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Preliminary communication

SYNTHESIS AND REACTIVITY OF TRIMETHYLPHOSPHITE COMPLEXES OF COBALT, RHODIUM AND IRIDIUM. CRYSTAL AND MOLECULAR STRUCTURE OF $[IrH(P(OMe)_3)_4(P(OMe)_2OSnMe_2Cl_2)][SnCl_3Me_2]$

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Summary

Syntheses of $[M(P(O)(OMe)_2)(P(OMe)_3)_4]$ (M = Co, Rh, Ir) are reported and variable temperature ^{31}P NMR studies on the iridium complex are described. Hydrogen reacts differently with the Ir and Rh complexes giving $[IrH_2(P(O)(OMe)_2)(P(OMe)_3)_3]$ and $[RhH(P(OMe_3)_4]$, respectively. The crystal and molecular structure of the novel compound $[IrH(P(OMe)_3)_4$-$(P(OMe)_2OSnMe_2Cl_2)][SnCl_3Me_2]$ is described.

The recent report [1] of the synthesis and chemistry of certain binary zerovalent transition metal-phosphite complexes prompts us to report related studies on Co^I, Rh^I and Ir^I compounds. Treatment of $[Ir(\eta^5\text{-}C_9H_7)(C_2H_4)_2]$ [2] with an excess of $P(OMe)_3$ affords the iridium(I) complex $[Ir(P(O)(OMe)_2)(P(OMe)_3)_4]$ (I), which was also obtained by treatment of $[IrCl(P(OMe)_3)_5]$ with: (a) Na in ether, (b) Na or K/Hg in ether or (c) with warm acetone. The $^{31}P\{^1H\}$ NMR spectrum of I at room temperature indicated that the complex is fluxional, exhibiting an A_4M spectrum ($\delta(P_A)$ −32.1, $\delta(P_M)$ −96.6 ppm, (relative to $P(OMe)_3$; $J(P_AP_M)$ 101.1 Hz). At −77°C (Fig. 1) the spectrum changes to an A_3BM spin system $\delta(P_A)$ −28.5, $\delta(P_B)$ −31.0, $\delta(P_M)$ −93.1 ppm; $J(P_AP_B)$ 55.8 Hz, $J(P_AP_M)$ 57.8 Hz, $J(P_BP_M)$ 569.1 Hz. Interestingly the appearance of the $P(O)(OMe)_2$ resonance at intermediate temperatures [2], is identical to that of the hydride resonance in $[IrH(P(OCH_2)_3CPr^n)_4]$, in which it has been proposed that the hydrogen is on a tetrahedral face and the lowest energy path for interchanging the phosphorus environments involves a tetrahedral-jump rearrangement mechanism [3,4]. We consider such a process unlikely for the bulkier $P(O)(OMe)_2$ group in I.

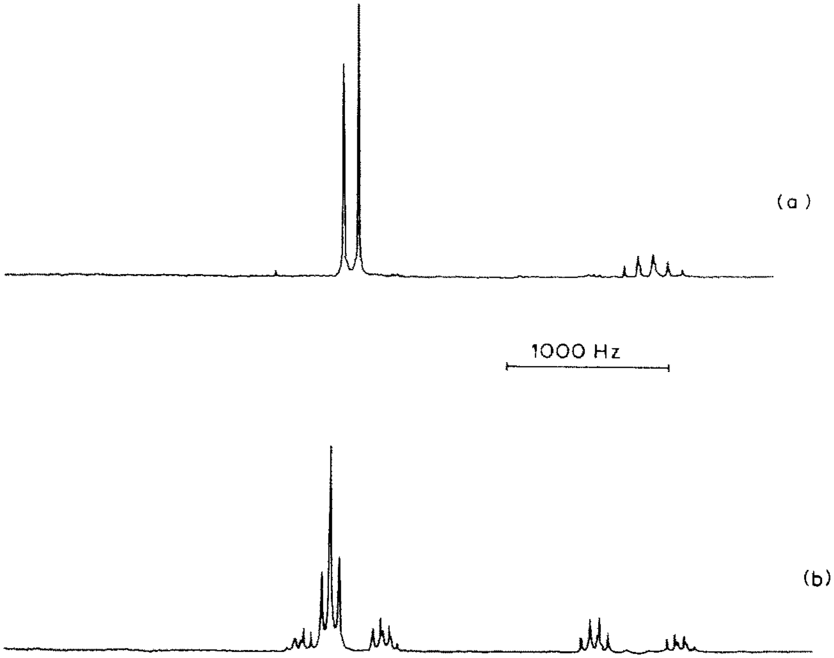
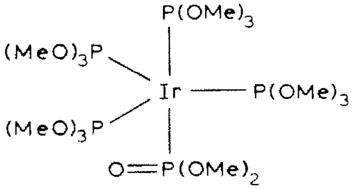
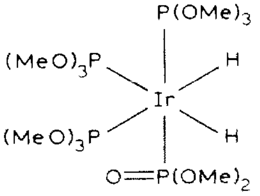


Fig. 1. $^{31}P\{^1H\}$ NMR spectrum of I, (a) at room temperature and (b) at −77°C in toluene.

Complex I adds hydrogen slowly at room temperature to yield the iridium(III) dihydride complex [$IrH_2P(O)(OMe)_2(P(OMe)_3)_3$] (II), whose *cis*-stereochemistry was unambiguously established by ^{31}P and ^1H NMR studies.



(I)

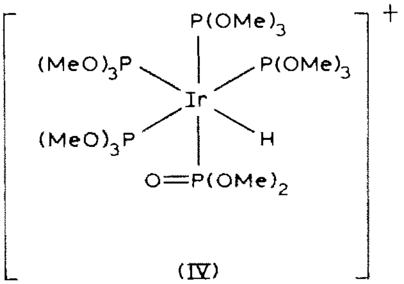


(II)

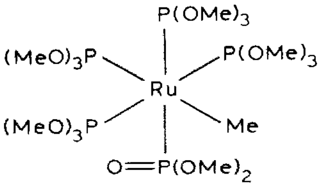
These results led us to reinvestigate the reaction of [$Rh(\eta^5$-$C_5H_5)(C_2H_4)_2$] and $P(OMe)_3$ which was reported [5] to form [$Rh_2(P(OMe)_3)_8$] largely based on ^{31}P NMR data. We now report that the product from this reaction is [$Rh(P(O)(OMe)_2(P(OMe)_3)_4$] (III) and that it exhibits a similar temperature dependent ^{31}P NMR spectrum to I.

Both I and III react quickly with MeI to form $M(P(OMe)_3)_5{}^+ I^-$ but in contrast to the behaviour of I, complex III reacts rapidly with hydrogen at room temperature to afford quantitative yields of $RhH(P(OMe)_3)_4$ and $PH(O)(OMe)_2$ as evidenced by carefully monitoring the reaction by ^{31}P NMR spectroscopy.

The basic nature of the metals in I and III is reflected by their ready reaction with HX (X = BF_4, p-$CH_3C_6H_4SO_3$) the products being $[IrH(P(O)(OMe)_2)(P(OMe)_3)_4]X$ (IV) and $[Rh(P(OMe)_3)_4X]$ plus $PH(O)(OMe)_2$. The ^{31}P NMR spectrum of the cation in IV established the *cis*-stereochemistry and it bears a close similarity to that of the neutral complex



(IV)



(V)

$[RuMe(P(O)(OMe)_2)(P(OMe)_3)_4]$ (V), formed [6] via a thermally induced methyl migration reaction of the zerovalent complex $[Ru(P(OMe)_3)_5]$.

We have confirmed independently the very recent report by Muetterties et al. [7] that $[Co(P(O)(OMe)_2)(P(OMe)_3)_4]$ is formed in the reaction between $[Co(P(OMe)_3)]_nCl$ (n = 3,4,5) with sodium or potassium amalgam and the existence of a paramagnetic monomer $[Co(P(OMe)_3)_4]$ and dinuclear $[Co_2(P(OMe)_3)_8]$ indicates the complexity of this type of system. By careful control of the phosphite concentration we have recently obtained NMR spectroscopic evidence for the complex $[Rh_2(P(OMe)_3)_8]$ and mercury contain-

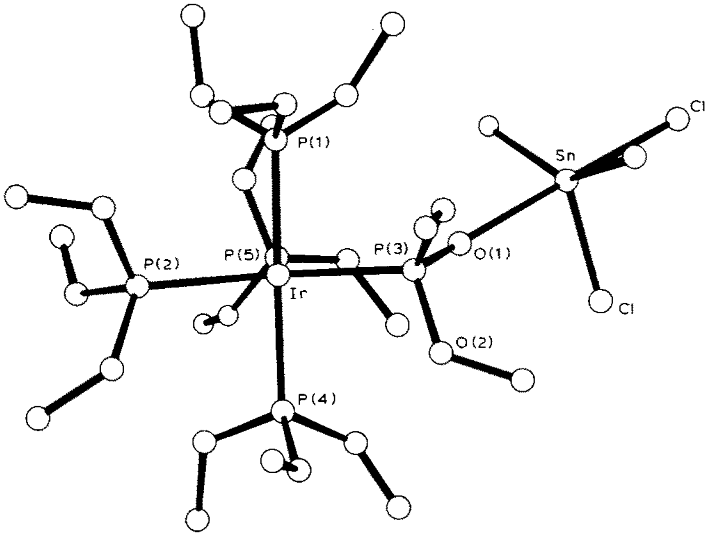


Fig. 2. Molecular Structure of the cation $[IrH(P(OMe)_3)_4(P(OMe)_2OSnCl_2Me_2)]^+$. Ir—P(1) 2.270(10); Ir—P(2) 2.382(13), Ir—P(3) 2.322(10); Ir—P(4) 2.331(11); Ir—P(5) 2.280(11); P(3)—O(1) 1.51(2); P(3)—O(2) 1.52(2); O(1)—Sn 2.30(2) Å.

ing products from the reaction between $[M(olefin)_2Cl]_2$ (M = Rh, Ir), $P(OMe)_3$ and Na/Hg [8]. The crystal structure of $Co_2Hg(P(OMe)_3)_8$ has recently been described [7].

The reaction of I with Me_2SnCl_2 in dry THF gave a single product whose ^1H and ^{31}P NMR spectra showed features similar to IV and elemental analysis and a single crystal X-ray structure determination confirmed the formation of the hydridoiridium(III) complex $[IrH(P(OMe)_3)_4(P(OMe)_2OSnCl_2Me_2)]$-$[SnCl_3Me_2]$ (VI), in which the oxygen of the coordinated $P(O)(OMe)_2$ ligand is the donor site towards tin (see Fig. 2). Formation of the hydride $CoH(P(OMe)_3)_4$ has been briefly noted [7] in reactions of Na/Hg with $CoCl_2$ in THF in the presence of excess $P(OMe)_3$ and from $NaCo(P(OMe)_3)_4$ with Hg in THF.

Crystal data: $C_{18}H_{55}Cl_5IrO_{15}P_5Sn_2$, orthorhombic, space group *Pnn2*, a 31.857(4), b 13.230(2), c 10.560(2) Å, $Z = 4$. The structure was determined by routine heavy atom methods and refined by least squares to $R = 0.077$ for 1972 reflections with $I > \sigma(I)$ measured on a CAD4 diffractometer. The cation structure is shown in Fig. 2 with some selected bond length data. The anion $[SnCl_3Me_2]^-$ has a trigonal bipyramidal structure with the methyl groups occupying equatorial positions.

Further studies on these systems will be reported separately.

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