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Synthesis and Reactivity of Anionic Mono- and Binuclear Pentachlorophenyl Complexes of Palladium(II) and Platinum(II)

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Arylation with C_6Cl_5Li or C_6Cl_5MgCl of several palladium or platinum substrates leads to new mono- or binuclear complexes of type $[MR_4]^{2-}$, $[M_2(\mu\text{-}X)_2R_4]^{2-}$, or $[trans\text{-}PtCl_2R_2]^{2-}$ (M = Pd or Pt; R = C_6Cl_5; X = Cl or Br) which have been isolated as tetraalkylammonium salts. Treatment of the anionic binuclear complexes with stoichiometric amounts of the ligand L produces anionic mononuclear derivatives of the type $[cis\text{-}MClR_2L]^-$ (M = Pd or Pt; R = C_6Cl_5; L = PPh_3, PEt_3, py, or $SbPh_3$) while the use of an excess of the ligand L affords the neutral derivatives *cis*-MR_2L_2 (M = Pd or Pt; R = C_6Cl_5; L = PPh_3, PEt_3, PPh_2Me, py, or $SbPh_3$; L_2 = bpy, dpe, or dae). The reactions of the binuclear complexes $[M_2(\mu\text{-}X)_2R_4]^{2-}$ with halides or pseudohalides give rise to substitution of the bridging halides (without cleavage of the bridges) and to the formation of $[M_2(\mu\text{-}X')_2R_4]^{2-}$ (X = Cl; X′ = Br, I, or SCN). $[MR_4]^{2-}$ reacts with the appropriate amount of HCl to give high yields of the anionic binuclear complexes $[M_2(\mu\text{-}Cl)_2R_4]^{2-}$. These compounds are the first anionic palladium or platinum complexes containing the pentachlorophenyl group to be reported.

Introduction

The arylation with C_6Cl_5Li or C_6Cl_5MgX of complexes of the type MX_2L_2 (M = Pd or Pt; X = halogen; L = phosphine) normally stops after the introduction of a single C_6Cl_5 group, leading to the formation of neutral monoaryl derivatives,[1,2] whereas the reaction of an excess of the lithium derivative with a substrate of the same type, but containing an N, As, or S donor ligand, allows the preparation of neutral bis(aryl)palladium complexes, $Pd(C_6Cl_5)_2L_2$.[3,4] If L = $AsPh_3$ or tht (tetrahydrothiophen), the ancillary ligands can be replaced by phosphines. This shows clearly that the diarylation of $PdCl_2(PR_3)_2$ is not prevented for steric but for kinetic reasons. For platinum no bis(pentachlorophenyl) complex has so far been reported and only *cis*- and *trans*-$PtX(C_6Cl_5)(PEt_3)_2$ have been reported;[2] their preparation presents, however, more difficulties than that of the corresponding palladium derivatives.

Recently we have described[5] the synthesis of anionic mono- and binuclear (pentafluorophenyl)palladium and -platinum complexes and have shown how the results of the reaction are influenced by the substrates and the arylating reagent as well as the reaction conditions (temperature, ratio of reagents, and reaction time).

In this paper we present a substantial extension of the field of (pentachlorophenyl)palladium(II) and especially -platinum(II) complexes, describing the first neutral bis(pentachlorophenyl)platinum(II) derivatives of the general formulas *cis*-PtR_2L_2 (L = N, P, As, or Sb donor and *trans*-$PtR_2(tht)_2$, as well as anionic mononuclear palladium and platinum complexes of type $Q[cis\text{-}MXR_2L_2]$ (X = Cl or Br; M = Pd or Pt; L = N, P, or Sb donor) and $Q_2[trans\text{-}PtR_2Cl_2]$ (Q = NBu_4) which contain two C_6Cl_5 groups linked to each metal atom. The anionic binuclear complexes $Q_2[M(\mu\text{-}X)R_2]_2$ (M = Pd or Pt; X = Cl, Br, I, or SCN; Q = NBu_4 or NEt_4) and the anionic mononuclear complexes $Q_2[MR_4]$ with four C_6Cl_5 groups are reported.

Results and Discussion

Synthesis of $Q_2[M(C_6Cl_5)_4]$ (M = Pd, Pt; Q = NBu_4, NEt_4). Several substrates have been tried for preparing anionic complexes of type $Q_2[M(C_6Cl_5)_4]$. Prolonged treatment (~24 h) of $K_2[PdCl_4]$ or $K_2[PtCl_4]$ (in ether solution) with C_6Cl_5Li in 1:8 ratio gave nothing but the unchanged starting compounds, while the reaction of $PdCl_2$ with C_6Cl_5Li resulted in decomposition and precipitation of metallic palladium, as has also previously been found for the reaction with C_6F_5Li.[5] The reaction of $PtCl_2$ with C_6Cl_5Li is described below.

The reaction of *trans*-$PdCl_2(tht)_2$ with an excess of C_6Cl_5Li (1:5 ratio) permitted isolation of the neutral disubstituted complex *trans*-$Pd(C_6Cl_5)_2(tht)_2$,[4] while the formation of any anionic species arising from the displacement of the neutral ligand tht could not be detected during the process. This shows C_6Cl_5Li to be less reactive than C_6F_5Li since under similar conditions the reaction with the latter leads to isolation of the anionic mononuclear complex $(NBu_4)_2[Pd(C_6F_5)_4]$.[5]

Nevertheless, treatment of $(NBu_4)_2[Pd(\mu\text{-}Br)Br_2]_2$ with C_6Cl_5Li (in diethyl ether, 1:14 molar ratio) allowed the isolation of $(NBu_4)_2[Pd(C_6Cl_5)_4]$ (I; 64% yield), after addition of NBu_4Br, along with small amounts of the binuclear complex $(NBu_4)_2[Pd(\mu\text{-}Br)(C_6Cl_5)_2]_2$ (VII; 9% yield; yields always referred to Pd or Pt in the starting compound) seemingly formed as an intermediate in the synthesis of I (see eq 1). In fact, VII reacted with C_6Cl_5Li,

$$Q_2[Pd(\mu\text{-}X)X_2]_2 + C_6Cl_5Li(\text{excess}) \rightarrow$$

$$Q_2[Pd(\mu\text{-}X)(C_6Cl_5)_2]_2 \xrightarrow{+C_6Cl_5Li} 2Q_2[Pd(C_6Cl_5)_4] \quad (1)$$

$$Q = NBu_4,\ X = Br;\ Q = NEt_4,\ X = Cl$$

yielding I after addition of NBu_4Br. Similarly, $(NEt_4)_2[Pd(\mu\text{-}Cl)Cl_2]_2$ reacted with C_6Cl_5Li (in diethyl ether, 1:20 ratio) to give II (13% yield) and $(NEt_4)_2[Pd(\mu\text{-}Cl)(C_6Cl_5)_2]_2$ (VI; 32% yield) (eq 1). $(NBu_4)_2[Pt(C_6Cl_5)_4]$ (III; 47% yield) has been prepared by reacting $PtCl_2$ with C_6Cl_5Li (in diethyl ether, 1:10 ratio) and subsequent addition of $(NBu_4)Br$; small amounts of $(NBu_4)_2[trans\text{-}PtCl_2(C_6Cl_5)_2]$

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(IV; 9% yield) also were formed during this process (eq 2).

$$\mathrm{PtCl_2 + C_6Cl_5Li \xrightarrow{+(NBu_4)Br}}$$
$$\mathrm{(NBu_4)_2[\mathit{trans}\text{-}PtCl_2(C_6Cl_5)_2] + (NBu_4)_2[Pt(C_6Cl_5)_4]} \quad (2)$$

Moreover, $K_2[PtCl_4]$ did not react with an excess of C_6Cl_5Li, whereas the reaction between *trans*-$PtCl_2(tht)_2$ and C_6Cl_5Li (1:3.5 ratio) afforded *trans*-$Pt(C_6Cl_5)_2(tht)_2$ (XXXI; 18% yield). Although anionic species seemingly also were formed during this process, addition of $(NBu_4)Br$ or $Cl(Ph_3P{=}N{=}PPh_3)$ to the solution led to the crystallization of mixtures which could not be separated.

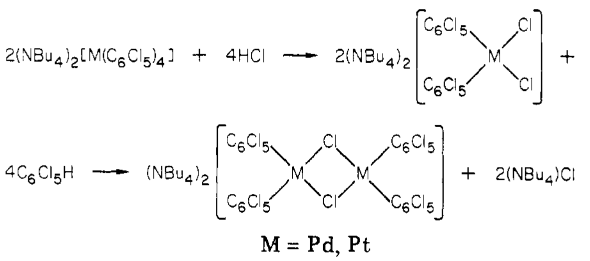
Synthesis of the Binuclear Complexes $(NBu_4)_2[M(\mu\text{-}X)(C_6Cl_5)_2]_2$. Although $(NBu_4)_2[Pd(\mu\text{-}Br)(C_6Cl_5)_2]_2$ could be obtained by reacting $(NBu_4)_2[Pd(\mu\text{-}X)X_2]_2$ with C_6Cl_5Li (eq 1), the process gave only low yields, which could be improved if $K_2[PdCl_4]$ or $PdCl_2$ were used as substrates and C_6Cl_5MgCl was employed as the arylating agent (1:4–6 ratio). Treatment of the reaction mixture with an excess of LiBr and addition of $(NBu_4)Br$ allowed the isolation of $(NBu_4)_2[Pd(\mu\text{-}Br)(C_6Cl_5)_2]_2$ (VII; 41% or, respectively, 54% yield).

Moreover, $(NBu_4)_2[Pd(\mu\text{-}Cl)(C_6Cl_5)_2]_2$ (V; 50% yield) resulted from the arylation of $PdCl_2$ with $(NBu_4)_2[Pd(C_6Cl_5)_4]$ (I) in refluxing acetone, according to (eq 3).

$$\mathrm{(NBu_4)_2[Pd(C_6Cl_5)_4] + PdCl_2 \rightarrow (NBu_4)_2[Pd(\mu\text{-}Cl)(C_6Cl_5)_2]_2} \quad (3)$$

Much poorer yields were obtained if these processes were carried out with platinum substrates. Thus the arylation of $PtCl_2$ with C_6Cl_5MgCl (1:5 ratio; 18 h reflux) and subsequent addition of an excess of $(NBu_4)Br$ gave $(NBu_4)_2[Pt(\mu\text{-}Br)(C_6Cl_5)_2]_2$ (XI) but in only 17% yield; whereas $(NBu_4)_2[Pt(C_6Cl_5)_4]$ reacted with $PtCl_2$ in refluxing acetone to give mainly the unchanged starting products along with $(NBu_4)_2[Pt(\mu\text{-}Cl)(C_6Cl_5)_2]_2$ (X; 18% yield). The yields of X could not be improved by more prolonged refluxing, which resulted in decomposition of the substrate or the reaction products and to the formation of metallic platinum.

Nonetheless, complexes V and X could be synthetized in high yield (86 and 87%, respectively) by reacting complexes I or III in acetone/ethanol with a ~2% aqueous solution of HCl (1:2 molar ratio), according to eq 4. The process, which causes cleavage of the M–C bonds, should lead to $(NBu_4)_2[\mathit{cis}\text{-}MCl_2(C_6Cl_5)_2]$ as an intermediate, which, however, could not be isolated and reacted further, under separation of $(NBu_4)Cl$, to give the binuclear species.



(4)

M = Pd, Pt

If the reactions described above were carried out with stoichiometric amounts of HCl (1:1 ratio), it was not possible to isolate $(NBu_4)_2[MCl(C_6Cl_5)_3]$ because cleavage of the M–C bonds is not selective and the reaction leads to a mixture which seemingly contains $(NBu_4)_2[M(C_6Cl_5)_4]$ and $(NBu_4)_2[M(\mu\text{-}Cl)(C_6Cl_5)_2]_2$ and in which the presence of $(NBu_4)_2[MCl(C_6Cl_5)_3]$ cannot be excluded either, although the very similar solubility of all these species prevented the isolation of the latter. Under the above-described conditions, process 4 is the most advantageous hitherto reported method for the synthesis of this type of anionic binuclear palladium and platinum complexes.

Reactions of the Anionic Binuclear Complexes. Treatment of these anionic binuclear chloro complexes with alkali-metal salts (LiBr, NaI, or KSCN), according to eq 5, resulted in substitution of the bridging group, without cleavage of the bridges nor of the M–C_6Cl_5 bonds.

$$\mathrm{(NBu_4)_2[M(\mu\text{-}X)(C_6Cl_5)_2]_2 + M'X' \rightarrow (NBu_4)_2[M(\mu\text{-}X')(C_6Cl_5)_2]_2 + M'X} \quad (5)$$

M = Pd, X = Cl, X′ = Br (VII), I (VIII); M = Pt, X = Cl, X′ = Br (XI), I (XII), SCN (XIII)

Nonetheless, for M = Pd and X′ = SCN the expected binuclear complex was not formed because of decomposition reactions which produced a mixture of products, which has not been investigated. Complex IX could, however, be obtained (69% yield) by treatment of solutions of $(NBu_4)[Pd(\mu\text{-}I)(C_6Cl_5)_2]_2$ (VIII) with AgSCN. On the other hand, the reaction of $(NBu_4)_2[M(\mu\text{-}Cl)(C_6Cl_5)_2]_2$ with neutral ligands (1:2 ratio) gives rise to the cleavage of the bridges and to the formation of the anionic complexes $(NBu_4)[\mathit{cis}\text{-}MCl(C_6Cl_5)_2L]$, according to eq 6, while addition of larger amounts of the neutral ligand L (1:4) or treatment of $(NBu_4)[MCl(C_6Cl_5)_2L]$ with L (1:1) allowed the isolation of the neutral mononuclear complexes *cis*-$M(C_6Cl_5)_2L_2$ (M = Pd, L = PEt_3 (XVIII), PPh_2Me (XIX), PPh_3 (XX), py (XXI), $SbPh_3$ (XXII), L_2 = bpy (XXIII); M = Pt, L = PPh_2Me (XXIV), PPh_3 (XXV), py (XXVI), $SbPh_3$ (XXVII), L_2 bpy (XXVIII), 1,2-bis(diphenylphosphino)ethane (dpe) (XXIX), 1,2-bis(diphenylarsino)ethane (dae) (XXX)).

$$\mathrm{(NBu_4)_2[M(\mu\text{-}Cl)(C_6Cl_5)_2]_2 + 2L \rightarrow 2(NBu_4)[\mathit{cis}\text{-}MCl(C_6Cl_5)_2L]} \quad (6)$$

M = Pd, X = Cl, L = PPh_3 (XIV); M = Pt, X = Cl, L = PPh_3 (XV), py (XVI), $SbPh_3$ (XVII)

Thus, when the proportions of the reactants are carefully adjusted, two types of complexes can be obtained: the anionic complexes *cis*-$[MX(C_6Cl_5)_2L]^-$ (XIV–XVII) and the neutral *cis*-$[M(C_6Cl_5)_2L_2]$ (XVIII–XXX). Their IR data (see below) indicate that all these complexes are the cis isomers. Although the neutral complexes *trans*-$Pd(C_6Cl_5)_2L_2$ with two C_6Cl_5 groups attached to each metal atom have been described[4] previously, the complexes described above are the first platinum derivatives which contain two C_6Cl_5 groups. Moreover, although the two platinum complexes $(NBu_4)_2[\mathit{trans}\text{-}PtCl_2(C_6Cl_5)_2]$ (IV) and *trans*-$Pt(C_6Cl_5)_2(tht)_2$ (XXXI) with the two C_6Cl_5 group in trans position could be prepared, attempts to obtain complexes of the series *trans*-$Pt(C_6Cl_5)_2L_2$ were unsuccessful since prolonged refluxing of IV or XXXI with an excess of the neutral ligand L (L = PPh_3 or PEt_3) did not result in a reaction.

The analytical results (C, H, N, and Cl), melting points, and conductivities for the new complexes are listed in Table I. For the complexes which have been obtained by several processes all the isolated samples gave satisfactory analyses. The syntheses to which the analytical data belong are marked by an asterisk (see Experimental Section). The conductivities of the complexes, in acetone solutions, are those expected for the electrolytes (1:1) and (2:1) or for the nonelectrolytes.[5,6] All the complexes are stable both in the solid state and in solution, although some decompose in refluxing ethanol.

IR Spectra. All the complexes show absorptions assignable to the C_6Cl_5 group,[4,7-9] some of which are of

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(7) Maslowsky, E. jun., "Vibrational Spectra of Organometallic Compounds"; Wiley: New York, 1977; p 437.

Table I. Analytical Results,[a] Conductivities, and Melting Points for the Novel Complexes[b]

		C		H		N		Cl[e]			Λ_M, Ω^{-1} cm^2 mol^{-1}
	complex	calcd	found	calcd	found	calcd	found	calcd	found	mp, °C	
I	$Q_2[Pd(C_6Cl_5)_4]$	42.33	42.18	4.53	4.39	1.73	1.96	44.63	45.45	205 dec	199
II	$Q'_2[Pd(C_6Cl_5)_4]$	35.20	35.54	2.93	2.82	2.05	1.96	51.96	51.06	234 dec	136.7
III	$Q_2[Pt(C_6Cl_5)_4]$	40.09	40.33	4.29	3.95	1.67	1.96	42.28	41.18	220 dec	180
IV	$Q_2[$*trans*-$PtCl_2(C_6Cl_5)_2]$	42.29	42.41	5.80	5.76	2.24	2.41	34.10	33.65	199	167
V	$Q_2[Pd(\mu\text{-}Cl)(C_6Cl_5)_2]_2$	38.06	38.02	4.08	3.90	1.59	1.70	44.16	43.16	203 dec	153
VI	$Q'_2[Pd(\mu\text{-}Cl)(C_6Cl_5)_2]_2$	31.16	31.46	2.59	2.41	1.81	1.81	50.65	49.81	223 dec	216.7
VII	$Q_2[Pd(\mu\text{-}Br)(C_6Cl_5)_2]_2$	36.25	36.53	3.88	3.42	1.51	1.37	*c*		144 dec	150.5
VIII	$Q_2[Pd(\mu\text{-}I)(C_6Cl_5)_2]_2$	34.51	34.43	3.72	3.66	1.43	1.43	*c*		195 dec	182
IX	$Q_2[Pd(\mu\text{-}SCN)(C_6Cl_5)_2]_2$	38.45	38.32	3.97	3.89	3.09	3.15	39.14	39.06	213 dec	193
X	$Q_2[Pt(\mu\text{-}Cl)(C_6Cl_5)_2]_2$	34.60	34.29	3.70	3.67	1.44	1.59	40.13	39.85	195 dec	171
XI	$Q_2[Pt(\mu\text{-}Br)(C_6Cl_5)_2]_2$	33.12	33.59	3.57	3.48	1.37	0.95	*c*		191 dec	200
XII	$Q_2[Pt(\mu\text{-}I)(C_6Cl_5)_2]_2$	31.62	31.81	3.38	3.17	1.31	1.34	*c*		203 dec	173
XIII	$Q_2[Pt(\mu\text{-}SCN)(C_6Cl_5)_2]_2$	35.05	35.34	3.65	3.55	2.82	3.16	35.66	34.42	245 dec	180
XIV	$Q[$*cis*-$PdCl(C_6Cl_5)_2PPh_3]$	48.24	48.13	4.45	4.48	1.22	1.33	34.05	34.45	163 dec	95
XV	$Q[$*cis*-$PtCl(C_6Cl_5)_2PPh_3]$	44.77	44.72	4.13	4.10	1.13	0.93	31.66	31.07	125 dec	95
XVI	$Q[$*cis*-$PtCl(C_6Cl_5)_2py]$	37.75	37.52	3.90	3.87	2.66	2.62	37.12	36.67	207	84
XVII	$Q[$*cis*-$PtCl(C_6Cl_5)_2SbPh_3]$	41.70	42.07	3.87	3.82	1.05	1.03	29.48	29.36	173 dec	86
XVIII	*cis*-$Pd(C_6Cl_5)_2(PEt_3)_2$	34.25	34.30	3.56	3.57			42.13	41.68	257 dec	no cond
XIX	*cis*-$Pd(C_6Cl_5)_2(PPh_2Me)_2$	45.39	45.51	2.60	2.71			35.25	35.74	168 dec	no cond
XX	*cis*-$Pd(C_6Cl_5)_2(PPh_3)_2$	51.03	51.33	2.67	2.90			31.38	31.12	200	no cond
XXI	*cis*-$Pd(C_6Cl_5)_2py_2$	34.60	34.81	1.31	1.68	3.67	3.48	46.44	45.91	237 dec	no cond
XXII	*cis*-$Pd(C_6Cl_5)_2(SbPh_3)_2$	43.96	44.45	2.28	2.29			27.03	27.46	200 dec	no cond
XXIII	*cis*-$Pd(C_6Cl_5)_2bpy$	34.70	34.40	1.05	1.11	3.67	3.56	46.50	45.56	334 dec	no cond
XXIV	*cis*-$Pt(C_6Cl_5)_2(PPh_2Me)_2$	41.71	41.72	2.39	2.48			32.41	31.40	233 dec	no cond
XXV	*cis*-$Pt(C_6Cl_5)_2(PPh_3)_2$	47.34	47.54	2.46	2.61			29.15	28.54	234 dec	no cond[d]
XXVI	*cis*-$Pt(C_6Cl_5)_2py_2$	31.02	30.61	1.18	1.19	3.28	3.13	41.60	41.05	204 dec	no cond[d]
XXVII	*cis*-$Pt(C_6Cl_5)_2(SbPh_3)_2$	41.18	40.99	2.15	2.32			25.33	24.98	190 dec	no cond[d]
XXVIII	$Pt(C_6Cl_5)_2bpy$	31.07	31.29	0.94	1.39	3.29	3.43	41.71	41.20	281 dec	no cond[d]
XXIX	$Pt(C_6Cl_5)_2dpe$	41.78	42.06	2.21	2.45			32.46	31.26	290 dec	no cond[d]
XXX	$Pt(C_6Cl_5)_2dae$	38.70	39.21	2.05	2.28			30.08	29.19	184 dec	no cond[d]
XXXI	*trans*-$Pt(C_6Cl_5)_2(tht)_2$	27.59	27.50	1.83	1.80			40.79	40.72	273 dec	no cond

[a] Calculated values in parentheses. [b] Q = NBu_4 and Q′ = NEt_4. [c] Cl could not be determined owing to the presence of other halogens. [d] Conductivities determined in 3×10^{-4} M solution because of low solubility. [e] In some cases the exact determination of Cl was not possible because of difficult combustion of the samples.

Table II. Absorption Assignable to the X-Sensitive Mode or to the Stretching Vibration ν(M–C)

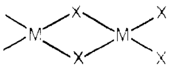
	complex	ν(X-sensitive)	ν(M–C)	
I	$Q_2[Pd(C_6Cl_5)_4]$	815 (s)	595 (s), 585 (m)	*a*
II	$Q'_2[Pd(C_6Cl_5)_4]$	815 (d)	602 (s), 585 (s)	*a*
III	$Q_2[Pt(C_6Cl_5)_4]$	820 (m)	590 (m)	*a*
IV	$Q_2[$*trans*-$PtCl_2(C_6Cl_5)_2]$	820 (m)	600 (m)	*a*
V	$Q_2[Pd(\mu\text{-}Cl)(C_6Cl_5)_2]_2$	835, 825 (m)	620, 610 (m)	*b*
VI	$Q'_2[Pd(\mu\text{-}Cl)(C_6Cl_5)_2]_2$	837, 830 (m)	620, 610 (m)	*b*
VII	$Q_2[Pd(\mu\text{-}Br)(C_6Cl_5)_2]_2$	832 (w), 825 (h)	618, 610 (m)	*b*
VIII	$Q_2[Pd(\mu\text{-}I)(C_6Cl_5)_2]_2$	830, 825 (m)	610, 600 (s)	*b*
IX	$Q_2[Pd(\mu\text{-}SCN)(C_6Cl_5)_2]_2$	832, 825 (m)	615, 605 (m)	*b*
X	$Q_2[Pt(\mu\text{-}Cl)(C_6Cl_5)_2]_2$	845, 835 (w)	633, 625 (m)	*b*
XI	$Q_2[Pt(\mu\text{-}Br)(C_6Cl_5)_2]_2$	845, 835 (w)	631, 625 (s)	*b*
XII	$Q_2[Pt(\mu\text{-}I)(C_6Cl_5)_2]_2$	842, 833 (w)	630, 620 (s)	*b*
XIII	$Q_2[Pt(\mu\text{-}SCN)(C_6Cl_5)_2]_2$	842, 833 (w)	630, 620 (s)	*b*
XIV	$Q[$*cis*-$PdCl(C_6Cl_5)_2PPh_3]$	833, 825 (m)	613, 605 (m)	*c*
XV	$Q[$*cis*-$PtCl(C_6Cl_5)_2PPh_3]$	840, 830 (w)	*f*	*c*
XVI	$Q[$*cis*-$PtCl(C_6Cl_5)_2py]$	845, 835 (w)	630, 625 (s)	*c*
XVII	$Q[$*cis*-$PtCl(C_6Cl_5)_2SbPh_3]$	840, 830 (w)	625, 610 (m)	*c*
XVIII	*cis*-$Pd(C_6Cl_5)_2(PEt_3)_2$	830, 825 (m)	605, 600 (m)	*d*
XIX	*cis*-$Pd(C_6Cl_5)_2(PPh_2Me)_2$	828, 820 (m)	610, 600 (m)	*d*
XX	*cis*-$Pd(C_6Cl_5)_2(PPh_3)_2$	820, 825 (m)	610, 600 (m)	*d*
XXI	*cis*-$Pd(C_6Cl_5)_2py_2$	838, 830 (m)	619, 610 (m)	*d*
XXII	*cis*-$Pd(C_6Cl_5)_2(SbPh_3)_2$	830, 825 (m)	610, 602 (m)	*d*
XXIII	*cis*-$Pd(C_6Cl_5)_2bpy$	839, 832 (m)	620, 610 (m)	*d*
XXIV	*cis*-$Pt(C_6Cl_5)_2(PPh_2Me)_2$	840, 830 (w)	620, 610 (w)	*d*
XXV	*cis*-$Pt(C_6Cl_5)_2(PPh_3)_2$	840, 835 (m)	620, 612 (m)	*d*
XXVI	*cis*-$Pt(C_6Cl_5)_2py_2$	847, 840 (m)	630, 623 (m)	*d*
XXVII	*cis*-$Pt(C_6Cl_5)_2(SbPh_3)_2$	840, 832 (w)	620, 610 (w)	*d*
XXVIII	$Pt(C_6Cl_5)_2bpy$	847, 842 (m)	630, 622 (m)	*d*
XXIX	$Pt(C_6Cl_5)_2dpe$	*f*	615, 607 (m)	*d*
XXX	$Pt(C_6Cl_5)_2dae$	838, 830 (w)	620, 610 (m)	*d*
XXXI	*trans*-$Pt(C_6Cl_5)_2(tht)_2$	833 (m)	605 (m)	*e*

[a-f] Symmetry group and number of expected of absorptions: (*a*) D_{4h}, 1(Eu); (*b*) D_{2h}, 2(B_{2u} + B_{3u}); (*c*) C_s, 2(2A′); (*d*) C_{2v}, 2(A_1 + B_1); (*e*) D_{2h}, 1(B_{2u}); (*f*) vibrations due to other ligands observed in this range do not allow any assignment to be made.

structural interest, as has been discussed for the analogous C_6F_5 derivatives.[5] The bands observed in the 850–820 cm^{-1} region are assigned to a X-sensitive mode[10] involving X–C_6Cl_5 stretching, while the absorptions near 600 cm^{-1} are assigned[8] to the M–C vibration. Table II lists the absorption bands observed for our complexes in these regions, which mostly coincide with the expected ones. $(NBu_4)_2[Pd(C_6Cl_5)_4]$ and $(NEt_4)_2[Pd(C_6Cl_5)_4]$ (D_{4h}) show, as expected, a single absorption assignable to the X-sensitive mode but exhibit two bands near 600 cm^{-1} (assignable to the ν(M–C) (E_u) stretch, both in the solid state and in solution, instead of the expected single one (Table II). Since repeated recrystallization did not change this situation and all the samples gave good analytical results, no impurity can be responsible for the second band. Nonetheless, $(NBu_4)_2[Pt(C_6Cl_5)_4]$ shows a single absorption at both ~800 and ~600 cm^{-1}. In all the other cases the observed spectra coincide with the expected ones (Table II). The complexes $M(C_6Cl_5)_2L_2$ (XVIII–XXX) show two absorptions in each of these regions, which confirms their cis configuration, while $Pt(C_6Cl_5)_2(tht)_2$ (XXXI) exhibits a single band in each of these regions, thus pointing to a trans configuration, as we had previously found[4] for the complexes *trans*-$Pd(C_6Cl_5)_2L_2$.

The anionic complexes $(NBu_4)[MX(C_6Cl_5)_2L]$ show also double bands in both regions. Moreover, because two IR-active modes (2A′ or $A_1 + B_1$) are predicted for both symmetries (C_s for the cis isomers and C_{2v} for the trans isomers), no structural assignment is possible. Since their reactions with neutral ligands L lead to neutral cis complexes, they are thought to be also the cis isomers.

As for the vibration arising from other ligands: $(NBu_4)_2$[*trans*-$PtCl_2(C_6Cl_5)_2$] (IV) shows a single band at 310 cm^{-1} assignable to the M–Cl stretching, thus confirming its trans configuration (see Table II). V, VI, and X exhibit broad or double bands at 250, 250, and 270–260 cm^{-1}, respectively, assignable to the



moiety, could not be observed for the Br and I derivatives in which it should appear beyond the range of our instrument. For IX and XIII the ν(CN) stretching vibration is located at 2160 (s) and 2164 (s) cm^{-1}, respectively. XIV, XV, and XVI show absorptions arising from ν(M–Cl) at 280 (m), 290 (m), and 290 (m) cm^{-1}, respectively. In the case of XVII this vibration is masked by others arising from internal absorptions of the $SbPh_3$ group. The absorptions assignable to L are detected for all complexes which contains a neutral ligand L. It seems noteworthy that XX and XXV exhibit four absorptions, due to PPh_3, in the 550–500 cm^{-1} region, thus confirming that their two PPh_3 groups are mutually cis.[11]

Experimental Section

C, H, and N analyses, conductance, and melting point determination were performed as described elsewhere.[5] Infrared spectra were recorded on a Perkin-Elmer 599 spectrophotometer. Quantitative Cl analyses were made as described by White,[12] a few milligrams of sucrose being added to facilitate combustion.[13]

The palladium and platinum starting complexes were prepared as described elsewhere.[5] C_6Cl_5Li was obtained as described in ref 14 and was directly used without further isolation. C_6Cl_5MgCl was prepared by reacting C_6Cl_6 with Mg and by using benzyl bromide as the initiator.[15] Complexes VI, VII, VIII, X, XVI, XIX, XXIV, XXVII, and XXX crystallize as solvates, and the solvent is eliminated without decomposition, by heating at ~80 °C for ca. 20 h.

Synthesis of $Q_2[M(C_6Cl_5)_4]$ (M = Pd or Pt). (a) Reaction of $K_2[MCl_4]$ with C_6Cl_5Li. The reaction of $K_2[MCl_4]$ with RLi (1:8 molar ratio, treatment up to 24 h) gave in every case the unchanged $K_2[MCl_4]$.

(b) Reaction of $(NBu_4)_2[Pd(\mu\text{-}Br)Br_2]_2$ with C_6Cl_5Li (1:14 Molar Ratio). $(NBu_4)_2[Pd(\mu\text{-}Br)Br_2]_2$ (1 g, 0.852 mmol) was added to an ether solution of C_6Cl_5Li (11.92 mmol) at −78 °C, and the mixture was allowed to warm to room temperature while stirring was continued for 17 h. Moist air was passed through the system to destroy the excess of C_6Cl_5Li, and the solution was evaporated to dryness. The residue was extracted with acetone and filtered, and the filtrate was concentrated to a few milliliters. Addition of 10 mL of ethanol caused crystallization of I. The yield of I was improved by addition of NBu_4Br (0.54 g, 1.67 mmol) to the mother liquor; total yield of I[16] 64%.

The remaining solution was concentrated almost to dryness and washed with hexane, and H_2O was added to precipitate the yellow complex VII, which was recrystallized from CH_2Cl_2/2-propanol (9% yield).

(c) Reaction of $(NBu_4)_2[Pd(\mu\text{-}Br)(C_6Cl_5)_2]_2$ with C_6Cl_5Li (1:10 Molar Ratio). $(NBu_4)_2[Pd(\mu\text{-}Br)(C_6Cl_5)_2]_2$ (0.3 g, 0.16 mmol) reacted with C_6Cl_5Li in ether (1.6 mmol), using the same conditions as described in b, yielding I (60%) after addition of NBu_4Br (0.10 g).

(d) Reaction of $(NEt_4)_2[Pd(\mu\text{-}Cl)Cl_2]_2$ with C_6Cl_5Li. $(NEt_4)_2[Pd_2Cl_6]$ (0.6 g, 0.87 mmol) was reacted with C_6Cl_5Li (17.4 mmol), and the workup was continued as for b (see above) to achieve the crystallization of complex II[16] (13% yield). The mother liquor was evaporated to dryness, the residue was treated with ethanol, and the solution was filtered. NEt_4Cl (0.288 g, 1.74 mmol) was added to the filtrate, and the solution was again filtered and left standing, causing VI to crystallize (0.43 g, 32% yield).

(e) Reaction of $PtCl_2$ with C_6Cl_5Li. Dry and finely powdered $PtCl_2$ (0.33 g, 1.24 mmol) was added to a solution of C_6Cl_5Li (13.209 mmol) in 65 mL of ether at −66 °C (~1:10 molar ratio). The solution was stirred for 5 h while it was allowed to warm to room temperature. In an air stream it was evaporated to dryness and the residue was extracted with CH_2Cl_2. The resulting solution was filtered. The filtrate was again evaporated to dryness, the residue was dissolved in methanol, and NBu_4Br (0.80 g, 2.488 mmol) was added. A few minutes of stirring resulted in crystallization of III,[16] which was filtered and washed repeatedly with hexane (47% yield).

The residue remaining after the extraction with CH_2Cl_2 was treated with acetone to give a suspension which was filtered and evaporated to dryness. The resulting residue was extracted with 2-propanol, $(NBu_4)Br$ (0.43 g, 1.33 mmol) was added, and the solution was partially evaporated to crystallize IV[16] (9% yield).

Decreasing the $PtCl_2$:C_6Cl_5Li ratio (1:7; 1:5) or the reaction time, with workup as above, did not lead to the expected improvement of the yield of IV but to a lower yield of III. Moreover, the reaction between $PdCl_2$ and C_6Cl_5Li, carried out under analogous conditions, led to decomposition and formation of metallic palladium, while below 0 °C no reaction took place.

Synthesis of $Q_2[M(\mu\text{-}X)(C_6Cl_5)_2]_2$. (a) Reaction of $K_2[PdCl_4]$ with C_6Cl_5MgCl. A mixture of $K_2[PdCl_4]$ (0.972 g, 2.9 mmol), Mg (0.41 g, 17 mmol), C_6Cl_6 (4.85 g, 17 mmol), 2 mL of benzyl bromide, 30 mL of THF, and 30 mL of benzene was refluxed for 4 h. The excess of the Grignard compound was hydrolyzed with 5 mL of water, and the solution was evaporated

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[16] Yields always referred to Pd or Pt in the starting compound.

to dryness. The residue was extracted with acetone, the solution was filtered, and the filtrate was treated (for 8 h at room temperature) with an excess of LiBr (0.78 g, 9 mmol). Evaporation to dryness gave a residue which was washed with water and extracted with ethanol. Addition of $(NBu_4)Br$ (0.91 g, 2.9 mmol), evaporation to dryness, and extraction with CH_2Cl_2 led to a solution to which dry $MgSO_4$ was added. Filtration and evaporation almost to dryness, followed by addition of 50 mL of ethanol, resulted in crystallization of VII (41% yield).

(b) Reaction of $PdCl_2$ with C_6Cl_5MgCl. To a solution of C_6Cl_5MgCl (22.5 mmol) in THF/benzene, prepared as in a, was added $PdCl_2$ (1 g, 5.63 mmol), and the mixture was refluxed for 7 h. The excess of the Grignard compound was hydrolyzed in air. The solution was evaporated to dryness, the residue was extracted with 50 mL of MeOH, and the resulting solution was filtered. The filtrate was stirred for 24 h with LiBr (1.45 g, 16.7 mmol), concentrated to 30 mL, and set aside for 20 h at -25 °C. The precipitate that formed (mainly LiBr and C_6Cl_5H) was filtered. Addition of $(NBu_4)Br$ (1.81 g, 5.63 mmol) to the filtrate led to instantaneous precipitation of VII,[16] which was recrystallized from CH_2Cl_2/2-propanol (54% yield).

(c) Reaction of $PtCl_2$ with C_6Cl_5MgCl. $PtCl_2$ (0.35 g, 1.31 mmol) was added to a solution of C_6Cl_5MgCl (6.55 mmol) in 40 mL of THF, and the mixture was refluxed for 18 h. After being hydrolyzed in an air stream, the suspension was evaporated to dryness. The residue was treated with 50 mL of MeOH and set aside for 12 h at -20 °C. Filtration and addition of $(NBu_4)Br$ (0.92 g, 2.85 mmol) gave a solution which was again filtered and evaporated to dryness. The residue was successively washed with hexane, water, and hexane and finally stirred with diethyl ether for 24 h. Partial evaporation led to the crystallization of XI (17% yield), which was washed with cyclohexane.

(d) Reaction of $Q_2[M(C_6Cl_5)_4]$ with MCl_2. (i) M = Pd and Q = NBu_4. $Q_2[Pd(C_6Cl_5)_4]$ (0.85 g, 0.535 mmol) was dissolved in 120 mL of acetone, and $PdCl_2$ (0.104 g, 0.588 mmol) was added. After 12 h of reflux and 15 h of stirring at room temperature, the solution was filtered and concentrated to ~5 mL and 15 mL of MeOH was added while the stirring was continued, in order to crystallize V.[16] Subsequent evaporation of the mother liquor led to the crystallization of more of V (overall yield 50%).

(ii) M = Pd and Q = NEt_4. Working under the conditions described in i led to VI[16] (56% yield).

(iii) M = Pt and Q = NBu_4. Finely powdered $PtCl_2$ (0.057 g, 0.215 mmol) was added to a solution of $Q_2[Pt(C_6Cl_5)]_4$ (0.25 g, 0.149 mmol) in 50 mL of acetone. After 8 h of reflux and 20 h of stirring at room temperature, the solution was filtered and the filtrate was evaporated almost to dryness. Addition of 20 mL of MeOH led to the crystallization of the starting complex III (34% yield). The mother liquor was treated with 15 mL of 2-propanol and evaporated almost to dryness to crystallize X (18% yield).

(e) Reaction of $(NBu_4)_2[M(C_6Cl_5)_4]$ with HCl. To a solution of $(NBu_4)_2[M(C_6Cl_5)_4]$ (0.2 g (0.125 mmol) for M = Pd or 0.9 g (0.537 mmol) for M = Pt) in 20 mL of acetone and 50 mL of ethanol was added HCl (aqueous; 0.464 M) in exactly 1:2 molar ratio (0.54 mL for the palladium complex and 2.31 mL for the platinum one), and the mixture was stirred for 2 h (M = Pd) or for 20 h (M = Pt). For M = Pd the solution was concentrated to ~5 mL and the resulting precipitate V was filtered and washed with 2-propanol and hexane (86% yield). For M = Pt the solution was concentrated to ~20 mL and 2-propanol was added to crystallize X,[16] which was filtered and washed with 2-propanol and hexane (87% yield).

(f) Substitution Reactions of X in $(NBu_4)_2[M(\mu\text{-}X)(C_6Cl_5)_2]_2$. (i) M = Pd, X = Cl, and X′ = I. $(NBu_4)_2[Pd(\mu\text{-}Cl)(C_6Cl_5)_2]_2$ (V) (0.2 g, 0.114 mmol) was dissolved in 35 mL of acetone, and NaI (0.034 g, 0.228 mmol) was added. The suspension was stirred for 15 h at room temperature, filtered, and concentrated to dryness, whereafter the residue was washed with MeOH. Treatment with CH_2Cl_2 and addition of MeOH (10 mL) led to the crystallization of VIII[16] (58% yield). $(NBu_4)_2[Pd(\mu\text{-}SCN)(C_6Cl_5)_2]_2$ (IX)[16] (69% yield) was obtained from $(NBu_4)_2[Pd(\mu\text{-}I)(C_6Cl_5)_2]_2$ (0.114 mmol) and AgSCN (0.228 mmol).

(ii) M = Pt, X = Cl, and X′ = Br, I, and SCN. Treatment of $(NBu_4)_2[Pt(\mu\text{-}Cl)(C_6Cl_5)_2]_2$ (0.2 g, 0.103 mmol), 40 mL of MeOH, and 10 mL of acetone with ~0.25 mmol of KX (X = Br, I, SCN) for ~5 h at reflux (X = Br, I) or 2 h at room temperature (X = SCN) and workup as in i yielded XI[16] (66%), XII[16] (59%), XIII[16] (69%), respectively.

Bridge-Cleavage Reactions with Neutral Ligands. (a) Synthesis of the Anionic Mononuclear Complexes $(NBu_4)[MX(C_6Cl_5)_2L]$. (i) M = Pt. $(NBu_4)_2[Pt(\mu\text{-}Cl)(C_6Cl_5)_2]_2$ (0.2 g, 0.1029 mmol) in 50 mL of acetone together with stoichiometric amounts of the respective ligand L (PPh_3, py, or $SbPh_3$) (0.206 mmol) was stirred for ~20 h at room temperature. Evaporation to almost dryness and addition of a few milliliters of 2-propanol led to the crystallization of XVI[16] (70% yield) or XVII[16] (71% yield). To crystallize XV[16] (65% yield) a few milliliters of methanol had to be added to the 2-propanol solution.

(ii) M = Pd. Shorter reaction time (~1 h, room temperature) and workup as above led—after addition of *n*-BuOH—to the crystallization of XIV[16] (65% yield).

Synthesis of Mononuclear Neutral Complexes. *cis*-$M(C_6Cl_5)_2L_2$: M = Pd, L = PEt_3 (XVIII), PPh_2Me (XIX), PPh_3 (XX), py (XXI), $SbPh_3$ (XXII), L_2 = bpy (XXIII); M = Pt, L = PPh_2Me (XXIV), PPh_3 (XXV), py (XXVI), $SbPh_3$ (XXVII), L_2 = bpy (XXVIII), dpe (XXIX), dae (XXX).

Refluxing of acetone (for Pd complexes) or ethanol (for Pt complexes) solutions of $(NBu_4)_2[M(\mu\text{-}X)(C_6Cl_5)_2]_2$ (0.1 mmol) with an excess of the neutral ligand L (1:5 ratio) for 3–5 h gave the neutral complexes. $Pt(C_6Cl_5)_2L_2$ crystallized directly from the ethanol solution, although in some cases partial concentration and addition of 2-propanol was necessary (yields:[16] XXIV, 65%; XXV, 90%; XXVI, 87%; XXVII, 79%; XXVIII, 65%, XXIX, 65%; XXX, 60%). For $Pd(C_6Cl_5)_2L_2$ the acetone solutions were evaporated almost to dryness and ethanol or 2-propanol was added to crystallize the complexes, which were washed with hexane (yields:[16] XVIII, 62%; XIX, 72%; XX, 72%; XXI, 75%; XXII, 63%; XXIII, 50%).

Synthesis of *trans*-$Pt(C_6Cl_5)_2(tht)_2$. *trans*-$PtCl_2(tht)_2$ (1.5 g, 3.4 mmol) was added to a solution of C_6Cl_5Li (11.9 mmol), and the mixture was stirred for 3 h at room temperature. Subsequent evaporation to dryness and extraction with CH_2Cl_2 left an insoluble solid, XXXI,[16] which was washed with H_2O and then repeatedly washed with MeOH (18% yield). $(NBu_4)Br$ was added to the CH_2Cl_2 solution to crystallize the anionic species. The resulting mixture of products could not be separated or identified in any case.

Registry No. I, 86391-95-9; II, 86409-33-8; III, 86391-97-1; IV, 86391-99-3; V, 80984-28-7; VI, 86392-00-9; VII, 86392-02-1; VIII, 86392-04-3; IX, 86392-06-5; X, 86392-08-7; XI, 86392-10-1; XII, 86392-12-3; XIII, 86392-14-5; XIV, 86392-16-7; XV, 86392-18-9; XVI, 86392-20-3; XVII, 86392-22-5; XVIII, 71536-69-1; XIX, 86392-23-6; XX, 86420-58-8; XXI, 86420-59-9; XXII, 86420-60-2; XXIII, 25916-95-4; XXIV, 86392-24-7; XXV, 86392-25-8; XXVI, 86409-34-9; XXVII, 86392-26-9; XXVIII, 86392-27-0; XXIX, 86392-28-1; XXX, 86392-29-2; XXXI, 86392-30-5.