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Preliminary communication

DEHYDROGENATION OF AN ALKANE CHAIN: RHODIUM(I) AND IRIDIUM(I) COMPLEXES OF 1,6-BIS(DIPHENYLPHOSPHINO)-*trans*-HEX-3-ENE

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Summary

Rhodium(I) and iridium(I) complexes effect the dehydrogenation of the alkane chain in the ligand 1,6-bis(diphenylphosphino)hexane forming the metal olefin complexes (BDPH)MCl where BDPH = 1,6-bis(diphenylphosphino)-*trans*-hex-3-ene and M = Rh or Ir.

The homogeneous hydrogenation of olefins using metal complexes as the active site is well known, e.g. the use of $[(C_6H_5)_3P]_3RhCl$ [1] is well documented. However the reverse reaction, i.e. the dehydrogenation of alkanes to give an olefin has not been studied in any great detail. The only reported dehydrogenation reaction of a saturated chain occurs in the reaction of 2,2'-bis(diphenylphosphino)bibenzyl with $[CODRhCl]_2$ (COD = 1,5-cyclooctadiene), to give 2,2'-bis(diphenylphosphino)stilbenechlororhodium(I) [2]. Coupling—dehydrogenation reactions also occur with *o*-tolylphosphines and ethanolic rhodium trichloride [3], and in the reaction of *o*-styryldiphenylphosphine with ruthenium carbonyl [4]. However all these reactions involve dehydrogenation of relatively active benzyl protons. We now wish to report the dehydrogenation occurring in the alkane chain of 1,6-bis(diphenylphosphino)hexane.

Upon refluxing 1,6-bis(diphenylphosphino)hexane with $[CODIrCl]_2$ in mesitylene under nitrogen for 4 hours, a clear orange solution is obtained. When this solution is allowed to cool to room temperature, orange crystals of the compound (BDPH)IrCl (Fig. 1), where M = Ir and BDPH = 1,6-bis(diphenylphosphino)-*trans*-hex-3-ene) form in a 90-95% yield. These crystals are analytically pure. The rhodium complex, (BDPH)RhCl, was prepared under similar conditions (solvent mesitylene, refluxing time ~ 1 h, yield 75%); and the compound was recrystallized from methylene chloride/methanol. The new tridentate ligand, BDPH, was isolated by treating (BDPH)RhCl with potassium

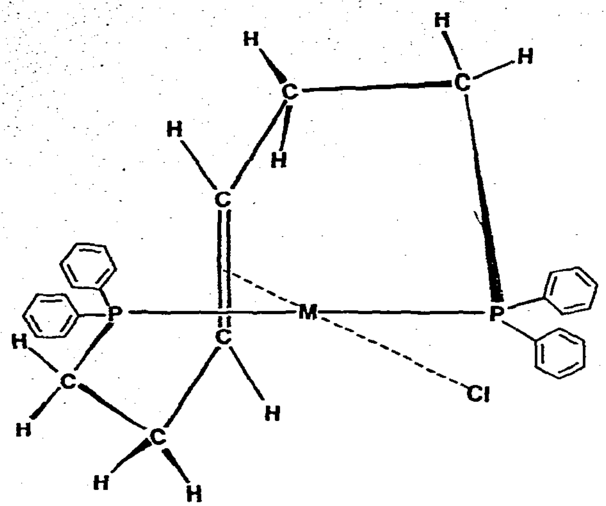

Fig.1. Proposed structure for the complexes (BDPH)MCl where BDPH = 1,6-bis(diphenylphosphino)-*trans*-hex-3-ene and M = Rh or Ir.

cyanide in ethanol at room temperature. The tertiary unsaturated diphosphine ligand [m.p. 191°C (decomp.); M^+, 452; mol.wt., 485 ($CHCl_3$ vapour phase osmometry (vpo))] has an intense sharp band in the infrared at 970 cm^{-1} typical of a C—H out of plane deformation vibrational frequency of a *trans*-disubstituted olefin [5]. This band is not present in the starting ligand 1,6-bis(diphenylphosphino)hexane. The band due to the C=C stretching mode is too weak to be observed, an observation which has been noted before in the similar ligand 2,2′-bis(di-*o*-tolylphosphino)stilbene [3]. The PMR spectrum of BDPH shows three distinct resonances at τ (ppm) 2.4—2.8 (phenyl, area 20), 4.50 (olefinic, area 2) and at 7.8—8.0 (overlapping methylenes, area 8). In the ^{13}C NMR spectrum, resonances occur at 137.3—127.1 ppm (phenyl), 129.2 ppm (olefinic) and at 28.6 ppm and 27.7 ppm (methylenes) downfield from TMS. Similar physical data were obtained for the rhodium and iridium complexes. (BDPH)RhCl [M^+, 590; mol.wt., 635 ($CHCl_3$, vpo)] has a strong band at 958 cm^{-1}, as well as new bands at 811, 825 and 835 cm^{-1}, and a ν(Rh—Cl) band at 288 cm^{-1} in the infrared spectrum. The olefinic resonance has been shifted upfield compared to the free ligand to τ 6.37 ppm in the PMR spectrum. In the ^{13}C NMR spectrum, resonances appear at 132.9—127.2 ppm (phenyl), 62.3 ppm (olefinic) with a J(Rh—C) 16.5 Hz, and at 30.0 and 20.8 ppm (methylenes) downfield from TMS. The magnitude of the upfield shift of the olefinic carbons compared to the free ligand, and the degree of rhodium coupling to the olefinic carbons are in agreement with previous ^{13}C NMR studies of rhodium olefin complexes [6]. (BDPH)IrCl [M^+, 680; mol.wt., 683 ($CHCl_3$, vpo)] has a band at 972 cm^{-1} and new bands at 820 and 839 cm^{-1}, and a ν(Ir—Cl) band at 300 cm^{-1} in the infrared spectrum. In the PMR spectrum, the olefinic resonance is again shifted well upfield compared to the free ligand and occurs at τ 7.46 ppm.

The activation of C—H bonds in the presence of metal complexes has resulted in much discussion in recent years [7], and most of the research has been concentrated on the more active phenyl C—H bonds. It has been shown, however, that alkyl C—H bonds can be reactive sites. For example, the alkyl as well as aryl protons of $(C_6H_5)_2P(CH_2CH_2CH_3)$ are exchanged with deuterium in the presence of $RuHCl[P(C_6H_5)_3]_3$ [8]. Similarly, the alkyl protons of the phosphines in the complexes $\{PtCl_2[P(C_3H_7)_3]\}_2$ and $\{PtCl_2[P(C_4H_9)_3]\}_2$ are exchanged with deuterium in a CH_3COOD/D_2O medium [9,10]. Such exchanges are proposed to proceed via metal—deuteride intermediates which involve the activation of the C—H bond by an oxidative addition reaction. Although it is quite obvious that the t-butyl groups in the diphosphines $(t\text{-Bu})_2P(CH_2)_nP(t\text{-Bu})_2$ ($n = 9$ or 10) play an important role in forcing the diphosphine to *trans*-chelate [11]; it is also apparent from molecular models that the alkane chain as well as the phenyl rings in 1,6-bis(phenylphosphino)hexane would exhibit steric hindrance if the diphosphine *cis*-chelated. It is therefore proposed that in the *trans*-chelating position, two of the protons in the 3 and 4 positions of the hexane chain of 1,6-bis(diphenylphosphino)hexane are so placed that there could be considerable overlap between the filled d_{xz} or d_{yz} orbitals of the metal complex (considering a square planar configuration with the ligands occupying the xy plane) and the empty *anti*-bonding orbitals of the C—H bond. This would then facilitate the transfer of electrons from the metal with the subsequent formation of a relatively unstable metal hydride species, and the formation of a stable metal—olefin bond. Although we have no direct evidence that this is the correct mechanism for the dehydrogenation step, we have found that the iridium complex (BDPH)IrCl activates hydrogen reversibly at low temperatures (*RT*) forming the *cis*-dihydride complex $(BDPH)IrH_2Cl$.

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