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Preliminary communication

The Synthesis of a Cationic Ylide Complex of Platinum(II) by the Reaction of Tetrakis(triphenylphosphine)platinum(0) with Chloroiodomethane.

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SUMMARY

The reaction of $Pt(PPh_3)_4$ with CH_2ClI in benzene yields the cationic ylide complex cis-$[Pt(PPh_3)_2(CH_2PPh_3)Cl]I$ in high yield. This complex has been converted to cis-$[Pt(PPh_3)_2(CH_2PPh_3)X]X$ (X = Br or I) by reaction with LiBr or NaI. Reaction of cis-$[Pt(PPh_3)_2(CH_2PPh_3)I]I$ with iodine yields cis-$[Pt(PPh_3)_2(CH_2PPh_3)I]I_3$. Nmr data are given in support of the suggested structures.

There is considerable current interest in the chemistry of transition metal ylide complexes.[1] Many such complexes have been prepared by the reaction of an ylide with a suitable transition metal complex.[2-5] The reaction of carbene complexes at low temperature has also yielded ylide complexes.[6]

During a study of possible synthetic routes to haloalkyl transition metal complexes, we have investigated the reaction of chloroiodomethane with $Pt(PPh_3)_4$. Instead of the expected oxidative addition reaction to yield a chloromethyl complex, we find that this reaction leads to a new

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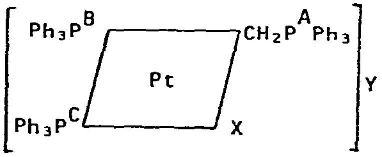
cationic ylide complex. This synthetic route to ylide complexes does not require the use of unstable ylides for their preparation. A related reaction, that of $Co(PMe_3)_4$ with 1,1-dichloroalkanes has been reported to yield bis-ylide complexes of the type $Co(CHRPMe_3)_2Cl_2$ (R = H or Me).[7] Thus, chloroiodomethane reacts with $Pt(PPh_3)_4$ in benzene at room temperature over 18 hours to give an off-white crystalline compound in ca. 80% yield. Recrystalization from dichloromethane/benzene gives white air-stable needles m.p. 161-165°. This compound behaves as a 1:1 electrolyte in nitrobenzene and has $\nu(Pt\text{-}Cl)$ at 307 cm^{-1}. Microanalytical data are consistent with the composition $[Pt(PPh_3)_2(CH_2PPh_3)Cl]I.C_6H_6$ (I) for the compound. The cis stereochemistry for (I) is suggested by the presence of a strong band in the IR spectrum at 543 cm^{-1}.[8]



(I) X = Cl , Y = I
(II) X = Br , Y = Br
(III) X = I , Y = I
(IV) X = I , Y = I_3

The reactions of (I) with an excess of lithium bromide or sodium iodide in acetone leads to compounds (II) and (III) respectively. The reaction of (III) with iodine at room temperature does not cause cleavage of the Pt-C bond but gives the tri-iodide salt (IV) thus demonstrating the high stability of the Pt-C bond in this complex.

The main evidence for the formulation of these complexes comes from ^{31}P, ^{13}C and ^{1}H NMR data. The ^{31}P NMR spectrum of (I) in CH_2Cl_2 with external H_3PO_4 as reference shows the following peaks: δP^A -31,63 ppm (doublet) $^3J(P^AP^C)$ 4,88 Hz with platinum satellites $^2J(PtP^A)$ 70,8 Hz; δP^B and δP^C -18,70 ppm (broad singlet) with platinum satellites (doublet) $^1J(PtP^B)$ 3987 Hz, $^2J(P^BP^C)$ 17,09 Hz and (double doublet) $^1J(PtP^C)$ 2244 Hz, $^2J(P^BP^C)$ 17,09 Hz, $^3J(P^AP^C)$ 4,88 Hz. The chemical shifts for P^B and P^C in (I) are coincident. The ^{31}P NMR spectrum of

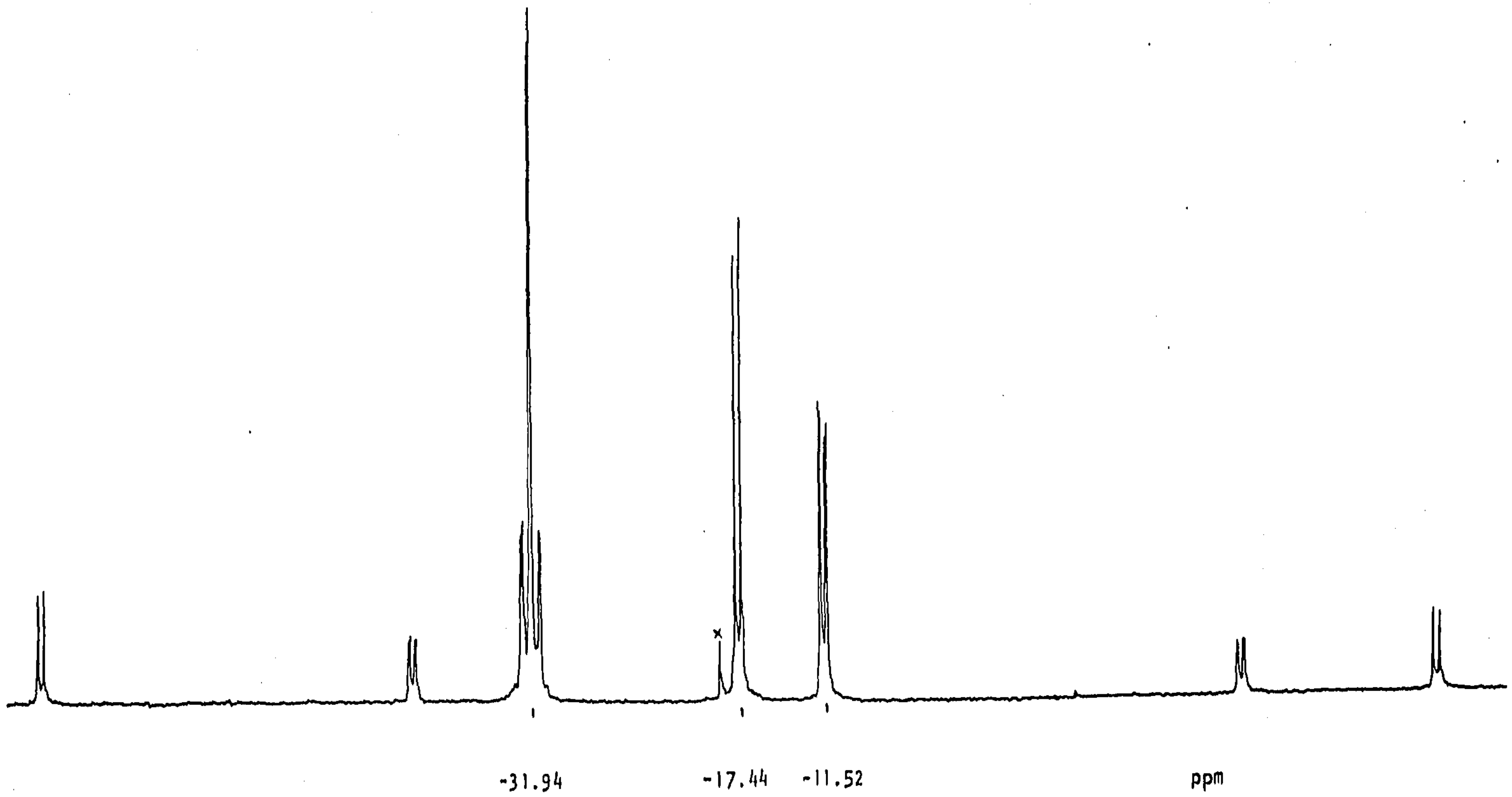


Fig. 1. The ^{31}P NMR spectrum of *cis*-$[Pt(PPh_3)_2(CH_2PPh_3)I]I$, (X = impurity)

(III) (see Figure) is similar to that of (I) but separate signals are now observed for P^B and P^C and these have the same multiplicity as the satellites. Thus for (III) δP^A -31,94 ppm (doublet) $^3J(P^AP^C)$ 3,66 Hz with platinum satellites $^2J(PtP^A)$ 47,61 Hz; δP^B -17,44 ppm (doublet) $^2J(P^BP^C)$ 16,48 Hz with platinum satellites $^1J(PtP^B)$ 3795 Hz; δP^C -11,52 ppm (double doublet) $^3J(P^AP^C)$ 3,66 Hz, $^2J(P^BP^C)$ 16,48 Hz with platinum satellites $^1J(PtP^C)$ 2258 Hz. The ^{13}C NMR spectrum of (I) in CH_2Cl_2 shows the ylide carbon atom as a doublet of doublets of doublets at δ 7,23 ppm to low field of TMS $^1J(P^AC)$ 105 Hz, $^2J(P^BC)$ 7,32 Hz, $^2J(P^CC)$ 37,23 Hz (the assignments of these coupling constants are made assuming $^1J(P^CC)$ > $^2J(P^CC)$ > $^2J(P^BC)$) with platinum satellites $^1J(PtC)$ 576 Hz. The ^1H NMR spectrum of (I) in CH_2Cl_2 shows a multiplet centred at δ2,52 ppm with platinum satellites $^2J(PtH)$ 69 Hz. The platinum satellites show an essentially first order spectrum (doublet of doublets of doublets) with $^2J(P^AH)$ = 14 Hz, $^3J(P^BH)$ = 6 Hz and $^3J(P^CH)$ = 9 Hz.

A possible mechanism for the formation of (I) may be as follows:

$$Pt(PPh_3)_4 \rightleftarrows Pt(PPh_3)_2 + 2PPh_3$$

$$PPh_3 + CH_2ClI \rightarrow [Ph_3PCH_2Cl]I$$

$$Pt(PPh_3)_2 + [Ph_3PCH_2Cl]I \rightarrow [Pt(PPh_3)_2(CH_2PPh_3)Cl]I.$$

We are at present carrying out further studies to determine the mechanism of this reaction and also investigating the generality of this reaction with other low-valent metal systems and other dihaloalkanes.

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