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Preliminary communication

The *trans*-influence of acyl groups in *trans*-[PtCl(COR)(PPh$_3$)$_2$] complexes

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SUMMARY

The ν(PtCl) band appears at 254–272 cm^{-1} in a range of acyl–platinum complexes, *trans*-[PtCl(COR)(PPh$_3$)$_2$], indicating that the acyl groups have a large *trans*-influence.

Baird and Wilkinson[1] observed a band at 337 cm^{-1} in the far IR spectrum of the complex *trans*-[PtCl(COPh)(PPh$_3$)$_2$], and assigned it to ν(PtCl), since on decarbonylation of the complex it was replaced by a band at 284 cm^{-1}. They tentatively concluded that the acyl group has a very low *trans*-influence, and a value of 337 cm^{-1} for ν(PtCl) would imply a *trans*-influence rather similar to that of chloride, since the ν(PtCl) band appears at 338 cm^{-1} in *trans*-[PtCl$_2$(PEt$_3$)$_2$][2]. However, in the Pt^{IV} complexes [PtClMe$_2$(X)(PMe$_2$Ph)$_2$] having X *trans* to Cl, Ruddick and Shaw found the ν(PtCl) values to be very similar (*viz.* 244 and 243 cm^{-1}, respectively) for X = Me and COMe[3].

In connection with other studies[4], we have prepared a range of *trans*-[PtCl(COR)(PPh$_3$)$_2$] complexes by treatment of the [Pt(PPh$_3$)$_2$C$_2$H$_4$] complex with the appropriate acyl chloride, and these are listed, along with their m.p.'s and some IR frequencies in Table 1. We find that for *trans*-[PtCl(COPh)(PPh$_3$)$_2$]*, there is a band at 338 ± 2 cm^{-1}, as noted by Baird and Wilkinson, but there is also a somewhat stronger band at 261 cm^{-1}, and we believe that the latter must be assigned to ν(PtCl), since it is absent in the spectrum of the corresponding bromide, *trans*-[PtBr(COPh)(PPh$_3$)$_2$], which, however, still shows the band at 338 cm^{-1}, along with a ν(PtBr) band at 176 cm^{-1} (polythene). This means that the benzoyl group does, in fact, have a large *trans* influence [*cf.* the ν(PtCl) values of 269 and 274 cm^{-1},

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* Our sample of this complex appears to be identical with that prepared by Baird and Wilkinson[1], except for the band at 261 cm^{-1}. They were not wholly certain that their complex was *trans*, but ours was shown to be so by the appearance of a sharp singlet (at δ(H$_3$PO$_4$) –20.0) with platinum satellites [J(Pt–P), 3328 Hz] in the ^{31}P NMR spectrum.

TABLE 1

PROPERTIES OF ACYL–PLATINUM COMPLEXES

trans-Complex	*m.p.* [a] *(°C)*	*ν(C=O) (Nujol)* *(cm^{-1})*	*ν(C=O) (CHCl$_3$)* *(cm^{-1})*	*ν(PtCl) (Nujol)* *(cm^{-1})*	*Other strong bands at 200–400 cm^{-1}* *(cm^{-1})*
[PtCl(COPh)(PPh$_3$)$_2$]	285–290	1625 [b]	1620	261	338
[PtCl(COC$_6$H$_4$OMe-*p*)(PPh$_3$)$_2$]	289–292	1614 [c]	1612 [c]	272	
[PtCl(COCH=CH$_2$)(PPh$_3$)$_2$]	[d]	1642	1605	254	292, 344
[PtCl(COCH=CH$_2$)(PMePh$_2$)$_2$]	141–143	1605	1605	272	331, 335
[PtCl(COCMe=CH$_2$)(PPh$_3$)$_2$]	215–218	1610	1605	256	350
[PtCl(COCH=CHMe-*trans*)(PPh$_3$)$_2$]	228–230	1597 [e]	1597 [e]	262	325
[PtCl(COCH=CHPh-*trans*)(PPh$_3$)$_2$]	227–230	1605	1587	269	

[a] In vacuo. Melting occurs with decomposition except where indicated. [b] Gradually changes to 1615 cm^{-1} in the Nujol mull. [c] Tentative assignment, since less intense, strong bands appear also at 1585 (Nujol) and at 1587 and 1595 cm^{-1} (CHCl$_3$). [d] Decomposes without melting at ca 150°.
[e] Less intense, strong bands appear at 1635 (Nujol) and 1642 (CHCl$_3$).

respectively, for *trans*-[PtCl(H)(PEt$_3$)$_2$] and *trans*-[PtCl(Me)(PEt$_3$)$_2$] [2]]. That this is general for acyl groups is indicated by the ν(PtCl) values for the other acyl complexes listed in Table 1, which fall in the range 254–272 cm^{-1}, and the influence of the COCH=CH$_2$ ligand appears to be not much smaller than that of the Ph$_2$MeSi ligand (*cf.* the ν(PtCl) value of 242 cm^{-1} for *trans*-[PtCl(SiMePh$_2$)(PPhMe$_2$)$_2$] [5], although the ν(PtCl) band is shifted to 272 cm^{-1} in *trans*-[PtCl(COCH=CH$_2$)(PMePh$_2$)$_2$].

The importance of this observation lies in the fact that the *trans* influence of various ligands is commonly associated with their inductive effects, and acyl groups are quite strongly electron-withdrawing by the inductive mechanism, as indicated by the following σ_I values[6]: Me, −0.05; SMe +0.19; OH, +0.27; COMe, +0.28; I, +0.39 .★ This is strong additional evidence that the identity of the ligating atom dominates the *trans* influence, the electronegativity of the ligand as a whole being of relatively little importance (*cf.* ref. 7). X-ray studies are planned, to ascertain whether the large *trans* influence of the acyl groups is reflected in the Pt–Cl bond length.

All the *trans*-[PtCl(COR)(PPh$_3$)] complexes undergo decarbonylation on heating. In the case of *trans*-[PtCl(COCH=CHPh-*trans*)(PPh$_3$)$_2$], heating the solid at 195° for ca. 15 min gives the styryl complex *trans*-[PtCl(CH=CHPh-*trans*)(PPh$_3$)$_2$], m.p. 228–230° (in vacuo), ν(PtCl) 290, ν(C=C) 1558, in virtually quantitative yield. Although only mixtures have so far been obtained from the other substituted acryloyl complexes listed in Table 1, this reaction may provide a useful route to certain substituted vinyl–platinum complexes, and we hope to study its scope.

★ In contrast to the benzoyl group, the benzenesulphonyl group has a medium *trans* influence, as indicated by our observation that ν(PtCl) appears at 315 cm^{-1} in the case of *trans*-[PtCl(SO$_2$Ph)(PPh$_3$)$_2$].

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