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Symmetrically Disubstituted Ferrocenes. III. Complexes of Ferrocene-1,1′-bis(dimethylarsine) and Ferrocene-1,1′-bis(diphenylarsine) with the Group VIII Metals[1]

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Received January 16, 1970

The chemistry of the ditertiary arsines ferrocene-1,1′-bis(dimethylarsine) (fdma) and ferrocene-1,1′-bis(diphenylarsine) (fdpa) functioning as ligands toward the metals of group VIII has been explored. The complexes $M(fdma)X_2$ (M = Pd; X = Cl, Br and M = Pt; X = Cl, Br, I) react with an excess of the diarsine fdma to produce solutions from which salts of the five-coordinate $M(fdma)_2X^+$ ions and the four-coordinate $M(fdma)_2{}^{2+}$ ions can be isolated. Reactions of this type do not occur for the more sterically crowded diarsine fdpa. The simple complexes $(fdma)NiX_2$ (X = Cl, Br, and I) and $(fdpa)NiX_2$ (X = Cl, Br) could not be prepared by a number of routes. One of these, however, the reaction of $(diars)Ni(CO)_2$ with iodine, led to the isolation of the species $(diars)Ni(CO)I_2$ (where diars = fdma or fdpa). These seem to be examples of carbonyl complexes of nickel in the +2 oxidation state.

Introduction

In its reaction chemistry and in the types of complexes it forms with transition metals, the ditertiary arsine chelate[3] ferrocene-1,1′-bis(dimethylarsine) (fdma) bears some superficial similarities to *o*-phenylenebis(dimethylarsine)[4] (diars). The latter ligand, largely in the hands of Nyholm and coworkers,[5] is proving undoubtedly to be one of the most versatile bidentate ligands studied. One significant difference between these two ligands, which is of practical importance in preparing their complexes, is that fdma is rapidly degraded to ferrocene by alcoholic acid solutions, while diars is stable in these media.

Unlike fdma and diars, which form mono- and bischelated metal complexes, ferrocene-1,1′-bis(diphenylarsine) fdpa has given complexes with only one chelate per metal atom. The latter diarsine's inability to form such compounds is presumably due to steric factors. Examination of molecular models of bis-chelated fdpa complexes confirmed this presumption.

Experimental Section

General Data.—Microanalyses were performed by Alfred Bernhardt Mikroanalytisches Laboratorium, Müllheim (Ruhr), West Germany; Galbraith Laboratories, Inc., Knoxville, Tenn.; Midwest Microlab, Inc., Indianapolis, Ind.; Spang Microanalytical Laboratory, Ann Arbor, Mich.; and at Massachusetts Institute of Technology by Dr. Stephen S. Nagy and Mrs. Nancy F. Alvord.

All melting points are corrected and were determined using a Thomas–Hoover "Unimelt" melting point apparatus on samples sealed in evacuated capillaries.

Molar conductances were determined at 25° with a Serfass conductivity bridge, Model RCM 15B1, and a Sargent Washburn type cell (cell constant 0.7965 ohm^{-1}). Conductometric titrations were carried out with the same bridge and an Industrial Instruments "dipping"-type cell, Model CEL-2A (cell constant 0.09952 ohm^{-1}), by adding from a buret tetraalkylammonium halide solutions to magnetically stirred metal complex solutions maintained at *ca.* 25° in tall-form beakers. The constants of both cells were determined from the conductances of 0.02 *N* potassium chloride prepared from distilled deionized water. The specific conductance of 0.02 *N* potassium chloride was taken to be 0.002768 $ohm^{-1}\ cm^{-1}$.[6]

The magnetic susceptibilities of solid samples were determined at four different field strengths by the Gouy method in double-ended glass Gouy tubes using $HgCo(SCN)_4$[7] as a calibrant. Corrections for diamagnetism of the ligands were made using values of -338×10^{-6} and -230×10^{-6} in χ_m (cgs units) for fdpa and fdma, respectively, and for other atoms of the complex using the values[8] given by Figgis and Lewis.

Where sensitive materials were involved, manipulations were carried out in an atmosphere of prepurified nitrogen.

Infrared spectra were recorded on a Perkin-Elmer 337 spectrophotometer. Visible and near-infrared spectra were determined with a Cary Model 14 spectrophotometer. Nuclear magnetic resonance spectra were recorded on Varian Associates T-60, A-60, and HA-100 spectrometers with tetramethylsilane as an internal reference.

Materials.—Reagent grade solvents were used and, when required, were degassed *in vacuo*. Hydrocarbons were dried by refluxing over and distilling from calcium hydride under nitrogen. Diglyme was dried as above over lithium aluminum hydride. "Spectrograde" nitromethane was dried over calcium sulfate, filtered, and fractionated under nitrogen.

The diarsines fdma and fdpa were prepared as described previously.[3] All other chemicals were of commercial reagent grade and, unless stated below, were used without purification.

Preparation of the Complexes.—The simple four-coordinate complexes $M(fdma)X_2$ (M = Pd, Pt; X = Cl, Br, I) and $M(fdpa)X_2$ (M = Pd; X = Cl, Br, I and M = Pt; X = Cl] were prepared from alcoholic solutions of the corresponding tetrahalometalates and a slight deficency of the arsine (*ca.* 1:0.96 molar ratios). The complexes are relatively insoluble in cold alcohols and are nonelectrolytes in dilute (*ca.* 10^{-3} *M*) nitromethane solutions.

Dichloroferrocene-1,1′-bis(dimethylarsine)palladium(II).—Red flakes decomposed without melting at *ca.* 255–260°. *Anal.* Calcd for $C_{14}H_{20}Cl_2FePd$: C, 29.43; H, 3.53; As, 26.23; Cl, 12.41. Found: C, 29.24; H, 3.60; As, 26.35; Cl, 12.35.

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Dibromoferrocene-1,1′-bis(dimethylarsine)palladium(II).—Red-brown flakes decomposed at 254–262°. *Anal.* Calcd for $C_{14}H_{20}As_2Br_2FePd$: C, 25.47; H, 3.05; Br, 24.21. Found: C, 25.40; H, 3.16; Br, 24.99.

Diiodoferrocene-1,1′-bis(dimethylarsine)palladium(II).—Dark red crystals decomposed at 282°. *Anal.* Calcd for $C_{14}H_{20}As_2FeI_2Pd$: C, 22.30; H, 2.67; I, 33.65. Found: C, 22.47; H, 2.82; I, 33.50.

Dichloroferrocene-1,1′-bis(diphenylarsine)palladium(II).—Dark red crystals decomposed at 240–242°. *Anal.* Calcd for $C_{34}H_{28}As_2Cl_2FePd$: C, 49.83; H, 3.44; Cl, 8.65. Found: C, 49.67; H, 3.53; Cl, 8.62.

Dibromoferrocene-1,1′-bis(diphenylarsine)palladium(II).—Dark red needles decomposed at 247.5–250°. *Anal.* Calcd for $C_{34}H_{28}As_2Br_2FePd$: C, 44.95; H, 3.11; Br, 17.59. Found: C, 46.04; H, 3.33; Br, 17.60.

Diiodoferrocene-1,1′-bis(diphenylarsine)palladium(II).—Shiny purple needles decomposed at 259.5–262°. *Anal.* Calcd for $C_{34}H_{28}As_2FeI_2Pd$: C, 40.74; H, 2.82; I, 25.32. Found: C, 40.77; H, 2.77; I, 24.78.

Dichloroferrocene-1,1′-bis(dimethylarsine)platinum(II).—Yellow crystals decomposed at 279–281°. *Anal.* Calcd for $C_{14}H_{20}As_2Cl_2FePt$: C, 25.48; H, 3.05; Cl, 10.75. Found: C, 25.86; H, 3.17; Cl, 11.00.

Dibromoferrocene-1,1′-bis(dimethylarsine)platinum(II).—Yellow needles decomposed at 304.5–305°. *Anal.* Calcd for $C_{14}H_{20}As_2Br_2FePt$: C, 22.45; H, 2.69. Found: C, 22.57; H, 2.82.

Diiodoferrocene-1,1′-bis(dimethylarsine)platinum(II).—Small orange plates decomposed at 310.5–311.5°. *Anal.* Calcd for $C_{14}H_{20}As_2FeI_2Pt$: C, 19.95; H, 2.39. Found: C, 20.18; H, 2.70.

Dichloroferrocene-1,1′-bis(diphenylarsine)platinum(II).—Recrystallization of the crude product from acetone gave a solvent adduct, as well-formed golden rhombs, mp 302.5–304.5° dec. *Anal.* Calcd for $C_{34}H_{28}As_2Cl_2FePt \cdot C_3H_6O$: C, 45.99; H, 3.55; Cl, 7.34. Found: C, 45.69; H, 3.26; Cl, 7.98.

The crude complexes are very soluble in polar solvents such as acetone, tetrahydrofuran, and chloroform and are quite often obtained with 1 mol of solvent of crystallization.

Chlorobis[ferrocene-1,1′-bis(dimethylarsine)]palladium(II) Hexafluorophosphate.—A hot solution of ammonium hexafluorophosphate (0.41 g, 2.51 mmol) in methanol (150 ml) was added dropwise to a stirred, refluxing solution of $Pd(fdma)Cl_2$ (1.14 g, 2.0 mmol), fdma (0.85, 2.14 mmol), and lithium chloride (0.34 g, 8.1 mmol) in 250 ml of the same solvent. Upon refluxing for 1 hr the solution was allowed to cool to ambient temperature, which caused the product to separate. Removal by filtration, followed by washing with methanol (four 25-ml portions) and then diethyl ether (two 25-ml portions), gave after drying *in vacuo* 1.59 g (74%) of very dark red-brown needles, mp 195.5–199.5°. *Anal.* Calcd for $C_{28}H_{40}As_4ClF_6Fe_2PPd$: C, 31.29; H, 3.75; Cl, 3.30; P, 2.88. Found: C, 31.61; H, 3.71; Cl, 3.56; P, 3.11.

Bromobis[ferrocene-1,1′-bis(dimethylarsine)]palladium(II) Hexafluorophosphate.—This complex was prepared similarly from $Pd(fdma)Br_2$, fdma, and sodium bromide in 83% yield as orange crystals, mp 231–233°. *Anal.* Calcd for $C_{28}H_{40}As_4BrF_6Fe_2PPd$: C, 30.05; H, 3.60. Found: C, 29.51; H, 3.75.

Bis[ferrocene-1,1′-bis(dimethylarsine)]palladium(II) Hexafluorophosphate.—A mixture of $Pd(fdma)Cl_2$ (1.15 g, 2.01 mmol) and fdma (0.81 g, 2.06 mmol) in methanol (100 ml) was heated until a dark red solution was obtained. The solution was filtered hot and added dropwise to a vigorously stirred refluxing solution of ammonium hexafluorophosphate (100 ml of a saturated methanolic solution diluted to 200 ml with methanol). During the addition, crystals developed in the hot solution. The mixture was refluxed for 1.25 hr and filtered hot. The fragile, dark blue plates were washed with hot methanol (seven 25-ml portions) followed by diethyl ether (two 25-ml portions) and dried *in vacuo*. The yield was 1.84 g (77%). Upon being heated in an evacuated capillary, the sample first became green, at *ca.* 210°, then gradually darkened until it became black at 280°, and finally melted at 282.5–285° dec. *Anal.* Calcd for $C_{28}H_{40}As_4F_{12}Fe_2P_2Pd$: C, 28.40; H, 3.40; P, 5.23. Found: C, 28.48; H, 3.37; P, 5.36.

Chlorobis[ferrocene-1,1′-bis(dimethylarsine)]platinum(II) Hexafluorophosphate.—The preparation of this complex was similar to that used for $[Pd(fdma)_2Cl][PF_6]$ with the exception that the reaction mixture was clarified, by filtration of the hot solution, before the product crystallized. The product was obtained in 84% yield as orange-red flakes, mp 224–228°. *Anal.* Calcd for $C_{28}H_{40}ClF_6Fe_2PPt$: C, 28.90; H, 3.47; Cl, 3.05. Found: C, 29.39; H, 3.65; Cl, 3.20.

Bromobis(ferrocene-1,1′-dimethylarsine)platinum(II) Hexafluorophosphate.—This complex was prepared similarly in 84% yield as an orange microcrystalline solid, mp *ca.* 262–267° (varied with heating rate). *Anal.* Calcd for $C_{28}H_{40}BrF_6Fe_2PPt$: C, 27.84; H, 3.34; Br, 6.62. Found: C, 27.96; H, 3.24; Br, 6.86.

Iodobis[ferrocene-1,1′-bis(dimethylarsine)]platinum(II) Hexafluorophosphate.—The iodo complex was prepared readily in a similar manner from $Pt(fdma)I_2$, fdma, and ammonium hexafluorophosphate, except that to prevent the formation of $[Pt(fdma)_2I]I$, molar ratios of 1.01:1.45:1.50, respectively, were used. The complex was obtained in 85% yield as red-orange flakes, mp 271–274.5°. *Anal.* Calcd for $C_{28}H_{40}As_4IF_6Fe_2PPt$: C, 26.80; H, 3.21. Found: C, 27.11; H, 3.47.

Iodobis[ferrocene-1,1′-bis(dimethylarsine)]platinum(II) Iodide.—A solution of sodium iodide (2.00 g, 13.3 mmol) in 25 ml of methanol was added dropwise to a well-stirred, refluxing solution of $Pt(fdma)I_2$ (0.602 g, 0.714 mmol) and fdma (0.514 g, 1.31 mmol) in 130 ml of the same solvent. The solution was set aside and allowed to stand at room temperature for 24 hr. During this time orange plates separated. These were collected and washed with ethanol (four 5-ml portions) and dried *in vacuo* to give 0.74 g (84%) of product, mp 238–247°. Recrystallization from hot ethanol (210 ml) containing fdma (0.21 g) under a nitrogen atmosphere gave 0.50 g of shiny, thin orange flakes, mp 242–246°. *Anal.* Calcd for $C_{28}H_{40}As_4Fe_2I_2Pt$: C, 27.19; H, 3.26; I, 20.52. Found: C, 27.92; H, 3.30; I, 20.12. The complex is soluble in hot methanol and in nitromethane, is sparingly soluble in hot chloroform, and is insoluble in hydrocarbons.

Bis[ferrocene-1,1′-bis(dimethylarsine)]platinum(II) Hexafluorophosphate.—This complex was prepared in the same manner as $[Pd(fdma)_2][PF_6]_2$. It was obtained as orange-red crystals, mp 316–318.5° dec, in 79% yield. Its solution behavior is similar to that of the corresponding palladium compound. *Anal.* Calcd for $C_{28}H_{40}As_4ClF_{12}Fe_2P_2Pt$: C, 26.42; H, 3.17; P, 4.87. Found: C, 26.39; H, 3.20; P, 5.22.

Dichlorobis[ferrocene-1,1′-bis(dimethylarsine)]ruthenium(II).—During 40 min ruthenium trichloride hydrate (1.02 g) in 150 ml of absolute ethanol was added dropwise to a magnetically stirred solution of fdma (4.45 g, 11.6 mmol) in 100 ml of the same solvent. The resulting green slurry gradually became, during 15 hr of reflux, a slurry of orange crystals of the product. These crystals were collected, washed with absolute ethanol (20 ml), and dried *in vacuo*; yield 3.18 g, mp 269.5–271.5°. The crude product was recrystallized from 220 ml of hot benzene–heptane (1:1 v/v), collected, washed with heptane (two 5-ml portions), and dried *in vacuo*. The purified sample (2.71 g) melted at 280.0–281.5°. *Anal.* Calcd for $C_{28}H_{40}As_4Cl_2Fe_2Ru$: C, 35.03; H, 4.20; Cl, 7.39. Found: C, 35.24; H, 4.33; Cl, 7.56.

The air-stable product is insoluble in ether and heptane and is soluble in acetone, chloroform, tetrahydrofuran, benzene, and hot butanol.

Dibromobis[ferrocene-1,1′-bis(dimethylarsine)]nickel(II).—A hot solution of fdma (3.25 g, 8.25 mmol) in butanol (20 ml) was added dropwise to a refluxing magnetically stirred slurry of anhydrous nickel bromide (0.88 g, 4.0 mmol) in butanol (100 ml). During the addition (*ca.* 10 min) the color changed from yellow through green to red-brown, and finally, when the addition was completed, the reaction mixture was an intense red-brown. It was refluxed for 1.5 hr and set aside to cool. After standing for 12 hr, the product separated. It was collected and washed first with butanol (three 10-ml portions) and finally with heptane (four 10-ml portions). Drying *in vacuo* gave 3.19 g (79%) of purple flakes, mp 154.5–156°. The melting point was unchanged after recrystallization from butanol (125 ml). *Anal.* Calcd for $C_{28}H_{40}As_4Br_2Fe_2Ni$: C, 33.41; H, 4.01; Br, 15.88. Found: C, 33.27; H, 4.00; Br, 16.41. The paramagnetic solid (μ_{eff} = 3.06 BM) is air stable. It is insoluble in water and cold 2-propanol and very slightly soluble in hot toluene.

Dicarbonylferrocene-1,1′-bis(dimethylarsine)nickel(0).—A solution of nickel tetracarbonyl (1.3 ml, *ca.* 10 mmol) and fdma (3.20 g, 8.13 mmol) in 50 ml of benzene was prepared, stirred at room temperature for 2 hr, heated over 1 hr to reflux, refluxed for 60 hr, cooled, and filtered through Celite. The clear filtrate was evaporated to dryness *in vacuo*. The orange residue was dissolved in 60 ml of oxygen-free methanol. The solution was filtered and the filtrate was slowly cooled to −15°. After 2 days, the crystalline product was collected, washed with two 5-ml portions of cold (*ca.* 0°) methanol, and dried *in vacuo*. The fine orange needlelike product weighed 2.84 g (60%), mp 106–107.5°. *Anal.* Calcd for $C_{16}H_{20}As_2FeNiO_2$: C, 37.78; H, 3.96. Found: C, 37.64; H, 4.12. In the solid state and in solution, Ni(fdma)(CO)$_2$ is decomposed by air. It is soluble in hydrocarbons and ethers and insoluble in water and reacts with carbon tetrachloride and carbon disulfide.

μ-Ferrocene-1,1′-bis(dimethylarsine)bis[tricarbonylnickel(0)].—A solution of fdma (2.8 g, 7.34 mmol) and nickel tetracarbonyl (9 ml, 7.0 mmol) in heptane (10 ml) was stirred magnetically at room temperature for 2 days. The solution was evaporated to dryness (25° (0.1 mm)). The residual red-orange crystalline solid was dissolved in 100 ml of oxygen-free methanol and the solution was filtered through Celite. The filtrate was cooled slowly to −15°. After several days the product crystallized and was collected from the cold mixture, washed twice with 10 ml of cold (−10°) methanol, and recrystallized similarly from 50 ml of methanol. A yield of 1.11 g (45%) of golden flakes, mp 58.0–59.0°, was obtained. An analytically pure sample, whose ir spectrum showed no trace of Ni(fdma)(CO)$_2$, was obtained by recrystallization of a small sample from a large volume of methanol. *Anal.* Calcd for $C_{20}H_{20}As_2FeNi_2O_6$: C, 35.35; H, 2.97. Found: C, 35.17; H, 3.31.

Unlike Ni(fdma)(CO)$_2$, dry solid μ-fdma[Ni(CO)$_3$]$_2$ is stable to air and dissolves without decomposition in oxygen-free carbon tetrachloride. Solutions of the compound are readily decomposed by heat or oxygen.

Dicarbonylferrocene-1,1′-bis(diphenylarsine)nickel(0).—To a magnetically stirred solution of fdpa (3.60 g, 5.62 mmol) in 45 ml of benzene, was added *via* a hypodermic syringe 1.5 ml (12 mmol) of nickel tetracarbonyl. After stirring the solution at room temperature for 1.5 hr, it was refluxed for 1.0 hr, and evaporated to dryness (60° (0.1 mm)). The dark yellow solid residue was extracted with 335 ml of boiling butanol. The extract was filtered hot through Celite on a medium-porosity fritted-glass disk. Slow cooling of the filtrate to room temperature gave the product, which was collected, washed with heptane (two 10-ml portions), and dried *in vacuo*. The yield of the golden needlelike crystals was 3.64 g (4.81 mmol, 86%), mp 204.5–207° dec. *Anal.* Calcd for $C_{36}H_{28}As_2FeNiO_2$: C, 57.12; H, 3.73. Found: C, 57.31; H, 3.98. As a dry solid, Ni(fdpa)(CO)$_2$ may be handled and stored in air, but in solution, it is slowly decomposed by air. It dissolves readily in benzene, chloroform, acetone, and hot higher alcohols.

Diiodocarbonylferrocene-1,1′-bis(dimethylarsine)nickel(II).—A solution of iodine (1.03 g, 4.07 mmol) in 30 ml of dry, oxygen-free benzene was added dropwise to a stirred solution of Ni(fdma)(CO)$_2$ (2.50 g, 4.93 mmol) in 30 ml of the same solvent. At the end of 0.75 hr the deep blue-green solution was set aside at 10° for 30.5 hr. The product, which separated, was collected and washed with cold, *ca.* 10°, benzene (two 10-ml portions) followed by heptane (two 10-ml portions) and dried *in vacuo* to give 1.70 g (57%) of very dark blue-green crystals which crumbled to a red powder at 145–155°, became sticky at 190–195°, and melted completely at 239–244° dec. *Anal.* Calcd for $C_{15}H_{20}As_2FeI_2O$: C, 24.53; H, 2.74; I, 34.55; O, 2.18. Found: C, 25.96, 25.79; H, 2.86, 2.82; I, 34.65; O, 2.20. The complex could not be recovered from solutions in degassed solvents.

Diiodocarbonylferrocene-1,1′-bis(diphenylarsine)nickel(II).—This complex was prepared in a similar manner from (fdpa)Ni(CO)$_2$ and iodine. It was obtained as dark red needles, mp 244.5–246°, in 66% yield. *Anal.* Calcd for $C_{35}H_{28}As_2FeI_2NiO \cdot C_6H_6$: C, 46.42; H, 3.23; I, 23.92; O, 1.51. Found: C, 46.45; H, 3.27; I, 25.24; O, 1.20. The complex could not be recrystallized.

Diiodoferrocene-1,1′-bis(diphenylarsine)nickel(II).—A refluxing solution of Ni(fdpa)(CO)$_2$ (2.50 g, 0.33 mmol) in 125 ml of oxygen-free benzene was treated dropwise, over 20 min, with a solution of iodine (0.84 g, 0.33 mmol) in 35 ml of the same solvent. The dark red solution was refluxed for 0.5 hr after the addition was completed and then set aside at 10° for 5 days. The product was collected, washed with benzene (three 10-ml portions), and dried *in vacuo*. The yield was 2.45 g (77.8%) of very dark red crystals, mp 235–237°. The effective magnetic moment was 3.37 BM at room temperature. *Anal.* Calcd for $C_{34}H_{28}As_2FeI_2Ni$: C, 42.77; H, 2.96; I, 26.58. Found: C, 43.01; H, 3.31; I, 28.71.

Conductance Data.—The values of the molar conductances for dilute solutions (*ca.* 1×10^{-3} *M*) in nitromethane at 25° are listed as follows in ohm^{-1} cm^2 mol^{-1}. Uni-unielectrolytes: [Pd(fdma)$_2$X][PF$_6$]: X = Cl, 86.1; X = Br, 85.5. [Pt(fdma)$_2$X][PF$_6$]: X = Cl, 88.8; X = Br, 87.0; X = I, 86.4. [Pt(fdma)$_2$I][I]: 81.6. Bi-unielectrolytes: [Pd(fdma)$_2$][PF$_6$]$_2$: 187. [Pt(fdma)$_2$][PF$_6$]$_2$: 191.

Nuclear Magnetic Resonance Spectral Data.—Pd(fdma)Cl$_2$: 5.35, triplet, J = 1.7 (1); 5.45, triplet, J = 1.7 (1); 8.64, singlet (3) [CD$_3$NO$_2$]. Pd(fdma)Br$_2$: 5.27, multiplet, 8.05, singlet [CD$_3$NO$_2$]. Pt(fdma)Cl$_2$: 5.45, multiplet (2); 8.17, irregular triplet, $|J_{^{195}Pt-H}|$ = 22 (3) [CD$_3$NO$_2$]. Pt(fdma)Br$_2$: 5.45, multiplet (2); 8.07, irregular triplet, $|J_{^{195}Pt-H}|$ = 22 (3) [CD$_3$NO$_2$]. [Pd(fdma)$_2$Cl][PF$_6$]: 5.36, multiplet (2); 8.13, singlet (3) [CD$_3$NO$_2$]. [Pd(fdma)$_2$Br][PF$_6$]: 5.15, triplet, J = 1.8 (1); 5.43, triplet, J = 1.8 (1); 8.03, singlet (3) [CD$_3$NO$_2$]. [Pt(fdma)$_2$Cl][PF$_6$]: 5.31; triplet, J = 1.7 (1); 5.43, triplet, J = 1.7 (1); 7.15, singlet (3) [CD$_3$NO$_2$]. [Pt(fdma)$_2$Br][PF$_6$]: 5.09, triplet, J = 1.8 (1); 5.43, triplet, J = 1.8 (1); 7.88, singlet (3) [CD$_3$NO$_2$]. [Pt(fdma)$_2$I][PF$_6$]: 5.12, triplet, J = 1.8 (1); 5.43, triplet, J = 1.8 (1); 7.82, irregular triplet, J = 1.8 (1); 7.82, irregular triplet, $|J_{^{195}Pt-H}|$ = 16 (3) [CD$_3$NO$_2$]. [Pt(fdma)$_2$I]I: 5.11, triplet, J = 1.6 (1); 5.42, triplet, J = 1.8 (1); 7.83, singlet (3) [CD$_3$NO$_2$]. [Pd(fdma)$_2$][PF$_6$]$_2$: 5.08, triplet, J = 1.7 (1); 5.32, triplet, J = 1.8 (1); 7.85, singlet (3) [CD$_3$NO$_2$]. [Pt(fdma)$_2$][PF$_6$]$_2$: 5.08, triplet, J = 1.8 (1); 5.28, triplet, J = 1.8 (1); 7.78, irregular triplet, $|J_{^{195}Pt-H}|$ = 20 (3) [CD$_3$NO$_2$]. Ru(fdma)$_2$Cl$_2$: 5.43, triplet, J = 1.6 (1); 5.72, triplet, J = 1.7 (1); 8.32, singlet (3) [DCCl$_3$]. Ni(fdma)(CO)$_2$: 6.0 singlet (2); 8.82, singlet (3) [C$_6$H$_6$].

Visible and Ultraviolet Spectral Data.—The visible and near-uv spectral data were obtained in nitromethane solutions and are listed as ν_{max}, cm^{-1} (ϵ_{max}, M^{-1} cm^{-1}). fdma: 22,700 (153). Pd(fdma)X$_2$: X = Cl, 21,300 (420); X = Br, 20,600 (sh) (530); X = I, 22,000 (3.3×10^3). Pt(fdma)X$_2$: X = Cl, 23,700 (167), 26,800 (384); X = Br, 22,700 (sh) (178), 26,800 (619); X = I, 25,600 (3.65×10^3). Pt(fdpa)X$_2$: X = Cl, 23,300 (227), 26,900 (542). Pd(fdma)$_2$X][PF$_6$]: X = Cl, 20,000 (3.2×10^3), 23,800 (3.1×10^3); X = Br, 21,800 (3.7×10^3). [Pt(fdma)$_2$X][PF$_6$]: X = Cl, 22,500 (sh) (1.2×10^3), 28,200 (2.9×10^3); X = Br, 25,000 (3.36×10^3); X = I, 23,100 (5.16×10^3). [Pt(fdma)$_2$I][I]: 23,100 (5.1×10^3). [Pd(fdma)$_2$][PF$_6$]$_2$: 17,200 (731). [Pt(fdma)$_2$][PF$_6$]$_2$: 22,900 (550).

Infrared Spectral Data (cm^{-1}).—Pd(fdma)Cl$_2$ (Nujol): 3074 (m), 1401 (m), 1320 (w), 1273 (w), 1257 (w), 1201 (w), 1159 (vs), 1036 (s), 1028 (s), 926 (s), 919 (s), 894 (vs), 884 (vs), 824 (s), 800 (w), 623 (w), 599 (m), 517 (m), 509 (m), 494 (m), 437 (w).

The infrared spectra of Nujol mulls of Pd(fdma)Br$_2$, Pd(fdma)I$_2$, Pt(fdma)Cl$_2$, Pt(fdma)Br$_2$, and Pt(fdma)I$_2$ are nearly identical with that of Pd(fdma)Cl$_2$.

Pd(fdpa)Br$_2$ (Nujol): 3105 (w), 3045 (w), 1573 (w), 1478 (m), 1423 (vs), 1309 (w), 1190 (m), 1156 (m), 1149 (m), 1080 (m), 1057 (w), 1034 (w), 1023 (m), 999 (m), 915 (vw), 900 (vw), 880 (w), 850 (w), 846 (w), 827 (w), 818 (m), 811 (m), 745 (vs), 731 (vs), 691 (vs), 618 (vw), 610 (w), 490 (m), 476 (m), 470 (m), 468 (s), 459 (m), 425 (w).

Pd(fdpa)Cl$_2$, Pd(fdpa)I$_2$, and Pt(fdpa)Cl$_2$ give spectra nearly identical with those of the above compounds.

[Pt(fdma)$_2$Br][PF$_6$] (Nujol): 1417 (m), 1382 (m), 1277 (m), 1265 (m), 1206 (m), 1159 (vs), 1066 (vw), 1056 (vw), 1044 (vs), 1037 (m), 1030 (s), 902 (vs), 850 (vb, vs), 616 (s), 600 (m), 576 (w), 548 (vs), 511 (vs), 485 (vs), 426 (w).

The spectra of [Pd(fdma)$_2$Cl][PF$_6$], [Pd(fdma)$_2$Br][PF$_6$], [Pt(fdma)$_2$Cl][PF$_6$], and [Pt(fdma)$_2$I][PF$_6$] are nearly identical with the spectrum of the above complex.

[Pt(fdma)$_2$][PF$_6$]$_2$ (Nujol): 1405 (w), 1321 (m), 1278 (s), 1268 (m), 1202 (m), 1153 (vs), 1063 (m), 1032 (vs), *ca.* 850 (vb, vs), 736 (m), 611 (m), 602 (m), 591 (m), 542 (vs), 502 (vs), 487 (s), 425 (w).

The spectrum of [Pd(fdma)$_2$][PF$_6$]$_2$ is nearly identical with that above.

Ni(fdma)$_2$Br$_2$ (Nujol and Kel-F): 3074 (w), 2980 (vw), 2112 (w), 1404 (m), 1374 (m), 1319 (m), 1266 (m), 1261 (w), 1251 (w), 1199 (w), 1154 (vs), 1056 (w), 1032 (m), 1021 (s), 894 (m), 854 (vs), 840 (sh, s), 815 (s), 616 (w), 595 (m), 577 (m), 494 (s), 487 (sh, m).

Ni(fdpa)I$_2$ (Nujol): 1560 (m), 1478 (s), 1433 (s), 1321 (w), 1308 (m), 1274 (w), 1200 (w), 1185 (m), 1154 (s), 1081 (m), 1077 (m), 1067 (w), 1058 (w), 1044 (m), 1026 (vs), 998 (m), 968 (vs), 916 (vw), 895 (vw), 882 (w), 873 (w), 847 (w), 834 (m), 827 (s), 740 (b, vs), 692 (vs), 678 (m), 674 (m), 599 (w), 495 (m), 489 (m), 471 (s), 457 (m), 416 (w).

Ni(fdma)(CO)$_2$ (cyclohexane): ν(CO) 2010 (s), 1950 (vs). Ni(fdma)(CO)$_2$ (Nujol): 3090 (vw), 2005 (vs), 1984 (vs), 1413 (w), 1320 (m), 1268 (m), 1248 (m), 1195 (m), 1150 (vs), 1067 (w), 1021 (vs), 898 (vs), 880 (m), 860 (s), 842 (vs), 828 (m), 817 (s), 811 (s), 796 (w), 612 (w), 602 (w), 594 (m), 586 (m), 579 (s), 500 (m), 485 (s), 479 (m), 452 (w), 421 (vw).

μ-fdma(NiCO$_3$)$_2$ (cyclohexane): ν(CO) 2070 (s), 2045 (s), 1993 (vs). μ-fdma(NiCO$_3$)$_2$ (Nujol): 2069 (vs), 2000 (b, vs), 1410 (w), 1322 (w), 1272 (w), 1260 (w), 1200 (m), 1170 (m), 1152 (m), 1054 (w), 1027 (s), 903 (s), 897 (sh, m), 865 (vs), 856 (vs), 844 (s), 834 (m), 811 (m).

Ni(fdpa)(CO)$_2$ (CCl$_4$): ν(CO) 2008 (vs), 1949 (vs). Ni(fdpa)(CO)$_2$ (Nujol): 3064 (w), 3049 (w), 2005 (vs), 1944 (vs), 1572 (w), 1564 (w), 1479 (s), 1429 (s), 1306 (m), 1271 (vw), 1194 (w), 1182 (m), 1171 (vw), 1149 (s), 1081 (sh, s), 1064 (m), 1053 (m), 1024 (s), 1021 (m), 998 (m), 968 (vw), 878 (vw), 876 (vw), 848 (vw), 830 (m), 817 (s), 744 (sh), (vs), 739 (vs), 734 (vs), 695 (vs), 691 (vs), 681 (m), 646 (w), 614 (w), 584 (vw), 488 (m), 474 (vs), 464 (vs), 439 (s), 442 (w).

Ni(fdma)(CO)I$_2$ (Nujol): 2054 (vs), 1405 (m), 1321 (m), 1271 (m), 1258 (m), 1202 (w), 1152 (vs), 1062 (m), 1038 (s), 1028 (s), 902 (vs), 895 (s), 888 (m), 875 (vs), 841 (m), 832 (vs), 803 (m), 611 (m), 602 (w), 588 (m), 508 (m), 502 (s), 479 (vs), 451 (vs), 422 (w).

Ni(fdpa)(CO)I$_2$ (Nujol): 2053 (vs), 1572 (w), 1478 (s), 1436 (vs), 1385 (m), 1323 (w), 1308 (w), 1275 (vw), 1202 (vw), 1184 (m), 1152 (m), 1079 (m), 1065 (w), 1044 (m), 1027 (s), 998 (m), 882 (m), 870 (w), 848 (w), 833 (w), 826 (s), 740 (sh, s), 732 (vs), 688 (s), 678 (s), 670 (s), 599 (vw), 500 (m), 470 (vs), 459 (m), 449 (m), 419 (vw).

Results and Discussion

Platinum, Palladium, and Ruthenium Compounds.—The relatively insoluble complexes M(fdma)X$_2$ (M = Pd; X = Cl, Br) react with excess of the diarsine fdma in lower alcohols and nitromethane to give intensely red solutions. Solutions of the analogous platinum species (M = Pt; X = Cl, Br, I) are orange. By suitably adjusting the experimental conditions, *viz.*, by having an excess of any of the halide ions and the stoichiometric amount of the precipitating agents, salts of the deep red Pd(fdma)$_2$X$^+$, yellow Pt(fdma)$_2$X$^+$, blue Pd(fdma)$_2$$^{2+}$, and orange Pt(fdma)$_2$$^{2+}$ cations were isolated with large anions such as B(C$_6$H$_5$)$_4$$^-$, PF$_6$$^-$, ClO$_4$$^-$, etc. With the exception of [Pt(fdma)$_2$I]I which is a uni-univalent electrolyte in nitromethane, no "M(fdma)$_2$X$_2$" species were isolated. However, the orange diamagnetic Ru(fdma)$_2$Cl$_2$, prepared from RuCl$_3$·3H$_2$O and excess fdma in refluxing ethanol, is a nonelectrolyte in nitromethane. The salts [M(fdma)$_2$X][PF$_6$] and [M(fdma)$_2$][PF$_6$]$_2$ gave molar conductances in nitromethane consistent[9] with their formulations as uni-uni- and bi-univalent electrolytes. Conductometric titrations of the [M(fdma)$_2$][PF$_6$]$_2$ with tetraalkylammonium halides in nitromethane gave equivalence points corresponding to the uptake of 1 equiv of halide ion. These facts suggest that the following equilibria are present in these solutions

$$\mathrm{M(fdma)X_2 + fdma \rightleftarrows M(fdma)_2X^+ + X^-} \qquad (1)$$

$$\mathrm{M(fdma)_2X^+ \rightleftarrows M(fdma)_2{}^{2+} + X^-} \qquad (2)$$

Because of the uncertainties in the values of their ionic conductances, no attempts were made to obtain from conductance data the degrees of dissociation of the M(fdma)$_2$X$^+$ species and the equilibrium constants of the above equilibria.

In contrast, the complexes M(fdpa)X$_2$ (M = Pd; X = Cl, Br, I and M = Pt; X = Cl) do not react with an excess of fdpa. However, these complexes react with an excess of fdma in alcohols to produce fdpa quantitatively and intensely colored solutions which are identical with those obtained from the M(fdma)X$_2$ complexes.

These results, however, show conclusively that fdma, like diars,[9,10] stabilizes both four- and five-coordinate cationic complexes of palladium and platinum.

The spectra of the Pd(fdma)$_2$X$^+$ species are quite characteristic and have a very intense absorption between 20,000 and 24,000 cm^{-1}. The spectrum of the dication Pd(fdma)$_2$$^{2+}$ is also quite characteristic and its deep blue color is due to a moderately intense absorption at 17,200 cm^{-1}. The platinum species have similar spectra but the absorption maxima occur at higher energies, 23,100–25,000 and 22,800 cm^{-1}, respectively. The solution and Nujol mull spectra are very similar, which indicates that the complexes are also four- and five-coordinate in the solid state. The nmr spectra for the complexes M(fdma)X$_2$, M(fdma)$_2$X$^+$, and M(fdma)$_2$$^{2+}$ in deuterionitromethane exhibit the cyclopentadienyl ring proton resonances characteristic of an AA'BB' pattern in which J_{AB} and $J_{\mathrm{A'B}}$ (or $J_{\mathrm{AB'}}$) are equal and considerably smaller than the chemical shift between A and B. The resonances of the methyl groups, which are shifted considerably downfield with respect to those of the uncomplexed ligand, appear as singlets for the M(fdma)$_2$X$^+$ (M = Pd, Pt) salts, as a

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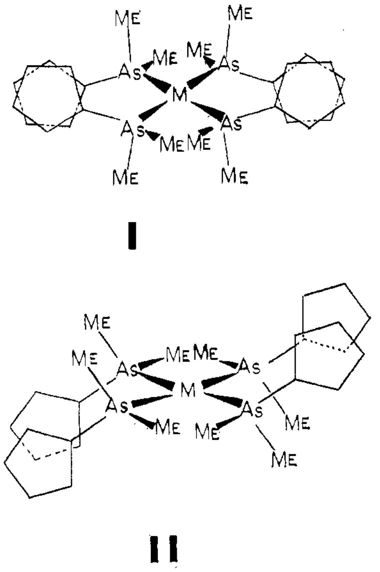


Figure 1.—Schematic representations of the two limiting structures for the cationic complexes $\mathrm{M(fdma)_2^{2+}}$. Structure I for which the angle of twist between the two five-membered rings, ω, is 36° is shown as the meso form. Structure II has $\omega = 0°$.

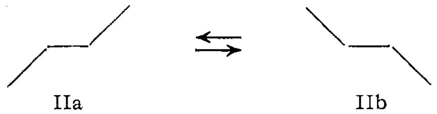
singlet for $\mathrm{Pd(fdma)_2^{2+}}$ but an irregular triplet for $\mathrm{Pt(fdma)_2^{2+}}$ ($J_{^{195}\mathrm{Pt-H}} = 20$ Hz), and as singlets for $\mathrm{Pd(fdma)X_2}$ or irregular triplets for $\mathrm{Pt(fdma)X_2}$ ($J_{^{195}\mathrm{Pt-H}} = 22$ Hz). The spectra are in accord with those expected for electron-withdrawing substituents on the ferrocene rings, namely, pronounced differences between the $H_{2,5}$ and $H_{3,4}$ resonances and considerable deshielding of both sets of resonances with respect to the protons of ferrocene. It has been generally assumed and recently confirmed[11] that, with the exception of vinylic substituted ferrocenes, the lower field triplet can be assigned the protons in the 2 and 5 ring positions and the higher field triplet the protons of the 3 and 4 positions. In this study the positions of the higher field triplet ($H_{3,4}$) remain fairly constant at *ca.* τ 5.4 for $\mathrm{M(fdma)_2X^+}$ and at τ 5.3 for $\mathrm{M(fdma)_2^{2+}}$. The lower field resonance depends on the metal, the charge, and the nature of the bound halide.

Like those for $\mathrm{M(fdma)X_2}$, the spectra of the $\mathrm{M(fdma)_2X^+}$ and $\mathrm{M(fdma)_2^{2+}}$ salts are too simple for static systems. The absence of platinum satellites on the methyl resonances in the spectra of the $\mathrm{Pt(fdma)_2X^+}$ complexes indicates that, in part at least, a rapid chemical exchange is giving rise to time-averaged and, hence, simplified spectra. This exchange is probably of the type

$$2\mathrm{Pt(fdma)_2X^+} = \mathrm{Pt(fdma)_2^{2+}} + \mathrm{Pt(fdma)X_2} + \mathrm{fdma} \qquad (3)$$

However, the presence of platinum satellites on the methyl resonances of $\mathrm{Pt(fdma)X_2}$ and $\mathrm{[Pt(fdma)_2][PF_6]_2}$ proves, for solutions of these species in which equilibria of types 1–3 are absent, that the averaging process which gives the simple spectra must be intramolecular.

The diamagnetic dications must have a structure which is based on a planar array of arsenic atoms about the central metal. The ligands in this structure, on the basis of examination of molecular models, would be unable to adopt a configuration in which the rings were eclipsed and in which the two iron atoms, the four arsenic atoms, and the central metal atom are coplanar. There are, however, two limiting structures which these complexes could adopt. These are shown in Figure 1. Stepped structures such as II have been observed previously for metal complexes which are sterically overcrowded.[12] Both limiting structures have quasi-axial and -equatorial methyl groups and four nonequivalent cyclopentadienyl protons. The two most probable mechanisms by which intramolecular averaging could occur are (i) a twist mechanism which interconverts the pairs of optical isomers M-*d*-(fdma)-*l*-(fdma)$^{2+}$ $\rightleftarrows$ M-*l*-(fdma)-*d*-(fdma)$^{2+}$ and M-*ll*-$\mathrm{(fdma)_2^{2+}}$ $\rightleftarrows$ M-*dd*-$\mathrm{(fdma)_2^{2+}}$ based on structures related to I and (ii) a mechanism which interconverts IIa and IIb shown schematically as



Both of these processes, as well as those for inversions of intermediate structures, will interconvert the quasi-axial and -equatorial groups and will average the pairs of ring protons $H_{2,5}$ and $H_{3,4}$. Similar processes can be envisaged for just one chelated ring in the species $\mathrm{M(fdma)X_2}$.

Nickel Compounds.—Attempts to prepare nickel complexes of the types $\mathrm{Ni(fdpa)X_2}$ and $\mathrm{Ni(fdma)X_2}$ (X = Cl, Br, I) produced some unexpected results. The reaction of anhydrous nickel bromide with fdma in hot butanol gave $\mathrm{Ni(fdma)_2Br_2}$ as red-brown paramagnetic ($S = 1$) crystals under a wide variety of experimental conditions. This complex, presumably, has a pseudooctahedral structure. The reaction of anhydrous nickel iodide with fdpa in refluxing *tert*-butyl alcohol gave dark red-brown paramagnetic crystals ($S = 1$) of $\mathrm{Ni(fdpa)I_2}$. This complex most likely has a distorted pseudotetrahedral structure. It could also be obtained by the reaction of the stoichiometric amount of iodine with $\mathrm{Ni(fdpa)(CO)_2}$ in refluxing benzene. In contrast, the analogous reaction with bromine gave essentially quantitative amounts of $\mathrm{NiBr_2}$ and fdpa. If, however, the dicarbonyls $\mathrm{Ni(fdpa)(CO)_2}$ and $\mathrm{Ni(fdma)(CO)_2}$ are treated with equivalent amounts of iodine at room temperature, dark red crystals of $\mathrm{Ni(fdpa)(CO)_2I_2}$ and dark blue crystals of $\mathrm{Ni(fdma)(CO)I_2}$ separate from the reaction mixture. These complexes show a single sharp absorption in the terminal CO stretching region at 2053 and 2054 cm^{-1}, respectively. The complexes underwent partial decomposition during attempts to recrystallize them from hot solutions; fresh solutions in benzene display sharp absorption at 2055 cm^{-1}. These

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complexes are clearly examples of carbon monoxide bonded to nickel in a +2 formal oxidation state.

Acknowledgments.—We gratefully acknowledge financial support by the National Science Foundation (Grants GP-6672 and GP-11001) and the American Chemical Society for a Petroleum Research Fund Graduate Fellowship, 1968–1969 (J. J. B.).

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The Stereochemistry of Four-Coordinate Bis(imidodiphosphinato)metal(II) Chelate Complexes

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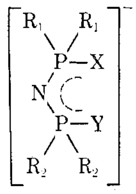
Received March 2, 1970

A series of bivalent metal complexes of the type $[X\text{-}PR_2NPR_2\text{-}X]_2M^{II}$ have been synthesized: M = Fe, Co, Ni, Zn, Pd, and Pt (X = S, R = CH_3, C_6H_5), M = Co, Ni (X = NH, R = C_6H_5), M = Co(X = O, R = C_6H_5). The sulfur complexes of Fe(II), Co(II), and Ni(II) include the first characterized tetrahedral four-coordinate complexes of these metals containing an MS_4 core. The ligand field spectral and magnetic data are discussed.

Introduction

There has been considerable interest in determining what factors influence the stereochemistry of four-coordinate metal(II) chelate complexes. The utility of employing bidentate chelates in which either the donor functions or the degree of steric overcrowding at the donor sites can be changed has been elegantly demonstrated.[3-8] Monomeric sterically unencumbered[7] chelates of nickel(II) with various donor sets have been found to be planar while those which are sterically overcrowded are usually[9,10] either fully tetrahedral ($S = 1$) or are involved in a planar ⇄ tetrahedral equilibrium. A series of β-difunctional ligands of the type **1**, where $R_1 = R_2 = CH_3$, C_6H_5 and X = Y = S, O, NH, have been synthesized.[11] This potentially large and versatile set of ligands can be named from the generic root "imidodiphosphinate" to simplify the collective nomenclature of the resulting metal complexes. This ligand system is ideally suited to studying the effect of the variation of the donor sets X and Y and the terminal substituents R_1 and R_2. While the earlier reports [11a] indicated that some metal complexes of these ligands could be prepared, no other information was given. This communication deals with the synthesis of bis-chelate complexes of the "imidodiphosphinates" and the establishment of their structures in both the solid and solution phases.



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Experimental Section

General Data.—Microanalyses were performed by Midwest Microlab Inc., Indianapolis, Ind., and at MIT by Mrs. Nancy F. Alvord. Molecular weights were determined osmometrically in dry benzene, toluene, or ethanol-free chloroform.

All melting points were determined using a hot-stage microscope.

The magnetic susceptibilities of the solid samples were determined using $HgCo(SCN)_4$ as a calibrant[12] either by the Gouy method, in double-ended glass Gouy tubes, or by the Faraday method. The diamagnetic susceptibility for $K[((C_6H_5)_2PS)_2N]$ was determined directly by the Gouy method, while those for the other ligands were obtained using Pascal's constants.[13] The values used were the following ($\times 10^{-6}$): $((C_6H_5)_2PS)_2N^-$, 198.8; $((CH_3)_2PS)_2N^-$, 188.4; $((C_6H_5)_2PNH)_2N^-$, 185.8; $((C_6H_5)_2PO)_2N^-$, 178.0. The magnetic susceptibilities of samples in solution were determined by the Evans[14] method.

Electronic spectra were recorded on a Cary (Model 14) spectrometer in dry methylene chloride. Infrared spectra were recorded on a Perkin-Elmer 337 spectrometer. Nuclear magnetic resonance spectra were recorded on Varian Associates T-60 and A-60 spectrometers.

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