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Preliminary communication

OXIDATIVE ADDITION OF DIMETHYLPHOSPHITE TO IRIDIUM(I) AND RHODIUM(I) COMPLEXES: STEREOSELECTIVE REDUCTION OF 4-t-BUTYLCYCLOHEXANONE

M.A. BENNETT and T.R.B. MITCHELL*

Research School of Chemistry, Australian National University, Box 4, P.O., Canberra, A.C.T. 2600 (Australia)

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Summary

Dimethylphosphite, $(CH_3O)_2P(O)H$, adds oxidatively to iridium(I) and rhodium(I) complexes to give hydrido-iridium(III) or -rhodium(III) dimethylphosphonate complexes. A complex $Ir(H)Cl[P(O)(OCH_3)_2][P(OH)(OCH_3)_2]_3$ obtained from $[IrCl(C_8H_{14})_2]_2$ and dimethylphosphite catalyses the stereoselective reduction of 4-t-butylcyclohexanone to 97/3 *cis/trans*-4-t-butylcyclohexanol, the ratio being identical with that obtained using the Henbest catalyst iridium(IV) chloride, phosphorous acid or one of its esters, and aqueous isopropanol.

Cyclohexanones can be stereoselectively reduced to mainly axial alcohols using the homogeneous Henbest catalyst, which consists of iridium(IV) chloride and phosphorous acid or one of its esters in aqueous isopropanol [1]; a similar rhodium-containing system has been applied to the reduction of steroidal ketones [2]. Since the nature and mode of action of the catalytic species is unknown, we have attempted to prepare well-defined dialkylphosphite and phosphorous acid complexes of iridium and rhodium by oxidative addition of the P—H bond in these ligands to low-valent metal complexes, and have examined the catalytic ability of the resulting adducts. Related oxidative additions of phosphine, PH_3, have recently been reported [3].

The red solution obtained by treating the cyclooctene complex $[IrCl(C_8H_{14})_2]$ with two equivalents of triphenylphosphine** reacts with two equivalents of dimethylphosphite, $(CH_3O)_2P(O)H$, to give a colourless solid which we formulate as the oxidative addition product (I) or (II) on the basis of analytical, molecular weight, and spectroscopic data. Its ^1H NMR spectrum in $CDCl_3$ shows signals at

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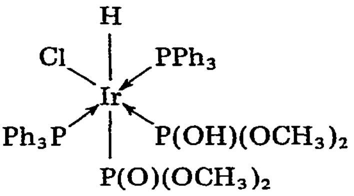
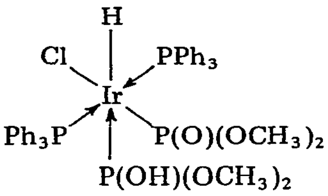
*Present address: Department of Chemistry, Queen's University, Belfast BT9 5AG, Northern Ireland.

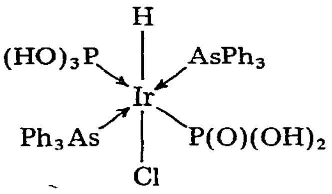
**This solution is thought to contain the monomeric, coordinately unsaturated species $IrCl(PPh_3)_2$ [4].



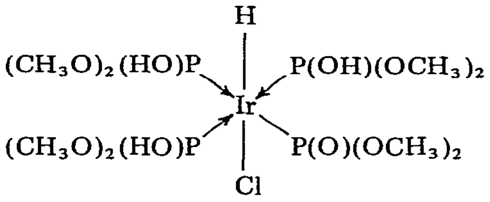
(I)



(II)



(III)



(IV)

τ 2.35, 2.65 (complex multiplet, aromatic protons), 6.96 (doublet, J 11 Hz, OCH_3), 7.47 (doublet, J 12 Hz, OCH_3) and 19.49 (overlapping triplets, J[H—P(*trans*)] 208, J[H—P(*cis*)] 13, 15 Hz, and its ^{31}P NMR spectrum in $CDCl_3$ (with proton- and noise-decoupling) shows signals at δ (ppm downfield of external H_3PO_4) 3.9 (triplet, $2PPh_3$), 44.5 (overlapping triplets, J 21 and 12 Hz) and 85.4 (multiplet, which appears as two multiplets with J[P—H] 207 Hz when not proton-decoupled). The large P—Ir—H coupling is typical of hydride *trans* to a tertiary phosphine [5], although the value of ν(Ir—H) [IR: 2180 (mull), 2150 cm^{-1} (CH_2Cl_2)] is ca. 100 cm^{-1} larger than the expected value for this arrangement. The spectroscopic data do not unambiguously distinguish between structures (I) (H *trans* to dimethylphosphonate) and (II) (H *trans* to dimethylphosphite). We have been unable to detect a signal due to P—OH in the range τ —10 to +10 in the ^1H NMR spectrum, probably because it is underneath the aromatic resonances. From $[MCl(C_8H_{14})_2]_2$ (M = Rh or Ir), the appropriate amount of tertiary phosphine or arsine, and dimethylphosphite we have similarly prepared $Ir(H)Cl[P(O)(OCH_3)_2][P(OH)(OCH_3)_2](AsPh_3)_2$ and $M(H)Cl[P(O)(OCH_3)_2][P(CH_3)_2Ph]_3$. Similar experiments using diethyl phosphite gave inseparable isomeric mixtures. Addition of phosphorous acid, $(HO)_2P(O)H$ to a mixture of $[IrCl(C_8H_{14})_2]_2$ and triphenylarsine in a 1/2 mole ratio gave the expected oxidative addition product $Ir(H)Cl[P(O)(OH)_2][P(OH)_3](AsPh_3)_2$ as a colourless solid, which shows a singlet at τ 31.26 in the ^1H NMR spectrum in $CDCl_3$, and a band at 2200 cm^{-1} in the IR spectrum (mull and CH_2Cl_2). Both values are typical of H *trans* to Cl [structure (III)].

From the reaction of dimethylphosphite in various proportions and $[IrCl(C_8H_{14})_2]_2$ in benzene a colourless solid and an oil of empirical formulae $Ir(H)Cl[P(O)(OCH_3)_2][P(OH)(OCH_3)_2]_n$ (n = 2 and 3 respectively) can be isolated. The ^1H NMR spectra of both compounds in CD_2Cl_2 show signals at τ ca. 6.2 (complex multiplet, OCH_3) and a concentration-dependent signal at τ ca. —2 (broad singlet, P—OH), the ratios being ca. 10/1 for the solid (calc. 9/1) and ca. 7/1 for the oil (calc. 8/1). In neither compound have we been able to locate a hydride resonance in the range τ 10—40 at room temperature, or, in the case of the solid, at —90°C in CD_2Cl_2, but both show a band at 2230 cm^{-1} (CH_2Cl_2) in their IR spectra, which must be due to ν(Ir—H). The oil is the only compound of this series which shows catalytic activity. It is an excellent catalyst for the reduction of 4-t-butylcyclohexanone to 97/3 *cis/trans*-4-t-butylcyclohexanol, the stereoselectivity thus being identical with that obtained using the Henbest catalyst. The reaction of $[RhCl(C_8H_{14})_2]_2$ with an excess of dimethylphosphite, and the complete hydrolysis of the P—F bonds in $IrCl(PF_3)_4$ [6], give as yet uncharacterised, hygroscopic solids which catalyse the reduction with similar stereoselectivity. These preliminary results suggest that the catalytically active species are octahedral iridium(III) or rhodium(III) hydrido complexes such as (IV)*. Further work is in progress to characterise and to determine the mode of action of these complexes.

Acknowledgement

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References

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[*] Except where stated, all compounds described herein gave satisfactory elemental analyses (C, H, P and Cl).