COPPER(I)-CATALYZED SYNTHESIS OF UNSYMMETRICAL TRIPHENYLPHOSPHINES

Derek Van Allen and D. Venkataraman*

Department of Chemistry, University of Massachusetts, 710 N. Pleasant Street, Amherst, MA 01003.

Contents:

1. General information	S1
2. Synthesis of Tris(triphenylphosphine)copper(I) bromide	S2
3. Synthesis of [Cu(neocup)(PPh ₃)Br].....	S2
4. Synthesis of [Cu(phen)(PPh ₃)Br].....	S3
5. Synthesis of [Cu(neocup) ₂ Br · H ₂ O].....	S3

General Information:

All of the reactions reported herein were conducted under an inert atmosphere of argon in oven-dried glassware. All reagents and solvents were obtained from commercial sources and were used without further purification. Cesium Carbonate was stored in an argon filled glove box. Purification was performed by flash chromatography using Silica Gel, 230-400 mesh. The yields given refer to isolated yields of the characterized compounds, deemed pure by elemental analyses, ¹H NMR, ¹³C NMR, and ³¹P NMR spectra were recorded on a 300 MHz, spectrometer. Chemical shifts were reported in parts per million (δ). The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; dd, doublet of doublets; dt, doublet of triplets; and m, multiplet. The coupling constants, J, are reported in Hertz (Hz). TMS was used as the internal reference for ¹H and ¹³C NMR. Phosphoric acid was used as an external standard for ³¹P NMR. Elemental analyses were performed at the University of Massachusetts at Amherst. The reported melting points were corrected using benzoic acid as a standard. X-ray data were collected using a CCD diffractometer with MoKα (λ=0.71073 Å) as the incident radiation. Diffraction data were collected at ambient temperature. The raw data were integrated, refined, scaled and corrected for Lorentz polarization and absorption effects. Structures solutions and refinements were done (on Fo2). All structures were checked for any missing symmetry. The Gas Chromatograph employed a 30-meter, 100% dimethylpolysiloxane capillary column.

Synthesis of Copper(I) Complexes:

Tris(triphenylphosphine)copper(I) bromide: In an Erlenmeyer flask equipped with a Teflon-coated stir bar, methanol (100 mL) was heated to boiling and triphenylphosphine (Alfa Aesar, 24.22 g, 92.34 mmol) was slowly added to the stirring methanol. After the complete dissolution of triphenylphosphine, CuBr_2 (Acros, 5.15 g, 23.09 mmol) was added in small portions. No special precautions were taken for the exclusion of air. Upon addition of the copper(II) bromide, a white precipitate formed. After the completion of the addition, the contents were stirred for 30 minutes and the flask was allowed to cool to ambient temperature. The reaction mixture was then filtered through a Buchner funnel and the white residue was washed repeatedly with ethanol and then with diethyl ether. The resultant white solid was dried under dynamic vacuum to give $\text{Cu}(\text{PPh}_3)_3\text{Br}$ (20.03 g, 93% yield). m.p. – 164-166 °C. The cell constants, contents and the space group are identical to that of the already reported structure of $\text{Cu}(\text{PPh}_3)_3\text{Br}$ (Cambridge Structural Database Refcode-FEYVAG).

[Cu(neocup)(PPh₃)Br]: In an Erlenmeyer flask equipped with a Teflon-coated magnetic stir bar, tris(triphenylphosphine)copper(I) bromide (2.61 g, 2.73 mmol) was added to chloroform (50 mL). After complete dissolution, neocuproine (2,9-dimethyl-1,10-phenanthroline (575 mg, 2.76 mmol) was then added. The colorless solution immediately turned yellow-orange. The contents of the flask were allowed to stir for 30 minutes at room temperature. Afterwards the solvent was removed *in vacuo* to afford a yellow solid. Recrystallization was achieved by layering 80 mL of diethyl ether onto a solution of the solid dissolved in 40 mL of dichloromethane (1.02 g, 61% yield). m.p. – 286-288 °C. The cell constants, contents and the space group are identical to that of the already reported structure of $\text{Cu}(\text{neocup})(\text{PPh}_3)\text{Br}$.¹

[Cu(phen)(PPh₃)Br]: In an Erlenmeyer flask equipped with a Teflon-coated magnetic stir bar, tris(triphenylphosphine)copper(I) bromide (1.40 g, 1.50 mmol) was added to chloroform (50 mL). After complete dissolution, 1,10-phenanthroline (856 mg, 1.50 mmol) was then added. The colorless solution immediately turned orange. The contents of the flask were allowed to stir for 30 minutes at room temperature. Afterwards the solvent was removed *in vacuo* to afford an orange solid. Recrystallization was achieved by layering 40 mL of diethyl ether onto a solution of the solid dissolved in 20 mL of dichloromethane (931 mg, 75% yield). m.p. – 252-253 °C. The cell constants, contents and the space group are identical to that of the already reported structure of Cu(phen)(PPh₃)Br (Cambridge Structural Database Refcode-BEQLAK).

[Cu(neocup)₂Br · H₂O]:² A solution of CuBr₂ (0.456g, 2.04 mmol) in minimal ethanol was added slowly to a stirring solution of neocuproine (1.738g, 8.00 mmol) in minimal ethanol. The solution was stirred at room temperature for 1 hour and became light green with a green precipitate. Afterwards the solvent was removed *in vacuo* and the residue was diluted with 150 mL distilled water. The solution was then boiled in an Erlenmeyer flask, during which time the solution became red. Upon cooling red crystals formed (1.06g, 90% yield). The cell constants, contents and the space group are identical to that of the already reported structure of Cu(neocup)₂Br·H₂O (Cambridge Structural Database Refcode-DAWKOB).

References:

- (1) Gujadhur, R.; Bates, C.; Venkataraman, D. *Org. Lett.* **2001**, *3*, 4315-4317.
- (2) Hall, J. R.; Marchant, N. K.; Plowman, R. A. *Aust. J. Chem.* **1962**, *15*, 480-485.