

"New Pincer-Type Diphosphinito (POCOP) Complexes of Ni^{II} and Ni^{III}"

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General considerations. Unless otherwise indicated, all manipulations were carried out under nitrogen using standard Schlenk procedures. Solvents were dried over sodium (hexane), sodium/benzophenone (toluene), or CaH₂ (acetonitrile), and then distilled under a nitrogen atmosphere. The reagents ClP(Prⁱ)₂, 4-dimethylaminopyridine (DMAP), CCl₄, and all the alkenes used as substrates in the Kharasch additions were purchased from Aldrich and used without further purification. Bruker ARX400 and AV400rg spectrometers were used for recording NMR spectra of CDCl₃ and C₆D₆ samples at ambient temperature (¹H and ¹H{³¹P} at 400 MHz; ³¹P{¹H} at 161.92 MHz; ¹³C{¹H} at 100.56 MHz). The ¹H, ¹H{³¹P}, and ¹³C{¹H} NMR spectra are referenced to the residual solvent signals, and the chemical shifts are reported in parts per million relative to TMS (7.26 and 77.16 ppm for CDCl₃; 7.16 and 128.06 ppm for C₆D₆). The ³¹P NMR spectra were referenced to an external 85% H₃PO₄ (0 ppm). The elementary analyses were performed by the Laboratoire d'Analyse Élémentaire, Département de chimie, Université de Montréal.

Preparation of ligands and Ni precursors

The pincer ligands {2,6-(OPPrⁱ)₂-C₆H₄}, **A**, and {(PrⁱPOCH₂)₂CH₂}, **B**, were prepared according to the slightly modified version of a literature procedure¹ (hexane was used as extraction solvent instead of toluene). The precursor [NiBr₂(THF)₂] was prepared according to a literature procedure;² following the same procedure, but using NCCH₃ instead of THF, gave [NiBr₂(NCCH₃)₂].³

Syntheses of Complexes.

[{2,6-(OPPrⁱ)₂-C₆H₃}NiBr] (1). Method A. A solution of ligand **A**, (0.5 g, 1.46 mmol) in toluene (20 mL) was slowly added to a stirred suspension of freshly prepared [NiBr₂(THF)₂] (0.636 g, 1.75 mmol) in toluene (20 mL), and the reaction mixture stirred at room temperature for one hour. The resulting residue was filtered (in the air) and the filtrate was evaporated to dryness. The crude product was extracted (in the air) with several portions of hexane and the combined extracts were concentrated to 10 mL. Slow evaporation of this solution gave the pincer complex as large, deep yellow crystals that were covered by oily residues. Rapidly washing the crystals with acetone and hexane, followed by drying under vacuum, gave analytically pure **1**. Yield: 0.561 g (80 %).

Method B. Inside the dry box, a 100 mL Schlenk vessel was charged with freshly prepared [NiBr₂(THF)₂] (0.636 mg, 1.75 mmol), toluene (40 mL), ligand **A** (500 mg, 1.46 mmol), and one equiv. of DMAP. The reaction vessel was taken out of the dry box and the mixture was heated to ca. 60 °C under nitrogen for one hour. Cooling to room temperature and filtration of the reaction mixture (in the air) gave a yellow-orange filtrate that was evaporated to dryness. The crude product was extracted with several portions of hexane and the combined extracts were evaporated to dryness. Analytically pure **1** was obtained as a deep yellow crystalline solid. Yield: 0.666 g (95 %). (Found: C, 45.2; H, 6.2. C₁₈H₃₁BrO₂P₂Ni requires C, 45.0 H, 6.5%). δ_H(400 MHz; CDCl₃; Me₄Si): 1.33 (12 H, dt, J_{HH} 7.0 and J^ν_{HP} 7.1, 4 x CH₃), 1.43 (12 H, dt, J_{HH} 7.1 and J^ν_{HP} 7.6, 4 x CH₃), 2.46 (4 H, m, J ~ 7, 4 x PCH(CH₃)₂), 6.42 (2 H, d, J_{HH} 8.0, ArH), 6.96 (1 H, t, J_{HH} 8.0, ArH); δ_H{³¹P}(400 MHz; CDCl₃; Me₄Si): 1.33 (12 H, d, J_{HH} 7.0, 4 x CH₃), 1.43 (12 H, d, J_{HH} 7.1, 4 x CH₃), 2.46 (4 H, m, J ~ 7, 4 x PCH(CH₃)₂), 6.42 (2 H, d, J_{HH} 8.0, ArH), 6.96 (1 H, t, J_{HH} 8.0, ArH); δ_C(400 MHz; CDCl₃; Me₄Si): 16.86 (4 C, s, 2 x PCH(CH₃)₂), 17.92 (4 C, s, 2 x PCH(CH₃)₂), 28.14 (4 C, vt, ^νJ_{PC} 11.4, 4 x PCH(CH₃)₂), 105.23 (1 C, vt, ^νJ_{PC} 6.2, ArC), 127.9 (1 C, vt, ^νJ_{PC} 20.8, ArC), 128.85 (1 C, s, ArC), 168.84 (1C, vt, ^νJ_{PC} 10.0, ArC); δ_P(400 MHz; CDCl₃; 85% H₃PO₄): 188.2 (s).

[{(Prⁱ)₂POCH₂]₂CH}NiBr] (2). To a stirred mixture of ligand **B** (0.5 g, 1.62 mmol, 1 equiv.) and freshly prepared [NiBr₂(NCCH₃)₂] (1.28 g, 3.24 mmol, 2 equiv.) in toluene (40 mL), was added one equiv. of DMAP. The mixture was heated to reflux under nitrogen for ca. 5 h, and then cooled to room temperature. The resulting mixture was

filtered (in the air) and the filtrate evaporated to dryness to give a crude product, which was extracted with several portions of hexane and the combined extracts were evaporated to dryness. Analytically pure **2** was obtained as a deep yellow crystalline solid. Yield 0.672 g (93 %). (Found: C, 40.4; H, 7.4. $C_{15}H_{33}BrO_2P_2Ni$ requires C, 40.4; H, 7.4 %). δ_H (400 MHz; C_6D_6 ; Me_4Si): 1.16 (6 H, dt^v, J_{HH} 6.9 and J_{HP}^N 6.8, 2 x CH_3), 1.23 (6 H, dt^v, J_{HH} 6.8 and J_{HP}^N 7.0, 2 x CH_3), 1.40 (6 H, dt^v, J_{HH} 7.0 and J_{HP}^N 7.6, 2 x CH_3), 1.50 (6 H, dt^v, J_{HH} 7.0 and J_{HP}^N 7.7, 2 x CH_3), 2.06 (2 H, bs, 2 x $PCH(CH_3)_2$), 2.31 (2 H, m, $J_{HH} \sim 7.1$, 2 x $PCH(CH_3)_2$), 2.83-2.92 (1 H, m, CH_2CHCH_2), 3.24 (2 H, dd, J_{HP} 11.6 and J_{HH} 9.5, CH_2CHCH_2), 3.41-3.54 (2 H, m, CH_2CHCH_2); $\delta_H\{^{31}P\}$ (400 MHz; C_6D_6 ; Me_4Si): 1.16 (6 H, d, J_{HH} 6.9, 2 x CH_3), 1.23 (6 H, d, J_{HH} 6.8, 2 x CH_3), 1.40 (6 H, d, J_{HH} 7, 2 x CH_3), 1.50 (6 H, d, J_{HH} 7.0, 2 x CH_3), 2.06 (2 H, m, $J \sim 7.0$, 2 x $PCH(CH_3)_2$), 2.31 (2 H, m, $J \sim 7.1$, 2 x $PCH(CH_3)_2$), 2.83-2.92 (1 H, m, CH_2CHCH_2), 3.24 (2 H, dd, J_{HP} 11.6 and J_{HH} 9.5, CH_2CHCH_2), 3.46-3.50 (2 H, m, CH_2CHCH_2); δ_C (400 MHz; C_6D_6 ; Me_4Si): 16.29 (2 C, s, 2 x CH_3), 17.16 (2 C, s, 2 x CH_3), 18.20 (2 C, s, 2 x CH_3), 18.87 (2 C, s, 2 x CH_3), 28.26 (2 C, vt, J_{PC} 13.2, 2 x $PCH(CH_3)_2$), 29.03 (2 C, vt, J_{PC} 11.1, 2 x $PCH(CH_3)_2$), 54.78 (1 C, vt, J_{PC} 11.1, CH_2CHCH_2), 75.97 (2 C, vt, J_{PC} 7.3, CH_2CHCH_2); δ_P (400 MHz; C_6D_6 ; 85% H_3PO_4): 186.33 (s).

[$\{(Pr^i_2POCH_2)_2CH\}NiBr_2$] (**3**). $CuBr_2$ (0.37 g, 1.681 mmol) was added to a solution of **2** (0.5 g, 1.121mmol) in a hexane/acetone mixture (30:5 mL; both solvents non-distilled). Stirring at room temperature and in the air caused an immediate colour change (yellow to red). The mixture was filtered (in the air) after 15 min of stirring, and the filtrate evaporated to dryness. Analytically pure **3** was obtained as a dark-red crystalline solid. Yield 0.562 g (95 %). (Found: C, 33.9; H, 5.9. $C_{15}H_{33}Br_2O_2P_2Ni$ requires C, 34.2; H, 6.3 %).

General procedure for Kharasch additions. For the large-scale reactions, a 25 mL two-necked round bottom flask equipped with a condenser and a rubber septum was charged with the desired mass of complex **3** to give a **3**: CCl_4 :olefin ratio of 1:1000:250 (for methyl acrylate, acrolein, acrylonitrile) or 1:4000:1000 (for styrene, 4-methyl styrene, methyl methacrylate). The reaction vessel was then purged with nitrogen for 15 min and

charged with dry, air-free acetonitrile (14 mL) and deoxygenated CCl₄ (12 mL) and olefin (3 mL). The reaction mixture was heated to reflux for 24 h under nitrogen. The final mixture was then evaporated to dryness (in the air) and purified by flash chromatography using hexane (acrylonitrile, methyl methacrylate, styrene, and 4-methylstyrene) or a 50:50 mixture of hexane and acetone (acrolein) as eluent. The reaction products were characterized by GC/MS and ¹H NMR. Smaller-scale reactions were carried out using 25% of the above quantities for all components. The yields of the styrene and methyl methacrylate runs were determined by direct isolation of the products and by GC/MS using a calibration curve based on *p*-Xylene as internal standard. For the other reactions, the yields were determined by direct isolation of the products, as indicated above.

Cyclic Voltammetry. Electrochemical measurements were performed on a three-electrode Epsilon potentiostat with platinum working and auxiliary electrodes. Electrochemical studies were made using 0.001 M solutions of **1** and **2** in a 0.1 M acetone solution of the supporting electrolyte Bu₄NPF₆. The potentials were referenced to an Ag/AgCl (0.1 mol dm⁻³ NaCl) reference electrode. Cyclic voltammetry measurements were performed in the potential range of 0 to 1.8 V using a scan rate of 0.2 V s⁻¹. Under these conditions, E_{1/2} for the FeCp₂⁺/FeCp₂ couple was 0.54 V.

Crystallographic data. The crystallographic data for all complexes were collected on Bruker AXS Smart 2K diffractometer using SMART.⁴ Graphite monochromatic Cu K_α radiation (λ=1.54178) was used at 100 K for **1** and **2** and 200 K for **3**. Cell refinement and data reduction were done using SAINT.⁵ All structures were solved by direct methods and refined by full-matrix least square and difference Fourier techniques using SHELXS-97⁶ and difmap synthesis using SHELXL97;⁷ the refinements were done on F² by full-matrix least squares. All non-hydrogen atoms were refined anisotropically while the hydrogen atoms (isotropic) were constrained to the parent atom using a riding model.

The crystal data and refinement parameters are presented in Table 1 while selected bond distances and angles are presented in Table 2. The complete crystallographic data

have also been deposited at the Cambridge Crystallographic Data Centre [deposition numbers are CCDC 620341 (1), CCDC 620342 (2), CCDC 620343 (3)].

Table1. Crystal Data Collection and Refinement Parameters for Complexes: 1, 2 and 3.

	1	2	3
Chemical formula	C ₁₈ H ₃₁ BrNiP ₂ O ₂	C ₁₅ H ₃₃ BrNiP ₂ O ₂	C ₁₅ H ₃₃ Br ₂ NiP ₂ O ₂
Fw	479.99	445.97	525.88
<i>T</i> (K)	100(2)	100(2)	200(2)
wavelength (Å)	1.542	1.542	1.542
space group	P-1	P2(1)2(1)2(1)	C2/c
<i>a</i> (Å)	12.9840(3)	8.7081(1)	34.4889(8)
<i>b</i> (Å)	13.0363(3)	13.9372(2)	7.0423(2)
<i>c</i> (Å)	13.4366(3)	17.1214(2)	22.1302(5)
α (deg)	78.494(2)	90	90
β (deg)	77.305(1)	90	127.664(1)
γ (deg)	88.467(2)	90	90
<i>Z</i>	4	4	8
<i>V</i> (Å ³)	2173.79(9)	2077.97(5)	4254.90(2)
ρ_{calc} (g cm ⁻³)	1.467	1.426	1.642
(cm ⁻¹)	48.89	50.62	71.63
θ range (deg)	3.44 to 72.61	2.58 to 72.86	3.24 to 68.9
R1 ^a [<i>I</i> > 2 σ (<i>I</i>)]	0.0358	0.0298	0.0520
wR2 ^b [<i>I</i> > 2 σ (<i>I</i>)]	0.0840	0.0698	0.1735
R1 [all data]	0.0482	0.0322	0.0546

$$^a R1 = \frac{\sum(|F_o| - |F_c|)}{\sum F_o} \quad ^b wR2 = \left\{ \frac{\sum [w(F_o^2 - F_c^2)^2]}{\sum [w(F_o^2)^2]} \right\}^{1/2}$$

Table 2. Selected Bond Distances (Å) and Angles (°) for Complexes 1, 2, and 3 and (PC_{sp3}P)NiBr⁸

	1	2	(PC _{sp3} P)NiBr	3
Ni – C2	1.885(3)	1.964(3)	1.971(4)	2.011(5)
Ni – P1	2.1534(8)	2.1574(8)	2.2182(1)	2.235(1)
Ni – P2	2.1422(8)	2.1527(8)	2.2123(1)	2.251(1)
Ni – Br1	2.3231(5)	2.3458(5)	2.3866(7)	2.3683(9)
Ni – Br2	-	-	-	2.436(1)
C2-Ni-Br1	178.10(8)	176.29(14)	169.89(13)	157.09(15)
P1-Ni-P2	164.92(4)	166.50(3)	170.16(5)	160.57(6)

References

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- ² A.L. Casalnuovo, T.V. RajanBabu, T.A. Ayers and T.H. Warren, *J. Am. Chem. Soc.* 1994, **116**, 9869.
- ³ The elementary analysis of this complex shows the presence of two solvent molecules. (Found: C, 15.6; H, 1.8; N, 8.9. Requires for C₄H₆Br₂Ni₁ C, 15.9; H, 2.0; N, 9.3).
- ⁴ SMART, Release 5.059; Bruker Molecular Analysis Research Tool, Bruker AXS Inc.: Madison, WI 53719-1173, 1999.
- ⁵ SAINT, Release 6.06; Integration Software for Single Crystal Data. Bruker AXS Inc.: Madison, WI 53719-1173, 1999.
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