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REACTIONS OF $[Pd(C_6F_5)_2(CNR)_2]$ WITH $[PdCl_2(NCPh)_2]$. INSERTION OF p-MeC_6H_4NC INTO Pd–C_6F_5 BONDS

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Summary

$[Pd(C_6F_5)_2(CNR)_2]$ (R = Cy, Bu^t, p-MeC_6H_4 (p-Tol)) react with $[PdCl_2(NCPh)_2]$ to give $[Pd_2(\mu\text{-}Cl)_2(C_6F_5)_2(CNR)_2]$. In refluxing benzene insertion of isocyanide into the C_6F_5–Pd bonds occurs only for R = p-Tol, to give a imidoyl bridged polynuclear complex *cis*-$[\{Pd_2(\mu\text{-}Cl)_2[\mu\text{-}C(C_6F_5)=N(Tol\text{-}p)]_2\}_n]$. This complex reacts with (a) Tl(acac) to give $[Pd_2\{\mu\text{-}C(C_6F_5)=N(Tol\text{-}p)\}_2(acac)_2]$; (b) neutral monodentate ligands to afford dimeric complexes $[Pd_2\{\mu\text{-}C(C_6F_5)=N(Tol\text{-}p)\}_2Cl_2L_2]$ (L = NMe_3, py, 4-Me-py, SC_4H_8), and (c) isocyanides to give insoluble complexes of the same composition which are thought to be polymeric, $[Pd(CNR)Cl\{\mu\text{-}C(C_6F_5)=N(p\text{-}Tol)\}]_n$ (R = p-Tol, Me, Bu^t). Thermal decomposition of *cis*-$[\{Pd_2(\mu\text{-}Cl)_2[\mu\text{-}C(C_6F_5)=N(p\text{-}Tol)]_2\}_n]$ gives the diazabutadiene species (p-Tol)N=C(C_6F_5)–C(C_6F_5)=N(p-Tol) in high yield.

Introduction

We recently described the synthesis of a novel type of imidoyl-bridged palladium complexes arising from insertion of MeNC into Pd–C_6F_5 bonds [1]. This insertion was noteworthy since the M–C bonds between transition metals and perfluoroaryl ligands are known to be remarkably inert towards insertions [2], and only one insertion of isocyanide into transition metal–perfluorocarbon bonds, namely that of CyNC into Ti–C_6F_5 bonds [3], had been reported before.

The results obtained with MeNC induced us to extend our work to other isocyanides RNC in order to examine the influence of the R group on the insertion process and on the stability of the imidoyl derivatives, when formed. The isocyanides Bu^{t}NC, CyNC and p-TolNC (p-Tol = p-tolyl) were chosen for this study; the last of these, containing an R group more electron-attracting than Me, was expected to be more reactive than MeNC, while the other two were expected to be less reactive than MeNC.

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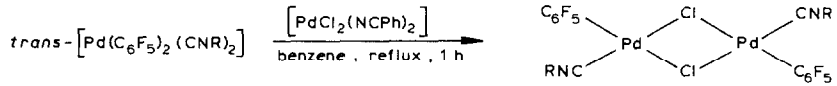
Results and discussion

Reactions involving Bu^{t}NC or CyNC

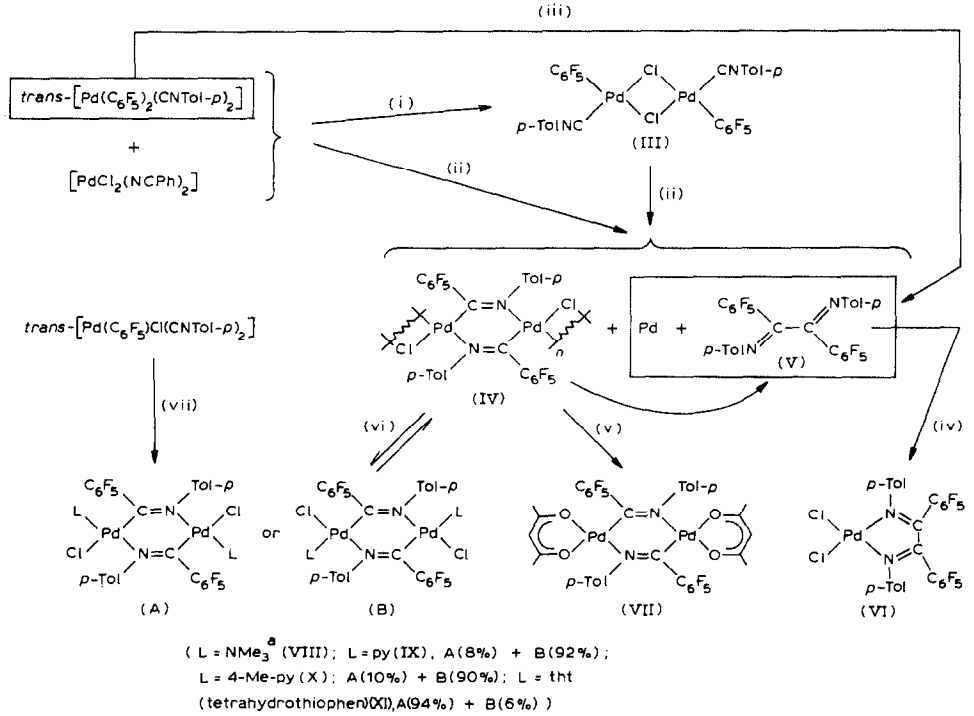
The complexes *trans*-$[Pd(C_6F_5)_2(CNR)_2]$ (R = Bu^t, Cy) react with $[PdCl_2(NCPh)_2]$ in refluxing benzene to give pale-yellow solutions, from which dinuclear chloro-bridged complexes $[Pd_2(\mu\text{-}Cl)_2(C_6F_5)_2(CNR)_2]$ can be isolated (eq. 1). Longer reaction times do not lead to insertion of the isonitrile into the C_6F_5–Pd bonds but to formation of black Pd.



(1)

(I, R = Bu^t; II, R = Cy)

The structure of complexes I and II is assigned on the basis of the analytical data (Table 1), IR spectra (Table 2) and ^{1}H NMR spectra (Table 3). In the light of the C_{2h} symmetry of these complexes one ν(C≡N) (B_u), one X-sensitive C_6F_5 (B_u) [4] and two ν(Pd–Cl) (2 B_u) IR active modes are to be expected, in good agreement with our observations.



(L = NMe$_3$[a] (VIII); L = py (IX), A(8%) + B(92%); L = 4-Me-py (X); A(10%) + B(90%); L = tht (tetrahydrothiophen) (XI), A(94%) + B(6%))

SCHEME 1. (i) Acetone, room temperature, 20 min; (ii) and (iii) Benzene reflux; (iv) $PdCl_2(NCPh)_2$, benzene; (v) Tlacac, CH_2Cl_2; (vi) L, CH_2Cl_2; (vii) Benzene reflux. [a] Possibly B isomer, as discussed in the text.

Reactions involving p-TolNC

The results of reactions starting from *trans*-$[Pd(C_6F_5)_2(CNTol\text{-}p)_2]$ are summarized in Schemes 1 and 2.

The complex *trans*-$[Pd(C_6F_5)_2(CNTol\text{-}p)_2]$ reacts with $[PdCl_2(NCPh)_2]$ in refluxing benzene (ii) to give the red polymeric imidoyl complex *cis*-$[\{Pd_2(\mu\text{-}Cl)_2[\mu\text{-}C(C_6F_5)\text{=}N(Tol\text{-}p)]_2\}_n]$ (IV, ca. 75% yield), traces of black Pd and some *N*, *N'*-*p*-tolyl bis(pentafluorophenyl)-1,2-ethanediimine (V, ca. 10% yield). In order to obtain the isonitrile chloro-bridged complex $[Pd(\mu\text{-}Cl)_2(C_6F_5)_2(CNTol\text{-}p)_2]$ (III) the reaction has to be carried out in acetone at room temperature (i); recrystallization from benzene gives $[Pd_2(\mu\text{-}Cl)_2(C_6F_5)_2(CNTol\text{-}p)_2]\cdot C_6H_6$ as pale-yellow crystals. Complex III is converted into IV by 20 min reflux in benzene.

Insertion of *p*-TolNC into Pd–C_6F_5 bonds in refluxing benzene is found to be faster than that of MeNC, whereas Bu^tNC and CyNC do not insert under similar conditions. Thus, the ease of insertion increases with the electrophilicity of the isocyanide, in agreement with previous observations [5].

TABLE 1

ANALYTICAL DATA (CALCULATED VALUES IN PARENTHESES) AND YIELDS

Compound		Analysis (%)			Yield (%)
		C	H	N	
$[Pd_2(\mu\text{-}Cl)_2(C_6F_5)_2(CNCy)_2]$	(I)	37.97 (37.75)	2.85 (2.65)	3.34 (3.35)	64
$[Pd_2(\mu\text{-}Cl)_2(C_6F_5)_2(CNBu^t)_2]$	(II)	33.75 (33.70)	2.43 (2.31)	3.58 (3.58)	89
$[Pd_2(\mu\text{-}Cl)_2(C_6F_5)_2(CNTol\text{-}p)_2]\cdot C_6H_6$	(III)	41.16 (41.78)	2.10 (1.92)	2.94 (3.14)	55
$[\{Pd_2(\mu\text{-}Cl)_2[\mu\text{-}C(C_6F_5)\text{=}N(Tol\text{-}p)]_2\}_n]$	(IV)	39.71 (39.47)	1.98 (1.66)	3.15 (3.29)	68
$(Tol\text{-}p)N\text{=}C(C_6F_5)\text{-}C(C_6F_5)\text{=}N(Tol\text{-}p)$	(V)	59.62 (59.16)	2.63 (2.49)	5.09 (4.93)	[a]
$[PdCl_2\{(Tol\text{-}p)N\text{=}C(C_6F_5)\text{-}C(C_6F_5)\text{=}N(Tol\text{-}p)\}]$	(VI)	44.80 (45.10)	2.04 (1.89)	3.87 (3.76)	77
$[Pd_2\{\mu\text{-}C(C_6F_5)\text{=}N(Tol\text{-}p)\}_2(acac)_2]$	(VII)	46.57 (46.60)	3.05 (2.88)	2.89 (2.86)	40
$[Pd_2\{\mu\text{-}C(C_6F_5)\text{=}N(Tol\text{-}p)\}_2Cl_2(NMe_3)_2]$	(VIII)	42.59 (42.35)	3.77 (3.34)	5.79 (5.81)	72
$[Pd_2\{\mu\text{-}C(C_6F_5)\text{=}N(Tol\text{-}p)\}_2Cl_2(py)_2]$	(IX)	45.61 (45.17)	2.61 (2.39)	5.63 (5.54)	70
$[Pd_2\{\mu\text{-}C(C_6F_5)\text{=}N(Tol\text{-}p)\}_2Cl_2(4Me\text{-}py)_2]$	(X)	46.00 (46.27)	3.09 (2.71)	5.16 (5.39)	64
$[Pd_2\{\mu\text{-}C(C_6F_5)\text{=}N(Tol\text{-}p)\}_2Cl_2(tht)_2]$	(XI)	41.34 (41.04)	2.92 (2.94)	2.72 (2.72)	46
$[\{Pd[\mu\text{-}C(C_6F_5)\text{=}N(Tol\text{-}p)]Cl(CNTol\text{-}p)\}_n]$	(XII)	49.11 (48.64)	2.90 (2.60)	5.05 (5.15)	75
$[\{Pd[\mu\text{-}C(C_6F_5)\text{=}N(Tol\text{-}p)]Cl(CNMe)\}_n]$	(XIII)	41.39 (41.14)	2.29 (2.16)	5.80 (6.00)	79
$[\{Pd[\mu\text{-}C(C_6F_5)\text{=}N(Tol\text{-}p)]Cl(CNBu^t)\}_n]$	(XIV)	44.43 (44.82)	3.42 (3.77)	5.38 (5.50)	78

[a] See experimental.

TABLE 2

RELEVANT IR ABSORPTIONS (cm^{-1})

Compound	ν(C≡N)	ν(C=N)	ν(Pd–Cl)	C_6F_5 absorptions				
I	2246	–	308,271	1630	1505	1065	963	795
II	2236	–	306,274	1630	1500	1065	962	791
III	2226	–	308,268	1630	1503	1063	960	797
IV	–	1578, 1560	273	1645;	1508,1493;	1129;	1019,986;	887
V	–	1628	–	1653;	1520,1490;	1131;	998,975;	848
VI	–	1598	352,345	1651	1510	1090	990	882
VII	–	1582 [a]	–	1644;	1514,1492;	1124;	1023,985;	890
VIII	–	1570,1536	311	1634;	1508,1490;	1117;	996,979;	867
IX	–	1578,1554	328,300	1642;	1509,1493;	1124;	1009,983;	886
X	–	1575,1551	311,301	1643;	1510,1488;	1123;	1015,980;	883
XI	–	1575,1543	297,278	1644;	1507,1488;	1121;	1009,979;	880
XII	2206	1600,1570	323,305	1645;	1513,1493;	1133;	1003,985;	875
XIII	2249	1605,1568	303,293	1650;	1518,1494;	1139;	1009,986;	875
XIV	2226	1609,1570	321,305	1649;	1513,1491;	1130;	1003,983;	817

[a] Overlap with acac absorptions occurs.

In the preparation of the red polymer (IV) some *N,N'-p*-tolylbis(pentafluorophenyl)-1,2-ethanediimine (V) and traces of black Pd are formed. The 1,4-diazabutadiene (V) is formally the coupling product of two imidoyl moieties, and its formation could be understood as arising from thermal decomposition of complex IV; in fact, when IV is refluxed in benzene for 30 d black Pd (98%) and V (80%) are formed. However *N,N'-p*-tolylbis(pentafluorophenyl)-1,2-ethanediimine is also formed in 26% yield, along with black Pd (92%) and unidentified gummy materials, when $[Pd(C_6F_5)_2(CNTol\text{-}p)_2]$ is refluxed in benzene for 26 h (iii), suggesting that the route to compound V may involve more than simple coupling.

The conditions defined in the experimental part for the preparation of IV are those which give the best yield of IV. Longer reflux times increase the amount of V and so lower the yield in IV, whereas with shorter times isolation of IV and V is complicated by the presence of unreacted starting materials.

The 1,4-diazabutadiene (V) was identified by elemental analysis, IR, ^1H and ^{19}F

TABLE 3

^1H NMR DATA (ppm, δ, in $CDCl_3$, ref. TMS)

Compound	
I	1.45(br.s, 6H); 1.75(br.s, 4H); 3.89(m, 1H)
II	1.42(s)
III	2.45(s, 3H); 7.27(s, 4H); 7.32(s, 3H, C_6H_6)
IV	2.27(s, 3H); 7.03(s, 4H)
V	2.30(s, 3H); 6.70(d, $2H_A$); 7.15(d, $2H_B$); J(AB) 8.4 Hz
VI	2.38(s, 3H); 7.18(m, 4H)
VII	1.80(s, 3H); 1.95(s, 3H); 2.26(s, 3H); 5.47(s, 1H); 7.10(s, 4H)
IX	2.19(s, 3H); 6.06(d, $2H_A$); 6.79(d, $2H_B$); 7.50(m, 2H); 7.85(m, 1H); 9.20(m, 2H); J(AB) 7.7 Hz
X	2.20(s, 3H); 2.43(s, 3H); 6.10(d, $2H_A$); 6.80(d, $2H_B$); 7.76(m, 2H); 9.01(m, 2H); J(AB) 7.8 Hz
XI	2.34(s, 3H); ca. 2.3(m, 4H); ca. 3.5(m, 4H); 7.22(d, $2H_A$); 7.47(d, $2H_B$); J(AB) 8.5 Hz

TABLE 4

^{19}F NMR DATA (ppm, δ, in $CDCl_3$, ref. $CFCl_3$)

Compound		F(2)	F(6)	F(4)	F(3)		F(5)	δ(F(2))–δ(F(6))	^3J(F(3)–F(4)) $\approx ^3J$(F(5)–F(4))
IV		−133.36	−141.26	−152.36	−160.36		−161.66	7.9	21.3
V		−138.13	−138.13	−152.33	−162.06		−162.06	0	20.7
VII		−135.91	−142.76	−156.93	−163.56		−164.51	10.85	20.9
IX	isomer *A*	−137.32	−139.15	−153.8	−161.2		[a]	1.83	[b]
	isomer *B*	−134.56	−141.88	−154.78	–	−162.55 [c]	–	7.32	20.8
X	isomer *A*	−137.22	−140.48	−153.9	[a]	[a]	[a]	3.26	[b]
	isomer *B*	−134.63	−141.83	−155.0	–	−162.56 [c]	–	8.20	21.0
XI	isomer *A*	−135.23	−139.66	−153.29	–	−161.50 [c]	–	4.43	21.1
	isomer *B*	−133.05	−141.57	−152.71	[a]	[a]	[a]	8.52	[b]

[a] Overlap with signals of the main isomer precludes assignation. [b] Not measured. [c] Signals of F(5) and F(6) overlap.

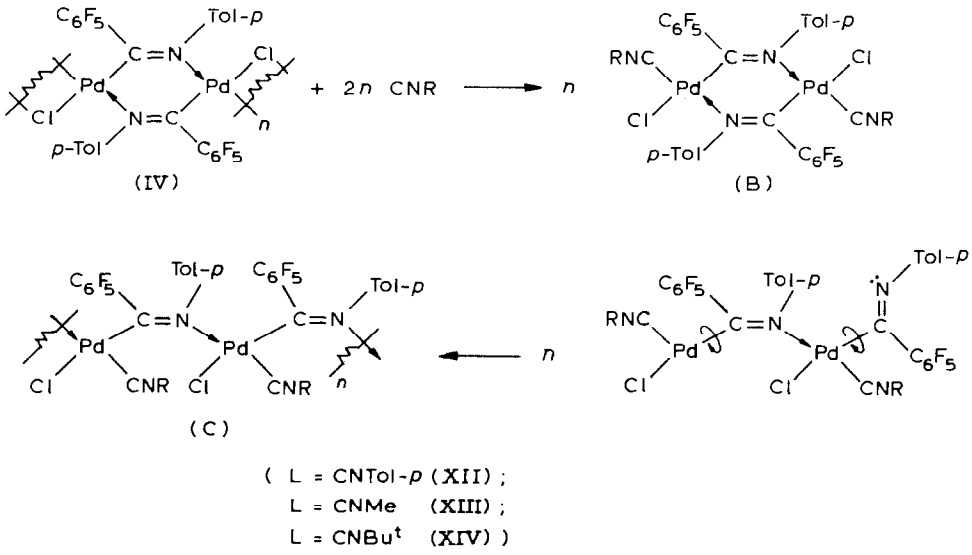
NMR, molecular weight (mass spectrometry, $m/e = 568$) and by its reaction with $[PdCl_2(NCPh)_2]$ (iv) to give $[PdCl_2\{(p\text{-Tol})N{=}C(C_6F_5)–C(C_6F_5){=}N(Tol\text{-}p)\}]$ (VI) where the 1,4-diazabutadiene is acting as a chelating ligand. As with other 1,4-diazabutadiene ligands [6], a shift of ν(C=N) to lower frequencies occurs upon coordination.

The ^{19}F NMR spectrum of compound (V), (Table 4) is, as expected, that of a typical AA'MXX' spin system. Complex (IV), however, shows five distinct signals, which indicates that the five fluorine atoms on each C_6F_5 group are non-equivalent. This effect arises because of the restriction to rotation of the C_6F_5 group, which gives rise to non-equivalence of the fluorine atoms *exo* (F(6) and F(5)) and *endo* (F(2) and F(3)) with respect to the rigid boat conformation of the dipalladiacycle, as we have discussed elsewhere for related complexes [1].

Complex IV reacts with Tlacac (v) to give the binuclear acetylacetonato complex (VII). On the other hand, the very labile complex $[Pd_2\{\mu\text{-}C(C_6F_5){=}NTol\text{-}p\}_2Cl_2(NMe_3)_2]$ (VIII) can be prepared as an orange solid by bubbling dry NMe_3 through a suspension of the red polymer (IV) in *n*-hexane (vi); this product can be stored for long periods at −20°C but loses NMe_3 immediately in solution and more slowly in the solid state at room temperature to regenerate IV.

Treatment of IV with stoicheiometric amounts of neutral ligands L (Pd/L = 1/1) affords dinuclear imidoyl complexes for L = py (IX), 4-Me-py (X) and tht (XI), as yellow solids very soluble in CH_2Cl_2 and acetone. Two isomers A and B shown in Scheme 1 are possible for these complexes. We have shown previously for similar complexes [1] that ^{19}F NMR spectroscopy is useful in distinguishing between such isomers as higher δ(F(2))–δ(F(6)) values are found for the B isomers. The ^{19}F NMR spectra of complexes IX–XI reveal the presence of both isomers in solution; isomer B is the major component for L = py (~ 92%) and 4-Me-py (~ 90%) and the minor component for L = tht (~ 6%), as expected in the light of the tendency of palladium (II) complexes to have the two softer ligands in mutually *cis* positions [7]. Distinct signals for the minor isomers could not be observed however in the ^1H NMR spectra under our resolution conditions.

In the solid state, two IR absorptions near 300 cm^{-1} are observed for the three



SCHEME 2

complexes (Table 2), and are assigned to the two IR active ν(Pd–Cl) modes ($A + B$) predicted for the C_2 symmetry of the complexes. These absorptions are at higher frequencies for IX and X than for XI, suggesting that the structure of the major isomer in solution is also predominant in the solid state; in complex XI, for which structure A is adopted, the higher *trans* influence of the C(imidoyl) atom leads to a lower ν(Pd–Cl) frequency.

The reactions of IV with a stoicheiometric amount of isonitrile (Pd/CNR = 1/1) behave differently in the sense that, although yellow solutions are formed at first, white solids XII–XIV separate from the solution within a few minutes. For R = *p*-Tol the same compound (XII) is obtained by heating *trans*-[Pd(C_6F_5)Cl(CNTol-*p*)$_2$] in refluxing benzene (vii). The compounds XII–XIV are insoluble in common organic solvents and this excludes the use of some identification techniques. Their elemental analyses and IR spectra are consistent with their formulation as imidoyl-bridged dimers, similar to those formed with other neutral ligands (VIII–XI) or to the related complex [Pd_2\{μ-C(C_6F_5)=N(Me)\}$_2$$Cl_2$(CNMe)$_2$] which was obtained by the same procedures [1]. However the differences in physical properties are too striking to be ignored. Thus, all the related \{μ-C(C_6F_5)=N(R)\}-bridged dimers prepared by us (R = Me, [1]; R = *p*-Tol, this paper) are yellow solids, very soluble in solvents such as acetone or dichloromethane; whereas complexes XII–XIV are colorless solids insoluble in these solvents. We suggest that the insolubility of the products may be due to the existence of a polymeric structure as shown in Scheme 2. The reaction of IV with CNR would lead in a first step to cleavage of the Cl bridges, thus giving a dimer B (presumably yellow and soluble) which in turn rearranges to give the polymeric structure C. The insolubility of complexes XII–XIV would force the equilibrium over towards them.

Experimental

The C, H and N analyses were carried out with a Perkin–Elmer 240-B microanalyzer. IR spectra were recorded on a Perkin–Elmer 599 spectrophotometer using Nujol mulls between polyethylene plates. ^1H NMR and ^{19}F NMR spectra were recorded on a Varian FT-80A instrument. . Molecular weights were determined in $CHCl_3$ solution on a Perkin–Elmer 115 apparatus. The mass spectrum was determined with a Hewlett–Packard 5930A mass spectrometer. *p*-TolNC, MeNC and Bu^tNC were prepared as described by Ugi and coworkers [8], and the complexes *trans*-$[Pd(C_6F_5)_2(CNR)_2]$ by published methods [9]. Since the methods used to prepare some of the complexes were very similar, only typical preparations are given.

Preparation of $[Pd_2(\mu\text{-}Cl)_2(C_6F_5)_2(CNR)_2]$*; R = Cy(I), Bu^t (II)*

A solution of *trans*-$[Pd(C_6F_5)_2(CNR)_2]$ (0.5 mmol) and $[PdCl_2(NCPh)_2]$ (0.5 mmol) in benzene (50 ml) is refluxed for 1 h, then filtered, to remove traces of black Pd, and concentrated to 1 ml. Addition of ethanol gives a pale-yellow precipitate which is filtered off, washed with cold ethanol, and dried. (Mol. weight: R = Cy, Found: 810, calcd.: 836.16; R = Bu^t, Found: 750, calcd.: 784.08).

Preparation of $[Pd_2(\mu\text{-}Cl)_2(C_6F_5)_2(CNTol\text{-}p)_2] \cdot C_6H_6$ *(III)*

$[PdCl_2(NCPh)_2]$ (113.7 mg, 0.296 mmol) is added to a suspension of *trans*-$[Pd(C_6F_5)_2(CNTol\text{-}p)_2]$ (200 mg, 0.296 mmol) in acetone (40 ml) and the mixture is stirred at room temperature for 20 min to give a clear yellow solution. The solution is cooled in an ice-bath and evaporated in vacuo to ca. 3 ml, and the product is precipitated as a pale-yellow solid by adding 20 ml of *n*-hexane. A solution of the product in 20 ml of benzene is evaporated in vacuo to ca. 5 ml and crystallized by addition of methanol and cooling in the freezer. Complex III has to be stored in the freezer.

Preparation of $[\{Pd_2(\mu\text{-}Cl)_2[\mu\text{-}C(C_6F_5)\text{=}N(Tol\text{-}p)]_2\}_n]$ *(IV)*

trans-$[Pd(C_6F_5)_2(CNTol\text{-}p)_2]$ (905.3 mg, 1.342 mmol) and $[PdCl_2(NCPh)_2]$ (511.7 mg, 1.342 mmol) are refluxed in 200 ml of benzene for 30 min. The resulting red solution is evaporated to give a red oil, which is stirred in 20 ml of acetone for 20 min. The suspension is evaporated to dryness and the resulting rose solid is stirred with 20 ml of acetone to give a red residue and a yellow-orange solution. The solid is filtered off and the solution is used to make *p*-TolN=$C(C_6F_5)$–$C(C_6F_5)$=NTol-*p* as described in the following preparation (method 1). The red solid (75% yield) is $[\{Pd_2(\mu\text{-}Cl)_2[\mu\text{-}C(C_6F_5)\text{=}N(Tol\text{-}p)]_2\} \cdot 1CH_3COCH_3]_n$ (Found: C, 40.77; H, 2.22; N, 2.88. Calcd.: C, 40.91; H, 2.21; N, 3.07%. IR: ν(C=O) in ca. 1720 cm^{-1}), and is contaminated with traces of black palladium. This crude product is dissolved in 150 ml of CH_2Cl_2 and the red solution is filtered through a cellulose-packed column (2 cm) and evaporated to ca. 10 ml. The red microcrystalline solid is filtered off, washed with 5 ml of cold CH_2Cl_2 and dried. The yield is ca. 70%.

Preparation of (p-Tol)N=$C(C_6F_5)$–$C(C_6F_5)$*=N(Tol-p) (V)*

Method 1. The yellow-orange solution from the above preparation is evaporated to dryness. Addition of 5 ml of ethanol gives a yellow solid which is filtered off, washed with cold ethanol, and dried (10% yield).

Method 2. Complex IV (100 mg) is refluxed in 50 ml of benzene for 30 d. The metallic palladium formed is filtered off (98% yield) and the yellow solution evaporated to dryness. Addition of 10 ml of ethanol gives a yellow solid, which is filtered off, washed with cold ethanol and air dried (80% yield).

Method 3. *trans*-$[Pd(C_6F_5)_2(CNTol\text{-}p)_2]$ (300 mg, 0.445 mmol) is refluxed in 50 ml of benzene for 26 h. The metallic palladium formed is filtered off (92% yield) and the reddish solution evaporated to dryness. Ethanol (10 ml) is added dropwise to the residue with stirring, to give a yellow solid, which is filtered off, washed with cold ethanol, and dried (26% yield).

Preparation of $[PdCl_2\{p\text{-}Tol)N{=}C(C_6F_5){-}C(C_6F_5){=}N(Tol\text{-}p)\}]$ *(VI)*

Compound V (74.1 mg, 0.130 mmol) is added to a solution of $[PdCl_2(NCPh)_2]$ (50 mg, 0.130 mmol) in 30 ml of benzene. Upon stirring a red microcrystalline solid separates within a few minutes, and this is filtered off, washed with 10 ml of benzene, and dried.

Preparation of $[Pd_2\{\mu\text{-}C(C_6F_5){=}N(Tol\text{-}p)\}_2(acac)_2]$ *(VII)*

Thallium acetylacetonate (106.7, 0.352 mmol) is added to a solution of complex (IV) (150 mg) in 50 ml of CH_2Cl_2. The mixture is stirred at room temperature for 4 h, and the white precipitate (TlCl) is filtered off. Evaporation of the yellow solution to ca. 2 ml and dropwise addition of 10 ml of ethanol affords a yellow precipitate which is filtered off, washed with 10 ml of cold ethanol, and dried (Mol. weight: Found: 990, calcd.: 979.43).

Preparation of $[Pd_2\{\mu\text{-}C(C_6F_5){=}N(Tol\text{-}p)\}_2Cl_2(NMe_3)_2]$ *(VIII)*

Trimethylamine is bubbled through a stirred suspension of complex IV (200 mg) in 20 ml of n-hexane for 10 min to give an orange solid (VIII), which is filtered off, washed with n-hexane, and dried. The product must be stored in the freezer. Complex VIII readily loses NMe_3 to regenerate the red polymer IV, as described below.

The complex $[Pd_2\{\mu\text{-}C(C_6F_5){=}N(Tol\text{-}p)\}_2Cl_2(NMe_3)_2]$ (100 mg, 0.105 mmol) is dissolved in 20 ml of acetone. The solution is concentrated on the rotary evaporator to small volume, whereupon the solution becomes red and a red solid is formed, which is identified as $[\{Pd_2\{\mu\text{-}C(C_6F_5){=}N(Tol\text{-}p)\}_2(\mu\text{-}Cl)_2\}\cdot 1CH_3COCH_3]_n$.

Preparation of $[Pd_2\{\mu\text{-}C(C_6F_5){=}N(Tol\text{-}p)\}_2Cl_2L_2]$*; L = py (IX), 4-Me-py (X), tht (XI)*

Pyridine (19 μl, 0.225 mmol) is added to a stirred solution of complex (IV) (100 mg) in 25 ml of CH_2Cl_2. The yellow solution is evaporated to ca. 1 ml, and 5 ml of ethanol are added to give a yellow product, which is recrystallized from dichloromethane/ethanol.

Preparation of $[\{Pd[\mu\text{-}C(C_6F_5){=}N(Tol\text{-}p)]Cl(CNR)\}_n]$*, R = p-Tol (XII), Me (XIII),* Bu^t *(XIV)*

Method 1 (general). *p*-Tolyl isocyanide (55 μl, 0.469 mmol) is added to a stirred solution of complex (IV) (200 mg) in 30 ml of CH_2Cl_2; the solution becomes yellow and a white solid separates within a few minutes. The solution is evaporated to a small volume, and the white precipitate is filtered off, washed with 5 ml of cold ethanol and dried.

Method 2 (for R = p-Tol). A solution of *trans*-[Pd(C_6F_5)Cl(CNTol-*p*)$_2$] (200 mg, 0.368 mmol) in 30 ml of benzene is refluxed for 2 h to give a yellow solution and a white precipitate. The solvent is evaporated to ca. 10 ml and the white precipitate is filtered off, washed with 10 ml of cold ethanol, and dried.

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