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Preliminary communication

ACYLPLATINUM COMPLEXES DERIVED FROM SALICYLALDEHYDE

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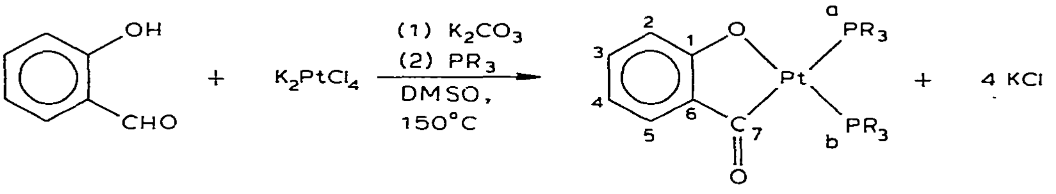
Summary

The reaction of salicylaldehyde with K_2PtCl_4, K_2CO_3 and 2 mol of tertiary phosphine, PR_3 in DMSO affords the novel acyl complex $[Pt(OC_6H_4CO)(PR_3)_2]$ in which both the phenolic oxygen and the aldehyde carbon are coordinated to platinum.

Although there are many examples of cyclometallation reactions [1,2] we know of no case of the formation of a platinum-acyl bond from aldehydes. We report here the synthesis of acylplatinum complexes I from salicylaldehyde and potassium tetrachloroplatinate, as shown in eq. 1.



(1)

(R = n-Bu, Ph, *p*-Tol)

(I)

The new complexes were characterized using NMR (^{13}C, ^1H and ^{31}P), mass and infrared spectroscopic methods. The compounds afforded satisfactory molecular weights (CH_2Cl_2) and microanalyses, although the latter were difficult because of the tendency of the complexes to lose carbon monoxide upon heating. The loss of carbon monoxide was also observed in the mass spectrum of the $P(p\text{-Tol})_3$ complex.

The P-n-Bu_3 complex was the most amenable to NMR study as it is readily soluble in $CDCl_3$ and shows no ^{13}C or ^1H resonances from arylphosphines. The $^{13}C\{^1H\}$ spectrum of this derivative shows a doublet of doublets for the acyl carbon, C(7), at 224.9 ppm (TMS), ($^2J(P_a,C)$ 113 Hz, $^2J(P_b,C)$ 3 Hz) flanked by platinum-195 satellites (^1J(Pt,C) 935 Hz). This ^{13}C chemical shift is consistent with that of an acyl carbon bound to platinum [3] and the one-bond platinum—carbon coupling is reasonable for a carbon *trans* to a phosphorus ligand [4]. The six remaining aromatic ^{13}C resonances are readily assigned and are in agreement with the literature [5,6].

^{1}H NMR spectrum (360 MHz) shows four distinct aromatic protons (δ(H(2)) 6.82 ppm, δ(H(3)) 7.18 ppm, δ(H(4)) 6.43 ppm and δ(H(5)) 7.33 ppm) with the appropriate proton—proton coupling patterns. The ^{31}P{^{1}H} NMR spectrum (H_3PO_4) shows P_a as a doublet at 6.5 ppm and P_b as a doublet at 4.9 ppm ^2J(P,P) 9.5 Hz. The ^1J(Pt,P) values of 1461 and 4107 Hz, for P_a and P_b, respectively, are consistent with the proposed structure [7].

For all three complexes there is a strong band in the IR corresponding to the C=O stretch (1615—1640 cm^{-1}). This is in keeping with the value of 1610—1636 cm^{-1} reported by Booth and Chatt [8] for the complex *trans*-[PtX(COR)-$(PEt_3)_2$].

To our knowledge this is the first report of the synthesis of an acylplatinum complex using an aldehyde as starting material. In view of the ready availability of aldehydes and the good yields (> 80%) obtained, this type of reaction may have synthetic potential.

Acknowledgments

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