

tetramethyl-1,4,8,11-tetraazacyclotetradecane) has been assigned as the $(d_{xy})^2 \rightarrow (d_{xy})^1(d\pi)^1 [d\pi = (d_{xz}, d_{yz})]$ transition (${}^1A_{1g} \rightarrow {}^1E_g$), which is vibronically coupled to the $A_{2u}(\text{Ru}-\text{O})$ vibrational stretching mode. This kind of vibronic structured d-d transition that is also commonly encountered in other d^2 *trans*-dioxo complexes¹⁰ should be regarded as an essential characteristic spectral feature for *trans*-Ru(VI)-dioxo species. The relative insensitivity of this 400-nm band of *trans*-[Ru^{VI}LO₂]²⁺ [L = (NH₃)₄, TMC,

(bpy)₂] with the nature of L⁹ is in accordance with its formulation as the electronic transition is primarily within the $d\pi$ levels. The observed decrease in the $\nu(\text{Ru}-\text{O})$ stretch ($\sim 620-650 \text{ cm}^{-1}$) in the excited state clearly indicates a weakening of the Ru-O bond in these dioxo species upon UV-vis excitation. This result together with its high oxidizing power ($E_1^\circ = 1.25 \text{ V}$ vs. NHE) strongly implies the potential usefulness of these species as powerful photochemical oxidative catalysts.

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Preparation, Characterization, and Chemistry of Activated Cobalt

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When anhydrous cobalt chloride or iodide was treated with solutions of lithium or potassium naphthalide in glyme at low temperature, slurries of very finely divided cobalt metal were obtained. The solid material obtained was a complex mixture of cobalt microparticles intimately mixed with the alkali halide coproduct and a carbonaceous material from solvent decomposition. X-ray photoelectron spectroscopy and the materials' chemical properties confirm the presence of metallic cobalt. The cobalt powder by itself or on alumina support was found to be a methanation and Fischer-Tropsch catalyst. Under some conditions high selectivity for formation of methanol and ethanol or methyl acetate was observed. Iodobenzene reacted with cobalt powders to give a low yield of biphenyl, while benzyl bromide gave a 63% yield of benzyl. Geminal dihalides such as dichlorodiphenylmethane reacted to give high yields of the unsaturated coupling product, tetraphenylethylene. Cobalt powders converted nitrobenzene to azobenzene in 37% yield.

Introduction

Highly dispersed and reactive metal powders have commanded a great deal of interest for their applications in catalytic and stoichiometric chemical syntheses as well as their uses in materials science. Numerous methods exist for the preparation of metal powders. Hydrogen reduction of metal oxides is one common method^{37,54} as is reduction of metal salts by other chemical means.^{54a,55} Pyrolysis of metal carboxylate derivatives has been used in some cases,^{54a,56} and condensation of metal atom vapors in a frozen solvent or other matrix^{25,26,42,57} is one of the more modern methods. A far-ranging review of unsupported metal particles and their preparation, reactivity, and physical properties has appeared.²⁷

Since 1972 we have published several reports describing convenient methods for the generation of reactive metal slurries in ethereal solvents and their use in organic synthesis.¹⁻²² Our

research on reactive cobalt was first reported in detail only recently.^{21,22} We have since developed a modified preparation for activated cobalt that gives a more reactive material, which we have used to prepare Co₂(CO)₈.¹ Further details of the nature of this new form of cobalt are the subject of this report. Included are the results of our attempts to form carbon-carbon bonds from organic halides using activated cobalt and the results of treating aromatic nitro compounds with activated cobalt.

Cobalt is an important constituent of some Fischer-Tropsch catalysts and, not surprisingly, our activated cobalt also displayed modest catalytic activity, which we shall describe.

Results

Preparation and Properties of Active Cobalt Powders. We have used two general approaches in preparing cobalt powders. The first method, reported previously,^{21,22} used a slight excess of lithium, usually 2.1-2.3 equiv in glyme (1,2-dimethoxyethane), to reduce anhydrous cobalt chloride to a dark gray powder, **1**. Use of cobalt bromide or iodide gave a somewhat less reactive form of **1**.²² These reductions also required the addition of a catalytic quantity of naphthalene, which acted as an electron carrier. This greatly shortened the time necessary for reduction and improved the reactivity of the metal. Slurries of **1** were very reactive toward strongly electrophilic aryl halides such as C₆F₅X (X = Br, I), yielding the solvated species Co(C₆F₅)₂ and CoX₂. The former was isolated as the bis(triethylphosphine) adduct. Attempts to extend this reaction to less reactive aryl halides met with disappointing results. In order to increase the reactivity of our cobalt powders, a new method of preparation was devised using a modification of a previously reported method.^{56b} This reactive cobalt, **2**, was prepared by dissolving lithium in glyme containing

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excess naphthalene. Excess naphthalene was used to ensure rapid and complete dissolution of all the lithium. Naphthalene radical anion is capable of slowly reductively cleaving ethereal solvents such as glyme, making it desirable to prepare and use such solutions as rapidly as possible. Use of the more polar solvent THF in place of glyme had some advantages, e.g., more rapid formation of naphthalide radical anion and improved solubility of the radical and cobalt halide. Unfortunately, THF was even more rapidly decomposed by naphthalide radical anion and/or active cobalt. Consequently, very few of our experiments used this solvent. Additions of cobalt chloride or iodide to cold glyme solutions of lithium naphthalide resulted in rapid formation of black-gray cobalt metal, **2**. Addition of dry cobalt halides or their suspensions in glyme gave a product with similar properties and reactivity.

In contrast to **1**, which rapidly settled out of suspension to give a clear solution, **2** remained suspended in an opaque black solution. Centrifugation of a suspension of **2** gave a black solution and sediment. Washing the sediment with fresh glyme produced a black solution even after several repetitions. Washing the sediment with less polar solvents, such as diethyl ether or light alkanes, gave clear or slightly cloudy colorless solutions. Switching back to glyme regenerated the black solutions. This suggests that an intimate mixture of cobalt microparticles and lithium chloride exists. As fresh glyme is added, part of the lithium chloride matrix is dissolved, liberating more cobalt particles, which color the suspension.

When dry, **2** was pyrophoric and almost completely nonferromagnetic; i.e., very little was attracted to a strong bar magnet. This was in marked contrast to **1** or commercial samples of 325-mesh cobalt powders, which were not pyrophoric and were strongly attracted to a magnet held in their vicinity. Qualitatively, the magnetic properties of **2** were suggestive of superparamagnetism.²³ Debye-Scherrer photographs from samples of **2** showed no, or at best weak and diffuse, lines that could not be assigned to any common modification of metallic cobalt. This suggested that the size of the cobalt crystallites was less than approximately 30 Å. Broadening of X-ray lines due to reduction of crystallite size is usually observed when the crystallite size falls between 30 and 500 Å.²⁴ Below approximately 30 Å broadening can be so severe as to render a line unobservable. Since a particle would have to be greater in size than 100–300 Å to support more than one magnetic domain, superparamagnetic behavior might be expected on the basis of our estimate of the crystallite size in **2**. Heating **2** to 300 °C resulted in a very strongly ferromagnetic material.

Nickel powders prepared by codeposition of nickel atoms and pentane show interesting magnetic properties,²⁵ which may be compared with our results. Depending on the length of time the cocondensate was annealed at –130 °C, nonferromagnetic or ferromagnetic nickel powders could be obtained after removal of the pentane. Both ferro- and nonferromagnetic nickel powders contained crystallites of similar sizes, which were well below 100–300 Å and thus of necessity contained single-domain particles. In both cases, the nickel crystallites were coated with a carbonaceous residue from reaction of the pentane with the metal. The thickness of this layer depended on the annealing time and determined the magnetic properties of the metal. Thick coats derived from lengthy annealing or highly dilute cocondensates prevented interdomain exchange, producing nonferromagnetic material. More concentrated cocondensates that were annealed gave thin coats, which allowed exchange to occur, producing ferromagnetic powders. In this same work, cobalt atom vapor cocondensed with pentane, giving powders that were always ferromagnetic regardless of the annealing time. Scott and co-workers were also able to prepare nickel powders with interesting magnetic properties by

the metal atom vaporization technique.²⁶ In their work, superparamagnetism was expected on the basis of crystallite size; however, quantitative measurements showed a considerable ferromagnetic contribution.

The apparent lack of gross ferromagnetism in **2** can qualitatively be explained, by analogy to the nickel systems, on the basis of thick carbonaceous layers coating the individual crystallites. From elemental and surface analyses, **1** and **2** are known to contain significant amounts of carbon. In the cobalt powders prepared here, the overcoat is undoubtedly thicker than in the case of nickel atom vapor studies due to the higher temperatures and more reactive solvent used. The onset of obvious ferromagnetism in **2** annealed at 300 °C probably reflects disruption of the carbonaceous overlayer and concomitant crystallite and domain growth. Finally, we note that **2** appears to consist of cobalt microparticles dispersed in an alkali-metal halide matrix, which also serves to dilute and isolate the magnetic centers from one another. Quantitative determination of magnetic properties would help establish the contribution, if any, that ferromagnetism makes in **2**.

Debye-Scherrer films obtained from several samples of **2** prepared by lithium reductions were remarkable in their lack of any readily identifiable phases. A sample of **2** annealed at 300 °C produced a few weak lines assignable in part to cubic cobalt. Agreement with literature data for cubic cobalt was not very satisfactory, and this identification was tentative. Also conspicuously absent from these films were lines expected for lithium chloride, which was known to be present in the sample from elemental analysis.

In contrast, **3** prepared by potassium reduction gave a diffraction pattern in good agreement with that expected for potassium chloride. In this case as well, no cobalt patterns were found. These X-ray data were consistent with diffraction from very small crystallites, less than 30–100 Å, or diffraction from an amorphous material. The latter explanation seemed unlikely since, to our knowledge, with the exception of thin films,^{27,28} no nonalloy metallic glasses have ever been prepared. In several other cases finely divided metals prepared by our techniques have failed to show metal lines in their X-ray powder patterns.^{13,29}

When treated with hydrochloric acid, **2** dissolved rapidly, evolving approximately 17% more gas than expected based on the cobalt present in the sample. The excess gaseous products were found to be composed of low-molecular-weight hydrocarbons, chiefly methane, with some C₂'s and C₃'s. The hydrocarbons are no doubt formed by hydrolysis of the carbonaceous residues resulting from solvent decomposition during reduction. Alcohols or other oxygenated products were probably also extant; however, no attempt was made to identify them. Since no appreciable amounts of solid residues were recovered after hydrolysis, the carbonaceous overlayer was probably composed chiefly of hydrocarbon rather than graphitic fragments.

Reactions of Cobalt Powders: Carbon Monoxide. We have previously reported on the use of **2** for the preparation of Co₂(CO)₈.¹ A slurry of **2** in hexanes reacted with CO at 1000–1400 psi at 80–110 °C to give cobalt carbonyl in yields up to 79%. We have since investigated the reactivity of dry **2** toward CO. Despite the consumption of considerable quantities of CO, very little Co₂(CO)₈ formed. Rather, **2** catalyzed the disproportionation of CO into CO₂ and carbon. Cobalt is considered to bind CO in a nondissociative manner at room temperature; however, at higher temperatures the adsorption becomes dissociative.^{30,31} Adsorption of CO on polycrystalline cobalt films is an exothermic process^{32,33} and is dependent on coverage and the type of binding

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site.³³⁻³⁵ At higher pressures such as those used in our experiments, the concentrated heat of adsorption might have been sufficient to initiate the disproportionation reaction. External heating failed to sustain the reaction, and attempts to duplicate this experiment with smaller samples of **2** failed even when the sample was heated. Catalytic CO disproportionation is apparently a short-lived phenomenon requiring a critical mass of cobalt to effect rapid sample heating. When a small amount of cobalt was used, the heat of adsorption was probably insufficient to initiate disproportionation, and externally supplied heat could only be applied slowly at a rate competitive with deactivation of the catalytic sites. Elemental analyses of the black solid recovered after the disproportionation reaction showed that **2** had suffered a great increase in its carbon content. Almost no change was found in the relative amounts of other elements including oxygen (assumed by difference). Carbon dioxide was qualitatively identified in the gases removed from the bomb.

These results provide an interesting contrast to a study of CO disproportionation on the 10 $\bar{1}2$ plane of single-crystal cobalt.³⁶ In this work it was found that CO was adsorbed in a nondissociative manner at room temperature. When this system was heated to 500 K, desorption and dissociation of CO was observed. Since no O 1s Auger signal was observed at the completion of the thermal treatment and no CO₂ was observed by mass spectroscopy, it was postulated that the adsorbed surface oxygen had diffused into the bulk to give a cobalt oxide. Low-energy electron diffraction data were consistent with the growth of Co₃C on the metal surface. When completely covered with Co₃C, the surface was no longer active for CO disproportionation. In another study CO did undergo disproportionation over a cobalt-silica catalyst at 300 °C.³¹

The black material recovered from our study did not have an increased amount of oxygen and had far too much carbon to be composed of Co₃C or other known cobalt carbide phases. In addition, when carburized **2** was dissolved in acid, most of the carbon was recovered as a black powder. We interpret these results as showing **2** to be catalyzing rapid CO disproportionation to give surface carbon or perhaps cobalt carbide and CO₂. The activity of the catalytic sites was rapidly destroyed by either thermal decomposition of the sites, "poisoning", or their decreased accessibility due to the buildup of surface carbon or unstable carbide phases. Carbides, if formed at all, were rapidly decomposed to unreactive carbon as shown by the composition and quantity of gases evolved and by the recovery of much of the excess carbon after hydrolysis. When hydrolyzed, carburized **2** evolved slightly less gas than **2**. Similar proportions and types of hydrocarbons were found in both cases. Examples of the formation of cobalt carbide³⁷ and graphitization of cobalt³⁸ by treatment of cobalt with CO at elevated temperatures are known.

Synthesis Gas. Some of the earliest Fischer-Tropsch catalysts employed cobalt species as key components.³⁹ We have found evidence for Fischer-Tropsch chemistry catalyzed by **2** in a variety of forms. In nearly all cases, methane was the dominant product. Under batch reactor conditions at elevated pressure and temperature, **2** had a rather limited lifespan for catalysis of hydrocarbon formation, due in part to sintering and/or coking. Recovered catalysts were also strongly ferromagnetic. Catalytic activity was not especially high and amounted to 4-7 mol of methane/mol of cobalt. It is important to note that hydrolysis of samples of **2** gave less than 0.1 mol of methane/mol of cobalt. In the batch reactor at higher pressures and lower H₂:CO ratios, **2** gave less methane and greater amounts of higher hydrocarbons. Some oxygenated hydrocarbons were formed but usually only in trace amounts. A striking exception was found in the liquid phase

isolated from one reaction (method 1), where a significant amount of methyl acetate formed almost to the exclusion of other oxygenates. The possibility that this product is formed by reaction with the solvent is currently under study. Esters are known to form with use of cobalt catalysts;^{40,41} however, if methyl acetate is in fact formed from synthesis gas rather than solvent reactions, the selectivity of this catalyst is most peculiar.

In an attempt to increase the catalyst's useful life, cobalt metal powders were dispersed on alumina in two ways. In the first, cobalt chloride was reduced with lithium naphthalide in a glyme slurry of alumina. This rather cumbersome procedure gave a catalyst with low activity for the formation of methane and C₄ hydrocarbons. The low activity of this catalyst, which was used in the absence of solvent, was probably due to the lack of free surface area available in the unagitated reactor. This may also be responsible for the unusual product distribution, where methane and C₄ species were the main volatile products.

In another experiment, **2** was dispersed on alumina by mixing glyme slurries of the two materials. A suspension of this catalyst in glyme reacted at elevated temperature and pressure to give methanol and ethanol as the major liquid-phase products. This catalyst also had a relatively limited active lifespan of a few hours, ultimately producing approximately 10 mol of methanol/mol of cobalt and 2 mol of ethanol/mol of cobalt.

We have also obtained data from the reaction of synthesis gas over cobalt catalysts in a flow reactor at 1 atm. By mixing glyme slurries of alumina and **2**, a catalyst was formed that was active primarily for methane formation. Methane and C₂ hydrocarbons were first formed in appreciable amounts at 540 K. At this temperature, these products may originate from hydrogenation and desorption of the carbonaceous portion of **2**. Methane was observed even at room temperature. Hydrocarbon production quickly tapered off at higher temperatures until ca. 590 K, when methane production resumed at a sustained high level. The catalyst prepared by reducing cobalt chloride in glyme in the presence of alumina was also active at a slightly lower temperature for the methanation reaction at 1 atm. This particular catalyst did not show the low-temperature hydrocarbon production observed with the previously described catalyst. This catalyst also gave trace amounts of C₂ hydrocarbons.

Nitro-Substituted Aromatics. The high oxophilic nature of the cobalt powders was readily demonstrated by its reaction with nitrobenzene at room temperature. Reductive coupling was found to be quickly effected by **2** to give azo and azoxy derivatives. Nitrobenzene reacted with **2** to give azobenzene in yields up to 37%. In some cases small amounts of azoxybenzene were also formed.

With 1-iodo-4-nitrobenzene **2** reacted to give low yields of 4,4'-diiodoazoxybenzene and 4,4'-diiodoazobenzene. Numerous other products that were not readily separated were also formed in this reaction. The expected C-C coupling product, 4,4'-dinitrobiphenyl, was not observed. If formed, it probably reacted further via the nitro groups to afford polymeric materials.

The reaction of 1,2-dinitrobenzene with **1** was attempted. Analysis of the reaction mixture showed only unreacted 1,2-dinitrobenzene, but recovery of this compound was incomplete. We are continuing to explore the general utility of these powders as reductive coupling agents.

Aryl and Alkyl Halides. Iodopentafluorobenzene reacted with **2** to give the solvated oxidative-addition products CoI₂ and Co-(C₆F₅)₂ or Co(C₆F₅)I. The compound Co(C₆F₅)₂·2PEt₃ was isolated in 54% yield by addition of triethylphosphine to the solvated materials. This compound had been prepared previously in comparable yield from **1** by a similar procedure^{21,22} and from the reaction of cobalt atom vapor with C₆F₅I.⁴²

Attempts to prepare Co(C₆F₅)₂(η⁶-C₆H₅CH₃) by replacing the glyme in which **2** was prepared with toluene were unsuccessful.

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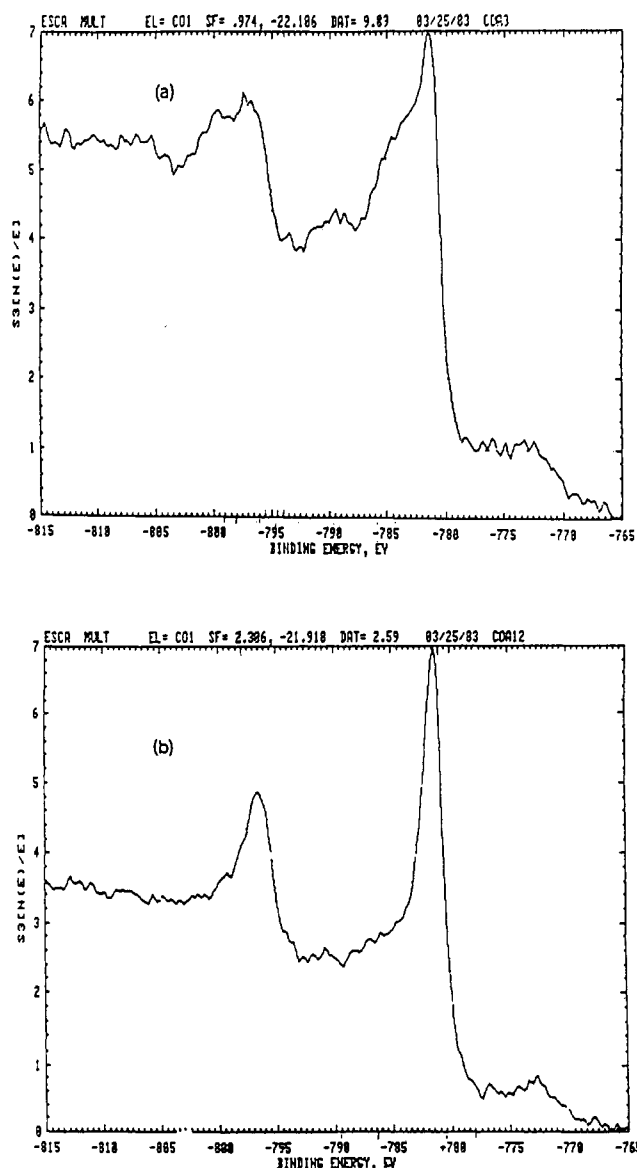


Figure 1. Co 2p X-ray photoelectron spectra of **2** from a potassium reduction of cobalt chloride: (a) as received; (b) as ion sputtered.

From the reaction of **2** with iodobenzene at reflux a low yield of biphenyl was obtained while much of the aryl halide remained unchanged. Reaction of **1** with iodobenzene was similar with respect to the amount of unreacted starting material; however, no biphenyl was formed.

Reactions of **2** with alkyl halides were generally more successful for C–C bond formation. For example, bibenzyl was formed in good yield from the reaction of **2** with benzyl bromide. Dichlorodiphenylmethane and **1** reacted to give tetraphenylethylene in 63% yield. Similarly, diiodomethane reacted with **1** to give ethylene.

Surface Analysis. A specimen of **3**, prepared by reducing cobalt chloride with potassium naphthalide in diglyme, was studied by X-ray photoelectron spectroscopy. Binding energies, spin-orbit coupling data, and compositional data are tabulated in Table IV. The binding energies of the most intense Co 2p peaks at 776.8 and 792.4 eV were consistent with zerovalent cobalt although the observed spin-orbit coupling was somewhat large compared to literature values.^{43,44} Shoulders and shake-up satellites were also observed that were consistent with cobalt oxides⁴⁵ (see Figure 1).

The O 1s signal agreed with that expected for cobalt(II) oxide.⁴⁵ Potassium 2p and Cl 2p peaks were unremarkable. After sputtering, two sharp, clearly defined peaks for metallic cobalt were observed and the cobalt oxide peaks, their associated shake-up peaks, and the O 1s peaks were greatly attenuated. The lack of shake-up peaks associated with the intense Co 2p peaks at 776.8 and 792.1 eV after sputtering served to further corroborate our assignment of these peaks to metallic cobalt.^{43–45} Sputtering is known to cause reduction of cobalt oxides to zerovalent cobalt.⁴⁵ We feel that this is unlikely to invalidate our conclusion that the metal in **3** is, for the most part, in the form of metallic cobalt to start with. Sputtering shows much of the oxygen to be on the surface, and the amount of carbon is also found to decrease with depth while the amounts of the other elements increase, reaching the limiting concentrations shown in Table IV.

To summarize, **3** appears to be composed largely of metallic cobalt in an alkali-metal halide matrix with some carbonaceous matter and cobalt oxide or possibly hydroxide on the surface.

Discussion

The highly reactive forms of cobalt described are very complex materials as shown by their physical properties and analyses. This is to be expected since metal powders prepared even under the relatively well-defined conditions used in metal atom vapor work can be quite complex.²⁷ The use of more reactive solvents (e.g., ethers) and higher temperatures (e.g., room temperature to -78°C) than those used in metal atom work are, in part, responsible for the complexity of **1**, **2**, and **3** and lead to metal dispersions that are quite different from those obtained from the metal atom technique.

The cobalt powders have been shown to exhibit catalytic activity for the Fischer–Tropsch reaction. Although methanation is the dominant reaction and catalyst longevity is a problem, these results are exciting. Dispersal of the cobalt powders on alumina was of some benefit in improving the catalyst's longevity. It is possible that selectivity of the catalyst toward higher hydrocarbons or oxygenated hydrocarbons might be improved by judicious choice of support and preparative details. Cobalt and other metals prepared by our method may be useful as catalysts for other transformations such as hydroformylation, hydrogenation, reformation, and so on. The possibility of custom designing bimetallic catalysts by coreduction of two metal halides is particularly exciting, and studies designed to test these suggestions are in progress. The usefulness of bimetallic SMAD (solvated metal atom dispersion) catalysts for olefin hydrogenation has recently been demonstrated by Klabunde and Imizu.⁴⁶

Cobalt powders were surprisingly reactive toward nitro groups, forming azo and azoxy derivatives via reductive coupling. The reaction of active cobalt with 1-iodo-4-nitrobenzene gave N–N coupling products but no C–C coupling products. In the same reaction, with use of active copper, however, C–C coupling was the dominant reaction, giving good yields of 4,4'-dinitrobiphenyl.⁴⁷ The cobalt-containing product of these reactions has not been identified; however, it is likely to be a cobalt oxide. Reduction of aromatic nitro compounds with zinc in alkaline methanol is the classic route to aromatic azo compounds.⁴⁸ Lead powders have also found application in the preparation of azoxy derivatives from the corresponding nitro-substituted aromatic precursors.⁴⁹ Although the mechanisms of zinc or lead reductions are probably quite different from that of cobalt, it is instructive to consider the enthalpy of formation of the simple metal monoxides, which are in the order of $\text{Zn} \gg \text{Co} \gg \text{Pb} \gg \text{Cu}$.^{50,51} This provides a

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Table I. Production from the Reaction of Synthesis Gas over Cobalt Powders

method	catalyst	pressure, psi	H ₂ :CO	analyzed phase	% CH ₄	% C ₂ H ₄	% C ₂ H ₆	% C ₃ H ₆	% C ₃ H ₈	% CH ₃ OH	% C ₄ ^d	% CH ₃ COOCH ₃
1	2	790	3:1	gas	88		5		5		2	
1	2	790	3:1	liquid	1		3		10	3	17	66
2	2	1060	24:1	gas	51	3	14	12	11	tr ^a	9	b
3	Co/Al ₂ O ₃	900	3.1:1	gas	56		3		6	tr ^a	35	
4	2/Al ₂ O ₃	830	3.1:1	liquid						82 ^c		

^a tr = trace. ^b Product obscured by internal standard. ^c Balance ethanol. ^d C₄ hydrocarbons.

convenient rationalization of the products observed upon reaction of the metals with nitrobenzene. Zinc, a strongly oxophilic metal, gives azobenzene, and lead, which is less oxophilic, gives azoxybenzene. Cobalt, which is intermediate in oxophilicity, gives a mixture of both azo and azoxy compounds, and copper gives neither. This elementary explanation, of course, has neglected solvent effects, which may be very important.

One of the most striking contrasts between active cobalt and other metals we have studied was its reactivity toward organic halides. Active nickel, for example, is a very good reagent for mediating the formation of carbon-carbon bonds from organic halides.^{4-6,10,21,22} Active cobalt, however, showed only limited reactivity, and we were able to couple only benzyl halides and geminal dihalides in appreciable yields using it.

Experimental Section

Procedures and Equipment. All manipulations involving air- or moisture-sensitive materials were performed on a dual-manifold vacuum line under argon or in an argon-filled Vacuum Atmospheres Corp. drybox. Vacuum-line argon was Linde "Prepurified" grade that was passed through a 0.8-m column of activated BASF R3-11 catalyst, a 0.8-m column of CaSO₄, and finally a 0.8-m column of 13X molecular sieves (Aldrich). Anhydrous cobalt halides were purchased from Cerac, stored in the drybox, and used as received. Reagent grade alkali metals, solvents, naphthalene, alkyl halides, aryl halides, nitro-substituted aromatics, acids, etc., were purchased from various commercial sources. Alkanes, diethyl ether, benzene, and toluene were distilled from blue solutions of sodium or potassium benzophenone. Glyme (1,2-dimethoxyethane) and THF were distilled from sodium-potassium alloy. Acetonitrile and methylene chloride were distilled under argon from calcium hydride. Alumina (Merck 71707) was dried at 500 °C for 14 h, cooled in a vacuum desiccator, and stored under argon. Mixtures of hydrogen and carbon monoxide (synthesis gas) were purchased from Linde. Analysis and separation of reaction mixtures were performed on a Hewlett-Packard 5730A gas chromatograph equipped with thermal conductivity and flame ionization detectors using a 1/8 in. × 10 ft stainless steel column containing 10% SE-30 on Chromasorb PA-W or a 1/8 in. × 8 ft stainless steel column containing Porapak-Q. Thin-layer chromatographic separations were performed on Merck 5775 silica gel plates. Compound identification was accomplished with a Perkin-Elmer PE-283 infrared spectrophotometer, Varian EM-390 NMR spectrometer, mixed melting points with authentic samples, and mass spectroscopy. Mass spectra were obtained in-house with the facilities of the Midwest Center for Mass Spectroscopy. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN 37921, or Spang Microanalytical Laboratory, Eagle Harbor, MI 49951. Cobalt was also estimated gravimetrically as Co₃O₄ according to published procedures.³⁹ X-ray powder patterns were obtained with use of Mo K α radiation (0.71069 Å) and a 104.6 mm diameter camera. Samples were loaded into 0.3-mm X-ray capillaries and flame-sealed.

Preparation of Cobalt Powder 1.^{21,22} The following describes a typical preparation of cobalt powder 1. In the drybox, lithium (0.2054 g, 29.6 mmol), naphthalene (0.4344 g, 3.4 mmol), and cobalt chloride (1.7683 g, 13.6 mmol) were charged into a flask equipped with a Teflon-clad stir bar and a vacuum adapter. On the vacuum line, 25 mL of freshly distilled glyme was added to the flask and the mixture was stirred for 14 h at room temperature. If desired, most of the naphthalene could then be removed from the mixture by allowing the dark gray product to settle out, decanting the supernatant, and repeating the process with fresh solvent.

Preparation of Cobalt Powder 2. The following describes a typical preparation of 2. In the drybox, lithium (0.3342 g, 48.2 mmol) and naphthalene (8.0600 g, 62.9 mmol) were placed in a flask equipped with

a Teflon-clad stir bar and vacuum adapter. On the vacuum line, 70 mL of freshly distilled glyme was added and the mixture stirred vigorously until all of the lithium had dissolved. The resulting black-green solution was cooled to -78 °C, and a slurry of cobalt chloride (3.0673 g, 23.6 mmol) in 30 mL of glyme was added. This mixture was stirred for 0.5 h at -78 °C and an additional 3 h at room temperature. The product obtained settled out of the opaque black supernatant very slowly. If desired, the powder may be separated by centrifugation. Washing the powder with fresh glyme always gave black supernatants whereas washing with diethyl ether or hexanes gave slightly cloudy supernatants. Typical elemental analyses were as follows. Anal. Found: C, 7.09; H, 0.89; Cl, 36.93; Co, 40.30; Li, 9.42.

Preparation of Cobalt Powder 3. Potassium (4.2592 g, 108.9 mmol) and naphthalene (20.0189 g, 156.2 mmol) were stirred in 100 mL of freshly distilled diglyme. When all of the potassium had dissolved, the solution was cooled to -60 °C, forming a thick slush. Dry cobalt chloride (6.0669 g, 46.7 mmol) was added in small portions from a preattached bent glass holding tube, rapidly turning the thick dark green slush to a mobile opaque brownish black slurry. When all of the cobalt chloride had been added, the mixture was warmed to -45 °C and allowed to stir for an additional 14 h. The black powder, isolated by centrifugation, was washed with 75 mL of fresh diglyme in three portions and 90 mL of hexanes in four portions and dried in vacuo overnight at room temperature. Anal. Found: C, 5.06; H, 0.60; Cl, 31.09; Co, 23.53; K, 35.17. From Debye-Scherrer X-ray powder diffraction photographs, potassium chloride was identified as the major diffracting phase. Interplanar distance (Å): calcd 3.149, 2.226, 1.819, 1.576, 1.426, 1.289; KCl (lit.⁵²) 3.146, 2.224, 1.816, 1.573, 1.407, 1.284.

Reaction of Co with Synthesis Gas: Method 1. A sample of 2 was prepared by adding CoCl₂ (3.0673 g, 23.6 mmol; 30 mL of glyme) to a solution of lithium naphthalide (0.3342 g, 48.2 mmol of lithium; 8.0600 g, 62.9 mmol of naphthalene; 70 mL of glyme) at -78 °C. From the well-stirred metal slurry was removed a 15-mL sample (containing ca. 5.1 mmol of Co), and this was transferred to a 125-mL bomb equipped with borosilicate glass liner and Teflon-clad magnetic stir bar. The gas lines connected to the bomb were flushed with synthesis gas (3:1 H₂-CO), and the bomb was filled to 790 psi with the gas. At 295 K, the pressure decreased rapidly to 758 psi and remained constant for the succeeding 106 min. The bomb was now heated in a sand bath while the pressure and temperature were monitored. At ca. 477 K, the pressure began to decline smoothly, ultimately stabilizing at 460 psi at 483 K after 1215 min. The apparatus was cooled to room temperature and the head space gases and liquid phase analyzed by GC, giving the results shown in Table I. Gas-phase products were identified by comparison of their retention time with authentic samples. Liquid-phase products were identified by retention time comparison and GC-MS. The recovered liquid phase was pale blue-green with most of the metal collected in a sticky mass.

Method 2. A 15-mL sample of the slurry described in method 1 was treated with 1060 psi of synthesis gas (2.4:1 H₂-CO) at 296 K. The pressure decreased to 985 psi within 0.5 h and remained constant over the succeeding 0.5 h. The reactor was heated to ca. 470 K and kept at that temperature for 427 min. A sample of gas for GC and GC-MS analyses was removed at this time, giving the results listed in Table I. GC-MS indicated that small amounts of formaldehyde, acetaldehyde, propanal, and acetic acid were also formed.

Method 3. Into a 250-mL round-bottom flask equipped with a Teflon-clad stir bar were placed the following materials: lithium (0.0258 g, 3.7 mmol); naphthalene (0.4816 g, 3.8 mmol); CoCl₂ (0.1818 g, 1.4 mmol); Al₂O₃ (19.9373 g, 195.5 mmol); glyme (175 mL). The mixture was stirred vigorously overnight. Even though all of the lithium had been consumed, much CoCl₂ remained adsorbed on the Al₂O₃ as evidenced by its blue color. A solution of lithium naphthalide was prepared from lithium (0.0207 g, 3.0 mmol) and naphthalene (0.6244 g, 4.9 mmol) in glyme (20 mL). This was added at once to the well-stirred slurry, causing the dark green color characteristic of naphthalide radical to disappear

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at once. The addition of further lithium (0.0654 g, 9.4 mmol) was necessary to reduce all of the obvious Co(II). By this time, the Al_2O_3 was a uniformly gray solid suspended in a colorless supernatant. The supernatant was removed and the solid washed with the following: glyme (100 mL); one 200-mL portion of 1:1 glyme-diethyl ether; diethyl ether (2×100 mL). The solid was dried for 14 h in vacuo at room temperature and an additional 1 h at 60 °C. The supernatant liquids were combined, evaporated, and partitioned into aqueous and organic fractions. In this way, 1.1716 g of white crystalline organic material (largely naphthalene) and 0.0277 g of pale blue water-soluble salts were recovered.

A 2.8476-g sample of the dry impregnated Al_2O_3 was loaded in a glass liner and placed into a 125-mL bomb, which was then filled to 900 psi with synthesis gas (3.1:1 H_2 -CO). After ca. 0.5 h, the pressure stabilized at 865 psi and 296 K. The reactor was heated in the sand bath to 500 K over a period of 200 min, attaining an equilibrium pressure of 1300 psi, which remained constant for the succeeding 685 min of the run. (Blank runs have shown that due to thermal gradients, heat loss, and gauge errors, the isochoric pressure change with temperature in this apparatus is approximately 92% of that expected for an ideal gas. In the present example, the pressure at 500 K was expected to be 1399 psi, suggesting that 99 psi of gas had been consumed.) No further pressure change was observed at 500 K. The gases were sampled at 500 K and analyzed with GC with the results shown in Table I.

Method 4. A slurry of **2** (0.0223 g, 3.2 mmol, of lithium; 1.0979 g, 8.6 mmol, of naphthalene; 0.1489 g, 1.2 mmol, of cobalt chloride; 90 mL of glyme) was added slowly to a well-stirred slurry of Al_2O_3 (15.8948 g, 155.9 mmol) in glyme (90 mL). After 4 h of vigorous stirring the faintly brown supernatant was removed and the gray solid washed with diethyl ether (3×100 mL). The solid was dried for 1 h at room temperature in vacuo and an additional 3 h at 60 °C. In the drybox, 15.9699 g of gray solid was recovered. From this quantity was taken 1.9355 g (corresponding to ca. 0.1 mmol of Co) and slurried with glyme (20 mL) and *n*-octane (0.0817 g, internal standard) in the glass-lined bomb. The bomb was filled with 830 psi of synthesis gas (3.1:1 H_2 -CO). The pressure decreased to ca. 800 psi in approximately 20 min and remained unchanged for an additional 70 min. The reactor was heated in the sand bath for 408 min at 468 K when the pressure stabilized at 1255 psi.

The reactor was cooled to 0 °C and vented, and the colorless liquid phase was analyzed by GC. The GC analysis revealed methanol (0.0452 g, 82%) and ethanol (0.0096 g, 18%) as the principal products (identification by comparison of retention times with authentic materials).

Method 5. Cobalt on alumina was prepared by the procedure described in method 4. A 5.6511-g sample (corresponding to ca. 0.4 mmol of Co) was placed in a tube reactor.

The tube reactor was 220 mm in length and 19 mm in diameter, with 14/20 standard taper joints on either end into which glass stopcocks were fitted. The catalyst was confined to the central 120 mm of the reactor by glass wool plugs. This central portion was wound with nichrome wire and insulated from the surroundings by a 20 mm thick winding of glass wool and a layer of aluminum foil. A thermometer was inserted into the windings, being placed as close to the reactor wall as possible.

Synthesis gas (3.1:1 H_2 -CO) was passed through a U-tube filled with $13\times$ molecular sieve at -78 °C to remove traces of moisture and $\text{Fe}(\text{C}-\text{O})_5$. Samples for GC analysis were removed through a septum-capped glass tee on the effluent side of the reactor. A CaSO_4 drying tube was included on the effluent side so that the amount of water formed could be estimated. Synthesis gas was passed through the reactor at 62 mL/min at 721.4 mm and 298 K for 2 h prior to heating the reactor to 618 K.

Periodically samples of the effluent gas from the reactor were analyzed by GC. Methane and C_2 hydrocarbons were the only products detected. From the mass increase of the drying tube, approximately 44% of the CO was converted to hydrocarbons or ca. 230:1 CO-Co at a space velocity of 11-44 min^{-1} . Here space velocity is defined by the volume of gas per unit time (62 mL/min) divided by the catalyst volume. We did not perform a quantitative determination of the catalyst density but rather used the quoted density of the alumina. The space velocities quoted represent reasonable upper and lower limits.

The catalyst recovered from the reactor was quite heavily coked.

Method 6. A 2.8476-g sample of cobalt on alumina (corresponding to ca. 0.2 mmol of Co) was prepared as described in method 3 and placed in the tube reactor. The products of the reaction were monitored by GC over the temperature range 298-633 K. Methane was the principal product, although much smaller amounts of other products, believed to be C_2 species, were also observed. Methane was observed at room temperature; however, the amount formed increased markedly at 505 K, fell, and peaked again at 572 K. After ca. 155 min, during which time the temperature increased from 572 to 636 K, the methane yield decreased to ca. 20% of its maximum value.

Table II. Weight Percent Composition of the Hydrocarbons Formed in the Hydrolysis of Cobalt Powders^d

	run 1 ^a	run 2 ^b	run 3 ^a	run 4 ^c
CH_4	50	24	50	46
C_2H_4	10	9	6	5
C_2H_6	19	8	10	9
C_3H_6	10	12	8	4
C_3H_8	10	12	5	7
C_4H_8		8	3	3
C_4H_{10}		8	3	6
C_5H_{10}		13		
C_5H_{12}		7	15	21

^a2. ^b2 after treatment with H_2 -CO, 1060 psi, 140 °C. ^c2 after CO, 1130 psi, 87 °C. ^dIn some cases, totals do not add to 100 due to a rounding off.

Table III. Calculated Lattice Spacings Found for Active Cobalt Powders

sample	lattice spacing, Å							
	5.50	3.44	2.78	2.30	2.05	1.82	1.71	1.54
2 carburized	5.55	3.43	2.81	2.30				
2 annealed	2.05	1.26	1.07					

At the completion of the experiment, the catalyst was observed to be caked and heavily coked.

Hydrolysis of Active Cobalt. A sample of **2** was prepared from 0.3727 g (53.7 mmol) of lithium, 8.9290 g (69.7 mmol) of naphthalene, and 3.3438 g (25.8 mmol) of cobalt chloride. The dark gray powder was separated by centrifugation, washed with four 40-mL portions of distilled diethyl ether, and dried overnight in vacuo at room temperature to give 3.3350 g of loose free-flowing solid. Hydrolyses of ca. 1-g samples of this material with concentrated hydrochloric acid produced 8.5 mmol of gas/g of material. If it is assumed that the hydrolyzed samples were representative of the whole, this was 17% more than the expected amount of gas if Co was the only reducing agent present; i.e., $2\text{H}^+ + \text{Co} \rightarrow \text{H}_2 + \text{Co}^{2+}$. Hydrolysis of commercial 325-mesh cobalt was found to give 2-5% less gas than that calculated from this equation. GC analysis of the hydrocarbon portion of the evolved gas from one of the hydrolysis experiments showed C_1 - C_3 hydrocarbons, which were identified by retention time and GC-MS (see Table II, run 1). The intensely blue acid solutions were clear or only slightly turbid when decomposition was complete.

In another experiment, 1.0108 g of cobalt powder from the same preparation was treated with 825 psi of H_2 for 12 min. By this time the pressure decreased to 810 psi. The H_2 was vented, and 250 psi of CO and 850 psi of H_2 were added sequentially. Within 3 min the pressure had decreased, stabilizing at 1060 psi. The bomb was heated to 413 K for 7 days. A plot of pressure vs. temperature during the heating and cooling period, and monitoring of the pressure at 413 K, indicated that little or no gas-consuming reactions had occurred. GC analysis of the bomb head-space gases showed no evidence for the formation of significant amounts of hydrocarbons. The recovered cobalt (0.9601 g) was gummy and the interior of the bomb was coated with sublimed naphthalene.

The recovered material was washed with pentane, leaving a free-flowing dark gray solid that was very strongly ferromagnetic.

Hydrolysis of a sample of the gummy material with concentrated hydrochloric acid gave a variety of hydrocarbons (see Table II, run 2).

Reaction of Dry Cobalt Powders with CO. A sample of **2** (0.7654 g, 110.0 mmol, of lithium; 14.8517 g, 115.9 mmol, of naphthalene; 6.8920 g, 53.1 mmol, of cobalt chloride; 150 mL of glyme) was prepared and the powder washed with four 50-mL portions of hexanes and diethyl ether. From these washings were obtained 13.98 g (ca. 94%) of the naphthalene and 7.2941 g of gray-black cobalt powder. The powder was not ferromagnetic; e.g., none was attracted to a strong bar magnet, and only a few particles were oriented by the magnet. Anal. Found: C, 7.09; H, 0.89; Cl, 36.93; Co, 40.30; Li, 9.42.

A 3.6065-g sample of this powder was treated with CO (1130 psi) at room temperature. The pressure dropped immediately, reaching 700 psi in 5 min with a large exotherm that made the bomb intolerably hot to the touch. Visual examination of the sample after the bomb was vented showed no obvious change in the powder. The sample was then repressurized to 1000 psi at room temperature. After 10 min, the pressure stabilized at 955 psi with no obvious exotherm. The bomb was placed in an 87 °C oil bath for 2 h and then cooled and vented. The powder

Table IV. Surface Analysis Results

sample state	Binding Energy (eV) and Spin-Orbit Coupling (SOC) Values								
	Co			K			Cl		O
	2p _{3/2}	2p _{1/2}	SOC	2p _{3/2}	2p _{1/2}	SOC	2p	1s	1s
received	776.8	792.4	15.6	292.6	295.3	2.7	198.0	530.0	284.6
sputtered 400 Å ^a	776.8	792.1	15.3	292.6	295.4	2.8	198.0	530.0	
Analytical Data (Atom %)									
	C	Cl	Co	K	O				
received	19.8	23.0	7.7	31.5	18.0				
bulk	5.1	31.1	23.5	35.2	4.5				
sputtered 400 Å ^a	8.3	33.0	14.1	40.0	4.6				

^aThe surface material was removed by Ar⁺ bombardment. The sputtering rate was determined from known thickness of Ta₂O₅ films. Since the sputtering rate of active cobalt relative to that of Ta₂O₅ is unknown, the absolute depth is approximate. The relative atomic percents are calculated by using experimental sensitivity factors and peak areas for each element shown. The relative concentrations show reproducibility to ±0.2% and are believed correct to ±5% of the absolute concentration.

was washed with hexanes to remove a small amount of Co₂(CO)₈ and naphthalene and then dried in vacuo to a constant mass of 4.4249 g. The Co₂(CO)₈ was oxidized by allowing the solution to stand in air, and the solid residues were collected on ashless filter paper and ignited to constant mass (0.00968 g). With the oxide residues weighed as Co₂O₄, it was calculated that less than 0.5% of the cobalt in the powder prior to treatment with CO was converted to Co₂(CO)₈. Anal. Found for the pentane-washed powder after CO treatment: C, 33.32; H, 1.10; Cl, 30.90; Co, 25.51; Li, 5.93.

Hydrolysis, with concentrated hydrochloric acid, of samples before and after treatment with CO, gave 9.0 and 8.0 mmol of gas/g, respectively, and the hydrocarbons shown in Table II, runs 3 and 4.

From hydrolysis of the carburized samples was obtained a finely divided black material that represented 29.89% of the sample mass. Ignition of this material resulted in a 95–99% decrease in mass and was accomplished with the formation of a small quantity of a refractory material.

In similar experiments CO₂ was shown to be present in the gases vented from the reactor by precipitation of CaCO₃ from a saturated Ca(OH)₂ solution through which the gases were dispersed.

Debye-Scherrer photographs of cobalt from this preparation before CO treatment, after CO treatment, and after annealing at 300 °C for 14 h under argon were obtained. Analysis of these films was inconclusive, the calculated interplanar distances being in poor agreement with known metallic oxidic or carbidic phases (see Table III).

Reaction of Cobalt with Aromatic Nitro Compounds: Nitrobenzene. A slurry of **2** (0.5861 g, 84.4 mmol, of lithium; 14.0901 g, 109.9 mmol, of naphthalene; 4.7055 g, 36.7 mmol, of CoCl₂) was prepared and the supernatant liquid removed by centrifugation. The metal powder was returned to the reaction flask via cannula with use of 100 mL of fresh glyme. Nitrobenzene (1.44 g, 11.7 mmol) was added at once to the well-stirred room-temperature slurry, resulting in a surprisingly vigorous exotherm. After ca. 2 min a 2-mL sample of the mixture was quenched with 5 drops of water. Analysis of the quenched reaction mixture by GC and thin-layer chromatography revealed that no nitrobenzene remained and that azobenzene and other highly colored products had formed. The reaction mixture was washed with five 40-mL portions of glyme, which were combined and extracted with diethyl ether–3 M HCl. The diethyl ether layer was extracted once again with water, dried over MgSO₄, and evaporated to give 3.28 g of a brown oil. The oil was placed on a silica gel column, from which 0.39 g (37%) of azobenzene was eluted with hexane–chloroform. Recrystallization from ethanol gave pure azobenzene, identified by comparison of its infrared spectrum and mixed melting point with authentic samples.

Other materials removed from the column included naphthalene and several highly colored oily components, which were not identified.

The aqueous extracts were combined, made basic (pH 9), and reextracted with diethyl ether to give a small amount (0.25 g) of brown oil. TLC analysis showed that a multicomponent mixture had resulted. This was not investigated further.

In another experiment, performed similarly but with 0.52 mol of PhNO₂/mol of Co, a 21% yield of azobenzene was obtained with numerous unidentified products. At reflux **2** also reacted with PhNO₂ (1 mol of PhNO₂/mol of Co) to give azobenzene (17%) or at room temperature to give azobenzene (18%) and azoxybenzene (9%), identified by their infrared spectra. Commercial 325-mesh cobalt powder was treated with a few drops of concentrated HCl in glyme until the strong blue color of Co(II) was observed, indicating that the surface oxide coating had been breached. The cleaned metal was washed with several portions of fresh glyme and treated with a nitrobenzene. No reaction was

observed at room temperature or at reflux.

1-Iodo-4-nitrobenzene. A slurry of **2** (0.2292 g, 33.0 mmol, of lithium; 6.3502 g, 49.5 mmol, of naphthalene; 1.830 g, 14.1 mmol, of CoCl₂) at –78 °C was treated with a room-temperature solution of 1-iodo-4-nitrobenzene (2.5853 g, 11.5 mmol, freeze–thaw degassed three times) in 20 mL of glyme. After 1 h the mixture was brought to reflux for 2 h. TLC examination of the products showed that no 1-iodo-4-nitrobenzene remained and that 4,4'-dinitrophenyl was not a materially significant product. The reaction mixture was divided into two equal portions, one of which was worked up from chloroform–water. From the crude product were isolated 4,4'-diiodoazobenzene (0.1315 g, 10%) and 4,4'-diiodoazoxybenzene (0.1585 g, 12%) by column chromatography, and the compounds were characterized by infrared spectroscopy, mixed melting point (azo compound only), and high-resolution mass spectroscopy. Other compounds were recovered from the column as impure, highly colored oils, which were not characterized.

1,2-Dinitrobenzene. Caution! 1,2-Dinitrobenzene is a high explosive that is known to detonate when subjected to shock or temperature above its melting point.⁵³ To reduce the potential hazards in this experiment, less reactive **1** was used. To a slurry of **1** (0.2054 g, 29.6 mmol, of lithium; 0.4344 g, 3.4 mmol, of naphthalene; 1.7683 g, 13.6 mmol, of cobalt chloride) was added a solution of 0.4740 g (2.8 mmol) of 1,2-dinitrobenzene in 40 mL of glyme at 0 °C over a period of ca. 3 h. The mixture was warmed to room temperature and stirred for 4 h. TLC analysis showed only naphthalene, 1,2-dinitrobenzene, and an unknown material with a strong blue fluorescence (also observed in the reaction of **2** with PhNO₂). The solvent was removed and the metal slurry washed several times with fresh portions of glyme. Water–diethyl ether extractions of the combined portions of glyme eventually yielded 0.3476 g of crystals. These were shown by TLC to be a mixture of naphthalene and 1,2-dinitrobenzene.

Reaction of Cobalt with C₆F₅I: Preparation of (C₆F₅)₂Co-2PEt₃. A slurry of **2** (0.2860 g, 41.2 mmol, of lithium; 6.8679 g, 53.6 mmol, of naphthalene; 2.2900 g, 17.8 mmol, of cobalt chloride) was prepared and the product centrifuged, washed with two 30-mL portions of diethyl ether, and slurried back into the reaction flask with 30 mL of glyme. Pentafluorophenyl iodide (5.38 g, 18 mmol) was added to the metal slurry at 0 °C. After 1 h, the blue-green mixture was warmed to room temperature for 14 h. The mixture was cooled to 0 °C, and 4.70 g (40 mmol) of triethylphosphine was added. It was stirred for 5 h at room temperature and then worked up as previously described^{21,22} to give 3.05

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g (54%) of crystalline $(C_6F_5)_2Co-2PEt_3$, whose physical and spectroscopic properties are consistent with those previously reported.

Reaction with Benzyl Bromide. A slurry of **2** (0.2812 g, 40.5 mmol, of lithium; 6.7343 g, 52.5 mmol, of naphthalene; 2.2540 g, 17.6 mmol, of cobalt chloride) was prepared and the product separated and washed with three 30-mL portions of diethyl ether. The metal powder in 30 mL of fresh glyme was treated at room temperature with 5.46 g (32 mmol) of benzyl bromide, causing a brisk exotherm after a brief induction period. After 14 h the products were quantitatively determined by GC as bibenzyl (63%) and toluene (6%) with use of a known quantity of *n*-nonane as an internal standard and application of response factor corrections.

Reaction with Phenyl Halides: Phenyl Iodide. Method 1. A slurry of **2** (0.2472 g, 35.6 mmol, of lithium; 5.9647 g, 46.5 mmol, of naphthalene; 1.9765 g, 15.4 mmol, of cobalt chloride) was prepared and the product washed once with glyme. It was then treated in 25 mL of glyme was 4.5955 g (22.5 mmol) of phenyl iodide. Quenches were taken periodically by withdrawing 1-mL samples and treating the samples with 2 drops of 1 M HCl. The samples were then quantitatively analyzed by GC with use of *n*-dodecane as an internal standard and application of response factor corrections. After 1 min, 59% of the phenyl iodide remained. After 20 h (last 3 h at reflux), 61% remained. No biphenyl was observed until the reaction mixture was refluxed, after which an 11% yield of that compound was found.

Method 2. A slurry of **1** (0.3166 g, 45.6 mmol, of lithium; 0.5889 g, 4.6 mmol, of naphthalene; 2.5429 g, 19.8 mmol, of cobalt chloride) was prepared and the powder washed once with 25 mL of glyme. It was then treated in 30 mL of glyme with 6.3406 g (31.1 mmol) of phenyl iodide. Quenches were taken as described in method 1 (vide supra) and showed 64% of the phenyl iodide remained unchanged after 1 min at room temperature. After 26 h (3 h at reflux) 60% of the phenyl iodide remained. No biphenyl was observed at any time.

Preparation of Tetraphenylethylene: Method 1. A slurry of **1** (0.3516 g, 50.7 mmol, of lithium; 1.3021 g, 10.2 mmol, of naphthalene; 7.7919 g, 24.9 mmol, of cobalt chloride) was prepared and the powder washed with 160 mL of glyme in two portions. The slurry in 20 mL of glyme was treated with 3.70 g (15 mmol) of dichlorodiphenylmethane, causing a brief mild exotherm. After 20 h, GC analysis revealed that only a trace of Ph_2CCl_2 remained in the green solution. The organic products were extracted from 3 M HCl with chloroform, washed with several portions of water, and dried over magnesium sulfate. After concentration in vacuo recrystallization of the residues from benzene-ethanol gave 1.58 g (63%) of pale yellow crystalline tetraphenylethylene, identified by its mixed melting point with an authentic sample and high-resolution mass spectroscopy.

Method 2. A slurry of **1** (0.1853 g, 26.7 mmol, of lithium; 0.2254 g, 1.8 mmol, of naphthalene; 4.002 g, 12.8 mmol, of cobalt iodide) was chilled to $-78^\circ C$, and 1.05 g (13 mmol) of cyclohexene and 1.48 g (6.2 mmol) of dichlorodiphenylmethane were added. After it was stirred for 48 h at room temperature, the mixture was refluxed for 3 h and worked up as described in method 1 to give 0.53 g (51%) of tetraphenylethylene.

Method 3. A slurry of **1** (0.2154 g, 31.0 mmol, of lithium; 0.1840 g, 1.4 mmol, of naphthalene; 4.5599 g, 14.6 mmol, of cobalt iodide; 45 mL of THF) was prepared. The metal powder was isolated by filtration under argon and dried in vacuo overnight. The cobalt powder (3.678 g) was slurried in 20 mL of distilled hexanes and treated with 2.72 g (11 mmol) of dichlorodiphenylmethane at room temperature, causing the formation of a green solution. After the mixture was stirred for 48 h, the products were worked up as previously described to give 0.80 g (42%) of tetraphenylethylene.

Reaction of Cobalt with Diiodomethane. A slurry of **1** (1.9500 g, 6.2 mmol, of cobalt iodide; 0.5009 g, 12.8 mmol, of potassium; 0.7878 g, 6.2 mmol, of naphthalene; 20 mL of THF) was treated with 5.2331 g (19.5 mmol) of diiodomethane and 0.0714 g of *n*-tridecane (GC standard). After 14 h ethylene was identified by mass spectroscopy in the gases above the reaction mixture. Analysis of the reaction mixture by GC showed that 57% of the diiodomethane remained unchanged.

X-ray Photoelectron Spectroscopy (XPS). Samples for XPS studies were sealed under argon in glass ampules. These were opened in an argon-filled drybox, and the metal powder was dusted onto aluminum-backed tape and transferred into the vacuum chamber of the XPS system (PHI Model 550) by means of a controlled-atmosphere specimen-transfer device (PHI Model 04-100). This device allows sample introduction with minimal contamination of the sample by air or moisture.

The spectra were obtained with use of a Mg anode for X-ray excitation with a vacuum of 10^{-9} torr. Sputtering was effected with a differentially pumped ion gun with an energy of 5 KeV and an ion current density of $5 A cm^{-2}$. Results from several experiments are collected in Table IV.

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Registry No. Co, 7440-48-4; CO, 630-08-0; $(C_6F_5)_2Co-2PEt_3$, 60528-59-8; nitrobenzene, 98-95-3; iodopentafluorobenzene, 827-15-6; iodobenzene, 591-50-4; benzyl bromide, 100-39-0; dichlorodiphenylmethane, 2051-90-3; diiodomethane, 75-11-6.

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Potential Lanthanide Ion Selective Reagents. 3.^{1,2} Metal Complex Formation with 1,7-Diaza-4,10,13-trioxacyclopentadecane-*N,N'*-diacetic Acid

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Stability constants for the ligand 1,7-diaza-4,10,13-trioxacyclopentadecane-*N,N'*-diacetic acid (dapda or K21DA) with the lanthanides and several other metal ions have been determined at $25^\circ C$ in aqueous 0.1 M $(CH_3)_4NCl$ medium by a potentiometric method. The results obtained are compared to those obtained for a similar ligand of larger cavity size, 1,10-diaza-4,7,13,16-tetraoxacyclooctadecane-*N,N'*-diacetic acid (dadca or K22DA), which has been previously studied and reported.¹ The stability of dapda is found to reach a peak at Eu(III) with the lanthanide series and is rationalized in terms of the matching of the ligand properties with metal ion characteristics. The transition-metal ions Ni(II), Cu(II), and Zn(II) all form stronger dapda (as compared to dadca) complexes due to a better match of the ligand cavity size and metal ion radius.

The past 20 years has witnessed a rapid growth in our knowledge and applications of the rare-earth elements. It was estimated that the total consumption of lanthanides was ~ 1.6

$\times 10^3$ metric tons in the early 1960s, which escalated to more than 20×10^3 metric tons in 1975.³ Also, their use was mainly in lighter flints, carbon arc electrodes, and glass polishing powders in the early 1960s; in recent years, it has changed to applications

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