Mono- and Bi-nuclear Anionic Pentafluorophenyl Complexes of Palladium(II) and Platinum(II)

By **Rafael Usón,* Juan Forniés, Francisco Martínez,** and **Milagros Tomás,** Department of Inorganic Chemistry, University of Zaragoza, Zaragoza, Spain

The arylation of $K_2[MCl_4]$, $[MCl_2(tht)_2]$, MCl_2, or $[NBu_4]_2[M_2(\mu\text{-}Br)_2Br_4]$ (M = Pd or Pt; tht = tetrahydrothiophen) with LiR or MgBrR ($R = C_6F_5$) leads to novel mono- and bi-nuclear anionic organo-derivatives of the general formulae $[MR_3(tht)]^-$, $[MR_4]^{2-}$, and $[M_2(\mu\text{-}Br)_2R_4]^{2-}$, which have been isolated as tetra-alkylammonium salts. Reaction of compounds of the $[MR_3(tht)]^-$ type with neutral ligands leads to the substitution of tht by L, that of $[PdR_4]^{2-}$ with $PdCl_2$ gives rise to the formation of $[Pd_2(\mu\text{-}Cl)_2R_4]^{2-}$, whilst $[M_2(\mu\text{-}X)_2R_4]^{2-}$ reacts with alkali-metal salts of Br^-, I^-, or SCN^- to give (without cleavage of the bridging system) the corresponding complexes. Twenty anionic complexes of these three novel types have been isolated and characterized.

ALTHOUGH most hitherto known σ-bonded organotransition-metal derivatives are kinetically stabilized by the simultaneous presence of π-acceptor Group 5B ligands, it is sometimes possible to dispense with the latter if the organic radical has been well chosen, so that decomposition pathways would be energetically unfavourable. Thus it has been possible to prepare stable homoleptic hydrocarbyls with CH_3,[1] C≡CR,[2] or neopentyl type[3] groups.

Moreover, the kinetic stabilization resulting from the presence of π-acceptor Group 5B ligands can also be an obstacle to the synthesis of other types of compounds, since the reactions come to a standstill as soon as relatively inert intermediate species are formed. Thus, the arylation of halogeno-complexes of the $[MX_2L_2]$ type (M = Pd or Pt; X = halide; L = a π-acceptor Group 5B ligand) with a large excess of an organo-magnesium or -lithium compound generally allows the introduction of a maximum of two radicals R, to give $[MR_2L_2]$. In some cases only compounds of the $[MX(R)L_2]$ type have been obtained, especially if R is a bulky or *ortho*-substituted group (*e.g.* 2,6-dimethylphenyl[4] or pentachlorophenyl[5]). This may be due to arylation reagents which are not sufficiently strong nucleophiles to displace the neutral ligands (nearly always phosphine or tertiary arsine groups) and are therefore only capable of substituting halide groups. The displacement of the ligand L by the reaction with an organolithium derivative has only been reported in a few cases, thus the homoleptic organo-anion $[PtMe_6]^{2-}$ was prepared[6] by treating LiMe with $[PtMe_5(PPh_3)]^-$, $[PtMe_5(PMePh_2)]^-$, or *cis*-$[PtMe_4(PMePh_2)_2]$.

There is some evidence that the arylation can progress even to the formation of anionic derivatives if the starting compounds do not contain ancillary π-acceptor ligands or if they do not contain any ancillary ligand. For example, $Li_2[NiPh_4]\cdot 4thf$ and $Li_2[NiMe_4]\cdot 2thf$[7] are obtained by treating $[Ni(dpi)_2]$ [dpi = monoanion of 1,3-bis(2-pyridylimino)isoindoline] with LiPh and LiMe in tetrahydrofuran (thf) solution whilst the reaction of $[NBu_4]_2[PtCl_6]$ with an excess of LiMe gives $[NBu_4]_2[PtMe_6]$,[8] which is stable as the solid under nitrogen, but unstable in solution. On the other hand, if $Li(C_6F_5)$ is treated with $[AuCl_4]^-$, $[AuCl(tht)]$, or $[AuCl_3(tht)]$ (tht = tetrahydrothiophen) it is possible to prepare[9] organo-anions of the type $[Au(C_6F_5)_4]^-$ or $[Au(C_6F_5)_2]^-$, the tetrabutylammonium salts of which are stable beyond 200 °C and do not decompose in air.

These considerations prompted us to study arylation reactions of readily available compounds, which do not belong to the usual $[MX_2L_2]$ type (L = Group 5B ligand), with LiR or MgBrR. We used $R = C_6F_5$ since this radical normally leads to stable products which do not easily undergo decomposition. It has thus been possible to achieve with both reagents the arylation of binary halides, and of palladium and platinum complexes, giving compounds which possess a greater degree of arylation than any previously known.

We describe herein the preparation of stable anionic organo-derivatives which contain six novel types of anions, $[MR_3L]^-$, $[MR_4]^{2-}$, and $[R_2M(\mu\text{-}X)_2MR_2]^{2-}$ (M = Pd or Pt; $R = C_6F_5$; L = tht or Group 5B ligand; X = halide or pseudohalide) and which were isolated as stable tetra-alkylammonium (Q) salts. We also synthesized one neutral and two anionic complexes of the novel types *cis*-$[PdBr(R)(PPh_3)_2]$, *trans*-$[PtR_2Cl_2]^{2-}$, and *cis*-$[PdR_2X(L)]^-$. Some of these results have already been the subject of a preliminary communication.[10]

RESULTS AND DISCUSSION

The salts $K_2[MCl_4]$, the neutral complexes $[MCl_2(tht)_2]$, the binary halides MCl_2, and the binuclear complexes $Q_2[M_2(\mu\text{-}Br)_2Br_4]$ were used as starting products. All are either commercially available or can readily be prepared. Although organolithium derivatives are generally more reactive than organomagnesium derivatives,[11] $Li(C_6F_5)$ is only slightly stable in solution at room temperature whilst $MgBr(C_6F_5)$ is stable even in refluxing diethyl ether and could therefore be more efficient in some cases.[12] For this reason both LiR and MgBrR ($R = C_6F_5$ throughout) were employed as arylating reagents.

The results of our study are collected in Table 1. The percentages given represent the optimum yields obtained for the compounds.

Arylation of Potassium Tetrachlorometallate, $K_2[MCl_4]$.—When M = Pd prolonged treatment (21 h) with LiR (1 : 8) leads to the substitution of all of the chlorine atoms and to the formation of $[PdR_4]^{2-}$, which can be crystallized as $Q_2[PdR_4]$, in low yield (26%).

Prolonged treatment (19 h) with MgRX (1 : 8) leads to the same final result, but with higher yields (54%). If the reaction time is reduced (5 h), or if stoicheiometric amounts of the Grignard compound are used, both short or prolonged treatment leads either to solutions which are thought to contain the partially arylated anions $[PdBr_xR_{4-x}]^{2-}$ and can be crystallized by addition of QBr as anionic binuclear complexes of the general formula $Q_2[Pd_2(\mu\text{-}Br)_2R_4]$, or non-crystallizable oils from which *trans*-$[PdBrR(PPh_3)_2]$, *cis*-$[PdBrR(PPh_3)_2]$, and Q[*cis*-$PdBrR_2(PPh_3)$] can successively be separated by addition of PPh_3. Products which contain chlorine are not obtained in any case, which shows that the chlorine of $[PdCl_4]^{2-}$ is always substituted by the bromine of the organomagnesium compound or of the QBr.

When M = Pt no reaction could be observed in any case with LiR or with MgBrR and the unchanged starting compound $K_2[PtCl_4]$ was recovered.

TABLE 1

Arylation of complexes of Pd and Pt

Starting complex	Arylating agent [a]: LiR	Arylating agent [a]: MgBrR
$K_2[PdCl_4]$	$Q_2[PdR_4]$ (26)	$Q_2[PdR_4]$ (54), $Q_2[Pd_2(\mu\text{-}Br)_2R_4]$ (37)
$K_2[PtCl_4]$	*b*	*b*
$[PdCl_2(tht)_2]$	$[PdR_2(tht)_2]$ (60), $Q[PdR_3(tht)]$ (24), $Q_2[PdR_4]$ (70)	$[PdR_2(tht)_2]$ (75), $Q[PdR_3(tht)]$ (7)
$[PtCl_2(tht)_2]$	$[PtR_2(tht)_2]$ (56), $Q[PtR_3(tht)]$ (56)	$[PtR_2(tht)_2]$ (8)
$PdCl_2$	*c*	$Q_2[Pd_2(\mu\text{-}Br)_2R_4]$ (46)
$PtCl_2$	$Q_2[PtR_4]$ (66), Q_2[*trans*-$PtCl_2R_2$] (60)	$Q_2[Pt_2(\mu\text{-}Br)_2R_4]$ (41)
$Q_2[Pd_2(\mu\text{-}Br)_2Br_4]$	$Q_2[PdR_4]$ (64)	$Q_2[Pd_2(\mu\text{-}Br)_2R_4]$ (81)
$Q_2[Pt_2(\mu\text{-}Br)_2Br_4]$	*b*	*b*

[a] $R = C_6F_5$; Q = tetra-alkylammonium. Yields (%) are given in parentheses. [b] No reaction. [c] Decomposition.

Tetrachlorometallates are not very convenient precursors, since no arylation can be achieved in the case of platinum and for palladium only a 100% excess of, and prolonged treatment with, the arylation agent yields the tetrakis(pentafluorophenyl) derivatives in low or medium yields.

Arylation of Dichlorobis(tetrahydrothiophen) Derivatives, $[MCl_2(tht)_2]$.—Treatment of $[MCl_2(tht)_2]$ with LiR (see Table 1) leads [equation (1)] to several reaction products which vary with the ratio organolithium : dichloroderivative and also with the reaction time. In both

$$[MCl_2(tht)_2] + LiR \longrightarrow [MR_2(tht)_2] \longrightarrow [MR_3(tht)]^- \longrightarrow [MR_4]^{2-} \quad (1)$$
$$(M = Pd \text{ or } Pt)$$

cases (M = Pd or Pt) the neutral and anionic complexes can readily be separated, since the neutral disubstituted compounds $[MR_2(tht)_2]$ are insoluble in ethanol, whilst crystallization of the anionic species requires the addition of the salt of a bulky cation.

By using a 2.2 : 1 mol ratio of LiR : $[MCl_2(tht)_2]$ it is possible to prepare the neutral compounds in *ca.* 60% yields. For M = Pt both the *cis*-$[PtR_2(tht)_2]$ and *trans*-$[PtR_2(tht)_2]$ isomers are obtained, whilst reaction with M = Pd only leads to the isolation of *trans*-$[PdR_2(tht)_2]$. The mixture of the platinum isomers can be separated by fractional crystallization (see Experimental section).

If the amount of LiR is increased to give a 3 : 1 ratio, the arylation affords the trisubstituted derivatives $[MR_3(tht)]^-$ which can be precipitated as tetra-alkylammonium salts. The yields are higher for the platinum than for the palladium compound since in the former the tht group is more strongly bonded. Small amounts of the neutral disubstituted derivative are again obtained in this case, although, as expected, in lower yields than in the previously described reactions (2.2 : 1 mol ratio).

An even greater excess of LiR (6 : 1) allows the isolation of the salt $Q_2[PdR_4]$, as the main product, along with small amounts of the neutral disubstituted complex. Nevertheless, in the case of platinum it has not been possible to isolate the tetrasubstituted derivative, even with a still larger excess of LiR. Increase of the LiR : $[PtCl_2(tht)_2]$ ratio (see Experimental section) leads only to a decrease in the yields of neutral and trisubstituted products. An even larger excess of LiR (8 : 1) gives an oily product, which probably contains $[PtR_4]^{2-}$, but which we were not able to resolve, even when using different bulky cations as precipitating agents.

These results show clearly that in both cases (palladium and platinum) the arylation process commences with the replacement of the halogens by aryl groups and formation of neutral disubstituted compounds, which can readily be isolated if the adequate amount of LiR has been used: also the presence of an excess of the organolithium derivative results in the successive substitution of the neutral tht ligands.

The reaction of $[PdCl_2(tht)_2]$ with MgBrR leads to the disubstituted derivative $[PdR_2(tht)_2]$ as the main product (75% yield). By using a very high MgBrR : $[PdCl_2(tht)_2]$ ratio (6 : 1) together with very prolonged treatment it is also possible to obtain a small amount of the trisubstituted salt $Q[PdR_3(tht)]$ (7% yield).

In the case of Pt, reaction with MgBrR gives only very low yields (8%) of the neutral disubstituted derivative $[PtR_2(tht)_2]$.

Arylation of Dichlorides, MCl_2.—The reaction of LiR with diethyl ether suspensions of $PdCl_2$ commences at slightly below room temperature and speeds up quickly until the ether begins to boil and simultaneous blackening of the solution and deposition of metallic palladium can be observed. Only once could the binuclear complex $Q_2[Pd_2(\mu\text{-}Br)_2R_4]$ be crystallized in low yields (15%) by further treatment of the filtrate. The reaction generally seems to lead to total decomposition to metallic palladium, even when it is slowed down by external cooling with water. This seems noteworthy, since all the possible reaction products could be obtained by other methods and are moreover fairly stable.

In the case of $PtCl_2$, the reaction with LiR takes place smoothly and allows the isolation (66% yield) of $Q_2[PtR_4]$, which could not be prepared by any other route, together with a very small amount (3% yield) of $Q_2[$*trans*-$PtCl_2R_2]$. The latter can also be obtained as the sole reaction product and in higher yields (60%) by using a smaller excess of LiR (2.3 : 1).

The arylation of MCl_2 with MgBrR leads in every case to the binuclear salts $Q_2[M_2(\mu\text{-}Br)_2R_4]$ (>40% yields), even when a large excess of the organomagnesium derivative is used.

Arylation of Binuclear Complexes, $Q_2[M_2(\mu\text{-}Br)_2Br_4]$.—The palladium complex reacts with LiR to give $Q_2[PdR_4]$ (64% yield), whilst the reaction with MgBrR leads to $Q_2[Pd_2(\mu\text{-}Br)_2R_4]$ (81% yield). The Grignard compound is obviously not capable of cleaving the bromine bridging system. This is also confirmed by the fact that $Q_2[Pd_2(\mu\text{-}Br)_2R_4]$ does not react with an excess or the organomagnesium compound, even after refluxing for several hours, whereas with LiR it is possible to prepare $Q_2[PdR_4]$ at room temperature.

The binuclear platinum complex does not react with LiR at room temperature nor with MgBrR at reflux.

Some Reactions of the Anionic Complexes.—Anionic complexes of the $Q[MR_3(tht)]$ type react readily with neutral ligands resulting in displacement of tht [equation (2)] and 50—80% yields of $Q[MR_3L]$. However, it has not been possible to obtain $[MR_2L_2]$ by displacing one of

$$Q[MR_3(tht)] + L \longrightarrow Q[MR_3L] + tht \qquad (2)$$

$$M = Pd,\ L = PPh_3 \text{ or } AsPh_3$$

$$M = Pt,\ L = PPh_3,\ AsPh_3,\ SbPh_3, \text{ or } Ph_2P(CH_2)_4PPh_2$$

the C_6F_5 groups, even by working with an excess of L.

On the other hand $Q_2[PdR_4]$ in acetone solution reacts[13] with $PdCl_2$ to give the binuclear salt (85% yield), according to equation (3). The corresponding

$$Q_2[PdR_4] + PdCl_2 \longrightarrow Q_2[Pd_2(\mu\text{-}Cl)_2R_4] \qquad (3)$$

platinum complex does not undergo a similar reaction and the unchanged starting products are recovered when working under mild conditions, whilst treatment in refluxing solvents of higher boiling points leads to decomposition and precipitation of metallic platinum. This also occurs if ' soluble $PtCl_2$ ' in the form of $[PtCl_2(NCCH_2Ph)_2]$ is used.

Finally, the anionic binuclear palladium and platinum complexes undergo interchange reactions with alkali-metal salts M'X' (LiBr, NaI, or K[SCN]), according to equation (4), without cleavage of the bridging system or any of the M–C bonds.

$$Q_2[M_2(\mu\text{-}X)_2R_4] + M'X' \longrightarrow M'X + Q_2[M_2(\mu\text{-}X')_2R_4] \qquad (4)$$

$$M = Pd,\ X = Cl,\ X' = Br,\ I, \text{ or } SCN$$

$$M = Pt,\ X = Br,\ X' = I \text{ or } SCN$$

The results of the C, H, and N analyses of the novel complexes are collected in Table 2. Since some compounds have been obtained by several methods, the preparation which gave the listed results is indicated by an asterisk in the Experimental section. All the other products gave satisfactory analyses. Table 2 also shows

TABLE 2

Analytical results, conductivities, and melting points for the novel complexes

Complex[a]	Analysis (%)[b]			Λ[c]/	
	C	H	N	$ohm^{-1}\ cm^2\ mol^{-1}$	M.p. (θ_c/°C)
(1) *trans*-$[PdR_2(tht)_2]$	37.8 (38.9)	2.50 (2.60)		0	150 (decomp.)
(2) *trans*-$[PtR_2(tht)_2]$	33.8 (34.0)	2.05 (2.30)		0	240 (decomp.)
(3) *cis*-$[PtR_2(tht)_2]$	33.7 (34.0)	2.35 (2.30)		0	174
(4) $Q[PdR_3(tht)]$	49.0 (48.6)	4.75 (4.70)	1.40 (1.50)	99	156 (decomp.)
(5) $Q[PdR_3(PPh_3)]$	55.9 (56.1)	4.40 (4.60)	0.95 (1.25)	97	173 (decomp.)
(6) $Q[PdR_3(AsPh_3)]$	53.3 (54.0)	4.80 (4.40)	0.95 (1.20)	98	156 (decomp.)
(7) $Q[PtR_3(tht)]$	45.3 (44.4)	4.10 (4.30)	1.35 (1.35)	100	160
(8) $Q'[PtR_3(tht)]$	39.2 (39.3)	2.75 (3.05)	1.50 (1.55)	122	190
(9) $Q''[PtR_3(tht)]$	36.0 (36.3)	2.05 (2.35)	1.55 (1.65)	98.5	192
(10) $Q[PtR_3(PPh_3)]$	51.4 (52.0)	4.15 (4.30)	1.10 (1.15)	92	172
(11) $Q[PtR_3(AsPh_3)]$	49.8 (50.1)	4.40 (4.10)	1.15 (1.10)	91	161
(12) $Q[PtR_3(SbPh_3)]$	48.5 (48.3)	4.10 (3.95)	1.10 (1.10)	90	133 (decomp.)
(13) $Q_2[R_3Pt\{Ph_2P(CH_2)_4PPh_2\}PtR_3]$	50.3 (50.0)	4.05 (4.35)	1.30 (1.20)	175	228 (decomp.)
(14) $Q_2[PdR_4]$	53.7 (53.4)	5.25 (5.75)	2.20 (2.20)	208	158
(15) $Q_2[PtR_4]$	49.9 (49.8)	4.80 (5.35)	2.15 (2.10)	165	151
(16) $Q_2[Pd_2(\mu\text{-}Cl)_2R_4]$	46.5 (46.8)	5.10 (5.00)	1.90 (1.95)	198	159 (decomp.)
(17) $Q_2[Pd_2(\mu\text{-}Br)_2R_4]$	44.6 (44.0)	4.95 (4.70)	1.80 (1.85)	198	147
(18) $Q_2[Pd_2(\mu\text{-}I)_2R_4]$	41.9 (41.5)	4.70 (4.45)	1.70 (1.75)	189	133
(19) $Q_2[Pd_2(\mu\text{-}SCN)_2R_4]$	46.9 (47.0)	5.20 (4.85)	3.70 (3.80)	176	191 (decomp.)
(20) $Q_2[Pt_2(\mu\text{-}Br)_2R_4]$	39.8 (39.4)	4.20 (4.25)	1.55 (1.65)	182.7	189
(21) $Q_2[Pt_2(\mu\text{-}I)_2R_4]$	37.8 (37.4)	4.30 (4.00)	1.45 (1.55)	156	186
(22) $Q_2[Pt_2(\mu\text{-}SCN)_2R_4]$	42.1 (41.9)	4.35 (4.35)	3.25 (3.35)	187.1	199
(23) $Q_2[$*trans*-$PtCl_2R_2]$	49.3 (48.7)	6.70 (6.65)	2.45 (2.60)	176	185 (decomp.)
(24) *trans*-$[PdBr(R)(PPh_3)_2]$	58.0 (57.4)	3.70 (3.40)		0	284
(25) *cis*-$[PdBr(R)(PPh_3)_2]$	57.3 (57.4)	3.60 (3.40)		0	257 (decomp.)
(26) $Q[$*cis*-$PdBrR_2(PPh_3)]$	54.2 (53.8)	5.10 (4.95)	1.40 (1.35)	87	151

[a] $R = C_6F_5$, $Q = [NBu_4]^+$, $Q' = [NEt_4]^+$, and $Q'' = [NMe_4]^+$. [b] Calculated values are given in parentheses. [c] In acetone.

the melting points and conductivities of the novel complexes. The conductivities correspond to those expected for 1 : 1 and 2 : 1 electrolytes or, respectively, for non-electrolytes.[14]

The described complexes are generally very stable both as solids and in solution, although most of them decompose when refluxed in ethanol.

Infrared Spectra.—The i.r. spectra of the novel compounds show bands characteristic of the C_6F_5 group.[15] It is noteworthy that the absorption at *ca.* 1 050 cm^{-1} appears as a broad and frequently split band, whilst that at 950 cm^{-1} is very broad in the case of $Q_2[MR_4]$ and $Q[MR_3L]$ but much narrower in the case of $Q_2[M_2(\mu\text{-}X)_2R_4]$.

The absorption at 800 cm^{-1}, which has already been used for structural elucidation [16] and which is assigned to an X-sensitive mode of mainly ν(M–C) character, points to the existence of a mixture of the *cis*-$[PtR_2(tht)_2]$ and *trans*-$[PtR_2(tht)_2]$ isomers formed in the reaction of $[PtCl_2(tht)_2]$ with LiR. It can be used for identifying each isomer after separation (see Experimental section). The compounds *cis*-$[PtR_2(tht)_2]$ (C_{2v}) exhibit two bands at 802 and 790 cm^{-1}, whilst *trans*-$[PtR_2(tht)_2]$ (D_{2h}) have a single absorption at 780 cm^{-1}, as expected for ν(M–C) stretching modes of the corresponding isomers: *cis*, $A_1 + B_2$; *trans*, (B_{2u}).

The complexes of the type $Q_2[M_2(\mu\text{-}X)_2R_4]$ (D_{2h}) show a double band at 780—790 cm^{-1}, whilst $Q_2[MR_4]$ have a single, very strong, band (E_u) at *ca.* 750 cm^{-1}. Although this absorption is in some cases broadened or even forms a shoulder, its location hardly changes with variation of central metal atom.

The i.r. spectra of $[MR_3L]^-$ are more complex in this region. If the ligand L does not absorb in this zone (*e.g.* tht) three absorptions assignable to the C_6F_5 group can clearly be distinguished, corresponding to the three ($2A_1 + B_1$) stretching modes expected for C_{2v} symmetry. The location of these bands is, however, influenced by the nature of the ligand L.

The complexes $Q[MR_3L]$ show characteristic absorptions of the ligand L at: 1 279m, (4); 1 276m, (7); 1 277m, (8); 1 277m, (9); 532s, 513m, 492m, (5); 542s, 522m, 500m, (10);[17] 485m, 475m, 466m, 340m, 333m, 319m, (6); 490m, 480m, 472m, 350m, 340m, 320m, (11); 465m, 458m, 451m, 285m, 279 (sh), 268m, (12); and 572s, 505s cm^{-1}, (13).

The binuclear complexes show absorptions to be assigned to the $Pd(\mu\text{-}X)_2Pd$ moiety at 290m (16), 220m (17), or 205m cm^{-1} (20). The absorptions to be expected for (18) and (21) are beyond the range of our instrument.[18] For (19) and (22), ν(CN) appears at 2 162s and 2 158s cm^{-1} respectively.[19] Complex (23) shows only a single absorption due to ν(Pt–Cl) at 320m, along with one absorption at 764s cm^{-1}, assignable to M-C_6F_5 (X-sensitive mode) which supports a *trans* configuration.

As already reported by Mastin,[17] *cis*-$[PdBr(R)(PPh_3)_2]$ shows a strong absorption at 540 cm^{-1}, which is not observed in the case of *trans*-$[PdBr(R)(PPh_3)_2]$ and can therefore also be used for structural assignment.

The presence of tetra-alkylammonium (Q) is unambiguously supported by a broad band of medium intensity at *ca.* 900 cm^{-1}, and by another strong one at 753 cm^{-1}.

EXPERIMENTAL

Infrared spectra, C, H, and N analyses, and conductance and melting-point determinations were performed as described elsewhere.[13]

The reactions with $Li(C_6F_5)$ were carried out under nitrogen. All the solvents were distilled prior to use, and the diethyl ether, used for the synthesis of $Li(C_6F_5)$ and $MgBr(C_6F_5)$, was rendered anhydrous by distillation with CaH_2. The salts $PtCl_2$ and $PdCl_2$ were finely powdered and desiccated at 110 °C.

The complexes $[PtCl_2(tht)_2]$ and $[PdCl_2(tht)_2]$ were prepared by treating a dichloromethane or chloroform solution of the neutral ligand with $PtCl_2$ or $PdCl_2$ until the halides were completely dissolved; the deep red solutions were partially evaporated and the required complexes (90% yields) were obtained after addition of light petroleum (40—50 °C) and cooling.

Arylation Reactions of $K_2[PdCl_4]$ *and* $K_2[PtCl_4]$ *with* LiR *or* MgBrR.—(*a*) $K_2[PdCl_4]$ *with* LiR. To a solution of $Li(C_6F_5)$ (2.17 g, 12.5 mmol) in diethyl ether (50 cm^3) at −78 °C was added $K_2[PdCl_4]$ (0.5 g, 1.53 mmol). The mixture was stirred for 21 h at room temperature, hydrolysed in air, and evaporated to dryness. The residue was extracted with acetone–dichloromethane (1 : 1, 60 cm^3) and filtered. Concentration to 15 cm^3 and addition of $[NBu_4]Br$ (0.9 g, 2.79 mmol) and isopropyl alcohol (30 cm^3) led, after partial evaporation, to 0.5 g (26% yield) of $[NBu_4]_2[Pd(C_6F_5)_4]$ (14).

(*b*) $K_2[PdCl_4]$ *with* MgBrR. The results of this reaction depend entirely upon the working conditions.

(*i*) To a fresh solution of $MgBr(C_6F_5)$ (4.64 g, 17.1 mmol) in diethyl ether (40 cm^3) was added desiccated (110—120 °C) and powdered $K_2[PdCl_4]$ (0.7 g, 2.14 mmol; 8 : 1). The mixture was refluxed for 4 h, stirred at room temperature for 15 h, hydrolysed with ether, and evaporated to dryness. The residue was extracted with acetone (30 cm^3), filtered through $Mg[SO_4]$–silica, and evaporated. The resulting black oil was dissolved in ethanol (20 cm^3). Addition of $[NBu_4]Br$ (1.37 g, 4.25 mmol) in ethanol (10 cm^3) and partial evaporation led to the crystallization of $[NBu_4]_2[Pd(C_6F_5)_4]$ (14), yield 1.47 g (56.6%).

(*ii*) Use of a 8 : 1 mol ratio but shorter treatment (3 h reflux, 2 h stirring at room temperature) and work-up as in (*i*) led, after addition of $[NBu_4]Br$ and evaporation, to a dark oil which was washed with water and hexane and dissolved in isopropyl alcohol (30 cm^3). Addition of hexane (15 cm^3) and stirring for 10 min resulted in the precipitation of 0.22 g (14% yield) of $[NBu_4]_2[Pd_2(\mu\text{-}Br)_2(C_6F_5)_4]$ (17).

(*iii*) A 4 : 1 mol ratio, 5 h reflux, and 17 h stirring at room temperature and work-up as in (*i*) led, after addition of $[NBu_4]Br$ and partial evaporation, to the crystallization of (17) (0.59 g, 37% yield).

(*iv*) A 4 : 1 mol ratio, but only 2 h refluxing and further work-up as in (*i*) gave, after addition of $[NBu_4]Br$ and 24 h stirring, $[NBu_4]_2[Pd_2(\mu\text{-}Br)_2Br_4]$ (0.2 g, 0.13 mmol). Evaporation of the filtrate gave a dark non-crystallizable oil which was dissolved in acetone–ethanol (40 cm^3). Addition of PPh_3 led to the successive crystallizations of *trans*-$[PdBr(C_6F_5)(PPh_3)_2]$ (24) (0.29 g, 15.7%)*, *cis*-$[PdBr(C_6F_5)(PPh_3)_2]$(25) (0.15 g, 8.2%)*, and $[NBu_4]$[*cis*-$PdBr(C_6F_5)_2(PPh_3)$] (26) (0.14 g, 6.4%)*.

Reaction of LiR or MgRX with $K_2[PtCl_4]$ (8 : 1 mol ratio and up to 20 h treatment) gave unchanged $K_2[PtCl_4]$ in each case.

Arylation Reactions of $[PdCl_2(tht)_2]$ *and* $[PtCl_2(tht)_2]$ *with* LiR *or* MgBrR.—(*a*) $[PdCl_2(tht)_2]$ *with* LiR. The results of this reaction depended closely upon the working conditions.

(*v*) To a solution of $Li(C_6F_5)$ (1.3 g, 7.47 mmol) in dry diethyl ether (50 cm^3) at −78 °C was added *trans*-$[PdCl_2(tht)_2]$ (1.2 g, 3.39 mmol) (2.2 : 1 mol ratio) and the mixture was stirred for 4 h at room temperature, hydrolysed with aqueous ether, and evaporated to a few cm^3 (2—4). Ethanol (30 cm^3) was added to crystallize *trans*-$[Pd(C_6F_5)_2(tht)_2]$ (1) (1.25 g, 60%)*.

(*vi*) Reaction of $Li(C_6F_5)$(0.98 g, 5.27 mmol) with *trans*-$[PdCl_2(tht)_2]$ (0.617 g, 1.75 mmol; 3 : 1) led to the crystallization of (1) (0.39 g, 36%). Addition of $[NBu_4]Br$ (0.32 g, 1 mmol) in ethanol (30 cm^3) to the filtrate and partial evaporation gave $[NBu_4][Pd(C_6F_5)_3(tht)]$ (4) (0.39 g, 24%) *. A higher proportion of $Li(C_6F_5)$ did not yield more (4) but led to the tetrasubstituted derivative (see below).

(*vii*) A 6 : 1 mol ratio, 24 h stirring at room temperature, and work-up as in (*vi*) afforded a small amount of (1) (0.14 g, 5% yield) and $[NBu_4]_2[Pd(C_6F_5)_4]$ (14)* (4.15 g, 70% yield).

(*b*) $[PdCl_2(tht)_2]$ *with* $MgBr(C_6F_5)$. (*viii*) To $MgBr(C_6F_5)$ (4.81 g, 17.7 mmol) in diethyl ether (40 cm^3) was added $[PdCl_2(tht)_2]$ (2 g, 5.6 mmol). The mixture was refluxed for 1.5 h, hydrolysed by stirring overnight in moist air, and evaporated to dryness. The residue was extracted with acetone (50 cm^3) and the extract filtered through $Mg[SO_4]$–silica. Evaporation of the filtrate to *ca.* 10 cm^3 and addition of ethanol (30 cm^3) gave (1) (2.60, 75% yield) which was washed with ethanol–hexane.

(*ix*) Reaction of $MgBr(C_6F_5)$ (4.60 g, 16.95 mmol) with $[PdCl_2(tht)_2]$ (1 g, 2.82 mmol; 6 : 1) led to (1) (0.94 g, 54% yield). Addition of $[NBu_4]Br$ (1.82 g, 5.65 mmol) to the ethanol filtrate gave, after evaporation, $[NBu_4][Pd(C_6F_5)_3(tht)]$ (4) (0.19, 7% yield).

(*c*) $[PtCl_2(tht)_2]$ *with* $Li(C_6F_5)$. The $[PtCl_2(tht)_2]$ used was a mixture of the *cis* and *trans* isomers.

(*x*) To a solution of $Li(C_6F_5)$ (1.14 g, 6.6 mmol) in diethyl ether (65 cm^3) at −78 °C was added $[PtCl_2(tht)_2]$ (1.34 g, 3.0 mmol; 2.2 : 1). The mixture was stirred for 4 h at room temperature, evaporated to dryness, and the residue extracted with dichloromethane (25 cm^3) to give a crystalline mixture of *trans*-$[Pt(C_6F_5)_2(tht)_2]$ (2) and *cis*-$[Pt(C_6F_5)_2(tht)_2]$ (3) (1.18 g, 56% yield), which were separated as described below.

(*xi*) To a solution of $Li(C_6F_5)$ (1.41 g, 8.10 mmol) in diethyl ether (60 cm^3) at −78 °C was added $[PtCl_2(tht)_2]$ (1.2 g, 2.71 mmol; 3 : 1). The mixture was stirred overnight at room temperature, hydrolysed, evaporated to dryness, and the residue extracted with dichloromethane (50 cm^3). Partial evaporation (*ca.* 10 cm^3) and addition of methanol (30 cm^3) gave a mixture of (2) and (3) (0.49 g, 26% yield). Addition of $[NBu_4]Br$ (0.87 g, 2.69 mmol) in methanol (10 cm^3) and partial evaporation led to $[NBu_4][Pt(C_6F_5)_3(tht)]$ (7) (1.55 g, 56% yield)*.

(*xii*) The compound $Li(C_6F_5)$ (1.88 g, 10.86 mmol) and $[PtCl_2(tht)_2]$ (1.2 g, 2.71 mmol; 4 : 1) and work-up as before yielded 0.23 g (12%) of a mixture of (2) and (3) along with (7) (0.78 g, 28%). Even after removal of (7) and evaporation of the solution to dryness, $[NBu_4]_2[Pt(C_6F_5)_4]$ could not be crystallized.

(*xiii*) When $Li(C_6H_5)$ (2.35 g, 13.50 mmol) and $[PtCl_2(tht)_2]$ (1.2 g, 2.71 mmol) were allowed to react as before it was possible to isolate 0.21 g (11% yield) of the mixture of (2) and (3) along with (7) (0.61 g, 22% yield). The tetrasubstituted complex could not be isolated from the oily residue.

(*xiv*) The above reaction undertaken with a 8 : 1 mol ratio $Li(C_6F_5)$ (3.77 g, 21.68 mmol) : $[PtCl_2(tht)_2]$ (1.2 g, 2.71 mmol) led to a non-crystallizable oil.

Pure samples of complexes (2)* and (3)* could be obtained by treating the mixture of both compounds with a small amount of dichloromethane in which (3) and some of (2) is soluble, so that the residue contained solely the *trans* derivative (2). The dichloromethane solution was evaporated to dryness and the residue was again treated with a small amount of dichloromethane to dissolve the *cis* complex (3) which was isolated by evaporation to dryness. The purity of both complexes was monitored by i.r. spectroscopy.

In experiments similar to that described in (*xii*) (4 : 1 mol ratio), $[NEt_4]Cl$ and $[NMe_4]Cl$ were used as cations to precipitate $[NEt_4][Pt(C_6F_5)_3(tht)]$ (8)* and $[NMe_4][Pt(C_6F_5)_3(tht)]$ (9)* in *ca.* 30% yields. It was not possible to isolate the tetrakis(pentafluorophenyl) compound.

(*d*) $[PtCl_2(tht)_2]$ *with* $MgBr(C_6F_5)$. The complex $[PtCl_2(tht)_2]$ (0.75 g, 1.69 mmol) was added to $MgBr(C_6F_5)$ (3.63 g, 13.38 mmol) (1 : 8 mol ratio) in diethyl ether (40 cm^3) and the solution refluxed for 5 h, hydrolysed in moist air, and evaporated to dryness. The residue was extracted with acetone (50 cm^3), the extract filtered through $Mg[SO_4]$–silica, and the filtrate was evaporated almost to dryness. Addition of ethanol (10 cm^3) led to the crystallization of 0.1 g (8% yield) of (2) and (3). Addition of $[NBu_4]Br$ (0.49 g, 1.5 mmol) to the filtrate did not give any anionic species but caused partial decomposition and separation of elemental platinum.

Arylation Reactions of $PdCl_2$ *and* $PtCl_2$ *with* LiR *and* MgBrR.—(*a*) $PdCl_2$ *with* $Li(C_6F_5)$. To a solution of $Li(C_6F_5)$ (5.84 g, 33.6 mmol) in diethyl ether (60 cm^3) at −78 °C was added $PdCl_2$ (1 g, 5.6 mmol). No reaction could be observed below −15 °C, however at *ca.* 0 °C a very exothermic reaction suddenly occurred resulting in boiling of the mixture and decomposition of metallic palladium. The resulting dark solution was filtered and the filtrate was evaporated almost to dryness. Addition of $[NBu_4]Br$ (1 g, 3.10 mmol) in ethanol (5 cm^3) and successive evaporation led to an oil which when treated with n-butanol gave crystals of $[NBu_4]_2[Pd_2(\mu\text{-}Br)_2(C_6F_5)_4]$ (17) (0.64 g, 15% yield). Repetition of this reaction under identical conditions led consistently to metallic palladium. If the temperature was carefully controlled and kept for 2 h below −5 °C, gradual decomposition to metallic palladium occurred and no anionic complex could be isolated from the residual solutions.

(*b*) $PdCl_2$ *with* $MgBr(C_6F_5)$. To a solution of $MgBr(C_6F_5)$ (9.98 g, 36.78 mmol) in diethyl ether (50 cm^3) was added $PdCl_2$ (0.82 g, 4.62 mmol) (mol ratio 8 : 1). The mixture was refluxed for 4 h, stirred for 18 h at room temperature, hydrolysed with ether, and evaporated to dryness. The residue was extracted with acetone (40 cm^3) and the extract filtered through $Mg[SO_4]$–silica. Evaporation of the filtrate led to an oily residue which was dissolved in ethanol (15 cm^3). Addition of $[NBu_4]Br$ (2.97 g, 9.21 mmol) in ethanol (10 cm^3) and partial evaporation afforded $[NBu_4]_2[Pd_2(\mu\text{-}Br)_2(C_6F_5)_4]$ (17) (1.62 g, 46%).

(*c*) $PtCl_2$ *with* $Li(C_6F_5)$. (*xv*) To a solution of $Li(C_6F_5)$ (0.59 g, 3.39 mmol) in diethyl ether (40 cm^3) at −78 °C was added $PtCl_2$ (0.39 g, 1.46 mmol) (2.3 : 1 mol ratio). The solution was allowed to slowly reach room temperature (in *ca.* 4 h), hydrolysed in moist air, and evaporated to dryness. The residue was extracted with acetone (40 cm^3), the extract filtered, again evaporated to dryness, and the residue dissolved in isopropyl alcohol (*ca.* 20 cm^3). Addition of $[NBu_4]Br$ (0.9 g, 2.80 mmol) led to its instantaneous dissolution and to gradual precipitation of $[NBu_4]_2$[*trans*-$PtCl_2(C_6F_5)_2$] (23) (0.95 g, 60% yield)*.

(*xvi*) The above reaction was carried out with a 8.5 : 1 mol ratio [$Li(C_6F_5)$ (2.6 g, 15 mmol); $PtCl_2$ (0.475 g, 1.78 mmol)]. After evaporating the acetone solution almost to dryness the residue was extracted with ethanol (20 cm^3). Addition of $[NBu_4]Br$ (1.28 g, 3.97 mmol) led to the crystallization of $[NBu_4]_2[Pt(C_6F_5)_4]$ (15) (1.58 g, 66% yield)*. Evaporation of the mother-liquors to dryness afforded a yellow oil which when washed with water and hexane and extracted with isopropyl alcohol yielded a small amount of (23) (0.061 g, 3.2% yield).

(*d*) $PtCl_2$ *with* $MgBr(C_6F_5)$. To a solution of $MgBr(C_6F_5)$ (8.13 g, 30 mmol) in diethyl ether (50 cm^3) was added $PtCl_2$ (1 g, 3.75 mmol) (8 : 1 mol ratio), and the work-up was continued as for $PdCl_2$. Addition of $[NBu_4]Br$ (2.42 g, 7.5 mmol) gave $[NBu_4]_2[Pt_2(\mu\text{-}Br)_2(C_6F_5)_4]$ (20) (1.31 g, 41% yield)*.

Arylation Reactions of the Binuclear Complexes, $[NR'_4]_2[M_2(\mu\text{-}Br)_2Br_4]$, *with* LiR *and* MgBrR (M = Pd *or* Pt).—(*a*) $[NBu_4]_2[Pd_2(\mu\text{-}Br)_2Br_4]$ *with* $Li(C_6F_5)$. The complex $[NBu_4]_2[Pd_2(\mu\text{-}Br)_2Br_4]$ (0.4 g, 0.34 mmol) was added to a solution of $Li(C_6F_5)$ (1.18 g, 6.8 mmol) in diethyl ether (50 cm^3) at −78 °C, stirred for 20 h at room temperature, hydrolysed with ether, and evaporated to dryness. The residue was extracted with acetone and filtered; the filtrate was again evaporated to dryness and treated with isopropyl alcohol (10 cm^3) to precipitate $[NBu_4]_2[Pd(C_6F_5)_4]$ (14). Addition of $[NBu_4]Br$ (0.22 g, 0.68 mmol) to the mother-liquors gave more (14) (total yield: 0.55 g, 64%).

(*b*) $[NBu_4]_2[Pd_2(\mu\text{-}Br)_2Br_4]$ *with* $MgBr(C_6F_5)$. To a solution of $MgBr(C_6F_5)$ (0.77 g) 2.85 mmol) in diethyl ether (50 cm^3) was added $[NBu_4]_2[Pd_2(\mu\text{-}Br)_2Br_4]$ (0.8 g, 0.68 mmol) (4.2 : 1 mol ratio). The mixture was refluxed for 2 h, hydrolysed with ether, evaporated to dryness, and the residue extracted with acetone at room temperature. The extract was filtered through $Mg[SO_4]$–silica and the dark filtrate was concentrated to 50 cm^3. Addition of ethanol (10 cm^3) and evaporation gave $[NBu_4]_2[Pd_2(\mu\text{-}Br)_2(C_6F_5)_4]$ (17) (0.84 g, 81% yield).

(*c*) $[NEt_4]_2[Pt_2(\mu\text{-}Br)_2Br_4]$ *with* $Li(C_6F_5)$. 1 : 1 Addition of $Li(C_6F_5)$ to $[NEt_4]_2[Pt_2(\mu\text{-}Br)_2Br_4]$ and treatment as for the similar palladium compound led to the recovery of the starting compounds.

(*d*) $[NEt_4]_2[Pt_2(\mu\text{-}Br)_2Br_4]$ *with* $MgBr(C_6F_5)$. As before, the reaction of the binuclear platinum complex with a large excess (1 : 8) of the organomagnesium derivative did not yield any organometallic complex, and only a small amount of the unchanged starting compound along with metallic platinum was recovered.

Reaction of $[NBu_4]_2[Pd(C_6F_5)_4]$ *with* $PdCl_2$.—To a solution of $[NBu_4]_2[Pd(C_6F_5)_4]$ (14) (1.3 g, 1.03 mmol) in acetone (200 cm^3) was added $PdCl_2$ (0.20 g, 1.13 mmol), which dissolved after 7 h refluxing. Partial evaporation of the yellow solution to *ca.* 10 cm^3 and addition of isopropyl alcohol (15 cm^3) gave $[NBu_4]_2[Pd_2(\mu\text{-}Cl)_2(C_6F_5)_4]$ (16) (1.26 g, 58% yield)*.

Substitution Reactions by Neutral Ligands L: $[NBu_4][M(C_6F_5)_3L]$ [M = Pd, L = PPh_3 (5)* *or* $AsPh_3$(6)*; M = Pt, L = PPh_3(10)*, $AsPh_3$(11)*, $SbPh_3$(12)*, *or* $\frac{1}{2}$ $Ph_2P(CH_2)_4PPh_2$ (13)*].—To a benzene solution of $[NBu_4][Pd(C_6F_5)_3(tht)]$ (4) or an ethanol solution of $[NBu_4][Pt(C_6F_5)_3(tht)]$ (7) were added stoicheiometric amounts of the ligand L in the same solvent and the mixture was refluxed for 3 h. For (5) and (6) the solution was evaporated to dryness, the oily residue was extracted with isopropyl alcohol, and the complexes crystallized after addition of n-hexane [50% yield (5)*; 60% yield (6)*]. Of the platinum complexes, (13)* crystallized during the reaction, was filtered off, and washed with n-hexane (50% yield); (10)* was obtained as white crystals after evaporation of the ethanol and treatment of the residue with methanol (5 cm^3) (65% yield), and (11)* and (12)* were obtained after partial evaporation of the ethanol solution and addition of a methanol–hexane mixture [75% yield (11)*; 80% yield (12)*].

Substitution Reactions of X *in* $[NBu_4]_2[M_2(\mu\text{-}X)_2(C_6F_5)_4]$.—(*a*) M = Pd; X = Br(17)*, I(18)*, *or* SCN (19)*. To a solution of (16) (0.22 g, 0.15 mmol) in acetone (30 cm^3) was added a slight excess of LiBr, NaI, or K[SCN]. The mixture was refluxed for 9 h (LiBr), treated at room temperature for 36 h (NaI), or for 2 h (K[SCN]), filtered, and the filtrate evaporated to *ca.* 10 cm^3. Complexes (18)* and (19)* crystallized after addition of ethanol in 65 and 74% yield respectively. Complex (17)* was isolated by a slightly different method. The acetone solution was evaporated to dryness and the yellow residue was washed several times with water, and finally treated with n-butanol (5 cm^3) and ethanol (5 cm^3) (77% yield).

(*b*) M = Pt; X = I (21)* *or* SCN (22)*. To a solution of (20) (0.5 g, 0.29 mmol) in acetone (20 cm^3) was added NaI. The mixture was refluxed for 2 h, stirred for 4 h at room temperature, filtered, and evaporated to dryness. The residue was washed several times with water and treated with cold methanol (5 cm^3) to crystallize (21)* (0.352 g, 67% yield). Similarly, complex (20) (0.28 g, 0.164 mmol) was added to K[SCN] (0.03 g, 0.31 mmol) in acetone (20 cm^3) and stirred for 5 h at room temperature. On working-up as above and treating the washed residue with isopropyl alcohol, complex (22) (0.108 g, 40% yield)* was obtained.

[9/996 *Received*, 26*th June*, 1979]

REFERENCES

[1] A. J. Shortland and G. Wilkinson, *J.C.S. Dalton*, 1973, 872; L. Galyer, K. Mertis, and G. Wilkinson, *J. Organometallic Chem.*, 1975, **85**, C37; E. L. Sigurdson and G. Wilkinson, *J.C.S. Dalton*, 1977, 812.

[2] R. Nast, *Angew. Chem.*, 1960, **72**, 26.

[3] P. J. Davidson, M. F. Lappert, and R. Pearce, *Accounts Chem. Res.*, 1974, **7**, 209; *Chem. Rev.*, 1976, **76**, 219; M. F. Lappert, *Pure Appl. Chem.*, 1978, **50**, 703.

[4] J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 1960, 1718.

[5] J. M. Coronas, O. Rosell, and J. Sales, *J. Organometallic Chem.*, 1976, **121**, 265.

[6] G. W. Rice and R. S. Tobías, *J.C.S. Chem. Comm.*, 1975, 994; *J. Amer. Chem. Soc.*, 1977, **99**, 2141.

[7] R. Taube and G. Honymus, *Angew. Chem. Internat. Edn.*, 1975, **14**, 261.

[8] C. S. Creaser and J. A. Creighton, *J. Organometallic Chem.*, 1978, **157**, 243.

[9] R. Usón, A. Laguna, and J. Vicente, *J.C.S. Chem. Comm.*, 1976, 353; *J. Organometallic Chem.*, 1977, **131**, 471.

[10] R. Usón, J. Forniés, P. Espinet, R. Navarro, F. Martínez, and M. Tomás, *J.C.S. Chem. Comm.*, 1977, 789.

[11] F. R. Hartley, ' The Chemistry of Platinum and Palladium,' Applied Science Publishers, London, 1973, pp. 325, 355; G. E. Coates, M. L. H. Green, and K. Wade, ' Organometallic Compounds, vol. II, The Transition Elements,' Chapman and Hall, London, 1968, p. 205.

[12] P. L. Coe, R. Stephens, and J. C. Tatlow, *J. Chem. Soc.*, 1962, 3227; S. C. Cohen, M. L. N. Reddy, D. M. Roe, A. J. Tomlinson, and A. G. Massey, *J. Organometallic Chem.*, 1968, **14**, 241; S. C. Cohen, D. E. Fenton, D. Shaw, and A. G. Massey, *ibid.*, 1967, **8**, 1.

[13] R. Usón, J. Forniés, R. Navarro, and M. P. García, *Inorg. Chim. Acta*, 1979, **33**, 69.

[14] W. J. Geary, *Co-ordination Chem. Rev.*, 1971, **7**, 81.

[15] D. A. Long and D. Steele, *Spectrochim. Acta*, 1961, **19**, 1955.

[16] G. B. Deacon and J. H. S. Green, *Spectrochim. Acta*, 1968, **A24**, 1125; R. Usón, J. Forniés, J. Gimeno, P. Espinet, and R. Navarro, *J. Organometallic Chem.*, 1974, **81**, 115; E. Maslowsky, jun., ' Vibrational Spectra of Organometallic Compounds,' Wiley, New York, 1977, p. 437.

[17] S. H. Mastin, *Inorg. Chem.*, 1974, **13**, 1003.

[18] D. M. Adams and P. J. Chandler, *J. Chem. Soc. (A)*, 1969, 588; B. Crociani, P. Uguagliati, T. Boschi, and U. Belluco, *ibid.*, 1968, 2869; B. Crociani, T. Boschi, R. Pietropaolo, and U. Belluco, *J.C.S. Dalton*, 1975, 531.

[19] R. A. Bailey, S. L. Kozak, T. W. Michelsen, and W. N. Mills, *Co-ordination Chem. Rev.*, 1971, **6**, 407.