

III. EXPERIMENTAL

Materials. Rhodium trichloride hydrate was purchased from Aldrich. The solvents used were purchased, purified by distillation, and degassed with argon before use.

Physical Measurements. ^{31}P NMR spectra were recorded on either a Bruker AC 250 spectrometer operating at a frequency of 101 MHz or on a Bruker AM 400 multinuclear spectrometer operating at 162 MHz. The external standard for ^{31}P spectra was 85% H_3PO_4 . Chemical shifts (δ) were reported in parts per million (ppm) with peaks downfield of the standard given positive values. Coupling constants were reported in Hz. Electrospray mass spectra were recorded on a VT Trio 2000 quadrupole mass spectrometer with a 100% methylene chloride mobile phase. A syringe pump was used to control the flow rate of the mobile phase.

Preparation of the Bis-phosphine Ligands

All the bisphosphine ligands are white solids which are slightly air sensitive; however, handling in air for short periods of time presents no problems.

DPPO was prepared as previously described.¹ The DPPB, DPPD, and DPPDOD were prepared as previously described.²

Preparation of Rhodium(I) Starting Materials

Preparation of Di- μ -chloro-bis[cycloocta-1,5-diene rhodium(I)]³

A 500 ml three-necked flask was fitted with a reflux condenser, nitrogen inlet, nitrogen outlet and magnetic stirrer. The flask was flushed with N₂ or Ar and 4.795 g (1.7 x 10⁻² mol) of RhCl₃·3H₂O added. The rhodium trichloride trihydrate was dissolved by the addition of 9 ml of deoxygenated water to yield a dark red/black solution. Cycloocta-1,5-diene (10 ml, an excess) and 120 ml of ethanol were added and the reaction mixture refluxed for 18 hours in an oil bath. After approximately 45 minutes an orange solid could be seen in the reaction mixture.

After cooling, the mixture was filtered through a Buchner funnel to yield the desired orange product. The solid washed with hexane and dried in vacuo. (90% yield).
¹H NMR (CDCl₃) 4.4 ppm (δ CH=CH, 4H), 2.5 ppm (δ CH₂, 4H) and 1.8 ppm (δ CH₂, 4H).

Preparation of Bis(acetonitrile)cycloocta-1,5-diene Rhodium(I) Tetrafluoroborate

A 50 ml round-bottomed flask with a side arm and magnetic stirrer was charged with 0.453 g (1.84×10^{-3} mol/Rh) of $[\text{Rh}(\text{COD})\text{Cl}]_2$. The orange solid was dissolved under argon in 20 ml of methylene chloride. Excess acetonitrile (3 ml) was added, followed by 0.3574 g (1.83×10^{-3} mol) of AgBF_4 in 3 ml of methanol. An immediate precipitate of silver chloride formed. The slurry was stirred for 30 minutes and AgCl removed by vacuum filtration to leave a yellow solution. This was added dropwise to diethyl ether under argon to yield a yellow precipitate. After 4 hours, the mixture was filtered and washed with three portions of diethyl ether. (85% yield)

Preparation of Rhodium Complexes

Preparation of *in situ* Cis-Cycloocta-1,5-diene-bis(phosphine) Rhodium(I) Tetrafluoroborate Complexes

A two-dram vial was charged with 0.0114 g (3×10^{-5} mol) of $[\text{Rh}(\text{COD})(\text{CH}_3\text{CN})_2]\text{BF}_4$ and an equimolar amount of the appropriate bis-phosphine. The vial was then fitted with a septum and flushed with argon for 10 minutes. 3 ml of methylene chloride were added and the vial swirled. A clear yellow solution (10^{-2} M) resulted which was used for the ^{31}P NMR studies.

For the ESMS samples a second vial was fitted with a septum and flushed with argon for 10 minutes. 1 ml of the above solution was then injected along with 9 ml of methylene chloride to create a 10^{-3} M solution.

Preparation of Alkyliminodiacetic Acids

Preparation of Dodecyliminodiacetic Acid⁴

A 250 ml Erlenmeyer flask was charged with 24 g (2.55×10^{-1} mol) of chlorothioacetic acid in 100 ml of ethanol and 10 ml of H₂O. This was neutralized to phenolphthalein with 10 N NaOH and 12 g (6.48×10^{-2} mol) of dodecylamine was added. 30 ml of 10 N NaOH was added slowly over the next three days, heating for the last 5 hours to 80-95° C. While heating everything dissolved and the solution became clear. Upon cooling the white product reappeared. The product was dissolved in ethanol and concentrated HCl added until the solution became acidic to blue litmus. The acidic form is insoluble and settled out leaving a clear solution. The product was filtered and washed with hexane to collect.

Preparation of Octadecyliminodiacetic Acid

A 250 ml Erlenmeyer flask was charged with 24 g (2.55×10^{-1} mol) of chlorothioacetic acid in 100 ml ethanol and 10 ml water. The acid was neutralized to phenolphthalein with 10 N NaOH before adding 33.69 g (1.25×10^{-1} mol) of octadecylamine. 30 ml of 10 N NaOH was added over the next 3 days, heating to 80-95° C for the final 5 hours of addition. The white product was recrystallized from boiling hot ethanol and collected via suction filtration.

Preparation of Dodecyliminodimethylacetate

A 250 ml Erlenmeyer flask was charged with 1.505 g (5.00×10^{-3} mol) of dodecyliminodiacetic acid, 2.295 g (1.2×10^{-2} mol) of triisopropanolamine, and 1.1 ml (1.2×10^{-2} mol) of dimethyl sulfate. 50 ml of acetone was added. The solution was heated uncovered over a steam bath until dissolved. The mixture was cooled to room temperature, then 0.5 ml of water and 1 ml of concentrated HCl were added to obtain the product as an oil.

Preparation of Arsenic-Containing Ligands

Reaction of 1,6-dibromohexane and Triphenylarsine

A 25 ml round-bottomed flask was charged with 1.0024 g of triphenylarsine and 5 ml of 1,6-dibromohexane and stirred. The mixture was heated gently with heating mantle but no product was obtained. To this was added 10 ml of DMF as a solvent and the mixture was heated to 70° C, still without result.

Preparation of Triphenyl(propyl)arsonium Iodide

To a 100 ml round-bottomed flask was added 1.0 g (3.3×10^{-3} mol) of triphenylarsine and 10 ml (1.0×10^{-1} mol) of 1-iodopropane in excess. The mixture was heated on a heating mantle to reflux at 110° C for 24 hours then 40 ml of diethyl ether was added. The yellow liquid was filtered and an impure white solid was collected.

Attempted Base Hydrolysis of Triphenylarsine

A 100 ml round-bottomed flask was charged with 1.0 g (3.3×10^{-3} mol) of triphenylarsine and 25 ml of 20% NaOH and heated overnight. The mixture was cooled and filtered; unreacted triphenylarsine was recovered.

Preparation of 1-diphenylarsino-3-triphenylphosphoniumpropyl Iodide

A 250 ml 3-neck round bottomed flask was charged with 100 ml of dry THF and 2 g (6.5×10^{-3} mol) of triphenylarsine. Li wire (0.0455 g, 6.5×10^{-3} mol) was added after pounding flat and dipping first in ethanol then dry THF to clean the surface (slight excess of lithium used to account for that lost during this process). The solution was refluxed for several hours until it turned dark red. After cooling to room temperature, 0.601 g (6.5×10^{-3} mol) of t-butyl chloride was added to kill off the lithium phenide byproduct. Next, 0.754 g (6.5×10^{-3} mol) of tetramethylethylenediamine (TMEDA) was added. The solution was cooled to 0° C on ice bath and 3.63 g (6.5×10^{-3} mol) of $[\text{Ph}_3\text{P}(\text{CH}_2)_3\text{I}]\text{I}$ was added in portions over 20 minutes. A few ml of water was added to kill off unreacted lithium, then the solvent was removed on a rotovap. The remaining solid was finally washed with methylene chloride and filtered to recover the white solid product.

Reaction of 1,4-bis(triphenylphosphonium) Iodide and Lithium Diphenylarsenide with TMEDA

A 250 ml 3-neck round-bottomed flask was charged with 100 ml of dry THF and 0.50 g (1.8×10^{-3} mol) of triphenylarsine. Li wire (0.012g, 1.8×10^{-3} mol) was added after pounding flat and dipping first in ethanol then dry THF to clean the surface (slight

excess of lithium used to account for that lost during this process). The solution was then refluxed for several hours until it turned dark red. After cooling to room temperature, 0.17 g (1.8×10^{-3} mol) of t-butyl chloride was added to kill off the lithium phenide byproduct. Next, 0.21 g (1.8×10^{-3} mol) of tetramethylethylenediamine (TMEDA) was added. The solution was cooled to 0° C on ice bath and 0.5 g (6.0×10^{-4} mol) of $[\text{Ph}_3\text{P}(\text{CH}_2)_4\text{PPh}_3]\text{I}_2$ was added in portions over 20 minutes. A few ml of water was added to kill off unreacted lithium, then the solution was filtered to recover the white-brown solid product.

Reaction of 1,4-Bis{diphenyl(3-triphenylphosphoniumpropyl)phosphonium}butane Iodide and Lithium Diphenylarsenide with TMEDA

A 250 ml 3-neck round-bottomed flask was charged with 50 ml of dry THF and 0.20 g (6.4×10^{-4} mol) of triphenylarsine. Li wire (0.0045 g, 6.4×10^{-4} mol) was added after pounding flat and dipping first in ethanol then dry THF to clean the surface (slight excess of lithium used to account for that lost during this process). The solution was refluxed for several hours until it turned dark red. The solution was cooled to room temperature and 0.060 g (6.4×10^{-3} mol) of t-butyl chloride was added to kill off the lithium phenide byproduct. Next, 0.075 g (6.4×10^{-3} mol) tetramethylethylenediamine (TMEDA) was added. After cooling the solution to 0° C on ice bath, 0.5 g (3.2×10^{-4} mol) of $[\text{Ph}_3\text{P}(\text{CH}_2)_3\text{PPh}_2(\text{CH}_2)_4\text{PPh}_2(\text{CH}_2)_3\text{PPh}_3]\text{I}_4$ was added in portions over 20 minutes. A few ml of water was added to kill off the unreacted lithium, then the solution was filtered to recover the white solid product.

References

1. Sekabunga, E.J., Ph.D. Dissertation, Auburn University, **1997**, 218.
2. Al-Baker, S., Ph.D. Dissertation, Auburn University, **1986**, 140-142.
3. Maier, L., *Prog. Inorg. Chem.*, **1963**, 5, 120.
4. Stein, A., Gregor, H.P., Spoerri, P.E., *J. Am. Chem. Soc.*, 77, **1955**, 191.