

Comparative Study of 1,1'-Bis(diphenylphosphino)cobaltocenium Hexafluorophosphate and 1,1'-Bis(diphenylphosphino)ferrocene as Bidentate Ligands

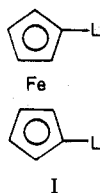
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The title compounds have been prepared and studied as bidentate phosphine ligands complexed to the group 6 carbonyls and several first-row transition-metal halides. The ferrocene ligand behaves much like standard aromatic phosphines such as bis(diphenylphosphino)ethane. In contrast the cationic cobaltocenium ligand requires new synthetic approaches to prepare some transition-metal halide complexes and, in the metal carbonyl complexes, results in a shift of the carbonyl stretching frequencies to higher wavenumbers.

Introduction

Nearly a decade has passed since the initial syntheses of the ferrocenyl-1,1'-bis(phosphines) and -(arsines)¹ (I). Although



I
L = PMe₂, PPh₂, AsMe₂, AsPh₂

there has been an extensive report on the syntheses and characterizations of transition-metal complexes of 1,1'-bis(diphenylarsino)ferrocene, fdpa, and 1,1'-bis(dimethylarsino)ferrocene,^{2,3} to date there has been very little reported on the ligand behavior of the phosphine analogues.⁴

The cobaltocenium cation, as a stable 18-electron metallocene, is an excellent candidate to extend the study of symmetrically disubstituted metallocene chelating ligands and provides a unique opportunity to study the effects of a positive charge on the ability of the ligand to form transition-metal complexes. It was also hoped that the readily reduced cobaltocenium fragment would increase the π -acid strength of the ligand and might produce interesting M \rightarrow Co charge-transfer complexes.

This article describes the preparation of the cationic diphosphine ligand 1,1'-bis(diphenylphosphino)cobaltocenium hexafluorophosphate, [cdpp]PF₆, from cyclopentadienyldiphenylphosphine⁵ and cobalt(II) chloride. Also described are the syntheses of several transition-metal complexes of [cdpp]PF₆ and some previously unreported transition-metal complexes of the ferrocene analogue 1,1'-bis(diphenylphosphino)ferrocene,⁶ fdpp. Of particular interest is the complex resulting from the reaction of [cdpp]PF₆ with copper(I) which yields the dark purple complex Cu(cdpp)Cl₂. This material displays a field-dependent paramagnetism indicative of an electron-transfer process between the cobaltocenium ligand and the copper ion in the complex.

Experimental Section

General Procedures and Starting Materials. With the exception of the reactions of fdpp with the transition-metal halides, all reactions were performed under an atmosphere of prepurified nitrogen using a drybox or standard Schlenk techniques. All products except the group 5 carbonyl metalates are air stable and can be isolated and recrystallized in air. However, as a precaution, the final recrystallizations, column chromatography, and Soxhlet extractions were routinely performed under a nitrogen atmosphere.

Reactions involving the group 5 metal carbonyl anions were performed under an atmosphere of prepurified nitrogen which was further purified by passage through a column of activated copper catalyst. The photolyses were conducted using a Hanovia lamp with a borosilicate reaction vessel equipped with a water-cooled quartz immersion well and two side arms.

Tetrahydrofuran (THF), diethyl ether, and hydrocarbons were distilled under nitrogen from sodium benzophenone ketyl. Diglyme was vacuum distilled from sodium benzophenone ketyl (15 mmHg, 85 °C) and dioxane was distilled under nitrogen from molten sodium metal. Acetonitrile and methylene chloride were purged with nitrogen and distilled under nitrogen from calcium hydride and phosphorus pentoxide, respectively. Distilled water and all alcohols were purged with a dispersed stream of nitrogen for at least 12 h, and acetone and xylene were purged with nitrogen for 3 h before use.

Chlorodiphenylphosphine (Alfa Ventron) was vacuum distilled prior to use. Bis(diglyme)sodium hexacarbonylvanadate(-I) was purchased from Strem Chemicals and was used without further purification. Anhydrous cobalt(II) chloride was obtained by heating the hydrate in vacuo to 180 °C overnight and was stored in a drying oven at 170 °C. 1,1'-Bis(diphenylphosphino)ferrocene,¹ (dimethoxyethane)sodium cyclopentadienide,⁷ the tetraethylammonium salts of tetrachloronickelate and tetrachlorocuprate,⁸ and tris(diglyme)potassium hexacarbonyltantalate⁹ were prepared by literature methods. Tris(diglyme)potassium hexacarbonyltantalate was metathesized to the tetraethylammonium salt before use.

Chemical analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn., Spang Microanalytical Laboratory, Ann Arbor, Mich., and the M.I.T. Microchemical Laboratory.

Melting points were determined on samples sealed in glass capillaries under an inert atmosphere. Infrared spectra were recorded on a Perkin-Elmer Model 457A spectrophotometer. Nuclear magnetic resonance spectra were recorded on a Varian Associates T-60 spectrometer. UV-vis-IR spectra were recorded on a Cary 17 spectrophotometer. Magnetic susceptibility measurements on the fdpp complexes were made by the Gouy method with mercury tetracyanocobalt(II) as a standard. The susceptibilities were determined at four different field strengths using a single solid sample of each compound at ca. 18 °C. The magnetic susceptibility measurements on the [cdpp]PF₆ complexes were made using the Faraday technique and are corrected for diamagnetism. Conductivity measurements were made on 1 mM acetonitrile solutions using a Serfass conductance bridge.

Preparation of the Complexes M(fdpp)X₂ (X = Cl, Br, I; M = Co, Ni). These complexes were prepared by adding a solution of 3.5 mmol of the hydrated metal(II) halide in 50 mL of hot 1-butanol to a solution of fdpp (3.5 mmol) in 125 mL of hot 1-butanol. The product crystallized on cooling and was collected by filtration. This was washed with 1-butanol (2 \times 10 mL) and pentane (3 \times 10 mL) and air-dried to give 50–60% yields of analytically pure product. Analyses are listed in Table I. The infrared spectra for these six complexes are all similar. The general features are (Nujol mull) 1475 (m), 1430 (s), 1160 (s), 1095 (s), 1025 (s), 830 (s), 730 (vs), and 700 (vs) cm⁻¹.

Iodo[1,1'-bis(diphenylphosphino)ferrocene]copper(I). A mixture of CuI (1.418 g, 7.77 mmol) and LiI (1.0 g, 7.0 mmol) was heated in 100 mL of hot butanol and filtered into a solution of fdpp (1.62 g, 2.92 mmol) in 75 mL of hot butanol. A finely crystalline yellow solid separated immediately. The product was filtered off, washed with two 25-mL portions of butanol and three 25-mL portions of pentane, and air-dried: yield 1.705 g (78.4%); mp >310 °C.

Tetracarbonyl[1,1'-bis(diphenylphosphino)ferrocene]chromium(0). Freshly sublimed Cr(CO)₆ (1.045 g, 4.75 mmol) and fdpp (2.637 g, 4.76 mmol) were refluxed in 100 mL of reagent grade xylene for 3 h. Intermittent agitation of the flask was found helpful in washing sublimed Cr(CO)₆ back into the solution from the condenser. After cooling of the mixture to room temperature, the addition of 150 mL

Table I. fdpp Complexes of the Cobalt(II) and Nickel(II) Halides: Melting Points, Elemental Analyses, and Magnetic Susceptibilities

| complex | color | mp, °C | anal., % | | | | μ_{eff} μ_{B} |
|-------------------------|-------------|---------|------------------|----------------|----------------|------------------|--|
| | | | C | H | P | X | |
| Co(fdpp)Cl ₂ | blue-green | 297–299 | 60.51 (59.68) | 4.28 (4.12) | 8.96 (9.05) | | 4.35 |
| Co(fdpp)Br ₂ | blue-green | 322–324 | 53.41 (52.82) | 3.73 (3.65) | 7.94 (8.01) | 20.67 (20.67) | 4.38 |
| Co(fdpp)I ₂ | green-black | 311–312 | | | | | |
| Ni(fdpp)Cl ₂ | dark green | 283–284 | 60.01 (59.70) | 4.20 (4.12) | | | 3.39 |
| Ni(fdpp)Br ₂ | olive | 298–300 | 53.65 (52.83) | 3.76 (3.65) | 7.80 (8.02) | | 3.13 |
| Ni(fdpp)I ₂ | red-brown | 262–264 | 47.52 (47.11) | 3.24 (3.26) | 7.15 (7.15) | 29.24 (29.28) | 3.12 |

^a Calculated values for C₃₄H₂₈P₂X₂FeM are in parentheses.

of pentane gave immediate crystallization of a golden yellow product, which was filtered off and washed with *n*-pentane; yield 2.536 g (73.1%) of golden yellow crystals. This product was dissolved in 60 mL of hot benzene. The addition of 140 mL of hot heptane to this solution, followed by slow cooling, caused golden yellow needles to separate; mp 258–259.5 °C (sealed tube). Anal. Calcd for C₃₈H₂₈CrFeP₂O₄: C, 64.13; H, 3.86. Found: C, 64.13; H, 4.02. NMR (CDCl₃): δ 4.35 (s, 8 H), 7.2–7.9 (mult, 20 H).

Tetracarbonyl[1,1'-bis(diphenylphosphino)ferrocene]molybdenum(0). A mixture of Mo(CO)₆ (1.51 g, 5.72 mmol) and fdpp (3.21 g, 5.79 mmol) was refluxed for 8 h in 110 mL of xylene. Addition of 250 mL of pentane to the cooled solution precipitated a mustard colored powder. Separation and washing with *n*-pentane gave 3.785 g (85.5%) of the complex. The crude product was dissolved in 100 mL of hot benzene. The solution was filtered and then diluted with 200 mL of hot heptane. Slow cooling gave golden yellow plates which were separated and washed with pentane; mp 269–270 °C. Anal. Calcd for C₃₈H₂₈MoFeO₄P₂: C, 60.49; H, 3.64; P, 8.00. Found: C, 59.90; H, 4.00; P, 8.01. NMR (CDCl₃): δ 4.35 (s, 8 H), 7.2–7.8 (mult, 20 H).

Tetracarbonyl[1,1'-bis(diphenylphosphino)ferrocene]tungsten(0). A mixture of W(CO)₆ (0.891 g, 2.53 mmol) and fdpp (1.41 g, 2.55 mmol) was refluxed in 100 mL of freshly distilled xylene for 49 h. After the mixture was cooled, the addition of heptane caused a partially crystalline yellow solid to separate. The crude material was dissolved in hot benzene. The addition of hot heptane, followed by slow cooling, gave golden yellow crystals. The yield, after filtration and washing with *n*-pentane, was 0.537 g (25.0%); mp 275–276 °C (sealed tube). Anal. Calcd for C₃₈H₂₈WFeO₄P₂: C, 54.32; H, 3.27. Found: C, 55.06; H, 3.39. NMR (CDCl₃): δ 4.35 (s, 8 H), 7.2–7.8 (mult, 20 H).

Tetraethylammonium Tetracarbonyl[1,1'-bis(diphenylphosphino)ferrocene]vanadate(-I). In a drybox, 2.7 g (5.4 mmol) of bis(diglyme)sodium hexacarbonylvanadate(-I) and 5.4 g (9.7 mmol, 80% excess) of fdpp were weighed into the photolysis reaction vessel (200-mL capacity). A stirring magnet was added and the vessel was sealed with the immersion well, a vacuum stopcock, and a rubber septum. This was passed out of the drybox and 200 mL of THF was added. A long syringe needle was inserted through the rubber septum to provide a nitrogen purge and the photolysis was started. After 2.5 h an IR spectrum of the crude reaction mixture showed extensive formation of the tetracarbonyl product and very little unreacted V(CO)₆⁻ so the photolysis was stopped. The solution was transferred into a nitrogen-filled 500-mL, three-necked flask and the solvent was removed in vacuo. The resulting orange solid was Soxhlet extracted with hexane to remove the unreacted phosphine. The Soxhlet-insoluble solids were suspended in 100 mL of acetone, filtered, and washed with two 10-mL portions of acetone. To the combined filtrate and washes was added 4.0 g (24 mmol) of tetraethylammonium chloride dissolved in 30 mL of distilled water. Another 70 mL of distilled water was added and the acetone was removed in vacuo. The resulting orange precipitate was collected by filtration and was washed with water (3 × 10 mL) and diethyl ether (4 × 20 mL), followed by hot hexane/benzene (2:1 v/v, 30 mL). The remaining solid was recrystallized from 50 mL of 1-propanol and 150 mL of acetone and washed with hexane to give 3.4 g of an orange solid. Another recrystallization from acetone/1-butanol gave a crystalline solid which was contaminated with acetone. This was transferred to a drying pistol and

dried in vacuo (acetone reflux) for 24 h to yield 2.0 g (2.4 mmol, 45%) of analytically pure [NEt₄][V(fdpp)(CO)₄], mp 206.5–207 °C. Anal. Calcd for C₄₆H₄₈NO₄P₂VFe: C, 65.18; H, 5.71; N, 1.65. Found: C, 64.87; H, 5.59; N, 1.39. NMR (Me₂SO-*d*₆): δ 1.2 (t of t, $J_{\text{HH}} = 6$ Hz, $J_{\text{NH}} = 2$ Hz, 12 H), 3.2 (q, $J_{\text{H}} = 6$ Hz, 8 H), 4.0 (t, 2 Hz, 4 H), 4.1 (t, 2 Hz, 4 H), 7.0–7.8 (mult, 20 H). IR (Nujol): ν_{CO} 1890 (s), 1780 (s), 1760 (s), 1720 (s) cm⁻¹. IR (THF): ν_{CO} 1900 (s), 1790 (s), 1770 (s), 1740 (s) cm⁻¹.

Tetraethylammonium Tetracarbonyl[1,1'-bis(diphenylphosphino)ferrocene]tantalate(-I). This reaction was carried out using the same procedure used in the synthesis of [NEt₄][V(fdpp)(CO)₄]. Since the reaction starts with a tetraethylammonium salt, the metathesis step was omitted. For this reaction, 1.5 g (3.1 mmol) of tetraethylammonium hexacarbonyltantalate(-I) and 2.6 g (4.7 mmol, 50% excess) of 1,1'-bis(diphenylphosphino)ferrocene were dissolved in 250 mL of THF and were photolyzed for 2 h. As in the previous reaction, this photolysis was carried out with a nitrogen purge and the progress of the reaction was monitored periodically using the carbonyl region of the infrared spectrum. The purification was accomplished by Soxhlet extraction with hexane and two recrystallizations from acetone/1-butanol. After 3 days of drying in vacuo at 56 °C, 1.0 g (1.1 mmol, 35% yield) of orange [NEt₄][Ta(fdpp)(CO)₄] was isolated; mp >200 °C dec without melting. Anal. Calcd for C₄₆H₄₈NO₄P₂FeTa: C, 56.51; H, 4.95; N, 1.43. Found: C, 57.45; H, 5.19; N, 1.22. NMR (Me₂SO-*d*₆): δ 1.2 (t of t, $J_{\text{HH}} = 6$ Hz, $J_{\text{HN}} = 2$ Hz, 12 H), 3.2 (q, $J_{\text{HH}} = 6$ Hz, 8 H), 4.1 (mult, 4 H), 4.2 (mult, 4 H), 7.1–7.8 (mult, 20 H). IR (THF): ν_{CO} 1905 (s), 1790 (s), 1775 (s), 1750 (s) cm⁻¹. IR (Nujol): ν_{CO} 1900 (s), 1775 (s), 1750 (sh), 1720 (s) cm⁻¹.

1,1'-Bis(diphenylphosphino)cobaltocenium Hexafluorophosphate, [cdpp]PF₆. A 1-L, three-necked, round-bottomed flask was equipped with an efficient stirring magnet and charged with 50 mL (59.45 g, 0.27 mol) of freshly distilled chlorodiphenylphosphine. THF (500 mL) was added to the flask and the solution was cooled to -78 °C. Using a solids addition tube, 44.5 g (0.25 mol) of (dimethoxyethane)sodium cyclopentadienide was added and the dry ice bath was removed for 30 min giving a cloudy yellow solution. This was cooled again to -78 °C and 135 mL (0.27 mol) of *n*-butyllithium in hexane was added. After 15 min 17.8 g (0.135 mol) of anhydrous CoCl₂ was added against a counter stream of nitrogen. The mixture was allowed to warm to room temperature and after 5 h it was oxidized by the addition of 8 mL (0.14 mol) of acetic acid, 20 mL of distilled water, and oxygen gas yielding a thick green suspension. After 15 min this suspension was filtered through a bed of filter aid. Ammonium hexafluorophosphate (26 g, 0.16 mol, 20% excess) was dissolved in a minimum of distilled water and added to the filtrate. The filtrate was diluted with 400 mL of 95% ethanol and the solvent volume was reduced using a roto-evaporator. This produced a brown solid which was collected by filtration and washed with ethanol. Recrystallization from acetone/ethanol gave a bright yellow powder which was chromatographed on silica gel with methylene chloride to remove the phosphine oxides. A final recrystallization from methylene chloride/ether gave 17 g (24 mmol, 20%) of a bright yellow crystalline solid, mp 189–191 °C dec. Anal. Calcd for C₃₃H₂₈F₆P₃Co: C, 58.13; H, 4.02; F, 16.23; P, 13.23. Found: C, 58.33; H, 3.92; F, 15.70; P, 13.37. NMR (CD₃CN): δ 5.2 (t, 2 Hz, 4 H), 5.7 (t, 2 Hz, 4 H), 7.5 (mult, 20 H). IR (Nujol): 3100 (m), 3050 (w), 1580 (w), 1478 (m), 1420 (m), 1383 (m), 1355 (w), 1315 (sh), 1305 (w), 1200 (m),

1185 (w), 1165 (w), 1155 (w), 1095 (m), 1075 (w), 1035 (m), 1025 (m), 1000 (w), 925 (w), 895 (s), 870–800 (s), 760 (m), 755 (m), 745 (m), 705 (m), 700 (m), 635 (m) cm^{-1} .

Tetracarbonyl[1,1'-bis(diphenylphosphino)cobaltocenium-*P,P'*]-molybdenum Hexafluorophosphate. In a typical reaction, 1.0 g (1.4 mmol) of $[\text{cdpp}]\text{PF}_6$ and 0.40 g (1.5 mmol) of molybdenum hexacarbonyl were loaded in a 100-mL, three-necked, round-bottomed flask fitted with a reflux condenser equipped with a nitrogen inlet. Dioxane (50 mL) was added and the reaction was heated to reflux for 1 h. The resulting dark brown solution was cooled and the solvent was removed to give a tan powder. The product was recrystallized from CH_2Cl_2 by the addition of diethyl ether. This was chromatographed on silica gel (CH_2Cl_2 as eluent) to give 0.85 g (0.93 mmol, 66%) of tan crystals. One more recrystallization from CH_2Cl_2 /hexane gave an analytical sample, mp 273 °C dec. Anal. Calcd for $\text{C}_{38}\text{H}_{28}\text{O}_4\text{F}_6\text{P}_2\text{CoMo}$: C, 50.13; H, 3.10; P, 10.20. Found: C, 50.16; H, 2.97; P, 10.14. NMR (acetone- d_6): δ 6.0 (t, 1 Hz, 4 H), 6.1 (t, 1 Hz, 4 H), 7.6 (mult, 20 H).

Tetracarbonyl[1,1'-bis(diphenylphosphino)cobaltocenium-*P,P'*]-chromium Hexafluorophosphate. This reaction was performed using the same basic procedure as in the synthesis of $[\text{Mo}(\text{CO})_4(\text{cdpp})]\text{PF}_6$. In this case 1.0 g (1.4 mmol) of $[\text{cdpp}]\text{PF}_6$ and 0.35 g (1.6 mmol, 14% excess) of $\text{Cr}(\text{CO})_6$ were refluxed in diglyme for 30 min. During the reflux, $\text{Cr}(\text{CO})_6$ sublimed into the condenser and had to be returned to the reaction mixture using a stainless steel wire inserted through a rubber septum at the top of the condenser. After cooling of the mixture, the product was precipitated by addition of 40 mL of hexane. The resulting precipitate was collected by filtration and air-dried to give 1.0 g of a tan microcrystalline powder. This material can be purified in the same manner as the molybdenum product. *Extra care must be taken in drying this material since it entrains solvents on crystallizing.* The final yield was 0.83 g (0.95 mmol, 68%) of $[\text{Cr}(\text{CO})_4(\text{cdpp})]\text{PF}_6$, mp 239–240.5 °C dec. Anal. Calcd for $\text{C}_{38}\text{H}_{28}\text{O}_4\text{F}_6\text{P}_2\text{CrCo}$: C, 52.67; H, 3.25; P, 10.72. Found: C, 52.29; H, 3.35; P, 11.31. NMR (acetone- d_6): δ 6.1 (mult, 8 H), 7.6 (mult, 20 H). NMR (CD_2Cl_2): δ 5.8 (mult, 4 H), 5.9 (mult, 4 H), 7.6 (mult, 20 H).

Tetracarbonyl[1,1'-bis(diphenylphosphino)cobaltocenium-*P,P'*]-tungsten Hexafluorophosphate. This reaction was carried out in the same manner as the $\text{Mo}(\text{CO})_6$ and $\text{Cr}(\text{CO})_6$ reactions. In this case 0.54 g (1.5 mmol, 10% excess) of $\text{W}(\text{CO})_6$ and 1.0 g (1.4 mmol) of $[\text{cdpp}]\text{PF}_6$ were refluxed in diglyme for 30 min. A precipitate developed upon cooling. This was collected by filtration and air-dried to give 0.43 g of dark brown crystals. Slow addition of hexane (15 mL) to the filtrate precipitated another 0.30 g of product for a total of 0.73 g (0.73 mmol, 52% yield) of product. This was purified in the same manner as $[\text{Mo}(\text{CO})_4(\text{cdpp})]\text{PF}_6$ to give 0.50 g (0.50 mmol, 30%) of a brown crystalline powder of $[\text{W}(\text{CO})_4(\text{cdpp})]\text{PF}_6$, mp 275 °C dec. Anal. Calcd for $\text{C}_{38}\text{H}_{28}\text{O}_4\text{F}_6\text{P}_2\text{CoW}$: C, 45.72; H, 2.83; P, 9.31. Found: C, 45.83; H, 2.72; P, 9.46. NMR (acetone- d_6): δ 6.07 (mult, 4 H), 6.14 (mult, 4 H), 7.62 (mult, 20 H).

Dichloro[1,1'-bis(diphenylphosphino)cobaltocenium]cobalt(II) Chloride. In a typical reaction 2.0 g (2.8 mmol) of $[\text{cdpp}]\text{PF}_6$ was dissolved in 25 mL of acetonitrile. On addition of 0.50 g (3.8 mmol, 30% excess) of anhydrous cobalt(II) chloride, the mixture turned dark green and a dark green precipitate developed. After 45 min, the precipitate was collected by filtration and was washed with THF to give 1.29 g (1.8 mmol, 64%) of a dark green microcrystalline solid. This solid was Soxhlet extracted with acetonitrile to give analytically pure $[\text{Co}(\text{cdpp})\text{Cl}_2]\text{Cl}$, mp 260–261 °C dec. Anal. Calcd for $\text{C}_{34}\text{H}_{28}\text{P}_2\text{Cl}_3\text{Co}$: C, 56.50; H, 3.90; P, 8.57; Cl, 14.72; Co, 16.31. Found: C, 56.47; H, 3.86; P, 8.70; Cl, 14.84; Co by difference, 16.13. IR (Nujol): 3100 (sh), 3090 (m), 3060 (w), 3040 (w), 1580 (w), 1570 (w), 1480 (m), 1430 (s), 1420 (m), 1390 (w), 1380 (s), 1195 (m), 1165 (w), 1155 (w), 1090 (m), 1070 (m), 1040 (m), 1020 (m), 1000 (w), 935 (w), 885 (m), 870 (m), 865 (m), 755 (s), 745 (s), 700 (s) cm^{-1} . Magnetic susceptibility $\mu_{\text{eff}} = 4.5 \mu_{\text{B}}$ at room temperature.

Dichloro[1,1'-bis(diphenylphosphino)cobaltocenium]nickel(II) Chloride. A small Erlenmeyer flask was charged with 0.20 g (0.43 mmol) of $[\text{NET}_4]_2[\text{NiCl}_4]$ and 0.35 g (0.50 mmol, 16% excess) of $[\text{cdpp}]\text{PF}_6$ and was capped with a rubber septum. Acetonitrile (5 mL) was added, and the contents of the flask were stirred giving a green solution and a brown precipitate. After 30 min the contents of the flask were filtered to give a dark brown, crystalline solid. The solid was Soxhlet extracted with acetonitrile to give 0.21 g (0.28 mmol, 65% yield) of $[\text{Ni}(\text{cdpp})\text{Cl}_2]$ as hygroscopic, dark brown plates, mp 160

°C dec. Anal. Calcd for $\text{C}_{34}\text{H}_{28}\text{P}_2\text{Cl}_3\text{CoNi}$: C, 56.52; H, 3.91; Cl, 14.72. Found: C, 56.29; H, 4.13; Cl, 14.12. IR (Nujol): 3100–3000 (m), 1580 (w), 1565 (w), 1480 (m), 1430 (s), 1380 (s), 1300 (m), 1190 (m), 1160 (m), 1090 (s), 1070 (w), 1055 (m), 1030 (s), 995 (w), 870 (s), 755 (sh), 745 (s), 700 (sh), 695 (s) cm^{-1} . Magnetic susceptibility $\mu_{\text{eff}} = 3.60 \mu_{\text{B}}$ at room temperature.

A. Reaction of $[\text{cdpp}]\text{PF}_6$ with $[\text{NET}_4]_2[\text{CuCl}_4]$. This reaction was performed in the same manner as that for $[\text{NiCl}_4]^{2-}$. Using 0.50 g (0.71 mmol) of $[\text{cdpp}]\text{PF}_6$ and 0.37 g (0.8 mmol, 10% excess) of $[\text{NET}_4]_2[\text{CuCl}_4]$, 0.41 g (0.59 mmol, 83% yield) of a dark red-brown crystalline product was isolated. Prolonged Soxhlet extraction with acetonitrile gave an analytically pure sample of $\text{Cu}(\text{cdpp})\text{Cl}_2$, mp 259–261 °C dec. Anal. Calcd for $\text{C}_{34}\text{H}_{28}\text{P}_2\text{Cl}_2\text{CoCu}$: C, 59.01; H, 4.08; Cl, 10.25. Found: C, 58.99; H, 4.07; Cl, 10.29. IR (Nujol): 3020 (m), 1475 (m), 1435 (s), 1410 (m), 1370 (m), 1310 (w), 1195 (w), 1155 (w), 1090 (m), 1070 (m), 1025 (m), 890 (w), 875 (w), 865 (m), 760 (sh), 745 (s), 690 (s), 635 (m) cm^{-1} . Magnetic susceptibility: χ is field dependent, ranging from 1.89×10^{-3} ($2.4 \mu_{\text{B}}$) at low field strengths to 0.16×10^{-3} cgsu ($1.2 \mu_{\text{B}}$) at high field strengths.

B. Reaction of $[\text{cdpp}]\text{PF}_6$ with CuCl and NET_4Cl . A 25-mL Erlenmeyer flask was charged with 0.50 g (0.71 mmol) of $[\text{cdpp}]\text{PF}_6$, 0.069 g (0.70 mmol) of CuCl , and 0.16 g (0.9 mmol, 30% excess) of NET_4Cl . The addition of 10 mL of acetonitrile gave a dark brown solution which quickly precipitated a red-brown microcrystalline powder. After 15 min of stirring, the powder was collected by filtration and washed with acetonitrile (2×5 mL) and methylene chloride (1×5 mL). This was dried in vacuo to give 0.39 g (0.57 mmol, 81%) of $\text{Cu}(\text{cdpp})\text{Cl}_2$, identified by comparison with the previous sample.

By use of this technique, a similar, dark red, iodide complex has also been obtained in 80% yield.

Results and Discussion

fdpp Complexes. The preparation of the nickel and cobalt halide complexes of fdpp was conducted using the procedures developed to prepare the analogous bis(triphenylphosphine)^{10,12} and dppe^{11,13} [1,2-bis(diphenylphosphino)ethane] compounds. The $\text{Co}(\text{fdpp})\text{X}_2$ complexes closely resemble the dppe¹¹ and bis(triphenylphosphine)¹⁰ analogues and presumably involve a similar pseudotetrahedral cobalt(II). The paramagnetic $\text{Ni}(\text{fdpp})\text{X}_2$ complexes resemble the high-spin, pseudotetrahedral bis(triphenylphosphine)nickel(II) halides¹² rather than the diamagnetic (dppe) NiX_2 compounds.¹³ The greater steric requirements and larger bite size of the fdpp ligand are probably responsible for this preference for the high-spin, tetrahedral geometry. The yellow cuprous iodide complex $\text{Cu}(\text{fdpp})\text{I}$ was prepared in a similar manner using excess iodide ion to increase the solubility of the copper reagent.

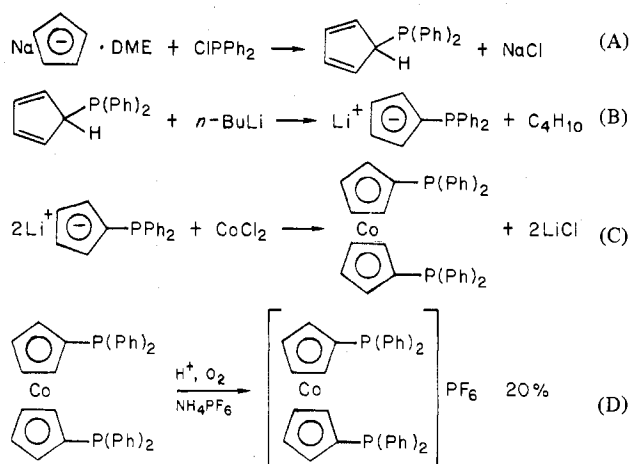
The group 6 metal tetracarbonyls $\text{M}(\text{fdpp})(\text{CO})_4$, $\text{M} = \text{Cr}$, Mo , and W , are readily prepared by refluxing a 1:1 mixture of the appropriate metal hexacarbonyl with fdpp in xylene. The reactions with the group 5 hexacarbonylmetalates were carried out using the procedure developed by Ellis and Davison to prepare the arsine analogue $[(\text{C}_2\text{H}_5)_4\text{N}][\text{V}(\text{CO})_4(\text{fdpa})]$.¹⁴ The addition of a nitrogen purge during the photolysis reaction resulted in a substantial increase in the rate of the reaction. For both the group 6 fdpp metal carbonyls and the group 5 fdpp tetracarbonylmetalates, the carbonyl region of the infrared spectra is typical of cis-disubstituted metal tetracarbonyls and is nearly identical with the carbonyl region of the analogous dppe compounds¹⁵ (Table III).

$[\text{cdpp}]\text{PF}_6$ and Its Transition-Metal Complexes. 1,1'-Bis(diphenylphosphino)cobaltocenium ion has been isolated as a hexafluorophosphate salt from the reaction sequence outlined in Scheme I.

IR, NMR, and elemental analyses are all consistent with the 1,1'-bis(diphenylphosphino)-substituted cobaltocenium hexafluorophosphate product.

The cationic ligand $[\text{cdpp}]\text{PF}_6$ reacts with molybdenum hexacarbonyl in refluxing dioxane to give the expected product $[\text{Mo}(\text{cdpp})(\text{CO})_4]\text{PF}_6$ in good yield. The reactions using $\text{Cr}(\text{CO})_6$ and $\text{W}(\text{CO})_6$ were similar but required a higher boiling solvent (diglyme) or longer reflux time to obtain good

Scheme I

Table II. Reaction Conditions for Preparing the Group 6 Tetracarbonyls of dppe, fdpp, and [cdpp]PF₆

| compound | conditions | reacn time, h | yield, % |
|---|------------------|---------------|----------|
| Cr(dppe)(CO) ₄ ^a | neat, 150–160 °C | 12 | 71 |
| Cr(fdpp)(CO) ₄ | xylene, 140 °C | 3 | 88 |
| [Cr(cdpp)(CO) ₄]PF ₆ | diglyme, 160 °C | 0.5 | 68 |
| Mo(dppe)(CO) ₄ ^a | neat, 150–170 °C | 9 | 67 |
| Mo(fdpp)(CO) ₄ | xylene, 140 °C | 8 | 86 |
| [Mo(cdpp)(CO) ₄]PF ₆ | dioxane, 101 °C | 1 | 66 |
| W(dppe)(CO) ₄ ^a | neat, 150–160 °C | 17 | 67 |
| W(fdpp)(CO) ₄ | xylene, 140 °C | 49 | 25 |
| [W(cdpp)(CO) ₄]PF ₆ | diglyme, 160 °C | 0.5 | 52 |

^a Reactions were carried out in sealed evacuated tubes.¹⁵

yields. The reactions performed in refluxing diglyme were stopped as soon as the metal carbonyls failed to sublime into the condenser. Longer reflux times resulted in reduced yields.

Table II lists the reaction conditions for the preparation of the group 6 tetracarbonyl complexes of [cdpp]PF₆, fdpp, and dppe.¹⁵ It is readily apparent that [cdpp]PF₆ compares favorably with the two neutral ligands in ability to complex with the group 6 metal hexacarbonyls.

Table III lists the carbonyl stretching frequencies for these same compounds.¹⁵ The carbonyl stretches for the three [cdpp]⁺ compounds are shifted 10–20 cm⁻¹ to higher wavenumbers indicating that [cdpp]⁺ is a “stronger π acid” than the neutral ligands.¹⁶ This shift has also been observed with the bis(diphenylphosphino-η⁶-benzene)chromium tetracarbonyl complexes of the group 6 metals and their first oxidation product.¹⁷

Attempts to prepare [cdpp]⁺ complexes with the cobalt(II) and nickel(II) chlorides in refluxing alcohols met with little success. An efficient reaction with cobalt(II) was achieved by using anhydrous cobalt(II) chloride in acetonitrile. Under these conditions the reaction occurred on mixing to yield a dark green, crystalline material which analyzed for Co(cdpp)Cl₃. Solution UV–visible spectra and the conductivity (100 Ω⁻¹ cm² in CH₃CN) indicate that the material is the chloride salt of the pseudotetrahedral¹⁰ cation [Co(cdpp)Cl₂]⁺. The solid-state UV–visible spectrum (KBr pellet) is very similar to the solid-state spectra¹⁰ of Co(PPh₃)₂Cl₂, ruling out the possibility of a five-coordinate geometry for the solid structure. The magnetic moment of 4.50 μ_B (298 K) is also indicative of a pseudotetrahedral, high-spin cobalt(II) in the powdered solid.

Attempts to prepare a nickel(II) complex from [cdpp]PF₆ and anhydrous nickel(II) chloride were also unsuccessful. A Ni^{II}(cdpp)⁺ complex was prepared using the tetrachloronickelate dianion and [cdpp]PF₆ in acetonitrile. This reaction

Table III. IR Spectra of the Group 6 Metal Tetracarbonyls, the Carbonyl Region

| | [cdpp]PF ₆ (CH ₂ Cl ₂) | fdpp (CH ₂ Cl ₂) | dppe ^a (1,2- Cl ₂ C ₂ H ₄) |
|---------------------|---|--|--|
| Cr(CO) ₄ | 2025 s | 2010 s | 2009 s |
| | 1935 s | 1915 s | 1914 sh |
| | 1903 s | 1890 s | 1899 vs 1877 s |
| Mo(CO) ₄ | 2040 s | 2022 s | 2020 s |
| | 1940 s | 1920 sh | 1919 sh |
| | 1912 vs | 1900 vs | 1907 vs 1881 s |
| W(CO) ₄ | 2030 s | 2018 s | 2016 s |
| | 1933 s | 1910 s | 1912 sh |
| | 1905 vs | 1890 vs | 1901 vs 1876 s |

^a Reference 15.

Table IV. UV–Visible Data for Selected Diphosphine Transition Metal Halide Complexes

| complex | solution | | solid state | |
|---|--|---|-------------|--------------------------|
| | medium | λ, nm (ε, M ⁻¹ cm ⁻¹) | medium | λ, nm |
| [cdpp]PF ₆ | CH ₃ CN | 375 (4100) | KBr pellet | 720 s 670 m 580 s |
| | | 265 (26 000) | | |
| | | 245 (29 000) | | |
| [Co(cdpp)- Cl ₂]Cl | CH ₃ CN | 685 (580) | KBr pellet | 740 m 645 s 615 sh |
| | | 665 sh | | |
| | | 630 sh | | |
| | | 590 (440) | | |
| | | 575 sh | | |
| | | 375 (4300) | | |
| Co(fdpp)Cl ₂ | CH ₂ Cl ₂ | 737 (470) | KBr pellet | 769 650 |
| | | 638 (700) | | |
| | | 610 sh | | |
| Co(PPh ₃) ₂ Cl ₂ ^a | CH ₃ CO- C ₂ H ₅ | 550 (240) | Nujol mull | 673 649 585 349 |
| | | 682 (310) | | |
| | | 638 (290) | | |
| Co(dppe)Cl ₂ ^b | CH ₂ Cl ₂ | 581 (235) | KBr pellet | 495 |
| | | 833 sh | | |
| | | 724 (440) | | |
| Cu(cdpp)Cl ₂ | Me ₂ SO, CH ₃ CN | 641 (410) | KBr pellet | 495 |
| | | 590 (600) | | |
| | | 520 (1600) | | |
| | | 272 (34 000) | | |

^a Reference 10. ^b Reference 11.

proceeds very rapidly to give an insoluble, brown crystalline solid which again does not contain PF₆⁻ and analyzes for Ni(cdpp)Cl₃. Due to the hygroscopic nature and poor solubility of this material, an adequate distinction could not be made between a five-coordinate geometry and a salt structure. However, the magnetic susceptibility of 3.60 μ_B (298 K, powdered sample) is consistent with a pseudotetrahedral nickel(II) in the solid state.

A similar reaction was performed with [cdpp]PF₆ and [NEt₄]₂[CuCl₄] in acetonitrile. This reaction gives a dark red-brown insoluble powder which analyzes as Cu(cdpp)Cl₂. Copper(II) halides are known to oxidize phosphines,¹⁸ so a copper(I) product is to be expected for this reaction. This same product can be prepared by mixing [cdpp]PF₆, NEt₄Cl, and CuCl in acetonitrile.

The physical data for Cu(cdpp)Cl₂ do not provide an unambiguous characterization of this material. An assignment of Cu^ICl₂[Co^{III}(CpPPh₂)₂] is consistent with the synthesis and the analysis but is inconsistent with the physical data. As a d¹⁰ metal ion, cuprous compounds are diamagnetic, and, except where the color results from the ligands or charge-transfer bands, the compounds are colorless.¹⁹ The cobaltocenium fragment of the molecule is yellow and diamagnetic so a

Co(III), Cu(I) formulation would expect a yellow, diamagnetic product similar to the Cu(fdpp)I material.

The UV-visible spectra, Table IV, demonstrate the electronic changes that have occurred in the (cdpp)⁺ fragment of the Cu(cdpp)Cl₂. In the spectrum of Cu(cdpp)Cl₂ there are no UV-visible absorptions which can clearly be attributed to the ligand [cdpp]⁺. In contrast the high-energy portion of the UV-visible spectrum for [Co(cdpp)Cl₂]Cl matches the UV-visible spectrum of [cdpp]PF₆ exactly.

A more acceptable valence assignment is Co^{II}/Cu^{II}. This assignment accounts for the changes in the ligand part of the UV-visible spectrum and the paramagnetism of the compound. Since this material would have two paramagnetic centers, it could display magnetic concentration effects such as field-dependent paramagnetism. Nevertheless, magnetic concentration effects are complex, and more extensive study is needed before any realistic assignment can be made for this material.

Conclusion

1,1'-Bis(diphenylphosphino)cobaltocenium hexafluorophosphate has been prepared and its behavior is contrasted to the isoelectronic neutral 1,1'-bis(diphenylphosphino)ferrocene. As a cationic phosphine ligand it is unique in that it has demonstrated an interaction of the positive charge with the complexed metal, in both the increased π -acid strength observed in the carbonyl stretching frequencies of the group 6 tetracarbonyl[1,1'-bis(diphenylphosphino)cobaltocenium] metal cations and the anomalous behavior of the Cu(cdpp)Cl₂ complex. In addition it has required fundamental changes in synthetic procedure such as the need for additional chloride ion to prepare the nickel(II) chloride complex Ni(cdpp)Cl₃. Cationic ligands using a quaternary ammonium or phosphonium ion as the source of the positive charge have failed to demonstrate either an extensive interaction of the positive charge with the complexed metal or a significant change in the reactivity of a cationic ligand over a neutral analogue.²⁰

Registry No. Co(fdpp)Cl₂, 67292-36-8; Co(fdpp)Br₂, 67292-37-9; Co(fdpp)I₂, 67292-35-7; Ni(fdpp)Cl₂, 67292-34-6; Ni(fdpp)Br₂,

67292-33-5; Ni(fdpp)I₂, 67292-32-4; Cr(fdpp)(CO)₄, 67292-31-3; [Cr(cdpp)(CO)₄]PF₆, 67292-30-2; Mo(fdpp)(CO)₄, 67292-28-8; [Mo(cdpp)(CO)₄]PF₆, 67292-27-7; W(fdpp)(CO)₄, 67292-26-6; [W(cdpp)(CO)₄]PF₆, 67292-25-5; [cdpp]PF₆, 67292-48-2; [Co(cdpp)Cl₂]Cl, 67292-46-0; Cu(cdpp)Cl₂, 67292-45-9; Cu(fdpp)I, 67292-44-8; [NEt₄][V(fdpp)(CO)₄], 67292-43-7; [NEt₄][Ta(fdpp)(CO)₄], 67292-41-5; [Ni(cdpp)Cl₂]Cl, 67292-39-1; Cr(CO)₆, 13007-92-6; Mo(CO)₆, 13939-06-5; W(CO)₆, 14040-11-0; bis(diglyme)sodium hexacarbonylvanadate(-I), 15531-13-2; tetraethylammonium hexacarbonyltantalate(-I), 67292-38-0.

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Hyrido Complexes of Ruthenium with Carborane Ligands

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The synthesis and characterization of the complexes 2,2-(PPh₃)₂-2,2-H₂-2,1,7-RuC₂B₉H₁₁ and 3,3-(PPh₃)₂-3,3-H₂-3,1,2-RuC₂B₉H₁₁ via the oxidative addition of 7,9- and 7,8-C₂H₅H₁₂⁻, respectively, to (PPh₃)₃RuHCl are described. These complexes are formulated as seven-coordinate formal Ru(IV) compounds. The 2,1,7 isomer was found to reversibly eliminate one molecule of H₂ with heating in vacuo to give a five-coordinate d⁶, formal Ru(II) complex. Both the 2,1,7 and 3,1,2 isomers readily lose hydrogen in their reactions with HCl and CO to give the corresponding substituted complexes. The pyridine-substituted complex 3,3-(PPh₃)₂-3-H-7-C₅H₅N-3,1,2-RuC₂B₉H₁₀ was also prepared and characterized.

The versatile homogeneous catalysts based on the rhodium and ruthenium metals include (PPh₃)₃RhCl and (PPh₃)₃RuHCl and many of their derivatives.^{1,2} Recently, we reported the preparation and characterization of a novel class of homogeneous catalysts based on carborane ligands and rhodium and iridium metals.^{3,4} These complexes are formed by the oxidative addition reaction of the isomeric C₂B₉H₁₂⁻ anions to coordinatively unsaturated d⁸ rhodium(I) and iridium(I) species. In two recent communications, we have further established that oxidative addition of *nido*- and *arachno*-carboranes to unsaturated transition-metal centers has

proved to be a general reaction.^{5,6} In this article we present details of the synthesis and characterization of several novel ruthenium complexes based on dicarbollide ligands and some of their reactions.

Results and Discussion

Synthesis. Both of the new ruthenium complexes were synthesized from the hydridotris(triphenylphosphine)ruthenium chloride complex (PPh₃)₃RuHCl. Oxidative addition of NHMe₃⁺ salts of the carborane anions⁷ 7,9- and 7,8-C₂B₉H₁₂⁻ to (PPh₃)₃RuHCl·PhCH₃⁸ in boiling ethanol gave