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DEHYDROGENATION OF 1,6-BIS(DIPHENYLPHOSPHINO)HEXANE BY RHODIUM(I) AND IRIDIUM(I) COMPLEXES; RHODIUM(I) AND IRIDIUM(I) COMPLEXES CONTAINING THE LIGANDS 1,6-BIS(DIPHENYLPHOSPHINO)HEXANE, 1,6-BIS(DIPHENYLPHOSPHINO)-TRANS-HEX-3-ENE, 1,6-BIS(DIPHENYLARSINO)HEXANE AND 1,6-BIS(DIPHENYLARSINO)-TRANS-HEX-3-ENE*

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Abstract

The ligand 1,6-bis(diphenylphosphino)hexane undergoes a dehydrogenation reaction with $M_2X_2(C_8H_{12})_2$, C_8H_{12} = *cis cis* cycloocta-1,5-diene to form MX(BDPH), M = Rh and X = Cl or Br, or M = Ir and X = Cl, and BDPH = 1,6-bis(diphenylphosphino)-*trans*-hex-3-ene. In the presence of carbon monoxide, 1,6-bis(diphenylphosphino)hexane and 1,6-bis(diphenylarsino)hexane react with $M_2Cl_2(C_8H_{12})_2$ to give the dimeric complexes $[M(CO)Cl(ligand)]_2$ which do not dehydrogenate. The ligands $(C_6H_5)_2P(CH_2)_nP(C_6H_5)_2$, n = 5, 7 or 8 and $(C_6H_5)_2As(CH_2)_6As(C_6H_5)_2$ do not undergo the dehydrogenation reaction under the same conditions. The ligands 1,6-bis(diphenylphosphino)-*trans*-hex-3-ene and 1,6-bis(diphenylarsino)-*trans*-hex-3-ene have been prepared and undergo normal substitution reactions with rhodium(I) and iridium(I) complexes. The square-planar complexes MCl(BDPH) react reversibly with carbon monoxide forming fluxional five coordinate complexes M(CO)Cl(BDPH), M = Rh or Ir and with excess carbon monoxide to form $[M(CO)_2(BDPH)]^+$, M = Ir,

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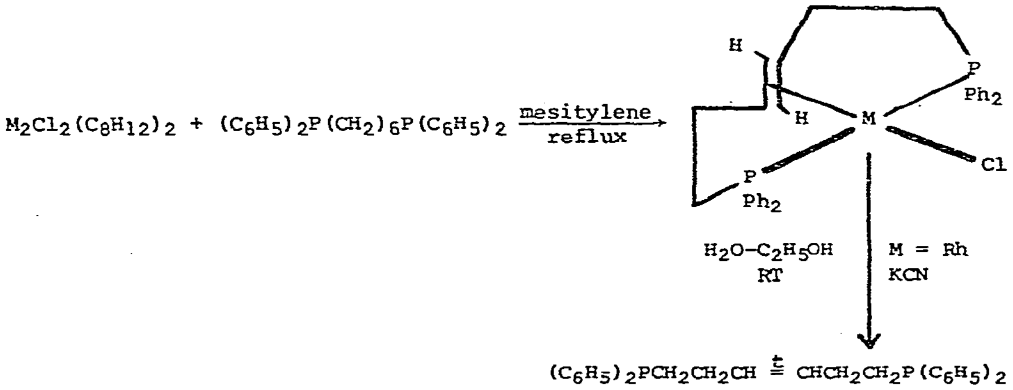
isolated as the tetraphenylborate salt. A possible mechanism for the dehydrogenation reaction is discussed. Analytical, mass spectral, infrared spectral, ^1H N.M.R. spectral and ^{13}C N.M.R. spectral data are consistent with the above reactions and formulations.

Introduction

In a preliminary communication of this work[1], it was reported that the diphosphine ligand 1,6-bis(diphenylphosphino)hexane, $(C_6H_5)_2P(CH_2)_6P(C_6H_5)_2$ undergoes a dehydrogenation reaction with $M_2Cl_2(C_8H_{12})_2$, where M = Rh or Ir and C_8H_{12} = *cis cis* cycloocta-1,5-diene to yield MCl(BDPH), where BDPH = 1,6-bis(diphenylphosphino)-*trans* hex-3-ene, $(C_6H_5)_2PCH_2CH_2CH \overset{t}{=} CHCH_2CH_2P(C_6H_5)_2$, in very good yields. (See Scheme 1). The ligand BDPH was then isolated by reacting the rhodium complex with potassium cyanide in aqueous ethanol.



Scheme 1. Preparation of MCl(BDPH) and BDPH; M = Rh or Ir, BDPH = 1,6-Bis(diphenylphosphino)-*trans*-hex-3-ene.

A similar dehydrogenation reaction occurs with the ligand 2,2'-bis (diphenylphosphino)bibenzyl and $Rh_2Cl_2(C_8H_{12})_2$ to yield

$\overline{\mathrm{RhCl[}o\text{-}(C_6H_5)_2PC_6H_4CH} \overset{t}{=} CHC_6H_4P(C_6H_5)_2\text{-}o]$[2,3]. Recently the results of another dehydrogenation reaction involving the ligand 1,6-bis(di-*t*-butylphosphino)hexane and rhodium trichloride trihydrate to yield $\overline{\mathrm{RhCl[Bu^t{}_2PCH_2CH_2CH}} \overset{t}{=} CHCH_2CH_2PBu^t{}_2]$ have been communicated[4]. Single crystal X-ray studies of the latter two complexes confirm the square-planar arrangement of ligands expected with the phosphorus atoms *trans* to each other and with the olefin occupying a coordination site and lying almost perpendicular to the square-plane. These structures have the same stereochemistry as that found for the closely related olefin and carbonyl complexes of rhodium(I) and iridium(I), *trans*-$MClL(PPh_3)_2$ where M = Rh or Ir and L = C_2H_4 or CO and M = Rh, L = C_2F_4 [5, 6, 7, 8]. These dehydrogenation reactions represent the first cases in which an alkane, although anchored by two phosphorus atoms, react with a metal site in a homogeneous situation to give an olefin. There has been considerable research in recent years[9] into the activation of C-H bonds, in particular the more active phenyl C-H bonds in the presence of transition metal complexes. More recently it has been shown that alkyl C-H bonds can also be activated [10, 11, 12]. In particular it was shown that the C-3 position of the alkyl chain in the straight chain phosphines $P(C_3H_7)_3$ and $P(C_4H_9)_3$ is much more activated than the other positions, giving rise to a favoured five membered ring intermediate[11, 12]. We were therefore interested in finding out if the other members of the diphosphine series $(C_6H_5)_2P(CH_2)_nP(C_6H_5)_2$, n = 5 - 8, and the diarsine $(C_6H_5)_2As(CH_2)_6As(C_6H_5)_2$ would undergo the dehydrogenation reaction. In view of recently reported *trans*-chelating preference of the similar diphosphine ligands $t\text{-}Bu_2P(CH_2)_nP\text{-}t\text{-}Bu_2$ (n = 9, 10 or 12), $t\text{-}Bu_2P(CH_2)_4C \equiv C(CH_2)_4P\text{-}t\text{-}Bu_2$, $o\text{-}(C_6H_5)_2PC_6H_4CH_2CH_2C_6H_4P(C_6H_5)_2\text{-}o$ and $o\text{-}(C_6H_5)_2AsC_6H_4CH_2CH_2C_6H_4As(C_6H_5)_2\text{-}o$ with platinum d^8 complexes [4, 13, 14, 15], it was also of interest to see if these ligands would *trans*-chelate. So that we could more easily investigate the coordination properties of the unsaturated ligand we have devised syntheses for both the diphosphine ligand $(C_6H_5)_2PCH_2CH_2CH{:}CHCH_2CH_2P(C_6H_5)_2$, (BDPH), and the new diarsine ligand $(C_6H_5)_2AsCH_2CH_2CH{:}CHCH_2CH_2AS(C_6H_5)_2$, (BDAH).

Experimental

1,5-Dibromopentane, 1,6-dibromohexane, 1,7-dibromoheptane, 1,8-dibromooctane and triphenylarsine were purchased from the Aldrich Chemical Company, triphenylphosphine was purchased from Fluka and carbon monoxide was obtained from CIG. These chemicals were used without further purification. Rhodium trichloride and iridium trichloride were purchased from Johnson Matthey Chemicals Ltd and Research Organic/Inorganic Chemical Corporation. Bis(cycloocta-1,5-diene)-μμ'-dichlorodirhodium(I)[16], bis(cycloocta-1,5-diene)-μμ'-dibromodirhodium(I)[16], bis(cycloocta-1,5-diene)-μμ'-dichlorodiiridium(I)[17], 1,6-dichloro-*trans*-hex-3-ene[18], lithium diphenylphosphide[19] and lithium diphenylarsenide[20] were prepared by standard literature methods. Infrared spectra were recorded on a JASCO IRA-2 spectrometer, ^1H N.M.R. spectra were recorded using a JEOL MH-100 spectrometer or a JEOL JNM-PS-100 spectrometer, ^{13}C N.M.R. spectra were recorded on a Brüker HX instrument operating at 67.87 MHz. The mass spectra were recorded on an AEI MS 902S instrument. Analyses were obtained from the University of Queensland Microanalytical Service and the Australian Microanalytical Service, CSIRO, Melbourne, Australia.

Preparation of Ligands

The diphosphines and diarsines used in this work were prepared by the general method of adding the ω,ω'-dihaloalkane or the ω,ω'-dihaloalkene to a freshly prepared solution of either lithium diphenylphosphide or lithium diphenylarsenide. Using the method of Aguiar *et.al.* [19, 20], by selectively decomposing the phenyllithium with *t*-butylchloride always resulted in lower yields (10-60%), but by using an excess of the dihalo-compounds good yields were always obtained. The preparation of 1,6-bis(diphenylphosphino)-*trans*-hex-3-ene is given. The other diphosphines and diarsines listed below were prepared in a similar fashion.

Preparation of 1,6-Bis(diphenylphosphino)-*trans*-hex-3-ene

A freshly prepared solution of lithium diphenylphosphide was made from 2.0g (286 mmol) of lithium and 20g (76.3 mmol) of triphenylphosphine in 60ml of tetrahydrofuran. The excess lithium was filtered off, and 10.7 g (69.9 mmol) of 1,6-dichloro-*trans*-hex-3-ene was added at 0°C. The solution was refluxed for 1hr and then reduced in volume to *ca*. 30ml. Aqueous ethanol (1:1) was added to precipitate the ligand which was then filtered off, washed with ethanol and dried. The yield of BDPH after recrystallisation from methylene chloride-methanol was 14.4g (91%).

Anal. Found: M.p. 192°C. Mol.wt., 485 (vapour pressure osmometry in chloroform), 453 (mass spectrum); C, 78.43; H, 6.58; P, 13.4. $C_{30}H_{30}P_2$. Calcd.: mol.wt., 452; C, 79.63; H, 6.68; P, 13.7.

$(C_6H_5)_2AsCH_2CH_2CH{:}CHCH_2CH_2As(C_6H_5)_2$ Anal. Found: mol.wt., 540 (vapour pressure osmometry in chloroform), 540 (mass spectrum); C, 66.12; H, 5.81; As, 27.8. $C_{30}H_{30}As_2$. Calcd.: mol.wt., 540; C, 66.68; H, 5.60; As, 27.7.

$(C_6H_5)_2P(CH_2)_6P(C_6H_5)_2$ Anal. Found: mol.wt., 467 (vapour pressure osmometry in chloroform), 454 (mass spectrum); C, 78.98; H, 7.21; P, 13.4. $C_{30}H_{32}P_2$ Calcd.: mol.wt., 454; C, 79.27; H, 7.10; P, 13.6.

All ligands were characterised by ^{1}H N.M.R., infrared and mass spectra.

Preparation and Reaction of Complexes

Preparation of 1,6-Bis(diphenylphosphino)-*trans*-hex-3-enechlororhodium(I), RhCl(BDPH).

(1) A mixture of 0.48g (1.06 mmol) of 1,6-bis(diphenylphosphino) hexane and 0.25g (5.08 x 10^{-1} mmol) of bis(cycloocta-1,5-diene)-μμ'-dichlorodirhodium(I) was heated in 30ml mesitylene under an atmosphere of nitrogen. Initially a yellow precipitate formed which later dissolved. The solution was refluxed for 2hr forming a clear amber

Ligand	Reactants	Yield(% Yield)	MP/BP
$(C_6H_5)_2P(CH_2)_5P(C_6H_5)_2$	Li, $(C_6H_5)_3P$ (57g, 218 mmol) $Br(CH_2)_5Br$ (50g, 217 mmol).	10.0g (10.4%)*	230°C, 0.1mmHg
$(C_6H_5)_2P(CH_2)_6P(C_6H_5)_2$	Li, $(C_6H_5)_3P$ (54g, 206 mmol), ^{t}BuCl(19.2g, 206 mmol), $Br(CH_2)_6Br$ (25g, 102 mmol).	22.4 g (48%)	124°C
$(C_6H_5)_2P(CH_2)_7P(C_6H_5)_2$	Li, $(C_6H_5)_3P$ (34g, 130 mmol), ^{t}BuCl (10.8g, 116 mmol), $Br(CH_2)_7Br$ (15g, 58 mmol).	15.0g (25%)*	140°C, 0.01mmHg
$(C_6H_5)_2P(CH_2)_8P(C_6H_5)_2$	Li, $(C_6H_5)_3P$ (48g, 183 mmol), ^{t}BuCl (15.5g, 167 mmol), $Br(CH_2)_8Br$ (25g, 92 mmol).	22.0g (49%)	105°C
$[(C_6H_5)_2AsCH_2CH_2CH:]_2$	Li, $(C_6H_5)_3As$ (20g, 65 mmol), $ClCH_2CH_2CH{:}CHCH_2CH_2Cl$ (9.1g, 59 mmol).	15.4g (96%)	96°C
$(C_6H_5)_2As(CH_2)_6As(C_6H_5)_2$	Li, $(C_6H_5)_3As$ (20g, 65 mmol) ^{t}BuCl (6g, 65 mmol), $Br(CH_2)_6Br$ (8g, 33 mmol).	10.5g (59%)	118°C

*Both $(C_6H_5)_2P(CH_2)_5P(C_6H_5)_2$ and $(C_6H_5)_2P(CH_2)_7P(C_6H_5)_2$ are high boiling viscous oils, hence lower than expected yields were obtained from isolating the pure products by vacuum distillation.

coloured solution and upon cooling to room temperature, the product precipitated from solution. The yellow crystalline product was filtered off, washed with ethanol and recrystallised from a methylene chloride-methanol mixture to yield 0.45g (75%) of RhCl(BDPH).

(ii) 1,6-Bis(diphenylphosphino)-*trans*-hex-3-ene (0.70g, 1.55 mmol) was added to a solution of 0.38g (0.77 mmol) of bis(cycloocta-1,5-diene)-μμ'-dichlorodirhodium(I) in 40ml of methylene chloride at room temperature under nitrogen. The solution was heated and methanol was added to crystallise the compound RhCl(BDPH). The yield of RhCl(BDPH) was 0.80g (88%).

Anal. Found: mol.wt., 635 (vapour pressure osmometry in chloroform), 591 (mass spectrum); C, 60.56; H, 5.13; P, 10.5; Cl, 6.3. $C_{30}H_{30}ClP_2Rh$. Calcd.: mol.wt., 591; C, 60.98; H, 5.12; P, 10.5; Cl, 6.0.

Isolation of 1,6-Bis(diphenylphosphino)-*trans*-hex-3-ene from RhCl(BDPH)

Potassium cyanide (2g) was added to a solution of RhCl(BDPH) (0.20g) in 20ml of 1:3 aqueous ethanol. The orange colour of RhCl(BDPH) quickly dissipated and a white precipitate formed. The solution was stirred for 2hr at room temperature. The white precipitate was filtered off, washed with water and ethanol and recrystallised from a methylene chloride-methanol mixture to yield 0.20g (87%) of BDPH. The ligand was characterised as above.

Preparation of 1,6-Bis(diphenylphosphino)-*trans*-hex-3-enebromorhodium(I), RhBr(BDPH).

This was prepared as above for RhCl(BDPH) from 1,6-bis(diphenylphosphino)hexane (0.37g, 8.15×10^{-1} mmol) and bis(cycloocta-1,5-diene)-μμ'-dibromodirhodium(I) (0.24g, 4.12×10^{-1} mmol) yielding 0.46g (89%) of RhBr(BDPH). Anal. Found: mol.wt., 672 (vapour pressure osmometry in chloroform); C, 56.63; H, 4.89; P, 9.6; Br, 12.5. $C_{30}H_{30}BrP_2Rh$. Calcd.: mol.wt., 635; C, 56.71; H, 4.76; P, 9.8; Br, 12.6.

Preparation of 1,6-Bis(diphenylarsino)-*trans*-hex-3-enechlororhodium(I), RhCl(BDAH)

A solution of 0.88g (1.6 mmol) of 1,6-bis(diphenylarsino)-*trans*-hex-3-ene in 20ml benzene was added dropwise to a refluxing solution of 0.40g (8.1×10^{-1} mmol) of bis(cyclooacta-1,5-diene)-μμ'-dichlorodirhodium(I) in 20ml of benzene. The solution was refluxed for 1 hr, cooled and the resultant yellow precipitate collected by filtration and recrystallised from a methylene chloride-methanol solution to yield 0.89g (81%) of RhCl(BDAH).

Anal. Found: mol.wt., 720 (vapour pressure osmometry in chloroform); C, 52.56; H, 4.55; As, 22.1. $C_{30}H_{30}ClAs_2Rh$. Calcd.: mol.wt., 679; C, 53.08; H, 4.46; As, 22.1.

Preparation of 1,6-Bis(diphenylphosphino)-*trans*-hex-3-enechloriridium(I), IrCl(BDPH).

(1) A solution containing 0.41g (9.0×10^{-1} mmol) of 1,6-bis-(phenylphosphino)hexane and 0.30g (4.5×10^{-1} mmol) of bis(cycloocta-1,5-diene)-μμ'-dichlorodiiridium(I) in 30ml mesitylene was refluxed for 4hr under a nitrogen atmosphere. The solution was then allowed to cool to room temperature whereupon orange crystals precipitated from solution. The crystals were filtered off, washed with mesitylene and ethanol and then dried *in vacuo* to yield 0.50g (95%) of IrCl(BDPH).

(11) A solution containing 0.54g (1.2 mmol) of 1,6-bis(diphenylphosphino)-*trans*-hex-3-ene and 0.40g (6.0×10^{-1} mmol) of bis(cycloocta-1,5-diene)-μμ'-dichlorodiiridium(I) in 20ml of benzene was refluxed for 1hr. The solution was cooled and the resultant orange crystals filtered off, washed with benzene and ethanol and then dried *in vacuo* to yield 0.59g (73%) of IrCl(BDPH).

Anal. Found: mol.wt., 683 (vapour pressure osmometry in chloroform), 680 (mass spectrum); C, 53.68; H, 4.55; P, 9.3; Cl, 5.4. $C_{30}H_{30}ClP_2Ir$. Calcd.: mol.wt., 680; C, 52.98; H, 4.45; P, 9.1; Cl, 5.2.

Preparation of 1,6-Bis(diphenylphosphino)-*trans*-hex-3-enecarbonylchlororhodium(I), Rh(CO)Cl(BDPH).

Carbon monoxide was bubbled through a solution of 0.10g (1.69×10^{-1}

mmol) of RhCl(BDPH) in 30ml of ether at room temperature for 1hr. The resulting yellow precipitate was filtered off and washed with ether and dried *in vacuo*. The yield was 0.10g (96%).

Anal. Found: C, 60.28; H, 5.32. $C_{31}H_{30}ClOP_2Rh$.

Calcd.: C, 60.16; H, 4.89.

Preparation of 1,6-Bis(diphenylphosphino)-*trans*-hex-3-enecarbonyl chloroiridium(I), Ir(CO)Cl(BDPH).

This was prepared as above for the rhodium carbonyl complex. The yield of Ir(CO)Cl(BDPH) was 97%. Anal. Found: C, 52.41; H, 4.22; Cl, 4.5. $C_{31}H_{30}ClOP_2Ir$. Calcd.: C, 52.57; H, 4.27; Cl, 5.0.

Preparation of 1,6-Bis(diphenylphosphino)-*trans*-hex-3-enedicarbonyl-iridium(I) Tetraphenylborate, $[Ir(CO)_2(BDPH)][B(C_6H_5)_4]$

Carbon monoxide was bubbled into a solution of 0.20g of IrCl(BDPH) in 5ml of methylene chloride. An excess of sodium tetraphenylborate in methanol was added and an immediate white precipitate formed. This was collected by filtration and recrystallised from chloroform-methanol to yield 0.18g (53%) of $[Ir(CO)_2(BDPH)][B(C_6H_5)_4]$. Anal. Found: C, 64.99; H, 4.99. $C_{56}H_{50}BO_2P_2Ir$. Calcd.: C, 65.94; H, 4.94.

Preparation of *trans*-μμ'-Di[1,6-bis(diphenylphosphino)hexane]dicarbonyl-dichlorodirhodium(I), $\{Rh(CO)Cl[(C_6H_5)_2P(CH_2)_6P(C_6H_5)_2]\}_2$.

Carbon monoxide was bubbled into a solution of 0.56g (1.2 mmol) of 1,6-bis(diphenylphosphino)hexane and 0.30g (6.1 mmol) of bis(cycloocta-1,5-diene)-μμ'-dichlorodirhodium(I) in 20ml benzene at room temperature. The benzene was then removed at reduced pressure and methanol added to yield a yellow precipitate which was recrystallised from methylene chloride-methanol mixture to yield 0.70g (93%) of $\{Rh(CO)Cl[C_6H_5)_2P-(CH_2)_6P(C_6H_5)_2]\}_2$. Anal. Found: mol.wt., 1142 (vapour pressure osmometry in chloroform); C, 59.37; H, 5.57; P, 10.1; Cl, 5.6; $C_{62}H_{64}Cl_2O_2P_4Rh_2$. Calcd.: mol.wt., 1242; C, 59.97; H, 5.20; P, 10.0; Cl, 5.7.

Preparation of *trans*-μμ'-Di[1,6-bis(diphenylarsino)hexane]dicarbonyldichlorodirhodium(I), $\{Rh(CO)Cl[C_6H_5)_2As(CH_2)_6As(C_6H_5)_2]\}_2$.

This was prepared as above from 0.55g (1.0 mmol) of 1,6-bis(diphenylarsino)hexane, 0.25g (5.1×10^{-1} mmol) of bis(cycloocta-1,5-diene)-μμ'-dichlorodirhodium(I) and an excess of carbon monoxide at room temperature to yield 0.62g (86%) of $\{Rh(CO)Cl[(C_6H_5)_2As(CH_2)_6$-$As(C_6H_5)_2]\}_2$. Anal. Found: C, 52.26; H, 4.64; Cl, 5.22. $C_{62}H_{64}Cl_2O_2As_4Rh_2$. Calcd.: C, 52.53; H, 4.55; Cl, 5.00.

Preparation of *trans*-μμ'-Di[1,6-bis(diphenylphosphino)hexane]dicarbonyldichlorodiiridium(I), $\{Ir(CO)Cl[(C_6H_5)_2P(CH_2)_6P(C_6H_5)_2]\}_2$.

This was prepared as above from 0.34g (7.5×10^{-1} mmol) of 1,6-bis(diphenylphosphino)hexane, 0.25g (3.7×10^{-1} mmol) of bis(cycloocta-1,5-diene)-μμ'-dichlorodiiridium(I) and an excess of carbon monoxide at room temperature to yield 0.31g (58%) of $\{Ir(CO)Cl[(C_6H_5)_2P(CH_2)_6$-$P(C_6H_5)_2]\}_2$. Anal. Found: mol.wt., 1477 (vapour pressure osmometry in chloroform); C, 52.53; H, 4.58; P, 7.8; Cl, 4.5. $C_{62}H_{64}Cl_2O_2P_4Ir_2$. Calcd.: mol.wt., 1420; C, 52,43; H, 4.54; P, 8.7; Cl, 5.0.

Preparation of *trans*-μμ'-Di[1,6-bis(diphenylarsino)hexane]dicarbonyldichlorodiiridium(I), $\{Ir(CO)Cl[C_6H_5)_2As(CH_2)_6As(C_6H_5)_2]\}_2$.

This was prepared as above from 0.25g (4.6×10^{-1} mmol) of 1,6-bis(diphenylarsino)hexane, 0.15g (2.2×10^{-1} mmol) of bis(cycloocta-1,5-diene)-μμ'-dichlorodiiridium(I) and an excess of carbon monoxide at room temperature to yield 0.25g (66%) of $\{Ir(CO)Cl[(C_6H_5)_2As(CH_2)_6$-$As(C_6H_5)_2]\}_2$. Anal. Found: C, 46.41; H, 4.09; Cl, 4.44. $C_{62}H_{64}Cl_2O_2As_4Ir_2$. Calcd.: C, 46.65; H, 4.04; Cl, 4.87.

Preparation of the Polymeric Compound 1,6-Bis(diphenylphosphino)chloroiridium(I) Dibenzene, $\{IrCl[(C_6H_5)_2P(CH_2)_6P(C_6H_5)_2].2C_6H_6\}_n$.

A solution of 0.41g (9.0×10^{-1} mmol) of 1,6-bis(diphenylphosphino)hexane in 20ml benzene was added dropwise to 0.30g (4.5×10^{-1} mmol) of bis(cycloocta-1,5-diene)-μμ'-dichlorodiiridium(I) in 10ml benzene at room temperature. The solution was stirred overnight and the resulting yellow precipitate separated by filtration and washed with benzene, then ethanol and dried *in vacuo* to yield 0.63g (84%).

Anal. Found: C, 59.60; H, 5.57; P, 7.1; $C_{42}H_{44}ClP_2Ir$

Calcd.: C, 60.17; H, 5.29; P, 7.4;

Results and Discussion

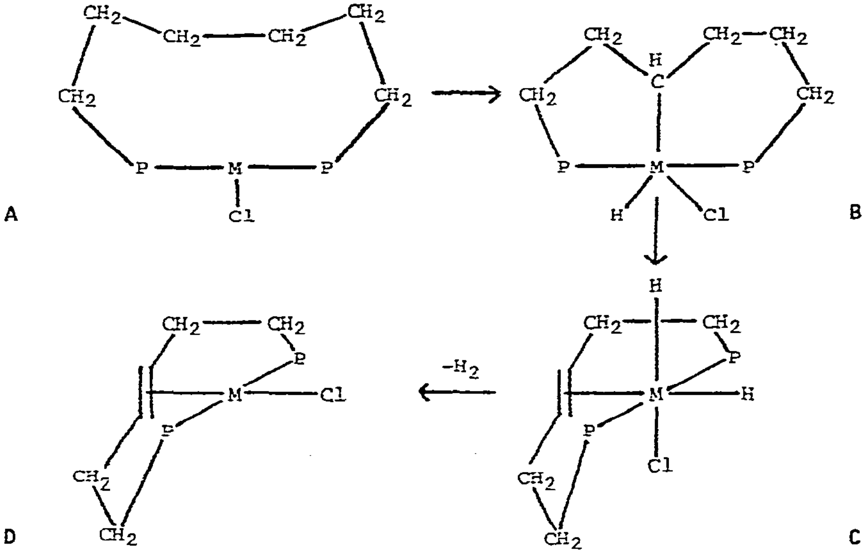
The Dehydrogenation Reaction

It has been reported that at ambient temperatures, the reaction of 1,6-bis(diphenylphosphino)hexane with the ethylene complex of rhodium(I), $Rh_2Cl_2(C_2H_4)_4$, in benzene gave the intermediate compound $RhCl[(C_6H_5)_2P(CH_2)_6P(C_6H_5)_2].C_6H_6$[21], the solution of which in benzene was used to study the homogeneous hydrogenation of styrene. In contrast to this, we find that the reaction of 1,6-bis(diphenylphosphino)hexane with $M_2Cl_2(C_8H_{12})_2$, M = Rh or Ir, C_8H_{12} = *cis cis* cycloocta-1,5-diene, in benzene at ambient temperatures leads to the formation of insoluble, presumably polymeric, compounds. In particular we analysed the iridium complex and found the formula approximated to $[IrCl[(C_6H_5)_2P(CH_2)_6P(C_6H_5)_2].2C_6H_6]_n$. The infrared spectra of the rhodium and iridium complexes were very similar to the infrared spectrum of the ligand.

However, when 1,6-bis(diphenylphosphino)hexane reacts with the cycloocta-1,5-diene complexes of rhodium(I) and iridium(I), $Rh_2Cl_2(C_8H_{12})_2$, $Rh_2Br_2(C_8H_{12})_2$ and $Ir_2Cl_2(C_8H_{12})_2$ in refluxing mesitylene under nitrogen, the very stable complexes RhX(BDPH), X = Cl or Br and IrCl(BDPH) are formed where BDPH = 1,6-bis(diphenylphosphino)-*trans*-hex-3-ene in good yields[1]. The same products MCl(BDPH) can be formed by heating the insoluble products as discussed above in mesitylene.

The dehydrogenation of 1,6-bis(diphenylphosphino)hexane by rhodium(I) and iridium(I) complexes most probably proceeds via a *trans*-chelating diphosphine *complex* - *A* (See Scheme 2). Similar diphosphines such as $^{t}Bu\ P(CH_2)_nPBu^{t}_2$, *o*-$(C_6H_5)_2PC_6H_4CH_2CH_2C_6H_4P(C_6H_5)_2$-*o* and *o*-$(C_6H_5)_2AsC_6H_4CH_2CH_2C_6H_4As(C_6H_5)_2$-*o* form *trans*-chelated rhodium(I) and iridium(I) [4,3,14,15] complexes and *trans*-stereochemistry is preferred in square planar Rh(I) and Ir(I) complexes.

The first step in the proposed mechanism leads to the abstraction of one proton from the hexane chain to give *complex - B*. The abstraction of a proton from the similar ligand o-$(C_6H_5)_2PC_6H_4CH_2CH_2C_6H_5P(C_6H_5)_2$-$o$ with Pd(II) and Pt(II) complexes is known[3]. The second step gives the olefin-dihydride complex $MCl(BDPH)\cdot H_2$. The iridium complex, $IrCl(BDPH)\cdot H_2$, has been isolated and it has been shown to have the stereochmistry as in *complex - C*[22]. It has also been shown that the complex $IrCl(BDPH)\cdot H_2$ readily loses molecular H_2 at higher temperatures to give IrCl(BDPH)[22].

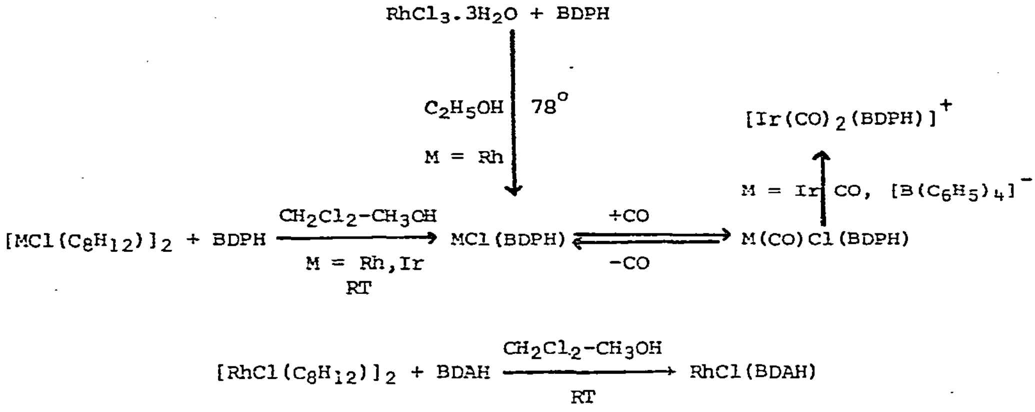


Scheme 2. Proposed Mechanism for the Dehydrogenation of 1,6-Bis-(diphenylphosphino)hexane with Rhodium(I) and Iridium(I) Complexes.

It has been shown that the C-3 position of the straight chain tertiary phosphines $P(CH_2CH_2CH_3)_3$ and $P(CH_2CH_2CH_2CH_3)_3$ is the position most easily metallated by platinum complexes[11,12] and this resulted in the expected five membered ring intermediate. We therefore have reacted the diphosphines $(C_6H_5)_2P(CH_2)_nP(C_6H_5)_2$, n = 5, 7 or 8 and the diarsine $(C_6H_5)_2As(CH_2)_6As(C_6H_5)_2$ with Rh(I) and Ir(I) complexes in refluxing mesitylene. Impure, difficult to isolate, complexes of the approximate formula $[MCl(ligand)]_n$ were formed for the diphosphine ligands. . The reaction with the diarsine ligand lead only to decomposition. In no case was metallation or dehydrogenation observed.

Complexes of BDPH and BDAH

(I) REACTIONS (See Scheme 3).



Scheme 3. Reactions of BDPH and BDAH with Rhodium(I) and Iridium(I) Complexes.

BDPH reacts smoothly with $Rh_2Cl_2(C_8H_{12})_2$ (C_8H_{12} = *cis cis* cycloocta-1,5-diene) or with rhodium trichloride to give the yellow rhodium(I) complex, RhCl(BDPH); and reacts with $Ir_2Cl_2(C_8H_{12})_2$ to give the orange iridium(I) complex, IrCl(BDPH). Both of these complexes can be prepared by the dehydrogenation reaction of 1,6-bis(diphenylphosphino) hexane with $M_2Cl_2(C_8H_{12})_2$, M = Rh or Ir as discussed earlier. In a similar fashion, BDAH reacts with $Rh_2Cl_2(C_8H_{12})_2$ to give the yellow complex RhCl(BDAH). Both the rhodium and iridium complexes, MCl(BDPH), react reversibly with carbon monoxide giving the five coordinate complexes M(CO)Cl(BDPH), and the iridium complex reacts with excess carbon monoxide in the presence of sodium tetraphenylborate to form the five coordinate cation $[Ir(CO_2(BDPH)]^+$. The bromo- and iodo- complexes IrX(BDPH) were prepared by the metathetical reactions of IrCl(BDPH) with lithium bromide and sodium iodide, and the carbonyl complexes Ir(CO)X(BDPH), X = Br or I were prepared *in situ* to study their infrared spectra. The bromo- and iodo-complexes were not characterised further.

(II) INFRARED DATA (See Table 1)

The ligands 1,6-bis(diphenylphosphino)-*trans*-hex-3-ene(BDPH) and 1,6-bis(diphenylarsino)-*trans*-hex-3-ene have an intense sharp band in the infrared at ∿970 cm^{-1} which is typical of an out-of-plane (oop) deformation vibrational frequency of a *trans*-disubstituted olefin[23]. The band due to the C=C vibrational stretching mode in these ligands is too week to be observed, an observation which has been recorded for similar ligands[3]. In the rhodium complexes, the oop deformation band is at slightly lower frequency (950-960 cm^{-1}) while in the iridium complexes, this band occurs at a slightly higher frequency. In all the four-coordinate complexes, there are two or more medium to strong bands which occur between 800-900 cm^{-1} which do not occur in the ligands. Such bands have been observed previously in rhodium complexes containing unsaturated tertiary phosphines[24,25]. The carbonyl complexes Rh(CO)Cl(BDPH) and Ir(CO)X(BDPH), X = Cl, Br or I contain three carbonyl bands indicating the occurrence of different isomers. The presence of multiple carbonyl bands is quite common in such complexes and has been recorded previously in unsaturated tertiary phosphine complexes of rhodium(I) and iridium(I) [26,27]. The metal-chlorine stretching frequencies of RhCl(BDPH), 283 cm^{-1}; RhCl(BDAH), 288 cm^{-1}; and IrCl(BDPH), 300 cm^{-1}; are close to those previously observed for chlorine *trans* to an olefin[3] and for chlorine *trans* to a carbonyl[28] for rhodium(I) and iridium(I) complexes.

(III) NUCLEAR MAGNETIC RESONANCE SPECTRA (See Table 2)

^{1}H N.M.R. Spectra. BDPH shows three distinct resonances at τ(ppm) 2.4 - 2.8 (phenyl, area 20), 4.50 (olefinic, area 2) and at

TABLE 1

Selected Infrared Data[a,b]

	ν(CO) nujol	ν(CO) solution	oop[c]	ν(M-Cl)
BDPH			970(s)	
BDAH			968(s)	
RhCl(BDPH)			958(s)	288(m)
RhBr(BDPH)			958(s)	
RhCl(BDAH)			951(s)	288(m)
IrCl(BDPH)			978(s) 986(s)	300(m)
Rh(CO)Cl(BDPH)		1994(s)[d]		h
		2019(s)		
		2074(w)		
Ir(CO)Cl(BDPH)	1975(s)	1970(s)[d]	982(m)	h
	2001(s)	2024(s)		
	2055(m)	2070(m)		
Ir(CO)Br(BDPH)		1994(s)[d]		
		2020(s)		
		2070(w)		
Ir(CO)I(BDPH)		1964(s)[d]		
		2018(s)		
		2068(m)		
$[Ir(CO)_2(BDPH)]^+$	2005(s)			
	2055(s)		e	
$[Rh(CO)ClL_1]_2$[g]	1950(s)			304(vw)
$[Rh(CO)ClL_2]_2$[g]	1955(s)			280(m)
$[Ir(CO)ClL_1]_2$[g]	1942(s)	1956(s)[f]		
		2005(s)		e
$[Ir(CO)ClL_2]_2$[g]	1940(s)	1950(s)[f]		286(m)
		2003(s)		

(For footnotes see next page)

Footnotes to Table 1

a all measurements are in cm^{-1}

b w = weak, m = medium, s = strong

c oop = out of plane deformation vibrational frequency of the olefinic protons.

d methylene chloride solution

e too weak to be observed

f chloroform solution

g $L_1 = (C_6H_5)_2P(CH_2)_6P(C_6H_5)_2$

$L_2 = (C_6H_5)_2As(CH_2)_6As(C_6H_5)_2$

h not measured

7.8 - 8.0 (overlapping methylenes, area 8); while for BDAH the olefinic resonance occurs at 4.55τ. Upon coordination, the olefinic resonance is shifted upfield which is typical for an olefin coordinated to a transition metal. The olefinic resonance in the ligands is a broad triplet while in the complexes it has sharpened and lost all visible couplings. There is no visible rhodium (I = ½) coupling to the olefinic protons. The olefinic resonance of the carbonyl complexes Rh(CO)Cl(BDPH) and Ir(CO)Cl(BDPH) is an unresolved broad singlet even at low temperatures (-61°C). This observation is in agreement with the occurrence of three carbonyl resonances in the infrared spectra of these complexes and indicative of a fluctional process occurring between the isomers. It should be noted that similar fluxional behaviour does not occur in the similar complexes M(CO)Cl(BDPPS), M = Rh or Ir [29] which is presumably a consequence of the 2,2'-bis(diphenylphosphino)-*trans*-stilbene (BDPPS) ligand being more rigid. In the BDPPS complexes the olefinic protons are inequivalent resulting in an AB pattern in the ^1H N.M.R. spectrum.

^{13}C N.M.R. Specta. A complete discussion regarding the ^{13}C N.M.R. spectra of rhodium and iridium olefin complexes containg

TABLE 2

Selected N.M.R. Data of the Olefinic Protons and Carbon Atoms.[a]

Compound	τ(H)[b]	δ(c)[c]	$J(^{103}Rh-^{13}C)$[d]
BDPH	4.50	129.2	
BDAH	4.55		
RhCl(BDPH)	6.34	62.3	16.5
RhBr(BDPH)	6.28		
RhCl(BDAH)	6.44		
IrCl(BDPH)	7.46	43.8	
Rh(CO)Cl(BDPH)[e]	4.96		
Ir(CO)Cl(BDPH)[e]	5.92		
$[Ir(CO)_2(BDPH)]^+$	6.42		

[a] ^{1}H N.M.R. spectra were recorded in $CDCl_3$ solutions at 100 MHz, ^{13}C N.M.R. spectra were recorded in CD_2Cl_2 solutions at 67.89 MHz.

[b] ^{1}H chemical shifts in ppm relative to TMS, $\tau = 10.0$, $J(^{103}Rh - ^1H) < 0.5$ Hz.

[c] ^{13}C chemical shifts in ppm relative to TMS, $\delta = 0$.

[d] in Hz accurate to ± 0.5Hz.

[e] ambient temperature spectrum.

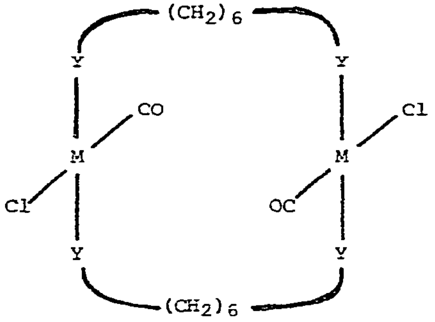
unsaturated tertiary phosphines will appear in the near future[30]. However, it should be noted here that the ^{13}C N.M.R. parameters are in agreement with the other physical data. The large upfield shift of the olefinic carbons in the complexes RhCl(BDPH), $\Delta\delta C = 66.9$ppm; and IrCl(BDPH), $\Delta\delta C = 85.4$ppm; and the $^{103}Rh-^{13}C$ coupling constant of 16.5Hz for RhCl(BDPH) are consistent with the olefin being firmly bound to the metal and are in agreement with ^{13}C N.M.R. parameters found previously for olefin complexes[1,31,32,33].

Dimeric Compounds Containing the Ligands 1,6-Bis(diphenylphosphino)hexane and 1,6-Bis(diphenylarsino)hexane.

Upon reacting the ligand 1,6-bis(diphenylphosphino)hexane or 1,6-bis(diphenylarsino)hexane with $M_2Cl_2(C_8H_{12})_2$, where C_8H_{12} = *cis cis* cycloocta-1,5-diene and M = Rh or Cl, in benzene or methylene chloride-methanol solutions saturated with carbon monoxide, the dimeric complexes $\{RhCl(CO)[(C_6H_5)_2P(CH_2)_6P(C_6H_5)_2]\}_2$ (I), $\{RhCl(CO)[(C_6H_5)_2As(CH_2)_6As(C_6H_5)_2]\}_2$ (II), $\{IrCl(CO[(C_6H_5)_2P(CH_2)_6P(C_6H_5)_2]\}_2$ (III), and $\{IrCl(CO)[(C_6H_5)_2As(CH_2)_6As(C_6H_5)_2]\}_2$ (IV), are formed in good yields. It should be noted that the diarsine complexes were too insoluble to obtain accurate molecular weight determinations. In no case was a monomeric compound containing a *trans*-chelating ligand formed. This is in direct contrast to the similar ligands 2,2'-bis(diphenylphosphino)bibenzyl and 2,2'-bis(diphenylarsino)bibenzyl which *trans*-chelate both rhodium and iridium complexes[15]. Furthermore, 2,2'-bis(diphenylphosphino)bibenzyl undergoes intramolecular metallation (including dehydrogenation) reactions with or without the presence of the extra ligand of carbon monoxide[2,3,15]. In none of the above cases (I to IV) was intramolecular metallation observed even at high temperatures. The complexes I to IV are very stable, and no change was observed with (I) even by refluxing the complex in mesitylene for 45 minutes. It has been shown that the ligand 1,10-bis-(di-t-butylphosphino)decane can form monomeric complexes $MCl(CO)[(Bu^t{}_2P(CH_2)_{10}PBu^t{}_2)]$, M = Rh or Ir, in which the diphosphine *trans*-chelates or a dimeric complex $\{RhCl(CO)[Bu^t{}_2P(CH_2)_{10}PBu^t{}_2]\}_2$. The complexes I - IV havea single carbonyl absorbance in nujol in the region 1940-1960 cm^{-1} which is in the region of carbonyl absorbances for carbon monoxide *trans* to chloride for square planar Rh(I) and Ir(I) complexes [5,34]. When chloroform solutions of the iridium complexes III and IV are prepared in the air, the complexes contain two carbonyl resonances at *ca.* 1950 cm^{-1} and at *ca.* 2005 cm^{-1}. The former is due to the parent complex while the latter is presumably due to the dioxygen adduct similar to the dioxygen adduct of Vaska's compound, $Ir(CO)Cl(O_2)[(C_6H_5)_3P]_2$ which has a ν(CO) 48 cm^{-1} higher than the parent compound $Ir(CO)Cl[(C_6H_5)_3P]_2$[5].

The M-Cl stretching frequencies for the complexes occur between 280 cm^{-1} and 304 cm^{-1}, typical of chloride *trans* to carbonyl for Rh(I) and Ir(I) square planar complexes. The metal-chlorine stretching frequencies for the analogous triphenylphosphine complexes, *trans*-$Rh(CO)Cl[(C_6H_5)_3P]_2$ and *trans*-$Ir(CO)Cl[(C_6H_5)_3P]_2$, occur at 309 cm^{-1} and 317 cm^{-1} respectively[28].

Although the complexes are not very soluble, d-chloroform solutions show that the ^1H N.M.R. spectra of the complexes are very similar to the ligands. However, the methylene resonances are broadened a little, but the variable temperature spectra of the complexes from +60°C to -60°C showed little change. We propose that in the solid state, the complexes have a structure similar to $\{RhCl(CO[Bu^t_2P(CH_2)_{10}PBu^t_2]\}_2$. (See below).



M = Rh or Ir,

Y = $(C_6H_5)_2P$ or $(C_6H_5)_2As$

Investigations into the dioxygen adducts and other oxidative addition reactions are in progress.

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