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THE PREPARATION OF ACYL— AND SULPHONATO—PLATINUM(II) COMPLEXES FROM BIS(TRIPHENYLPHOSPHINE)PLATINUM ETHYLENE

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Summary

The acyl—platinum complexes *trans*-[PtCl(COR)L_2] (L = PPh_3) have been obtained in high yield from the reaction between [$PtL_2(C_2H_4)$] and the acyl chlorides RCOCl (where R = Ph, C_6H_4OMe-*p*, C_6H_4Cl-*p*, CH=CH_2, CH=CHMe, CMe=CH_2, CH=CHPh). The sulphonato complexes *trans*-[PtCl(SO_2R)L_2] (with R = Ph or Me) have been obtained analogously from the sulpholyl chlorides, RSO_2Cl.

The complex *trans*-[PtCl(COCH=CHPh-*trans*)L_2] undergoes decarbonylation on heating to give *trans*-[PtCl(CH=CHPh-*trans*)L_2].

Introduction

In connection with an investigation of the interaction of acyl and sulphonyl chlorides with triethylsilane in the presence of transition metal complexes [1-3], we needed certain acyl— and sulphonato—platinum complexes. It is known that such complexes can be obtained by treatment of [$Pt(PR_3)_n$] (n = 3 or 4) with acyl or sulphonyl chlorides [4-7], and we found that the analogous reaction with [$PtL_2(C_2H_4)$] (L = PPh_3) gives the expected [PtCl(COR)L_2] and [PtCl(SO_2R)L_2] complexes in high yield. Some properties of the products are discussed.

Results and discussion

All the acyl halides and the two sulphonyl halides used reacted readily. The use of the platinum ethylene complex has the advantage that the only by-product, ethylene, volatilizes from the system. The benzoyl chlorides and benzenesulphonyl chloride could be added directly to the platinum—ethylene complex, but with the aliphatic acyl chlorides and methanesulphonyl chloride the reaction was so vigorous that benzene had to be used as solvent to moderate the reaction.

The melting points of the acyl complexes prepared, along with relevant IR data, are listed in Table 1, and some ^1H NMR data in Table 2. All the acyl complexes were white or pale yellow solids, stable in air as solids and in solution. They

TABLE 1

MELTING POINTS AND IR SPECTROSCOPIC DATA FOR *trans*-$[PtCl(COR)(PPh_3)_2]$

R	M.p. (°C)[a]	$\nu(C{=}O)$[b] (Nujol)	$\nu(C{=}O)$[b] ($CHCl_3$)	$\nu(Pt{-}Cl)$[b] (Nujol)	Other strong bands at 200-400 cm^{-1}
C_6H_5	285-290	1625[c]	1620	261	338
p-$MeOC_6H_4$	290-292	1614[d]	1612[d]	272	
p-ClC_6H_4	299-304		1629[e]	267	
CH_3	275-277	1653		269	343
$CH_2{=}CH$	*f*	1642	1605	254	292, 344
$MeCH{=}CH$[h]	228-230	1597[g]	1597[g]	262	325
$PhCH{=}CH$[h]	228-230	1605	1587	269	
$CH_2{=}CMe$	215-218	1610	1605	256	350

[a] In vacuo. Melting occurs with decomposition. [b] in cm^{-1}. [c] Gradually changes to 1615 cm^{-1} in the mull. [d] Tentative assignment, since less intense but still strong bands appear also at 1585 (Nujol) and at 1587 and 1595 cm^{-1} ($CHCl_3$). [e] Other strong bands at 1609, 1581, and 1569 cm^{-1}. [f] Decomposes at ca. 150°C without melting. [g] Less intense but strong bands appear also at 1635 (Nujol) and 1642 cm^{-1} ($CHCl_3$). [h] *Trans.*

are readily soluble in chloroform, moderately soluble in benzene, and insoluble in light petroleum.

The properties show some features of interest, as follows:

(*a*). Decarbonylation of the $[PtCl(COC_6H_4X)L_2]$ complexes (X = H, *p*-OMe, *p*-Cl) takes place on heating with partial melting, but the material resolidifies, and the observed final m.p. is that of the decarbonylated $[PtCl(C_6H_4X)L_2]$; decarbonylation ranges were (X =) H, 212-220; *p*-OMe, 203-210; *p*-Cl; 180-190°C. There have been attempts to interpret the decarbonylation temperatures of acyl—platinum complexes in terms of the electronic characteristics of the ligands [6], but we think it likely that decomposition usually occurs as a consequence of melting, the temperature of which depends mainly on the strength of the intermolecular interactions in the crystal.

(*b*). In keeping with that view, we found that *trans*-[PtCl(COCH=CHPh-*trans*)-L_2] decomposed to [PtCl(CH=CHPh-*trans*)L_2] at 195°C when heated alone, and also when its solution in mesitylene (b.p. 164°C) was refluxed. The stereochemistry about the double bond is retained, but we cannot rule out the possibility that the *cis*-styryl complex is first produced and undergoes isomerization at the high temperature involved.

TABLE 2

^1H NMR DATA (IN $CDCl_3$) FOR $[PtCl(COCR^1{=}CR^2R^3)(PPh_3)_2]$ COMPLEXES

Acyl ligand	τ_1	τ_2	τ_3	$J(1{-}2)$[a]	$J(1{-}3)$[a]	$J(2{-}3)$[a]
$COCH_2{=}CH_2$	*b*	*b*	3.86		15.0	3.5
COCH=CHMe-*trans*	5.18	8.75[c]	3.34	1.5[d]	15.0	6.5[d]
COCH=CHPh-*trans*	4.65	*b*			15.5	
$COCMe{=}CH_2$	9.30[c]	4.39	3.20			

[a] Hz. [b] Masked by other resonances. [c] Methyl proton resonances. [d] $H{-}CH_3$ proton coupling.

Attempts to prepare alkenyl—platinum complexes analogously from the other alkenoyl complexes were unsuccessful. Decarbonylation occurred at 150-200°C, but was accompanied by extensive decomposition, and the only pure product isolated was *cis*-[$PtCl_2L_2$].

(*c*). The ν(Pt—Cl) stretching frequencies for the acyl complexes fall in the range 252-272 cm^{-1} and give rise to the strongest bands in the 200-400 cm^{-1} region. For *trans*-[$PtCl(COPh)L_2$], the assignment was confirmed by conversion of the complex into the corresponding bromo complex, *trans*-[$PtBr(COPh)L_2$], which showed the expected ν(Pt—Br) band at 176 cm^{-1}. The ν(Pt—Cl) frequencies indicate that the acyl ligands have high trans-influences. The frequencies are mostly somewhat lower than for Cl *trans* to H, Me, or Ph, and in some cases approach those for Cl *trans* to R_3Si and R_3Ge groups. The significance of this observation, viz. that the *trans*-influence of a ligand appears to depend predominantly on the nature of the ligating atom and little on the overall inductive effect of the ligand, has been pointed out previously [8].

(*d*). In the ^1H NMR spectrum, all the acyl complexes prepared showed a broad complex resonance centred at τ 2.22-2.26 and a sharper complex resonance centred at τ 2.59-2.65, both due to protons of the phosphine ligands. The resonances associated with the alkenoyl groups (Table 2) show the expected features. The ^{31}P NMR spectrum of *trans*-[$PtCl(COPh)L_2$] showed a sharp singlet at $\delta(H_3PO_4)$ —20.0 ppm., *J*(Pt—P) 3328 Hz, confirming the *trans*-configuration.

(*e*). The ν(Pt—Cl) bands of *trans*-[$PtCl(SO_2Ph)L_2$] and *trans*-[$PtCl(SO_2Me)L_2$] in Nujol appeared at 315 and 302 cm^{-1}, respectively, which is consistent with data for related complexes [9,10], and indicates a medium *trans*-influence.

Experimental

The light petroleum used had a b.p. of 40-60°C. All reactions were carried out under dry nitrogen. The m.p.'s were in vacuo.

Preparation of trans-[$PtCl(COR)L_2$] complexes

(*i*). Benzoyl chloride (1 ml) was added to [$PtL_2(C_2H_4)$] (0.300 g, 0.404 mmol). Gas evolution began immediately, and a pale yellow-green solution was formed. This was kept at room temperature for 1 h, during which pale green crystals separated. Hexane (ca. 20 ml) was added to precipitate more solid. The solid was filtered off, dried (0.321 g, 93%), and recrystallized from benzene/light petroleum to give *trans*-[$PtCl(COPh)L_2$], m.p. 285-290°C (dec.) (lit. [6], 285-291°C (dec.)). (Analysis found: C, 60.2; H, 4.3. $C_{45}H_{35}ClOP_2Pt$ calcd.: C, 60.0; H, 4.1%.)

(*ii*). Similar procedures gave the complexes *trans*-[$PtCl(COC_6H_4X)L_2$] with X = *p*-OMe (86%), m.p. 289-292°C (dec.) (Analysis found: C, 59.3; H, 4.2. $C_{44}H_{37}ClO_2P_2Pt$ calcd.: C, 59.35; H, 4.2%), and X = *p*-Cl (90%), m.p. 299-304°C (dec.) (Analysis found: C, 57.1; H, 3.9. $C_{43}H_{34}Cl_2Pt$ calcd.: C, 57.7; H, 3.8%.)

(*iii*). Crotonyl chloride (0.25 ml) was added dropwise to [$PtL_2(C_2H_4)$] (0.300 g, 0.404 mmol) in benzene (3 ml). Gas evolution began immediately. The pale yellow solution was set aside for 1 h at room temperature, the small amount of white solid was filtered off, and light petroleum (b.p. 40-60°C) (25 ml) was added to the filtrate to precipitate a cream solid (0.307 g, 92%). Recrystallization from benzene/light petroleum gave (PtCl(COCH=CHMe-*trans*)L_2], m.p. 228-230°C (dec.) (Analysis found: C, 58.4; H, 4.3. $C_{40}H_{35}ClOP_2Pt$ calcd.: C, 58.3; H, 4.3%.) The ^1H NMR spectrum (Table 2) indicated the *trans*-configuration about the double bond.

(*iv*). Similar procedures gave *trans*-[PtCl(COR)L_2] with R = CMe=CH_2 (88%), m.p. 215-218°C (dec.), (Analysis found: C, 58.3, H, 4.4. $C_{40}H_{35}ClOP_2Pt$ calcd.: C, 58.3; H, 4.3%); R = CH=CH_2 (86%), decomposes above 150°C in vacuo. (Analysis found: C, 57.9; H, 4.4. $C_{39}H_{33}ClOP_2Pt$ calcd.: 57.3; H, 4.1%.) R = CH_3, m.p. 275-277°C (dec.), ν(CO) 1653 cm^{-1} (lit. [5], 1652 cm^{-1}).

(*v*). Warm cinnamoyl chloride (1 ml) was added dropwise to [PtL_2(C_2H_4)] (0.300 g, 0.404 mmol). Gas evolution began immediately. The orange-yellow solution was warmed in a bath at 50°C for 1 h, during which yellow crystals separated. After cooling, light petroleum (3 ml) was added, and additional yellow solid separated. The solid was filtered off and washed with hot light petroleum and dried to give pale yellow crystals (0.329 g, 92%). Recrystallization from benzene/light petroleum gave *trans*-[PtCl(COCH=CHPh-*trans*)L_2], m.p. 227-230°C (dec.). (Analysis found: C, 60.9; H, 4.4. $C_{45}H_{37}ClOP_2Pt$ calcd.: C, 61.0; H, 4.2%.) The *trans*-configuration about the double bond was shown by the NMR spectrum (Table 2).

Decarbonylation of trans-[PtCl(COCH=CHPh-trans)L_2]

(*i*). The [PtCl(COCH=CHPh)L_2] (0.500 g, 0.562 mmol) was dissolved in warm mesitylene (6 ml). The yellow solution was boiled under reflux for 10 min, during which it turned light brown. Cooling and addition of light petroleum (30 ml) gave an off-white solid (0.304 g, 60%), which was recrystallized from toluene and shown to be *trans*-[PtCl(CH=CHPh-*trans*)L_2], m.p. 228-230°C (lit. [11], 215-217°C). (Analysis found: C, 61.8; H, 4.5. $C_{44}H_{37}ClP_2Pt$ calcd.: C, 61.6; H, 4.35%).

(*ii*). The [PtCl(COCH=CHPh)L_2] (0.200 g, 0.226 mmol) was heated under nitrogen to 195°C. The product (0.189 g, 97%) was shown by its IR and NMR spectra to be *trans*-[PtCl(CH=CHPh-*trans*)L_2].

Decarbonylation of trans-[PtCl(COPh)L_2]

The [PtCl(COPh)L_2] (0.200 g, 0.232 mmol) was heated under vacuum at 230°C for 30 min. After cooling, the off-white solid (0.186 g, 96%) was recrystallized from chloroform/methanol to give *trans*-[PtClPhL_2], m.p. 287-290°C (lit. [6], 287-292°C).

Preparation of trans-[PtBr(COPh)L_2]

Anhydrous lithium bromide (0.126 g, 1.45 mmol) was added to *trans*-[PtCl(COPh)L_2] (0.125 g, 0.145 mmol) in acetone (2 ml). The suspension was stirred at room temperature for 2 h, then the acetone was evaporated off, and the solid residue extracted with benzene. The extract was treated with light petroleum to give *trans*-[PtBr(COPh)L_2], (0.115 g, 88%), m.p. 284-285°C (dec.). (Analysis found: C, 57.4; H, 4.1. $C_{43}H_{35}BrOP_2Pt$ calcd.: C, 57.1; H, 3.9%.)

Preparation of trans-[PtCl(SO_2R)L_2]

(*i*). Benzenesulphonyl chloride (1 ml) was added dropwise to [PtL_2(C_2H_4)]

(0.150 g, 0.202 mmol). Gas evolution began immediately. The solution was set aside at room temperature for 1 h. Addition of light petroleum (20 ml) and methanol (2 ml) gave a white solid (0.159 g, 88%) which was recrystallized from chloroform/light petroleum to give the 1/1 chloroform adduct *trans*-[PtCl(SO_2Ph)-L_2]. $CHCl_3$, m.p. 270-274°C (dec.). IR (Nujol): $\nu_{asym.}(SO_2)$ 1210, $\nu_{sym.}(SO_2)$ 1057 and ν(Pt—Cl) 315 cm^{-1}. (Analysis found: C, 50.5; H, 3.7. $C_{43}H_{36}Cl_4O_2SP_2Pt$ calcd.: C, 50.85; H, 3.6%.)

(*ii*). Methanesulphonyl chloride (0.5 ml) was added dropwise to a solution of [$PtL_2(C_2H_4)$] (0.300 g, 0.404 mmol) in benzene (4 ml). Gas evolution began immediately. The solution was set aside for 1 h at room temperature, during which white crystals separated. Addition of light petroleum caused separation of additional solid. The solid (0.312 g, 93%) was recrystallized from benzene/light petroleum to give *trans*-[PtCl(SO_2Me)L_2], m.p. 254-255°C (dec.). IR (Nujol): $\nu_{asym.}(SO_2)$ 1218, $\nu_{sym.}(SO_2)$ 1071. ν(Pt—Cl) 302 cm^{-1}. (Analysis found: C, 52.8; H, 4.0. $C_{37}H_{33}ClO_2SP_2Pt$ calcd.: C, 53.3; H, 4.0%.)

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References

1 S.P. Dent, C. Eaborn and A. Pidcock, Chem. Commun., (1970) 1703.
2 B. Courtis, S.P. Dent, C. Eaborn and A. Pidcock, J.Chem. Soc., Dalton Trans., (1975) in press.
3 S.P. Dent, C. Eaborn and A. Pidcock, J. Chem. Soc., Dalton Trans., (1975) in press.
4 U. Belluco, Organometallic and Coordinations Chemistry of Platinum, Academic Press, London and New York, 1974, pp. 9, 229.
5 C.D. Cook and G.S. Jauhal, Can. J. Chem., 45 (1967) 301.
6 M.C. Baird and G. Wilkinson, J. Chem. Soc. A, (1967) 865.
7 A.J. Murkhedkar, M. Green, and F.G.A. Stone, J. Chem. Soc. A, (1969) 3023; (1970) 947.
8 S.P. Dent, C. Eaborn, A. Pidcock and B. Ratcliff, J. Organometal. Chem., 46 (1972) C68.
9 J. Chatt and D.M.P. Mingos, J. Chem. Soc. A, (1969) 1770.
10 B. Faraone, L. Silvestro, S. Sergi and R. Pietropaolo, J. Organometal. Chem., 34 (1972) C55.
11 B.E. Mann, B.L. Shaw, and N.I. Tucker, J. Chem. Soc. A, (1971) 2667.