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REACTIONS OF THE TERTIARY PHOSPHINES $R_2P\overline{C{=}CCl(C}F_2)_n$ WITH GROUP VI HEXACARBONYLS AND SALTS OF PLATINUM AND PALLADIUM

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SUMMARY

The tertiary phosphines $R_2P\overline{C{=}CCl(C}F_2)_n$ (R = C_6H_5 or C_6H_{11}; n = 2,3, or 4) react with $M(CO)_6$ (M = Cr, Mo, W) to give $R_2P\overline{C{=}CCl(C}F_2)_nM(CO)_5$ in which the ligand is bonded to M through P alone. Similar bonding is found in some chloro-complexes of platinum and palladium.

INTRODUCTION

For a number of years we have been studying the preparation and complexing ability of fluorocarbon bridged ditertiary arsines and phosphines such as $(CH_3)_2As\overline{C{=}CAs(CH_3)_2(C}F_2)_2$ [1-3]. In spite of the presence of three donor sites the >C=C< moiety in the bridging group is only directly involved in the bonding in complexes of formula $(L\text{-}L)M_2(CO)_6$ where (L-L) is the ligand and M is Fe, Ru, Os, [4-6]. We have also observed the formation of complexes with unusual geometry when an $-As(CH_3)_2$ group becomes detached from the fluorocarbon group during the reaction. This often forces the >C=C< fragment to bond to the metal in an η^2 and/or η^1 manner [7,8]. In one case the related ligand cis-$(CH_3)_2AsC(CF_3){=}C(CF_3)As(CH_3)_2$ was found to react with $Mn_2(CO)_8$ to give a complex in which the >C=C< had been converted into a η^3-allyl group by loss of fluorine as well as the $-As(CH_3)_2$ moiety [9].

The structural requirement for this sort of reactivity seems to be the presence of $R_2E\text{-}\overset{|}{C}{=}\overset{|}{C}\text{-}As(CH_3)_2$ (E = P or As) and with this in mind we have initiated studies on the reactions of tertiary phosphines and arsines of formula $R_2E\overline{C{=}CCl(C}F_2)_n$ in the belief that the reactivity of the vinylic chlorine atom should lead to some interesting metal complex chemistry.

The approach has born fruit in the case of the reaction of $R_2P\overline{C{=}CCl(C}F_2)_3$ with $Fe(CO)_5$ ($R = C_6H_5$, C_6H_{11}) [10,11] and the structure of the product obtained when $R = C_6H_{11}$ is shown in Figure 1. Here the loss of chlorine and fluorine atoms from the ring results in the formation of an η^3-allyl system with respect to one iron atom which is also η^1 with respect to the second.

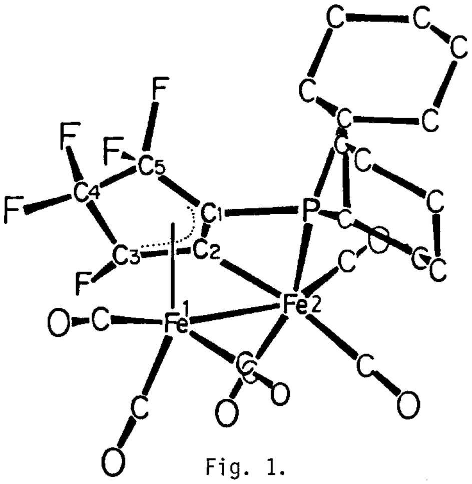

Fig. 1.

The present communication describes some experiments designed to investigate the possibility of forming similar complexes from the Group VI hexacarbonyls and from Pt(II) and Pd(II) derivatives by reacting them with $(C_6H_5)_2P\overline{C{=}CCl(C}F_2)_{n/2}$, L_n, $(C_6H_{11})_2P\overline{C{=}CCl(C}F_2)_{n/2}$, L'_n ($n = 4, 6, 8$) and $(CH_3)_2As\overline{C{=}CCl(C}F_2)_3$, L''_6.

RESULTS AND DISCUSSION

The new tertiary phosphines $R_2P\overline{C{=}CCl(C}F_2)_4$ ($R = C_6H_5$, C_6H_{11}), L_8 and L'_8, are prepared in moderate yield according to equation 1 [3].

$$R_2PH + ClC\overline{{=}CCl(C}F_2)_4 \xrightarrow{DMF} R_2P\overline{C{=}CCl(C}F_2)_4 + HCl \qquad (1)$$

When $R = C_6H_5$ the known [1] ditertiary phosphine $(C_6H_5)_2P\overline{C{=}CP(C_6H_5)_2(C}F_2)_4$ is also a reaction product.

We deliberately chose to react L_n and L'_n with the metal hexacarbonyls $M(CO)_6$ (M = Cr, Mo, W) under severe conditions (Carius tube, 115-150°C) in the hope that ligand fragmentation and/or rearrangement processes would occur. However, the results listed in Table 1 show that the only products isolated are the monosubstituted derivatives $(L_n)M(CO)_5$ or $(L'_n)M(CO)_5$. The yields are low.

All the new complexes have the expected mass spectrum consisting of a parent ion followed by peaks corresponding to the stepwise loss of five carbonyl groups. The spectroscopic properties in Table 3 are unremarkable and as expected. Some complexes show more $\nu(CO)$ bands than the three expected for a molecule with strict C_{4v} symmetry because of ligand asymmetry. All complexes show strong $\nu(C{=}C)$ and $\nu(C{-}Cl)$ bands (not listed) at essentially the same positions as the free ligand. All these data indicate that there is no interaction between the metal and the fluorocarbon moiety. The structure in the case of $(C_6H_{11})_2P\overline{C{=}CCl(C}F_2)_2Mo(CO)_5$ has been confirmed [12]. The C=C bond length is 1.326(8)Å and the cyclobutene ring is rotated so that the chlorine atom is almost as far away from the metal centre as possible.

Reactions between fluorocarbon containing ligands and salts of platinum and palladium have been little investigated [13,14]. In a particularly interesting case Carty and coworkers [15] obtained the ditertiary phosphine derivatives $(C_6H_5)_2PCH_2C(CF_3){=}CHP(C_6H_5)_2MCl_2$ (M = Pt, Pd) when MCl_4^{2-} was treated with $(C_6H_5)_2PC{\equiv}CCF_3$.

In the present investigation we find that L_n or L'_n reacts with MCl_4^{2-} to give $(L_n)_2PtCl_2$ or $(L'_n)_2PdCl_2$ (n = 6) and the chlorine bridged $(L_n)_2Pd_2Cl_4$ (n = 4, 6). The analytical data and spectroscopic results confirm these formulations and in particular the $\nu(M{-}Cl)$ bands show that the phosphines are cis in the MCl_2 complexes [16,17].

Other workers [18] report that bulky ligands tend to form bridged species $L_2M_2Cl_4$ in preference to L_2MCl_2 types. The dicyclohexylphosphino derivative L'_6 is expected to be more bulky than its diphenylphosphino analogue L_6 [3]; however the bridged complex is not obtained from the former but is obtained from the latter.

TABLE 1 Preparative data for metal carbonyl complexes

L_n or L'_n	$M(CO)_6$	Reaction Temp (°C)	Reaction Time (h)	Product	Yield %
L'_4 0.36 g 1.0 mmol	$Cr(CO)_6$ 0.22 g 1.0 mmol	130	24	$(L'_4)Cr(CO)_5$	10
L'_4 0.32 g 0.89 mmol	$Mo(CO)_6$ 0.23 g 0.89 mmol	130	20	$(L'_4)Mo(CO)_5$	35
L'_4 0.57 g 1.6 mmol	$W(CO)_6$ 0.56 g 1.6 mmol	140	120	$(L'_4)W(CO)_5$	9.0
L_4 0.45 g 1.3 mmol	$Cr(CO)_6$ 0.29 g 1.3 mmol	128	46	$(L_4)Cr(CO)_5$	11
L_4 0.50 g 1.45 mmol	$Mo(CO)_6$ 0.38 g 1.45 mmol	125	40	$(L_4)Mo(CO)_5$	25
L_4 0.75 g 2.18 mmol	$W(CO)_6$ 0.77g 2.18 mmol	125	72	$(L_4)W(CO)_5$	15
L_4 0.27 g 0.67 mmol	$Cr(CO)_6$ 0.14 g 0.67 mmol	130	44	$(L_4)Cr(CO)_5$	34
L'_6 0.35 g 0.87 mmol	$Mo(CO)_6$ 0.14 g 0.55 mmol	130	44	$(L'_6)Mo(CO)_5$	32
L'_6 0.33 g 0.82 mmol	$W(CO)_6$ 0.29 g 0.82 mmol	150	92	$(L'_6)W(CO)_5$	16

TABLE 1 - continued

L_6 0.47 g 1.2 mmol	$Cr(CO)_6$ 0.26 g 1.2 mmol	130	77	$(L_6)Cr(CO)_5$	46
L_6 0.43 g 1.07 mmol	$Mo(CO)_6$ 0.28 g 1.07 mmol	120	50	$(L_6)Mo(CO)_5$	45
L_6 0.5 g 1.2 mmol	$W(CO)_6$ 0.44 g 1.2 mmol	150	99	$(L_6)W(CO)_5$	38
L''_6 0.47 g 1.50 mmol	$Cr(CO)_6$ 0.33 g 1.50 mmol	130	95	$(L''_6)Cr(CO)_5$	25
L''_6 0.38 g 1.2 mmol	$Mo(CO)_6$ 0.32 g 1.2 mmol	115	60	$(L''_6)Mo(CO)_5$	18
L''_6 0.35 g 1.13 mmol	$W(CO)_6$ 0.39 g 1.13 mmol	150	108	$(L''_6)W(CO)_5$	14
L'_8 0.25 g 0.54 mmol	$Cr(CO)_6$ 0.12 g 0.54 mmol	130	50	$(L'_8)Cr(CO)_5$	16
L'_8 0.32 g 0.71 mmol	$Mo(CO)_6$ 0.188 g 0.71 mmol	130	46	$(L'_8)Mo(CO)_5$	34
L_8 0.29 g 0.65 mmol	$Cr(CO)_6$ 0.14 g 0.65 mmol	140	96	$(L_8)Cr(CO)_5$	36
L_8 0.32 g 0.72 mmol	$Mo(CO)_6$ 0.19 g 0.72 mmol	130	46	$(L_8)Mo(CO)_5$	45

TABLE 2 Analytical data for metal carbonyl complexes

Compound	Colour	mp(°C)	Analyses %			
			C		H	
			calc.	found	calc.	found
$(L'_4)Cr(CO)_5$	pale yellow	103	46.0	46.2	4.04	4.02
$(L'_4)Mo(CO)_5$	pale green	106	42.6	42.7	3.74	3.56
$(L'_4)W(CO)_5 \cdot 1/2C_6H_{14}$	yellow	115	39.8	39.4	3.99	3.78
$(L_4)Cr(CO)_5$	yellow	92	47.0	47.1	1.87	2.00
$(L_4)Mo(CO)_5$	pale yellow	97	43.4	43.5	1.73	1.71
$(L_4)W(CO)_5$	pale yellow	115	37.7	37.5	1.50	1.37
$(L'_6)Cr(CO)_5$	yellow	91	45.1	45.3	3.70	3.83
$(L'_6)Mo(CO)_5$	yellow	123	41.1	41.4	3.45	3.48
$(L'_6)W(CO)_5$	yellow	128	36.2	36.9	3.03	3.19
$(L_6)Cr(CO)_5$	greenish yellow	114	45.0	45.3	1.71	2.00
$(L_6)Mo(CO)_5$	green	116	41.9	41.7	1.60	1.56
$(L_6)W(CO)_5$	yellow	117	36.8	37.4	1.40	1.49

$(L''_6)Cr(CO)_5$	yellow	39	28.5	28.8	1.20	1.34
$(L''_6)MO(CO)_5$	greenish yellow	27	26.2	26.6	1.09	1.10
$(L''_6)W(CO)_5$	greenish yellow	52	22.5	22.8	0.94	1.01
$(L'_8)Cr(CO)_5$	yellow	92	42.6	42.5	3.42	3.39
$(L\ _8)Mo(CO)_5$	yellow	145	39.9	39.6	3.20	3.12
$(L_8)Cr(CO)_5$	yellow	67	43.4	43.7	1.58	1.67
$(L_8)Mo(CO)_5$	yellow	138	40.5	40.9	1.48	1.51

TABLE 3 NMR and IR spectroscopic data for metal carbonyl complexes

Compound	^{19}F nmr	$\nu(CO)$ cm^{-1}				
$(L'_4)Cr(CO)_5{}^a$	102.0(m,1) 111.2(m,1)	2080(s)	1970(sh)	1955(vs)	1940(sh)	1910(sh)
$(L'_4)Mo(CO)_5{}^a$	102.4(m,1) 111.6(m,1)	2080(s)	1965(sh)	1950(vs)	1935(sh)	1920(w)
$(L'_4)W(CO)_5{}^a$	103.5(m,1) 113.8(m,1)	2080(s)	1955(sh)	1940(vs)	1920(sh)	1900(w)
$(L_4)Cr(CO)_5{}^b$	108.9(m,1) 115.8(m,1)	2082(s)	1995(sh)	1965(s,sh)	1962(vs)	1920(sh)
$(L_4)Mo(CO)_5{}^b$	109.2(m,1) 116.0(m,1)	2082(s)	1990(sh)	1962(s,sh)	1960(vs)	1920(sh)
$(L_4)W(CO)_5{}^b$	109.2(m,1) 116.2(m,1)	2080(s)	1990(sh)	1962(s,sh)	1962(vs)	1920(sh)
$(L_4)Cr(CO)_5{}^a$	104.0(m,1) 112.0(m,1) 131.1(m,1)	2072(s)	1981(m)	1952(sh)	1945(vs)	1908(sh)
$(L'_6)Mo(CO)_5{}^a$	104.1(m,1) 112.0(m,1) 131.4(m,1)	2080(s)	1988(m)	1955(sh)	1945(vs)	1914(sh)
$(L'_6)W(CO)_5{}^a$	104.6(m,1) 111.6(m,1) 130.8(m,1)	2082(s)	1990(m)	1955(sh)	1945(vs)	1920(sh)
$(L_6)Cr(CO)_5{}^b$	104.5(m,1) 113.0(m,1) 129.6(m,1)	2075(s)	1990(sh)	1960(sh)	1945(vs)	1920(m)
$(L_6)Mo(CO)_5{}^b$	104.4(m,1) 112.6(m,1) 129.8(m.1)	2079(s)	1990(sh)	1958(sh)	1950(vs)	1920(m)

TABLE 3 - continued

$(L_6)W(CO)_5$[b]	104.2(m,1) 112.2(m,1) 129.2(m,1)	2082(s)	1985(sh)	1958(sh)	1950(vs)	1920(m)
$(L''_6)Cr(CO)_5$[c]	104.0(m,1) 113.4(m,1) 129.6(m,1)	2075(s)	1988(sh)	1960(s,sh)	1950(vs)	1920(sh)
$(L''_6)Mo(CO)_5$[c]	103.6(m,1) 113.0(m,1) 129.4(m,1)	2080(s)	1992(sh)	1965(s,sh)	1955(vs)	1922(sh)
$(L''_6)W(CO)_5$[c]	103.6(m,1) 113.2(m,1) 129.6(m,1)	2082(s)	1992(sh)	1965(s,sh)	1958(vs)	1925(sh)
$(L'_8)Cr(CO)_5$[a]	104.2(m,1) 110.4(m,1) 134.6(m,2)	2071(s)	1989(w,sh)	1955(sh)	1948(vs)	1910(sh)
$(L'_8)Mo(CO)_5$[a]	104.1(m,1) 110.6(m,1) 134.6(m,2)	2080(s)	1989(w,sh)	1960(sh)	1955(vs)	1915(sh)
$(L_8)Cr(CO)_5$[b]	103.5(m,1) 110.6(m,1) 134.6(m,2)	2075(s)	1989(w,sh)	1959(sh)	1950(vs)	1920(sh)
$(L_8)Mo(CO)_5$[b]	103.4(m,1) 110.4(m,1) 134.6(m,2)	2082(s)	1995(w,sh)	1962(sh)	1960(vs)	1930(sh)

[a] ^1H NMR spectrum of all complexes consists of a broad multiplet in the region 1.0 - 2.2.

[b] ^1H NMR 7.4(m).

[c] ^1H NMR 1.83(m).

Although unsymmetrical ligands of the type $(CH_3)_2As\overline{C=CP(C_6H_5)_2(C}F_2)_n$ are known [1] attempts to prepare related ditertiary phosphines $R_2P\overline{C=CPR'_2(C}F_2)_n$ using analogous procedures have been unsuccessful [11]. In the hope that a complex of such an unsymmetrical ditertiary phosphine could be formed diphenylphosphine was reacted with $(L'_4)Mo(CO)_5$. The expected $Mo(CO)_4$ derivative was not isolated.

EXPERIMENTAL

All reactions were carried out either in conventional reaction flasks under a nitrogen atmosphere or in a sealed evacuated Carius tubes.

Infrared spectra were recorded on a Perkin-Elmer Model 457 spectrometer and were calibrated using polystyrene; only selected bands are quoted. All nmr spectra were run using $CDCl_3$ solutions and Varian T-60 and XL-100 instruments. Chemical shifts are given in ppm downfield from internal TMS (^1H) and upfield from internal $CFCl_3$ (^{19}F). Mass spectra were recorded using an AEI MS-9 spectrometer. Melting points were determined on a Gallenkamp apparatus and are uncorrected. Microanalyses were performed by Mr. Peter Borda of the Department of Chemistry, U.B.C.

The hexacarbonyls $M(CO)_6$ (M = Cr, Mo, W) and dicyclohexylphosphine were obtained from Strem Chemical Incorporated. Fluorocarbons were purchased from PCR Incorporated, and platinum and palladium salts from Platinum Chemicals Inc. All were used without further purification.

Preparation of 1-chloro-2-dicyclohexylphosphinooctafluorocyclohexene, L'_8

Dicyclohexylphosphine (2.9 g, 14.8 mmol) in DMF (14 ml) was added to a stirred solution of 1,2-dichlorooctafluorocyclohexene (4.36 g, 14.7 mmol) in DMF (10 ml) at 0°C. After an hour the solution was warmed to 20°C, left for 4 h and refluxed for 5 h. The resulting red solution was cooled to 20°, poured into water (150 ml), and extracted with ether. The extracts were dried ($MgSO_4$). Removal of solvent gave an orange oil which was dissolved in a small volume of dichloromethane and chromatographed on a Florisil column. A yellow band was eluted with petroleum ether (b.p. 40-60°C). The solvent was evaporated and the yellow solid residue was recrystallized from hexane and identified as 1-chloro-2-dicyclohexylphosphinooctafluorocyclohexene (1.2 g, 17.8% yield) m.p. 47°C. ^1H nmr:

1.0-2.2(m); ^{19}F nmr: 104.0 (area 1), 110.4 (area 1), 134.4 (area 2) all multiplets; mass spec: m/e 456 (M^+); i.r. 1585(m) (C=C), 1345(m), 1230(vs), 1210(vs), 1170(vs), 1140(s), 1118(s), 1040(m), 990(s), 870(m), (C-Cl), 800 cm^{-1}. Anal. calc. for $C_{18}H_{22}ClF_8P$: C, 47.3; H, 4.85, Found: C, 47.8, H, 4.88%.

Preparation of 1-chloro-2-diphenylphosphinooctafluorocyclohexene, L_8

Diphenylphosphine (2.42 g, 13.0 mmol) in DMF (15 ml) was added to 1,2-dichlorooctafluorocyclohexene (3.83 g, 12.9 mmol) at 0°C. The reaction mixture was treated as described above and on cooling to 0°C an orange solid precipitated. This solid was recrystallized from hexane affording orange crystals of 1,2-bis(diphenylphosphino)octafluorocyclohexene (0.98 g, 25.4%) of known spectroscopic properties [1].

The filtrate was poured into water and extracted with ether as described above. Chromatography on Florisil afforded a yellow band which was eluted with petroleum ether. This gave yellow crystals of 1-chloro-2-diphenylphosphinooctafluorocyclohexene on recrystallization from hexane (1.2 g, 21.05%) m.p. 63°C, ^{1}H nmr: 7.4(m); ^{19}F nmr 103.5 (area 1); 110.6 (area 1); 134.4 (area 2) all multiplets; mass spec. m/e 444 (M^+); i.r. 1585(m) (C=C), 1345(m), 1230(vs), 1210(vs), 1170(vs), 1135(s), 1120(s), 990(s), 870(m) (C-Cl); 800(m), 750(s) cm^{-1}. Anal. calc. for $C_{18}H_{10}ClF_8P$: C, 48.6; H, 2.26, Found: C, 49.2, H, 2.51%.

Reactions of the tertiary phosphines, L_n and L'_n with group VI hexacarbonyls

The general procedure for the preparation of the $LM(CO)_5$ complexes is as follows and specific details are given in Table 1. A benzene solution containing ligand and hexacarbonyl (1:1 mole ratio) was heated in a Carius tube. At the end of the reaction period the tube was opened and the solvent removed at reduced pressure. The solid residue was dissolved in a small volume of dichloromethane and chromatographed on a Florisil column. The complexes were eluted with diethyl ether/petroleum ether (b.p. 40-60°C) 1/99. Evaporation of the solvent gave the desired solids which were then recrystallized from hexane.

TABLE 4 Preparative data for platinum and palladium complexes

L_n or L'_n	M'_2MCl_4	Product	Yield %
L_4 0.28 g 0.82 mmol	Na_2PdCl_4 0.24 g 0.82 mmol	$[(L_4)PdCl_2]_2$ [a]	45
L'_6 0.34 g 0.84 mmol	Na_2PdCl_4 0.25 g 0.84 mmol	$(L'_6)_2PdCl_2$ [d]	60
L'_6 0.30 g 0.75 mmol	K_2PtCl_4 0.31 g 0.74 mmol	$(L'_6)_2PtCl_2$ [d]	69
L_6 0.37 g 0.94 mmol	Na_2PdCl_4 0.28 g 0.94 mmol	$(L_6)_2PdCl_2$ [b] and	56
		$[(L_6)PdCl_2]_2$ [c,d]	19
L_6 0.32 g 0.81 mmol	K_2PtCl_4 0.34 g 0.82 mmol	$(L_6)_2PtCl_2$ [d]	44

[a] Recrystallized from hexane.

[b] Recrystallized from ethanol.

[c] Isolated by cooling the orange filtrate obtained after filtering off $(L_6)_2PdCl_2$.

[c] Recrystallized from dichloromethane.

TABLE 5 Analytical and spectroscopic data for platinum and palladium complexes

Compound	Colour	mp(°C)	C		H		Cl		^{19}F NMR[c]	ν(M-Cl) cm^{-1}[d]		
			calc.	found	calc.	found	calc.	found				
$[(L_4)PdCl_2]_2$	orange	177	38.6[a]	38.4	2.50[a]	2.51	20.4[b]	20.8	109.2 116.6	358(m)	299(w)	260(m)
$(L'_6)_2PdCl_2$	pale yellow	254	41.2	41.3	4.47	4.48	14.3	14.1	104.4 114.8 132.6	355(m)	310(w)	
$(L'_6)_2PtCl_2$	pale yellow	294	37.8	37.8	4.11	4.04	13.1	13.1	104.6 114.6 132.8	340(w)	300(m)	
$(L_6)_2PdCl_2$	yellow	202	42.2	42.1	2.08	2.21	14.6	14.6	105.4 115.1 130.0	357(m)	318(w)	
$[(L_6)PdCl_2]_2$	orange	207	35.7	35.9	1.76	1.88	18.6	17.1	105.2 115.1 130.0	360(m)	300(w)	265(m)
$(L_6)_2PtCl_2$	yellow	248	36.7	36.4	4.20	4.02			105.4 115.0 130.2	342(w)	305(m)	

[a] Anal calc. for $C_{32}H_{20}Cl_6F_8P_2Pd_2 \cdot 0.5\ C_6H_{14}$.

[b] Anal. calc. for $C_{32}H_{20}Cl_6F_8P_2Pd_2$ (sample recrystallized from ethanol).

[c] All bands are multiplets.

[d] Nujol mull.

Reaction of $(C_6H_{11})_2P\overline{C=CCl(C}F_2)_2Mo(CO)_5$ with diphenylphosphine

Diphenylphosphine (0.148 g, 0.79 mmol) and the complex (0.47 g, 0.79 mmol) in benzene (8 ml) were heated in a Carius tube at 115° for 24 h. Chromatography of the reaction mixture on Florisil afforded only a green band which contained unreacted $Mo(CO)_5$ derivative (0.135 g, 28% recovery).

When the reaction was carried out at 150°C considerable charring took place. The i.r. spectrum showed the absence of the expected $Mo(CO)_4$ derivative.

Reaction of the tertiary phosphines L_n and L'_n with sodium tetrachloropalladate(II) and potassium tetrachloroplatinate(II)

In general a solution of the metal halide in water (15-20 ml) was added dropwise to a solution of the ligand in acetone (10-15 ml). An immediate precipitate was formed and the resulting suspension was stirred for 24 h (20°C). The solid was isolated and recrystallized. Analytical and spectroscopic data are noted in Table 5.

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