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Cationic Cyanobenzylpalladium(II) Complexes. Synthesis and Reactivity of the CN Group towards Nucleophiles

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The addition of alcohols, thiols, water and amines to the σ-coordinated CN group of cis-$[Pd(o\text{-}CH_2C_6H_4CN)L_2]_2(BF_4)_2$ *(L_2 = $2PPh_3$, 1,2-bis(diphenylphosphino)ethene or -ethane) yields stable N-bonded iminoether, iminothioether, amide and amidine complexes, respectively. Thiophenols, ArSH (Ar =* p-$C_6H_4CH_3$, p-C_6H_4Br*) break the σ-Pd–C bond, forming* o*-cyano toluene and complexes of the type* $[Pd(SAr)L_2]_2(BF_4)_2$. *The azido complex* $PdN_3(o\text{-}CH_2C_6H_4CN)(Ph_2PCH_2CH_2PPh_2)$ *is stable in the solid state but in solution it undergoes an intramolecular 1,3-cycloaddition yielding the corresponding tetrazolate complex.*

Introduction

In recent years many cyanoalkyl complexes of transition metals have been prepared [1–12]. This class of organometallic compounds presents some interesting features: i) the strength of the M–C bond is considerably greater than that of analogous alkyl compounds, as shown by the difficulty of obtaining insertion reactions [10, 12, 13], electrophilic attacks [14] and reductive eliminations [13], ii) the cyanoalkyl moiety may behave either as a mono- or a bidentate ligand and promote *cis–trans* isomerisation reactions [10, 15, 16], and iii) the σ- (or eventually π-) bonded CN group should be activated in addition reactions of nucleophiles such as alcohols, water and amines giving iminoether, amide and amidine complexes respectively [17, 18]. Of particular interest are the *o*-cyanobenzyl derivatives of manganese(I), iron(I) and platinum(II). The latter compounds show the widest range of reactions [15–18]. We have described recently the synthesis, spectroscopic properties and some reactions of palladium(II) complexes of the type $PdCl(CH_2C_6H_4CN)L_2$ ($L_2 = 2PPh_3$, diphosphine, *o*-phenanthroline) [19]. This paper deals with the synthesis and the reactivity of the cationic complexes $[Pd(o\text{-}CH_2C_6H_4CN)L_2]_2(BF_4)_2$.

Results and Discussion

Immediate precipitation of AgCl is observed when mixing a dichloromethane solution of *cis*- or *trans*-$PdCl(o\text{-}CH_2C_6H_4CN)L_2$ with the stoichiometric amount of $AgBF_4$ in acetone and cationic complexes of the type $[Pd(o\text{-}CH_2C_6H_4CN)L_2]_2(BF_4)_2$ (L = PPh_3, complex 1a; L_2 = diphos 1b, [19]) can be recovered from the filtered solution. The *m*-$CH_2C_6H_4CN$ derivatives can be obtained similarly. These complexes show an intense IR absorption in the ν(C≡N) region, about 30 cm^{-1} higher than that of the uncoordinated CN group of $PdCl(o\text{-}CH_2C_6H_4CN)L_2$. This indicates the presence of a σ Pd–NC bond in the cationic complexes. The dimeric formula of these complexes is supported by the following considerations: i) Dreiding molecular models show that the *o*-cyanobenzyl group is too strained in a chelating σ Pd–NC intramolecular arrangement, ii) the analogous platinum complex $[Pt(o\text{-}CH_2C_6H_4CN)(cis\text{-}Ph_2PCH{=}CHPPh_2)]_2(BF_4)_2$ was found to be dimeric by an X-ray determination of its crystal structure [20] and iii) molecular weight measurements showed that the manganese(I) complex $[Mn(o\text{-}CH_2C_6H_4CN)(CO)_4]_2$ is dimeric in solution [15]. It is likely that also in the case of palladium the cyanobenzyl group acts as a bidentate ligand bridging two metal atoms in a dimeric complex of *cis* geometry.

All complexes have been characterized by ^1H NMR, IR spectroscopy (Table I) and elemental analyses (Experimental).

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TABLE I. ^{1}H NMR and IR Spectral Data for Cyanobenzyl–Pd(II) Complexes and Products of Nucleophilic Attack.

Complex	$\delta(CH_2)^a$ (ppm)	^3J(PPdCH) (Hz)	δ (others) (ppm)	ν(C=N) region^h (cm^{-1})	ν(others) (cm^{-1})
1a *cis*-$[Pd\{o\text{-}CH_2C_6H_4CN\}(PPh_3)_2]_2(BF_4)_2$	3.44m		7.3m $PC_6H_5{}^e$		2260m ν(C≡N) 1056vs, br $\nu(BF_4)$ 537s^e
2a *cis*-$[Pd\{m\text{-}CH_2C_6H_4CN\}(PPh_3)_2]_2(BF_4)_2$	2.95m, br 3.16m, br		7.3m $PC_6H_5{}^e$		2264m ν(C≡N) 1059vs, br $\nu(BF_4)$ 537s^e
3a *cis*-$[Pd\{o\text{-}CH_2C_6H_4C(=NH)OCH_3\}(PPh_3)_2]BF_4$	3.10dd	6.6 *cis* 7.5 *trans*	3.20s OCH_3 5.95br NH 7.3m $PC_6H_5{}^e$	1625s	3345w ν(NH) 1215m $\nu(COC)_{as}$ 1056vs, br $\nu(BF_4)$ 538s^e
3b $[Pd\{o\text{-}CH_2C_6H_4C(=NH)OCH_3\}(Ph_2PCH_2CH_2PPh_2)]BF_4$	2.95dd	4.6 *cis* 9.8 *trans*	3.86s OCH_3 6.23br NH	1618s	3347w ν(NH) 1211m $\nu(COC)_{as}$ 1048vs, br $\nu(BF_4)$
3c $[Pd\{o\text{-}CH_2C_6H_4C(=NH)OCH_3\}(Ph_2PCH{=}CHPPh_2)]BF_4$	3.11dd	5.0 *cis* 10.0 *trans*	4.00s OCH_3 6.21br NH	1620s	3344w ν(NH) 1218m $\nu(COC)_{as}$ 1055vs, br $\nu(BF_4)$
4b $[Pd\{o\text{-}CH_2C_6H_4C(=NH)SCH_3\}(Ph_2PCH_2CH_2PPh_2)]BF_4$	2.92dd	4.5 *cis* 9.5 *trans*	2.38s SCH_3 6.17br NH	1570m 1540m	3315w ν(NH) 1055vs, br $\nu(BF_4)$
4c $[Pd\{o\text{-}CH_2C_6H_4C(=NH)SCH_3\}(Ph_2PCH{=}CHPPh_2)]BF_4$	3.01dd	5.0 *cis* 9.7 *trans*	2.45s SCH_3 6.28br NH	1568m 1540m	3320w ν(NH) 1056vs, br $\nu(BF_4)$
5b $[Pd\{o\text{-}CH_2C_6H_4C(=NH)SCH_2C_6H_5\}(Ph_2PCH_2CH_2PPh_2)]BF_4$	3.01dd^b	4.4 *cis* 9.5 *trans*	4.30s SCH_2 6.07br NH	1570m 1533m	3332w ν(NH) 1057vs, br $\nu(BF_4)$
5c $[Pd\{o\text{-}CH_2C_6H_4C(=NH)SCH_2C_6H_5\}(Ph_2PCH{=}CHPPh_2)]BF_4$	3.02dd	4.7 *cis* 9.5 *trans*	4.27s SCH_2 6.18br NH	1571m 1540m	3338w ν(NH) 1057vs, br $\nu(BF_4)$
6b $[Pd\{o\text{-}CH_2C_6H_4C(=NH)N(CH_3)_2\}(Ph_2PCH_2CH_2PPh_2)]BF_4$	2.74s, br^b	c	3.09s $NCH_3{}^f$ 6.10br NH	1576s 1544s	3353w ν(NH) 1053vs, br $\nu(BF_4)$
6c $[Pd\{o\text{-}CH_2C_6H_4C(=NH)N(CH_3)_2\}(Ph_2PCH{=}CHPPh_2)]BF_4$	2.72s, br^b	d	3.14s $NCH_3{}^g$ 6.22br NH	1575s 1543s	3350w ν(NH) 1053vs, br $\nu(BF_4)$
7b $[Pd\{o\text{-}CH_2C_6H_4CONH_2\}(Ph_2PCH_2CH_2PPh_2)]BF_4$	2.83dd^b	3.0 *cis* 9.0 *trans*	6.15br NH	1642s, br^i 1520s, br	3435w, 3340w 3262w, ν(NH) 1054vs, br $\nu(BF_4)$
8b $PdN_3\{o\text{-}CH_2C_6H_4CN\}(Ph_2PCH_2CH_2PPh_2)$	2.90dd	4.4 *cis* 11.6 *trans*			2220m ν(C≡N) 2035vs $\nu(N_3)_{as}$
9b $Pd\{o\text{-}CH_2C_6H_4CN_4\}(Ph_2PCH_2CH_2PPh_2)$	2.86dd	6.0 *cis* 10.0 *trans*			

10b $[Pd\{p\text{-}SC_6H_4CH_3\}(Ph_2PCH_2CH_2PPh_2)]_2(BF_4)_2$	2.27 s CH_3 6.2–6.8 m C_6H_4	1057vs, br $\nu(BF_4)$
11b $[Pd\{p\text{-}SC_6H_4Br\}(Ph_2PCH_2PPh_2)]_2(BF_4)_2$	6.4–6.7 m C_6H_4	1056vs, br $\nu(BF_4)$

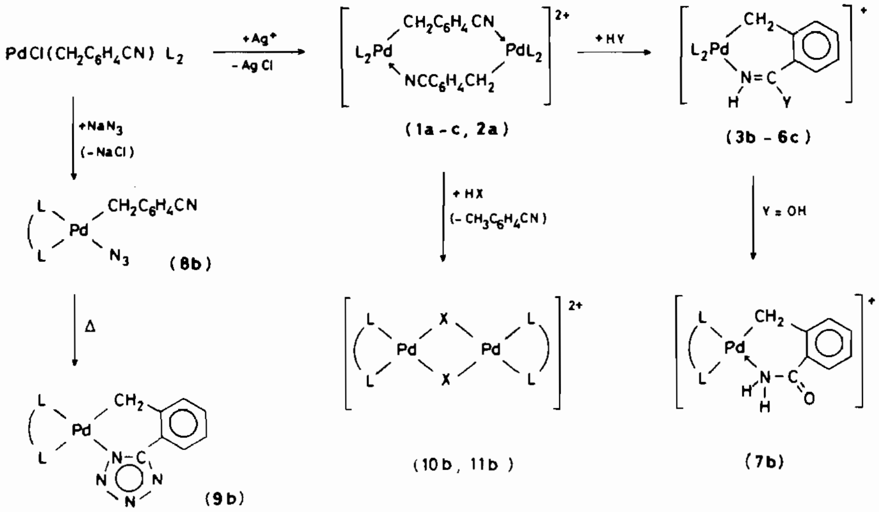
[a] ^1H NMR spectra at 34 °C in $CDCl_3$, unless stated otherwise. TMS as internal standard; s: singlet; d: doublet; m: multiplet; br: broad. All derivatives of bis(diphenylphosphino)ethane showed broad multiplet CH_2 resonances at 2.1–2.5 ppm. [b] In CD_2Cl_2. [c] The $PdCH_2$ resonance is split upon cooling into two broad singlets, and at lower temperature (−25 °C) into a multiplet superposed on the multiplet of the diphosphine CH_2. [d] The $PdCH_2$ resonance is split into a multiplet centered at 2.6 ppm upon cooling at *ca.* −30 °C; this multiplet coalesces into two broad singlets at *ca.* 10 °C. [e] See text. [f] The NCH_3 resonance is split inot a doublet centered at 3.12 ppm at *ca.* −30 °C which coalesces at *ca.* 0 °C. [g] The NCH_3 resonance is split into a doublet centered at 3.15 ppm at *ca.* −35 °C which coalesces at *ca.* −5 °C. [h] Nujol or hexachlorobutadiene mull, NaCl or CsI windows. m: medium; s: strong; vs: very strong; w: weak. [i] Attributable to "amide I" and "amide II" bands respectively.

The assignment of a *cis* geometry for complexes 1a, 2a and 3a is based on the following observations: i) the $^{31}P\{^1H\}$NMR spectrum of 1a in CD_2Cl_2 appears as a doublet of doublets (δ(P) = 23.1 and 35.5 ppm, $^2J(PP) \sim 18$ Hz relative to H_3PO_4 85%) indicating that the two PPh_3 are magnetically nonequivalent, ii) for those three complexes as for *cis*-$PdXY(PPh_3)_2$, the phenyl proton resonance of PPh_3 appears as a broad singlet, whereas two broad multiplets are observed for *trans*-$PdXY(PPh_3)_2$ [21] and iii) 1a, 2a and 3a show a strong IR band at *ca.* 540 cm^{-1} which is absent in the *trans* derivatives of the type $PdClX(PPh_3)_2$ (X = CH_2CN, CF_3, CH_2CF_3, Cl [22]; *o*-, *m*- and *p*-$CH_2C_6H_4CN$ [19]). The latter criterion was proposed by Mastin [23] for the assignment of *cis* or *trans* geometry to bis(triphenylphosphine)platinum(II) complexes. The ^1H NMR spectrum of $[Pd(o\text{-}CH_2C_6H_4CN)L_2]_2(BF_4)_2$ (L_2 = 1,2-bis-(diphenylphosphino)ethane, 1b, or -ethene, 1c [19]) presents the usual doublet of doublets for the benzylic methylene protons coupling with two nonequivalent phosphorus atoms. For 1a and 2a, the methylene resonance in the −10– + 40 °C range appears as one and two broad multiplets respectively, suggesting that the two CH_2 protons are not magnetically equivalent. This fact may be related to the higher bulkiness of the two PPh_3, compared with that of a diphosphine, forcing the cyanobenzyl moiety out of the PPdP plane. In addition the flipping movement of the cyanoalkyl group above and below the PPdP plane should give rise to unresolved multiplets, as found previously for the analogous Pt(II) compounds $[Pt(o\text{-}CH_2C_6H_4CN)L_2]_2(BF_4)_2$ (L = PPh_3, $AsPh_3$) [16, 17].

The nitrile group of the cyanobenzylpalladium(II) complexes 1a–c is prone to nucleophilic attack and reacts with alcohols, thiols, amines and water giving the corresponding iminoether (3a–c), iminothioether (4b–5c), amidine (6b, c) and amide (7b) N-coordinated derivatives (Scheme 1).

The IR spectrum of these complexes presents a band around 3340 cm^{-1} (ν(NH)) and one or two bands in the region 1540–1620 cm^{-1} which can be assigned to the N–H bending and the C=N stretch. The benzyl methylene ^1H resonance pattern is the doublet of doublets expected for a *cis* geometry. However, for 6b and 6c, only a broad singlet can be detected at room temperature. On lowering progressively the temperature, two broad singlets appear and then a multiplet at −40 °C. For the same complexes, the NCH_3 resonance is a singlet at room temperature and a doublet at −40 °C. This temperature dependent spectrum can be accounted for the rotational barrier around the $=C\text{–}N\text{–}CH_3$ bonds of the amidino group [24].

Less basic thiols, such as *p*-thiocresol and *p*-bromothiophenol do not add to the CN group but cleave the Pd–C bond leading to a quantitative elimination of



L = PPh₃ or 1/2 diphos; L–L = diphos; CH₂C₆H₄CN = *o*-cyanobenzyl; for 2a, *m*-cyanobenzyl;
Y = OH, OCH₃, SCH₃, SCH₂C₆H₅, N(CH₃)₂; X = *p*-SC₆H₄CH₃ or *p*-SC₆H₄Br.

o-cyanotoluene and to the formation of the cationic sulphur bridged dimers 10b and 11b. The azido complex 8b has been prepared by metathetical exchange from the analogous chloro complex. This complex is stable in the solid state, but in solution it undergoes a 1,3-intramolecular cycloaddition of N_3 on the CN group, giving the tetrazolate complex 9b. The same intramolecular cyclization has been observed in the case of the platinum(II) derivative *cis*-$PtN_3(o\text{-}CH_2C_6H_4CN)(PPh_3)_2$ [18]. Intermolecular cycloaddition of nitriles to azido complexes of platinum and palladium have also been reported [25, 26].

A slow hydrolysis occurs even for the uncoordinated cyano group of the neutral dimeric complex $[PdCl(o\text{-}CH_2C_6H_4CN)PPh_3]_2$. This reaction is promoted by triethylamine:

$$[PdCl(o\text{-}CH_2C_6H_4CN)PPh_3]_2 \xrightarrow[-Et_3NHCl]{H_2O + NEt_3}$$

$$[Pd(o\text{-}CH_2C_6H_4CONH)PPh_3]_n$$

12a

The white insoluble product 12a, obtained in quantitative yield, shows the characteristic infrared absorptions of imide group and its elemental analysis corresponds to this formulation. Its extreme insolubility in most solvents is probably related to its polymeric nature.

As a conclusion, the palladium derivatives of the type $[Pd(o\text{-}CH_2C_6H_4CN)L_2]_2(BF_4)_2$ show, by comparison with the corresponding platinum complexes, an easier addition of nucleophiles to the coordinated cyano group and a facile cleavage of the Pd–C bond by means of acidic thiols. In particular they allow the hydrolysis of a nitrile under rather mild and neutral conditions.

Experimental

^1H NMR spectra were recorded with a Varian NV-14 or a EM-390 spectrometer, IR spectra with the Perkin-Elmer 457 or 180 spectrometers. GLC were performed with a Hewlett-Packard 5730A Gas-Chromatograph equipped with flame ionization detectors and with a Hewlett-Packard 3380A integrator. *o*-Cyanotoluene and thiophenols were analyzed on a 5-ft Chromosorb 20M column at 150 °C.

The complexes *trans*-$PdCl(o\text{-}CH_2C_6H_4CN)(PPh_3)_2$, *trans*-$PdCl(m\text{-}CH_2C_6H_4CN)(PPh_3)_2$, $[Pd(o\text{-}CH_2C_6H_4CN)(diphos)]_2(BF_4)_2$ and $[PdCl(o\text{-}CH_2C_6H_4CN)(PPh_3)]_2$ were prepared as reported previously [19]. All solvents were purified and dried by standard methods. Microanalyses were performed by the Institute of Organic Chemistry, Padua.

Preparation of Complexes

cis-*$[Pd(o\text{-}CH_2C_6H_4CN)(PPh_3)_2]_2(BF_4)_2$ (1a), and*
cis-*$[Pd(m\text{-}CH_2C_6H_4CN)(PPh_3)_2]_2(BF_4)_2$ (2a)*

A solution of $AgBF_4$ (0.58 g, 3.0 mmol) in acetone (10 ml) was added to a solution of *trans*-$PdCl(o\text{-}CH_2C_6H_4CN)(PPh_3)_2$ or *trans*-$PdCl(m\text{-}CH_2C_6H_4CN)(PPh_3)_2$ (2.35 g, 3.0 mmol) in dichloromethane (70 ml) under nitrogen. AgCl was filtered and the filtrate reduced to *ca.* 35 ml. Addition of ether gave a yellow precipitate which was recrystallised from dichloromethane/ether. Yields 85–90%. M.p. (°C, dec) 134–139 (1a), 136–143 (2a). *Anal.* 1a:

found (calc.) C 62.86 (63.37), H 4.22 (4.35), N 1.57 (1.68); 2a: C 62.48 (63.37), H 4.14 (4.35), N 1.67 (1.68) %.

cis-$[Pd\{o\text{-}CH_2C_6H_4C(=NH)OCH_3\}(PPh_3)_2]BF_4$ (3a)

NEt_3 (0.05 ml) was added to a suspension of 1a (0.5 g) in methanol (25 ml). The reaction mixture was stirred for 20 min at 30 °C under nitrogen. After being allowed to stand at room temperature for 40 min, the yellow solution was evaporated to 10 ml under reduced pressure; 3a was precipitated by adding ether, and was recrystallized from dichloromethane/ether. Yield 0.295 g. In absence of NEt_3 the reaction is too slow and the complex decomposes into a brown product. M.p. 191–193°. *Anal.* C 61.74 (62.41), H 4.73 (4.66), N 1.49 (1.62) %.

$[Pd\{o\text{-}CH_2C_6H_4C(=NH)OCH_3\}(L\text{–}L)]BF_4$ (3b, $L\text{–}L = Ph_2PCH_2CH_2PPh_2$; 3c, $L\text{–}L$ = cis-$Ph_2PCH=CHPPh_2$)

A suspension of $[Pd(o\text{-}CH_2C_6H_4CN)(L\text{–}L)]_2(BF_4)_2$ (0.4 g) in degassed methanol (25 ml) was stirred at 35 °C until complete dissolution (20–30 min), and set aside for 2 h. The solvent was removed under reduced pressure giving a yellow oil, which was treated dropwise with ether/n-hexane (1:1). The resulting solid was recrystallized from dichloromethane/ether. Yields 75–85% M.p. 201–203° (3b), 210–214° (3c). *Anal.* 3b: C 57.08 (56.82), H 4.75 (4.63), N 1.73 (1.89); 3c: C 56.64 (56.98), H 4.22 (4.37), N 1.91 (1.90) %.

$[Pd\{o\text{-}CH_2C_6H_4C(=NH)SCH_3\}(L\text{–}L)]BF_4$ (4b, $L\text{–}L = Ph_2PCH_2CH_2PPh_2$; 4c, $L\text{–}L$ = cis-$Ph_2PCH=CHPPh_2$)

CH_3SH was bubbled into a suspension of $[Pd(o\text{-}CH_2C_6H_4CN)(L\text{–}L)]_2(BF_4)_2$ (0.4 g) in acetone (15 ml) for 3 min and the mixture stirred for 55 min. Solvent was removed under reduced pressure and the yellow residue was recrystallized from dichloromethane/ether. Yields 60–80%. M.p. 175–190° (4b), 181–188° (4c). *Anal.* 4b: C 54.82 (55.61), H 4.61 (4.53), N 1.68 (1.85); 4c: C 55.48 (55.84), H 4.07 (4.28), N 1.70 (1.86) %.

$[Pd\{o\text{-}CH_2C_6H_4C(=NH)N(CH_3)_2\}(L\text{–}L)]BF_4$ (6b, $L\text{–}L = Ph_2PCH_2CH_2PPh_2$; 6c, $L\text{–}L$ = cis-$Ph_2PCH=CHPPh_2$)

These pale yellow complexes were prepared as described above, using $(CH_3)_2NH$. Yields 50–80%, after recrystallization of the crude oily product from acetone/ether. M.p. 188–196° (6b), 186–192° (6c). *Anal.* 6b: 57.56 (57.43), H 5.22 (4.95), N 3.54 (3.72); 6c: C 57.81 (57.59), H 4.77 (4.70), N 3.59 (3.75) %.

$[Pd\{o\text{-}CH_2C_6H_4C(=NH)SCH_2C_6H_5\}(L\text{–}L)]BF_4$ (5b, $L\text{–}L = Ph_2PCH_2CH_2PPh_2$; 5c, $L\text{–}L$ = cis-$Ph_2PCH=CHPPh_2$)

$PhCH_2SH$ (0.2 ml) was added to a suspension of $[Pd(o\text{-}CH_2C_6H_4CN)(L\text{–}L)]_2(BF_4)_2$ (0.4 g) in acetone (15 ml), and the mixture stirred for 70 min under nitrogen. A yellow precipitate formed on addition of ether/n-hexane and was recrystallized from acetone/ether. Yields 88–95%. M.p. 165–174° (5b), 163–169° (5c). *Anal.* 5b: C 58.83 (59.19), H 4.48 (4.60), N 1.55 (1.68); 5c: C 59.05 (59.33), H 4.27 (4.37), N 1.54 (1.69) %.

$[Pd(o\text{-}CH_2C_6H_4CONH_2)(Ph_2PCH_2CH_2PPh_2)]BF_4$ (7b)

$[Pd(o\text{-}CH_2C_6H_4CN)(Ph_2PCH_2CH_2PPh_2)]_2(BF_4)_2$ (0.75 g) was added to a mixture of acetone (30 ml) and water (10 ml) and heated at 50 °C for 3 h. The acetone was evaporated and water added. The pale yellow precipitate was washed with water and recrystallized from dichloromethane/ether. Yield 0.58 g. M.p. 176–184°. *Anal.* 7b: C 56.53 (56.27), H 4.56 (4.44), N 1.82 (1.93).

$[Pd(o\text{-}CH_2C_6H_4CONH)(PPh_3)]_n$ (12a)

$[PdCl(o\text{-}CH_2C_6H_4CN)(PPh_3)]_2$ (0.25 g) and NEt_3 (0.15 ml) were added to a mixture of acetone (10 ml) and water (5 ml) and stirred for 75 h. The insoluble white solid was filtered and washed with water and acetone, and dried in vacuo. Yield 0.23 g. M.p. 223–227°. *Anal.* C 61.97 (62.27), H 4.68 (4.42), N 2.75 (2.80) %. IR bands: 1574s, br; 1519vs, br (ν(CONH)); 3271 w cm^{-1} (ν(NH)).

$PdN_3(o\text{-}CH_2C_6H_4CN)(Ph_2PCH_2CH_2PPh_2)$ (8b) and $Pd(o\text{-}CH_2C_6H_4CN_4)(Ph_2PCH_2CH_2PPh_2)$ (9b)

NaN_3 in excess was added to a suspension of $PdCl(o\text{-}CH_2C_6H_4CN)(Ph_2PCH_2CH_2PPh_2)$ (0.6 g) in 30 ml acetone/water (~3:1) and stirred at room temperature. After 2 h the acetone was evaporated under reduced pressure and precipitation was completed by adding water (30 ml). The yellow solid was washed with water, then methanol, and was recrystallized from dichloromethane/ether. Yield 0.58 g. 8b (0.4 g) was heated under reflux in methanol (25 ml) for 2.5 h. The volume was reduced to 5 ml, and the yellow complex 9b was precipitated by adding ether. Yield 0.37 g. M.p. 192–195° (8b), 222–226° (9b). *Anal.* 8b: 61.26 (61.59), H 4.50 (4.56), N 8.63 (8.45); 9b: C 61.33 (61.59), H 4.60 (4.56), N 8.00 (8.45) %.

$[Pd(SAr)(Ph_2PCH_2CH_2PPh_2)]_2(BF_4)_2$ (10b, Ar = p-$C_6H_4CH_3$; 11b, Ar = p-C_6H_4Br)

$[Pd(o\text{-}CH_2C_6H_4CN)(Ph_2PCH_2CH_2PPh_2)]_2(BF_4)_2$ (0.4 g) was stirred for 2 h in acetone (15 ml) with a threefold excess of *p*-thiocresol or *p*-bromothiophenol, at room temperature. The red-orange solution was reduced to 5 ml, the yellow complex was precipitated by adding ether, and was recrystallized from dichloromethane/ether. Yields 85–90%. GLC analysis of both filtered solutions showed quantitative amounts of *o*-toluonitrile. M.p. 256–258° (10b), 282–287° (11b). *Anal.* 10b : C 54.97 (55.45), H 4.15 (4.37); 11b: C 48.88 (49.29), H 3.54 (3.62) %.

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