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2,2′-Bis((di-*tert*-butylphosphino)methyl)-1,1′-biphenyl (ditbi): a bulky analogue of bisbi. The crystal structure of $[Rh_2Cl_2(1,5\text{-cod})_2(\mu\text{-ditbi})]$

Lee J. Higham *,[1], Katie Heslop, Paul G. Pringle *, A. Guy Orpen

School of Chemistry, University of Bristol, Bristol BS8 1TS, UK

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Abstract

Diphosphine 2,2′-bis(di-*tert*-butylphosphino)methyl)-1,1′-biphenyl (ditbi) is synthesised by the addition of $Bu^t_2P(BH_3)Li$ to 2,2′-bis(bromomethyl)-1,1′-biphenyl, followed by deprotection with diethylamine. Treatment of $[Rh_2Cl_2(1,5\text{-cod})_2]$, with ditbi gives $[Rh_2Cl_2(1,5\text{-cod})_2(\mu\text{-ditbi})]$ (**2**) as confirmed by its X-ray crystal structure determination. Hydroformylation of 1-hexene using $[Rh(acac)(CO)_2]$/ditbi as catalyst gave *n*- and *iso*-heptanal in a ratio of 1:1.

Keywords: Diphosphine; Hydroformylation; Rhodium; Synthesis and characterisation

1. Introduction

The diphosphine bisbi ((2,2′-bis(diphenylphosphino)methyl)-1,1′-biphenyl) [1] has attracted much attention because it is an outstanding ligand for hydroformylation catalysis: its rhodium complexes are highly active under mild conditions and *n*:*i* product ratios of 66:1 have been achieved [2]. The flexibility of the bisbi backbone enables this ligand to span angles at the metal ranging from 90–120° and it is this property that may be at the root of its success [3]. We are interested in other ligands that contain the bisbi backbone and here we report the bulky diphosphine ditbi (**1**).

2. Results and discussion

The synthesis of ditbi was carried out according to Scheme 1. Difficulties were encountered in the final borane deprotection step including the regeneration of Ph_2PH and the formation of many by-products, as evidenced by the complicated ^{31}P NMR spectra. Several amines (morpholine, diazabicyclo[2.2.2]octane (DABCO), triethylamine and diethylamine) were investigated as deprotecting reagents and the reactions were carried out at different temperatures, concentrations of amine and reaction times; the most convenient procedure used diethylamine under the conditions given in the Section 4.3.

Reaction of ditbi with one equivalent of $[Rh_2Cl_2(1,5\text{-cod})_2]$ in CH_2Cl_2 yielded an orange solution which ^{31}P NMR spectroscopy showed contained a single P-containing species with a chemical shift of 40.6 ppm ($^1J_{Rh-P} = 137.7$ Hz). Orange crystals that deposited from this solution were suitable for X-ray crystallography. The crystal structure (see Fig. 1 and Tables 1 and 2)

* Corresponding authors.
E-mail address: lee.higham@ucd.ie (L.J. Higham).
[1] Present address: Chemistry, University College Dublin, Belfield, Dublin, Ireland. Tel.: +35-317-162-316; fax: +35-317-162-308.

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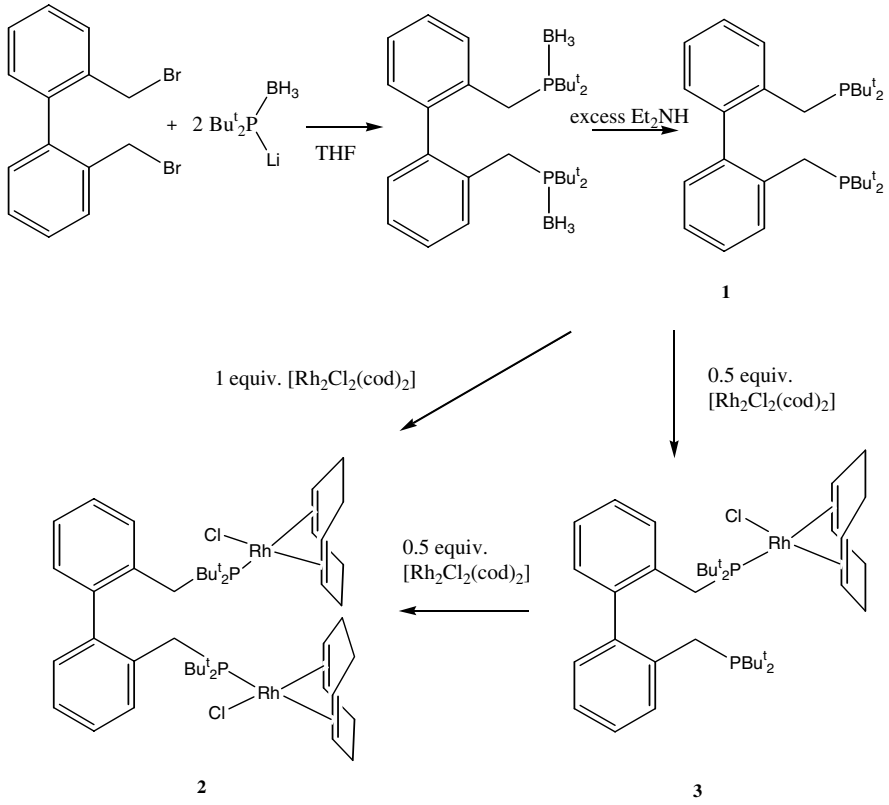

Scheme 1. Synthesis of ditbi (**1**) and its reactions with [$Rh_2Cl_2(cod)_2$].

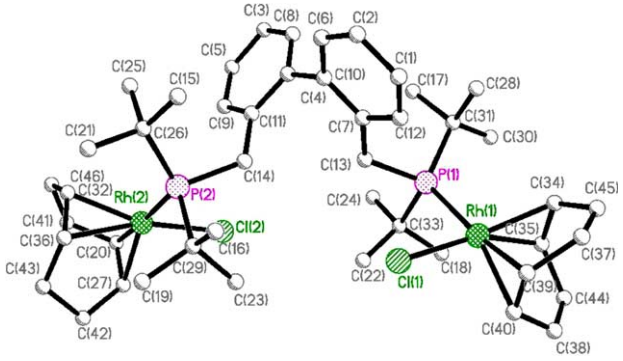

Fig. 1. Crystal structure of [Rh_2Cl_2(1,5-cod)$_2$(μ-ditbi)] (**2**).

Table 1
Bond distances (Å) and angles (°) for [Rh_2Cl_2(1,5-cod)$_2$(μ-ditbi)] (**2**)

Bond lengths (Å)		Angles (°)	
Rh(1)–P(1)	2.390(3)	Cl(1)–Rh(1)–P(1)	89.80(10)
Rh(2)–P(2)	2.407(3)	Cl(2)–Rh(2)–P(2)	88.40(11)
Rh(1)–Cl(1)	2.381(3)	C(35)–Rh(1)–C(40)	81.3 (5)
Rh(2)–Cl(2)	2.370(3)	C(13)–P(1)–C(31)	102.3(5)
P(1)–C(13)	1.860(10)	C(14)–P(2)–C(26)	102.5(5)
P(2)–C(14)	1.853(11)	C(7)–C(13)–P(1)	121.6(7)
C(1)–C(2)	1.399(16)	C(28)–C(31)–C(30)	110.7(10)
C(2)–C(8)	1.407(15)		
C(34)–C(35)	1.398(15)		
C(38)–C(44)	1.475(19)		

Table 2
Crystal and refinement data for [Rh_2Cl_2(1,5-cod)$_2$(μ-ditbi)] (**2**)·$CHCl_3$

Crystal	[Rh_2Cl_2(1,5-cod)(μ-ditbi)] (**2**)·$CHCl_3$
Colour, habit	Orange block
Size (mm)	0.4×0.35×0.2
Formula	$C_{47}H_{73}Cl_5P_2Rh_2$
Formula weight	1083.06
Crystal system	Monoclinic
Space group (No.)	$P2_1/c$(14)
a (Å)	12.0851(14)
b (Å)	20.188(2)
c (Å)	23.201(3)
β (°)	95.553(2)
V (Å^3)	5633.8(11)
Z	4
μ (mm^{-1})	0.907
Reflections collected	27474
Unique data	8832
R_{int}	0.0662
Final $R_1[I>2\sigma(I)]$	0.0814
Max, min difference map features (eÅ^{-3})	0.78, −0.98

confirmed the binuclear structure of **2**. Binuclear complexes have previously been reported when 1,*n*-bis(diphenylphosphino)alkanes ($n=3$–6) reacted with [Rh_2Cl_2-(diolefin)$_2$] [4].

A space-filling model of **2** (see Fig. 2) shows the twisted bisbi backbone and the crowded nature of the structure.

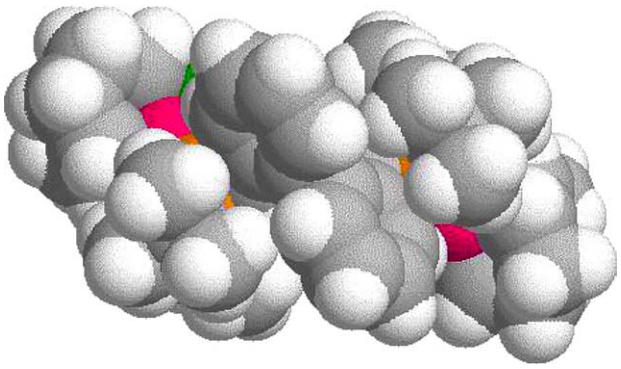

Fig. 2. Space-filling model of $[Rh_2Cl_2(1,5\text{-cod})_2(\mu\text{-ditbi})]$ (**2**).

The bulk of the PBu^t_2 groups may explain why ditbi seems reluctant to *cis*-chelate; addition of ditbi to 0.5 equivalents of $[Rh_2Cl_2(1,5\text{-cod})_2]$ gave a species characterised in solution as the mononuclear ditbi complex **3** from the ^{31}P NMR spectrum. The coordinated phosphine appears as a doublet at δ 38.6 ppm ($^1J_{Rh-P}$ = 145.7) and the non-coordinated phosphine at δ 28.2 ppm. Treatment of solutions of **3** with 0.5 equivalents of $[Rh_2Cl_2(1,5\text{-cod})_2]$ gave **2**.

We compared ditbi and bisbi in rhodium-catalysed hydroformylation of hex-1-ene. Under the reaction conditions employed (9.0 bar H_2/CO, 36 °C, 11 h) the alkene had completely reacted but the *n*:*iso* ratio of product aldehydes was found to be ca. 1:1 with ditbi. Others have shown [2] that using bisbi under similar conditions led to an *n*:*i* ratio of greater than 66:1

3. Conclusion

The bulky diphosphine ditbi has been made and shown to bridge in a dirhodium(I) complex. The great steric bulk of ditbi perhaps inhibits the formation of *cis*-chelates which may explain the low *n*:*i* ratio in the hydroformylation of 1-hexene.

4. Experimental

4.1. General methods

All operations were carried out under a N_2 atmosphere using standard Schlenk-line techniques. Toluene, CH_2Cl_2 and THF were dried using the Grubbs drying system [5] and purged with nitrogen; CH_3OH was refluxed and distilled under nitrogen from Mg/I_2. Et_3N and Et_2NH were dried and distilled from P_2O_5 and KOH respectively. Anhydrous *n*-pentane, 2,2′-bis(bromomethyl)-1,1′-biphenyl, morpholine, diazabicyclo[2.2.2]octane (DABCO) and $[Rh(acac)(CO)_2]$ were all purchased from Aldrich. 1-Hexene was purchased from Aldrich and purged with nitrogen prior to use. C_6D_6 and $CDCl_3$ were degassed with nitrogen and stored over molecular sieves. $[Rh_2Cl_2(1,5\text{-cod})_2]$ was synthesised according to a literature procedure [6]. The NMR spectra were recorded at 23 °C on a Jeol ecp300 spectrometer with chemical shifts relative to tetramethylsilane for ^1H and ^{13}C spectra and 85% H_3PO_4 for ^{31}P spectra.

4.2. Synthesis of $Bu^t_2PH \cdot BH_3$

To Bu^t_2PH (5.00 g, 34.0 mmol) in THF (50 cm^3) at room temperature, was slowly added BH_3·THF (40 cm^3 of a 1 M solution in THF, 40 mmol). The reaction mixture was stirred for 1 h and then the solvent and other volatiles were removed under reduced pressure. The residue was dissolved in *n*-pentane (40 cm^3) and the solution was set-aside at 0 °C for 7 days to give the crystalline product (5.03 g, 92%). ^{31}P NMR ($CDCl_3$): 48.3 (q, $^1J_{B-P}$ = 53.0 Hz) ppm.

4.3. Synthesis of 2,2′-bis((di-tert-butylphosphino)methyl)-1,1′-biphenyl (ditbi) (*1*)

1.25 g (7.80 mmol) of $Bu^t_2PH \cdot BH_3$ was dissolved in THF (20 cm^3) and cooled to 0 °C. To this was added *n*-BuLi (4.9 cm^3, 1.6 M solution in hexanes, 7.8 mmol). The resulting pale yellow solution was allowed to warm to room temperature and stirred for 1 h. The solution was then cooled to 0 °C, and bis(bromomethyl)-1,1′-biphenyl (1.33 g, 3.90 mmol) was added as a solid, generating a yellow solution which became colourless after 5 min. The ice-bath was removed and the reaction mixture allowed to warm to room temperature. After 2 h, the mixture was heated to 35 °C and then a large excess of diethylamine (20 cm^3, 14.14 g, 0.20 mol) was added by syringe to give a suspension which was then stirred for a further 60 h. The volatiles were then removed and CH_2Cl_2 (50 cm^3) added. The solution was filtered from the ammonium salt and then the solvent removed to yield an oil. Methanol (30 cm^3) was added to this oil to give a colourless solution which was filtered from a small quantity of an oily solid and then cooled to 0 °C overnight. The resultant white solid product was filtered off and dried (0.66 grams, 51.3%). EI mass spectrum: *m*/*z* 470 (M^+). Elemental composition to within 1.7 ppm. ^1H NMR ($CDCl_3$): 7.69 (m, 2H, Ar*H*), 7.0–7.3 (m, 6H, Ar*H*), 2.59 (m, 4H, C*H H* b), 1.03 (d, 18H, $^3J_{P-H}$ = 11.0 Hz, CH_3), 0.77 (d, 18H, $^3J_{P-H}$ = 10.7 Hz, CH_3) ppm. ^{13}C NMR ($CDCl_3$): 25.6 (d, $^1J_{P-C}$ = 22.5 Hz, *C* H_2), 29.7 (m, 13.3 Hz, *C*H_3), 31.4 (d, $^1J_{P-C}$ = 20.7 Hz, *C* Me_3), 32.0 (d, $^1J_{P-C}$ = 23.0 Hz, *C* Me_3), 125.3–130.4 (m, CH, aromatic) 139.7 (d, $^1J_{P-C}$ = 12.1 Hz, *o C* 2), 141.3 (br, *ipso C* 1) ppm. ^{31}P NMR: 31.6 (s) ppm. IR (solid, cm^{-1}): *v*(aryl-H) 3059 (w), 756 (s), 737 (s), *v*(C═C) 1597 (m), *v*(C–H) 1469 (m), *v*(aryl-P) 1432 (m).

4.4. Synthesis of [Rh_2Cl_2(1,5-cod)$_2$(μ-ditbi)] (**2**)

To a solution of ditbi (0.19 g, 0.4 mmol) in CH_2Cl_2 (10 cm^3) was added [Rh_2Cl_2(1,5-cod)$_2$] (0.16 g, 0.4 mmol). The resulting deep-red solution was stirred for 1 h and then the volatiles were removed. The residue was dissolved in $CDCl_3$ (2 cm^3) and after 2 weeks red crystals of **2** had formed. ^{31}P NMR: 40.6 (d, $^1J_{P-Rh}$ = 137.7 Hz) ppm. FAB mass spectrum: *m/e* 987 ([MNa]$^+$).

4.5. Catalytic hydroformylation of 1-hexene

The diphosphine ditbi (9.0 mg, 0.019 mmol) was added to a solution of [Rh(acac)(CO)$_2$] (5.0 mg, 0.019 mmol) in anhydrous C_6D_6 (3 cm^3) and the emerald green solution became orange. The solution was transferred under nitrogen to the autoclave which was then evacuated and refilled 3 times with a 1:1 mixture of H_2 and CO. The reaction mixture was stirred for 1 h at 36 °C and 9.0 bar of syngas. 1-Hexene (1.2 cm^3, 9.6 mmol) was injected into the autoclave and the reaction monitored by syngas uptake. After 11 h the uptake was complete but the conditions were maintained for a further 5 h. The pressure was released slowly and the autoclave purged with nitrogen. The ratio of linear:branched products was calculated by integrating the ^{1}H NMR signals for the aldehyde protons at 9.22 (*n*) and 9.15 (*i*) in C_6D_6.

4.6. X-ray crystal structure of [Rh_2Cl_2(1,5-cod)$_2$(μ-ditbi)] (**2**)

X-ray diffraction experiments on [Rh_2Cl_2(1,5-cod)$_2$(μ-ditbi)] (**2**) as a chloroform solvate were carried out at −100 °C on a Bruker SMART diffractometer using Mo Kα X-radiation, $\alpha = 0.71073$ Å. Crystal and refinement data are given in Table 2. Absorption corrections were based on equivalent reflections and structures refined against all F_o^2 data with hydrogen atoms riding in calculated positions. A disordered chloroform solvate molecule was found in the electron density difference map. Attempts to model this disorder produced unsatisfactory results and an improved model was obtained by applying a diffuse solvent correction to the data using the Squeeze routine in the Platon suite of software [7].

5. Supplementary material

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 241328 for **2**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(1223)336033 or e-mail: deposit@ccdc.cam.ac.uk or www.ccdc.cam.ac.uk/conts/retrieving.html.

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