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SYNTHESIS OF MONO- AND BI-NUCLEAR PERHALOPHENYL-PALLADIUM(II) COMPLEXES

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Summary

New routes for the preparation of the binuclear complexes $Cl_4Pd_2L_2$ and $X_2(Ar_X)_2Pd_2L_2$ (X = halide or pseudohalide, $(Ar_X) = C_6F_5$ or C_6Cl_5 , and L = phosphine or arsine) are described Cleavage of the halogen-bridge by ligands leads to mononuclear complexes of the $X(Ar_X)PdL_2$ and $X(Ar_X)PdLL'$ -type

Introduction

We have recently shown [1] that the reactions of compounds of the Cl_2PdL_2 type with $BrTl(C_6F_5)_2$ lead to mixtures of neutral mononuclear and binuclear halogen-bridged pentafluorophenyl palladium(II) complexes, which, since the binuclear complexes are less soluble, can be resolved by fractional crystallization The reaction unfortunately is not general, and does not, for example, take place when $L = PEt_3$, PBu_3 , PPh_2Et , py or quin

In the present paper we describe the preparation of binuclear organopalladium (II) complexes and their arylation to give complexes of the $X_2(Ar_X)_2Pd_2L_2$ type. Finally, the cleavage of the halogen-bridge leads to monomeric complexes of the $X(Ar_X)PdL_2$ or $X(Ar_X)PdLL'$ type ($Ar_X = C_6F_5$ or C_6Cl_5 , L or L' are neutral ligands with N, P or As as donor atoms).

Results and discussion

Preparation of chloro-bridged palladium(II) complexes

Complexes of this type are usually prepared by refluxing Cl_2PdL_2 with ammonium [2] or, better, sodium [3] tetrachloropalladate(II) in aqueousalcoholic solution However, we made the binuclear complexes $Cl_4Pd_2L_2$ (L = PEt_3 , PBu_3 , PPh_3 or $AsPh_3$) in 80–90% yield by iefluxing for 30 min mixtures of the corresponding Cl_2PdL_2 in ethanol or acetone solution with $PdCl_2$ (90% of the theoretic amount) in 2 N HCl solution

$$Cl_2PdL_2 + PdCl_2 \rightarrow Cl_4Pd_2L_2$$

Com	vəldi	noj sisvlind	ud (caled) (%)					
		C	= = =	z	ßr	CI	pa	M p (°C)
_	Br2(C6+5)2Pd2(PFt3)2	,1131	3 09	an an air an	16.46		21 85	509
		(30 56)	(191)		(16 92)		(22 58)	
п	Bt2(C6 h 5)2Pd2(PBu3)2	3862	545		1393		18 5 4	141
		(0686)	(486)		(66 17)		(1916)	
Ξ	Br ₂ (C ₆ I 5) ₂ Pd ₂ (PPh 3) ₂	4748	279					285 (dec.)
		(4681)	(243)					
2	Cl2(C6Cl5)2Pd2(PLt3)2	2827	3 00			40.91		284 (dec)
	6 6 1 1 1 1	(2829)	(967)			(11 18)		
>	Br2(C6Cl5)2Pd2(PFt1)2	2671	297					310 (dec)
		(26 00)	(2 10)					
И	12(C ₆ Cl ₅)2Pd2(Ph13)2	24 65	2 66					308 (dec)
	1 - - -	(2 1 9 7)	(249)					
ΝI	(SCN)2(C6Cl5)2Pd2(PI 11)2	2912	2 49	2 88		12 4 3		284 (dec)
		(2923)	(787)	(797)		(32 90)		

ANALYTICAL RESULTS I OR BINUCLI AR COMPLEXI 5 OBTAINI D ACCORDING TO 1 Q5 2, 3, 4

1 LIBLI 1

Process (1) can, of course, not be used in this form when L is an easily protonated ligand, e g a nitrogen ligand.

Synthesis of chloro-bridged perhalophenyl palladium(II) complexes

The only previous direct alkylation or arylation of binuclear palladium(II) complexes appears to be that by Calvin and Coates [4]. who reported the alkylation of $(\mu$ -SEt)₂Cl₂Pd₂(PBu₃)₂ with LiCH₃, leading to $(\mu$ -SEt₂)₂(CH₃)₂ - Pd₂(PBu₃)₂. The Cl-bridged binuclear palladium(II) complex $(\mu$ -Cl₂)Cl₂Pd₂ - (PBu₃)₂ reacted with LiCH₃ to give metallic palladium even at -45° C

We have studied the introduction of C_6F_5 and C_6Cl_5 groups into the binuclear complexes, according to eqs. (2) and (3),

$$Cl_4Pd_2L_2 + BrMgC_6F_5 \rightarrow Cl_2(C_6F_5)_2Pd_2L_2 + MgX_2$$
(2)

$$(L = PEt_3, PBu_3, PPh_3 \text{ or } AsPh_3)$$

$$Cl_4Pd_2(PEt_3)_2 + C_6Cl_6 + Mg \rightarrow Cl_2(C_6Cl_5)_2Pd_2(PEt_3)_2 + MgCl_2$$
 (3)

Process (2) normally leads to a mixture of $Cl_2(C_6F_5)_2Pd_2L_2$ and $Br_2(C_6F_5)_2$ -Pd₂L₂ The terminal halogens are replaced by C_6F_5 groups and the chlorinebridging atoms are partially replaced by bromine atoms. On treating the mixture with LiBr, only the bromine derivative is obtained as the end-product. When $L = AsPh_3$, partial cleavage of the chlorine-bridges takes place during process (2), leading to mixtures which were not studied further Process (3) was only studied with $L = PEt_3$.

The other binuclear C_6Cl_5 complexes were prepared by substitution reactions (see below).

Analytical data for the new complexes are listed in Table 1

Synthesis of other binuclear complexes $X_2(C_6Cl_5)_2Pd_2(PEt_3)_2$

Other binuclear complexes were prepared by substitution reactions according to eq. 4 starting from $Cl_2(C_6Cl_5)_2Pd_2(PEt_3)_2$ The ease of substitution increases

$$Cl_2(C_6Cl_5)_2Pd_2(PEt_3)_2 + 2MX \rightarrow 2MCl + X_2(C_6Cl_5)_2Pd_2(PEt_3)_2$$
 (4)

 $(MX = L_1Br, NaI \text{ or } KSCN)$

in the sequence LiBr < NaI < KSCN, i.e. with the increasing nucleophilic character of the anion X, agreeing with results obtained [1] with $Cl_2(C_6F_5)_2$ - $Pd_2(PPh_3)_2$ (Analytical data are listed in Table 1)

Bridge-cleavage reactions

A major application of the halogen-bridged organo complexes is in reactions in which the bridge is cleaved to give monomeric complexes. The cleavage can



C II N Br CI Mp (C) VII $BC(a_1^{a_1})^{p_1} M(Pl_1)_1$ 30.4 50.4 50.4 10.4 120 $Mp (C)$ X $BC(a_1^{a_1})^{p_1} M(Pl_1)_1$ (76.4) (71.6) (71.6) (71.6) (71.6) (71.6) (71.6) (71.6) (21.6)	Compl	lex	Analysis found	l (calcd) (^c ?)		Alla Annala	a called an allow of any data called and	
VIII $\mathbb{R}(\mathbb{C}_{0}^{1}\mathcal{F})^{1} \mathbb{Q}(\mathbb{P}(1)^{1}, \mathbb{I})$ \mathbb{I}_{0} \mathbb{I}_{1} <t< th=""><th></th><th></th><th>c</th><th>II</th><th>Z</th><th>Br</th><th>c1</th><th>M p (°C)</th></t<>			c	II	Z	Br	c1	M p (°C)
X $HrG_6F_5 PM(PB_4)_2$ (7.6) (7.1) (6.6) (11.60) (7.1) (16.6) (11.60) (21.60) (11.60) (21.60) (11.60) (21.60) (11.60) (21.60) (11.60) (21.60) $($	VIII	Br(C ₆ F5)Pd(P11,1)2	36.04	5 04	en un malfer a de la de la del	1361		120
IX $B(C_d_1; j)^{B}(C^{B}(h_1)_2)$ $17, i1$ 6.65 $10, i5$ $10, i6$ $10, $		•	(30-66)	(12,09)		(1356)		
X $R(G_6^{1})$ plu($\Gamma_{1,1}(\Lambda sH_{2})$) (776) (713) (716) (713) (716) (713) (702) (710) <th< td=""><td>XI</td><td>Br(C₆F₅)Pd(PBu₃)2</td><td>17 31</td><td>6.85</td><td></td><td>1016</td><td></td><td>84</td></th<>	XI	Br(C ₆ F ₅)Pd(PBu ₃)2	17 31	6.85		1016		84
X $M(G_6^1; j) M(P(1; j) (\Lambda^*P_1_j))$ 41 % 4.2 h 9.7 h 2.1 h(G_6) XI $B(G_6^1; j) P(P(1; j) (P(1_j))$ (41 %) (10 %) 221 XII $B(G_6^1; j) P(P(1; j) (P(1_j))$ (41 %) (10 %) 221 XII $B(G_6^1; j) P(P(1; j) (P(1_j))$ (41 %) (10 %) 120 XII $B(G_6^1; j) P(P(1; j) (Q_10)$ (40 %) (41 %) (10 %) 120 XII $B(G_6^1; j) P(P(1; j) (Q_10)$ (40 %) (41 %) (40 %) (41 %) 120 XIV $B(G_6^1; j) P(P(1; j) Q_10)$ (40 %) (41 %) 240 1271 178 (dec) XVI $G(G_6^1; j) P(P(1; j) Q_10)$ (41 %) 240 1271 178 (dec) XVI $G(G_6^1; j) P(P(1; j) Q_10)$ (41 %) 240 1271 178 (dec) XVI $G(G_6^1; j) P(P(1; j) Q_10)$ (41 %) 240 1271 178 (dec) XVI $G(G_6^1; j) P(P(1; j) Q_10)$ (41 %) 240 1271 120 XVI $G(G_6^1; j) P(P(1; j) Q_10)$			(17 54)	(11)		(10 55)		
Xi $\operatorname{BrCd}(\Gamma_2)\operatorname{Prl}(\operatorname{Prl}_1)(\operatorname{Prl}_1)$ (65.2) (3.66) (10.21) Xi $\operatorname{BrCd}(\Gamma_2)\operatorname{Prl}(\operatorname{Prl}_1)(\operatorname{PrOPl}_1)$ (10.10) (10.12) Xi $\operatorname{BrCd}(\Gamma_2)\operatorname{Prl}(\operatorname{Prl}_1)(\operatorname{PrOPl}_1)$ (10.10) (10.12) Xi $\operatorname{BrCd}(\Gamma_2)\operatorname{Prl}(\operatorname{Prl}_1)(\operatorname{ProPl}_1)$ (10.10) (10.12) Xi $\operatorname{BrCd}(\Gamma_2)\operatorname{Prl}(\operatorname{Prl}_1)(\operatorname{Prl}_1)$ (10.10) (10.22) Xi $\operatorname{BrCd}(\Gamma_2)\operatorname{Prl}(\operatorname{Prl}_1)(\operatorname{Prl}_1)$ (10.10) (10.22) Xi $\operatorname{BrCd}(\Gamma_2)\operatorname{Prl}(\operatorname{Prl}_1)(\operatorname{Prl}_1)$ (10.10) (10.22) (10.22) Xi $\operatorname{BrCd}(\Gamma_2)\operatorname{Prl}(\operatorname{Prl}_1)$ (11.10) (10.10) (10.12) Xi $\operatorname{CCd}(\Gamma_2)\operatorname{Prl}(\operatorname{Prl}_1)$ (11.10) (10.10) (10.12) Xi $\operatorname{CCd}(\Gamma_2)\operatorname{Prl}(\operatorname{Prl}_1)$ (11.10) (10.10) (10.10) (10.10) Xi $\operatorname{CCd}(\Gamma_2)\operatorname{Prl}(\operatorname{Prl}_1)$ (10.10) (10.10) (10.10) (10.10) Xi $\operatorname{CCd}(\Gamma_2)\operatorname{Prl}(\operatorname{Prl}_1)$ (10.10) (10.10) (10.10) (10.10) Xi $\operatorname{CCd}(\Gamma_2)\operatorname{Prl}(\operatorname{Prl}_1)$ (10.10) (10.10) (10.10) (2.16) (10) Xi $\operatorname{CCd}(\Gamma_2)\operatorname{Prl}(\operatorname{Prl}_1)$ (10.10) (10.10) (2.16) (×	Br(C ₆ I [,] 5)Pd(Pl 1, 1)(AsPh ₃)	46 35	4 26		04.0		219 (dec)
XI $Br(G_6\Gamma_5)Pid(Pl1_4)(PPh_3)$ $q^{0}08$ d^{27} 1007 221 XII $Br(G_6\Gamma_5)Pid(Pl1_3)(P(OPh_3))$ $(f^{0}0)$			(46 32)	(386)		(1028)		
XII $\operatorname{Irr}(c_6 I_5)\operatorname{Pri}(\operatorname{FrI}_1)$ (19 10) (10 0) (10 8 f) (12 2) (10 16) (12 2) (10 2 2) (10 2 2) (10 2 2) (10 2 2) (10 2 2) (10 2 2) (10 2 2) (10 1 2 2) (10 1 2 2) (10 1 2 2) (10 2 2) (10 2 2) (10 2 2) (10 2 2) (10 2 2) (10 2 2) (10 2 2) (10 2 2) (10 2 2) (10 2 2) (11 7 3) (11 8 3) (11 3 1) (11 3 1) (11 3 1) (11 3 1) (11 3 1) (11 3 1) (11 3 1) (11 3 1) (11 3 1) (11 3 1) (11 3 1) (11 3 1) (11 3 1) (12 3 1) (13 3 10) (13 3 10) (13 3 10) (13 3 10) (13 3 10) (13 3 10) (13 3 10) (13 3 10) (13 3 10) (13 3 10)	×	Br(C ₆ F 5) Pd(Pf 13)(PPh3)	49 08	4 27		1007		221
XII Br(G_61 c) Pa(PT t_3) P(QPT t_3) 4579 132 1016 120 XII $Br(G_61 c) Pa(QP1 t_3) P(S)$ 6803 (384) (1022) 150 (dc) XIV $Br(G_61 c) Pa(QP1 t_3) P(S)$ 6103 (384) (177) (163) 231 1277 1277 1260 (dc) XIV $Br(G_61 c) Pa(PP1 t_3)$ (1198) (166) 2.313 (1131) 150 (dc) XV $SCN(G_6 r_5) Pa(PP1 t_3)$ (1198) (528) 240 13271 173 (dc) XVI $CI(G_6 G_{12}) Pa(PP1 t_3)$ 4141 498 240 3306 169 XVII $Br(G_6 CI_5) Pa(PP1 t_3)$ (3116) (381) 3306 169 XVII $Br(G_6 CI_5) Pa(PP1 t_3)$ 214 465 240 3306 169 XVII $Br(G_6 CI_5) Pa(PP1 t_3)$ (311) (381) (310) 190 207 203 XVII $Br(G_6 CI_5) Pa(PP1 t_3)$ (310) (411) 210			(19 10)	(4 00)		(1087)		
XII $hr(c_{1}; ph(rPl t_{1})(py))$ (40.0B) (JB4) (10.22) XIV $hr(c_{1}; ph(rPl t_{1})(py))$ (3 B) 3 B) 2 B) 1 A 2? 1 B (G_{1}) XIV $hr(c_{1}; ph(rPl t_{1})(quin))$ (1 B) (3 G) (2 B) 2 B) (1 B (G_{1})) (1 B (G_{1})) (1 B (G_{1})) (1 B (B))	XII	Br(C6I 5)Pd(PI 13)[P(OPh)]]	45 79	1 32		1016		120
XIII $\mathrm{Br}(G_{4}; p)\mathrm{Pl}(\mathrm{Pl}; q)(\mathrm{Ql}(\mathrm{Pl}))$ 16 0.2 3 0.5 2 3.1 14 2? 15 0. (dic.) XIV $\mathrm{Br}(G_{6}\Gamma_{5})\mathrm{Pl}(\mathrm{Pl}; q)(\mathrm{QlI})$ 4071 (163) 2 3.3 14 7.3 178 (dac.) XV 5 CN(G_{6}\Gamma_{5})\mathrm{Pl}(\mathrm{Pl}; q)(\mathrm{QlI}) 4011 (5 4.9) (1 3 31) 178 (dac.) XV 5 CN(G_{6}\Gamma_{5})\mathrm{Pl}(\mathrm{Pl}; q)_{2} 41 4.6 2.13 (1 3 31) 178 (dac.) XV1 Cl(G_{6}G_{5})\mathrm{Pl}(\mathrm{Pl}; q)_{2} 41 4.9 2.40 33.06 169 XV1 Br(G_{6}G_{1})\mathrm{Pl}(\mathrm{Pl}; q)_{2} (4 15) (4 81) (2 4.0) 33.06 169 XV1 Br(G_{6}G_{1})\mathrm{Pl}(\mathrm{Pl}; q)_{2} (4 4.0) 2.40 33.06 169 XV1 Br(G_{6}G_{1})\mathrm{Pl}(\mathrm{Pl}; q)_{2} (4 4.0) 2.07 2.3 190 XV11 Br(G_{6}G_{1})\mathrm{Pl}(\mathrm{Pl}; q)_{1} 2.91 4.45 2.07 2.03 2.04 XV11 Br(G_{6}G_{1})\mathrm{Pl}(\mathrm{Pl}; q)_{1} 2.3 4.45 2.07 2.07 2.04			(46-08)	(1, 84)		(10.22)		
XIV $\operatorname{HrC}_{6}[^{5}]\operatorname{Pl}(\operatorname{Pl}_{1})(\operatorname{Gul})$ (71 07) (71,1) (2 64) (14 73) (14 73) XV $\operatorname{SCNC}_{6}[^{5}]\operatorname{Pl}(\operatorname{Pl}_{1})(\operatorname{Gul})$ (11 93) (11 31) (15 24) (2 40)	ШХ	Br(C ₆ I 5)Pd(Pl 13)(py)	7698	395	233	1422		150 (dic)
XIV $\operatorname{BrC}_{G}(\Gamma_5)\operatorname{Pd}(\operatorname{Pt}_1)(\operatorname{Guin})$ 40 71 181 2.49 12 71 171 178 (dec) XV $\operatorname{SCN}(G_6 \Gamma_5)\operatorname{Pd}(\operatorname{Pt}_1)_2$ (198) (3.66) (2.31) (1131) 150 150 XV1 $\operatorname{Cl}(G_6(\Gamma_5)\operatorname{Pd}(\operatorname{Pt}_1)_2$ (4019) (5.29) (2.41) 33.06 169 XV1 $\operatorname{BrC}_6(\Gamma_5)\operatorname{Pd}(\operatorname{Pt}_1)_2$ (4119) (5.29) (2.41) 33.06 169 XV1 $\operatorname{BrC}_6(\Gamma_5)\operatorname{Pd}(\operatorname{Pt}_1)_2$ (3.190) (3.190) 190 XV1 $\operatorname{BrC}_6(\Gamma_5)\operatorname{Pd}(\operatorname{Pt}_1)_2$ (2.16) (4.10) (3.190) 190 XV1 $\operatorname{BrC}_6(\Gamma_5)\operatorname{Pd}(\operatorname{Pt}_1)_2$ (2.16) (4.10) (2.16) (3.190) 190 XV1 $\operatorname{BrC}_6(\Gamma_5)\operatorname{Pd}(\operatorname{Pt}_1)_2$ (2.16) (4.10) (2.16) (3.190) 190 XV1 $\operatorname{BrC}_6(\Gamma_5)\operatorname{Pd}(\operatorname{Pt}_1)_2$ (2.14) (4.17) (2.16) (3.190) 190 XV1 $\operatorname{BrC}_6(\Gamma_5)\operatorname{Pd}(\operatorname{Pt}_1)_2$ (3.194) (4.17) (2.16) (2.16) (3.732) 191 XX $\operatorname{ClC}_6(\Gamma_5)\operatorname{Pd}(\operatorname{Pt}_1)/\operatorname{Arbh}_3$ (4.17) (2.16) (2.16) (2.761) 191 XX $\operatorname{ClC}_6(\Gamma_5)\operatorname{Pd}(\operatorname{Pt}_1)/\operatorname{Prb}_3$ (4.17) (2.16) (2.16) (2.761) 160 XXI $\operatorname{ClC}_6(\Gamma_5)\operatorname{Pd}(\operatorname{Pt}_1)/\operatorname{Prb}_3$ (4.17) (2.15) (2.16) (2.761) 160 XXI $\operatorname{ClC}_6(\Gamma_5)\operatorname{Pd}(\operatorname{Pt}_1)/\operatorname{Prb}_3$ (4.10) (2.15) (2.16) (2.761) 160 XXII $\operatorname{ClC}_6(\Gamma_5)\operatorname{Pd}(\operatorname{Pt}_1)/\operatorname{Pr}_3$ (3.70) (2.17) (2.61) (2.761) 160 XXII $\operatorname{ClC}_6(\Gamma_5)\operatorname{Pd}(\operatorname{Pt}_1)/\operatorname{Pr}_3$ (3.90) (4.10) (2.17) (2.761) (2.761) 160 XXII $\operatorname{ClC}_6(\Gamma_5)\operatorname{Pd}(\operatorname{Pt}_1)/\operatorname{Pr}_3$ (3.90) (3.70) (2.17) (3.61) (2.761) (2.60) (0.60) (0.60) (2.61) (2.60) (0.60) (2.61) (2.60) (0.60) (2.61) (2.60) (2.61) (2.60) (2.61) (2.60) (2.61) (2.60) (2.61) (2.60) (2.61) (2.60) (2.60) (2.61) (2.60) (2.61) (2.60) (2.61) (2.60) (2.61) (2.61) (2.60) (2.61)			(37 07)	(3 63)	(2 64)	(1473)		
XV $5CN(G_6F_5)Pd(Pt1_1)_2$ (1198) $(16,6)$ (2.13) (1131) XVI $CIC_6G_{15}Pd(Pt_{1})_2$ (010) 549 2.11 103 XVI $CIC_6G_{15}Pd(Pt_{1})_2$ $(14,15)$ (181) (528) (241) 3306 169 XVI $Br(G_6G_{15})Pd(Pt_{1})_2$ $(14,15)$ (181) $(34,90)$ 100 XVII $Br(G_6G_{15})Pd(Pt_{1})_2$ (2210) (440) (417) 207 $26,35$ 210 XVIII $CG_6G_{15}Pd(Pt_{1})_2$ 291 417 207 $26,35$ 210 204 XXI $CIC_6G_{15}Pd(Pt_{1})(PPh_{3})$ (411) (215) $26,37$ 210 2732 210 XXI $CIC_6G_{15}Pd(Pt_{1})(PPh_{3})$ (411) (215) $26,37$ 210 2732 210 XXII $CIC_6G_{15}Pd(Pt_{1})(PPh_{3})$ (411) (215) 213 210 210 210 210 210 210 210 210 <	ΧIV	Br(C ₆	40 71	181	2.49	1271		178 (dec)
XVSCN(G_6 \Gamma_5)Pd(P1 t_1)_240 405 492 11150XVICl(G_6 \Gamma_5)Pd(P1 t_1)_2(40 1'1)(5 28)(2 4u)33 0u169XVIIBr(G_6 C1_5)Pd(P1 t_1)_2(41 1)(4 1)(5 28)(2 4u)33 0u169XVIIBr(G_6 C1_5)Pd(P1 t_1)_2(3 1 10)(4 10)(3 1 10)(3 1 00)190XVIIIBr(G_6 C1_5)Pd(P1 t_1)_2(2 1u)(4 4u)(3 1 10)204XXIII(1 2 1u)(4 11)2 072b 37210XXIICl(G_6 C1_5)Pd(P1 t_1)(PPh_3)47 404 472 072b 37210XXIICl(G_6 C1_5)Pd(P1 t_1)(A8Ph_1)(4 11)(2 15)2b 37210XXIICl(G_6 C1_5)Pd(P1 t_1)(A8Ph_1)47 404 472 072b 37261XXIICl(G_6 C1_5)Pd(P1 t_1)(P(Dh)_1)43 313 70(2 15)2b 33210XXIIICl(G_6 C1_5)Pd(P1 t_1)(P(Dh)_1)43 313 70(2 15)2b 100XXIIICl(G_6 C1_5)Pd(P1 t_1)(P(Dh)_1)43 313 70(2 15)2b 100XXIIICl(G_6 C1_5)Pd(P1 t_1)(P(Dh)_1)43 313 70(2 17)2b 100XXIIICl(G_6 C1_5)Pd(P1 t_1)(P(Dh)_1)43 313 70(2 17)2b 100XXIIICl(G_6 C1_5)Pd(P1 t_1)(P(Dh)_1)43 313 70(2 17)2b 10XXIIICl(G_6 C1_5)Pd(P1 t_1)(P(Dh)_1)43 313 70(2 17)2b 10XXIIICl(G_6 C1_5)Pd(P1 t_1)(P(Dh)_1)41 3190(2 17)2b 1			(11 98)	(3 66)	(2.33)	(181)		
XVI $C(C_6C_5)$ $Pa(Pr_{1})_2$ (40 19) (5 28) (2 4h) 33 06 169 XVII $B(C_6C_5)$ $Pa(Pr_{1})_2$ (34 96) (34 17) (36 96) (36 16	X۷	SCN(C ₆ F ₅)Pd(PI t ₃) ₂	40 40	5 49	2 31			150
XVI $Cl(C_6Cl_5)Pd(Pt_1)_2$ $J_4 J_1$ $4 98$ $J_3 00$ $I69$ $J_3 00$ $J_4 I_5$ $J_5 I_5$ $J_6 I$			(40 19)	(5 28)	(2 46)			
XVII $Br(C_6Cl_5)Pd(P1 t_3)_2$ (1415) (411) (45) (33.96) XVIII $Br(C_6Cl_5)Pd(Pt_1)_2$ 22.84 4.65 20.91 4.0 XVIII $(C_6Cl_5)Pd(Pt_1)_2$ 20.71 4.29 20.7 20.3 XIX $SCN(C_6Cl_5)Pd(Pt_1)_2$ 33.65 4.17 2.07 26.35 210 XIX $SCN(C_6Cl_5)Pd(Pt_1)_2$ 34.65 4.17 2.07 26.35 210 XX $Cl(C_6Cl_5)Pd(Pt_1)_2$ 34.65 4.13 2.07 26.35 210 XXI $Cl(C_6Cl_5)Pd(Pt_1)(AsPh_3)$ 4.749 4.7 2.07 25.32 210 XXI $Cl(C_6Cl_5)Pd(Pt_1)(AsPh_3)$ 4.749 4.72 4.72 2.07 25.12 191 XXII $Cl(C_6Cl_5)Pd(Pt_1)(P(OPh))_1$ 4.331 3.57 2.733 26.02 210 26.00 XXII $Cl(C_6Cl_5)Pd(Pt_1)(P(OPh))_1$ 4.331 3.57 2.33 $3.65.63$ $310 (dec)$ XXII $C(C_6Cl_5)Pd(Pt_1)(P(OPh))_1$ 4.331 3.57 2.33 $3.65.63$ $310 (dec)$ XXII $C_6Cl_5)Pd(Pt_1)(P(OPh))_1$ 4.390 (3.60) (2.17) (26.00) $310 (dec)$ XXIV $C_6Cl_5)Pd(Pt_1)_2$ 38.41 9.66 (3.70) (2.71) (26.00) XXIV $C_6Cl_5)Pd(Pt_1)_2$ (2.71) (2.71) (2.71) (2.60) XXIV $C_6Cl_5)Pd(Pt_1)_2$ (2.71) (2.71) (2.71) (2.60) XXIV $C_6Cl_5)Pd(Pt_1)_3$ <t< td=""><td>ХVI</td><td>Cl(C₆Cl₅)Pd(PFt₃)₂</td><td>3441</td><td>4 98</td><td></td><td></td><td>33 06</td><td>169</td></t<>	ХVI	Cl(C ₆ Cl ₅)Pd(PFt ₃) ₂	3441	4 98			33 06	169
XVII $\operatorname{Br}(\operatorname{Gc}(\operatorname{Gl}_5)\operatorname{Pd}(\operatorname{Pl}_1)_2$ 32 84 465 190 190 (410) (410) (410) (410) (410) (410) (410) (411) (410) (411) (410) (411) (41			(31 12)	(481)			(33.96)	
XVIII $(C_6Cl_5)Pd(Pt_1)_2$ (12 16)(4 16)204XIX $SCN(C_6Cl_5)Pd(Pt_1)_2$ 29 314 2920726 35210XIX $SCN(C_6Cl_5)Pd(Pt_1)_2$ (30 05)(4 17)2 0726 35210XX $Cl(C_6Cl_5)Pd(Pt_1)_3$ (35 09)(4 61)(2 15)26 12191XXI $Cl(C_6Cl_5)Pd(Pt_1)(AsPh_1)$ (4 68)(4 21)(2 15)26 92180XXI $Cl(C_6Cl_5)Pd(Pt_1)(P(0Ph)_1)$ (4 18)(3 70)25 92180XXII $Cl(C_6Cl_5)Pd(Pt_1)(P(0Ph)_1)$ 43 313 5725 33310 (dec)XXIII $Cl(C_6Cl_5)Pd(Pt_1)(P(0Ph)_1)$ 3 3572 333563310 (dec)XXIII $Cl(C_6Cl_5)Pd(Pt_1_3)(PP)$ 3 16(2 49)(2 51)116XXIII $Cl(C_6Cl_5)Pd(Pt_1_3)(PP)$ 3 16(3 66)2 333563310 (dec)XXIV $(C_6F_5)C(C_6Cl_5)Pd(Pt_1_3)(PP)$ (3 96)(2 17)(2 17)(2 17)(2 17)XXIV $(C_6F_5)C(C_6Cl_5)Pd(PE1_3)_2$ 3 11(3 96)(2 17)(2 17)(2 17)XXIV $C_6F_5)(C_6Cl_5)Pd(PE1_3)_2$ 3 419 6(2 17)(2 17)(2 17)XXIV $C_6F_5)(C_6Cl_5)Pd(PE1_3)_2$ 3 419 6(2 17)(2 17)(2 16)XXIV $C_6F_5)(C_6Cl_5)Pd(PE1_3)_2$ 3 11(3 96)(2 17)(2 17)(2 17)XXIV $C_6F_5)(C_6Cl_5)Pd(PE1_3)_2$ 3 149 6(2 17)(2 18)(2 16)XXIV $C_6F_5)(C_6Cl_5)Pd(PE1_3)_2$ (3 16)(3 95)(2 17)(2 18)XXIV $C_6F_5)Pd(PE1_3)_2$ (3 16)(IIVX	Br(C ₆ Cl ₅)Pd(PI t ₃) ₂	32 84	4 65				190
XVIII $I(C_6CI_5)Pd(Pt_{1})_2$ 29 11 4 29 204 XVIII $I(C_6CI_5)Pd(Pt_{1})_2$ (30 05) (4 17) (2 15) 26 35 210 XX $SCN(C_6CI_5)Pd(Pt_{1})_2$ (35 09) (4 61) (2 15) 26 35 210 XX $CI(C_6CI_5)Pd(Pt_{1})(PPh_{3})$ 47 49 4 47 (2 15) (2 15) 26 12 191 XXI $CI(C_6CI_5)Pd(Pt_{1})(A^{P}h_{3})$ (4 6 8) (4 21) (2 15) (2 15) 26 12 191 XXI $CI(C_6CI_5)Pd(Pt_{1})[P(OPh)_{1}]$ (4 18) (3 70) 25 92 180 XXII $CI(C_6CI_5)Pd(Pt_{1})[P(OPh)_{1}]$ (4 18) (3 70) (2 15) 26 12 116 XXII $CI(C_6CI_5)Pd(Pt_{1})[P(OPh)_{1}]$ (3 3 3 7 2 3 57 (2 10) (2 17) (2 10) (3 16) (2 6 10) (3 167) (3 161) (3 161) (3 161) (3 161) (2 10) (3 167) (3 19) (2 17) (3 19) (2 17) (3 19) (2 17) (2 17) (2 18) (3 10) (4ec) (2 10) (2 17) (2 17) (2 18) (2 17) (2 18) (2 17) (2 18			(32 16)	(4 46)				
XIX $SCN(C_6Cl_5)Pd(Pt_4)_2$ (30 05) (417) XX $SCN(C_6Cl_5)Pd(Pt_3)_2$ (35 09) (41) (215) (215) (27 32) XX $Cl(C_6Cl_5)Pd(Pt_3)(PPh_3)$ (35 09) (441) (216) (216) (27 61) XX $Cl(C_6Cl_5)Pd(Pt_4)(A_8Ph_4)$ (46 68) (4 21) (216) (25 61) (27 61) (25 61) (25 61) (25 61) (25 61) (26	IIIVX	I(C ₆ Cl ₅)Pd(PFt ₃)2	29 31	4 29				204
XIX $\text{SCN}(\text{C}_6\text{Cl}_5)\text{Pd}(\text{Pt}_1)_2$ 34 & 5 4 13 2 07 26 35 210 XX $\text{Cl}(\text{C}_6\text{Cl}_5)\text{Pd}(\text{Pt}_1)_3$) 47 49 447 (215) (27 32) (27 32) XX $\text{Cl}(\text{C}_6\text{Cl}_5)\text{Pd}(\text{Pt}_1)(\text{APh}_3)$ 47 49 447 (21) (216) (27 61) (27 61) XXI $\text{Cl}(\text{C}_6\text{Cl}_5)\text{Pd}(\text{Pt}_1) \text{P}(\text{OPh})_1 $ 44 72 4 02 (26 12) (26 12) (26 12) XXII $\text{Cl}(\text{C}_6\text{Cl}_5)\text{Pd}(\text{Pt}_1) \text{P}(\text{OPh})_1 $ 43 31 3 57 (26 12) (26 12) (26 12) (44 18) (3 60) (217) (26 12) (26 12) (44 18) (3 70) (26 12) (26 12) (26 12) (26 12) (26 12) (26 12) (27 61) (28 00) (28 11) (28 11) (28 01) (28 11) (28 01) (28 11) (28 11) (28 01) (28 11)			(30 05)	(417)				
XX $Cl(C_6Cl_5)Pd(Pl_3)(PPh_3)$ (4 61) (2 15) (2 7 32) XX $Cl(C_6Cl_5)Pd(Pl_4)(Pl_4)(A^{2}Ph_3)$ 4 7 4 9 4 4 7 2 5 12 191 (2 7 61) 25 92 180 XXI $Cl(C_6Cl_5)Pd(Pl_4)(Pl_4)(A^{2}Ph_3)$ 4 7 2 4 02 25 92 180 XXII $Cl(C_6Cl_5)Pd(Pl_4)(Pl_4)(19)$ 4 3 3 7 3 70) 25 13 116 XXII $Cl(C_6Cl_5)Pd(Pl_4)(Pl_4)(19)$ 3 5 7 2 3 3 5 7 2 3 3 3 7 2 3 5 3 3 10 (dec) (2 6 0) XXII $Cl(C_6Cl_5)Pd(PL_3)(12)$ 3 7 2 3 6 2 2 3 3 3 6 3 3 10 (dec) (3 6 1 0) (3 6 1 0) (3 6 1 0) (3 6 1 0) (3 6 1 0) (3 6 1 0) (3 6 1 0) (3 6 1 0) (3 6 1 0) (3 6 1 0) (3 6 1 0) (3 6 1 0) (3 6 1 0) (3 7 0) (3 7 0) (3 7 0) (3 7 0) (3 7 0) (2 17) (2 17) (2 3 80) (2 3 80) (2 17) (2 3 80) (2 17) (2 3 80) (2 17) (2 3 80) (2 17) (2 3 80) (2 17) (2 3 80) (2 17) (2 3 80) (2 17) (2 3 80) (2 17) (2 3 80) (2 17) (2 3 80) (2 17) (2 3 80) (2 17) (2 16) (2 17) (2 16) (2 16) (2 17) (2 16) (2 16) (2 16) (2 16) (2 16) (2 16) (2 17) (2 16) (2 17) (2 16) (2 17) (2 17) (2 16) (2 16) (2 16) (2 16) (2 16) (2 16) (2 16) (2 16) (2 16) (2 16) (2 16) (2 16) (2 16) (2 16) (2 16) (2 16) (2 17) (2 16) (ХІХ	SCN(C ₆ Cl ₅)Pd(Pi [,] t ₃) ₂	34 85	4 13	2 07		2635	210
XX $C(C_6C(5)Pd(P1_5))(PPh_3)$ 47 49 447 2612 191 XXI $C(C_6C(5)Pd(P1_4))(A_8Ph_4)$ 44 72 4 02 (27 61) (27 61) XXI $C(C_6C(5)Pd(P1_4))(A_8Ph_4)$ 44 72 4 02 (26.12) 180 XXII $C(C_6C(5)Pd(P1_5))[P(OPh)_1]$ 43 31 3 57 (26.12) XXII $C(C_6C(5)Pd(P1_5))(P(OPh_1)]$ 43 31 3 57 (26.00) XXIII $C(C_6C(5)Pd(P1_5))(P(OPh_3)]$ 33 72 3 52 2 33 35 53 J10 (dec) (31 67) (3 96) (2 17) (2 17) (36.19) XXIV $(C_6F_5)(C_6C(5)Pd(PE1_3)_2$ 38 41 3 96 (2 17) (2 17) (22 82 249) XXIV $(C_6F_5)(C_6C(5)Pd(PE1_3)_2$ (37 98) (3 95) (2 17) (2 3 89)			(35 09)	(4 61)	(215)		(27 32)	
XXI $Cl(C_6Cl_5)Pd(Pl_{1})(\Lambda_8Ph_{1})$ (466) (421) (2761) XXI $Cl(C_6Cl_5)Pd(Pl_{1})(\Lambda_8Ph_{1})$ (472 402 2592 180 XXII $Cl(C_6Cl_5)Pd(Pl_{1})[P(OPh)_{1}]$ 43 31 357 (26.12) (26.12) XXII $Cl(C_6Cl_5)Pd(Pl_{1})[P(OPh)_{1}]$ 43 31 357 (26.0) (26.0) XXII $Cl(C_6Cl_5)Pd(Pl_{1})(DY)$ 3372 352 233 3553 J10 (dec) (3167) (379) (277) (277) (236) (3798) (395) (277) (2389) (2389)	xx	Cl(C ₆ Cl ₅)Pd(Pl L ₃)(PPh ₃)	47 49	4 47			2612	191
XXI $Cl(G_6Cl_5)Pd(Pl t_3)(A_8Ph_3)$ 44 72 4 02 25 92 180 XXII $Cl(G_6Cl_5)Pd(Pt_3)[P(OPh)_1]$ 43 31 3 57 (26.12) XXII $Cl(G_6Cl_5)Pd(Pt_3)[P(OPh)_1]$ 43 31 3 57 (26.00) XXIII $Cl(G_6Cl_5)Pd(Pt_3)(12Y)$ 33 72 3 52 2 33 35 53 J10 (dec) (31 67) (3 96) (2 17) (2 16) (36.19) XXIV $(G_6F_5)(G_6Cl_5)Pd(PEt_3)_2$ 38 41 3 96 (2 17) (2 17) (22 82 249 (37 96) (3 95) (2 17) (2 36) (2 36)			(46 68)	(421)			(7 61)	
XXII $Cl(C_6Cl_5)Pd(Pf_{1})[P(OPh)_1]$ (3 70) (26.12) (44 18) (3 70) (3 57 (26.12) 116 (41 0) (41 0) (3 6) (3 6) (26 0) (26 0) (26 0) (31 0) (46 0) (3 6) (3 6) (2 33 (2 0) (2 6) (36.19) (36.19) (36.19) (36.19) (36.19) (37 0) (37 0) (37 0) (39 0) (2 7) (2 7) (23 89) (23 89)	IXX	Cl(C ₆ Cl ₅)Pd(Pl 1 ₁)(AsPh ₁)	44 72	4 02			26 92	180
XXII $Cl(C_6Cl_5)Pd(Pfl_3)[P(OPh)_1]$ 43 31 3 57 26 1J 116 XXII $Cl(C_6Cl_5)Pd(Pfl_3)[P(OPh)_1]$ 43 94) (3 66) (26 00) (26 00) (26 00) XXIII $Cl(C_6Cl_5)Pd(Pfl_3)$ 33 72 3 52 2 33 35 53 J10 (dec) (31 67) (4 39) (2 17) (36,19) (36,19) (26 19) (2 17) (22 82 249) XXIV $(C_6F_5)(C_6Cl_5)Pd(PEl_3)_2$ 38 41 3 96 (2 17) (2 37) (23 89) (23 89)			(4418)	(3 70)			(26.12)	
XXIII Cl(C ₆ Cl ₅)Pd(PT L ₃)(DY) (3 04) (3 06) (26 00) (26 00) (33 72 3 52 2 33 35 53 310 (dec) (31 67) (3 79) (2 17) (36.19) (36.19) (XXIV (C ₆ F ₅)(C ₆ Cl ₅)Pd(PEL ₃)2 38 41 3 96 22 82 249 (37 98) (3 95) (2 36) (23 89) (2 38 9)	ІІХХ	Cl(C ₆ Cl ₅)Pd(PFt ₃)[P(OPh) ₁]	43 3 1	3 57			2613	116
XXIII Cl(C ₆ Cl ₅)Pd(PT L ₃)(DY) 33 72 3 52 2 33 35 53 310 (dec) (31 67) (3 79) (2 17) (36.19) (36.19) XXIV (C ₆ F ₅)(C ₆ Cl ₅)Pd(PEL ₃)2 249 (37 98) (3 95) (2 37 98) (3 95)			(43 04)	(3 66)			(26 00)	
(3 1 67) (3 39) (2 37) (3 6.19) (3 1.10	ихх	Cl(C6Cl ₅)Pd(PT t ₃)(py)	33 7 2	3 52	2 34		35 53	J10 (dec)
XXIV (C ₆ F ₅)(C ₆ Cl ₅)Pd(PEt ₃)2 38 44 3 96 22 82 249 (37 98) (3 95) (2 23 89)			(31 67)	(6E F)	(2 17)		(36,19)	
(37.98) (3.95) (3.95)	XXIV	(C ₆ F ₅)(C ₆ Cl ₅)Pd(PDt ₃) ₂	3841	968			22 82	249
			(37.98)	(395)			(23 89)	

432

TABLL 2

obviously be brought about by the same ligand L which is already present in the binuclear complex to afford complexes of the $X(Ar)PdL_2$ type (eq 5), or by a different ligand L' which leads to complexes of the X(Ar)PdLL' type (eq 6). Processes (5) and (6) take place under mild conditions The addition of L or L' in some cases does not require any special precautions, but in other cases it is best carried out below room temperature to prevent decomposition and precipitation of metallic palladium These complications were never observed when working at 0°C

Data for the complexes obtained according to eqs 5 and 6 are listed in Table 2.

Substitution reactions of mononuclear complexes

The ligand X of the mononuclear complexes obtained as described above, may be replaced by other anionic ligands Thus the complexes $(SCN)(C_6F_5)$ -Pd(PEt₃)₂ and Y(C₆Cl₅)Pd(PEt₃)₂ (Y = Br, I, SCN) were obtained (For analytical data see Table II)

The preparation of $(C_6Cl_5)(C_6F_5)Pd(PEt_3)_2$ according to eq 7 is noteworthy

$$Cl(C_6Cl_5)Pd(PEt_3)_2 + L_1C_6F_5 \rightarrow L_1Cl + (C_6F_5)(C_6Cl_5)Pd(PEt_3)_2$$
(7)

It is interesting that a second C_6Cl_5 group cannot be introduced into $Cl(C_6Cl_5)Pd(PEt_3)_2$ by using $L_1C_6Cl_5$. C_6Cl_5 could not be introduced into $Cl(C_6F_5)Pd(PEt_3)_2$, by use of either LiC_6Cl_5 or $ClMgC_6Cl_5$ Furthermore, it was not possible to bring about process (7) with the Grignard compound $XMgC_6F_5$, whatever excess was used Although the failure of some of the attempts could arise from steric factors, the main reason must be kinetic effects, since even $Cl(C_6Cl_5)Pd(PEt_3)_2$ does not undergo reaction with $XMgC_6H_5$ or with LiC_6H_5 .

Only one complex $(C_6F_5)(C_6Cl_5)N_1(PPh_2Me)_2$ containing both a C_6F_5 and a C_6Cl_5 group attached [5] to the same metal was previously known. In this complex the M-C distance is shorter for Ni-C₆Cl₅ than for Ni-C₆F₅ (1 905 ± 0.010 and 1.978 ± 0.009 Å respectively). This could indicate a stronger bond in the case of M-C₆Cl₅.

Conductivities and melting points

All the complexes are essentially non-conducting, their conductivities (in acetone or chloroform solution, depending on the solubility) are very low $(\Lambda_M \sim 0-1 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1})$

As will be seen from Table 1, the binuclear complexes show a good thermal stability All except two melt at high temperature (> 280° C) with decomposition, while the two complexes which melt at lower temperatures, do so without decomposition

The mononuclear complexes (see Table 2) generally melt without decomposition.

IR spectra

Both the binuclear and mononuclear complexes exhibit the bands due to the C_6F_5 group [6] (at 1635, 1505, 950 and 800 cm⁻¹) or the C_6Cl_5 group [7] (at 1320, 1295, 1230 and 675 cm⁻¹). The complex $(C_6F_5)(C_6Cl_5)Pd(PEt_3)_2$ shows

both series of vibrations. All the complexes exhibit the bands characteristic of the various ancillary ligands.

The binuclear complex $(SCN)_2(C_6Cl_5)_2Pd_2(PEt_3)_2$ shows a very clear band at 2145 cm⁻¹, i.e. in a zone which is free from other bands and the location of which practically coincides with that found for $(SCN)_2(C_6F_5)_2Pd_2(PEt_3)_2$ [1] at 2148 cm⁻¹. This is to be accepted as a reliable indication of the symmetrical arrangement of the thiocyanato-bridging groups [8].

The mononuclear complexes $(SCN)(C_6F_5)Pd(PEt_3)_2$ and $(SCN)(C_6Cl_5)Pd(PEt_3)_2$, obtained from the corresponding chlorocomplexes by substitution reactions, show the $\nu(CN)$ vibration below 2100 cm⁻¹. This indicates that the SCN group is attached to the metal via the N atom [7]. The same type of binding was also found for $(SCN)(C_6Cl_5)N1(PPh_3)_2$ [7] and $(SCN)(C_6Cl_5)-Pd(PPh_3)_2$ [7] as well as for $(SCN)(C_6F_5)Pd(PPh_3)_2$ [10]

 $(SCN)(C_6Cl_5)Pd(PEt_3)_z$ can also be prepared by adding PEt₃ to acetone solutions of the binuclear complex $(SCN)_2(C_6Cl_5)_2Pd_2(PEt_3)_2$ The IR spectrum of the resulting complex completely coincides with that prepared by substitution.

Experimental

IR spectra were recorded on a Beckman IR 20A spectrophotometer (over the range 4000–250 cm⁻¹) using Nujol mulls between polyethylene sheets Conductivities were measured in approx 5×10^{-4} M solutions with a Philips PW 9501/01 conductimeter

The C, H and N analyses were made with a Perkin—Elmer 240 microanalyzer Halogen analyses were performed as described by White [11], a few milligrams of sucrose being added to the sample to facilitate its combustion

For determination of Pd the samples were dissolved first in fuming nitric acid and then in perchloric acid, and the metal was precipitated with dimethyl-glyoxime [12]

Preparation of Cl_2PdL_2 ($L = PPh_3$, PBu_3 , $AsPh_3$ or PEt_3)

An ethanol solution of the ligand was added dropwise to an aqueous solution of K_2PdCl_{\star} . The resulting yellow precipitates were recrystallized from dichloromethane (L = PPh₃ or AsPh₃) or acetone (L = PBu₃) In the case of L = PEt₃, the initially formed reddish precipitate redissolved after completion of the addition of the ligand

Upon adding 6 N HCl, a yellow solid precipitated The mixture was stirred for 24 h. and the solid recrystallized from ethanol/water. (approx 90% yield)

Preparation of $Cl_Pd_2L_2$ ($L = PPh_3$, PEt_3 , PBu_3 or $AsPh_3$)

An ethanol solution of Cl_2PdL_2 was refluxed for 30 min with 90% of the calculated amount (according to eq 1) of $PdCl_2$ in 2N HCl solution. The resulting dark-red solution was filtered to remove a small quantity of precipitated metallic Pd. The filtrate was concentrated, and the binuclear complexes separated in 90% or even higher yields.

Preparation of $Br_2(C_6F_5)_2Pd_2L_2$ (I-III) ($L = PPh_3$, PEt_3 , PBu_3) An (3 5 1) excess of the Grignard compound $BrMg(C_6F_5)$ was added to an ether solution or suspension of $Cl_4Pd_2L_2$ The mixture was stirred for 30 min at room temperature and then refluxed for 1 h. After evaporation of the solution to dryness, warm water was added to destroy the Grignard compound The residue was extracted with acetone, and water was added to give a brown product This was extracted with ether After partial evaporation of the ether, yellow crystals were obtained, these were, in every case, a mixture of $Cl_2(C_6F_5)_2Pd_2L_2$ and $Br_2(C_6F_5)_2Pd_2L_2$ The mixture was quantitatively transformed into the bromo-derivative by treatment with an acetone solution of LiBr The solution was evaporated to dryness and repeatedly washed with water to remove all the soluble halide (40-50% yields).

For $L = AsPh_3$ the reaction with the Grignard compound resulted in the cleavage of the halogen-bridge and in the formation of mixtures which were not further studied

Preparation of $Cl_2(C_6Cl_5)_2Pd_2(PEt_3)_2$ (IV)

Dry N₂ was passed through a 250 ml flask containing 2 5 g (4 4 mmol) of $Cl_4Pd_2(PEt_3)_2$, 0.82 g of Mg and 9.64 g (33 8 mmol) of C_6Cl_6 and 40 ml of tetrahydrofuran and 40 ml of benzene were added with stirring The mixture was heated to the reflux temperature, and 2 ml of benzyl chloride were added as initiator. The refluxing was continued until the magnesium was completely dissolved. The solution was evaporated to dryness and the residue hydrolyzed to destroy the Grignard compound. The precipitate was filtered off and washed with n-hexane and then ether. The residue was extracted with dichloromethane and the resulting solution was filtered and evaporated. Pale-yellow crystals of $Cl_2(C_6Cl_5)_2Pd_2(PEt_3)_2$ were obtained upon addition of benzene (41 2% yield)

Preparation of $X_2(C_6Cl_5)_2Pd_2(PEt_3)_2$ (V-VII)

To a dichloromethane solution of 0 5 mmol of $Cl_2(C_6Cl_5)_2Pd_2(PEt_3)_2$ were added 1 1 mmol of MX (LiBr. NaI or KSCN) in 10 ml of acetone The resulting complex was in every case less soluble than the starting complex, so partial precipitation of the former was observed The mixture was evaporated to dryness, the residue was washed with water to remove the halogen of pseudohalogen and the complex was recrystallized from CH_2Cl_2/e ther (~90% yield)

Preparation of $Br(C_6F_5)PdL_2$ and $Br(C_6F_5)PdLL'$ (VIII-XIV)

The conditions for each synthesis are summarized in Table 3 The starting complex dissolved in 20 ml of the appropriate solvent After the reaction time shown, the solution was vacuum-concentrated until crystals of the end product were observed. The mononuclear complexes were generally soluble in ether, benzene, acetone, or chloroform, and insoluble in water and, in some cases, in ethanol

Preparation of $Cl(C_6Cl_5)PdL_2$ and $Cl(C_6Cl_5)PdLL'$ (XVI, XX-XXIII)

The syntheses were carried out as summarized in Table 3 Suspensions of the starting complex $Cl_2(C_6Cl_5)_2Pd_2(PEt_3)_2$ in 20–40 ml of the appropriate solvent were completely dissolved during the reaction. The resulting solution was finally vacuum-concentrated to cause crystallization of the mononuclear complexes. These are soluble in benzene, chloroform and acetone, and insoluble in ethanol and water

RI ACTION CONDITIONS	FOR THL PRI PA	RATION OF X(Ar ₃	k)PdL2 (or LL)				
Starting complex	(lonim)	ligand	(mmol)	Solvent	T (°C)	Reaction time (mun)	Yield (%)
Br2(C6F5)2Pd2(PFt3)2	0 44	PE41	0.96	ether	0	1	89
; ; ; ;	049	PPh ₃	1 06	acetone	0	0.5	76
	0 49	AsPh3	1 06	acetone	0	1	97
	0 53	P(OPh) ₃	1 06	ether	0	1	52
	080	ЪУ	1 76	penzene	0	-1	88
	0 52	umb	114	pen/one	0	-1	60
Br2(C6F5)2Pd2(Phu3)2	0 38	PBu ₃	082	ether	18	05	76
Cl2(C6Cl5)2Pd2(Pl·t3)2	1 66	PL43	310	benzone	18	2	72
1 1 1 1 1	0 60	PPh3	1 10	acetone	0	1	78
	0 50	AsPh 3	110	henzone	0	1	75
	0 50	P(OPh) ₃	1 10	acetone	0	1	31
	0 50	ЪУ	1 10	acetone	0	1	49

TABLF }

Preparation of $X(C_6Cl_5)Pd(PEt_3)_2$ (XVII-XIX)

To a solution of 0.8 mmol of $Cl(C_6Cl_5)Pd(PEt_3)_2$ in 20 ml of acetone were added 0.9 mmol of MX (LiBr, NaI, KSCN), and the mixture was stirred for 1 h at room temperature. After evaporation to dryness, the residue was washed with water to remove the halogen or pseudohalogen and the resulting residue was recrystallized from benzene/ethanol or ether/ethanol (~100% yield)

 $(SCN)(C_6F_5)Pd(PEt_3)_2$ was obtained in the same way (60% yield) starting from $Cl(C_6F_5)Pd(PEt_3)_2$.

 $(SCN)(C_6Cl_5)Pd(PEt_3)_2$ was also prepared by bridge-cleavage of $(SCN)_2 - (C_6Cl_5)_2Pd_2(PEt_3)_2$ with an excess of PEt₃ To 0 10 mmol of the binuclear complex in 10 ml of acetone were added 0 22 mmol of PEt₃ The suspension was stirred at room temperature until the complex completely dissolved After partial evaporation and addition of ethanol, white crystals formed, and were filtered off (50 0% yield)

Preparation of $(C_6F_5)(C_6Cl_5)Pd(PEt_3)_2$ (XXIV)

2 mmol of $Cl(C_6Cl_5)Pd(PEt_3)_2$ were added to a solution of 6 mmol of LiC_6F_5 in 25 ml of ether at $-78^{\circ}C$, and the mixture was stirred for 30 min at this temperature and for another 3 h at room temperature. The precipitate of lithium halide was separated from the off-white solution by centrifuging. The solution was evaporated to dryness, the residue was extracted with benzene, and the solution filtered. White crystals of the complex were obtained by partially evaporating the solution and adding ethanol (52.9% yield). They are soluble in chloroform, benzene and acetone, and insoluble in ethanol, water, and nitromethane

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