

Catalytic Hydrogenation of Aryl Phosphines by Niobium Aryloxy Compounds: High Yield and Efficient Synthesis of Cyclohexyl Phosphine Ligands

Joyce S. Yu and Ian P. Rothwell*

Department of Chemistry, 1383 Brown Building, West Lafayette, IN 47907-1393, USA

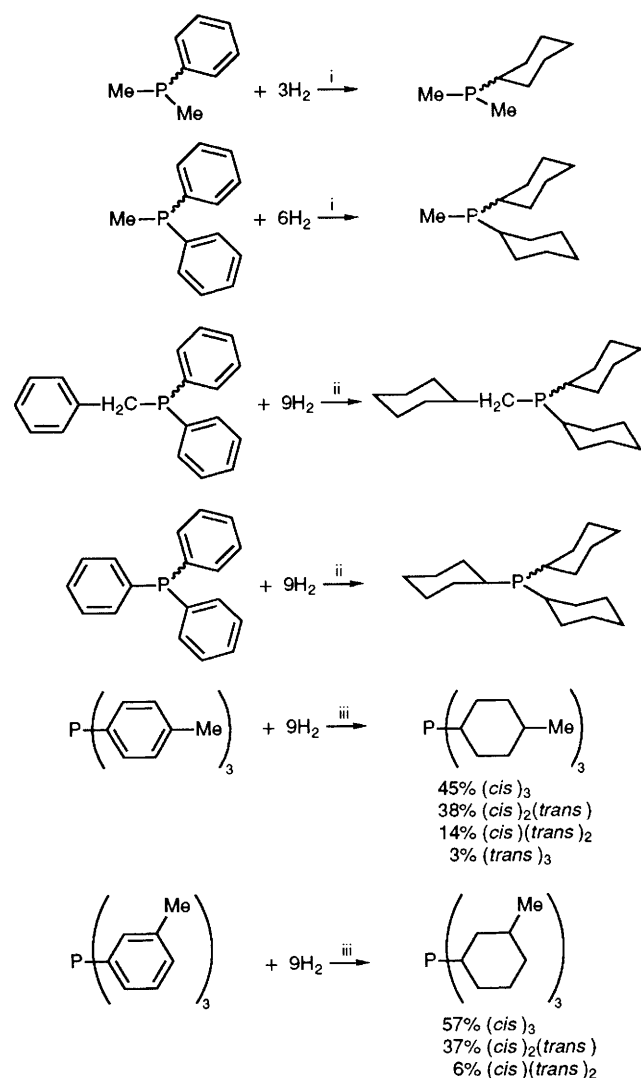
The tris(4-methylbenzyl) compound $\text{Nb}(\text{OC}_6\text{H}_3\text{Ph}_{2-2,6})_2(\text{CH}_2\text{C}_6\text{H}_4\text{-4Me})_3$ **1** ($\text{OC}_6\text{H}_3\text{Ph}_{2-2,6}$ = 2,6-diphenylphenoxide) acts as a catalyst precursor for the hydrogenation of a variety of aryl phosphine ligands.

There has been considerable recent research interest into the chemistry of transition metal complexes containing bi- and tri-dentate phosphine ligands containing electron-donating substituents at phosphorus.¹ We communicate here our development of a new process for the catalytic hydrogenation of aryl phosphines by a niobium aryloxy compound.² The process provides an efficient method for the synthesis of more basic cyclohexyl phosphine ligands from their aromatic counterparts in a one-step reaction.

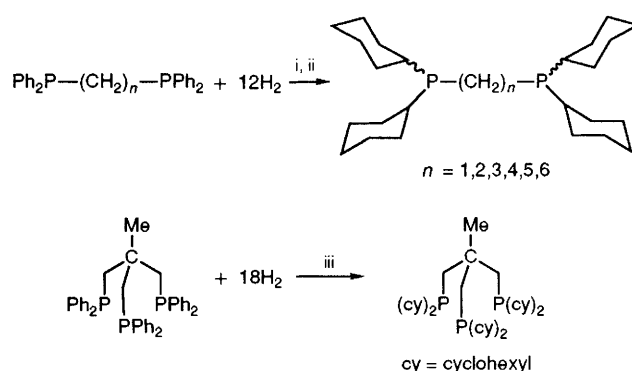
The tris(4-methylbenzyl) compound $\text{Nb}(\text{OC}_6\text{H}_3\text{Ph}_{2-2,6})_2(\text{CH}_2\text{C}_6\text{H}_4\text{-4Me})_3$ **1**³ acts as a catalyst precursor for the hydrogenation of a wide variety of aryl phosphine ligands (Scheme 1). The reactions are carried out in cyclohexane as the solvent at 80–100 °C with hydrogen pressures of 1200 psi

(1 psi = 6.895×10^3 Pa). During the course of the reaction, the three $\text{Nb-CH}_2\text{C}_6\text{H}_4\text{-4Me}$ bonds undergo hydrogenolysis to produce *p*-xylene, while hydrolysis of the final reaction mixture shows that the two 2,6-diphenylphenoxide groups initially bound to niobium, undergo hydrogenation to produce 2,6-dicyclohexylphenoxide ligands.⁴

Hydrogenation of the monodentate phosphine ligands PMe_2Ph , PMePh_2 and PPh_3 proceeds to eventually generate their totally saturated counterparts. Analysis of the reaction mixture by ³¹P NMR spectroscopy at intermediate times failed to detect any cyclohexenyl- or cyclohexadienyl-phosphine compounds. Triphenylphosphine was observed to produce



Scheme 1 Reaction conditions: i compound **1**: 0.1 mmol, substrate: 2 mmol, 80 °C, 24 h, solvent: 3 ml of C_6H_{12} ; ii, compound **1**: 0.1 mmol, substrate: 0.3 mmol, 80 °C, 24 h, solvent: 3 ml of C_6H_{12} ; iii, compound **1**: 0.1 mmol, substrate: 0.3 mmol, 100 °C, 48 h, solvent: 3 ml of C_6H_{12} ; product >99% pure based on ³¹P NMR spectra



Scheme 2 Reaction conditions: i, compound **1**: 0.09 g (0.1 mmol), substrate: 0.3 mmol, 80 °C, 24 h, solvent: 3 ml of C_6H_{12} ; ii, compound **1**: 2.2 g (2.5 mmol), dppm ($n = 1$): 25 g (65 mmol), 100 °C, 96 h, solvent: 55 ml C_6H_{12} , dcpm: 25.5 g (62.4 mmol, 96% isolated yield), compound **1**: 1 g (1.1 mmol), dppb ($n = 4$): 10 g (23 mmol), 80 °C, 48 h, solvent: 15 ml C_6H_{12} , dcpb: 8.9 g (19.3 mmol, 85% isolated yield); iii, compound **1**: 1.5 g (1.6 mmol), substrate: 4.6 g (7.5 mmol), 100 °C, 48 h, solvent: 15 ml of C_6H_{12} ; product: 4.1 g (6.4 mmol, 85% isolated yield)

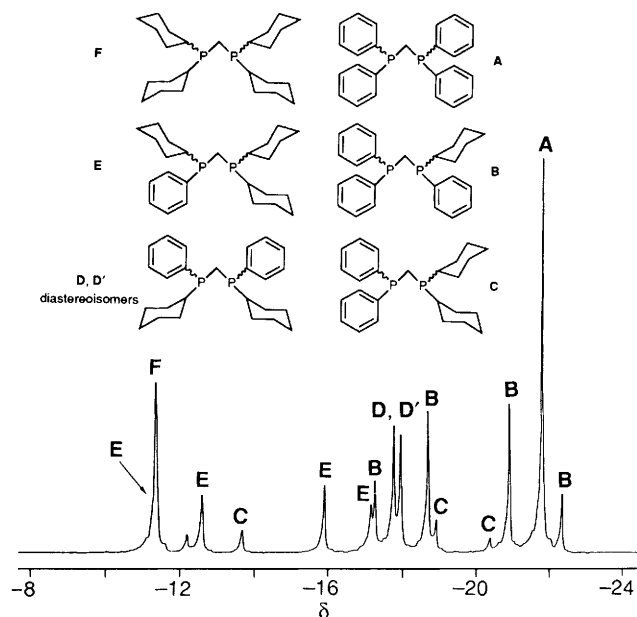


Fig. 1 ³¹P NMR spectra of the mixed cyclohexyl and phenyl phosphine intermediates

$\text{PPh}_2(\text{C}_6\text{H}_{11})$ and $\text{PPh}(\text{C}_6\text{H}_{11})_2$ as the only detectable intermediates. The hydrogenation of the tolyl-phosphine substrates $\text{P}(\text{C}_6\text{H}_4\text{-4Me})_3$ and $\text{P}(\text{C}_6\text{H}_4\text{-3Me})_3$ generated the corresponding tris(methylcyclohexyl) products. Analysis of the ^{31}P NMR spectra of the product mixture indicated the stereochemistry of the resulting rings to be predominantly (but not exclusively) *cis* in both cases (Scheme 1). It is of interest that both the benzyl and phenyl substituents in $(\text{PhCH}_2)\text{PPh}_2$ are hydrogenated (Scheme 1).

The catalyst precursor **1** will also allow hydrogenation of a range of bi- and tri-dentate aryl phosphines (Scheme 2).[†] Within the series $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$ ($n = 1, 2, 3, 4, 5, 6$) the ligand *dppe* [ethylenebis(diphenylphosphine)] ($n = 2$) was found to undergo hydrogenation slower than the rest of the series. This process can be scaled up to produce useful quantities of the corresponding cyclohexyl phosphines in high yield. Hence the ligand bis(dicyclohexylphosphino)methane (*dcpm*) has been obtained in 96% yield (25.5 gm) from bis(diphenylphosphino)methane (25 gm). During the course of this synthesis, all of the mixed cyclohexyl and phenyl phosphine intermediates were identified by ^{31}P NMR spectroscopy (Fig. 1). There has recently been research interest into the chemistry of tridentate phosphine ligands containing cyclohexyl substituents.⁵ The compound 1,1,1-tris(diphenylphosphinomethyl)ethane can be hydrogenated in the presence of **1** to produce 1,1,1-tris(dicyclohexylphosphinomethyl)ethane in 85% yield[†] (Scheme 2). Although the exact nature of the active catalyst in these systems is still under investigation, hydrogenation of **1** in the presence of PMe_3 has led to an isolable tri-hydride, $\text{Nb}(\text{OC}_6\text{H}_3\text{cy}_2\text{-2,6})_2(\text{H})_3(\text{PMe}_3)_2$.⁶

[†] A 300 ml stainless steel high pressure reactor was charged under N_2 at ambient temperature with a solution of $\text{Nb}(\text{OC}_6\text{H}_3\text{Ph}_2\text{-2,6})_2(\text{CH}_2\text{C}_6\text{H}_4\text{-4Me})_3$, **1** (2.2 g, 2.5 mmol) and bis(diphenylphosphino)methane (*dppm*, 25.0 g, 65.1 mmol) in cyclohexane (55 ml). The reactor was initially pressurized with H_2 (1200 psi) and heated at 100 °C for 4 days. During the course of the reaction the pressure dropped and the reactor was re-pressurized four times. After cooling and venting the H_2 gas, the cyclohexane was removed *in vacuo* and H_2O (30 ml) was then added to the mixture. Extraction of the resulting mixture with diethyl ether (4×200 ml) gave a clear colourless solution. Removal of the ether followed by recrystallization of the crude from hot ethanol (120 ml) produced the product *dcpm* as white crystal, yield = 25.5 g (96%). A similar procedure to that used for the synthesis of *dcpm* except using 1.5 g of $\text{Nb}(\text{OC}_6\text{H}_3\text{Ph}_2\text{-2,6})_2(\text{CH}_2\text{C}_6\text{H}_4\text{-4Me})_3$ and 4.6 g of $\text{MeC}(\text{CH}_2\text{PPh}_2)_3$ in 15 ml of cyclohexane allowed the isolation of the white crystalline product, $\text{MeC}(\text{CH}_2\text{Pcy}_2)_3$; yield = 4.1 g (85%).

We thank the National Science Foundation (Grant CHE-8915573) for financial support of this research.

Received, 22nd November 1991; Com. 1/05923H

References

- 1 F. L. Joslin, J. T. Mague and D. M. Roundhill, *Polyhedron*, 1991, **10**, 1713; M. Hackett and G. M. Whitesides, *J. Am. Chem. Soc.*, 1988, **110**, 1449; A. Del Zotto, A. Mezzetti, N. B. Pahor and P. Rigo, A. E. Mezzetti, N. B. Pahor and R. Rigo, *J. Chem. Soc., Dalton Trans.*, 1989, 1045; A. Del Zotto, A. Mezzetti and R. Rigo, *J. Chem. Soc., Dalton Trans.*, 1990, 2515; C. Landis and D. R. Schaad, *J. Am. Chem. Soc.*, 1990, **112**, 1628; C. Krüger and Y.-H. Tsay, *Acta Crystallogr. Sect. B*, 1972, **28**, 1941; C. Krüger and Y.-H. Tsay, *J. Organomet. Chem.*, 1972, **34**, 387; T.-S. Chou, C.-H. Tsao and S.-C. Hung, *J. Org. Chem.*, 1985, **50**, 4329; M. Hackett, J. A. Ibers and G. M. Whitesides, *J. Am. Chem. Soc.*, 1988, **110**, 1436; H. C. Clark and M. J. Hampden-Smith, *J. Am. Chem. Soc.*, 1986, **108**, 3829; G. Ferguson, M. J. Hampden-Smith and B. L. Ruhl, *Acta Crystallogr. Sect. C*, **43**, 788; P. Diversi, G. Ingosso, A. Lucherini, T. Lumini, F. Marchetti, V. Adovasio and M. Nardelli, *J. Chem. Soc., Dalton Trans.*, 1988, 1045; M. D. Fryzuk and W. E. Piers, *Polyhedron*, 1988, **7**, 1001.
- 2 E. L. Muetterties and J. R. Blecke, *Acc. Chem. Res.*, 1979, **12**, 324; J. R. Blecke and E. L. Muetterties, *J. Am. Chem. Soc.*, 1981, **103**, 556 and references cited therein; M. Bennett, *Chemtech* 1980, 444; M. D. Ward and J. Schwartz, *J. Am. Chem. Soc.*, 1981, **103**, 5253; R. Wilczynski, W. A. Fordyce and J. Halpern, *J. Am. Chem. Soc.*, 1987, **109**, 2969; I. Amer, H. Amer, R. Ascher, J. Blum, Y. Sasson and K. C. P. Vollhardt, *J. Mol. Catal.*, 1987, **39**, 189; P. P. Fu, H. M. Lee and R. G. Harvey, *J. Org. Chem.*, 1980, **45**, 2797; M. Yalpani, *Chem. Ber.*, 1990, **123**, 719 and references cited therein; R. A. Grey, G. P. Pez and A. Wallo, *J. Am. Chem. Soc.*, 1980, **102**, 5948; S. R. Stobart and M. J. Zawrotko, *J. Chem. Soc., Chem. Commun.*, 1985, 1700; E. H. Kelle Zeiher, D. G. DeWit and K. G. Caulton, *J. Am. Chem. Soc.*, 1984, **106**, 7006; T. Arliguie, T. B. Chaudret, F. Jalon and F. Lahoz, *J. Chem. Soc., Chem. Commun.*, 1988, 998; B. Chaudret, F. Dahan and X. D. He, *J. Chem. Soc., Chem. Commun.*, 1990, 1111.
- 3 R. W. Chesnut, G. G. Jacob, J. S. Yu, P. E. Fanwick and I. P. Rothwell, *Organometallics*, 1991, **10**, 321.
- 4 B. D. Steffey, R. W. Chesnut, J. L. Kerschner, P. Pellechia, P. E. Fanwick and I. P. Rothwell, *J. Am. Chem. Soc.*, 1989, **111**, 378; B. D. Steffey and I. P. Rothwell, *J. Chem. Soc., Chem. Commun.*, 1990, 213; B. C. Ankaniec, P. E. Fanwick and I. P. Rothwell, *J. Am. Chem. Soc.*, 1991, **113**, 4710; J. S. Yu, B. C. Ankaniec, M. T. Nguyen and I. P. Rothwell, *J. Am. Chem. Soc.*, 1992, **114**, 1927.
- 5 Y. Kim, H. Deng, D. W. Meek and A. Wojcicki, *J. Am. Chem. Soc.*, 1990, **112**, 2798; G. Jia, D. W. Meek and J. C. Gallucci, *Organometallics*, 1990, **9**, 549; Y. Kim, J. C. Gallucci and A. Wojcicki, *J. Am. Chem. Soc.*, 1990, **112**, 8600.
- 6 P. E. Fanwick, personal communication.