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Cyanobenzylpalladium(II) Complexes. Synthesis and Spectroscopic Properties

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The oxidative addition of benzyl, o-, m- *and* p-*cyanobenzyl chlorides to* $Pd(PPh_3)_4$ *yields* trans-$PdCl(CH_2C_6H_4Y)(PPh_3)_2$ *(Y = H or CN) (1a–d). In solution, these complexes are in equilibrium with the dimers* $[PdCl(CH_2C_6H_4Y)PPh_3]_2$ *(2a–d) which are obtained in quantitative yields upon shifting the equilibria by oxidation of the free* PPh_3 *with* H_2O_2. PPh_3 *in both the monomers and the dimers is readily displaced by bidentate ligands yielding* $PdCl(CH_2C_6H_4Y)(L–L)$ *(3). Chloride abstraction from 3 gives dimeric cationic complexes* $[Pd($o-$CH_2C_6H_4CN)(L–L)]_2(BF_4)_2$ *having a σ-coordinated CN group. Insertion of carbon monoxide in the Pd–C bonds is quantitative.*

Introduction

The reaction of haloalkanes with transition metal complexes of low oxidation states gives a convenient route to σ-alkyl complexes. When the halo-alkane contains a reactive substituent such as CN, this synthesis is nearly the only possible one since the normal Grignard techniques use lithium or sodium alkyls reacting with the CN group [1]. Recently, we have reported the preparation, spectroscopic properties and the reactivity of various cyanoalkyl complexes of platinum [2]. When σ-bonded to platinum, the CN group is easily attacked by nucleophiles (alcohols, water, amines) giving iminoether, amide and amidine complexes, respectively [3]. The enhanced strength of the M–C bond of cyanoalkyl complexes compared to that of the parent alkyl complexes allows the coexistence of M–H and σM–C bond in the same compound, whether its geometry is *cis* or *trans* [4].

trans-$PdCl(CH_2C_6H_5)(PPh_3)_2$ has been prepared by Fitton *et al.* [5], but was uncompletely characterized. This paper deals with the preparation and some properties of benzyl and cyanobenzyl complexes of palladium(II), with emphasis on substitution reactions, CO insertion in the Pd–C bond and on the coordination of the CN group to palladium.

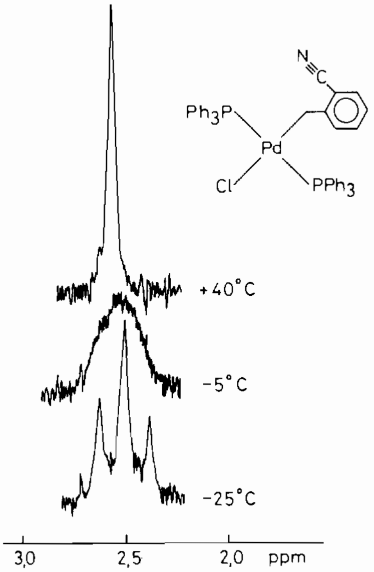


Figure. Methylene resonance of *trans*-$PdCl(o\text{-}CH_2C_6H_4CN)(PPh_3)_2$ in $CDCl_3$.

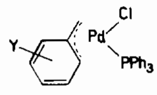
Results and Discussion

The oxidative addition of $ClCH_2C_6H_4Y$ (Y = H, *o*-CN, *m*-CN, *p*-CN) to $Pd^0(PPh_3)_4$ in benzene yields *trans*-$PdCl(CH_2C_6H_4Y)(PPh_3)_2$ (1a–d), the by-products being *trans*-$PdCl_2(PPh_3)_2$ and $[PPh_3(CH_2C_6H_4CN)]Cl$. The compounds have been characterized by ^1H NMR, IR and Raman spectroscopy (Table I).

TABLE I. IR, Raman and ^{1}H NMR Spectral Data.

Complex	Color	M.p. (°C, dec)	ν(C≡N)[a] (cm^{-1})	Others (cm^{-1})	δ(CH$_2$)[b] (p.p.m)	^{3}J(PPdCH) (Hz)
1a *trans*-PdCl($CH_2C_6H_5$)(PPh_3)$_2$	White	163–167	–	264s ν(Pd–Cl)	2.73(t)[c]	6.5 at –60 °C.
1b *trans*-PdCl(*o*-$CH_2C_6H_4CN$)(PPh_3)$_2$	White	160–162	IR 2224m R 2225s	285s ν(Pd–Cl)	2.51(t)[c]	7.5 at –25 °C.
1c *trans*-PdCl(*m*-$CH_2C_6H_4CN$)(PPh_3)$_2$	Yellow	167–169	IR 2230m	273s ν(Pd–Cl)	2.52(t)[c]	7.0 at –20 °C.
1d *trans*-PdCl(*p*-$CH_2C_6H_4CN$)(PPh_3)$_2$	Pale Yellow	158–160	IR 2223m	285s ν(Pd–Cl)	2.65(t)[c]	6.5 at –25 °C.
2a [PdCl($CH_2C_6H_5$)PPh_3]$_2$	Yellow	205–207	–	256m ν(Pd–Cl) 223s	2.94(d)	2.8
2b [PdCl(*o*-$CH_2C_6H_4CN$)PPh_3]$_2$	Yellow	203–206	IR 2221m R 2220s	267s ν(Pd–Cl) 218m	2.77(d)	4.3
2c [PdCl(*m*-$CH_2C_6H_4CN$)PPh_3]$_2$	Yellow	214–215	IR 2228m	267s ν(Pd–Cl) 220m	2.95(d)	3.5
2d [PdCl(*p*-$CH_2C_6H_4CN$)PPh_3]$_2$	Yellow	194–197	IR 2220m	262s ν(Pd–Cl) 223m	2.96(d)	3.4
3b PdCl(*o*-$CH_2C_6H_4CN$)(*o*-phen)	Yellow	213–217	IR 2216m	325s ν(Pd–Cl)	3.64(s)	–
4b PdCl(*o*-$CH_2C_6H_4CN$)($Ph_2PCH_2CH_2PPh_2$)	Yellow	210–214	IR 2219m	305s ν(Pd–Cl)	3.20(dd)	4.0 J_{cis} 12.0 J_{trans}
4c PdCl(*m*-$CH_2C_6H_4CN$)($Ph_2PCH_2CH_2PPh_2$)	Yellow	195–197	IR 2228m	309s ν(Pd–Cl)	3.08(dd)	4.3 J_{cis} 11.2 J_{trans}
5b PdCl(*o*-$CH_2C_6H_4CN$)($Ph_2PCH{=}CHPPh_2$)	Yellow	207–209	IR 2218m	318m ν(Pd–Cl)	3.37(dd)	4.0 J_{cis} 12.5 J_{trans}
6b [Pd(*o*-$CH_2C_6H_4CN$)($Ph_2PCH_2CH_2PPh_2$)]$_2$(BF_4)$_2$	Yellow	205–210	IR 2250m R 2251 m	1060vs ν(BF_4)	3.02(dd)	3.5 J_{cis} 11.5 J_{trans}
7b [Pd(*o*-$CH_2C_6H_4CN$)($PH_2PCH{=}CHPPh_2$)]$_2$(BF_4)$_2$	Yellow	208–214	IR 2250m R 2252 m	1055vs ν(BF_4)	3.20(dd)	3.0 J_{cis} 11.0 J_{trans}
8a *trans*-PdCl($COCH_2C_6H_5$)(PPh_3)$_2$	Pale Yellow	135–140	–	258s ν(Pd–Cl) 1697vs ν(CO)	3.37(s)	(in CD_2Cl_2)
8b *trans*-PdCl(*o*-$COCH_2C_6H_4CN$)(PPh_3)$_2$	Pale Yellow	125–140	IR 2223m R 2222s	267s ν(Pd–Cl) 1671vs ν(CO)	3.83(s)	(in CD_2Cl_2)
9a [PdCl($COCH_2C_6H_5$)PPh_3]$_2$	Yellow	165–175	–	264s ν(Pd–Cl) 1714s ν(CO)	insoluble in CD_2Cl_2	
9b [PdCl(*o*-$COCH_2C_6H_4CN$)PPh_3]$_2$	Yellow	170–176	IR 2225m R 2220s	267s ν(Pd–Cl) 226s 1705vs ν(CO)	insoluble in CD_2Cl_2	

[a] IR: nujol mulls, R: powdered sample. [b] In $CDCl_3$, TMS as internal standard. [c] Coalescence temperature: –30 °C for 1a, –5 °C for 1b, +15° for 1c, +5° for 1d.



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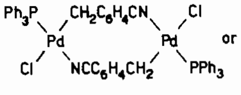

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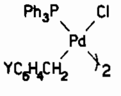
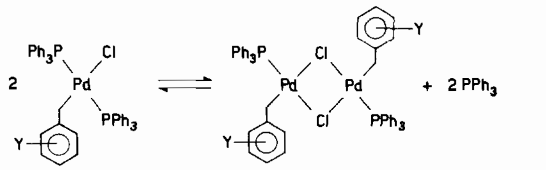


(2a - d)

At low temperature the methylene resonance of 1a–d is split into a triplet (1/2/1) by the two equivalent phosphorus atoms due to the *trans* position of the two triphenylphosphines. Upon heating, coupling is lost and the signals coalesce into a singlet (Figure 1), due to a fast exchange between coordinated and free PPh_3. Loss of PPh_3 from 1a–d could occur by formation of π-benzylbis(triethylphosphine)palladium(II) tetrafluoroborate as has been reported by Stevens *et al.* [6]. Neither the π-benzyl complex (I) nor the CN bridged dimers (II) were observed in this case, whereas the dimers $[PdCl(CH_2C_6H_4Y)PPh_3]_2$ (2a–d) were quantitatively isolated from solutions of complexes 1a–d by oxidising the free triphenylphosphine with H_2O_2. Thus, PPh_3 is liberated by the following equilibrium which has been proposed by Fitton [5] in the case of the benzyl ligand



The coalescence temperatures for 1b–d are higher than that of 1a, probably because of the presence of an electron attracting group on the benzyl moiety. The methylene resonance of 2a–d is split into a doublet with a coupling constant $^3J_{PPdCH}$ of 3–4 Hz, characteristic of a PPh_3 in *cis* position (compare with 3b–c in Table I). The IR spectra show a ν(C≡N) in the range 2220–2230 cm^{-1}, corresponding to an uncoordinated CN group. Two bands attributable to ν(Pd–Cl) are observed in accordance with a chloro bridged structure [7].

Substitution of PPh_3 by bidentate ligands L–L (*o*-phenanthroline, *cis*-1,2-bis(diphenylphosphino)-ethane, *cis*-1,2-bis(diphenylphosphino)ethylene) in dichloromethane readily yields $PdCl(CH_2C_6H_4Y)(L–L)$ (3b, 4b–c, 5b). The methylene resonance of 4b and 5b is split into a doublet by the two non equivalent phosphorus atoms.

Abstraction of chloride with $AgBF_4$ yields the dimeric cationic complexes $[Pd(o\text{-}CH_2C_6H_4CN)(L–L)]_2$ (6b, 7b). Their ν(C≡N) occur around 2250 cm^{-1} (IR and Raman), about 30 cm^{-1} higher than those of 4b and 5b. This indicates a σ coordination of the CN group to palladium, even though Dreiding molecular models show a favourable geometry for π-coordination of CN.

Insertion of carbon monoxide into the Pd–C bond of 1a–b and 2a–b occurs at room temperature and 1 atm CO in 1,2-dichloroethane leading to the acyl complexes *trans*-$PdCl(COCH_2C_6H_4Y)(PPh_3)_2$ (8a–b) and $[PdCl(COCH_2C_6H_4Y)PPh_3]_2$ (9a–b), respectively. The intermediate $PdCl(CH_2C_6H_4Y)(CO)PPh_3$ resulting from the bridge splitting of complex 2 by CO was not observed in the reaction mixture prior to the formation of the acyl complexes 9. We are currently examining the reactivity of the σ-Pd–NC bond towards various nucleophiles.

Experimental

^{1}H NMR spectra were recorded with a Bruker WP-60 and a Varian NV-14 spectrometers, IR spectra with Perkin–Elmer 457 and 180 spectrophotometers, and Raman spectra with a Spex Compact 1403 spectrometer equipped with an Ar source. The Institute of Organic Chemistry of Padua carried out the microanalyses. $Pd(PPh_3)_4$ [8], *o*-, *m*- and *p*-$ClCH_2C_6H_4CN$ were prepared as reported in the literature [9, 10]. All solvents were purified and dried by standard methods [11].

Preparation of Complexes

Trans-*$PdCl(CH_2C_6H_4Y)(PPh_3)_2$ (1a–d)*

$ClCH_2C_6H_4Y$ (6.0 g) was added under nitrogen to a suspension of $Pd(PPh_3)_4$ (20.0 g) in benzene (150 ml). The reaction mixture was stirred at 55 °C for one hour, then at room temperature for 70 h (1a), 35 h (1b), 80 h (1c) and 25 h (1d). Precipitation was completed by adding diethylether or hexane. The crude product was dissolved in dichloromethane, the insoluble byproduct *trans*-$PdCl_2(PPh_3)_2$ filtered and the filtrate reduced to *ca.* 50 ml. Addition of methanol gave a precipitate which was recrystallised from CH_2Cl_2/ether in the presence of PPh_3 (1 g) to hinder dimerization into complexes 2a–d. Yields 60–75%. *Anal.* 1a: found (calc.) C 67.89 (68.17), H 5.13 (4.92), Cl 5.03 (4.68); 1b: C 67.63 (67.53), H 4.79 (4.64), N 1.81 (1.79), Cl 4.79 (4.53); 1c: C 67.46, H 4.89, N 1.83, Cl 4.67; 1d: C 67.04, H 4.87, N 1.58, Cl 4.68.

$[PdCl(CH_2C_6H_4Y)PPh_3]_2$ (2a–d).

trans-$PdCl(CH_2C_6H_4Y)(PPh_3)_2$ (3.0 g) was stirred with H_2O_2 30% (5 ml) in acetone (150 ml). After 2 hours, the yellow microcrystals of 2a–d were filtered and washed with acetone. Yields 90–98%. The mother liquor evaporated to dryness gave the stoichiometric amount of $OPPh_3$. *Anal.* 2a: C 60.45 (60.63), H 4.63 (4.48), Cl 7.35 (7.16); 2b: C 60.23 (60.02), H 4.25 (4.07), N 2.72 (2.69), Cl 6.69 (6.81); 2c: C 60.35, H 4.25, N 2.66, Cl 6.80; 2d: C 60.12, H 4.20, N 2.58, Cl 6.99.

$PdCl(o\text{-}CH_2C_6H_4CN)(o\text{-}phen)$ (3b)

trans-$PdCl(o\text{-}CH_2C_6H_4CN)(PPh_3)_2$ (3.5 g) was stirred with *o*-phenanthroline (2.0 g) in dichloromethane (30 ml) for 2 hours. Precipitation was completed by adding benzene (150 ml), the yellow crystals were washed with ether. Yield 95%. *Anal.* 3b: C 54.47 (54.82), H 3.38 (3.22), N 9.42 (9.59), Cl 8.27 (8.09).

$PdCl(CH_2C_6H_4Y)(Ph_2PCH_2CH_2PPh_2)$ (4b–c)

A solution of *trans*-$PdCl(CH_2C_6H_4Y)(PPh_3)_2$ (3.0 g) in dichloromethane was stirred overnight with 1,2-bis(diphenylphosphino)ethane (2.0 g) at room temperature. The volume was reduced to 25 ml; the yellow complex was precipitated by adding ether and recrystallised from CH_2Cl_2/MeOH. Yields 92–96%. *Anal.* 4b: C 62.00 (62.21), H 4.70 (4.61), N 2.04 (2.13), Cl 5.61 (5.40); 4c: C 61.85, H 4.52, N 2.20, Cl 5.31.

$PdCl(o\text{-}CH_2C_6H_4CN)(Ph_2PCH{=}CHPPh_2)$ (5b)

Complex 1b (2.5 g) was stirred with *cis*-1,2-bis-(diphenylphosphino)ethylene (1.5 g) in benzene (50 ml) for 20 hours at room temperature. The white precipitate was filtered and washed with benzene and ether. Yield 89%. *Anal.* 5b: C 62.08 (62.40), H 4.38 (4.32), N 2.03 (2.14), Cl 5.85 (5.42).

$[Pd(o\text{-}CH_2C_6H_4CN)(L{-}L)]_2(BF_4)_2$ (6b, 7b)

A solution of $AgBF_4$ (2 mmol) in acetone (10 ml) was added to a solution of 4b or 5b (2 mmol) in dichloromethane (50 ml) under nitrogen. AgCl was filtered and the filtrate reduced to a small volume. Addition of ether gave a yellow precipitate which was recrystallized from CH_2Cl_2/ether. Alcohols, especially hot methanol, have to be avoided as solvents, as 6b and 7b are converted into iminoether complexes. Yields 90–95%. *Anal.* 6b: C 57.44 (57.70), H 4.19 (4.27), N 2.03 (1.98), F 11.02 (10.74); 7b: C 57.20 (57.86), H 4.24 (4.00), N 1.95 (1.98), F 10.86 (10.77).

trans-$PdCl(COCH_2C_6H_4Y)(PPh_3)_2$ (8a–b)

A suspension of 1a or 1b (2 g) in benzene (40 ml) was stirred for 6 hours under CO (1 atm) at room temperature. Precipitation was completed by adding ether (100 ml). The pale yellow products were recrystallized from CH_2Cl_2/ether in the presence of PPh_3 (0.2 g) Yields 80–90% *Anal.* 8a: C 67.03 (67.27), H 4.81 (4.74), Cl 4.62 (4.51); 8b: C 66.31 (66.55), H 4.50 (4.48), N 1.68 (1.73) Cl 4.44 (4.37).

$[PdCl(COCH_2C_6H_4Y)PPh_3]_2$ (9a–b)

A suspension of 2a or 2b (1.0 g) in 1,2-dichloroethane (30 ml) was stirred under CO (1 atm) at room temperature for 6 and 20 hours respectively. The yellow products were filtered and washed with ether. Yields 78–92%. *Anal.* 9a: C 59.22 (59.68), H 4.07 (4.24), Cl 6.89 (6.77); 9b: C 58.56 (59.15), H 3.77 (3.86), N 2.49 (2.55), Cl 6.91 (6.47).

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