J. Iran. Chem. Soc., Vol. 8, No. 1, March 2011, pp. 240-246.

JOURNAL OF THE
Iranian
Chemical Society

Phosphine-Borane Complexes: *in situ* Deprotection and Application as Ligands in the Rh- or Pd-Catalysed Hydroformylation Reaction

D.B.G. Williams*, P.D.R. Kotze, A.C. Ferreira and C.W. Holzapfel
Department of Chemistry, University of Johannesburg, P.O. Box 524, Auckland Park, Johannesburg, South Africa

(Received 4 June 2010, Accepted 29 July 2010)

Triarylphosphine-borane complexes are directly useful in the Rh-catalysed hydroformylation reaction of 1-octene (or Pd-catalysed hydroformylation of 1-pentene). Mild reaction conditions provide similar yields and selectivities of the anticipated aldehyde products to reactions making use of the corresponding free phosphines as ligands. The mono- or bidentate P-B adducts undergo *in situ* CO-mediated deprotection the produce the free phosphine ligands. The results demonstrate that phosphine-borane complexes may be directly applied to carbonylation reactions without a prior deprotection step, with little to no change in the reaction outcome.

Keywords: Carbonylation, Hydroformylation, Palladium, Phosphanes, Rhodium

INTRODUCTION

Phosphines often suffer instability towards air, water and acids. Once oxidised, they are rendered practically useless in reactions where free phosphines are required as metal-modifying ligands in catalytic processes. Therefore, a number of methods have been developed to overcome the instability of phosphines [1,2,3], the most effective of which is probably borane protection of the phosphine. Burg *et al*. [4] reported the first synthesis of a phosphine-borane complex. This method has been extensively utilised for the preparation of a wide range of phosphine-borane compounds, generally to protect the P atom in the (III) oxidation state against oxidation [5] employing BH_3.THF and BH_3.DMS as reagents, amongst others [5-9]. In such complexes, the P-B donor-acceptor bond is unusually strong and the B-H bonds show signs of an Umpolung effect [10]. Consequently, these complexes are inert towards oxygen, many nucleophiles, moisture and most acids; this has been attributed to the fact that the P-B and B-H bonds have low polarity and polarisability [11]. P-B complexes cannot normally be used to modify transition metal catalysts: a separate deprotection step to release the free P ligand is usually called for, after which complexation to the metal in question ensues. Deprotection is usually effected *ex situ* (when the free phosphine is to be used to modify a catalyst) by amines in a separate step. We have previously investigated the suitability of several amines and other deprotection agents to cause this deprotection [12], which typically proceeds in high yield. Purification of the free phosphine is effected by removal of the new N-BH_3 complex from the free phosphine by extraction into a second liquid phase, which most frequently is water. The need for an independent deprotection procedure to provide the free ligand adds cost and an additional step to the process.

It is known that diborane (B_2H_6) forms a BH_3.CO complex with carbon monoxide [13]. Additionally, B-CO complexes are intermediates in the synthesis of alcohols, aldehydes and ketones from alkylborane precursors [14]. The present study

*Corresponding author. E-mail: bwilliams@uj.ac.za

proposed to determine whether *in situ* deprotection of phosphine-borane complexes in carbonylation reactions would be possible (*i.e.* where the CO present serves to deprotect the P-BH_3 complex). Here, the free phosphine ligand is intended to bind to, and therefore modify, a transition metal as the ligand is released from the borane complex. Our approach successfully paves the way for the direct employment of phosphine-borane complexes in such reactions without the need for a separate deprotection step. The investigation was pursued by performing the Rh-catalysed hydroformylation reaction using a series of triarylphosphine-borane complexes and comparing the results with those obtained when making use of the corresponding free phosphine ligands. The Pd-catalysed hydroformylation reaction, making use of bidentate phosphines, was also successfully investigated. No additional reagents were added with which to effect the deprotection, rendering this method advantageous over procedures requiring extra reagents and separate deprotection steps.

EXPERIMENTAL

General

All experiments were performed using standard Schlenk techniques under an atmosphere of dry argon. ^{1}H and $^{13}C\{H\}$ NMR spectra were recorded by means of a Varian Gemini 2000, 300 MHz spectrometer in $CDCl_3$ and were referenced to $SiMe_4$. $^{31}P\{H\}$ NMR spectra were run in $CDCl_3$ and referenced to external 85% aqueous phosphoric acid. Gas chromatography (GC) was carried out on a Varian Spectrum 3400 CX gas chromatograph, using nitrogen as the carrier gas with a flow pressure of 1 bar. A DB1 30 m column, which separated components on the basis of boiling points, was used. Mass spectrometry was performed on a Varian Spectrum 3400 CX mass spectrometer at an ionisation potential of 70 eV. GC-MS analyses were performed on a Varian Spectrum 3400 CX. High pressure IR spectroscopy was performed a high pressure Parr reactor fitted with opposing ZnS windows. The turnover frequencies of the catalyst systems were calculated from CO uptake measurements using a Danfoss gas flow meter coupled to a high-pressure ballast vessel (turnover frequency is measured in mol product/mol cat.h) and were calculated using the linear part of the CO uptake curve.

Synthesis of Triarylphosphine Ligands

All of the phosphines of this study are commercially available or have been prepared and characterised [15]. The following method is given for ease of reference (see also Ref. [16]). The aryl halide (0.049 mol, 1.2 equiv.) was added to a THF (20 ml) mixture containing magnesium turnings (1.0 g, 0.041 mol, 1.0 equiv.) and a few iodine crystals. The suspension was allowed to stir under reflux for several hours. The solution was cooled to -40 °C after which it was slowly added to a cold (-40 °C) THF solution of the relevant P-Cl reagent (chlorodiphenyl-phosphine, 2.5 ml, 0.021 mol, 0.5 equiv.; dichlorophenyl-phosphine, 1.86 ml, 0.014 mol, 0.33 equiv; or trichloro-phosphine, 0.72 ml, 0.008 mol, 0.2 equiv). The resulting solution was allowed to stir overnight while slowly warming to room temperature. The product was extracted using DCM and H_2O and the solvent was removed *in vacuo*. The product was isolated by flash column chromatography using hexane as the eluent.

General Synthesis of Phosphine-Borane Complexes (see Ref. [5])

The free phosphine ligand (1 equiv.) was dissolved in THF (20 ml), unless otherwise stated, and cooled to 0 °C. To this mixture was added a THF solution containing the BH_3.THF complex (1 M, 4 equiv.). The resulting solution was allowed to stir overnight at room temperature. The product was extracted with DCM and H_2O and the solvent was removed *in vacuo*. The product was isolated by flash column chromatography (hexane:EtOAc in v/v ratios as indicated). Borane complexes not mentioned below have been [17] prepared and characterised.

Diphenyl-*o*-tolylphosphine-borane (4c). The title compound was prepared as described in the general synthesis method, using diphenyl-*o*-tolylphosphine (0.0018 mol), providing the product as a white powder (0.0014 mol, 79%). m.p.: 135-136 °C; TLC: R_f 0.51 (19:1 hexane:EtOAc); ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 7.33-7.16 (m, 10H), 7.05-7.03 (m, 2H), 6.94 (t, 1H, J = 7.5 Hz), 6.81 (dd, 1H, $J_{H\text{-}H}$ = 6.6 Hz, $J_{H\text{-}P}$ = 6.0 Hz), 2.06 (s, 3H), 1.70-0.60 (br m, 3H, BH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 142.8 (d, 1C, J = 10.6 Hz), 134.0 (d, 2C, J = 8.6 Hz), 133.1 (d, 4C, J = 8.7 Hz), 131.8 (d, 1C, J = 8.9 Hz), 131.3 (d, 1C, J = 2.6 Hz), 131.1 (d, 2C, J = 2.3

Hz), 129.0 (d, 2C, J = 57.2 Hz), 128.8 (d, 4C, J = 10.0 Hz), 127.5 (d, 2C, J = 55.3 Hz), 125.8 (d, 1C, J = 9.4 Hz), 22.4 (d, 1C, J = 4.9 Hz); ^{31}P NMR (121 MHz, $CDCl_3$) δ_P 20.8 (d, J = 90.9 Hz); IR: ν_{max} ($CHCl_3$)/cm^{-1} 3067, 3009, 2389, 1438, 1105, 1063; EIMS: *m/z* 290 [M^+], 276 [M-BH_3]$^+$.

(*o*-Ethylphenyl)diphenylphosphine-borane (4d). The title compound was prepared as described in the general procedure, starting with (*o*-ethylphenyl)diphenylphosphine (0.0017 mol), which provided the product as colourless crystals (0.0012 mol, 71%). m.p.: 129-132 °C; TLC: R_f 0.53 (19:1 hexane:EtOAc); ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 7.30-7.20 (m, 10H), 7.08-7.03 (m, 2H), 7.00 (t, 1H, J = 7.4 Hz), 6.86 (dd, 1H, $J_{H\text{-}H}$ = 7.4 Hz, $J_{H\text{-}P}$ = 4.5 Hz), 2.68 (q, 2H, J = 7.5 Hz), 0.95 (t, 3H, J = 7.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 148.9 (d, 1C, J = 10.3 Hz), 134.2 (d, 2C, J = 16.3 Hz), 133.2 (d, 4C, J = 9.5 Hz), 131.5 (d, 1C, J = 2.3 Hz), 131.1 (d, 2C, J = 2.3 Hz), 129.9 (d, 1C, J = 8.6 Hz), 129.6 (d, 2C, J = 58.4 Hz), 128.8 (d, 4C, J = 9.9 Hz), 127.1 (d, 1C, J = 55.5 Hz), 125.8 (d, 1C, J = 9.7 Hz), 27.8 (d, 1C, J = 5.7 Hz), 15.0 (s, 1C); ^{31}P NMR (121 MHz, $CDCl_3$) δ_P 20.9 (d, J = 64.0 Hz); IR: ν_{max} ($CHCl_3$)/cm^{-1} 3058, 3009, 2965, 2932, 2386, 1465, 1436, 1068; EIMS: *m/z* 304 [M^+], 290 [M-BH_3]$^+$.

Phenyl-di-*p*-tolylphosphine-borane (4e). The title compound was synthesised as described in the general procedure with phenyl-di-*p*-tolylphosphine (0.0017 mol) as the starting material, yielding the product as colourless crystals (0.0017 mol, 100%). m.p.: 183-185 °C; TLC: R_f 0.51 (19:1 hexane:EtOAc); ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 7.41-7.21 (m, 9H), 7.06 (d, 4H, J = 7.8 Hz), 2.21 (s, 6H), 1.63-0.63 (br m, 3H, BH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 141.6 (d, 2C, J = 2.6 Hz), 133.1 (d, 4C, J = 10.0 Hz), 133.0 (d, 2C, J = 9.7 Hz), 131.0 (d, 1C, J = 2.6 Hz), 129.5 (d, 4C, J = 10.5 Hz), 129.1 (d, 1C, J = 51.0 Hz), 128.6 (d, 2C, J = 9.9 Hz), 125.8 (d, 2C, J = 59.8 Hz), 21.4 (s, 2C); ^{31}P NMR (121 MHz, $CDCl_3$) δ_P 20.1 (d, J = 72.9 Hz); IR: ν_{max} ($CHCl_3$)/cm^{-1} 3058, 3009, 2381, 1500, 1435, 1091; EIMS: *m/z* 304 [M^+], 290 [M-BH_3]$^+$.

Phenyl-di-*o*-tolylphosphine-borane (4f). The borane complex was synthesised as described in the general synthesis using toluene (20 ml) as solvent with phenyl-di-*o*-tolylphosphine (0.0017 mol) as the starting material, affording the product as a white amorphous solid (0.0016 mol, 95%). m.p.: 155-157 °C; TLC: R_f 0.52 (19:1 hexane:EtOAc); ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 7.35-7.19 (m, 5H), 7.04-7.00 (m, 4H), 6.97 (t, 2H, J = 7.6 Hz), 6.82 (dd, 2H, $J_{H\text{-}H}$ = 7.1 Hz, $J_{H\text{-}P}$ = 4.7 Hz), 2.10 (s, 6H), 1.70-0.60 (br m, 3H, BH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 143.1 (d, 2C, J = 11.0 Hz), 133.7 (d, 2C, J = 9.0 Hz), 133.5 (d, 2C, J = 8.6 Hz), 131.9 (d, 2C, J = 9.0 Hz), 131.3 (d, 2C, J = 2.5 Hz), 131.2 (d, 1C, J = 2.6 Hz), 128.7 (d, 2C, J = 9.5 Hz), 128.6 (d, 1C, J = 56.6 Hz), 127.6 (d, 2C, J = 54.0 Hz), 126.0 (d, 2C, J = 9.0 Hz), 22.7 (d, 2C, J = 4.6 Hz); ^{31}P NMR (121 MHz, $CDCl_3$) δ_P 21.6 (d, J = 54.9 Hz); IR: ν_{max} ($CHCl_3$)/cm^{-1} 3068, 3010, 2387, 1437, 1105,1059; EIMS: *m/z* 304 [M^+], 290 [M-BH_3]$^+$.

Di-(*o*-ethylphenyl)phenylphosphine-borane (4g). Phosphine-borane **7** was generated as described the general synthesis method, using toluene (20 ml) as solvent with di-(*o*-ethylphenyl)phenylphosphine (0.0016 mol) as the substrate, providing the product as a white powder (0.0011 mol, 70%). m.p.: 132-134 °C; TLC: R_f 0.51 (19:1 hexane:EtOAc); ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 7.28-7.21 (m, 5H), 7.07-7.02 (m, 4H), 6.96 (t, 2H, J = 7.5 Hz), 6.85 (dd, 2H, $J_{H\text{-}H}$ = 7.5 Hz, $J_{H\text{-}P}$ = 4.5 Hz), 2.70 (q, 4H, J = 7.5 Hz), 0.96 (t, 6H, J = 7.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 149.0 (d, 2C, J = 10.5 Hz), 133.8 (d, 2C, J = 9.0 Hz), 133.6 (d, 2C, J = 8.6 Hz), 131.4 (d, 2C, J = 2.5 Hz), 131.0 (d, 1C, J = 2.0 Hz), 130.0 (d, 2C, J = 9.0 Hz), 128.9 (d, 1C, J = 52.0 Hz), 128.7 (d, 2C, J = 10.0 Hz), 127.8 (d, 2C, J = 54.6 Hz), 125.8 (d, 2C, J = 9.5 Hz), 27.9 (d, 2C, J = 5.5 Hz), 14.8 (s, 2C); ^{31}P NMR (121 MHz, $CDCl_3$) δ P 20.8 (d, J = 61.1 Hz); IR: ν_{max} ($CHCl_3$)/cm^{-1} 3060, 3008, 2967, 2933, 2870, 2385, 1465, 1438, 1065; EIMS: *m/z* 332, 318 [M-BH_3]$^+$.

Rh-Catalysed Hydroformylation of 1-Octene

Acetylacetonatodicarbonylrhodium(I) (1.1 mg, 0.0000043 mol, 0.0091 mol% *vs*. 1-octene) and the triarylphosphine-BH_3 complex or the corresponding free phosphine ligand (0.043 mol, 10 equiv. with respect to Rh) were dissolved in toluene (5 ml) in a high pressure autoclave reactor. 1-Octene (7.4 ml, 0.047 mol) was added after which the reactor was sealed and pressurised with 2500 kPa of syngas (H_2:CO = 1:1, constant pressure). The reaction mixture was allowed to stir at 100 °C for 5 h using a stirrer speed of 1000 rpm. The reaction mixture was filtered through silica and analysed using GC-FID (30 m Zebron ZB1 analytical column with a 0.2 mm internal diameter and 0.5 μm film thickness and He as the carrier gas, with the following temperature programme: 50 °C starting

oven temperature, hold 4 min, 10 °C min^{-1} ramp to 300 °C, total run time 29 min). Products were compared against authentic samples of the product aldehydes.

Pd-Catalysed Hydroformylation of 1-Pentene

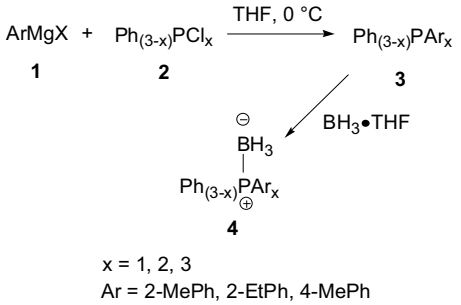
In a glovebox, $Pd(OC(O)CF_3)_2$ (112 mg, 0.337 mmol), 1,3-*bis*(diphenylphosphino)propane.$2BH_3$ (148 mg, 0.337 mmol) [17] and trifluoroacetic acid (282 mg, 2.47 mmol) were dissolved in THF (10 ml). THF (29 ml), 1-pentene (39.0 ml, 25.0 g, 0.356 mol) and the catalyst solution were transferred to the autoclave under inert conditions. The reactor was sealed, pressurised to 5000 kPa with 1:1 H_2/CO, heated to 100 °C and the contents were stirred at 1000 rpm. Readings on the flow meter were initiated after the system had stabilised (approximately 10 min) and the reaction was allowed to proceed for 3 h. The reaction mixture was filtered through silica and analysed as for the Rh-catalysed reactions.

RESULTS AND DISCUSSION

With the exception of triphenylphosphine (obtained from a commercial source), all phosphines used in this study were prepared according to the method of Steube [16], using aryl-Grignard reagents **1** with various P-Cl electrophiles **2** in THF as solvent (Scheme 1). The phosphines **3** (Fig. 1) were borane-protected [5] by treatment thereof with four equivalents of BH_3·THF at 0 °C for several hours, affording the corresponding phosphine-borane complexes **4** in good yields (Table 1).

A diagnostic change in the ^{31}P NMR signals was observed upon phosphine-borane complex formation. The P-B complex afforded a line-broadened doublet resonance with a significant down-field shift (Table 1) *vs*. the higher-field sharp singlet peaks observed for the free phosphines. This shift provides ready proof of complexation. IR spectroscopy using the borane complexes showed a broad absorption peak in the area of 2385 cm^{-1} with a shoulder at about 2350 cm^{-1}, which was indicative of the presence of the borane complexed to the phosphine [5].

The Rh-catalysed hydroformylation reaction of 1-octene (Scheme 2) was performed with the phosphine-borane complexes and their corresponding free phosphine ligands, respectively. The reactions were performed using a catalyst



Scheme 1. Preparation of phosphine-borane complexes

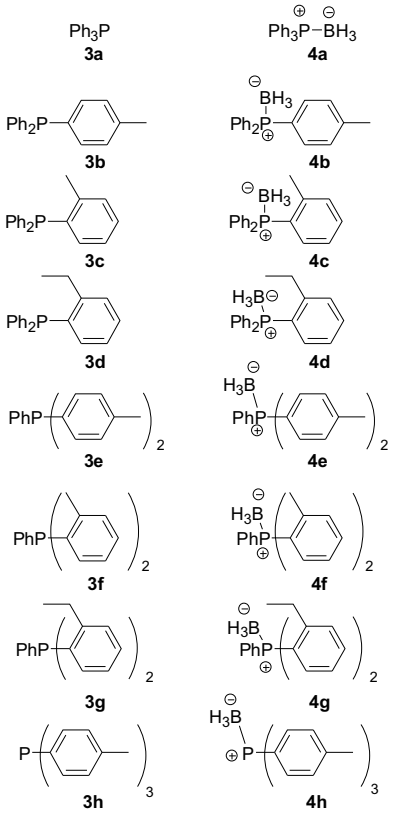


Fig. 1. Phosphines and their corresponding borane complexes.

loading of only 0.0091 mol% (*ca*. 11 000:1 ratio of 1-octene/Rh) and a rhodium to ligand ratio of 1:10. These reactions were intentionally limited to 5 h in order to determine ligand effects, especially on the conversions of the substrate to product. (Higher (quantitative) conversions to aldehyde products are readily attainable using higher

Table 1. Phosphine-Borane Complexes and Their ^{31}P NMR Data

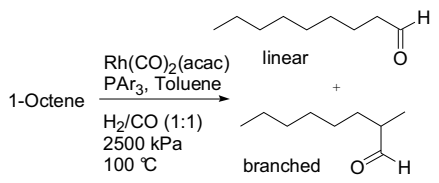
Complex	Yield (%)	^{31}P NMR (ppm)	^{31}P NMR (ppm) free phosphine
4a	100[a]	21.0	-5.1
4b	100	19.9	-5.9
4c	79[a]	21.1	-13.4
4d	71[a]	20.9	-14.8
4e	100[a]	20.1	-6.2
4f	95[b]	21.6	-20.4
4g	70[b]	20.8	-24.2
4h	100[a]	19.5	-7.5

[a]Borane protection performed in THF. [b]Borane protection performed in toluene.

Table 2. Hydroformylation Results with Free Ligands and Phosphine-Borane Complexes

Entry	Ligand	Yield[a] aldehydes	*l*/*b*[a,b]	TOF[c] $\times 10^2$	Entry	P-B complex	Yield[a] aldehydes	*l*/*b*[a,b]	TOF[c] $\times 10^2$
1	**3a**	77	1.7	16.9	9	**4a**	79	1.7	17.4
2	**3b**	60	1.9	13.2	10	**4b**	71	1.9	15.6
3	**3c**	59	1.6	13.0	11	**4c**	95	1.6	13.9
4	**3d**	58	1.5	12.7	12	**4d**	94	1.6	13.2
5	**3e**	58	1.8	12.7	13	**4e**	65	1.5	14.3
6	**3f**	44	1.5	9.7	14	**4f**	42	1.5	9.2
7	**3g**	39	1.4	8.6	15	**4g**	34	1.8	7.5
8	**3h**	54	1.8	11.9	16	**4h**	61	1.4	13.4

[a]Average of four independent experiments with individual yield deviations less than 3% from the average. Selectivity to aldehydes > 98%. Reactions limited to 5 h. [b]*l*/*b* = linear/branched ratio. [c]TOF = turnover frequency in mol product/mol Rh.h.



Scheme 2. Hydroformylation of 1-octene

temperatures, pressures and/or longer reaction times). The resulting reaction mixtures were analysed by GC-FID (Table 2) against authentic samples of the aldehyde products.

The hydroformylation reactions provided similar results (Table 2) for the phosphine-borane and the free phosphine ligand systems in terms of yields and ratios of the aldehydes.

Decreasing turnover frequencies were observed, as a trend, along the series mono-, di- and tri-substituted triarylphosphine free ligands. The phosphine-borane adducts followed a similar

trend. This trend is anticipated [18] for phosphine ligands bearing increasing electron density on the P atom, arising from the positive inductive effects of the alkyl substituents. The electronic effect of alkyl substituents on arylphosphines is readily demonstrated by investigating the CO stretching frequencies of the Rh-Vaska's type complexes of the ligands [19]. The good correlation between the reactions performed with a given ligand and its corresponding borane complex provided convincing indirect evidence that the complexes underwent deprotection under the reaction conditions. What may be further noted from Table 2 is that the linear/branched ratio of aldehyde products remained fairly constant across most of the series, suggesting that the presence of the borane had no significant effect on the alkene co-ordination and hydride migration processes (which determine the ratio of aldehyde products obtained) [20].

The *in situ* deprotection technique was also applied to the borane complex of a bidentate ligand (1,3-*bis*(diphenylphosphino)propane.2BH_3; dppp.2BH_3) [17] in a $Pd(OC(O)CF_3)_2$-catalysed hydroformylation reaction of 1-pentene. The benchmark reactions performed in the presence of the free ligand afforded a linear/branched ratio of aldehyde products of 3.3:1 while those performed with the dppp.2BH_3 provided a ratio of 3.2:1. The turnover frequency of the catalyst system calculated from CO uptake measurements was 450 for the reaction performed with free dppp *vs*. 400 for the reaction with the dppp.2BH_3 complex, showing little difference between the two reactions. Selectivity for aldehyde products was determined to be greater than 98% in all instances, by GC-FID. These two successful outcomes (with Rh and Pd) hint that the *in situ* deprotection protocol is not limited to only one type of ligand/catalyst precursor combination. This method may well hold the potential to simplify a variety of reactions outside of the hydroformylation transformation making use of CO, eliminating one step in the series of events leading up to the catalytic transformation. For example, a supported pyridylphosphine ligand has recently been prepared and applied in the Pd-catalysed alkoxycarbonylation of alkenes [21]. The ligand synthesis involved borane protection/deprotection steps, while the catalysed reaction makes use of CO pressure and the process may therefore benefit from the current approach.

IR spectroscopy was performed in an effort to investigate the reaction between CO and the triphenylphosphine-borane complex. This was carried out by pressurising a solution of triphenylphosphine-borane in toluene in a high pressure Parr reactor fitted with opposing ZnS windows. The solution was subjected to conditions similar to those of the Rh-catalysed hydroformylation reaction detailed above. IR spectroscopy was performed on the mixture at regular intervals. The peak indicative of the phosphine-borane complex at around 2385 cm^{-1} disappeared fully within 45 min, clearly demonstrating the efficiency of the high pressure CO at effecting this *in situ* deprotection step. Additionally, NMR studies in a sapphire high-pressure NMR tube showed an interesting solvent effect. Attempted deprotection reactions under CO pressure (4000 kPa CO, 120 °C) in toluene failed to demonstrate any deprotection at all during the course of one hour. In contrast, those performed in THF (3000 kPa CO, 80 °C) showed 100% deprotection within one hour, but failed to show any deprotection under milder conditions (100 kPa CO, 25 °C). This effect is ascribed to solvent participation in the deprotection reaction in the case of THF. (Ethers have been shown to catalyse the reaction of diborane with Lewis bases-a similar effect may account for the present observations [22]. Indeed, the requirement of performing the borane protection reaction of ligands **3f** and **3g** to form complexes **4f** and **4g** (Table 1) in toluene where reactions in THF were less successful also alludes to solvent participation). Mass transfer of CO into solution is slow in 5 mm NMR tubes given the small surface-to-volume ratio, explaining the differences observed between the high pressure IR reactions performed in a well-stirred Parr reactor vessel and the NMR results in toluene as solvent. While THF is not typically employed as a solvent for hydroformylation reactions, the current observations may prove useful in other carbonylation reactions where THF is more frequently relevant as a solvent.

CONCLUSIONS

A series of triarylphosphine-borane complexes was prepared and employed without prior deprotection in the hydroformylation reaction with results that largely mimicked those obtained with the corresponding free phosphine ligands.

CO used in this reaction as a reagent readily causes deprotection of the phosphine-borane complex, allowing ligand-modified Rh and Pd catalysts to be generated. We show for the first time that mono- and bidentate phosphine-borane complexes can be directly utilised in hydroformylation reactions without the need for an independent deprotection step. Pleasingly and importantly, the outcomes demonstrate that there is no need for the employment of conventional deprotection agents such as amines that produce additional waste and that the putative BH_3.CO complex does not inhibit the reaction in any way. It is highly likely that other carbonylation reactions will benefit from this *in situ* deprotection protocol, an aspect that we are investigating, especially since phosphine-borane complexes are very commonly used as part of the P-atom protection strategy in ligand synthesis.

ACKNOWLEDGEMENTS

We thank Sasol, THRIP and the University of Johannesburg for generous financial support.

Supplementary Data

Supplementary data associated with this article can be found at doi:

^{13}C NMR spectra of all new phosphine-borane complexes.

REFERENCES

[1] F. Wang, W. Schwabacher, J. Org. Chem. 64 (1999) 8922.

[2] B.H. Lipshutz, D.J. Buzard, C.S. Yun, Tetrahedron Lett. 31 (1990) 201.

[3] P. Pellon, Tetrahedron Lett. 33 (1992) 4451.

[4] A.B. Burg, R.I. Wagner, J. Am. Chem. Soc. 75 (1953) 3872.

[5] J.M. Brunel, B. Faure, M. Maffei, Coord. Chem. Rev. 178-180 (1998) 665.

[6] M. Ohff, J. Holz, M. Quirmbach, A. Borner, Synthesis (1998) 1391.

[7] R.C. Moore, S.S. White, H.C. Kelly, Inorg. Synth. 12 (1970) 109.

[8] R.W. Parry, T.C. Bissot, J. Am. Chem. Soc. 78 (1956) 1525.

[9] J. McNulty, Z. Yuehui, Tetrahedron Lett. 45 (2004) 407.

[10] A.H. Cowley, M.C. Damasco, J. Am. Chem. Soc. 93 (1971) 6815.

[11] H. Schmidbaur, J. Organomet. Chem. 200 (1980) 287.

[12] D.B.G. Williams, H. Lombard, M. van Niekerk, P.P. Coetzee, C.W. Holzapfel, Phosphorus, Sulfur and Silicon 177 (2002) 2799

[13] F.A. Cotton, G. Wilkinson, Advanced Inorganic Chemistry, John Wiley and Sons, Brisbane, 1988.

[14] a) H.C. Brown, M.W. Rathke, J. Am. Chem. Soc. 89 (1967) 2738; b) H.C. Brown, T.E. Cole, M. Srebnik, K.-W. Kim, J. Org. Chem. 51 (1987) 4925.

[15] **3a**: commercially available. **3b**: commercially available. **3c**: commercially available. **3d**: S. Vuoti, M. Haukka, J. Pursiainen, J.J. Organomet. Chem. 692 (2007) 5044. **3e**: K. Kikukawa, T. Yamane, Y. Ohbe, Y. Takagi, T. Matsuda, Bull. Chem. Soc. Jpn. 52 (1979) 1187. **3f**: M.A. Bennett, P.A. Longstaff, J. Am. Chem. Soc. 91 (1969) 6266. **3g**: M.A. Moreno, M. Haukka, S. Jaeaeskelaeinen, S. Vuoti, J. Pursiainen, T.A. Pakkanen, J. Organomet. Chem. 690 (2005) 3803. **3h**: M. Nakamura, M. Miki, T. Majima, Perkin Trans. 2 (2000) 1447; dppp.2BH_3: T. Imamoto, T. Oshiki, T. Onozawa, T. Kusumoto, K. Sato, J. Am. Chem. Soc. 112 (1990) 5244.

[16] C. Steube, W.M. LeSeur, G.R. Norman, J. Am. Chem. Soc. 77 (1955) 3526.

[17] **4a**: Commercially available. **4b**: M.K. Das, S. Roy, Synth. React. Metal-Org. Chem. 16 (1986) 67. **4c**: L. Monnier, J.-G. Delcros, B. Carboni, Tetrahedron 56 (2000) 6039.

[18] A. Kamal, M. Naseer, A. Khan, K. Srinivasa Reddy, Y.V.V. Srikanth, T. Krishnaji, Tetrahedron Lett. 48 (2007) 3813.

[19] A. Roodt, S. Otto, G. Steyl, Coord. Chem. Rev. 245 (2003) 121.

[20] S.C. van der Slot, P.C.J. Kamer, P.W.N.M. van Leeuwen, J.A. Iggo, B.T. Heaton, Organometallics 20 (2001) 430.

[21] S. Doherty, J.G. Knight, M. Bentham, Chem. Commun. (2006) 88.

[22] E. Mayer, Monatsh. Chem. 102 (1971) 940.