### Insertion Reactions of 1,4-Diisocyanobenzene in Binuclear Pd(I) Complexes

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Reactions between  $XPd(\mu - dpm)_2 PdX'$  (X = X' = Cl, Br, I, NCO, SCN,  $N_3$  or  $C_6F_5$ ;  $X = C_6F_5$ , X' =Cl, Br or NCO) with 1,4-diisocyanobenzene lead to the tetranuclear complexes  $[(\mu,\mu'-CNC_6H_4NC)]$  XPd- $(\mu dpm)_2 P dX'_2$ , where both ends of the diisocyanide are inserted in a metal-metal bond. The cationic derivatives  $[(\mu,\mu'-CNC_6H_4NC)](RNC)Pd(\mu-dpm)_2Pd-$ (CNR)<sub>2</sub> $(BPh_4)_4$  and  $[(\mu,\mu'-CNC_6H_4NC){(RNC)Pd}$  $(\mu - dpm)_2 Pd(C_6F_5)_2 ](BPh_4)_2 (R = p - Tol, Cy or {}^tBu)$ are obtained by reacting  $[(\mu,\mu'-CNC_6H_4NC)]$ {CIPd- $(\mu$ -dpm)<sub>2</sub>PdX}<sub>2</sub>] (X = Cl or C<sub>6</sub>F<sub>5</sub>) with RNC in the presence of NaBPh<sub>4</sub>. Treatment of  $[(\mu,\mu'-CNC_6H_4-$ NC { $ClPd(\mu-dpm)_2Pd(C_6F_5)$ } with NaBPh<sub>4</sub> causes the de-insertion and subsequent coordination of the isocyanide, yielding [(C<sub>6</sub>F<sub>5</sub>)Pd(µ-dpm)<sub>2</sub>Pd(CN-C<sub>6</sub>H<sub>4</sub>-NC) $Pd(\mu$ - $dpm)_2Pd(C_6F_5)/(BPh_4)_2$ .

#### Introduction

Recently we have prepared [1] palladium(I) pentafluorophenyl derivatives of the type  $XPd(\mu dpm)_2Pd(C_6F_5)$  (X = halogen, pseudohalogen or  $C_6F_5$ ) and have studied the insertion of monoiso-cyanides in the metal-metal bond, as well as their coordination to one of the Pd(I) atoms.

In the present paper we describe the insertion of a rigid bidentate isocyanide (1,4-diisocyanobenzene) [2] into different binuclear Pd(I) derivatives, which leads to the formation of tetranuclear neutral or cationic complexes.

#### **Results and Discussion**

The coordinating properties of monoisocyanides have been extensively studied [3, 4], but only a few references on reactions with diisocyanides [5-8] can be found. The latter lead to the formation of different types of complexes whose character depends upon the type of the isocyanide used and the ratio of the reactants. The use of 1,4-diisocyanobenzene, a rigid non-chelating isocyanide, gives rise to the synthesis of mononuclear complexes with the diisocyanide acting as a unidentate ligand [7], or of mono- or heteropolynuclear complexes [6-8] if both ends of the diisocyanide are coordinated.

Treatment of the binuclear Pd(I) complexes  $[XPd(\mu-dpm)_2PdX']$  (X = X' = Cl, Br, I, NCO, SCN, N<sub>3</sub> [14] or C<sub>6</sub>F<sub>5</sub> [1]; X = C<sub>6</sub>F<sub>5</sub>, X' = Cl, Br or NCO [1]) in deoxygenated CH<sub>2</sub>Cl<sub>2</sub> (in the case of X = X' = C<sub>6</sub>F<sub>5</sub> benzene is used as solvent) with 1,4-diisocyanobenzene (1:0.5 molar ratio) leads to the insertion of each end of the isocyanide in the Pd--Pd bond (eqn. 1) and to the formation of the neutral tetranuclear derivatives.

Most of the resulting complexes crystallize with  $CH_2Cl_2$ , which can be removed without decomposi-



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$ (\mu \mu' CNC_{\phi} H_{A}VC) (GCN)Pd(\mu dpm)_{P} Pd(XCO))_{2} - CH_{2}Cl_{2} (1V) \qquad (34.33) \qquad (3.53) \qquad (3.51) \qquad (3.66) \qquad (3.$	$ (\mu,\mu'-CNC_6H_4NC)\{(OCN)Pd(\mu-dpm)_2Pd(NCO)\}_2\cdot CH_2Cl_2(IV) (48.78) (3.53) (48.78) (5.53) (4.04) (\mu,\mu'-CNC_6H_4NC)\{(SCN)Pd(\mu-dpm)_2Pd(SCN)\}_2 (V) (57.89) (4.04) (57.89) (3.99) (4.04) (\mu,\mu'-CNC_6H_4NC)\{(N_3Pd(\mu-dpm)_2PdN_3\}_2 \cdot CH_2Ch_2(V) (57.89) (57.89) (3.99) (4.04) (\mu,\mu'-CNC_6H_4NC)\{(N_3Pd(\mu-dpm)_2PdN_3\}_2 \cdot CH_2Ch_2(VI) (55.84) (4.04) (55.84) (4.04) (57.86) (4.04) (\mu,\mu'-CNC_6H_4NC)\{(C_6F_5)Pd(\mu-dpm)_2Pd(C_6F_5)\}_2 (VII) (57.86) $	(48.78) (3 58.30 (48.78) (3 57.50 (44 57.50 (4) 57.50 (4) 57.89) (3 55.84) (4) 55.84) (4) (57.73) (3 55.62 (3 55.62 (3) 33	53) 551 04) 99) 855 04) 144 136) 21)	(1.04) 3.49 (3.58) (3.58) (3.51) (3.61) (3.61) (3.61) (3.61) (3.61) (3.53) (0.99) (1.01) (1.01)	orange yellow pale- orange orange orange yellow	က် န န က က် ရ ကို	87 60 63 53
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$ (\mu \mu^{-C} CNC_{\theta}H_{N} C) [(SCN)Pd(\mu-dpm)_{2}Pd(SCN)]_{2} (V) \qquad 57.50 \qquad 4.28 \qquad 3.74 \qquad pale \qquad h \qquad 60 \\ (\mu \mu^{-}CNC_{\theta}H_{N} C) [(N_{0})Pd(\mu-dpm)_{2}Pd(S,F_{2})]_{2} (VI) \qquad 57.50 \qquad 4.38 \qquad 8.19 \qquad 6.15 \\ (\mu \mu^{-}CNC_{\theta}H_{N} C) [(N_{0})Pd(\mu-dpm)_{2}Pd(S,F_{2})]_{2} (VI) \qquad 57.86 \qquad 4.04 \qquad 8.39 \qquad 6.10 \\ (\mu \mu^{-}CNC_{\theta}H_{N} C) [(C_{0}F_{2})Pd(\mu-dpm)_{2}Pd(S_{1}F_{2})]_{2} (VII) \qquad 57.86 \qquad 4.04 \qquad 8.36 \qquad 6.36 \\ (\mu \mu^{-}CNC_{\theta}H_{N} C) [(C_{0}F_{2})Pd(\mu-dpm)_{2}Pd(S_{1}F_{2})]_{2} (VII) \qquad 57.86 \qquad 4.04 \qquad 8.36 \\ (\mu \mu^{-}CNC_{\theta}H_{N} C) [(D_{1}U_{1}-dpm)_{2}Pd(S_{1}F_{2})]_{2} (VII) \qquad 57.70 \qquad 4.14 \qquad 1.28 \\ (\mu \mu^{-}CNC_{\theta}H_{N} C) [(D_{1}U_{1}-dpm)_{2}Pd(S_{1}F_{2})]_{2} (VII) \qquad 57.70 \qquad 5.52 \qquad 3.93 \qquad 1.14 \qquad 0.09 \qquad 0.00 \\ (\mu \mu^{-}CNC_{\theta}H_{N} C) [(D_{1}U_{1}-dpm)_{2}Pd(S_{1}F_{2})]_{2} (N) \qquad 55.62 \qquad 3.93 \qquad 1.14 \qquad 0.09 \qquad 0.01 \\ (\mu \mu^{-}CNC_{\theta}H_{N} C) [(D_{1}U_{1}-dpm)_{2}Pd(S_{1}F_{2})]_{2} (BPh_{4})_{2} (X) \qquad 55.62 \qquad 3.93 \qquad 1.14 \qquad 0.09 \qquad 0.01 \\ (\mu \mu^{-}CNC_{\theta}H_{N} C) [(D_{1}U_{1}-dpm)_{2}Pd(S_{1}F_{2})]_{2} (BPh_{4})_{2} (XI) \qquad 55.62 \qquad 2.15 \qquad 0.010 \qquad 0.01 \\ (\mu \mu^{-}CNC_{\theta}H_{N} C) [(D_{1}U_{1}-dpm)_{2}Pd(S_{1}F_{2})]_{2} (BPh_{4})_{2} (XI) \qquad 73.63 \qquad 5.61 \qquad 2.25 \qquad 0.010 \qquad 0.01 \\ (\mu \mu^{-}CNC_{\theta}H_{N} C) [(D_{1}U_{1}-dpm)_{2}Pd(S_{1}F_{2})]_{2} (BPh_{4})_{4} (XII) \qquad 73.81 \qquad 5.61 \qquad 2.50 \qquad 0.010 \qquad 0.01 \\ (\mu \mu^{-}CNC_{\theta}H_{N} C) [(D_{1}U_{1}-dpm)_{2}Pd(S_{1}F_{2})]_{2} (BPh_{4})_{4} (XII) \qquad 73.28 \qquad 5.61 \qquad 2.50 \qquad 0.010 \qquad 0.01 \\ (\mu \mu^{-}CNC_{\theta}H_{N} C) [(D_{1}U_{1}-DNC)Pd(\mu-dpm)_{2}Pd(S_{1}F_{2})]_{2} (BPh_{4})_{4} (XII) \qquad 73.28 \qquad 5.61 \qquad 2.50 \qquad 0.010 \qquad 0.01 \\ (\mu \mu^{-}CNC_{\theta}H_{N} C) [(D_{1}U_{1}-DNC)Pd(\mu-dpm)_{2}Pd(S_{1}F_{2})]_{2} (BPh_{4})_{4} (XII) \qquad 73.28 \qquad 5.61 \qquad 2.50 \qquad 0.010 \qquad 0.01 \\ (\mu \mu^{-}CNC_{\theta}H_{H} NC) [(D_{1}U_{1}-DNC)Pd(\mu-dpm)_{2}Pd(S_{1}F_{2})]_{2} (BPh_{4})_{2} (X) \qquad 5.60 \qquad 2.27 \\ (\mu \mu^{-}CNC_{\theta}H_{H} NC) [(D_{1}U_{1}-DNC)Pd(\mu-dpm)_{2}Pd(S_{1}F_{2})]_{2} (BPh_{4})_{2} (X) \qquad 5.60 \qquad 2.27 \\ (\mu \mu^{-}CNC_{\theta}H_{H} NC) [(D_{1}U_{1}-DNC)Pd(\mu-dpm)_{2}Pd(S_{1}F_{2})]_{2} (BPh_{4})_{2} (X) \qquad 0.010 \qquad 0.010 \qquad 0.010 \qquad 0.010 \qquad 0$	$ (\mu,\mu'-CNC_6H_4NC)\{(SCN)Pd(\mu-dpm)_2Pd(SCN)\}_2 (V) \qquad 57.50 \qquad 4.28 \\ (\mu,\mu'-CNC_6H_4NC)\{(SCN)Pd(\mu-dpm)_2PdN_3\}_2 \cdot CH_2 CI_2 (VI) \qquad 55.22 \\ (\mu,\mu'-CNC_6H_4NC)\{N_3Pd(\mu-dpm)_2PdN_3\}_2 \cdot CH_2 CI_2 (VII) \qquad 55.84 \\ (\mu,\mu'-CNC_6H_4NC)\{(C_6F_5)Pd(\mu-dpm)_2Pd(C_6F_5)\}_2 (VII) \qquad 57.86 \\ (27.45) \qquad (27.45) \\ (27.45) \qquad (27.45) \\ (27.45) \qquad (27.45) \\ ($	57.50 57.50 (57.89) 56.22 (55.84) (55.84) 57.86 (57.45) (3 (3 (3 (3 (3 (3 (3 (3 (3 (3 (3 (3 (3	28 99) 85 04) 02 36) 14	3.74 (3.61) 8.19 (8.36) 0.99 (1.01)	pale- orange dark- orange orange yellow	ى تە 4 ھ ئ ئ	60 67 53
$ (\mu \mu^{-CNC_{6}} H_{4}NC) (N_{3} P d(\mu d pm)_{2} P dN_{3})_{2} \cdot CH_{3} C T_{3} (V1) $ $ (57.2) (4.3) (5.3$	$(\mu,\mu'-CNC_6H_4NC)[N_3Pd(\mu-dpm)_2PdN_3]_2 \cdot CH_2 Cl_2 (VI) $ $(\mu,\mu'-CNC_6H_4NC)[N_3Pd(\mu-dpm)_2PdN_3]_2 \cdot CH_2 Cl_2 (VI) $ $(55.84) $ $(4.04) $ $(55.84) $ $(4.04) $ $(57.86 $ $(4.02) $ $(57.86 $ $(57.86) $ $(57.86 $ $(57.86) $ $(57$	(57.89) (3 56.22 4 4 (55.84) (4 57.86 4 (57.45) (3 57.70 4 (57.73) 3 55.62 3	.99) .85 .04) .02 .14 .14	(3.61) 8.19 (8.36) 0.99 (1.01) 1.28	orange dark- orange orange yellow	ۍ a 4 ک d	67 63 53
$ (\mu \omega' CNC_6 H_4 NC) [N_3 Pd(\omega - dpm)_2 Pd(N_3)_2 - CH_5 C_1 (V1) $ $ (J2) (L \omega' CNC_6 H_4 NC) [(C_6 F_5) Pd(\omega - dpm)_2 Pd(C_6 F_3)]_2 (V11) $ $ (J3) (J4) (J4) (J4) (J4) (J4) (J4) (J4) (J4$	$(\mu,\mu'$ -CNC <sub>6</sub> H <sub>4</sub> NC){N <sub>3</sub> Pd( $\mu$ -dpm) <sub>2</sub> PdN <sub>3</sub> } <sub>2</sub> ·CH <sub>2</sub> Cl <sub>2</sub> (VI) 56.22 4.85 ( $\mu,\mu'$ -CNC <sub>6</sub> H <sub>4</sub> NC){(C <sub>6</sub> F <sub>5</sub> )Pd( $\mu$ -dpm) <sub>2</sub> Pd(C <sub>6</sub> F <sub>5</sub> )} <sub>2</sub> (VII) 57.86 4.02 ( $\mu,\mu'$ -CNC <sub>6</sub> H <sub>4</sub> NC){(C <sub>6</sub> F <sub>5</sub> )Pd( $\mu$ -dpm) <sub>2</sub> Pd(C <sub>6</sub> F <sub>5</sub> )} <sub>2</sub> (VII) 57.86 4.02 (57.45) (3.35)	56.22       4         (55.84)       (4         (57.86       4         (57.45)       (3         (57.70)       4         (57.73)       (3         (55.62)       3		8.19 (8.36) 0.99 1.28 1.28	dark- orange orange yellow	ი ი ი ი ი	67 63 53
$ (\mu \mu' CNC_6 H_4 NC) \{ (C_6 F_5) Pd(\mu - dpm)_2 Pd(C_6 F_3) \}_2 (VII) $ $ (\mu \mu' CNC_6 H_4 NC) \{ (CPd(\mu - dpm)_2 Pd(C_6 F_3) \}_2 (VII) $ $ (J.12) (J.$	$(55.84) \qquad (4.04) (2.0C_6H_4NC)\{(C_6F_5)Pd(\mu-dpm)_2Pd(C_6F_5)\}_2 (VII) \qquad 57.86 \qquad 4.02 \qquad (57.45) \qquad (57.45) \qquad (7.35)$	(55.84) (4 57.86 4 (57.45) (3 57.70 4 (57.73) (3 55.62 3	.04) .02 .14 .14	(8.36) 0.99 1.28 1.28	orange orange yellow	s Sb	63 53
$ (\mu \omega' CNC_6 H_4 NC) \{ (C_6 F_5) Pd(\mu dpm)_2 Pd(C_6 F_5) \}_2 (VII) $ $ (\mu \omega' CNC_6 H_4 NC) \{ (CPd(\mu dpm)_2 Pd(C_6 F_5) \}_2 (VII) $ $ (\mu \omega' CNC_6 H_4 NC) \{ (PPd(\mu dpm)_2 Pd(C_6 F_5) \}_2 (VII) $ $ (Y, 1) $ $ (\mu \omega' CNC_6 H_4 NC) \{ (PPd(\mu dpm)_2 Pd(C_6 F_5) \}_2 (X) $ $ (Y, 1) $ $ (Y, 2) $ $ (\mu \omega' CNC_6 H_4 NC) \{ (PPd(\mu dpm)_2 Pd(C_6 F_5) \}_2 (X) $ $ (Y, 2) $ $ (\mu \omega' CNC_6 H_4 NC) \{ (PPd(\mu dpm)_2 Pd(C_6 F_5) \}_2 (X) $ $ (Y, 2) $ $ (\mu \omega' CNC_6 H_4 NC) \{ (PPd(\mu dpm)_2 Pd(C_6 F_5) \}_2 (X) $ $ (Y, 2) $ $ (\mu \omega' CNC_6 H_4 NC) \{ (PTONC) Pd(\mu dpm)_2 Pd(C_6 F_5) \}_2 (X) $ $ (Y, 2) $ $ (\mu \omega' CNC_6 H_4 NC) \{ (PTONC) Pd(\mu dpm)_2 Pd(C_6 F_5) \}_2 (X) $ $ (Y, 2) $ $ (\mu \omega' CNC_6 H_4 NC) \{ (PTONC) Pd(\mu dpm)_2 Pd(CNP^{-1}OI) \}_2 ( BPh_4 \lambda_4 (XII) $ $ (Y, 2) $ $ (\mu \omega' CNC_6 H_4 NC) \{ (PTONC) Pd(\mu dpm)_2 Pd(CNP^{-1}OI) \}_2 ( BPh_4 \lambda_4 (XII) $ $ (Y, 3) $ $ (Y, 2) $ $ (\mu \omega' CNC_6 H_4 NC) \{ (PTONC) Pd(\mu dpm)_2 Pd(CNP^{-1}OI) \}_2 ( BPh_4 \lambda_4 (XII) $ $ (Y, 2) $ $ (Y, 2) $ $ (\mu \omega' CNC_6 H_4 NC) \{ (PTONC) Pd(\mu dpm)_2 Pd(CN^{-1}DI) \}_2 ( BPh_4 \lambda_4 (XII) $ $ (Y, 2) $ $ (Y$	$(\mu,\mu'-CNC_6H_4NC)\{(C_6F_5)Pd(\mu-dpm)_2Pd(C_6F_5)\}_2$ (VII) 57.86 4.02 (57.45) (57.45) (57.45)	57.86 4 (57.45) (3 57.70 4 (57.73) (3 55.62 3	.02 .36) .14	0.99 (1.01) 1.28	orange yellow	Sb 4	63 53
$ (\mu \mu' CNC_6 H_4 NC) \{ CIPd(\mu - dpm)_2 Pd(C_6 F_5) \}_2 (VIII) $ $ (\mu \mu' CNC_6 H_4 NC) \{ CIPd(\mu - dpm)_2 Pd(C_6 F_5) \}_2 (XI) $ $ (\mu \mu' CNC_6 H_4 NC) \{ RPd(\mu - dpm)_2 Pd(C_6 F_5) \}_2 (X) $ $ (X) (X) (X) (X) (X) (X) (X) (X) (X) (X)$	(31 2)	(57.45) (3 57.70 4 (57.73) (3 55.62 3	.36) .14 71)	(1.01) 1.28	yellow	Sb	53
$ (\mu \mu^{-C} CNC_6 H_4 NC) (CPB(\mu-dpm)_2 Pd(C_6 F_5))_2 (YII) $ $ (\mu \mu^{-C} CNC_6 H_4 NC) (CPB(\mu-dpm)_2 Pd(C_6 F_5))_2 (X) $ $ (\mu \mu^{-C} CNC_6 H_4 NC) (BrPd(\mu-dpm)_2 Pd(C_6 F_5))_2 (X) $ $ (55.75) $ $ (55.75) $ $ (55.75) $ $ (55.75) $ $ (55.75) $ $ (55.75) $ $ (55.75) $ $ (55.75) $ $ (55.75) $ $ (55.75) $ $ (55.75) $ $ (55.75) $ $ (55.75) $ $ (55.75) $ $ (55.75) $ $ (55.75) $ $ (55.8) $ $ (1.08) $ $ (1.08) $ $ (1.08) $ $ (1.08) $ $ (1.08) $ $ (1.08) $ $ (1.08) $ $ (1.08) $ $ (1.08) $ $ (1.08) $ $ (1.08) $ $ (55.75) $ $ (55.5) $ $ (55.75) $ $ (55.9) $ $ (1.08) $ $ (1.09) $ $ (1$		51.70 4 (57.73) (3 55.62 3	.14	1.28	yellow	20	ŝ
$ (\mu\mu'-CNC_6H_4NC) \{ BiPd(\mu-dpm)_2 Pd(C_6F_5) \}_2 (X) $ $ (J.1.2) (J.1.2) (J.1.2) (J.1.2) (J.1.2) (J.1.2) (J.1.2) (J.1.2) (J.1.2) (J.2.2) (J.$	$(\mu,\mu'$ -CNC <sub>6</sub> H <sub>4</sub> NC){ClPd}(\mu-dpm)_2Pd(C <sub>6</sub> F <sub>5</sub> )] <sub>2</sub> (VIII) 57.70 4.14	(57.73) (3 55.62 3				•	
$ (\mu_{\mu}^{-L} - CNC_6 H_4 NC) [BiFd(\mu - dpm)_2 Pd(C_6 F_5)]_2 (X) $ $ (\mu_{\mu}^{-L} - CNC_6 H_4 NC) [BiFd(\mu - dpm)_2 Pd(C_6 F_5)]_2 (X) $ $ (X) $ $ (\mu_{\mu}^{-L} - CNC_6 H_4 NC) [(OCN) Pd(\mu - dpm)_2 Pd(C_6 F_5)]_2 (X) $ $ (SS.75) $ $ (SS$	(57.73) (3.71)	55.62 3	(1)	(71.1)		q	ţ
$ (\mu\mu'-CNC_6H_4NC) (0CN)Pd(\mu-dpm)_2 Pd(C_6F_5)]_2 (X) $ $ (55.75) (55.75) (55.9) (1.06) (1.08) (1.0$	(μ.μ. CNC <sub>6</sub> H₄NC){BrPd(μ-dpm) <sub>2</sub> Pd(C <sub>6</sub> F <sub>5</sub> )} <sub>2</sub> (IX) 55.62 3.93		.93	1.14	orange	52	67
$ (\mu_{\mu}'-CNC_6H_4NC)[(OCN)Pd(\mu-dpm)_2Pd(C_6F_5)](BPh_4)_2 (X) 58.84 4.56 2.15 yellow a 71 (C_6F_5)Pd(\mu-dpm)_2Pd(C_6F_5)](BPh_4)_2 (XI) 58.84 4.56 2.15 yellow 139 66 (3.36) (3.56) (3.36) (3.22) (3.36) (3.37) (3.36) (3.36) (3.37) (3.36) (3.36) (3.37) (3.36) (3.36) (3.37) (3.36) (3.37) (3.36) (3.36) (3.37) (3.36) (3.36) (3.37) (3.36) (3.36) (3.36) (3.37) (3.36) (3.36) (3.37) (3.36) (3.37) (3.36) (3.37) (3.36) (3.37) (3.36) (3.37) (3.36) (3.37) (3.36) (3.37) (3.36) (3.37) (3.36) (3.37) (3.36) (3.37) (3.36) (3.37) (3.36) (3.36) (3.36) (3.37) (3.36) (3.37) (3.36) (3.37) (3.36) (3.37) (3.36) (3.37) (3.36) (3.37) (3.36) (3.37) (3.36) (3.37) (3.36) (3.37) (3.36) (3.37) (3.36) (3.37) (3.36) (3.37) (3.36) (3.37) (3.36) (3.37) (3.36) (3.37) (3.37) (3.36) (3.37) (3.36) (3.$	(55.75) (3.59)	(55.75) (3	.59)	(1.08)			
$ [(G_6F_5)Pd(\mu dpm)_2 Pd(CNC_6H_4NC)Pd(\mu dpm)_2 Pd(C_6F_5)](BPh_4)_2 (XI) (58.39) (3.69) (2.23) (2.23) (0.91) (0$	(μ,μ <sup>,</sup> -CNC <sub>6</sub> H <sub>4</sub> NC){(OCN)Pd(μ-dpm) <sub>2</sub> Pd(C <sub>6</sub> F <sub>5</sub> )} <sub>2</sub> (X) 58.84 4.56	58.84 4	.56	2.15	yellow	5	71
$ [(C_6F_5)Pd(\mu dpm)_2Pd(CN-C_6H_4NC)Pd(\mu dpm)_2Pd(C_6F_5)](BPh_4)_2 (XI) 64.93 4.26 0.94 yellow 139 66 (4.34) (0.91) (5.55) (1.91) (6.5.86) (4.34) (0.91) (6.5.86) (4.34) (0.91) (5.55) (2.19) (1.91) (7.2.1) (7.2.1) (7.2.1) (7.2.1) (7.2.1) (7.2.1) (7.2.1) (7.2.1) (7.2.1) (7.2.1) (7.2.1) (7.2.1) (7.2.1) (7.2.1) (7.2.1) (7.2.1) (7.2.1) (7.2.2) (7.2.1) (7.2.1) (7.2.2) (7.2.1) (7.2.2) (7.2.1) (7.2.2) (7.2.1) (7.2.2) (7.2.1) (7.2.2) (7.2.1) (7.2.2) (7.2.1) (7.2.2) (7.2.2) (7.2.2) (7.2.1) (7.2.2) (7.2.1) (7.2.2) (7.2.1) (7.2.2) (7.2.2) (7.2.1) (7.2.2) (7.2.2) (7.2.1) (7.2.2$	(58.39) (3.69)	(58.39) (3	(69)	(2.23)			
$ [(\mu,\mu'\text{-CNC}_6H_4\text{NC})[(p-\text{TolNC})Pd(\mu-\text{dpm})_2Pd(\text{CN}p-\text{Tol})]_2[(BPh_4)_4(\text{XII}) 73.03 5.61 2.50 \text{ orange} 258 42 \\ [(\mu,\mu'\text{-CNC}_6H_4\text{NC})[(C_{\text{VNC}})Pd(\mu-\text{dpm})_2Pd(\text{CNC})]_2](BPh_4)_4(\text{XII}) 73.61 8.14 2.13 \text{ orange} 243 57 \\ [(\mu,\mu'\text{-CNC}_6H_4\text{NC})[(C_{\text{VNC}})Pd(\mu-\text{dpm})_2Pd(\text{CN}^4\text{Bu})]_2](BPh_4)_4(\text{XII}) 73.61 8.14 2.13 \text{ orange} 243 57 \\ [(\mu,\mu'\text{-CNC}_6H_4\text{NC})[(p-\text{TolNC})Pd(\mu-\text{dpm})_2Pd(\text{CN}^4\text{Bu})]_2](BPh_4)_4(\text{XII}) 73.61 8.14 2.13 \text{ orange} 243 57 \\ [(\mu,\mu'\text{-CNC}_6H_4\text{NC})[(p-\text{TolNC})Pd(\mu-\text{dpm})_2Pd(\text{C}^4\text{F}_3)]_2](BPh_4)_2(\text{XV}) 66.69 2.56 (2.277) 0.7200 0.7200 0.7200 0.7207 \\ [(\mu,\mu'\text{-CNC}_6H_4\text{NC})[(p-\text{TolNC})Pd(\mu-\text{dpm})_2Pd(\text{C}_6\text{F}_5)]_2](BPh_4)_2(\text{XV}) 66.49 4.61 (1.70) 0.7200 0.7200 0.7206 157 \\ [(\mu,\mu'\text{-CNC}_6H_4\text{NC})[(t^{\text{B}}\text{UNC})Pd(\mu-\text{dpm})_2Pd(\text{C}_6\text{F}_5)]_2](BPh_4)_2(\text{XV}) 66.60 (4.73 4.87 2.00 0.7200 0.7206 157 88 \\ [(\mu,\mu'\text{-CNC}_6H_4\text{NC})[(t^{\text{B}}\text{UNC})Pd(\mu-\text{dpm})_2Pd(\text{C}_6\text{F}_5)]_2](BPh_4)_2(\text{XV}) 66.60 (4.73 4.87 2.00 0.7206 0.7206 157 88 \\ [(\mu,\mu'\text{-CNC}_6H_4\text{NC})[(t^{\text{B}}\text{UNC})Pd(\mu-\text{dpm})_2Pd(\text{C}_6\text{F}_5)]_2](BPh_4)_2(\text{XV}) 66.60 (4.73 4.64 1.73) (1.71) 0.7206 0.7206 \\ [6.19) (6.19) (4.68 (1.71) 65.70 4.64 1.84 0.717 \\ (6.19) (4.68 (1.71) 65.70 4.64 1.84 0.717 \\ (6.19) (4.68 (1.71) 65.70 4.64 1.84 0.717 \\ (6.19) (4.68 (1.71) 65.70 4.64 1.84 0.717 \\ (6.19) (4.68 (1.71) 65.70 4.64 1.84 0.717 \\ (6.19) (6$	$[(C_6F_5)Pd(\mu-dpm)_2Pd(CN-C_6H_4NC)Pd(\mu-dpm)_2Pd(C_6F_5)](BPh_4)_2$ (XI) 64.93 4.26	64.93 4	.26	0.94	yellow	139	99
$ [(\mu,\mu'\text{-CNC}_6H_4\text{NC})[(p\text{-TolNC})Pd(\mu\text{-dpm})_2Pd(\text{CN}p\text{-Tol})]_2[(BPh_4)_4(\text{XII}) 73.63 5.61 2.50 \text{ orange} 258 42 \\ [(\mu,\mu'\text{-CNC}_6H_4\text{NC})[(Cy\text{NC})Pd(\mu\text{-dpm})_2Pd(\text{CNC}y)]_2](BPh_4)_4(\text{XIII}) 73.61 8.14 2.13 \text{ orange} 243 57 \\ [(\mu,\mu'\text{-CNC}_6H_4\text{NC})[(Cy\text{NC})Pd(\mu\text{-dpm})_2Pd(\text{CN}^4\text{Bu})]_2](BPh_4)_4(\text{XIIV}) 73.61 8.14 2.13 \text{ orange} 243 57 \\ [(\mu,\mu'\text{-CNC}_6H_4\text{NC})[(^4\text{BuNC})Pd(\mu\text{-dpm})_2Pd(\text{CN}^4\text{Bu})]_2](BPh_4)_4(\text{XIIV}) 72.87 6.06 2.50 \text{ orange} 243 54 \\ [(\mu,\mu'\text{-CNC}_6H_4\text{NC})[(^4\text{-TolNC})Pd(\mu\text{-dpm})_2Pd(\text{CN}^6\text{F}_5)]_2](BPh_4)_2(\text{XV}) 6.6.49 4.30 2.00 \text{ deep} 149 \\ [(\mu,\mu'\text{-CNC}_6H_4\text{NC})[(p\text{-TolNC})Pd(\mu\text{-dpm})_2Pd(\text{C}_6\text{F}_5)]_2](BPh_4)_2(\text{XV}) 6.6.49 4.30 2.00 \text{ deep} 149 \\ [(\mu,\mu'\text{-CNC}_6H_4\text{NC})[(p\text{-TolNC})Pd(\mu\text{-dpm})_2Pd(\text{C}_6\text{F}_5)]_2](BPh_4)_2(\text{XV}) 66.49 4.30 2.00 \text{ deep} 153 89 \\ [(\mu,\mu'\text{-CNC}_6H_4\text{NC})[(p\text{-TolMC})Pd(\mu\text{-dpm})_2Pd(\text{C}_6\text{F}_5)]_2](BPh_4)_2(\text{XV}) 66.10 (4.73 (1.70) \text{ orange} 153 89 \\ [(\mu,\mu'\text{-CNC}_6H_4\text{NC})[(p\text{-TolMC})Pd(\mu\text{-dpm})_2Pd(\text{C}_6\text{F}_5)]_2](BPh_4)_2(\text{XV}) 66.10 (4.73 (1.71) \text{ orange} 153 \\ (6.10) (6.10) (4.64 (1.70) \text{ orange} 153 \\ (1.71) \text{ orange} 153 \\ (1.71) \\ (6.6.0) (4.73 (1.71) \\ (6.10) (4.68) (1.73) \\ (1.71) \\ (6.10) (4.68) (1.73) \\ (1.74) \\ (1.74) \\ (1.74) \\ (1.74) \\ (1.74) \\ (1.74) \\ (1.74) \\ (1.74) \\ (1.74) \\ (1.74) \\ (1.74) \\ (1.74) \\ (1.74) \\ (1.74) \\ (1.74) \\ (1.74) $	(65.86) (4.34)	(65.86) (4	.34)	(0.91)			
$ [(\mu,\mu'-CNC_6H_4NC)[(CyNC)Pd(\mu-dpm)_2Pd(CNCy)]_2](BPh_4)_4 (XIII) $ (73.87) (5.25) (2.19) (73.61 8.14 2.13 0range 243 57 (73.23) (8.05) (2.22) (2.22) 0range 263 54 ((\mu,\mu'-CNC_6H_4NC)[(p-TolNC)Pd(\mu-dpm)_2Pd(C_6F_5)]_2](BPh_4)_4 (XIV) 72.87 6.06 2.50 0range 263 54 ((\mu,\mu'-CNC_6H_4NC)[(p-TolNC)Pd(\mu-dpm)_2Pd(C_6F_5)]_2](BPh_4)_2 (XV) 66.49 4.30 2.00 deep- 149 71 ((\mu,\mu'-CNC_6H_4NC)[(r-TolNC)Pd(\mu-dpm)_2Pd(C_6F_5)]_2](BPh_4)_2 (XVI) 66.49 4.30 2.00 deep- 149 71 ((\mu,\mu'-CNC_6H_4NC)[(r-TolNC)Pd(\mu-dpm)_2Pd(C_6F_5)]_2](BPh_4)_2 (XVI) 66.72 4.87 2.00 0range 153 89 ((\mu,\mu'-CNC_6H_4NC)[(r-TolNC)Pd(\mu-dpm)_2Pd(C_6F_5)]_2](BPh_4)_2 (XVI) 66.60) (4.73) (1.71) 0range 153 89 ((\mu,\mu'-CNC_6H_4NC)[(r-TolNC)Pd(\mu-dpm)_2Pd(C_6F_5)]_2](BPh_4)_2 (XVII) 66.10) (4.64 1.70) 0range 153 89 ((\mu,\mu'-CNC_6H_4NC)[(r-TolNC)Pd(\mu-dpm)_2Pd(C_6F_5)]_2](BPh_4)_2 (XVII) 66.10) (4.68 (1.71) 0range 153 89)	$[(\mu,\mu'-CNC_6H_4NC)](p-TolNC)Pd(\mu-dpm)_2Pd(CNp-Tol)]_2[(BPh_4)_4(XII)$ 73.03 5.61	73.03 5	.61	2.50	orange	258	42
$ [(\mu,\mu'-CNC_6H_4NC)[(CyNC)Pd(\mu-dpm)_2Pd(CNCy)]_2](BPh_4)_4 (XIII) 73.61 8.14 2.13 orange 243 57 \\ [(\mu,\mu'-CNC_6H_4NC)[(^{t}BuNC)Pd(\mu-dpm)_2Pd(CN^{t}Bu)]_2](BPh_4)_4 (XIV) 72.87 6.06 2.50 orange 263 54 \\ [(\mu,\mu'-CNC_6H_4NC)[(p-TolNC)Pd(\mu-dpm)_2Pd(C_6F_5)]_2](BPh_4)_2 (XV) 66.49 4.30 2.00 deep- 149 71 \\ [(\mu,\mu'-CNC_6H_4NC)[(p-TolNC)Pd(\mu-dpm)_2Pd(C_6F_5)]_2](BPh_4)_2 (XVI) 66.49 4.30 2.00 deep- 149 71 \\ [(\mu,\mu'-CNC_6H_4NC)[(r-VNC)Pd(\mu-dpm)_2Pd(C_6F_5)]_2](BPh_4)_2 (XVI) 66.60 (4.73 4.87 2.00 orange 153 89 \\ [(\mu,\mu'-CNC_6H_4NC)[(r^{t}BuNC)Pd(\mu-dpm)_2Pd(C_6F_5)]_2](BPh_4)_2 (XVI) 66.10 (4.73 (1.71) 0range 153 89 \\ [(\mu,\mu'-CNC_6H_4NC)[(r^{t}BuNC)Pd(\mu-dpm)_2Pd(C_6F_5)]_2](BPh_4)_2 (XVII) 66.10 (4.73 (1.71) 0range 153 89 \\ [(\mu,\mu'-CNC_6H_4NC)[(r^{t}BuNC)Pd(\mu-dpm)_2Pd(C_6F_5)]_2](BPh_4)_2 (XVII) 66.10 (4.73 (1.71) 0range 153 89 \\ [(\mu,\mu'-CNC_6H_4NC)[(r^{t}BuNC)Pd(\mu-dpm)_2Pd(C_6F_5)]_2](BPh_4)_2 (XVII) 66.10 (4.68 (1.71) 0range 153 89 \\ [(\mu,\mu'-CNC_6H_4NC)[(r^{t}BuNC)Pd(\mu-dpm)_2Pd(C_6F_5)]_2](BPh_4)_2 (XVII) 66.10 (4.68 (1.71) 0range 153 89 \\ [(\mu,\mu'-CNC_6H_4NC)[(r^{t}BuNC)Pd(\mu-dpm)_2Pd(C_6F_5)]_2](BPh_4)_2 (XVII) 66.10 (4.73 (1.71) 0range 153 89 \\ [(\mu,\mu'-CNC_6H_4NC)[(r^{t}BuNC)Pd(\mu-dpm)_2Pd(C_6F_5)]_2](BPh_4)_2 (XVII) 66.10 (4.73 (1.71) 0range 153 89 \\ [(\mu,\mu'-CNC_6H_4NC)[(r^{t}BuNC)Pd(\mu-dpm)_2Pd(C_6F_5)]_2](BPh_4)_2 (XVII) 66.10 (4.68 (1.71) 0range 153 89 \\ [(\mu,\mu'-CNC_6H_4NC)[(r^{t}BuNC)Pd(\mu-dpm)_2Pd(C_6F_5)]_2](BPh_4)_2 (XVII) 66.10 (4.68 (1.71) 0range 169 81 \\ [(\mu,\mu'-CNC_6H_4NC)[(r^{t}BuNC)Pd(\mu-dpm)_2Pd(C_6F_5)]_2](BPh_4)_2 (XVII) 66.10 (4.68 (1.71) 0range 169 81 \\ [(\mu,\mu'-CNC_6H_4NC)[(r^{t}BuNC)Pd(\mu-dpm)_2Pd(C_6F_5)]_2](BPh_4)_2 (XVII) (66.10 (4.68 (1.71) 0range 169 81 \\ [(\mu,\mu'-CNC_6H_4NC)[(r^{t}BuNC)Pd(\mu-dpm)_2Pd(C_6F_5)]_2](BPh_4)_2 (XVII) (6.10 (1.71) 0range 169 81 \\ [(\mu,\mu'-CNC_6H_4NC)[(r^{t}BuNC)Pd(\mu-dpm)_2Pd(C_6F_5)]_2](BPh_4)_2 (XVII) (6.10 (1.71) 0range 169 81 \\ [(\mu,\mu'-CNC_6H_4NC)[(r^{t}BuNC)Pd(\mu-dpm)_2Pd(C_6F_5)]_2](BPh_4)_2 (XVII) (6.10 (1.71) 0range 169 81 \\ [(\mu,\mu'-CNC_6H_4NC)[(r^{t}BuNC)Pd(\mu-dpm)_2Pd(C_6F_5)]_2](BP$	(13.87) (5.25)	(73.87) (5	.25)	(2.19)			
$ [(\mu,\mu'-CNC_6H_4NC)[(^{t}BuNC)Pd(\mu-dpm)_2Pd(CN^{t}Bu)]_2](BPh_4)_4 (XIV) (73.23) (8.05) (2.22) (2.22) (2.23) (8.05) (2.27) (2.27) (2.6) (2.6) (2.27) (2.6) (2.6) (2.6) (2.2) (2.6) (2.$	$[(\mu,\mu'-CNC_6H_4NC)](CyNC)Pd(\mu-dpm)_2Pd(CNCy)]_2](BPh_4)_4$ (XIII) 73.61 8.14	73.61 8	.14	2.13	orange	243	57
$ [(\mu,\mu^{-C}NC_{6}H_{4}NC)](TBUNC)Pd(\mu^{-d}pm)_{2}Pd(CN^{-B}U)]_{2} ](BPh_{4})_{2} (XU) (72.70) (5.66) (2.27) 0 0 Tange 203 0.71 (1.1) 0 Tange 203 0.71 (1.1) 0 Tange 203 0 T$	(73.23) (8.05) (73.23) (8.05)	(73.23) (8	.05)	(2.22)		636	54
$ [(\mu,\mu'-CNC_6H_4NC)\{(p-TolNC)Pd(\mu-dpm)_2Pd(C_6F_5)\}_2](BPh_4)_2(XV) \qquad (5.49) \qquad (2.00) \qquad (4.46) \qquad (1.70) \qquad (4.9) \qquad (7.10) \qquad (1.70) \qquad (1.71) \qquad (1.7$	$[(\mu,\mu + CNC_6H_4NC)]([BUNC)]rd(\mu - dpm)_2 rd(CN_BU)]_2](Brn_4)_4 (AIV) = 12.87 = 0.00$	3) (0L CL)	00.	UC.2	orange	C 07	•
$[(\mu,\mu'-CNC_6H_4NC)[(CyNC)Pd(\mu-dpm)_2Pd(C_6F_5)]_2](BPh_4)_2(XVI) (67.01) (4.46) (1.70) 0range 153 89 \\[(\mu,\mu'-CNC_6H_4NC)[(CyNC)Pd(\mu-dpm)_2Pd(C_6F_5)]_2](BPh_4)_2(XVII) (66.0) (4.73) (1.71) 0range 153 89 \\[(\mu,\mu'-CNC_6H_4NC)[(^{t}BuNC)Pd(\mu-dpm)_2Pd(C_6F_5)]_2](BPh_4)_2(XVII) (66.19) (4.68) (1.73) (1.71) 0range 149 65 \\[(\mu,\mu'-CNC_6H_4NC)[(^{t}BuNC)Pd(\mu-dpm)_2Pd(C_6F_5)]_2](BPh_4)_2(XVII) (66.19) (4.68) (1.73) (1.71) 0range 149 65 \\[(\mu,\mu'-CNC_6H_4NC)[(^{t}BuNC)Pd(\mu-dpm)_2Pd(C_6F_5)]_2](BPh_4)_2(XVII) (66.19) (4.68) (1.73) (1.71) 0range 149 65 \\[(\mu,\mu'-CNC_6H_4NC)[(^{t}BuNC)Pd(\mu-dpm)_2Pd(C_6F_5)]_2](BPh_4)_2(XVII) (66.19) (4.68) (1.73) (1.71) 0range 149 \\[(\mu,\mu'-CNC_6H_4NC)[(^{t}BuNC)Pd(\mu-dpm)_2Pd(C_6F_5)]_2](BPh_4)_2(XVII) (66.19) (4.68) (1.73) (1.71) 0range 149 \\[(\mu,\mu'-CNC_6H_4NC)[(^{t}BuNC)Pd(\mu-dpm)_2Pd(C_6F_5)]_2](BPh_4)_2(XVII) (66.19) (4.68) (1.73) (1.73) 0range 149 \\[(\mu,\mu'-CNC_6H_4NC)[(^{t}BuNC)Pd(\mu-dpm)_2Pd(C_6F_5)]_2](BPh_4)_2(XVII) (66.19) (4.68) (1.73) 0range 149 \\[(\mu,\mu'-CNC_6H_4NC)[(^{t}BuNC)Pd(\mu-dpm)_2Pd(LAB) 0range 149 \\[(\mu,\mu'-CNC_6H_4NC)Pd(\mu-dpm)_2Pd(\mu-dpm)_2Pd(\mu-dpm)_2Pd(\mu-dpm)_2Pd(\mu-dpm)_2Pd(\mu-dpm)_2Pd(\mu-dpm)_2Pd(\mu-dpm)_2Pd(\mu-dpm)_2Pd(\mu-dpm)_2Pd(\mu-dpm)_2Pd(\mu-dpm)_2Pd(\mu-dpm)_2Pd(\mu-dpm$	$(12.0) \qquad (12.0) \qquad (12.0) \qquad (2.00) \qquad ($	(17.10) (J	30	2 00	deen-	149	71
$[(\mu,\mu'-CNC_6H_4NC)\{(CyNC)Pd(\mu-dpm)_2Pd(C_6F_5)\}_2](BPh_4)_2(XVI) (66.72) (4.73) (1.70) (1.70) (1.73) (1.73) (1.71) (1.7$		(10 23)	161	102.17	Orande	n G	
$[(\mu,\mu'-CNC_6H_4NC)\{(^{t}BuNC)Pd(\mu-dpm)_2Pd(C_6F_5)\}_2](BPh_4)_2(XVII) (66.60) (4.73) (1.71) (1.71) (4.69) (1.71) (55.70) (4.64) (1.71) (66.19) (4.68) (1.71) (66.19) (4.68) (1.71) (66.19) (4.68) (1.72) (66.19) (4.68) (1.73) (66.19) (4.68) (1.73) (66.19) (4.68) (1.73) (66.19) (4.68) (1.73) (66.19) (4.68) (1.73) (66.19) (66.19) (4.68) (1.73) (66.19)$	$[(i, i, 'CNC, H, NC)]((C, NC)]pd((i, dim), pd((C, F_i)), [(RPh_i), (XU)] $ $4.87$ $4.87$	4 (TO. 10)	87	2.00	orange	153	89
$[(\mu,\mu'-CNC_6H_4NC)](^{t}BuNC)Pd(\mu-dpm)_2Pd(C_6F_5)]_2](BPh_4)_2(XVII) 65.70 4.64 1.84 0range 149 65 (1.73) (4.68) (1.73) (4.68) (1.73) (4.68) (1.73) (4.68) (1.73) (4.68$		(4) (1997) (14	.73)	(1.71)	þ		
(66.19) (4.68) (1.73)	$[(\mu,\mu'-CNC_6H_4NC)](^{t}BuNC)Pd(\mu-dpm)_2Pd(C_6F_5)]_2](BPh_4)_2$ (XVII) 65.70 4.64	65.70 4	.64	1.84	orange	149	65
	(66.19) (4.68)	(66.19) (4	(89)	(1.73)			

Complex	ν(C≡N) <sup>a</sup>	q	x	$c_{6}F_{5}^{f}$
(μ,μ'-CNC <sub>6</sub> H4NC){CIPd(μ-dpm)2PdCl] <sub>2</sub> (I)	1	1599, 1571		
$(\mu, \mu'$ -CNC <sub>6</sub> H <sub>4</sub> NC){BrPd( $\mu$ -dpm) <sub>2</sub> PdBr} <sub>2</sub> (II)	1	1607, 1571		
$(\mu, \mu'$ -CNC <sub>6</sub> H <sub>4</sub> NC){IPd( $\mu$ -dpm) <sub>2</sub> PdI} <sub>2</sub> (III)	I	1621, 1569		
(μ,μ'.CNC <sub>6</sub> H <sub>4</sub> NC){(NCO)Pd(μ-dpm) <sub>2</sub> Pd(NCO)} <sub>2</sub> (IV)	1	1599, 1566	2199 <sup>c</sup>	
$(\mu,\mu'$ -CNC <sub>6</sub> H <sub>4</sub> NC){(SCN)Pd( $\mu$ -dpm) <sub>2</sub> Pd(SCN)} <sub>2</sub> (V)	i	1605, 1557	2075 <sup>d</sup>	
$(\mu,\mu'-CNC_6H_4NC)[N_3Pd(\mu-dpm)_2PdN_3]_2$ (VI)	I	1598, 1571	2035 <sup>e</sup>	
$(\mu,\mu'$ -CNC <sub>6</sub> H <sub>4</sub> NC){(C <sub>6</sub> F <sub>5</sub> )Pd( $\mu$ -dpm) <sub>2</sub> Pd(C <sub>6</sub> F <sub>5</sub> )}2 (VII)	I	1593		
$(\mu,\mu'$ -CNC <sub>6</sub> H <sub>4</sub> NC)(CIPd( $\mu$ -dpm) <sub>2</sub> Pd(C <sub>6</sub> F <sub>5</sub> )} <sup>2</sup> (VIII)	I	1618, 1604, 1571		942(941)
(μ,μ, cNC6H4NC){BrPd(μ-dpm) <sub>2</sub> Pd(C <sub>6</sub> F <sub>5</sub> )} <sub>2</sub> (IX)	I	1619, 1602, 1570		943(940)
(μ,μ'-CNC <sub>6</sub> H4NC)((CNO)Pd(μ-dpm) <sub>2</sub> Pd(C <sub>6</sub> F <sub>5</sub> )] <sub>2</sub> (X)	I	1600, 1570	2196 <sup>c</sup>	942(942)
$[(C_6 F_6)Pd(\mu-dpm)_2 Pd(CNC_6H_4NC)Pd(\mu-dpm)_2 Pd(C_6 F_5)](BPh_4)_2$ (XI)	2149(2122)	1590		942
$[(\mu,\mu' \cdot CNC_6H_4NC)](p \cdot ToINC)Pd(\mu \cdot dpm)_2Pd(CNp \cdot Tol)]_2[(BPh_4)_4 (XII)]$	2177(2132)	1622, 1577		
$[(\mu,\mu',CNC_6H_4NC)](CyNC)Pd(\mu-dpm)_2Pd(CNCy)]_7](BPh_4)_4$ (XIII)	2207(2143)	1622, 1578		
$\left[\left(\mu,\mu'-CNC_{6}H_{4}NC\right)\left(t^{4}BuNC\right)Pd(\mu-dpm)_{2}Pd(CN^{4}Bu)\right]_{2}\left[(BPh_{4})_{4}(XIV)\right]$	2186(2143)	1619, 1577		
$[(\mu,\mu' \cdot CNC_6H_4NC)](p \cdot ToINC)Pd(\mu \cdot dpm)_2Pd(C_6F_5)]_2](BPh_4)_2$ (XV)	2160(2132)	1630, 1580		944
$[(\mu,\mu'-CNC_6H_4 NC)](CyNC)Pd(\mu-dpm)_2Pd(C_6F_5)]_2](BPh_4)_2$ (XVI)	2202(2143)	1614, 1580		945
$[(\mu,\mu'\text{-CNC}_6\text{H}_4\text{ NC})](^{t}\text{BuNC})\text{Pd}(\mu\text{-d}\text{pm})_2\text{Pd}(\text{C}_6\text{F}_5)]_2](\text{BPh}_4)_2 \text{ (XVII)}$	2193(2143)	1618, 1580		946
<sup>a</sup> In parentheses the $\nu(C=N)$ for the free isocyanide. <sup>b</sup> Absorptions in the ~1600	cm <sup>-1</sup> region including the t	(C=N) and the internal aromatic ri	ng vibrations.	<sup>c</sup> ν(C≡N) of the

CNO group [15].  $a_{\nu}(C\equiv N)$  of the SCN group [16, 17].  $e_{\nu_{as}(N_3)}$  [18]. <sup>f</sup>In parentheses the corresponding absorption in the palladium(I) precursor.

### Insertion of Di-isocyanide in Pd(I) Complexes

TABLE II. Some IR Relevant Data.

tion by heating in a vacuum-oven at 60  $^{\circ}\!\mathrm{C}$  for 20 h (Table I).

Neutral complexes are only sparingly soluble in CHCl<sub>3</sub> but molecular weight determinations could be made for IV (previously removing the solvent of crystallization), VIII and IX. The results are in accordance with the formulae proposed: IV, 2339 (2259.40); VIII, 2551 (2496.35); IX, 2422 (2585.26).

The IR spectra of these complexes (see Table II) show absorptions in the 1600 cm<sup>-1</sup> region arising from the stretching vibration  $\nu(C=N)$  of the inserted diisocyanide. Another weaker absorption, probably due to the aromatic ring of the diisocyanide, can also be observed in this zone. No absorption is found in the 2200 cm<sup>-1</sup> region, which indicates that all the diisocyanide is inserted. The pentafluorophenyl derivatives show the bands which are characteristic of this ligand [9]. Table II lists those at  $\cong 950 \text{ cm}^{-1}$ , whose location depends upon the oxidation state of the central atom [10, 11]. As may be seen, in accordance with the results reported for other palladium(I) complexes [1], there is no substantial shift of this vibration from the palladium(I) starting complexes to the resulting insertion products. This coincides with the results reported by Balch et al. [12], who have shown by X-ray photoelectron spectroscopy that the insertion of isocyanides does not change the electron density on the metal.

Contrary to our previous observations for  $[(\mu-CyNC){ClPd(\mu-dpm)_2Pd(C_6F_5)}]$  (which undergoes a reversible de-insertion-coordination rearrangement [1])  $[(\mu,\mu'-CNC_6H_4NC){ClPd(\mu-dpm)_2Pd-(C_6F_5)}_2]$  (VIII) needs to be treated with NaBPh<sub>4</sub> (room temperature, benzene) in order to provoke the de-insertion leading to a cationic complex with coordinated diisocyanide (eqn. 2):

 $(\mu,\mu'-CNC_6H_4NC)[ClPd(\mu-dpm)_2Pd(C_6F_5)]_2 +$ 

 $2NaCl + [(C_6F_5)Pd(\mu-dpm)_2Pd(\mu,\mu'-CNC_6H_4NC)-$ 

$$Pd(\mu - dpm)_2 Pd(C_6 F_5)](BPh_4)_2 \qquad (2)$$
(XI)

The IR spectrum of (XI) exhibits a strong absorption at 2149 cm<sup>-1</sup>, assignable to the stretching vibration  $\nu(C\equiv N)$  of the coordinated diisocyanide, whereas the strong absorption at 1618 cm<sup>-1</sup> shown by the starting compound cannot any longer be observed. This confirms that both ends of all the diisocyanide present in complex (XI) are coordinated to a palladium atom.

Treatment of complexes (I) or (VIII) with RNC (R = p-Tol, Cy or <sup>t</sup>Bu) (1:4 molar ratio or respec-

tively excess) and NaBPh<sub>4</sub> (1:4.1 or, respectively, 1:2.1) in acetonitrile yields the corresponding cationic derivatives (eqns. 3 and 4):

 $(\mu,\mu'-CNC_6H_4NC)[CIPd(\mu-dpm)_2PdCI]_2 + 4RNC +$   $+ 4BPh_4Na \longrightarrow [(\mu,\mu'-CNC_6H_4NC)](RNC)Pd(\mu-dpm)_2Pd(CNR)]_2](BPh_4)_4 + 4NaCl (3)$   $R = p-Tol(XII), Cy(XIII), ^tBu(XIV)$   $(\mu,\mu'-CNC_6H_4NC)[CIPd(\mu-dpm)_2Pd(C_6F_5)]_2 + 2RNC +$   $+ 2BPh_4Na \longrightarrow [(\mu,\mu'-CNC_6H_4NC)](RNC)Pd(\mu-dpm)_2Pd(C_6F_5)]_2 + 2NC +$   $(dpm)_2Pd(C_6F_5)]_2](BPh_4)_2 + 2NaCl (4)$ 

R = p-Tol(XV), Cy(XVI), <sup>t</sup>Bu(XVII)

The IR spectra of these complexes show a sharp absorption in the 2000 cm<sup>-1</sup> region, along with another one at *ca.* 1600 cm<sup>-1</sup>, due to the stretching vibration  $\nu$ (C=N) of the coordinated isocyanide and to  $\nu$ (C=N) of the inserted diisocyanide respectively (Table II). Another absorption in the 1600 cm<sup>-1</sup> zone, already present in the free diisocyanide, becomes stronger in our compounds. The single absorption at approx. 2000 cm<sup>-1</sup> points to the presence of only one type of complex. Although a rearrangement leading to the formation of species with inserted monoisocyanides and coordinated diisocyanides of the type {( $\mu$ -RNC)<sub>2</sub>[(C<sub>6</sub>F<sub>5</sub>)Pd( $\mu$ dpm)<sub>2</sub>Pd( $\mu$ , $\mu'$ -CNC<sub>6</sub>H<sub>4</sub>NC)Pd( $\mu$ -dpm)<sub>2</sub>Pd(C<sub>6</sub>F<sub>5</sub>)] }-(BPh<sub>4</sub>)<sub>2</sub> cannot completely be ruled out, the abovementioned data seem to make it improbable.

The cationic complexes exhibit a strong absorption at 610 cm<sup>-1</sup> due to the anion BPh<sub>4</sub><sup>-</sup>. They are conducting in acetone solution (C  $\cong 3 \times 10^{-4} M$ ), their molar conductivities being lower than those expected for 2:1 or, respectively, 4:1 electrolytes, as usual in the case of cationic complexes with BPh<sub>4</sub><sup>-</sup> [13] (Table I).

### Experimental

C, H and N analyses were determined with a Perkin-Elmer 240 microanalyzer; IR spectra were recorded (over the range  $4000-200 \text{ cm}^{-1}$ ) on a Perkin-Elmer 599 spectrophotometer, using Nujol mulls between polyethylene plates; conductivities were determined with a Philips PW 9501/01 conductimeter.

 $Pd_2X_2(\mu$ -dpm)<sub>2</sub> (X = Cl, Br, I, CNO, SCN, N<sub>3</sub>) were prepared according to [14],  $XPd(\mu$ -dpm)<sub>2</sub>- $Pd(C_6F_5)$  (X = Cl, Br, CNO,  $C_6F_5$ ) were obtained according to [1] and 1,4-diisocyanobenzene was prepared as described in [2]. All the reactions were carried out under nitrogen; deoxygenated solvents were used throughout. Some typical syntheses are described in the following.

 $[(\mu,\mu'-CNC_6H_4NC){Pd_2X_2(\mu-dpm)_2}_2nCH_2Cl_2]$  (X = Cl, n = 1(I); X = Br, n = 0(II); X = I, n = 1(III); X = OCN, n = 1(IV); X = SCN, n = 0(V); X = N\_3, n = 1(VI)

To a solution of 0.095 mmol of  $[Pd_2X_2(\mu-dpm)_2]$ in 40 ml of  $CH_2Cl_2$  was added dropwise 0.047 mmol of p-CNC<sub>6</sub>H<sub>4</sub>NC (in the same solvent). After ~3 h stirring the solution was concentrated to *ca*. 5 ml. Addition of ethanol led to the precipitation of the respective complex, which was filtered off and washed with ether. Complexes I, III, IV and VI required 20 h storage in a vacuum-oven at  $\cong$ 60 °C to remove the crystal solvent. Subsequent analyses coincided with those calculated for the solvent-free complexes.

## $[(\mu,\mu'-CNC_6H_4NC)\{XPd(\mu-dpm)_2Pd(C_6F_5)\}_2]; X = C_6F_5(VII), Cl(VIII), Br(IX) or CNO(X)$

To 0.169 mmol of  $CIPd(\mu-dpm)_2Pd(C_6F_5)$  in 30 ml of  $CH_2Cl_2$  was added 0.084 mmol of p-CNC<sub>6</sub>-H<sub>4</sub>NC (in the same solvent) and stirred for 2 h. Concentration to  $\cong$ 3 ml and addition of ethanol led to the crystallization of (VIII). (IX) and (X) were obtained similarly, whilst in the case of (VII) benzene was used as solvent.

# $[(C_6F_5)Pd(\mu dpm)_2Pd(CNC_6H_4NC)Pd(\mu dpm)_2 - Pd(C_6F_5)](BPh_4)_2 (XI)$

To a solution of (VIII) (0.180 g, 0.072 mmol) in 50 ml of benzene was added NaBPh<sub>4</sub> (0.095 g, 0.277 mmol), and the mixture stirred at room temperature for 30 min. The complex formed (XI) was filtered off and washed with water and ethanol.

# $[(\mu,\mu'-CNC_6H_4NC)\{(RNC)Pd(\mu-dpm)_2Pd(CNR)\}_2] - (BPh_4)_4; R = p-Tol(XII), Cy(XIII) or {}^{t}Bu(XIV)$

To an orange-coloured suspension of (I) (0.150 g, 0.065 mmol) in 20 ml of acetonitrile were added NaBPh<sub>4</sub> (0.093 g, 0.271 mmol) and <sup>t</sup>BuNC (29  $\mu$ l, 0.258 mmol). The formed solution was stirred at room temperature for 30 min, filtered and concentrated. Addition of ethanol gave rise to the precipi-

tation of XIV, which was washed with ethanol, water and diethylether.

Complexes XII and XIII were obtained similarly.

 $[(\mu,\mu'-CNC_6H_4NC)\{(RNC)Pd(\mu-dpm)_2Pd(C_6F_5)\}_2] - (BPh_4)_2; R = p-Tol(XV), Cy(XVI) or ^tBu(XVII)$ 

To a suspension of VIII (0.150 g, 0.060 mmol) in 15 ml of acetonitrile were added NaBPh<sub>4</sub> (0.045 g, 0.131 mmol) and an excess of *p*-TolNC and the mixture was stirred for 45 min. The deep-orange solution was filtered and concentrated to  $\cong$ 3 ml. 10 ml of ethanol was added to crystallize (XV), which was filtered off and washed with ethanol.

Complexes (XVI) and (XVII) were obtained similarly.

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