]	C_6D_6	1.10 t'(7.2)	13.6 t'(31.1)	[d]	[d]
17	2120 vs	CD_2Cl_2	1.70 s	17.5 s	77.4	104.5
18	2034 vs	C_6D_6	[e]	27.1 s[f]	123.0[g]	109.5[c]
19	2121 w	D_6-acetone	1.61 s	17.3 s	85.8	112.1
20	2123 w	D_6-acetone	1.61 t'(8.7)	17.2 d (26.2)	89.8	105.1
21	2133 m	D_6-acetone	1.63 s	17.6 t'(30.5)	87.6	103.1
22	2040 vs	D_6-acetone	1.57 s	15.6 s	86.1	104.2
23	-	CD_2Cl_2	[i]	132.4 t'(49.3)[j]	78.2	120.2
24	-	CD_2Cl_2	[e]	132.5 t'(49.2)[j]	78.1	108.3
25	-	CD_2Cl_2	[e]	133.7 t'(50.0)[j]	[d]	[d]
26	2112 m	C_6D_6	1.28 t'(7.2)	13.6 t'(29.0)		
	2020 w					
27	2113 w	C_6D_6	1.41 t'(7.5)	16.2 t'(29.3)		
	2017 w					
28	2191 w[a]	CD_2Cl_2	1.26 t'(6.9)	13.6 t'(30.1)		
29	2198 w[a]	CD_2Cl_2	1.40 t'(7.3)	14.7 t'(30.5)	See Table 8	
30	2195 w[a]	CD_2Cl_2	1.49 t'(7.0)	16.4 t'(31.7)		
31	2191 w	C_6D_6	1.38 t'(7.2)	14.4 t'(28.8)		
32	2192 w	C_6D_6	1.50 t'(7.2)	16.2 t'(30.1)		

[a] ν(OH) **2** 3455 s, **10** 3434 s, **11** 3455 s, **28** 3425 s, **29** 3440 s, **30** 3440 s. – [b] t', not dissolved. – [c] t', ^3J(PC) **3** 11.2, **9** 7.0, **11** 11.4, **12** 12.0, **18** 7.3 Hz. – [d] Not observed. – [e] δSiCH_3 **9** 0.00 s (9H), **18** 0.00 s (9H), **24** 0.47 s (9H), **25** 0.51 s (9H). – [f] δPC$^1H_2$ J(PC). – [g] t', ^2J(PC) **9** 30.6, **10** 33.9, **11** 33.5, **12** 34.0, **18** 28.2 Hz. – [h] $\nu_{as}(N_3)$ 2047 vs. – [i] δCCH_3 **23** 0.34 s (9H). – [j] δP$C_{(Ph)}$ (J_{PC}).

triphenyl phosphite and methylmagnesium chloride. Other chemicals (Merck-Schuchardt, Fluka) were used as purchased. – IR: Nujol mulls between KBr discs, Perkin-Elmer, Type 397. – ^{1}H and ^{13}C NMR: Bruker WM 300 (300 MHz), ^{13}C (75.4 MHz).

General Synthetic Methods: trans-Alkynylbis(trimethylphosphane)palladium Halides

a) *trans*-$PdX_2(PR_3)_2$[1] (R = PMe_3, PBu_3) in 100 ml of triethylamine and 50 ml of ethanol at 20°C were combined with equimolar amounts of 1-alkyne and stirred until a clear solution was obtained (16–48 h). The volatile products were removed in vacuo, and the residue was extracted with *n*-hexane over a glass-sinter disc (G 3). Crystallization at −25°C, decantation with washing (cold hexane) and drying in vacuo yielded analytically pure products as compiled in Table 2.

b) *trans*-Chloro(alkynyl)bis(triorganophosphane)palladium and powdered sodium salt in 30–60-fold excess were stirred for 48 h. After evaporation of the volatile components in vacuo and extraction of the solid residue with hexane workup was carried out as in method a) (Table 3).

c) $Pd(PR_3)_4$[1] (R = PMe_3, PPh_3) in 100 ml of ether at 0°C were combined with equimolar amounts of 1-halogen-1-alkyne, and the mixture was stirred overnight. The volatile products were removed in vacuo, and the residue was extracted with hexane; further

Table 8. Characteristic ^{13}C-NMR data for coupling products **27**–**32**

	^{13}C NMR shifts						
No.	C^1	C^2	C^3	C^4	C$^{1'}$	C$^{2'}$	others
27	136.9	137.4	115.4	85.0	97.5	82.8	^{2}C$\underline{C}$H$_3$ 31.7, C^5$\underline{C}$H$_3$ 31.1, C$^{3'}$$\underline{C}H_3$ 30.4, ^{2}$\underline{C}$ 38.0 $\underline{C}^5$ 29.1
26	132.2	138.2	111.9	84.0	98.1	82.9	^{2}C$\underline{C}$H$_3$ 31.8, C^5$\underline{C}$H^3 31.0, C$^{3'}$$\underline{C}H_3$ 28.6, ^{2}$\underline{C}$ 38.7 $\underline{C}^5$ 29.4, $\underline{C}^{3'}$ 28.6
28	141.9	-	132.7	100.0	110.9	92.4	^{2}C$\underline{C}$H$_3$ 32.0, C^5$\underline{C}$H$_3$ 26.6, C$^{3'}$$\underline{C}H_3$ 24.1, ^{2}$\underline{C}$ 79.7 $\underline{C}^{3',5}$ 65.8
29	141.8	164.3	134.0	99.7	114.5	92.7	^{2}C$\underline{C}$H$_3$ 32.1, $\underline{C}^5$CH$_3$ 26.7, C$^{3'}$$\underline{C}H_3$ 23.9, ^{2}$\underline{C}$ 79.8 $\underline{C}^5$ 66.1, $\underline{C}^{3'}$ 66.0
30	141.8	164.5	134.5	100.0	114.4	92.6	^{2}C$\underline{C}$H$_3$ 32.0, C^5$\underline{C}$H^3 26.6, C$^{3'}$$\underline{C}H_3$ 23.9, ^{2}$\underline{C}$ 79.7 $\underline{C}^5$ 66.1, $\underline{C}^{3'}$ 65.9
31	136.9[a]	138.0[b]	85.0	107.0	94.4	83.6	$\underline{C}^{11}$H 44.7, $\underline{C}^5$H 31.3, $\underline{C}^{3'}$H 30.7, $\underline{C}^{12,16}$H$_2$ 25.5, $\underline{C}^{4',8',6,10}H_2$ 25.1, $\underline{C}^{13,15}$H$_2$ 32.5, $\underline{C}^{7,9}$H$_2$ 33.9, $\underline{C}^{14}$H$_2$ 27.4, $\underline{C}^{5',7'}$H$_2$ 33.7, $\underline{C}^8$H$_2$ 26.9, $\underline{C}^{6'}$H$_2$ 26.6
32	136.9[c]	140.5[d]	84.3	107.6	94.6	83.4	$\underline{C}^{11}$H 44.8, $\underline{C}^5$H 31.0, $\underline{C}^{3'}$H 30.4, $\underline{C}^{12,16}$H$_2$ 25.18, $\underline{C}^{4',8',6,10}H_2$ 24.8, $\underline{C}^{13,15}$H$_2$ 32.1, $\underline{C}^{7,9}$H$_2$ 33.6, $\underline{C}^{14}$H$_2$ 27.0, $\underline{C}^{5',7'}$H$_2$ 33.4, $\underline{C}^8$H$_2$ 26.6, $\underline{C}^{6'}$H$_2$ 26.3

[a] t', ^2J(PC) = 11.6 Hz. – [b] t', not dissolved. – [c] t', ^2J(PC) = 11.8 Hz. – [d] t', ^3J(PC) = 7.2 Hz.

Table 9. Thermal transformation of PdI(C≡CCMe$_2$OH)(PMe$_3$)$_2$ (**11**) and PdI[C≡C(*n*-Pr)](PMe$_3$)$_2$ (**20**) in mixture **A** by method d)

11 [mg] [mmol]	**20** [mg] [mmol]	Yield **A** [mg]	Habitus
2170 4.64	1050 2.32	930 -	red brown oil

Table 10. Mass analyses of mixture **A** (compounds **30** and **33**–**35**)[a]

No.	formula	mass calcd.	m/e (%) M$^+$ found
30	C$_{21}$H$_{39}$IO$_3$P$_2$Pd	634.8	634 (31)
33	C$_{21}$H$_{39}$IO$_2$P$_2$Pd	618.8	618 (60)
34	C$_{21}$H$_{39}$IOP$_2$Pd	602.8	602 (62)
35	C$_{21}$H$_{39}$IP$_2$Pd	586.8	586 (33)

m/e (%)	other fragments found
316 (8)	Pd[C≡C-(n-Pr)]$_2$(PMe$_3$)$^+$
310 (19)	C[C≡C-CMe$_2$(OH)][C≡C-(n-Pr)]=C[C≡C-CMe$_2$(OH)](PMe$_3$)$^+$
300 (26)	C[C≡C-CMe$_2$(OH)][C≡C-(n-Pr)]=C[C≡C-CMe$_2$(OH)][C≡C-(n-Pr)]$^+$

[a] As products can be separated from the byproducts PdX$_2$(PMe$_3$)$_2$ and "Pd(PMe$_3$)$_2$" but not from each other, mixtures of products were detected by mass spectrometry. IR and ^{1}H-NMR spectra contain a large number of overlapping signals and are not useful, whereas ^{13}C-NMR spectra show the correct number of peaks but without the possibility of assignment.

workup was performed in method a) yielding analytically pure products compiled in Table 4.

d) *Thermal transformation of* **1**, **2**, **10**–**13**, and **19**: Crystalline samples of *trans*-alkynylhalogenobis(trimethylphosphane)palladium were heated in vacuo to a temp. of 10°C above the melting or decomposition point and kept for 2 h at that temp. The dark residue was extracted with 30 ml of pentane over a glass-sinter disc

Table 11. Thermal transformation of PdBr(C≡CSiMe$_3$)(PMe$_3$)$_2$[1], PdBr[C≡C(*n*-Pr)](PMe$_3$)$_2$[1], and PdI[C≡C(*n*-Pr)](PMe$_3$)$_2$ (**20**) in mixture **B** by method d)

PdBr(C≡C-SiMe$_3$)L$_2$[1] [mg] [mmol]	PdBr[C≡C-(n-Pr)]L$_2$[1] [mg] [mmol]	**20** [mg] [mmol]	Yield **B** [mg]	Habitus
550 1.26	130 0.32	290 0.64	320 -	red brown oil

Table 12. Mass analyses of mixture **B** (compounds PdBr[C(C≡CSiMe$_3$)=C(C≡CSiMe$_3$)(SiMe$_3$)](PMe$_3$)$_2$[1], PdBr{C[C≡C-(*n*-Pr)]=C[C≡C(*n*-Pr)](*n*-Pr)}(PMe$_3$)$_2$[1], and **35**–**40**) (see footnote[a] in Table 10)

No.	formula	mass calcd.	m/e (%) M$^+$ found
[1]	C$_{21}$H$_{45}$BrP$_2$PdSi$_3$	630.1	628 (61)
36	C$_{21}$H$_{43}$BrP$_2$PdSi$_2$	600.0	598 (100)
37	C$_{21}$H$_{41}$BrP$_2$PdSi	569.9	568 (91)
38	C$_{21}$H$_{39}$BrP$_2$Pd	539.8	538 (53)
[1]	C$_{21}$H$_{45}$IP$_2$PdSi$_3$	677.1	676 (39)
39	C$_{21}$H$_{43}$IP$_2$PdSi$_2$	646.9	648 (16)
40	C$_{21}$H$_{41}$IP$_2$PdSi	616.9	616 (23)
35	C$_{21}$H$_{39}$IP$_2$Pd	586.8	586 (16)

m/e (%)	other fragments found
504 (10)	{[BrC(n-Pr)=CI][C(C≡C-SiMe$_3$)=C[C≡C-(n-Pr)](n-Pr)]}$^+$
462 (27)	[C(C≡C-SiMe$_3$)=C[C≡C-(n-Pr)](n-Pr)]$_2^+$
310 (19)	C[C≡C-CMe$_2$(OH)][C≡C-(n-Pr)]=C[C≡C-CMe$_2$(OH)](PMe$_3$)$^+$
262 (23)	HC(C≡C-SiMe$_3$)=C(C≡C-SiMe$_3$)(n-Pr)$^+$

Table 13. Thermal transformation of PdI[C≡C(*c*-Hex)](PMe$_3$)$_2$ (**12**) and PdBr[C≡C(*n*-Pr)](PMe$_3$)$_2$[1] in mixture **C** by method d)

11 [mg] [mmol]	**20** [mg] [mmol]	Yield **C** [mg]	Habitus
140	1400	430	red brown
0.31	3.45	-	oil

(G 3) and the solution kept at −25°C. Yields of crystalline material in Table 5 are based on Pd in Equation (1).

Table 14. Mass analyses of mixture **C** (compounds **31**, **38**, **41**, and **42** (see footnote[a] in Table 10)

No.	formula	mass calcd.	m/e (%) M$^+$ found
31	$C_{30}H_{51}BrP_2Pd$	660.0	658 (3)
41	$C_{27}H_{47}BrP_2Pd$	620.0	618 (36)
42	$C_{24}H_{43}BrP_2Pd$	579.9	578 (20)
38	$C_{21}H_{39}BrP_2Pd$	539.8	538 (22)

m/e (%)	other fragments found
321 (8)	C[C≡C-(c-Hex)]=C[C≡C-(c-Hex)](c-Hex)$^+$
281 (21)	C[C≡C-(c-Hex)]=C[C≡C-(c-Hex)](n-Pr)$^+$
241 (8)	C[C≡C-(c-Hex)]=C[C≡C-(n-Pr)](n-Pr)$^+$
202 (8)	HC[C≡C-(n-Pr)]=C[C≡C-(n-Pr)](n-Pr)$^+$

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