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Synthesis and reactivity of palladium complexes with *N,N′*-di-*p*-tolyl-formamidine, -triazene or -formamidinato ligands. Insertion of CNC_6H_4Me-*p*, CS_2 or CO_2 into a Pd–N bond

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Abstract

The syntheses of complexes containing the HL ligands *N,N′*-di-*p*-tolylformamidine (TolNCHNHTol) (Tol = *p*-MeC_6H_4) and *N,N′*-di-*p*-tolyltriazene (TolNNNHTol) are described. The complexes are of the types *cis*-$[Pd(C_6F_5)_2(HL)_2]$, *trans*-$[Pd(C_6F_5)Cl(HL)_2]$ and *cis*-$[Pd(C_6F_5)_2(PPh_3)(HL)]$, with the HL ligands acting as monodentate ligands via the imino N atom. A *N,N′*-di-*p*-tolylformamidinato complex, *cis*-$(NBu^n_4)[\overline{Pd(C_6F_5)_2\{N(tol)CHN}(Tol)\}]$ is also described. It undergoes irreversible insertion of CNTol of CS_2, or reversible insertion of CO_2, into one N–Pd bond. While the CS_2 insertion product is an *S,S*-bonded dithiocarbamate-type complex, the product arising from the CO_2 insertion contains a six-membered palladiacycle with the ligand *O,N*-bonded to the Pd atom.

Introduction

Formamidine and triazene ligands, RNYN′HR′ (Y = CH, N) and their deprotonated forms are a rich source of transition-metal complexes of a variety of structural types. Thus, formamidinato and triazenido ligands can bond in a monodentate σ-N′ (a), bidentate chelate σ-N,N′ (b) or bidentate bridging σ,σ′-N,N′ (c) fashion; the situations most commonly met are (b) [1] and (c) [2], and monodentate behaviour (a) has been reported in only a few complexes [3]. In addition there is the possibility of η^3-pseudoallyl coordination (d), as yet unknown, or of bridging heterodinuclear systems (e). Complexes of the latter type, in which metal–metal bonds are stabilized, have been reported recently [4,5]. Additional modes of coordination are

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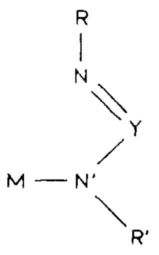
possible in systems of higher nuclearity, and some new bridging possibilities have been observed in osmium clusters [6].



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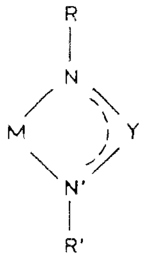

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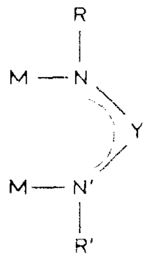

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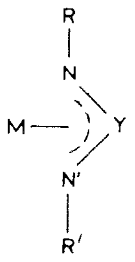

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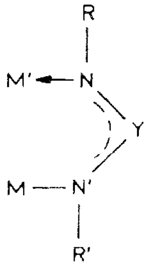


(e)

There have been few reports on the reactivity of formamidinato or triazenido ligands [2d,7] or on the coordination behaviour of their neutral parents formamidines and triazenes, RN=YNHR [8]. We describe here the synthesis of some complexes containing the neutral ligands *N,N′*-di-*p*-tolylformamidine (Hdptf) and *N,N′*-di-*p*-tolyltriazene (Hdptt) and one complex with a *N,N′*-di-*p*-tolylformamidinato ligand bonded in a bidentate chelate form (b). We also report on the reactions of the last-mentioned complex with CNTol, CS_2 and CO_2, which insert into the Pd–N bond.

Results and discussion

(a) Synthesis of complexes with neutral ligands (complexes I–VI)

The complexes *cis*-$[Pd(C_6F_5)_2(HL)_2]$ (HL = Hdptf (I), Hdptt (II)) were prepared by treating $(NBu^n_4)_2[Pd_2(\mu\text{-Br})_2(C_6F_5)_4]$ [9] with *N,N′*-di-*p*-tolylformamidine (Hdptf) or, *N,N′*-di-*p*-tolyltriazene (Hdptt), according to eq. 1.

$$\tfrac{1}{2}(NBu^n_4)_2[Pd_2(\mu\text{-Br})_2(C_6F_5)_4] + 2\,HL \xrightarrow{CH_2Cl_2} cis\text{-}[Pd(C_6F_5)_2(HL)_2] + (NBu^n_4)Br \qquad (1)$$

Addition of HL to CH_2Cl_2 solutions of $[Pd_2(\mu\text{-Cl})_2(C_6F_5)_2(tht)_2]$ [10] (tht = tetrahydrothiophen) causes cleavage of the cloride bridges and displacement of the

Table 1

Analytical data

Complex	Analysis (Found (calcd.) (%))		
	N	C	H
cis-$[Pd(C_6F_5)_2(TolNHCHNTol)_2]$ (I)	6.23	56.76	3.59
	(6.30)	(56.74)	(3.63)
cis-$[Pd(C_6F_5)_2(TolNHNNTol)_2]$ (II)	9.53	53.51	3.11
	(9.43)	(53.92)	(3.40)
trans-$[Pd(C_6F_5)Cl(TolNHCHNTol)_2]$ (III)	7.49	56.75	4.06
	(7.40)	(57.08)	(4.26)
trans-$[Pd(C_6F_5)Cl(TolNHNNTol)_2]$ (IV)	10.95	53.58	3.90
	(11.06)	(53.78)	(3.98)
cis-$[Pd(C_6F_5)_2(PPh_3)(TolNHCHNTol)]$ (V)	3.09	57.73	3.50
	(3.02)	(58.30)	(3.26)
cis-$[Pd(C_6F_5)_2(PPh_3)(TolNHNNTol)]$ (VI)	4.53	56.24	3.35
	(4.47)	(56.94)	(3.26)
cis-$(NBu^n_4)[Pd(C_6F_5)_2(TolNCHNTol)]$ (VII)	4.55	56.20	5.56
	(4.64)	(56.99)	(5.67)
cis-$(NBu^n_4)[\overline{Pd(C_6F_5)_2\{N(Tol)CHN(Tol)C}NTol\}]$ (VIII)	5.45	59.01	5.99
	(5.47)	(59.85)	(5.91)
cis-$(NBu^n_4)[Pd(C_6F_5)_2\{S_2C\text{-}N(Tol)CHNTol\}]$ (IX)	3.83	53.40	5.34
	(4.28)	(53.79)	(5.23)
$[Ag\{S_2CN(Tol)CHNTol\}]$ (X)	7.11	47.16	3.43
	(6.88)	(47.18)	(3.72)
cis-$(NBu^n_4)[\overline{Pd(C_6F_5)_2\{N(Tol)CHN(Tol)O}CO\}]$ (XI)	4.12	55.46	5.88
	(4.42)	(55.61)	(5.41)

tht ligand to give *trans*-$[Pd(C_6F_5)Cl(HL)_2]$ (HL = Hdptf (III), Hdptt (IV)), according to eq. 2.

$$[Pd_2(\mu\text{-}Cl)_2(C_6F_5)_2(tht)_2] + 2\ HL \xrightarrow{CH_2Cl_2} trans\text{-}[Pd(C_6F_5)Cl(HL)_2] + tht \quad (2)$$

Treatment of I or II with a stoicheiometric amount ($Pd/PPh_3 = 1/1$) of PPh_3 in CH_2Cl_2 gives *cis*-$[Pd(C_6F_5)_2(HL)(PPh_3)]$ as white (HL = Hdptf (V)) or orange (HL = Hdptt (VI)) crystals, according to eq. 3. IR spectroscopy shows that the *cis* configuration is retained throughout the reaction, a common feature for pentafluorophenyl-derivatives of palladium [11].

$$cis\text{-}[Pd(C_6F_5)_2(HL)_2] + PPh_3 \xrightarrow{CH_2Cl_2} cis\text{-}[Pd(C_6F_5)_2(HL)(PPh_3)] + HL \quad (3)$$

Complexes I–VI are stable as solids, but the triazene derivatives slowly decompose in solution. The analyses results and yields for the complexes are listed in Table 1.

(b) Structural study

The structural assignments of the complexes are based on their IR (Table 2), ^1H NMR (Table 3), and ^{19}F NMR (Table 4) spectra.

The IR spectra of all complexes I–VI show absorption bands characteristic of coordinated HL ligands, namely, $\nu(NH)$ absorptions at 3400–3200 cm^{-1}, $\nu(NYN)$ bands (Y = CH, N) at 1670–1520 cm^{-1}, and several bands in the ranges 1530–1400 and 1400–1200 cm^{-1} [8]. X-sensitive C_6F_5 bands [12] are observed near 800 cm^{-1};

Table 2

Relevant IR absorptions ($\mathrm{cm^{-1}}$)

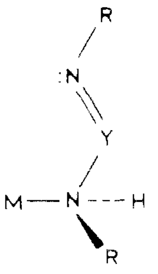
Compound	ν(NH)	ν(N–Y–N) (Y = CH, N)	X-sensitive C_6F_5	ν(Pd–Cl)
I	3370(s),3350sh)	1642(vs)	788(s),776(s)	–
II	3369(vs),3348(sh),3328(sh)	1522(vs)	788(s),778(s)	–
III	3215(sh),3160(vs)	1670(vs,br)	788(s)	285(vs)
IV	3140(s,br)	1520(vs)	788(s)	296(vs)
V	3340(s)	1650(vs,br)	787(s),770(s)	
VI	3200(w,br)	1520(vs)	786(s),770(s)	–
VII	–	1530(vs,br)	788(s),778(s)	
VIII	–	1592(vs) [a]	788(s),770(s)	–
IX	–	1643(vs),1630(vs)	788(s),775(s)	
X	–	1629(vs),1597(s)		

[a] ν(C=N) 1628(vs).

as expected from the respective symmetries, complexes I, II, V and VI, with two mutually *cis*-C_6F_5 groups, show two such bands, and complexes III and IV display only one.

The ^{19}F NMR spectra confirm the assignment of the geometry as far as the C_6F_5 groups are concerned. Complexes I–IV show only one type of C_6F_5 group, with a typical AA′MXX′ pattern, whereas complexes V and VI show signals corresponding to two chemically inequivalent C_6F_5 groups.

Formamidine and triazene ligands have two possible monodentate bonding modes, and their coordination behaviour has been the subject of some controversy [8]. In contrast to earlier suggestions of coordination (f) through the more basic amine-N atom [8b], Vrieze et al. have recently shown [3d] that coordination (g) through the imine-N atom occurs in the complexes $[\mathrm{M}\{\mathrm{C_6H_3(CH_2NMe_2)_2}$-2,6$\}(\mathrm{Hdptf})]X$ (M = Pd, Pt), both in solution and in the solid state.



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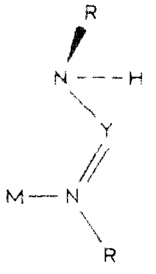


(g)

In our complexes a monodentate rigid bonding mode of the Hdptf and Hdptt ligands is inferred from the observation of two inequivalent *p*-tolyl systems in the ^{1}H NMR spectra at room temperature. The amino NH and imino CH protons in the formamidine derivatives are well separated, with ^3J(H–H) values of ca. 12.5 Hz: these coupling values and the strong shielding of the NH resonances in all the complexes are consistent with a coordination mode of the HL ligands via the imino-N atom. In addition, as for complex $[\mathrm{Pt}\{\mathrm{C_6H_3(CH_2NMe)_2}\}$-2,6$\}(\mathrm{Hdptf})]X$

Table 3

^{1}H NMR resonances (δ (ppm), $CDCl_3$, J(Hz), ref. TMS)

CH_3		Amidino or triazene resonances			Other
		Aryl	CH	NH	
I	2.23(6H,s); 2.33(6H,s)	7.13(4H,d),6.77(4H,d) $J_{AB} \simeq 8.23$; 7.21(4H,d),7.05(4H,d) $J_{A'B'} \simeq 8.29$	7.57(2H,d)	8.62(2H,d), J(NH–CH) $\simeq$ 12.54 Hz	
II	2.20(6H,s); 2.36(6H,s)	7.61(4H,d),7.03(4H,d) $J_{AB} \simeq 8.4$; 7.17(4H,d),7.11(4H,d) $J_{A'B'} \simeq 8.6$			
III	2.31(6H,s); 2.32(6H,s)	7.22(4H,d),7.06(4H,d) $J_{AB} \simeq 8.23$; 7.00(4H,d),7.13(4H,d) $J_{A'B'} \simeq 8.38$	7.58(2H,d)	9.43(2H,d) J(NH–CH) $\simeq$ 12.3	
IV	2.36(6H,s); 2.37(6H,s)	7.95(4H,d),7.16(4H,d) $J_{AB} \simeq 8.47$; 7.27(4H,d),7.12(4H,d) $J_{A'B'} \simeq 8.41$			
V	2.34(3H,s); 2.36(3H,s)	7(m)		8.92(2H,d), J(NH–CH) $\simeq$ 12.7	
VI	2.09(3H,s); 2.18(3H,s)	7(m)			
VII	2.18(6H,s)	6.82(4H,d), 6.48(4H,d) $J_{AB} \simeq 8.3$	9.28(1H,s)		
VIII	2.19(3H,s), 2.39(3H,s)	7.24(2H,d),7.11(2H,d),6.58(2H,d) 6.4(2H,d) $J_{AB} \simeq 9.4$	7.74(1H,s)		2.05(3H,s),6.79(4H,s)
IX	2.29(3H,s), 2.36(3H,s)	7.26(2H,d),7.14(2H,d) $J_{AB} \simeq 8.22$; 7.07(2H,d),6.90(2H,d) $J_{AB} \simeq 8.33$	9.46(1H,s)		
X	2.11(3H,s), 2.14(3H,s)	7.06(4H,s),6.91(2H,d), 6.74(2H,d) $J_{AB} \simeq 7.84$			

Table 4

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

	F(2), F(6)	F(4)	F(3), F(5)
cis-$[Pd(C_6F_5)_2(TolNHCHNTol)_2]$ (I)	−115.43	−161.87	−164.23
cis-$[Pd(C_6F_5)_2(TolNHNNTol)_2]$ (II)	−115.33	−160.14	−163.20
trans-$[Pd(C_6F_5)Cl(TolNHCHNTol)_2]$ (III)	−120.61	−161.03	−163.98
trans-$[Pd(C_6F_5)Cl(TolNHNNTol)_2]$ (IV)	−118.62	−159.04	−162.75
cis-$[Pd(C_6F_5)_2(PPh_3)(TolNHCHNTol)]$ (V)	−113.75, −117.22	−161.59, −163.61	−164.48
cis-$[Pd(C_6F_5)_2(PPh_3)(TolNHNNTol)]$ (VI)	−113.89, −116.86	−161.09, −162.66	−163.33, −164.27
cis-$(NBu^n_4)[\underline{Pd(C_6F_5)_2(TolNCHNTol)}]$ (VII)	−115.23	−164.25	−166.14
cis-$(NBu^n_4)[Pd(C_6F_5)_2\{(Tol)NCHN(Tol)C(NTol)\}]$ (VIII)	−112.35, −114.39	−165.97, −166.15	−168.14, −168.59
cis-$(NBu^n_4)[\underline{Pd(C_6F_5)_2\{S_2CN(Tol)CHN(Tol)}\}]$ (IX)	−113.51	−164.57	−166.00
cis-$(NBu^n_4)[Pd(C_6F_5)_2\{(Tol)NCHN(Tol)OCO\}]$ (XI)		−165.47, −165.57	

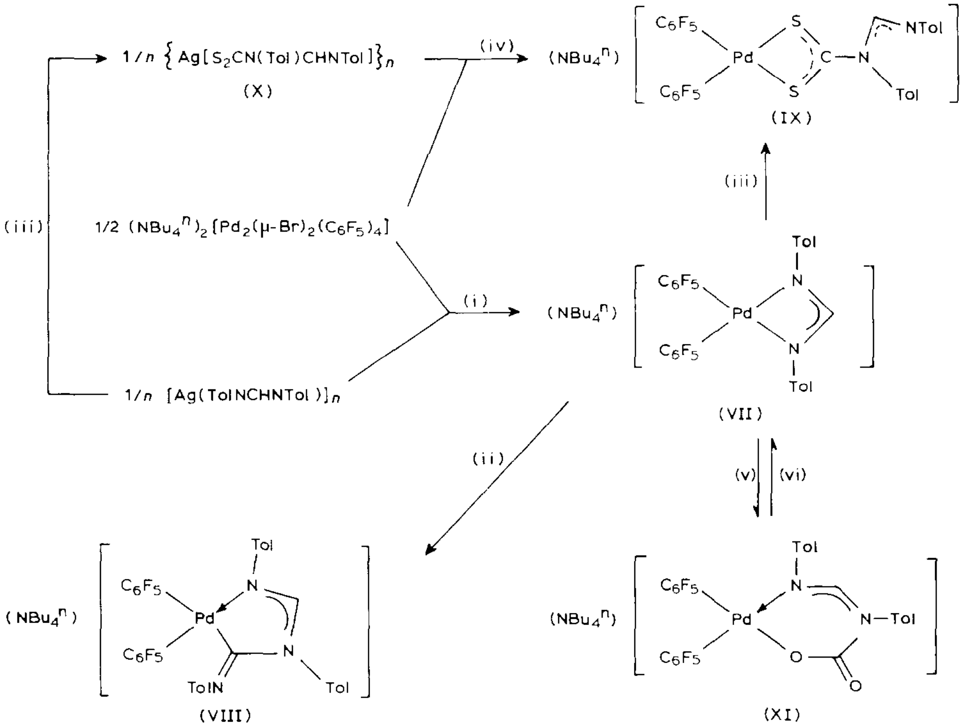
[3d], the ^{1}H NMR spectra of our complexes show one of the four aromatic resonances of the *p*-tolyl groups at lower field than the others. This resonance can be assigned to the two *ortho*-protons of the tolyl group bound to the imine-N atom.

(c) Synthesis and reactivity of a N,N′-di-p-tolylformamidinato derivative

We attempted to make derivatives containing a triazenido group but these turned out to be unstable, and the reactions were accompanied by extensive decomposition to black palladium. A formamidinato complex was prepared, and its synthesis and reactions with small molecules are summarized in Scheme 1.

The complex $(NBu^n_4)[Pd(C_6F_5)_2(TolNCHNTol)]$ (VII) was obtained in high yield by treating a dichloromethane solution of $(NBu^n_4)_2[Pd_2(\mu\text{-}Br)_2(C_6F_5)_4]$ with $[Ag(TolNCHNTol)]_n$ (Br/Ag ratio 1/1). Attempts to answer the question of whether the formamidinato group acts as a bridging or as a chelate ligand by a X-ray diffraction study were frustrated because we were unable to obtain good crystals. Equivalent conductivity measurements for complex VII in acetone at various concentrations [13] gave a value for the $\Lambda_0 - \Lambda_e/\sqrt{N}$ slope in the range of the values found for 1/1 electrolytes, and a long way from those found for 2/1 electrolytes. This suggests that, as in related derivatives [1], the formamidinato group is acting as a chelate ligand. The observation of a strong band at 1530 cm^{-1} assigned to $\nu(N{=}C{=}N)$ (120 cm^{-1} lower than in the free amidine) is indicative of extensive electronic delocalization within the NCN moiety. As expected the ^{1}H and ^{19}F NMR spectra of VII at room temperature reveal chemical equivalence of both N-substituents and of both C_6F_5 groups.

Complex VII reacts with CNTol to give a yellow complex VIII that we formulate as resulting from insertion of CNTol in a Pd–N bond. This is supported by the absence of absorptions in the $\nu(C{\equiv}N)$ region (2000–2300 cm^{-1}), and the observation of two strong absorptions at 1592 and 1628 cm^{-1} which are related to $\nu(N{=}C{=}C)$ and $\nu(C{=}N)$, respectively. As expected from the proposed structure, signals for two inequivalent C_6F_5 groups are observed in the ^{19}F NMR spectrum of



Scheme 1. (i) CH_2Cl_2, 1 day; (ii) stoicheiometric amount of CNTol, CH_2Cl_2, 10 min; (iii) CS_2 in CH_2Cl_2, 1 h; (iv) CH_2Cl_2, 15 h; (v) CH_2Cl_2, bubbling CO_2; (vi) spontaneously or on bubbling of N_2.

complex VIII, whereas the ^1H NMR spectrum displays three singlets corresponding to the three inequivalent methyl groups at 2.05, 2.19 and 2.30 ppm (δ, $CDCl_3$).

Complex VII also reacts with CS_2 to give the yellow complex IX. As shown in Scheme 1, IX can also be obtained by treating $(NBu^n_4)_2[Pd_2(\mu\text{-}Br)_2(C_6F_5)_4]$ with the silver complex X, obtained from the corresponding silver formamidinato and CS_2. The suggestion of a dithiocarbamate type of bonding for complex IX, resulting from a formal insertion of CS_2 into the Pd–N bond, is supported by the observed equivalence of the two C_6F_5 groups in the ^{19}F NMR spectrum; the alternative structures $|Pd(C_6F_5)_2\{N(Tol)CHN(Tol)C(S)S\}|^-$ and $|Pd(C_6F_5)_2\{N(Tol)\text{-}CHN(Tol)SC(S)\}|^-$ should give rise to inequivalence of the two C_6F_5 groups. In keeping with the proposed structure, two sharp methyl signals are observed at 2.29 and 2.36 ppm (δ, $CDCl_3$) in the ^1H NMR spectrum, and two absorptions in the IR spectrum at 1643 and 1630 cm^{-1} are assigned to the $\nu(C{=}N)$ stretches.

When CO_2 is bubbled through a yellow solution of complex VII in CH_2Cl_2 (0 °C) the yellow colour disappears, and addition of n-hexane allows the isolation of a white complex XI, which analyzes satisfactorily for the product of insertion of CO_2 into the Pd–N bond. Complex XI is very labile, and quickly loses CO_2 even in the solid state at room temperature, and very rapidly in solution. Bubbling of N_2 through solutions of complex XI leads to complete loss of CO_2 and regenerates complex VII. The extreme instability of complex XI complicates its spectroscopic study. ^{19}F NMR spectra are blurred in the range of the *ortho*- and *meta*-fluorines because of overlap of the signals of complex XI and those of its decomposition product VII; luckily the region of the *para*-fluorines is very informative, and in addition to the triplet assigned to the *para*-F of complex VII at −164.25 ppm, there are two more triplets of equal intensity at −165.47 and −165.57 ppm. This means that the two C_6F_5 groups in the complex are inequivalent, and rules out formulation of XI as a carbamato derivative isostructural with IX. The mode of bonding proposed in Scheme 1 seems the most reasonable one, and is consistent with the spectroscopic data. Although many examples of reversible CO_2 insertion into H-, C- and O-transition metal bonds have been reported [14] the first genuine example of CO_2 insertion into a N-transition metal bond was reported only recently [15], and the reaction described here is the first example of a reversible insertion of CO_2 into a Pd–N bond.

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. ^{1}H and ^{19}F NMR spectra were recorded on a Varian XL-200 instrument. Conductivities were measured on a Philips PW 9501/01 apparatus with ca. 10^{-4} *M* acetone solutions.

N,N'-Di-*p*-tolyltriazene, *N,N'*-di-*p*-tolylformamidine and silver(I) *N,N'*-di-*p*-tolylformamidinate were prepared by published methods [16,17,18].

Since the methods used to prepare some of the complexes are very similar to one another only typical procedures are given.

cis-[Pd(C_6F_5*)*$_2$*(TolNHCHNTol)*$_2$*] (I)*

$(NBu^n_4)_2[Pd_2(\mu\text{-}Br)_2(C_6F_5)_4]$ (0.3 g, 0.1966 mmol) in 30 ml of CH_2Cl_2 is stirred with of *N,N'*-di-*p*-tolylformamidine (0.176 g, 0.7864 mmol) for 30 min. The solution is then evaporated to dryness and 10 ml of ethanol are added. The white solid formed is filtered off and washed with ethanol (15 ml). 80% yield.

cis-[Pd(C_6F_5*)*$_2$*(TolNHNNTol)*$_2$*] (II)*

N,N'-Di-*p*-tolyltriazene (0.133 g, 0.5903 mmol) are added to a solution of 0.212 g (0.1475 mmol) of $(NBu^n_4)_2[Pd_2(\mu\text{-}Br)_2(C_6F_5)_4]$ in 25 ml of CH_2Cl_2 and the mixture is stirred. The orange solution obtained is evaporated to dryness and 10 ml of ethanol are added. The yellow solid is filtered off and washed with 10 ml of ethanol, 73% yield.

trans-[Pd(C_6F_5*)ClL*$_2$*] (L = Hdptf (III); L = Hdptt (IV))*

$[Pd_2(\mu\text{-}Cl)_2(C_6F_5)_2(tht)_2]$ (0.2 g, 0.2518 mmol) and L (L = Hdptt, 0.227 g, 1.0072 mmol III); (L = Hdptt, 0.226 g, 1.0072 mmol IV) are stirred in 30 ml of CH_2Cl_2 for 4 h to give either a yellow (in the case of III) or a red (in the case of IV) solution. Evaporation to dryness and addition of ether (15 ml) gives yellow crystals of III (80% yield) or IV (70% yield).

cis-[Pd(C_6F_5*)*$_2$*L(PPh*$_3$*)] (L = Hdptf (V); L = Hdptt (VI))*

Triphenylphosphine (0.029 g, 0.1112 mmol or 0.044 g 0.1685 mmol) is added to a solution of complex I (0.100 g, 0.1112 mmol) or II (0.150 g, 0.1685 mmol) in 30 ml of CH_2Cl_2. The mixture is stirred at room temperature for 5 h. In the case of complex V the colourless solution is concentrated to a small volume (~ 1 ml) and ethanol (~ 10 ml) is added to give white crystals of V (68% yield). In the case of complex VI, the red solution is evaporated to dryness and 30 ml of ether are added, and the solute is cooled to give orange crystals of VI (60% yield).

$(\mathrm{NBu^n_4})[\overline{\mathrm{Pd(C_6F_5)_2(TolNCHNTol)}}]$ *(VII)*

Silver(I) *N,N'*-di-*p*-tolylformamidinate (0.087 g, 0.2621 mmol) is added to a solution of $(\mathrm{NBu^n_4})_2[\mathrm{Pd_2}(\mu\text{-Br})_2(\mathrm{C_6F_5})_4]$ (0.200 g, 0.1311 mmol) in 50 ml of CH_2Cl_2. The mixture is stirred for one day and AgBr is then filtered off. Evaporation of the yellow solution to dryness and dropwise additon of ~ 10 ml of ether produces yellow crystals of VII (74% yield).

cis-$(\mathrm{NBu^n_4})[\overline{\mathrm{Pd(C_6F_5)_2\{N(Tol)CHN(Tol)C}}\mathrm{NTol\}}]$ *(VIII)*

p-Tolylisocyanide (15 μl, 0.1103 mmol) is added to a solution of complex VII (0.100 g, 0.1103 mmol) in 20 ml of CH_2Cl_2. The initially yellow solution becomes pale yellow within a few minutes. The solution is evaporated to dryness and 15 ml of diethyl ether is added to the residue. The pale yellow solid (VIII) is filtered off and washed with 10 ml of diethyl ether (85% yield).

cis-$(\mathrm{NBu^n_4})[\mathrm{Pd(C_6F_5)_2\{S_2CN(Tol)CHN(Tol)\}}]$ *(IX)*

Method I. CS_2 (1 ml) is added to a stirred solution of complex VII (0.3 g, 0.3310 mmol) in 25 ml of CH_2Cl_2. The orange solution is evaporated to dryness. The resulting oil is dissolved in ether (60 ml) and the solution is filtered, evaporated to ca. 3 ml, and cooled in the freezer to give a yellow solid, which is filtered off and washed with 5 ml of cold ethanol (yield 50%).

Method II. A solution of $(\mathrm{NBu^n_4})_2[\mathrm{Pd_2}(\mu\text{-Br})_2(\mathrm{C_6F_5})_4]$ (0.264 g, 0.1732 mmol) in 30 ml of CH_2Cl_2 is stirred with 0.141 g (0.1732 mmol) of complex X for 15 h. The AgBr is filtered off, the yellow solution evaporated to dryness and ethanol is added to the residue. The yellow crystals of IX are filtered off, and washed with 5 ml of cold ethanol (yield 90%).

$[\mathrm{Ag(S_2C\text{-}N(Tol)CHNCTol)}]$ *(X)*

CS_2 (1 ml) is added to a colourless solution of silver(I) *N,N'*-di-*p*-tolylformamidinate in 30 ml of CH_2Cl_2. After 3 h stirring the resulting orange solution is evaporated to dryness and 10 ml of ethanol are added to the residue. The orange solid is filtered off and washed with ethanol (15 ml) (90% yield).

cis-$[\overline{\mathrm{Pd(C_6F_5)_2\{N(Tol)CHN(Tol)O}}\mathrm{C(O)\}}]$ *(XI)*

CO_2 is bubbled through a cold yellow solution of complex VII (0.2 g, 0.2206 mmol) in CH_2Cl_2 (3 ml). After 15 min the solution becomes colourless and n-hexane (50 ml) is added. The solution is cooled in the freezer to give a white solid, which is filtered off under a CO_2 atmosphere and washed with n-hexane.

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